

การเสริมแรงด้วยซิลิกาอินซิทูของน้ำยางธรรมชาติพรีวัลคาไนซ์ด้วยรังสี



นางสาว กมลฉัตร จรุงจิตอารีย์

สถาบันวิทยบริการ จุฬาลงกรณ์มหาวิทยาลัย

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต

สาขาวิชาปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์

คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

ปีการศึกษา 2550

ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

IN SITU SILICA REINFORCEMENT OF RADIATION PREVULCANIZED NATURAL
RUBBER LATEX



Miss Kamolchat Charungchitaree


สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

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 2007
Copyright of Chulalongkorn University


501699

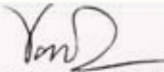
Thesis Title *IN SITU* SILICA REINFORCEMENT OF RADIATION
PREVULCANIZED NATURAL RUBBER FILMS
By Miss Kamolchat Charungchitaree
Field of study Petrochemistry and Polymer Science
Thesis Advisor Assistant Professor Varawut Tangpasuthadol, Ph.D.
Thesis Co-advisor Professor Suda Kiatkamjornwong, Ph.D.
Associate Professor Jariya Boonjawat, 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, Ph.D.)


THESIS COMMITTEE


.....Chairman
(Professor Pattarapan Prasassarakich, Ph.D.)


.....Thesis Advisor
(Assistant Professor Varawut Tangpasuthadol, Ph.D.)


.....Thesis Co-advisor
(Professor Suda Kiatkamjornwong, Ph.D.)


.....Thesis Co-advisor
(Associate Professor Jariya Boonjawat, Ph.D.)


.....Member
(Phiriyatorn Suwanmala, Ph.D.)

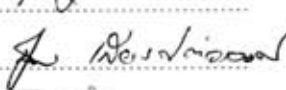
กมลฉัตร จรุงจิตอารีย์: การเสริมแรงด้วยซิลิกาอินซิทูของน้ำยางธรรมชาติพรีวัลคาไนซ์ด้วยรังสี (*IN SITU SILICA REINFORCEMENT OF RADIATION PREVULCANIZED NATURAL RUBBER LATEX*) อ.ที่ปรึกษา: ศศ.ดร. วราวุฒิ ตั้งพสุธาตล, อ.ที่ปรึกษาร่วม: ศศ.ดร. สุดา เกียรติกำจรวงศ์, รศ.ดร. จริญญา บุญญวัฒน์; 62 หน้า.

ในงานวิจัยนี้ได้รายงานวิธีสำหรับเตรียมแผ่นยางธรรมชาติซึ่งวัลคาไนซ์ด้วยรังสีและมีซิลิกาแบบเกิดขึ้น ณ จุดเกิดปฏิกิริยา โดยใช้ปริมาณรังสีแกมมา 15 กิโลเกรย์ ฉายไปที่น้ำยางที่มีเนื้อยางแห้งร้อยละ 50 หลังจากนั้นนำน้ำยางพรีวัลคาไนซ์ที่ได้มาผสมกับอัลคอกซีไฮเลนซึ่งเป็นสารตั้งต้นของซิลิกา ตามด้วยการอบของผสมที่ 50 °ซ เพื่อริเริ่มกระบวนการ โชล-เจลของสารไฮเลนไปเป็นอนุภาคซิลิกาภายในเนื้อยาง ได้ศึกษาอัลคอกซีไฮเลนจำนวน 3 ชนิดคือ เทตระเอทอกซีไฮเลน (TEOS), ไวนิลไทรเอทอกซีไฮเลน (VTOS) และเอทิลไทรเอทอกซีไฮเลน (ETOS) ลำดับของร้อยละการเปลี่ยนรูปจากไฮเลนไปเป็นซิลิกาคือ TEOS>VTOS>ETOS ซึ่งสะท้อนถึงขนาดเชิงปริมาตรและข้อของหมู่แทนที่ไวนิลและเอทิลของไฮเลน จากผลการวิเคราะห์ด้วย SEM พบว่าอนุภาคซิลิกาที่เกิดขึ้นจากไฮเลนทั้งสามชนิดกระจายตัวในเนื้อยางได้อย่างทั่วถึง อนุภาคซิลิกาที่เกิดขึ้นจาก TEOS จับตัวเป็นกลุ่มก้อนขนาดต่างๆ ประมาณ 1 ไมโครเมตร แต่เมื่อใช้ VTOS และ ETOS อนุภาคซิลิกาที่ได้จะมีขนาด 0.1 ไมโครเมตรและไม่จับตัวกัน และยังได้ศึกษาผลของชนิดและปริมาณของอัลคอกซีไฮเลนที่ใช้ต่อพฤติกรรมการบวมในโทลูอินและน้ำ สมบัติเชิงกลและสมบัติทางความร้อนของคอมโพสิตซิลิกาอินซิทู-ยางธรรมชาติฉายรังสี

สถาบันวิทยบริการ จุฬาลงกรณ์มหาวิทยาลัย

สาขาวิชา วิศวกรรมและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต กมลฉัตร จรุงจิตอารีย์

ปีการศึกษา 2550 ลายมือชื่ออาจารย์ที่ปรึกษา 

ลายมือชื่ออาจารย์ที่ปรึกษาร่วม 

ลายมือชื่ออาจารย์ที่ปรึกษาร่วม 

4772207223: MAJOR PETROCHEMISTRY AND POLYMER SCIENCE

KEYWORD: RADIATION VULCANIZATION/ NATURAL RUBBER/ IN SITU SILICA/ SOL-GEL PROCESS/ COMPOSITES

KAMOLCHAT CHARUNGCHITAREE: *IN SITU* SILICA REINFORCEMENT OF RADIATION PREVULCANIZED NATURAL RUBBER LATEX. THESIS ADVISOR: ASST. PROF. VARAWUT TANGPASUTHADOL, Ph.D. THESIS CO-ADVISOR: PROF. SUDA KIATKAMJORNWONG, Ph.D., ASSOC. PROF. JARIYA BOONJAWAT; 62 pp.

A method to prepare radiation-vulcanized NR sheets containing *in situ* generated silica was reported. The NR latex having 50% dry rubber content was irradiated under gamma rays with a total radiation dose of 15 kGy. The prevulcanized latex was then mixed with alkoxysilanes, precursors of silica. The latex mixture was heated at 50 °C for 48 hours in order to initiate the sol-gel process of the silane to form silica particles inside the rubber matrix. Three types of alkoxysilanes were studied-tetraethoxysilane (TEOS), vinyltriethoxysilane (VTOS), and ethyltriethoxysilane (ETOS). The percentage of conversion from silanes to silica were in the order of TEOS (80%)>VTOS (60%)>ETOS (10%), reflecting the bulkiness and polarity of the vinyl and ethyl substituent of the silane. The silica particles obtained from all silanes dispersed evenly in the rubber matrix as observed by SEM. The silica particles generated from TEOS formed various aggregate sizes of about 1 μm. The sizes of silica particles generated from either VTOS or ETOS were found to be about 0.1 μm and aggregation was not found. Swelling behavior in toluene and water, physical properties and thermal properties of the *in situ* silica/radiation vulcanized natural rubber composites were also investigated as a function of type and amount of alkoxysilanes used.

Field of study Petrochemistry and Polymer Science Student's signature Kamolchat Charungchitaree

Academic year 2007 Advisor's signature [Signature]

Co-advisor's signature [Signature]

Co-advisor's signature [Signature]

ACKNOWLEDGEMENTS

I would like to express gratitude to my advisor, Assistant Professor Varawut Tangpasuthadol, Ph.D. and my co-advisors, Professor Suda Kiatkamjornwong, Ph.D. and Associate Professor Jariya Boonjawat, Ph.D. for their invaluable suggestions, guidance and kindness throughout the course of this work.

I am sincerely grateful to Professor Pattarapan Prasassarakich and Dr. Phiriyatorn Suwanmala, Thailand Institute of Nuclear Technology, for their invaluable comments and suggestions as serving on the committee members.

I am also thankful for the research financial supports from Research Team Aid (RTA) Grant, Thailand Research Fund contract number RTA 4780004 to Professor Suda Kiatkamjornwong and Office of the National Research Council of Thailand to Associate Professor Jariya Boonjawat. I thank the technical assistance given by the staff from National Metal and Materials Technology Center (MTEC) and from Scientific and Technological Research Equipment Center (STREC), Chulalongkorn University.

Moreover, I appreciate comments, help, and warm friendship from all members of Varawut and Voravee groups in Organic Synthesis Research Unit. Finally, I would like to express my deepest gratitude to my family for their love, encouragement and support throughout my entire study.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

CONTENTS

	Page
ABSTRACT IN THAI.....	iv
ABSTRACT IN ENGLISH.....	v
ACKNOWLEDGEMENTS.....	vi
CONTENTS.....	vii
LIST OF FIGURES.....	x
LIST OF TABLES.....	xiii
LIST OF SCHEMES.....	xiv
LIST OF ABBREVIATIONS.....	xv
CHAPTER I INTRODUCTION.....	1
1.1 Statement of problems.....	1
1.2 Objectives.....	2
1.3 Scope of the investigation.....	2
CHAPTER II THEORY AND LITERATURE REVIEW.....	3
2.1 Natural Rubber	3
2.2 Radiation vulcanization of natural rubber	4
2.3 Reinforcement.....	8
2.4 Silica.....	9
2.5 Sol-Gel process.....	10
2.6 Mechanical Testing.....	13
2.6.1 Tensile stress-strain.....	13
2.6.2 Tear resistance.....	14
2.6.3 Hardness.....	16
2.6.4 Tension set.....	16
2.7 Swelling behavior.....	16
2.8 Thermal analysis.....	17

	Page
CHAPTER III MATERIALS AND METHODS.....	18
3.1 Materials.....	18
3.2 Experimental Methods.....	18
3.2.1 Determination of dry rubber content (%DRC) of latex.....	18
3.2.2 Preparation of pre-vulcanized NR latex.....	18
3.2.3 <i>In situ</i> generation of the silica in pre-vulcanized NR latex	19
3.2.4 Determination of silica content in the composites.....	20
3.2.5 Swelling study.....	20
3.2.5.1 Swelling in toluene.....	20
3.2.5.2 Swelling in water	21
3.2.6 Microscopic Analysis.....	21
3.2.7 NMR analysis of the <i>in situ</i> silica/RVNR composites.....	21
3.2.8 Measurement of physical properties.....	21
3.2.8.1 Tensile strength.....	21
3.2.8.2 Tear strength.....	22
3.2.8.3 Hardness.....	22
3.2.8.4 Tension set.....	22
3.2.9 Thermal properties.....	23
CHAPTER IV RESULTS AND DISCUSSION.....	24
4.1 Effect of radiation dose on crosslinking of natural rubber	24
4.2 <i>In situ</i> formation of silica in radiation-prevulcanized natural rubber latex by sol-gel process.....	27
4.2.1 TEOS mixing step before and after irradiation.....	27
4.2.2 Dry rubber content in RVNR latex affecting the sheet casting process.....	28
4.3 Variation of alkoxysilane in the preparation of the <i>in situ</i> silica/RVNR composites.....	30
4.3.1 Extent of <i>in situ</i> silica formation in the RVNR composites.....	31

	Page
4.3.2 Morphology and distribution of silica in the composites.....	33
4.4 Preparation of the <i>in situ</i> silica/RVNR composites using mixed silanes.....	35
4.4.1 General observation.....	35
4.4.2 Extent of <i>in situ</i> silica formation from mixed silane in the RVNR composites.....	38
4.4.3 Morphology of the <i>in situ</i> silica in the composites using the mixed silanes.....	39
4.5 Solid state ^{29}Si NMR analysis.....	40
4.6 Swelling behavior of the <i>in situ</i> silica/RVNR composites.....	43
4.7 Physical properties of the <i>in situ</i> silica/RVNR composites.....	44
4.8 Relationship between chemical structure of silica and physical properties of rubber.....	49
4.9 Thermal properties of the <i>in situ</i> silica/RVNR composites.....	50
CHAPTER V CONCLUSIONS AND FUTURE DIRECTION.....	52
5.1 Conclusions.....	52
5.2 Future Direction.....	53
REFERENCES.....	54
APPENDIX.....	57
VITAE.....	62

LIST OF FIGURES

Figure	Page
2.9 cis-1,4-polyisoprene.....	3
2.10 Sketches of primary particle, aggregate and agglomerates occurring in silica.....	9
2.11 Typical shape of a flat polymer sample used stress-strain test.....	14
2.12 Mechanical testing: a) Tensile stretching of a bar; b) Shear of a rectangular block.....	14
2.13 Shaping of standard tear specimens, A, B, C, and T.....	15
3.1 Shape of rubber sample for tear test.....	22
3.2 Shape of rubber sample for tension set test.....	22
4.1 Degree of swelling in toluene of the RVNR films after various doses of radiation on the latex. (Each data point was averaged from 3 sample sets).....	25
4.2 Water absorption of the RVNR films after various doses of radiation on the latex. (Each data point was averaged from 3 sample sets).....	25
4.3 Modulus at 300% elongation (M300) of RVNR films after various doses of radiation on the latex. (Each data point was averaged from 5 sample sets).....	26
4.4 Tension set (%) of RVNR films after various doses of radiation on the latex. (Each data point was averaged from 3 sample sets).....	26
4.5 SEM micrographs of fractured surface of <i>in situ</i> silica which were generated (a) before and (b) after gamma irradiation. [upper images 2,000x; lower images,10,000x].....	28
4.6 Photographs of the <i>in situ</i> silica/RVNR films, prepared from latex containing (a) 30%, (b) 40%, (c) 50%, and (d) 60% DRC.....	29
4.7 Changes of silica content and %conversion of TEOS to silica as a function of heating time for the <i>in situ</i> silica/RVNR composites.....	30
4.8 Chemical structures of TEOS, VTOS, and ETOS.....	30

	page
4.9 Photographs of the <i>in situ</i> silica/RVNR films; (a) from green NR, (b) from RVNR, (c) RVNR added with TEOS, (d) RVNR added with VTOS, and (e) RVNR added with ETOS (<i>note-</i> the amount of all added silane was 50 phr).....	31
4.10 SEM micrograph of the fractured surface of <i>in situ</i> silica/RVNR composites prepared from RVNR latex mixed with 50 phr of (a) TEOS, (b) VTOS (left images, 2,000x; right image, 10,000x).....	34
4.11 Photograph of the <i>in situ</i> silica/RVNR films using TEOS/VTOS mixed with (a) T5V45, (b) T15V35, (c) T25V25, (d) T35V15 and (e) T45V5 (Total silane = 50 phr).....	36
4.12 Photograph of the <i>in situ</i> silica/RVNR films using TEOS/ETOS mixed with (a) T5E45, (b) T15E35, (c) T25E25, (d) T35E15 and (e) T45E5 (Total silane = 50 phr).....	37
4.13 SEM images of the fractured surface of the <i>in situ</i> silica/RVNR composites using 'TEOS/VTOS' mixed with (a) T5V45 and (b) T45V5.....	39
4.14 SEM images of the fractured surface of the <i>in situ</i> silica/RVNR composites using 'TEOS/ETOS' mixed with (a) T5E45 and (b) T45E5.....	40
4.15 ²⁹ Si CP/MAS NMR spectra of (a) T50, (b) V50, (c) E50, (d) T45V5 and (e) T45E5.....	42
4.16 Degree of swelling in toluene of the <i>in situ</i> silica/RVNR composites prepared from different amounts of alkoxy silanes. (Each data point was averaged from 3 sample sets).....	43
4.17 Water absorption of the <i>in situ</i> silica/RVNR composites prepared from different silanes. (Each data point was averaged from 3 sample sets).....	44
4.18 Changes in modulus at 300% elongation of the <i>in situ</i> silica/RVNR sheet as a function of silica content (Each data point was averaged from 5 sample sets.).....	45

	Page
4.19 Changes in modulus at 300% elongation of the <i>in situ</i> silica/RVNR sheet as a function of silane type (Each data point was averaged from 5 sample sets.).....	46
4.20 Changes in hardness of the <i>in situ</i> silica/RVNR sheet as a function of added alkoxy silane loading (Each data point was averaged from 5 point in a sample.).....	46
4.21 Changes in tension set of the <i>in situ</i> silica/RVNR sheet as a function of silica content(Each data point was averaged from 3 sample sets).....	47
4.22 Changes in tension set of the <i>in situ</i> silica/RVNR sheet as a function of silane type (Each data point was averaged from 3 sample sets).....	48
4.23 Changes in tear strength of the <i>in situ</i> silica/RVNR sheet as a function of silica content(Each data point was averaged from 3 sample sets).....	49
4.24 Changes in tear strength of the <i>in situ</i> silica/RVNR sheet as a function of silane type(Each data point was averaged from 3 sample sets).....	49
4.25 TGA thermogram of the <i>in situ</i> silica/RVNR composites.....	50

LIST OF TABLES

Table	Page
2.1 The composition of typical field latex.....	3
2.2 Types of preservative system used in centrifuged NR latex concentrate..	4
2.3 Formulation of vulcanization of NR latex.....	5
3.1 Variation of silane for the formation of silica in RVNRL.....	19
4.1 Content and %conversion of silica generated in the RVNR composites	32
4.2 Silica content and %conversion of silica generated in the RVNR composites by mixed silanes.....	38
4.3 Designation of the various structural units of silicon atoms in TEOS and alkyltrialkoxysilane.....	41
4.4 Onset temperature, mass change and residual mass of the <i>in situ</i> silica/RVNR composites.....	51
A-1 Water absorption (%) of the <i>in situ</i> silica/RVNR composites.....	58
A-2 Hardness (shore A) of the <i>in situ</i> silica/RVNR composites.....	58
A-3 Stress of the <i>in situ</i> silica/RVNR composites at various elongation.....	59
A-4 Tension set (%) of the <i>in situ</i> silica/RVNR composites.....	60
A-5 Tear strength of the <i>in situ</i> silica/RVNR composites.....	60
A-6 TGA analysis of the <i>in situ</i> silica/RVNR composites	61

LIST OF SCHEMES

Scheme	Page
2.1 Radioactive decay of cobalt.....	6
2.2 Primary and secondary processes in irradiated polymers.....	7
2.3 Natural rubber formation by radiation.....	8
2.4 Hydrolysis and condensation reaction of TEOS to form silica.....	10
2.5 Acid-Catalyzed Hydrolysis.....	11
2.6 Base-Catalyzed Hydrolysis.....	11
2.7 Hydrolysis and condensation of trialkoxysilanes to give polysilsesquioxane.....	12
3.1 Chemical equation for the conversion of TEOS to silica.....	20
3.2 Chemical equation for the conversion of alkyltriethoxysilane to silica	20



 สถาบันวิทยบริการ
 จุฬาลงกรณ์มหาวิทยาลัย

LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
BA	Boric acid
BTOS	butyltriethoxysilane
°C	Degrees Celsius
CP MAS NMR	Cross-polarization magic angle spinning nuclear magnetic resonance
DRC	Dry rubber content
DTA	Dynamic thermal analysis
ETOS	Ethyltriethoxysilane
HA	High ammonia
kGy	kilogray
LA	Low ammonia
mm	Millimeter
MPa	Megapascal
M300	modulus at 300% elongation
N	Newton
NR	Natural rubber
phr	Part per 100 grams of rubber

PVA	Polyvinyl alcohol
RVNR	Radiation vulcanized natural rubber
RVNRL	Radiation vulcanization of natural rubber latex
SBR	Styrene-butadiene rubber
SEM	Scanning electron microscopy
SPP	Sodium pentachlophenate
TEM	Transmission electron microscopy
TEOS	Tetraethoxysilane
TGA	Thermal gravimetric analysis
TMOS	Tetramethoxysilane
TMTD	Tetramethyl thiuram disulfide
TZ	Tetramethyl thiuram disulfide and zinc oxide
VTOS	Vinyltriethoxysilane
ZnO	Zinc oxide

CHAPTER I

INTRODUCTION

1.1 Statement of problems

Natural rubber is vulcanized to improve the physical properties of rubber making it suitable for manufacturing a large number of products. Vulcanization is in fact a crosslinking process and can be carried out by adding chemicals such as sulfur and peroxide compounds or by gamma irradiation. The radiation vulcanization of rubber latex is an emerging technology whereby radiation is used in place of sulfur in the conventional vulcanization process. The radiation vulcanized natural rubber latex (RVNRL) has many advantages over conventional vulcanizates such as the absence of toxic nitrosamines, better degradability, transparency and softness [Ratnam, 1999].

However, their physical properties not all only tear strength are known to be inferior to those of sulfur vulcanizates. Therefore reinforcement is necessary to improve the mechanical properties of designated products. Beside carbon black, silica is the other importance filler used in the rubber industry. Conventionally, precipitated silica is mixed with rubber gum by mechanical mixing. This often lead to agglomeration of silica particles inside the rubber composite, resulting in a poor dispersion of these particles. One of the methods for overcoming these difficulties is generation of silica in the rubber matrix. The *in situ* formation of silica is achieved by polymerization of tetraethoxysilane (TEOS) via a sol-gel process. The advantage of *in situ* generation over mechanical mixing is that rubber and silica are able to interact more intimately, lowering the agglomeration of each particle. In 2003, the sol-gel reaction of TEOS was carried out in natural rubber latex for compounding rubber and silica. The composite containing *in situ* silica had a higher tensile modulus and tear strength than the composite prepared by conventionally mixing with silica powder [Daranee, 2003].

In this work, the focus was to reinforce the radiation-prevulcanized natural rubber by silica generated *in situ*. Three types of silanes; tetraethoxysilane (TEOS), vinyltriethoxysilane (VTOS), and ethyltriethoxysilane (ETOS), were used as precursors

to generate the silica particles. The silane was added to the prevulcanized latex. Then the mixture was heated at 50 °C in order to completely cure the rubber and to initiate the sol-gel process of the silane to form silica inside the rubber matrix. It was hypothesized that the *in situ*-generated silica particle can disperse evenly in the rubber vulcanizate. Swelling behavior and mechanical properties of silica-RVNR sheets were also investigated as a function of type and amount of alkoxy silanes used.

1.2 Objectives

To reinforce the radiation-vulcanized natural rubber by silica generated *in situ*. Distribution, morphology of silica particles and mechanical properties of the *in situ* silica-filled RVNR sheets were studied as a function of type and amount of alkoxy silanes.

1.3 Scope of the investigation

The stepwise investigation was carried out as follows:

1. Preparation of radiation-prevulcanized natural rubber latex
2. *In situ* generation of the silica in pre-vulcanized natural rubber latex using single and mixed silanes
3. Determination of silica content in the composites and %conversion of silane to silica
4. Microscopic analysis of the *in situ* silica/RVNR composites by using SEM
5. Measurement of mechanical properties of the *in situ* silica/RVNR composites- modulus at 300% elongation (M300), tear strength, tension set, and hardness
6. Measurement of thermal properties of the *in situ* silica/RVNR composites by TGA

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Natural rubber

Natural rubber is obtained from the milky white fluid called “latex”, found in many plants. The most important of these plants are the tree *Hevea brasiliensis*. Natural rubber is known chemically as polyisoprene and consists of the simplest unit, isoprene, which has the chemical formula C_5H_8 (Figure 2.1). In its natural state, rubber exists as a colloidal suspension in the latex. The colloid is stabilized by naturally occurring proteins and phospholipids at the surface of the rubber particles. It also contains other materials such as sugars, resins, mineral salts and alkaloids. The composition of typical field latex is shown in Table 2.1.

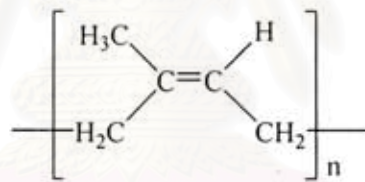


Figure 2.1 cis-1,4-polyisoprene

Table 2.1 The composition of typical field latex

Constituent	Composition (%)
water	55-65
rubber particles	30-40
protein	2.0-3.0
resins	1.5-3.5
sugars	1.0-2.0
ash	0.5-1.0
sterol glycosides	0.1-0.5

Field latex is not utilized in its original form due to its high water content. Latex concentrate usually made by centrifugation-spinning at high speed to separate a cream containing 60% dry rubber content. A small amount of ammonia and/or some chemical is added to the concentrated latex to prevent it from coagulation. Details of the preservation systems used in centrifuged concentration are given in Table 2.2.

Table 2.2 Types of preservative system used in NR latex.

Designation	Abbreviation	Preservative system (%by weight)
High or full ammonia	HA	min 0.6% ammonia
Low ammonia TZ	LA-TZ	max 0.29% ammonia, max 0.1% zinc oxide, max 0.1% tetramethylthiuram disulphide
Low ammonia pentachlorophenate	LA-SPP	max 0.3% ammonia, max 0.2% sodium pentachlorophenate
Low ammonia boric acid	LA-BA	max 0.3% ammonia, max 0.24% boric acid

2.2 Radiation vulcanization of natural rubber

Natural rubber is sticky and non-elastic. The crosslinking of NR molecules makes NR elastic. Crosslinking is a reaction of polymers to form a three-dimensional network, resulting in changes in the physical properties of polymers. Tensile strength and modulus increase, while the elongation at break decreases by the crosslinking. NR is too weak for practical uses without crosslinking. Heat and solvent resistance are improved by crosslinking.

Sulfur vulcanization, peroxide vulcanization and radiation vulcanization are known methods for the vulcanization of NR latex. Generally, the sulfur vulcanization system is still the most popular one which is widely used in the rubber industry. It has

been evolving over time. However, radiation vulcanization of natural rubber latex (RVNRL) is an emerging technology whereby radiation is used in place of sulfur in the conventional vulcanization process for the manufacture of dipped NR latex products. The radiation process involves the irradiation of natural rubber latex in the presence of sensitizers resulting in the crosslinking of the latex. The products obtained have noticeable advantage over the conventionally vulcanized natural rubber latex due to the absence of the carcinogenic nitrosamines derived from the common accelerators of the sulfur vulcanized natural rubber latex, lower levels of cytotoxicity and allergic reactions, faster degradation in the environment, and absence of acid combustion gases. The rise in the environmental consciousness among consumers has boosted the potential for RVNRL.

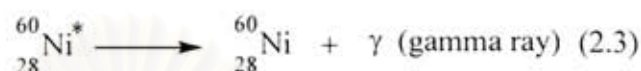
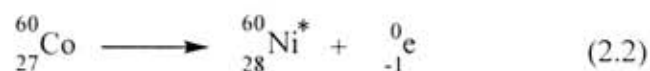
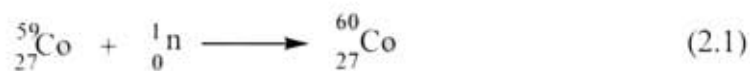
Table 2.3 Formulation of vulcanization of NR latex [Makuuchi, 2003]

Ingredient	Vulcanization technique	
	Sulfur	Radiation
HA NR latex	167 g	167 g
10% KOH	2.5 g	2.5 g
20% potassium laurate	1.3 g	-
50% Sulfur	2.0 g	-
50% ZDEC	0.8 g	-
50% ZnO	0.4 g	-
n-BA	-	5 g
water	-	30 g

Radiation source

Gamma rays (γ) are widely used for the sterilization of medical devices and food irradiation on a large scale. Gamma rays are electromagnetic waves. The most widely used gamma rays emitter is cobalt-60, a radioisotope produced by the activation

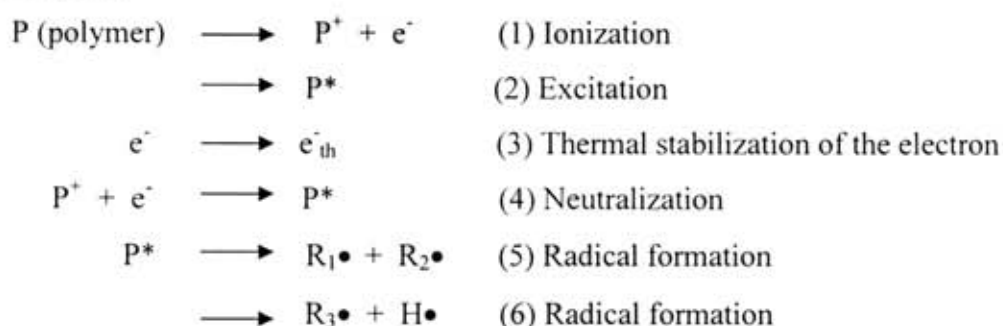
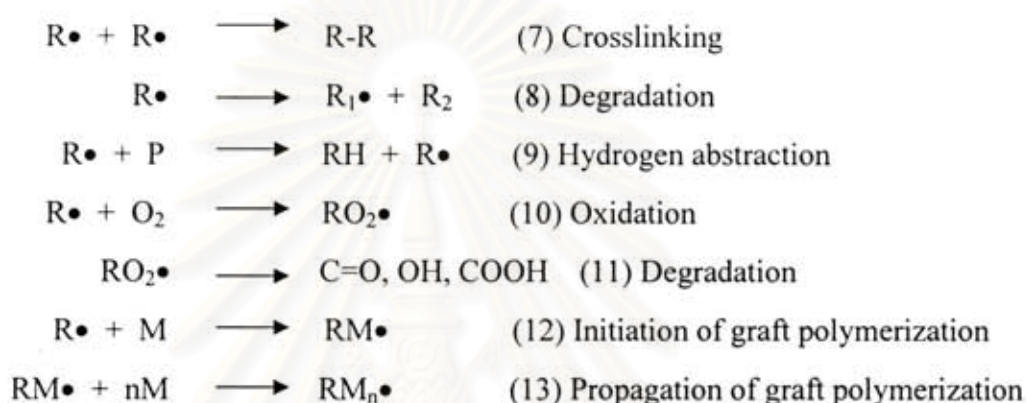
of Co-59 in a nuclear reactor. The gamma ray decay of Co-60 produces the stable isotope Ni-60 (Scheme 2.1), [Makuuchi, 2003].



Scheme 2.1 Radioactive decay of Cobalt

Radiation reaction

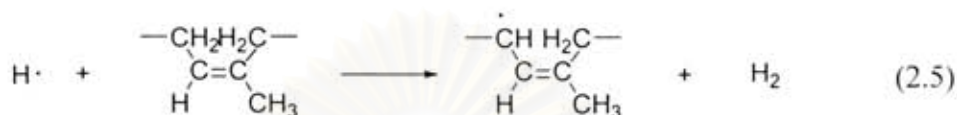
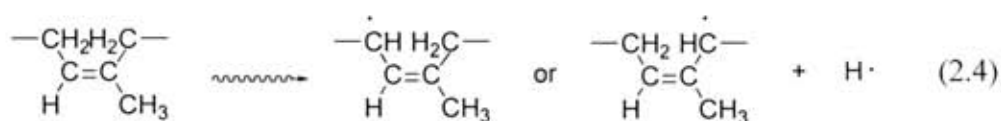
The principal chemical reactions of a polymer induced by radiation are shown in Scheme 2.2. The primary reactions of radiation with polymers are the production of electron, positively charged polymer and excited polymer. These reactions occur in a very short time. The ions, electrons and excited polymers undergo further reactions and produce polymer radicals and other reactive species in the secondary process. Excitation is immediately followed by the dissociation of the resulting electronically excited molecule into free radicals ((5) and (6)). The reaction (5) leads to degradation of the polymer. All radiation-induced reactions result from the interaction of these active species with themselves or with the molecules of the surrounding medium. Free radicals are responsible for a large variety of chemical changes induced by radiation. The recombination of polymer radicals formed during the radiolysis of a polymer results in crosslinking (7). If the irradiated medium contains polymerizable unsaturated molecules (C=C), the primary radicals add to the double bonds, thereby initiating polymerization. Irradiation of a polymer in the presence of a monomer results in graft polymerization by the sequence of reaction given in equations (12) and (13) [Makuuchi, 2003].

Primary ProcessSecondary Process**Scheme 2.2** Primary and secondary processes in irradiated polymersRadiation crosslinking of natural rubber

The main components of the NR latex are rubber particles and water. NR and water molecules independently absorb radiation energy such as gamma radiation. The NR radicals are generated by radiolysis of the NR molecules in the NR particles. The natural rubber radicals recombine with each other to form crosslink.

Polyisoprene contains unsaturated C=C bond that is crosslinkable. Two types of allyl radicals are formed by the abstraction of a hydrogen atom from methylene by the action of radiation (reaction (1) in Scheme 2.3). The hydrogen atom abstracts another hydrogen from the immediate vicinity, resulting in hydrogen gas evolution and the formation of an allyl radicals (reaction (2) in Scheme 2.3). The reactions of NR radicals are recombination, abstraction of hydrogen atom and addition to an unsaturated C=C bond provides formation of a crosslink. However, the radiation crosslinking efficiency of natural rubber is not as high as expected. This is probably due to the loose packing of natural rubber molecules with the *cis* structure and the presence of methyl groups.

These make it difficult for natural rubber radicals to approach an unsaturated C=C bond [Makuuchi, 2003].



Scheme 2.3 Natural rubber formation by radiation

RVNRL has been investigated for a long time. The first report appeared in 1956 as a patent which claimed a successful crosslinking of natural rubber latex by irradiating latex with the dose more than 300 kGy and without a sensitizer [Gehman and Auerbach, 1956]. Later on, several kinds of sensitizers were used to reduce the radiation dose, such as carbon tetrachloride, 2-ethylhexyl acrylate (2-EHA) and N-butyl acrylate (n-BA), etc. n-BA, which is a sensitizer, has higher vapour pressure than 2-EHA and tends to reduce the stability of natural rubber latex. Thus some stabilizers are used to prevent the latex from coagulation due to the addition of sensitizer. Zhonghai and Makuuchi (1989) obtained the optimum vulcanization dose of 15 kGy using 5 phr of n-BA with potassium hydroxide as a stabilizer.

2.3 Reinforcement

Although NR is known to exhibit numerous outstanding properties, reinforcing fillers are necessarily added into natural rubber in most cases in order to gain the appropriate properties for specific applications. Reinforcement is primarily the enhancement of strength and strength-related properties, abrasion resistance, hardness and modulus. In most applications, carbon black and silica have been used as the main reinforcing fillers that increase the usefulness of rubbers.

The increase in stiffness imparted by the filler particles involves a hydrodynamic effect which depends on the filler volume fraction, but the occlusion of

rubber by the aggregate and the rubber trapped within the filler agglomerates may increase the effective filler volume. On the other hand, the shape factor (anisometry) also contributes to the increase in moduli.

However, the most important contribution to the elastic modulus arises from polymer/filler interactions which can be increased if a good dispersion of the filler is achieved. These interactions depend on the surface characteristics of the particles (active sites and surface free energy) and also on the chemical nature of the polymer [Bokobza, 2005].

2.4 Silica

In rubber industry, besides carbon black, silica is the other reinforcing filler used to impart specific properties to rubber compounds. Silica is an inorganic material which consists of ultimate particles of the silicon dioxide $(\text{SiO}_2)_n$. Silicon atom is covalently bonded in a tetrahedral arrangement to four oxygen atoms. Each of the four oxygen atoms is covalently bonded to either one silica atom forming a siloxane (-Si-O-Si-) or to a hydrogen forming a silanol (-Si-O-H) functionality.

Aggregates are three-dimensional clusters of ultimate particles. Aggregates can physically agglomerate through intermolecular hydrogen bonding of surface silanol groups of one aggregate to a silanol group of other aggregate.

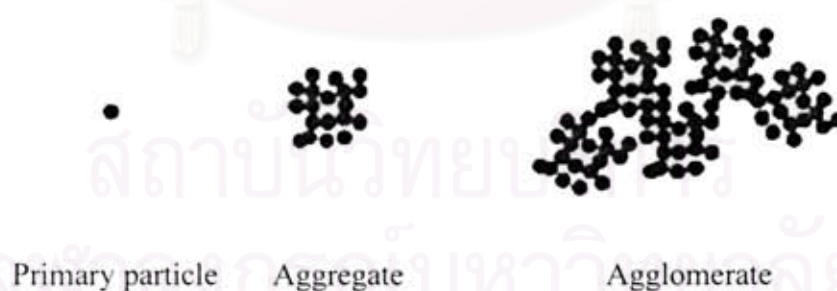


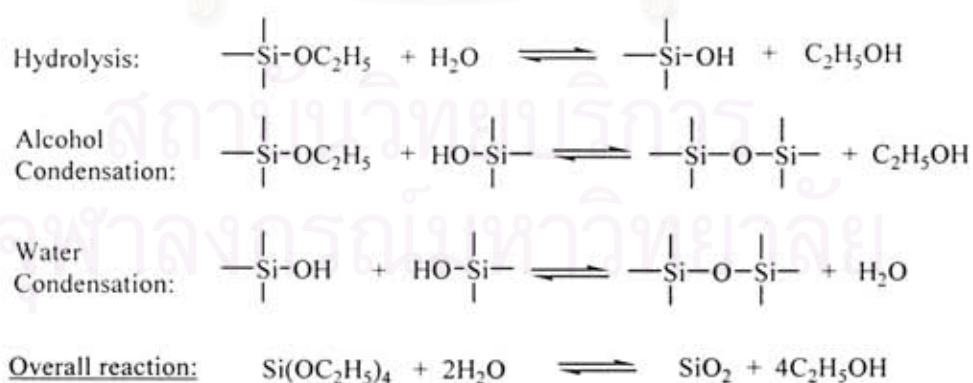
Figure 2.2 Sketches of a primary particle, aggregates and agglomerates occurring in silica [Mark, J.E., 2005]

In 2003, Thiangchanya *et. al.* prepared the RVNRL film filled fumed silica and hydroxy apatite. Concentrated HA latex was diluted to 50%DRC using 1% ammonia solution and stabilized by 0.2 phr of KOH. 5 phr of n-BA was added as sensitizer. The

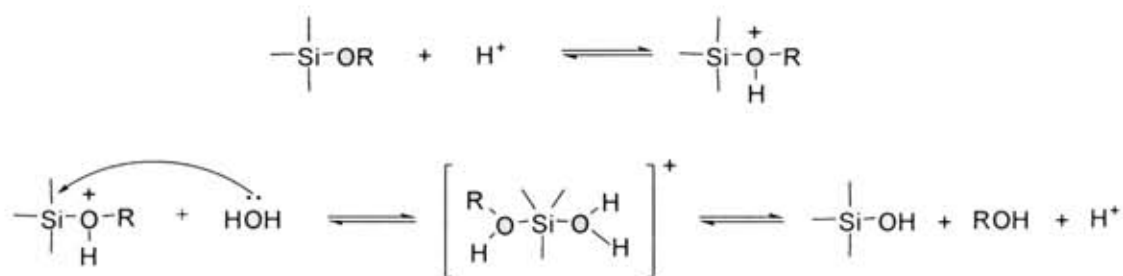
mixture was irradiated in a gamma irradiator with a total vulcanization dose of 13.5 kGy. The RVNRL was mixed with fume silica or hydroxyl apatite dispersion. Maturation of the mixture was for at least 3 days before casting into films. They reported that, at 2 phr for both fume silica and hydroxyl apatite in RVNRL, tear and aging properties of the latex films were improved. Trouser tear strength of the films increased from 5 kN/m to 10 kN/m, while the tensile strength was unchanged. The absence of the mastication might probably be the reason since mastication could induce filler-rubber interaction.

2.5 Sol-gel process for polymer reinforcement

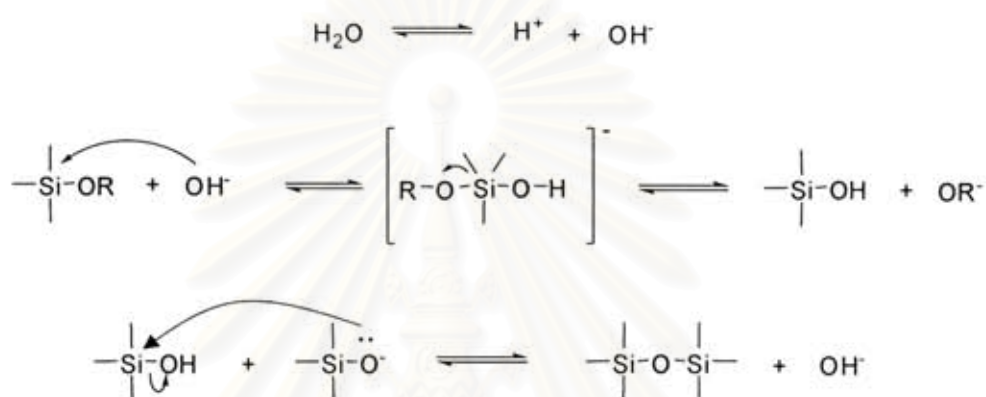
This process occurs in liquid solution of metal alkoxide precursors (TMOS, TEOS, etc.), which, by means of hydrolysis and condensation reactions, leading to the formation of a new phase-called 'sol'. The sol is made of solid particles of a diameter of few hundreds of nanometer suspended in a liquid phase. Then the particles condense into a new phase, called 'gel' in which a solid macromolecule is immersed in a liquid phase (solvent). Hydrolysis and condensation reaction of TEOS to form silica is shown in Scheme 2.4. The mechanisms of acid-catalyzed hydrolysis and base-catalyzed hydrolysis are shown in Schemes 2.5 and 2.6, respectively. The fundamental property of the sol-gel process is that it is possible to generate a ceramic material at a temperature close to room temperature.



Scheme 2.4 Hydrolysis and condensation reactions of TEOS to form silica



Scheme 2.5 Acid-catalyzed hydrolysis



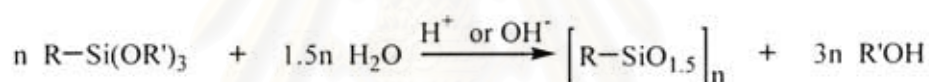
Scheme 2.6 Base-catalyzed hydrolysis

Recently, the sol-gel process has been widely applied to generate *in situ* reinforcing material for a number of systems such as butadiene rubber [Kohjiya,1996], styrene-butadiene rubber [Ikeda, 1997], polyamide-6,6 [Bhowmick, 2005], urethane acrylate [Han, 2007], PVA [Jia, 2007], and natural rubber [Kohjiya, 2001; Ansarifar, 2005; Bokobza, 2005].

In situ reinforcement of natural rubber was extensively studied by Kohjiya and Ikeda. In 2000, Kohjiya *et al.* prepared the *in situ* silica filling in the rubber matrix before vulcanization. The NR sheet of ca. 1 mm thickness was immersed in TEOS and aqueous solution of *n*-butylamine to follow the sol-gel reaction of TEOS. The *in situ* silica-filled NR was then compounded with ingredients for the sulfur vulcanization reaction on a two-roll mill and vulcanized at 150 °C in the compression mold. Fine and well-dispersed *in situ* silica particles were generated by the sol-gel reaction of TEOS in the rubber matrix before vulcanization. The silica did not inhibit much the crosslinking reaction of the NR compound by sulfur, which suggested that the amount of silanol groups on the surface of *in situ* silica was lower than that of conventional silica and *in*

situ silica-filled NR vulcanizates improved the mechanical properties. Since the filling of *in situ* silica was conducted before curing, this method is more useful as an industrially practical technique than the method in which the sol-gel reaction of TEOS was carried out after the rubber vulcanization. However, the degree of TEOS diffusion into rubber matrix could be a limitation for this method.

Organotrialkoxysilanes, $\text{RSi}(\text{OR}')_3$, are sol-gel precursors. They are commonly used to modify surfaces for composite materials, to prepare coatings for microelectronics and photonics applications, and as monomers for forming hybrid organic-inorganic materials. For the latter, organotrialkoxysilanes are typically copolymerized with another sol-gel monomer—generally tetramethoxysilane (TMOS) or tetraethoxysilane (TEOS). The sol-gel polymerization of organotrialkoxysilanes involving hydrolysis and condensation usually results in the formation of low molecular weight silica (Scheme 2.7).



Scheme 2.7 Hydrolysis and condensation of trialkoxysilanes to give polysilsesquioxane

The remaining substituent is an organic group attached to the silicon atom through a silicon-carbon single bond. The formation of interaction or chemical bonds between the inorganic and organic components is expected to be of great importance in guarantee a durable chemical junction between the two incompatible phases.

In 1999, Hsiue *et al.* prepared polyimide-silica (PI-SiO₂) hybrids with silica particles at a nanometer scale. Polyimide-silica hybrids were obtained using the nonaqueous sol-gel process by polycondensation of phenyltriethoxysilane (PTEOS) in a poly(amic acid) solution. PTEOS and poly(amic acid) react in a flask in tetrahydrofuran (THF) as a solvent. The mixture was then stirred for about 24 h until the reaction solution became homogeneous. They found that PTEOS introduced phenyl groups into the final formed silica network, to increase the compatibility between the organic polyimide and the inorganic silica network. Since the resulting polyimide-silica hybrids are transparent while containing a high silica content of 45%. The increase of the silica

contents in the hybrid, promotes the compatibility of polyimide and silica, and, consequently, brings about some benefits in improving their physical and mechanical properties.

In 2005, Siramanon prepared NR vulcanizates filled with silica using alkyltrialkoxysilanes (VTOS, ETOS and BTOS) and TEOS as precursors to generate the silica *in situ*. Conversion of the silanes to silica in the NR matrix is in order TEOS > VTOS > ETOS > BTOS. The *in situ* generated silica particles from TEOS alone and alkyltriethoxysilanes/TEOS were well dispersed in the NR matrix without noticeable agglomeration, as was observed in the mechanically mixed silica-filled vulcanizate. The size of the *in situ* silica particles in the vulcanizate observed by TEM is approximately 40 nm, and not depending on the silane types. The mechanical properties of the *in situ* silica-filled NR vulcanizates are higher than NR vulcanizate filled with silica powder (Hisil-255). Furthermore, these three mechanical properties of the *in situ* silica-filled NR vulcanizates were increased with increasing amount of VTOS in the VTOS/TEOS formulation from 5 to 20% of the total silanes.

2.6 Mechanical Testing [Morton, 1973]

2.6.1 Tensile stress-strain

Physical testing of rubber often involves application of a force to a specimen and measurement of resultant deformation or application of a deformation and measurement of the required force. In practice, stress-strain experiments are often carried out on a flat sample that has been shaped into the form as shown in Figure 2.3.

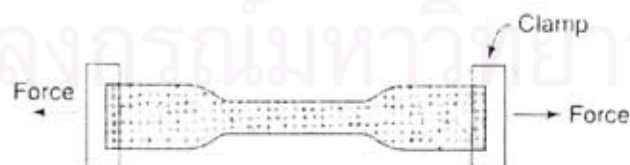


Figure 2.3 Typical shape of a flat polymer sample used for stress-strain test

Two common modes of deformation, tensile and shear are shown in Figure 2.4. Stress is the force per unit cross sectional area (F/A). Strain is the deformation per unit

of the original length ($\Delta L/L$) in tensile tests or deformation per unit distance between the contacting surfaces (S/D) in shear tests. Stress is usually expressed in a unit of Newton per square meter ($N\ m^{-2}$). Strain is usually expressed in percent. Material stiffness is determined by modulus, which is defined as the ratio of stress to strain.

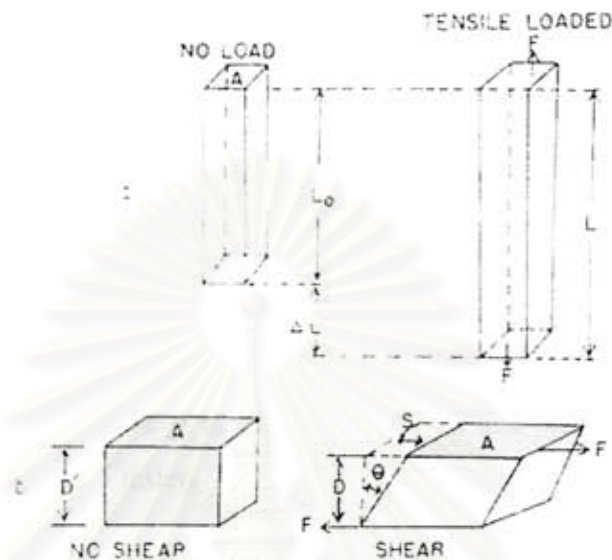


Figure 2.4 Mechanical testing: a) Tensile stretching of a bar; b) Shear of a rectangular block

2.6.2 Tear resistance

High stress concentration on a rubber product applied at a cut or defect area during service can lead to the propagation of a tear or rupture. Different rubber vulcanizates show different resistance to tear. Tear characteristics for a compound can be related to the compound's crosslink density and state of cure, as well as filler type and loadings. The force to initiate a tear is quite different from the forces required to propagate a tear. Various tear tests place a deliberate flaw in a rubber specimen to try to relate to the tear propagating force.

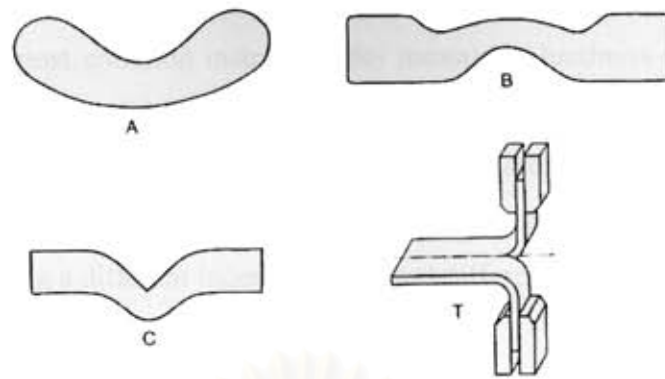


Figure 2.5 Shapes of the standard tear specimens, A, B, C, and T

Figure 2.5 shows the shapes of some commonly used tear test pieces which are described in ASTM D624. Die B is a crescent-shaped test piece with large ends for better gripping in a tensile tester. This specimen is nicked with a razor blade to a specified depth to help initiate a tear. The Die C test piece has an angle to help initiate a tear and does not necessarily require a cut nick. The Die T Trouser tear specimen is separated by a shear force from the tension applied in opposite directions to each leg at right angles to the plane of the test piece. The tear strength (T_s) is reported as kilonewton meter⁻¹ of thickness from the formula:

$$T_s = F/d \quad (1)$$

where F = maximum force (in N), for dies B and C, and the median or mean for die T (trouser), and d = test piece thickness in mm.

In accordance with the fracture mechanics, tearing energy theoretically is a basic material property that is truly independent of the cut geometry and geometry of the rubber specimen. Most standard tear tests do not measure tearing energy. A modified Trouser tear comes closed to relating to true tearing energy; however, features such as the width of the cut and variations in cut geometry, among others, can greatly affect accuracy of the results.

2.6.3 Hardness

Hardness, as applied to rubber, may be defined as the resistance to indentation under conditions which do not puncture the rubber. Hardness must be expressed in

terms of instrument parameters rather than in basic units. The spring-loaded pocket durometer is the most common instrument for measuring hardness of elastomers. The shore durometer (ASTM D2240) in particular is generally used. In this instrument the scale runs from zero hardness for a liquid to 100 for a hard plane surface such as glass. The type A durometer is used for soft stocks, up to a reading of 90. Above 90 the type D durometer, having a different indenter shape and different stiffness spring, is used.

2.6.4 Tension set

The term “tension set” refers to the strain remaining after complete release of the load producing a deformation. ASTM D412 describes methods for evaluating tension set. The usual measurement of the set is intended to evaluate delayed elastic recovery. If chemical changes have occurred, however, the residual deformation may be permanent. It is expressed as a percentage of the original length or distance between gauge marks.

2.7 Swelling behavior

Two of the most widely recognized effects of reinforcing fillers are changes in the mechanical properties of the composites and their swelling. A reinforced vulcanized rubber possesses a substantial increase in stiffness (modulus) and a reduction in the extent to which the vulcanizate will swell in a rubber solvent. Both of these effects can also be achieved quantitatively by increasing the degree of crosslinking of the rubber. Reinforcing fillers such as carbon black interact strongly with unsaturated hydrocarbon rubbers during milling or during mastication in an internal mixer. The amount of rubber which remains associated with the filler when the mixture is subsequently immersed in a rubber solvent (‘bound rubber’) is often used as a measure of this interaction (The quantity of bound rubber normally increases on storage or heating of the rubber-filler ‘mix’). Thus, the rubber is adsorbed on the filler surface and this alters the stress-strain properties and reduces the extent of swelling in a solvent. Since stress-strain and equilibrium volume swelling measurements are the principal means of assessing crosslink density, it becomes very difficult to measure crosslink density when a reinforcing filler is present in the rubber because the effects of crosslink cannot be readily distinguished from the effects of rubber-filler interaction.

2.8 Thermal Analysis

Thermal analysis generally covers three different experimental techniques: Thermo Gravimetric Analysis (TGA), Differential Thermal Analysis (DTA), and Differential Scanning Calorimetry (DSC). For all experiments a selection of crucibles are available (platinum, gold, aluminum, quartz) and the measurements can be done in a flow of different gases.

The basic principle in TGA is to measure the mass of a sample as a function of temperature. It is a measurement of weight loss when the cured adhesive is gradually heated ($10\text{-}20\text{ }^{\circ}\text{C min}^{-1}$). In principle, this simple measurement is an important and powerful tool in solid state chemistry and materials science. The method for example can be used to determine water of crystallisation, follow degradation of materials, determine reaction kinetics, study oxidation and reduction, or to teach the principles of stoichiometry formula and analysis.



สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

CHAPTER III

MATERIALS AND METHODS

3.1 Materials

Natural rubber latex, a high ammonia (HA, min 0.6%) type with 60% dry rubber content (DRC) without TMTD and ZnO, was obtained from Pan Asia Biotechnology Co., Ltd., Thailand. Tetraethoxysilane (TEOS), vinyltriethoxysilane (VTOS), ethyltriethoxysilane (ETOS), normal-butyl acrylate (n-BA) were purchased from Fluka, Germany. Potassium hydroxide pellet and acetic acid were purchased from Merck, Germany. Ammonia solution was purchased from BDH, England.

3.2 Experimental Methods

3.2.1 Determination of dry rubber content (%DRC) of latex

An aliquot of 1 g of latex was weighed in a Petri dish and coagulated with 5% acetic acid in water. After complete coagulation, the coagulum was removed, washed with water, squeezed and dried in an oven at 70 °C until it became transparent. The dried coagulum was weighed. The DRC was calculated by the equation below :

$$\%DRC = W_r/W_l \times 100 \quad (3.1)$$

where W_l = latex weight (g), W_r = dried rubber weight (g).

3.2.2 Preparation of pre-vulcanized NR latex

High-ammonia concentrated NR latex with 60%DRC (without TMTD and ZnO) was diluted with 0.7% v/v ammonia solution to obtain a 50%DRC latex. In order to stabilize the latex during gamma radiation, KOH solution (10% w/v) was added to the diluted latex to obtain a final KOH content of 0.2 phr. Then 5 phr of n-BA was added dropwise to the mixture while stirring with a mechanical stirrer. After completing the addition of n-BA, the mixture was continuously stirred for 30 min and left overnight. About 1 liter

of the mixture was irradiated in a gamma irradiator, Co-60. The radiation dose was varied at a dose rate of 16.2 kGy h⁻¹. Radiation vulcanized natural rubber latex (RVNRL) was used in this study without adding any antioxidant.

3.2.3 *In situ* generation of silica in pre-vulcanized NR latex

Single or mixed silanes at various amount (Table 3.1) was added to the RVNRL while stirring to obtain a homogeneous milky mixture. The films of about 1 mm thick were prepared by pouring about 12.5 g of the latex mixture onto a circular glass plate having 9.5 cm in diameter and the plate was tightly closed with a cover glass to reduce silane and ammonia evaporation. The cover mold was heated at 50 °C. The heating time (gelation time) was varied from 6 hours to 7 days. After the closed heating step, the films were further dried at 50 °C for 1 day.

Table 3.1 Variation of silane amount for the formation of silica in RVNRL

No.	Code	Silane amount (phr)		
		TEOS	VTOS	ETOS
1	T50	50	-	-
2	V50	-	50	-
3	E50	-	-	50
4	T5V45	5	45	-
5	T15V35	15	35	-
6	T25V25	25	25	-
7	T35V15	35	15	-
8	T45V5	45	5	-
9	T5E45	5	-	45
10	T15E35	15	-	35
11	T25E25	25	-	25
12	T35E15	35	-	15
13	T45E5	45	-	5

3.2.4 Determination of silica content in the composites

Small pieces of composite films (50-60 mg) were placed in aluminum oxide cups and heated under air atmosphere, from room temperature to 850 °C in an oven (Carbolite GM 11/7). The temperature was kept at 850 °C for 15 minutes. The remaining ash was weighed. Silica content was calculated by

$$\text{Silica content (phr)} = [(W_1 - W_2)/W_3] \times 100 \quad (3.2)$$

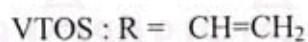
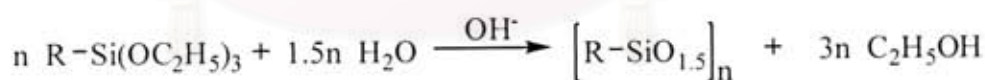
The conversion of silanes to silica was calculated by

$$\text{Conversion (\%)} = (W_4/W_5) \times 100 \quad (3.3)$$

where W_1 was the weight of remaining ash of silica-filled sample, W_2 was the weight of remaining ash of silica-free sample, W_3 was the weight of the initial silica/rubber sample, W_4 was the amount of *in situ* generated silica in the sample obtained from Eq. 3.2, and W_5 was the theoretical amount of silica generated assuming a quantitative conversion of silanes to silica by Schemes 3.1 and 3.2.



Scheme 3.1 Chemical equation for the conversion of TEOS to silica



Scheme 3.2 Chemical equation for the conversion of alkyltriethoxysilanes to silica

3.2.5 Swelling study

3.2.5.1 Swelling in toluene

Equilibrium swelling was measured using specimens having a 2.5 cm in diameter. The specimen was immersed in toluene for 24 hours. The excess solvent was padded off

before the samples were weighed. The swelling ratio was calculated using the following equation :

$$\text{Degree of swelling (\%)} = (W_s - W_i) / W_i \times 100 \quad (3.4)$$

where W_i = the initial weight of sample, W_s = the weight of swollen sample.

3.2.5.2 Swelling in water

Water absorption of the composites films was measured using specimens having a 2.5 cm in diameter. The sample was immersed in water at room temperature for 24 hours. Excess solvent was padded off before the sample was weighed. The water absorption was calculated by using Eq 3.4.

3.2.6 **Microscopic analysis**

The *in situ* silica-filled RVNR composites were fractured under liquid nitrogen. The samples were then sputter-coated with gold and the micrographs were taken by JEOL JSM-6400 scanning electron microscope (SEM). The SEM photographs were used to determine the dispersion and size of the silica particles in the rubber matrix.

3.2.7 **NMR Analysis of *in situ* silica/RVNR composites**

Solid-state ^{29}Si cross-polarization magic angle spinning (CP MAS) NMR spectra of the rubber composites were collected at 59.6 MHz on Bruker DPX-300. Up to 10,000 scans were carried out to obtain the appropriate signal-to-noise ratio. The aim of the ^{29}Si -NMR experiments was to identify the local environments of the silicon atoms bridging structures in the composites.

3.2.8 **Measurement of physical properties**

3.2.8.1 Tensile strength

Rubber films were stamped with a die cutter into a dumbbell shape, die E. Tensile properties were measured according to ASTM D412 using LLOYD Instruments

LS at a crosshead speed of 500 mm min^{-1} . The value reported for each sample was based on an average of five specimens.

3.2.8.2 Tear strength

Rubber films were cut into trousers shape as illustrated in Figure 3.1. Tear strength was measured using LLOYD Instruments LS at a crosshead speed of 250 mm min^{-1} . The value reported for each sample was based on an average of three specimens.

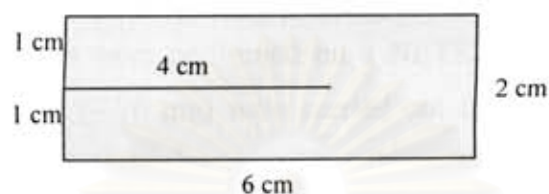


Figure 3.1 Shape of the rubber sample for tear test

3.2.8.3 Hardness

Hardness was measured using Durometer Hardness System (Shore A) Model 716 according to ASTM D2240. Measurements were taken from five different points distributed over the specimen.

3.2.8.4 Tension set

The rubber films were cut into a size of $0.5 \text{ cm} \times 6 \text{ cm}$. Two points which had about 1 cm apart were marked on the sample. The distance of the two points was measured by a Vernier caliper. The sample was extended until the distance between the two points was twice of the original length, and was held for 10 min. The sample was then allowed to retrace for 10 min. The final distance between the two points was measured.

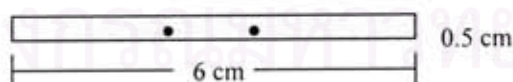


Figure 3.2 Shape of the rubber sample for tension set test

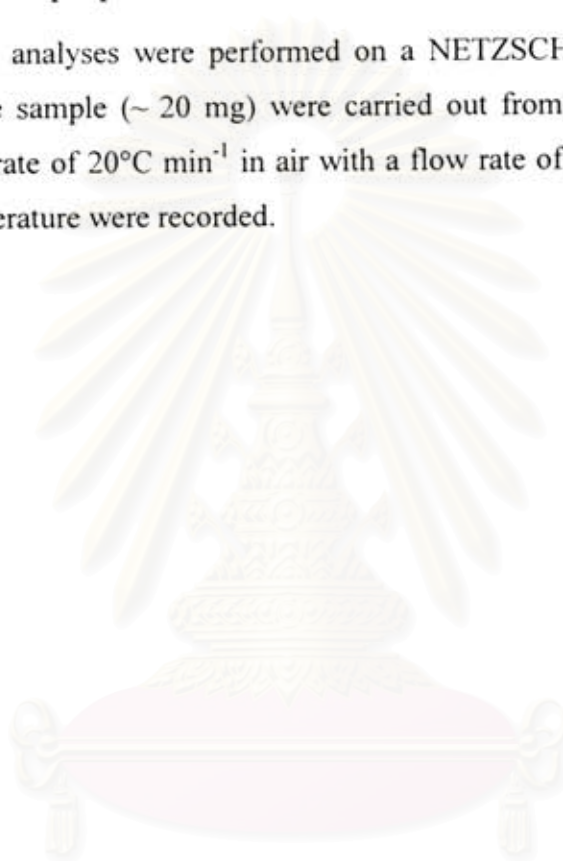
The tension set was calculated using the following equation:

$$\text{Tension set (\%)} = (L_f - L_i) / L_i \times 100 \quad (3.5)$$

where L_i = the initial distance between two points, L_f = the final distance of between two points

3.2.9 Thermal properties

Thermogravimetical analyses were performed on a NETZSCH STA 409 C/D. The measurements of the sample (~ 20 mg) were carried out from room temperature to 900 °C at a heating rate of 20°C min⁻¹ in air with a flow rate of 50 ml min⁻¹. Weight changes versus temperature were recorded.



สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

CHAPTER IV

RESULTS AND DISCUSSION

The results and discussion are divided into 7 parts as follows:

- 4.1 Effect of radiation dose on crosslinking of natural rubber
- 4.2 *In situ* formation of silica in radiation-vulcanized natural rubber latex by sol-gel process
- 4.3 Variation of alkoxy silanes in the preparation of the *in situ* silica/RVNR composites
- 4.4 Preparation of the *in situ* silica/RVNR composites using mixed silanes
- 4.5 Solid-state ^{29}Si NMR analysis
- 4.6 Study of swelling behavior of the *in situ* silica/RVNR composites
- 4.7 Physical properties of the *in situ* silica/RVNR composites
- 4.8 Relationship between chemical structure of silica and physical properties of rubber
- 4.9 Thermal properties of the *in situ* silica/RVNR composites

4.1 Effect of radiation dose on crosslinking of natural rubber

The latex used in the radiation process contained 50% dry rubber, 5 phr n-BA, and 0.2 phr KOH. n-BA was a sensitizer for radiation crosslinking that could enhance the formation of radical species required for crosslinking the polyisoprene chains. KOH was added in order to maintain a basic condition of the latex.

Upon irradiation, the rubber underwent predominantly a crosslinking process and, as a result, a three-dimensional network of polymer chains was formed. The crosslinking of natural rubber was determined by measuring the degree of swelling in toluene. Swelling study was also performed in water in order to evaluate the film performance in biological environment.

Figure 4.1 shows the degree of swelling in toluene of the radiation-vulcanized natural rubber (RVNR) films after exposure to various radiation doses. With the

increases in radiation dose, the degree of swelling (%) decreased and remained almost constant when the radiation dose was higher than 10 kGy. A similar trend was observed for the swelling for the RVNR films in water as shown in Figure 4.2.

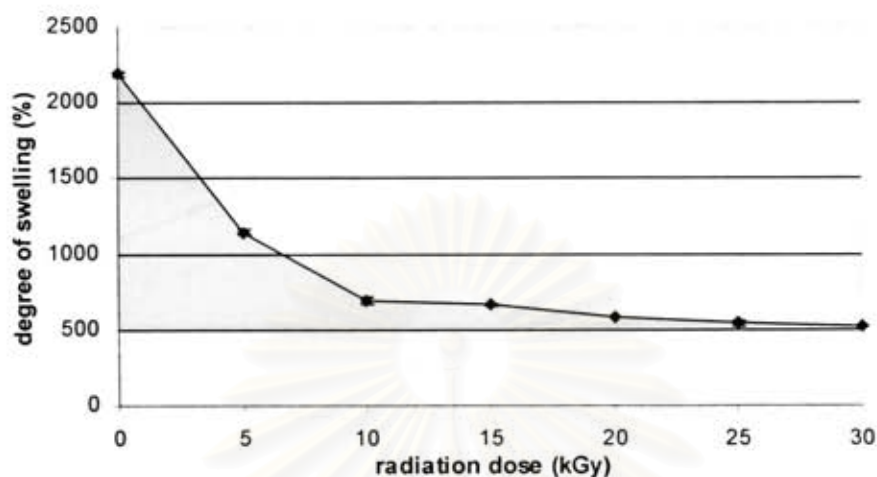


Figure 4.1 Degree of swelling in toluene of the RVNR films after various doses of radiation on the latex (Each data point was averaged from 3 sample sets.)

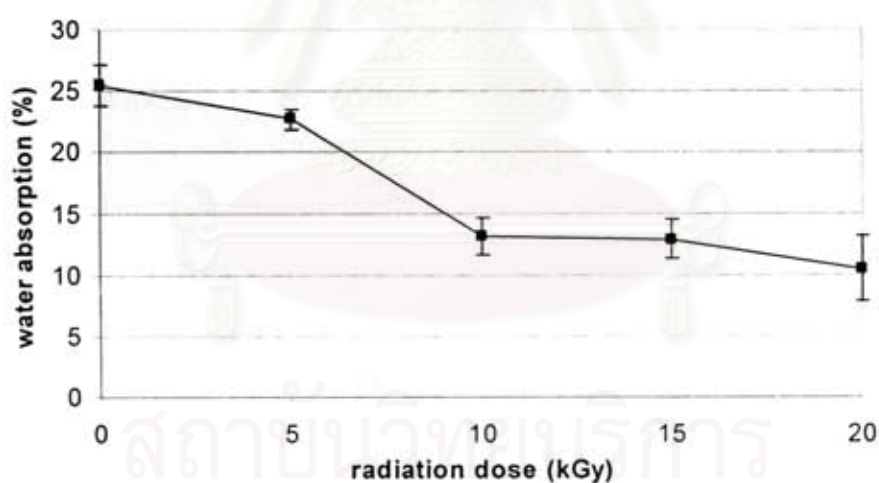


Figure 4.2 Water absorption of the RVNR films after various doses of radiation on the latex (Each data point was averaged from 3 sample sets.)

Generally the tensile properties of the rubber represent in terms of tensile strength, elongation at break, and modulus. Unexpectedly during the tensile measurement, about 90% of specimens slipped from the sample grips before they were stretched to breakage, therefore only modulus at 300% elongation (M300) was shown

in this report. Figure 4.3 reveals the M300 of the RVNR films increased with increasing the radiation dose from 0 to 30 kGy.

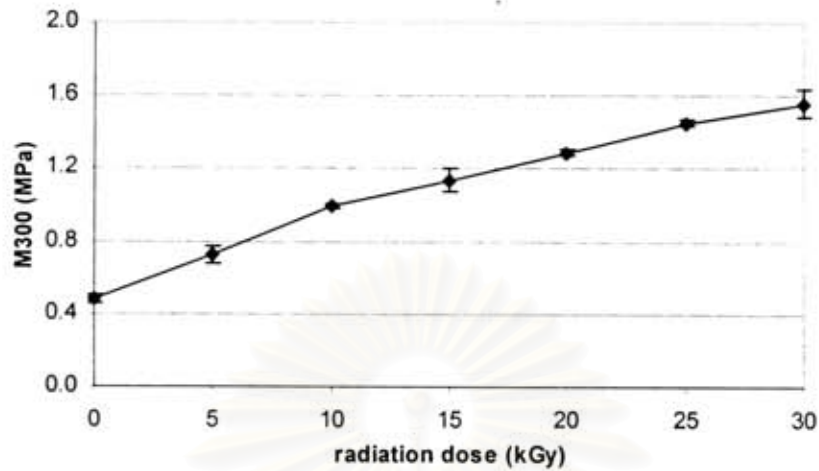


Figure 4.3 Modulus at 300% elongation (M300) of RVNR films after various doses of radiation on the latex (Each data point was averaged from 5 sample sets.)

In addition the ability for the vulcanized rubber to recover after being mechanically loaded was evaluated via tension set whose results are shown in Figure 4.4. Generally a decrease in tension set indicates a good elastic property of the rubber. It was observed that the tension set (%) decreased with increasing the radiation dose.

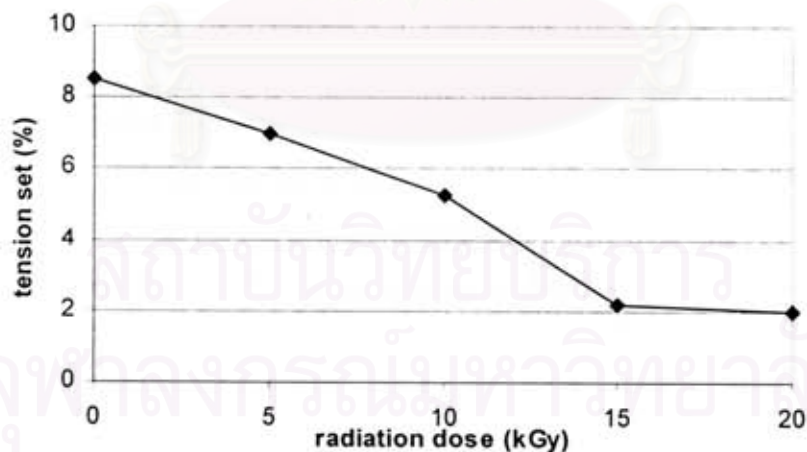


Figure 4.4 Tension set (%) of RVNR films after various doses of radiation on the latex (Each data point was averaged from 3 sample sets.)

According to these results, it seems that only 15 kGy of the radiation dose was enough for irradiation of the natural rubber latex. Although M300 of RVNR films at the

radiation dose of 15 kGy is lower than those of Haque (1996), Dafader (2006) etc., the radiation dose of 15 kGy was selected for further use in the work.

4.2 *In situ* formation of silica in radiation-pretreated natural rubber latex by sol-gel process

Following the studies reported by Nantivanich (2003) and Siramanon (2005), TEOS is immiscible with water, but natural emulsifier present in the latex can aid the mixing. When adding a small amount of TEOS, the mixture remains homogeneous and become more viscous when increasing the TEOS content. But, when the TEOS loading is more than 70 phr, the mixture becomes very viscous, as well as aggregation of the latex is observed. Thus the amount of TEOS in this study is limited at 50 phr.

4.2.1 TEOS mixing step before and after irradiations

As mentioned earlier, TEOS can be mixed into the NR latex (50%DRC) without difficulties as long as the silane amount was kept at and below 50 phr. In this section, the focus was to determine whether the order of TEOS mixing and irradiations steps had any effects on the silica morphology and preparation.

Figure 4.5 shows scanning electron micrographs of the resulting *in-situ* silica-filled composites. In each micrograph, the white spots are the silica particles and the dark background is the rubber matrix. For both cases, the silica particles are dispersed in the NR matrix. Agglomeration of the silica is also clearly observed. Each agglomeration is limited to an approximate diameter of 1 μm or less. When comparing the elementary particle, the silica formed in the 'before irradiation' sample are smaller than the ones obtained from 'after irradiation' samples. This suggests a good mixing between TEOS and latex when TEOS was added before the irradiation step. Usually small particles lead to better reinforcement than big particles. It was however found that after adding TEOS, the mixture became increasingly viscous with time even when the mixture was left stand at room temperature. Complete coagulation was reached after about 1 hour. Thus it was impossible to further cast the coagulated latex into sheets. In addition, the silica particles, which were generated before the rubber vulcanization, may inhibit the crosslinking of the rubber chains as reported earlier by Bokobza (2005).

Because of these reasons, the alkoxy silane was added after the gamma ray irradiation step.

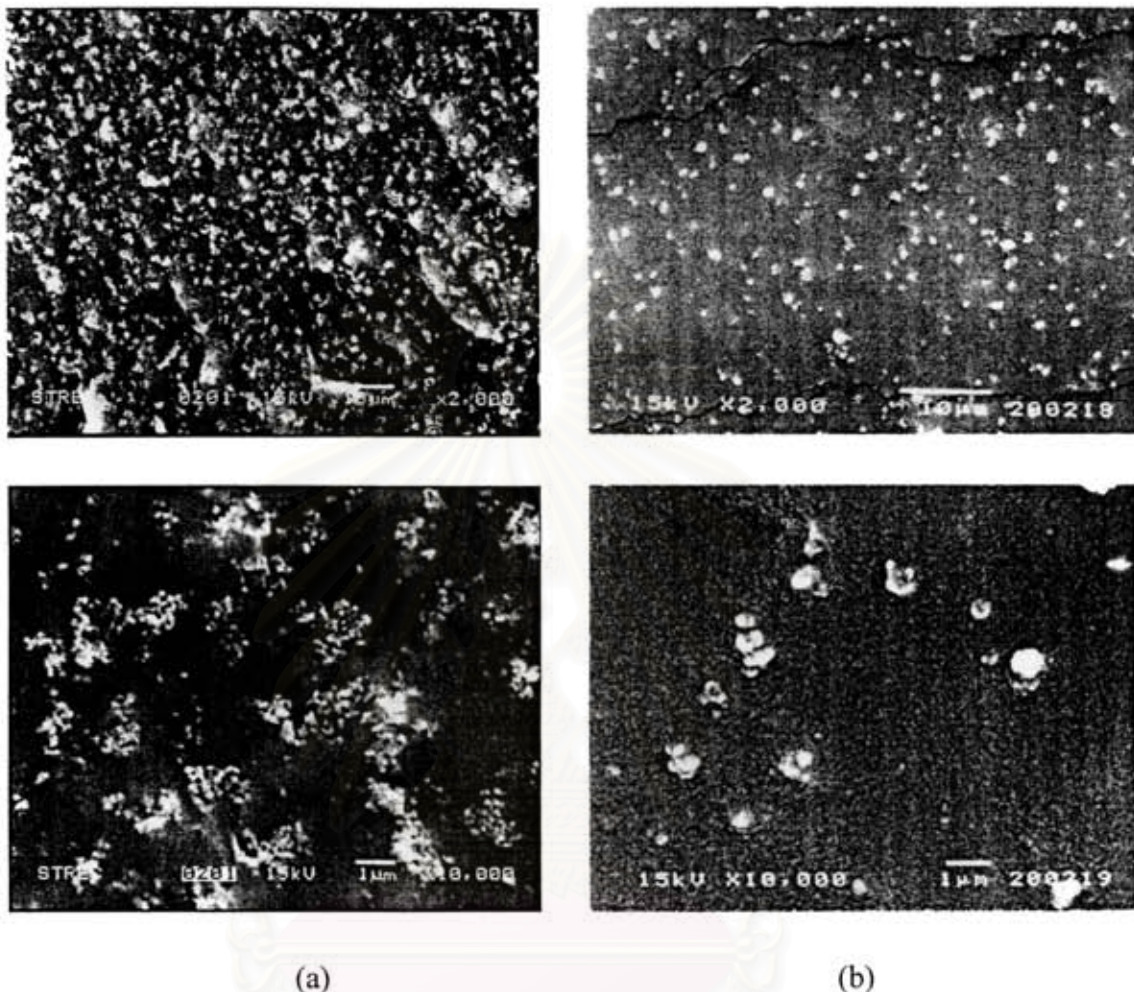


Figure 4.5 SEM micrographs of the fractured surface of the *in situ* silica/RVNR composites, which were generated (a) before and (b) after gamma irradiation [upper images, 2,000 \times ; lower images, 10,000 \times]

4.2.2 Dry rubber content in RVNR latex affecting the sheet casting process

The effect of rubber content in RVNR latex on the composite preparation was studied. The %DRC being investigated were 30, 40, 50, and 60 %. In each latex, 50 phr TEOS was added following the methods explained in Section 3.3.3. After the heating at 50 $^{\circ}\text{C}$ for 2 days, each of the resulting radiation-vulcanized rubber-silica sheets was visually observed for the homogeneity of silica dispersion. The photographs are shown in Figure

4.6. It is clearly visible that the latex concentration does affect the silica dispersion in the cured films. The non-homogeneous rubber sheets were obtained in the case of latex having 30 and 40% DRC. Some silica powders loosely attached on the surface of the film (a), while some blemish and scratches were observed on the film (b). This was due to the fact that TEOS could not be homogeneously dispersed in the RVNR latexes having 30 and 40% DRC during the mixing by the mechanical stirrer. Layers of TEOS on the latex surface were seen after the mixing.

At the higher DRC values, the mixing of TEOS in the 50 and 60% DRC latexes were compatible resulting in smooth films with homogeneous textures. These results can be explained in terms of the polarity of TEOS and the rubber latex. It is known that TEOS and rubber particles are both hydrophobic substances while water is highly polar. Therefore the compatibility between TEOS and the latex increases with increasing the dry rubber content. Thus the appropriate latex concentrations in TEOS mixing step are 50 and 60% DRC.

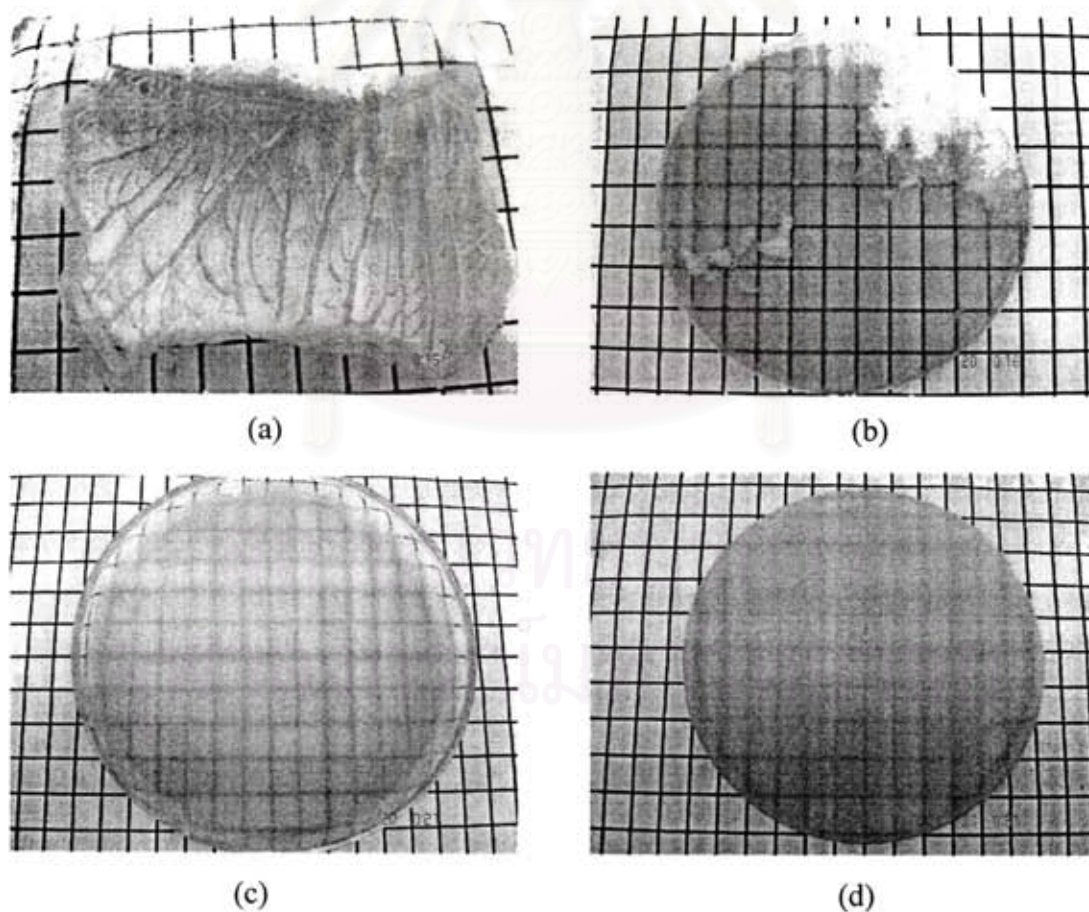


Figure 4.6 Photographs of the *in situ* silica/RVNR films, prepared from latex containing (a) 30%, (b) 40%, (c) 50%, and (d) 60% DRC

The effect of gelation time (or heating time) on silica content in the composites prepared from RVNR latex mixed with 50 phr of TEOS and %conversion of the silane to silica is shown in Figure 4.7. It was found that the amount of silica generated in the rubber increased as the heating time increased, and remained constant when the heating time was longer than 2 days. The heating period was therefore set at 2 days for all other samples in this study.

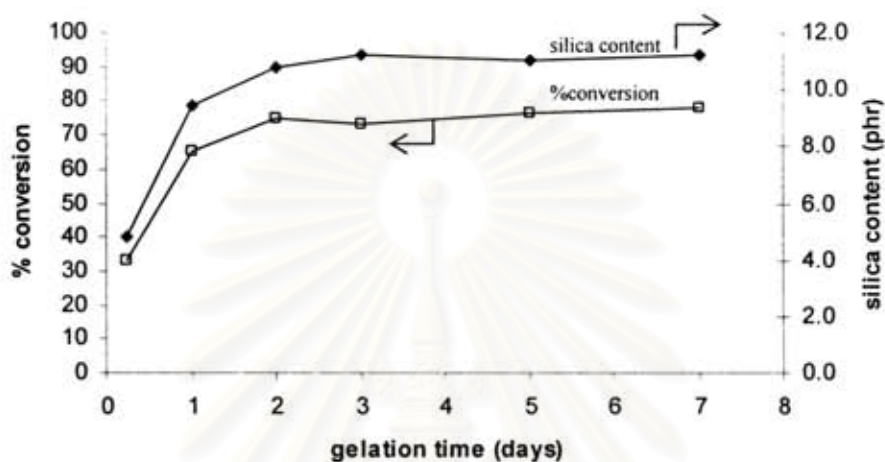


Figure 4.7 Changes of silica content and %conversion of TEOS to silica as a function of heating time for the *in situ* silica/RVNR composites

4.3 Variation of alkoxy silane in the preparation of the *in situ* silica/RVNR composites

In this section, the focus was concerned with the type of alkoxy silanes: tetraethoxysilane, vinyltriethoxysilane, and ethyltriethoxysilane, used in the composites preparation. The structure of each silane differed from the others by one of the four substituents on the silicon atom as shown in Figure 4.8.

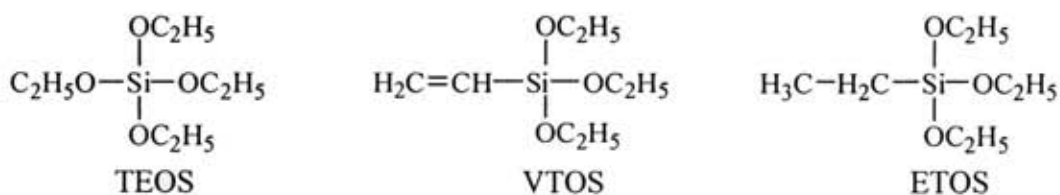


Figure 4.8 Chemical structures of TEOS, VTOS, and ETOS

The appearances of the composite films prepared in this study are shown in Figure 4.9. The green and RVNR latex gave transparent films (Figure 4.9 a and b). When the silane was added, the films turned opaque due to the formation of silica particles in the rubber matrix (Figure 4.9 c, d, and e).

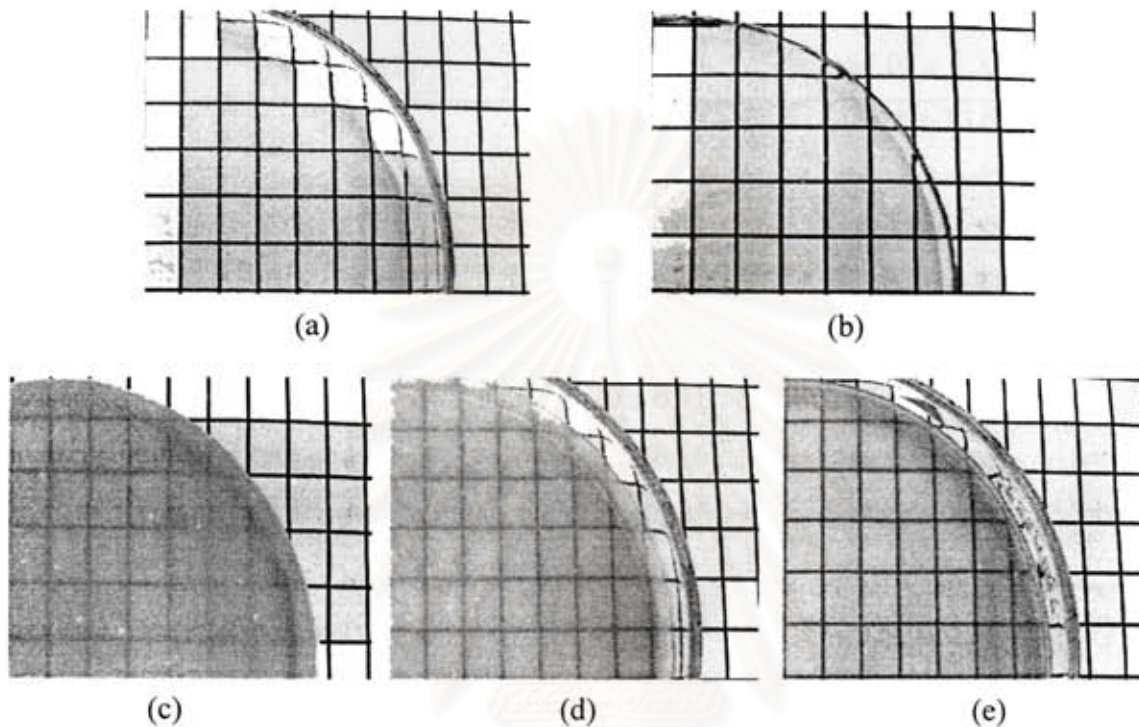


Figure 4.9 Photographs of the *in-situ* silica/RVNR films prepared from (a) green NR, (b) RVNR, (c) RVNR added with TEOS, (d) RVNR added with VTOS, and (e) RVNR added with ETOS (*note*: the amount of all added silane was 50 phr.)

4.3.1 Extent of *in situ* silica formation in the RVNR composites

The *in situ* formation of silica particles in the RVNR sheets were studied in terms of silica content and %conversion from each silane type to silica. The results are listed in Table 4.1.

Table 4.1 Content and %generation of silica generated in the RVNR composites

sample	%Si (Theory)	%silica content	%conversion
T10	2.88	2.74 ± 0.31	95.11 ± 10.78
T20	5.77	4.82 ± 0.23	83.59 ± 4.07
T30	8.66	6.98 ± 0.20	80.62 ± 2.35
T40	11.54	9.22 ± 0.20	79.82 ± 1.72
T50	14.42	11.70 ± 0.18	81.02 ± 1.25
V10	4.16	2.35 ± 0.57	56.28 ± 13.64
V20	8.32	5.04 ± 0.54	60.44 ± 6.45
V30	12.47	7.15 ± 0.48	57.14 ± 3.85
V40	16.63	8.12 ± 0.73	48.63 ± 4.41
V50	20.79	11.5 ± 0.67	55.14 ± 3.22
E10	4.22	0.70 ± 0.31	16.70 ± 7.41
E20	8.44	0.94 ± 0.16	11.12 ± 1.90
E30	12.66	0.89 ± 0.35	7.02 ± 2.77
E40	16.88	0.89 ± 0.47	5.27 ± 2.79
E50	21.10	0.82 ± 0.19	3.89 ± 0.91

The results in Table 4.1 indicate that, for TEOS and VTOS, the silica contents generated in the composites increased with increasing the silane loading from 10 to 50 phr. This is, however, not the case for ETOS, where the silica contents remained less than 1 phr independent of added ETOS amounts. The results suggest that the chemical structure of silane plays an important role in the sol-gel process. TEOS molecule contains four ethoxy groups, while either VTOS or ETOS molecule contains three ethoxy groups and one non-reactive alkyl group. Therefore TEOS undergoes hydrolysis and condensation to form silica almost completely at an average conversion of 80%. Rankin and Tan (2006) reported similar results and explained that the substitution of an ethoxy group with an ethyl group (in ETOS) or a vinyl group (in VTOS) became more electron-donating than the ethoxy group. The alkyl group increased the electron density at the silicon and in turn slowed down the hydrolysis under a basic condition.

In addition, increasing the steric bulkiness of the organic substituent has an inhibitory effect on the hydrolysis and condensation reaction during the sol-gel process.

The silanes with smaller vinyl groups are more readily hydrolyzed and condensed to afford large silica than those with bulkier ethyl group. ETOS therefore forms only low molecular weight resin and tends to phase-separate out of the polar medium due to the low polarity of the ethyl group.

Moreover, Loy (2000) reported that ETOS formed gels was completed only after 8 days with NaOH as the catalyst. In this study, the sol-gel process in 2 days with ammonia as the catalyst. Therefore the reaction condition reported here can be concluded as a 'milder' condition for converting ETOS to silica.

Therefore the presence of the alkyl group in the silane resulted in a remarkable reduction in the conversion of alkoxy silane to silica in the RVNR latex.

4.3.2 Morphology and distribution of silica in the composites

The fractured surfaces of the *in situ* silica/RVNR composites were analyzed by SEM (Figure 4.10). The silica particles obtained from TEOS and VTOS dispersed evenly in the rubber matrix. The elementary particles are almost spherical. For ETOS, only a few white spots were seen in the sample E50 (Figure 4.10c), in good agreement with the low silica content of silica reported in Table 4.1. The silica generated from TEOS tended to agglomerate and form clusters having various sizes. It is due to the hydrophilicity of silanol groups on the surface of silica particles that attract other nearby particles. On the other hand, those from VTOS and ETOS remained finely dispersed inside the rubber matrix. The silica particles obtained from these two alkyltriethoxysilanes should have the corresponding alkyl groups on the particle surfaces. This therefore reduces the particle aggregation within the similar hydrophobic rubber domain. However when comparing between the vinyl and ethyl groups, it seems that the type of alkyl group in the alkyltriethoxysilanes used in this work have no effect on the size distribution of the silica particles generated in the rubber matrix.

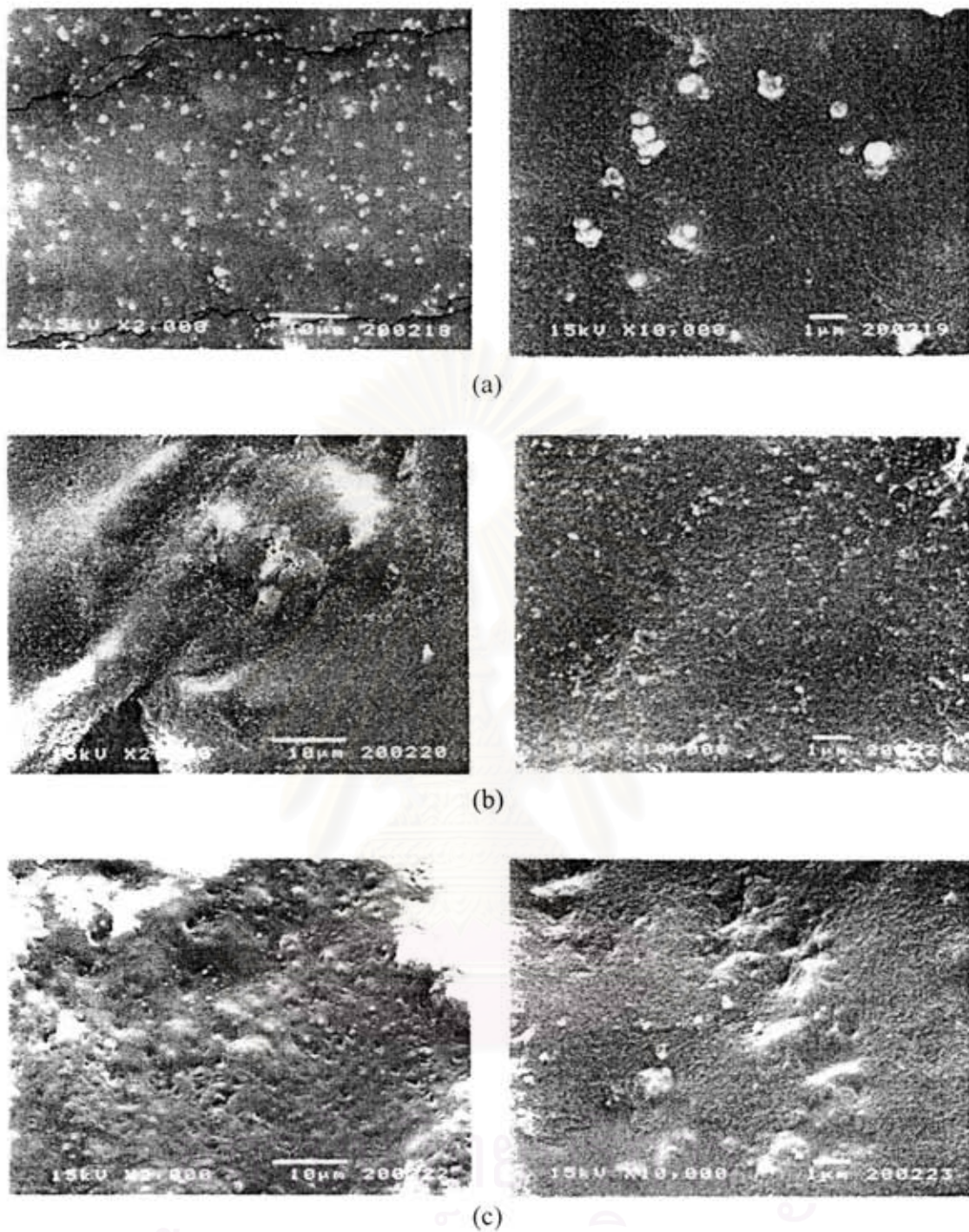


Figure 4.10 SEM micrographs of the fractured surface of the *in situ* silica/RVNR composites prepared from RVNR latex mixed with 50 phr of (a) TEOS, (b) VTOS, and (c) ETOS [left images, 2,000 \times ; right images, 10,000 \times]

4.4 Preparation of the *in situ* silica/RVNR composites using mixed silanes

According to Section 4.3, the %conversion of silane to silica in this study was in the order of TEOS>VTOS>ETOS. Importantly, it gave only 10%conversion when ETOS was used. In this section, attempts were made to generate silica inside the rubber matrix using a mixture of TEOS and alkyltriethoxysilane as the precursors. The experiment was designed such that the total amount of mixed silanes in all samples were equal to 50 phr.

4.4.1 General observation

The appearances of silica filled RVNR generated from 'TEOS/VTOS' and 'TEOS/ETOS' are shown in Figures 4.11-4.12, respectively. The silica dispersion in the cured rubber films prepared from 5-phr TEOS mixed with 45-phr VTOS (Fig. 4.11a) and 45-phr TEOS and 5-phr VTOS (Fig. 4.11e) were homogeneous. It was however from that loose and large silica powder appeared on the film surface prepared from other TEOS/VTOS ratio (Figure 4.11b, c and d). These TEOS/VTOS film sets were repeatedly prepared and the same results were still obtained. It is clear that the silane ratio when mixed with the irradiated latex affects the homogeneity of the latex mixture. A certain reason for this phenomena cannot yet be elucidated.

The appearances of TEOS/ETOS cured rubber films shown in Fig. 4.12a to 4.12e indicated that the *in situ* silica particles were buried inside the rubber matrix. No loosely bound silica was observed.

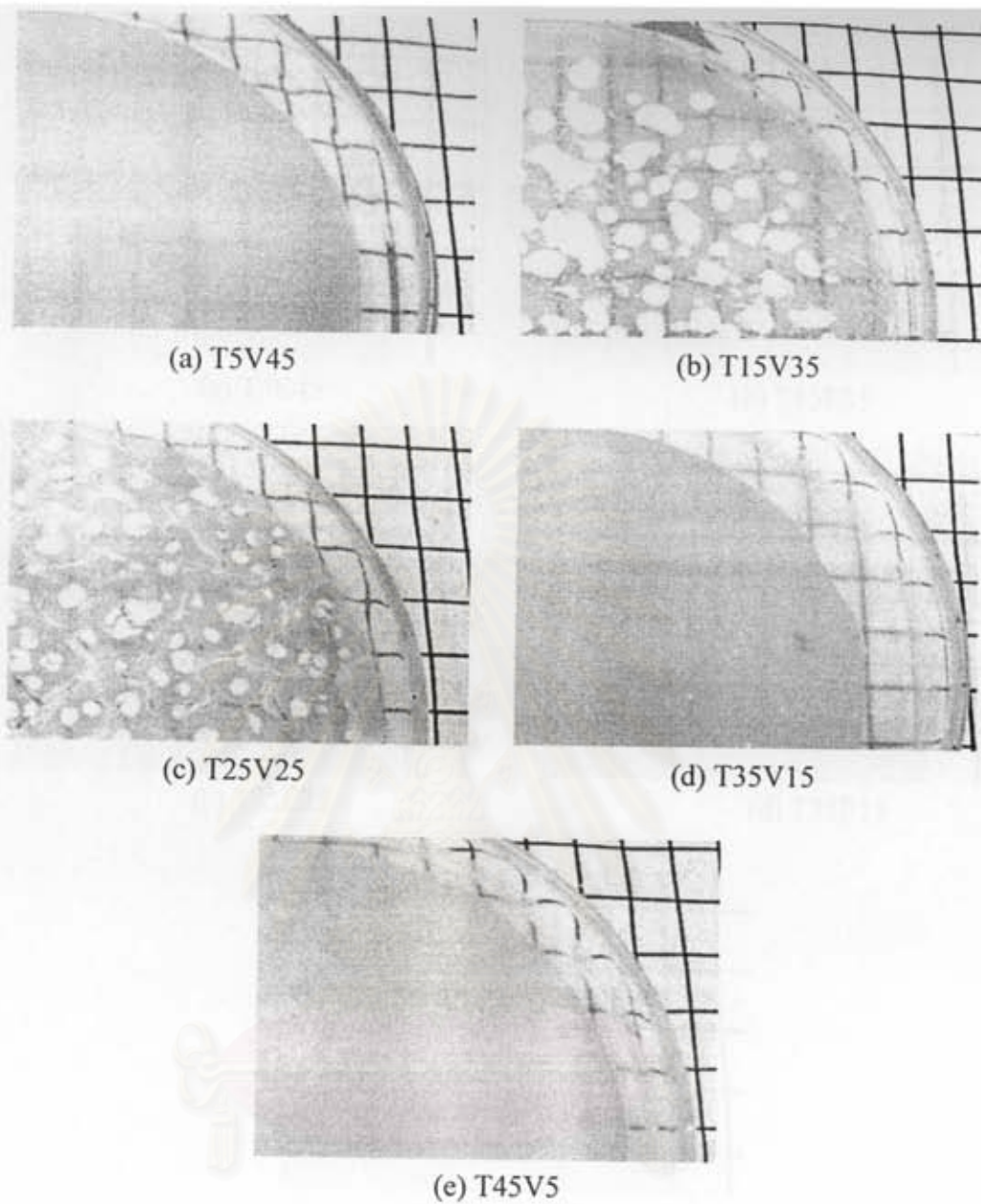


Figure 4.11 Photographs of the *in situ* silica/RVNR films prepared by adding mixtures of TEOS/VTOS as silica precursor: (a) T5V45, (b) T15V35, (c) T25V25, (d) T35V15 and (e) T45V5. (Total silane = 50 phr)

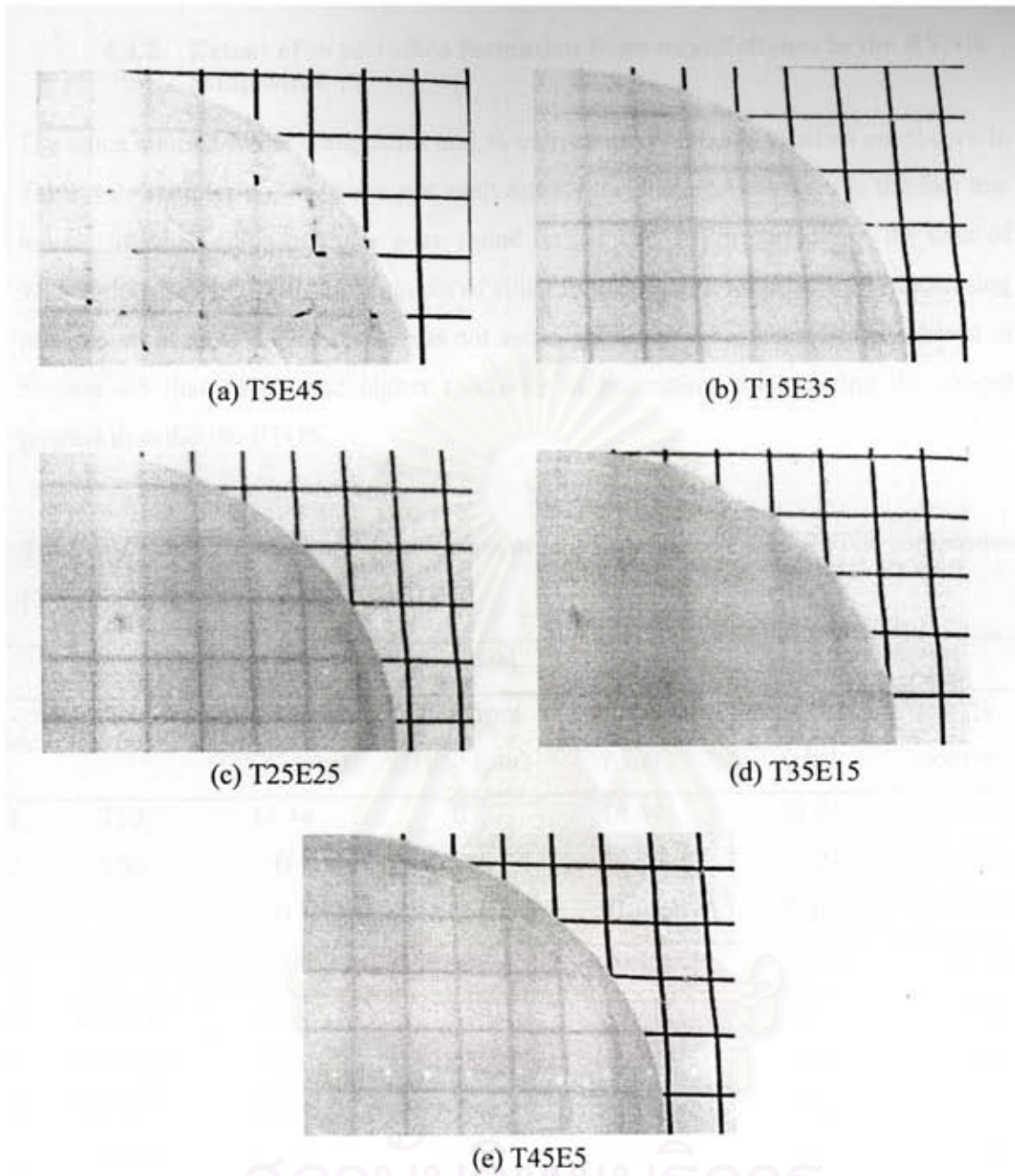


Figure 4.12 Photographs of the *in situ* silica/RVNR films prepared by adding mixtures of TEOS/VTOS as silica precursor: (a) T5E45, (b) T15E35, (c) T25E25, (d) T35E15 and (e) T45E5. (Total silane = 50 phr)

4.4.2 Extent of *in situ* silica formation from mixed silanes in the RVNR composites

The silica content in the composites and % conversion of silanes to silica are shown in Table 4.2. Samples no. 5-7 were not analyzed for the silica content due to the fact that loosely attached silica particles were found on the cured film surface. In the case of TEOS mixed with ETOS, the amounts of silica formed *in situ* increased with increasing the amount of TEOS. This result was not surprising since it has been already shown in Section 4.3 that TEOS had higher reactivity in generating silica during the sol-gel process than did the ETOS.

Table 4.2 Silica content and %conversion of silica generated in the RVNR composites [T = TEOS, V = VTOS, and E = ETOS]

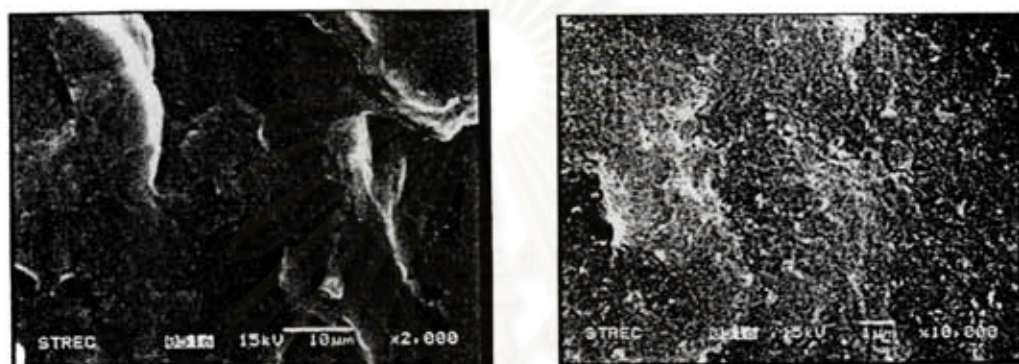
No.	Sample	Theoretical			Experimental	
		Silica from TEOS (phr)	Silica from OTES ¹ (phr)	Total Silica (phr)	Total Silica (phr)	% conversion
1	T50	14.44	0	14.44	10.26	71.05
2	V50	0	20.86	20.86	10.27	49.23
3	E50	0	21.06	21.06	2.18	10.35
4	T5V45	1.44	18.71	20.15	12.15	60.29
5	T15V35	4.33	14.55	18.88	n/a ²	n/a
6	T25V25	7.21	10.39	17.61	n/a	n/a
7	T35V15	10.10	6.24	16.33	n/a	n/a
8	T45V5	12.98	2.08	15.06	11.88	78.89
9	T5E45	1.44	18.98	20.43	4.14	20.27
10	T15E35	4.33	14.77	19.09	6.16	32.26
11	T25E25	7.21	10.55	17.76	8.86	49.89
12	T35E15	10.10	6.33	16.42	10.03	61.07
13	T45E5	12.98	2.11	15.09	11.47	76.01

¹OTES = organotriethoxysilane

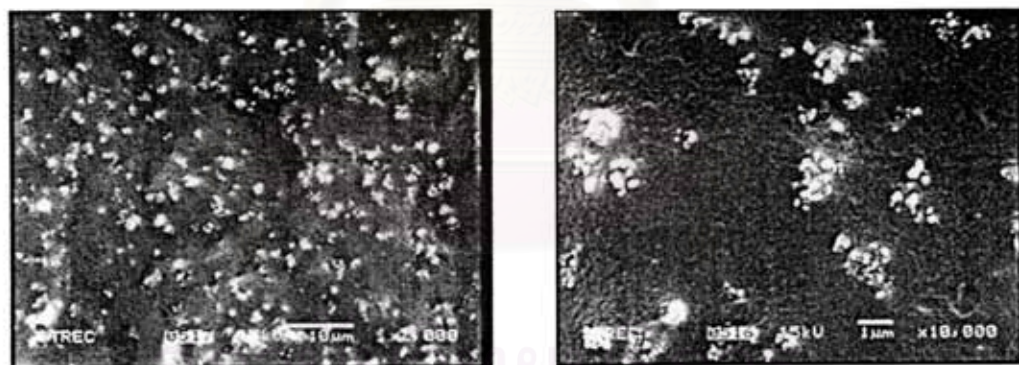
²n/a = loosely attached silica particles were found on the film surface

4.4.3 Morphology of the *in situ* silica in the composites using the mixed silanes

The fractured surfaces of the composites were analyzed using SEM (Figures 4.13 and 4.14). The *in situ* silica particles seen as white dots were homogeneously dispersed in the NR matrix. The primary silica particles are spherical. Silica particle aggregation is clearly observed and increased in size when the added amount of added TEOS was increased. These results agreed well with the results stated in the section 4.3.2 for the characteristic of silica generated from a single silane.

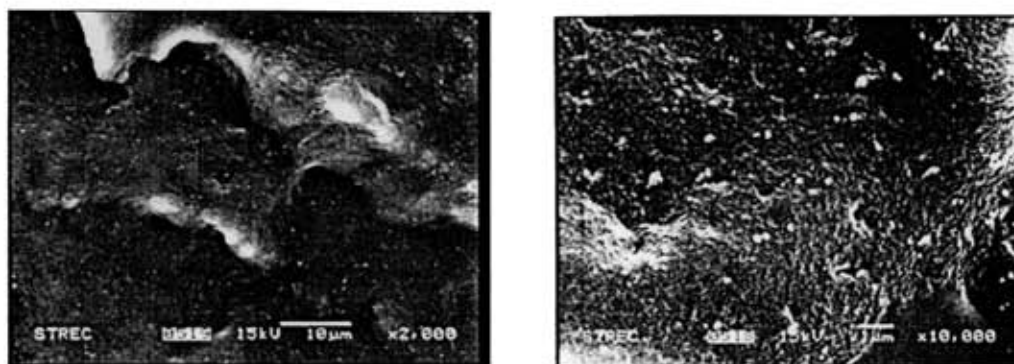


(a) T5V45 (silica content = 12.15 phr)

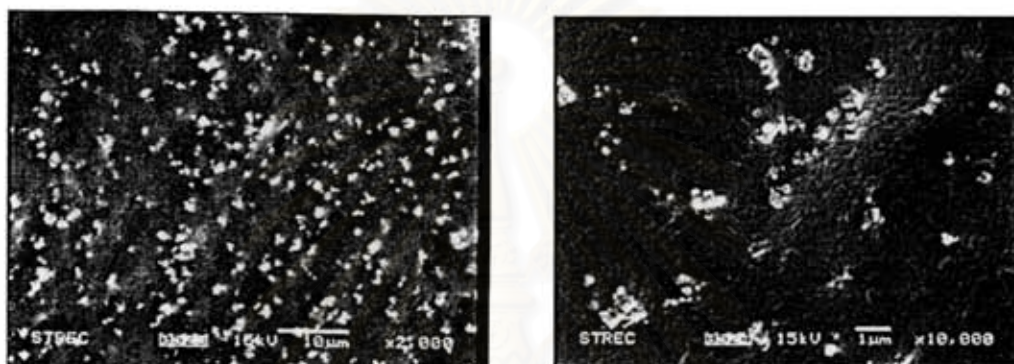


(b) T45V5 (silica content = 11.88 phr)

Figure 4.13 SEM micrographs of the fractured surface of the *in situ* silica/RVNR composites prepared from RVNR latex mixed with (a) T5V45 and (b) T45V5 [left images, 2,000×; right images, 10,000×]



(a) T5E45 (silica content = 4.14 phr)



(b) T45E5 (silica content = 11.47 phr)

Figure 4.14 SEM micrographs of the fractured surface of the *in situ* silica/RVNR composites prepared from RVNR latex mixed with (a) T5E45 and (b) T45E5 [left images, 2,000 \times ; right images, 10,000 \times]

4.5 Solid-state ^{29}Si NMR analysis

Solid-state ^{29}Si cross-polarization magic angle spinning (CPMAS) NMR was used to analyze the chemical content of the alkylated silica, as also reported by Han et al.(2007). Figure 4.15 shows the designation of the various structure units of silicon atoms in TEOS and alkyltriethoxysilane. A Q species is one in which the silicon atom is capable of producing four siloxane bonds, whereas a T species is one which can only achieve three siloxane bonds, such as a silane which has a single R group directly bonded to a silicon atom. Therefore, if there was complete hydrolysis and condensation reaction in sol-gel process as a result, only T³ and Q⁴ species would be detected in the ^{29}Si NMR spectra.

Table 4.3 Designation of the various structural units of silicon atoms in TEOS and alkyltrialkoxysilane [Han, 2007]

T-SPECIES			Q-SPECIES			
T	T ²	T ³	Q	Q ²	Q ³	Q ⁴
<i>Structural units in various atoms</i>						
R	Si	Si	R	Si	Si	Si
O	O	O	O	O	O	O
R-Si-O-Si	R-Si-O-Si	R-Si-O-Si	R-O-Si-O-Si	R-O-Si-O-Si	R-O-Si-O-Si	Si-O-Si-O-Si
O	O	O	O	O	O	O
R	R	Si	R	R	Si	Si

The NMR spectra of the *in situ* silica/RVNR composites are shown in Figure 4.15. For T50 (Figure 4.15a), the signal at -109 ppm is assigned to the siloxane group which are attributed to the silicon atom without the hydroxyl group, $\text{Si}(\text{O-Si})_4$ (conventionally called Q⁴). The signal at -102 ppm represents free silanols which are attributed to the silicon atoms that have one hydroxyl group, $(\text{Si-O})_3\text{Si-OH}$ (Q³). Figure 4.15b shows the NMR spectra of V50. The signal at about -75 ppm is assigned to a silicon atom in which one bond is connected to the alkyl group, $(\text{Si-O})_3\text{Si-R}$ (T³). The signal at about -60 ppm is assigned to a silicon atom in which one bond is connected to the alkyl group and one bond is connected to the alkoxy group, $(\text{Si-O})_2(\text{OR})\text{Si-R}$ (T²). Figure 4.15c shows the NMR spectra of E50. The signal at about -60 ppm is assigned to a silicon atom in which one bond is connected to the alkyl group and one bond is connected to the alkoxy group, $(\text{Si-O})_2(\text{OR})\text{Si-R}$ (T²). The signal at about -50 ppm is assigned to a silicon atom in which one bond is connected to the alkyl group and two bond are connected to the alkoxy group, $(\text{Si-O})(\text{OR})_2\text{Si-R}$ (T¹). These indicate that the hydrolysis and condensation reactions of TEOS and VTOS are more complete than those of ETOS in the RVNR latex. Moreover, these results correspond to the silica content stated in Section 4.3.1.

Representative NMR spectra of the composites prepared from the mixed silanes (T45V5 and T45E5) are shown in Figure 4.15d and 4.15e. The Q³ and Q⁴ signals are seen in both spectra at about -102 and -109 ppm, respectively. A T signal from alkylated silicon is not visible probably because of its low abundance.

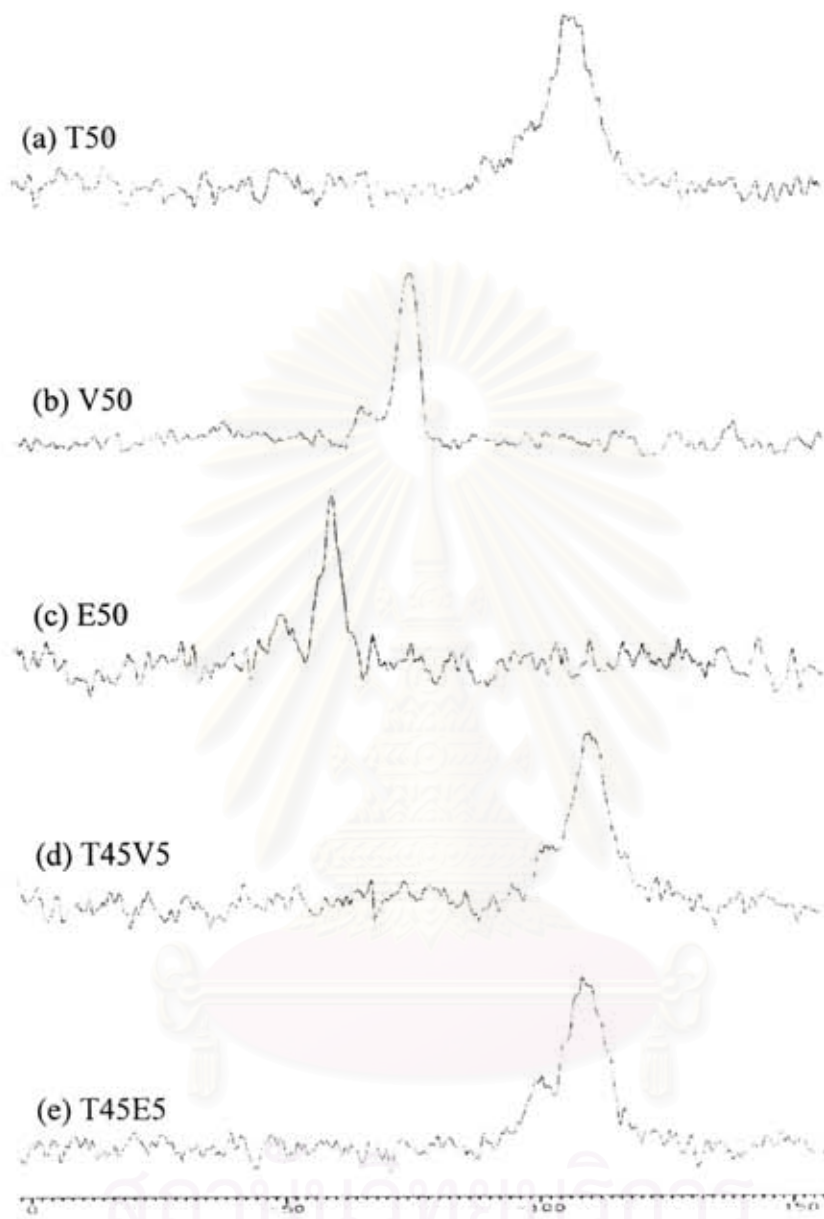


Figure 4.15 ^{29}Si CP/MAS NMR spectra of (a) T50, (b) V50, (c) E50, (d) T45V5 and (e) T45E5

4.6 Swelling behavior of the *in situ* silica/RVNR composites

Figure 4.17 shows the degree of swelling in toluene of the RVNR sheets filled with silica generated *in situ*. The swelling was found to decrease with increasing the silica content. This is due to the fact that rubber chain motion in the composites become restricted by the presence of silica. When comparing among the different silanes, the swelling of the composites with silica generated from TEOS and VTOS were similar. It seemed that using the alkyltriethoxysilane with one vinyl group did not significantly affect the swelling under the circumstance that the contents of silica generated from TEOS and VTOS in the composites were equal.

The unexpected results were observed from the composites containing silica generated from ETOS. The amount of silica in the ETOS composite was rather low, and yet the degree of swelling was somehow similar to the samples with high silica contents prepared from TEOS and VTOS. A proper explanation for this observation has not been reached.

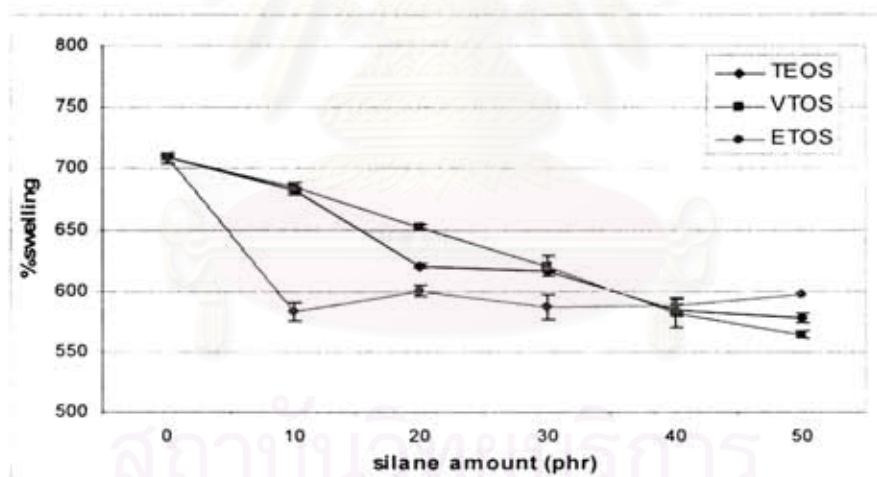


Figure 4.17 Degree of swelling in toluene of *in situ* silica/RVNR composites prepared from different amounts of alkoxysilanes (Each data point was averaged from 3 sample sets.)

Figure 4.18 shows water absorption of the *in situ* silica/RVNR composites. When comparing among the composites which had the same level of silica content, the water absorption of T50, T45V5 and T45E5 were the same, except those from V50. It seems that the use of VTOS to prepare the filler lowers the water absorption. It is most

likely due to the presence of vinyl group on the silica surface, which was generated from VTOS. This vinyl group was less polar than the usual hydroxy group on a simple silica. This type of 'vinylated' silica therefore tended to expel water from the composite. Moreover, the unreacted VTOS molecules might occupy free volume of the rubber matrix, the composites had less free volume available for absorption of water molecules.

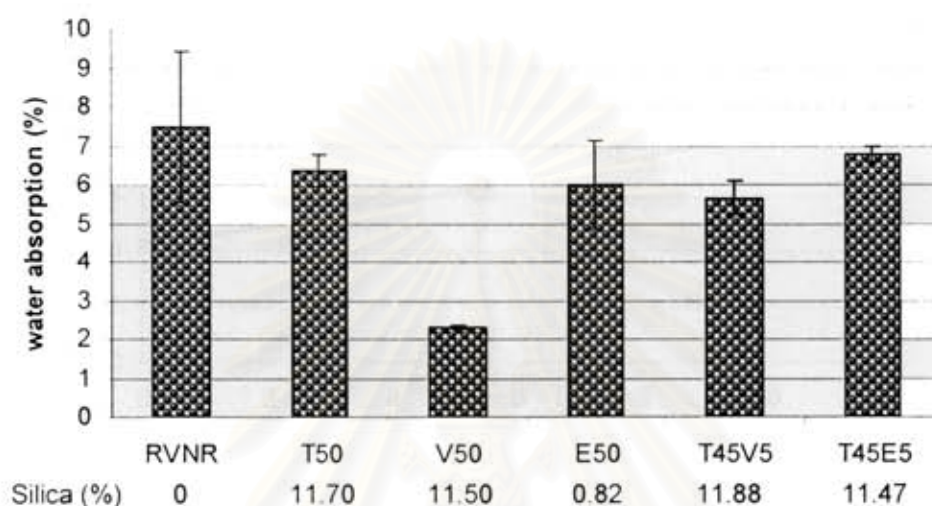


Figure 4.18 Water absorption of the *in situ* silica/RVNR composites prepared from different silanes (Each data point was averaged from 3 sample sets.)

4.7 Physical properties of the *in situ* silica/RVNR composites

The modulus at 300% elongation (M300) of the NR films filled with *in situ* silica increases with increasing the amount of silica in the composite films (Figure 4.19). It can be explained by the reinforcing effect of the silica. Generally, when silica is added into rubber at a sufficiently high loading, the distance between silica aggregates becomes close enough to induce strong interaction between aggregates giving rise to an additional network, namely filler-filler network. This filler-filler network should result in increases in strength and hardness at a high silica content [Sae-oui, 2007].

Different silanes in fact produced composites with different modulus. The silica generated from TEOS resulted in the composite having higher M300 than those from VTOS. The M300 of rubber sheet filled silica obtained from ETOS was the lowest since the amounts of silica formed in these samples were also the lowest (see Table 4.1). The result was somewhat not following the hypothesis that the vinyl group

obtained from VTOS which had vinyl group on the silica surface and the sizes of the silica particle participated in the reinforcement of the composites via filler-rubber interaction. If the filler-rubber interaction between the inorganic silica and organic polyisoprene chain had affected, one might expect to see an increase in modulus of the rubber filled with VTOS over that of TEOS system.

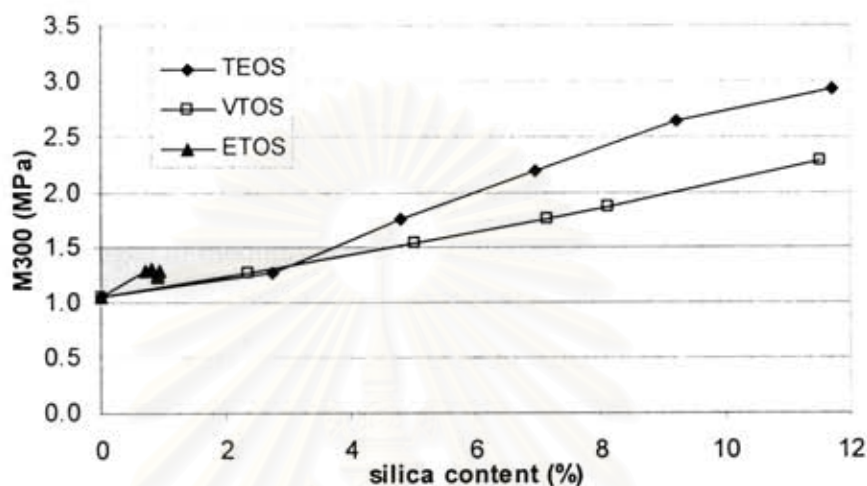


Figure 4.19 Changes in modulus at 300% elongation of the *in situ* silica/RVNR sheets as a function of silica content prepared from either TEOS, VTOS or ETOS (Each data point was averaged from 5 sample sets.)

Comparison of M300 among samples prepared from various single and mixed silane types are shown in Figure 4.20. The mixed silanes used in the formulation to prepare the composites T45V5 and T45E5 resulted in the increase of M300 over the value of T50, V50, and E50, which were the composites prepared from the single silane. It is possible that not only the filler-filler interaction from TEOS-generated silica, but also filler-rubber interaction from alkyltriethoxysilane-generated silica affects the modulus of the composites. Alkyltriethoxysilane promotes the phase compatibility between the rubber phase and the silica phase through the alkyl group and thus enhances the mechanical properties. The vinyl group is more effective than the ethyl group in promoting modulus of the composites.

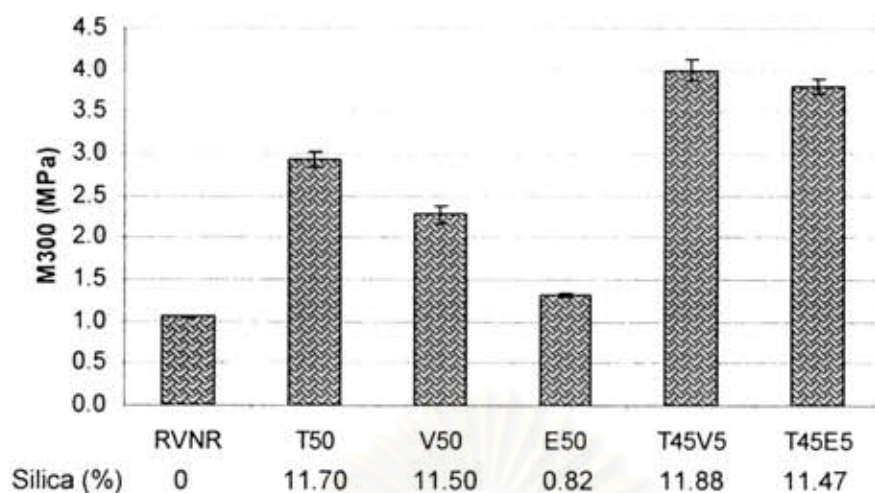


Figure 4.20 Changes in modulus at 300% elongation of the *in situ* silica/RVNR sheets as a function of silane type (Each data point was averaged from 5 sample sets.)

As hardness (Figure 4.21) is closely related to the modulus of the composites, it was also found that the hardness of the *in situ* silica/RVNR composites increased with increasing the silica content for the TEOS precursor. The composite with vinylated silica (V50) showed lower hardness than those of T50 although they both possessed similar silica contents. The composite E50 had the lower hardness due to low silica contents.

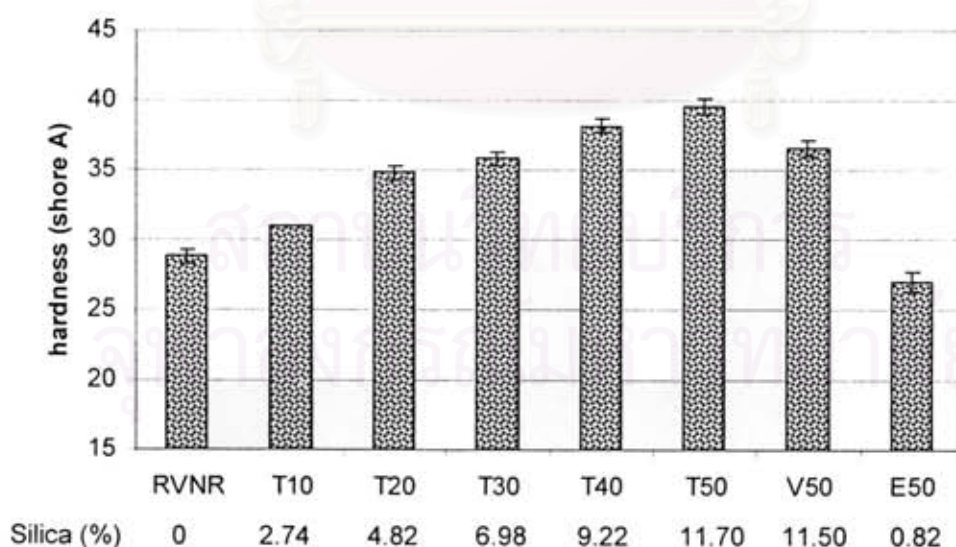


Figure 4.21 Changes in hardness of the *in situ* silica/RVNR sheets as a function of added alkoxysilane loading (Each data point was averaged from 5 point in a sample.)

Figures 4.22 and 4.23 show the results of tension set analysis of the *in situ* silica/RVNR composites. It was found that tension set slightly increased with increasing silica content generated in the composites. This is due to the fact that silica particles limit the mobility of polymer chains. It was also found that the higher the silica content, the lower the elasticity of the rubber composites. This gives the same trend as the tensile properties of the composites. Silica particles can limit the extension of the polymer chain, they can also limit the retraction of the polymer chain. However, tension set of the *in situ* silica /RVNR composites (5%) is lower than the one of standard material (10%).

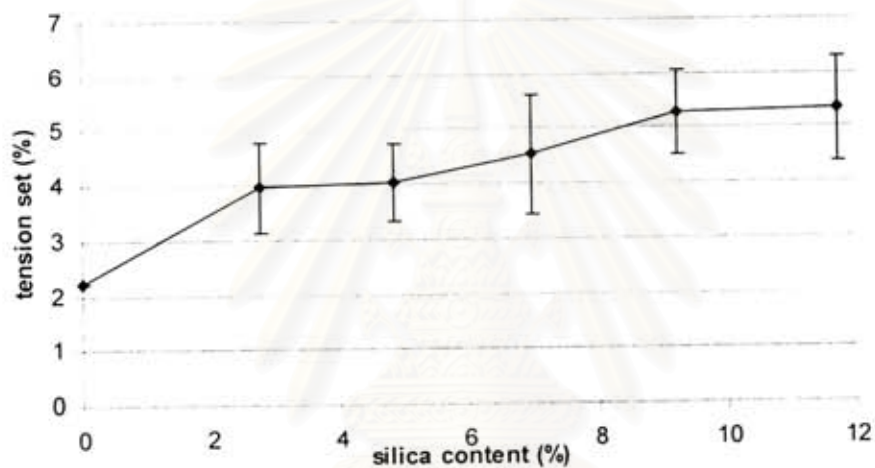


Figure 4.22 Changes in tension set of the *in situ* silica/RVNR sheets as a function of silica content (Each data point was averaged from 3 sample sets.)

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

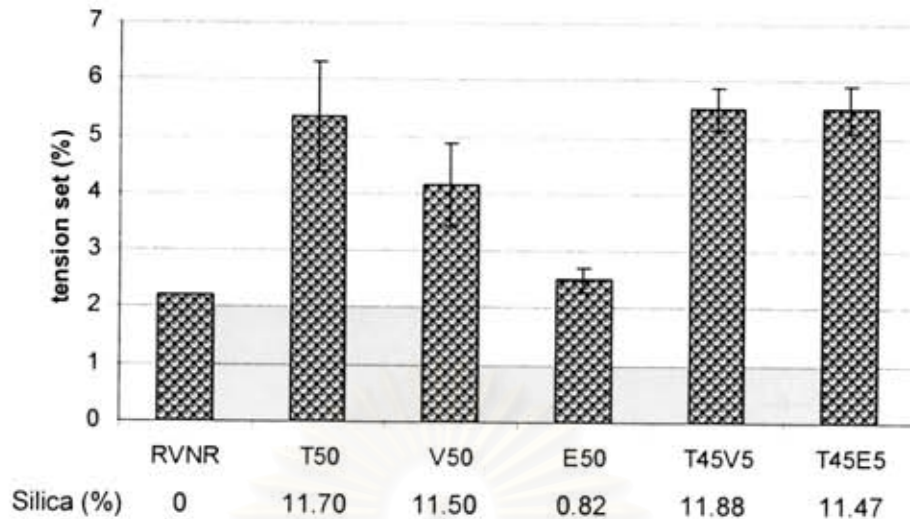


Figure 4.23 Changes in tension set of the *in situ* silica/RVNR sheets as a function of silane type (Each data point was averaged from 3 sample sets.)

Plots of tear strengths of the *in situ* silica/RVNR sheets versus silica contents are illustrated in Figures 4.24-4.25. It was found that the tear strength of the composites increased with increasing the silica content. In general the tear strength of VTOS-generated silica was higher than those of TEOS-generated silica (Figure 4.24). When comparing among different silanes (Figure 4.25), the composites V50 and E50 were the highest among all others. This was expected since the changes in tear strength for the composites could be discussed in term of phase continuity and interaction between silica particle and rubber molecules (Sombatsompop, 2007). The silica generated from VTOS and ETOS had either vinyl or ethyl groups on the particle surface, leading to an improved compatibility between the silica and the rubber phase. While TEOS generated silica had only silanol group on the surface, therefore poor interaction occurred between the silica particles and the rubber phase.

จุฬาลงกรณ์มหาวิทยาลัย

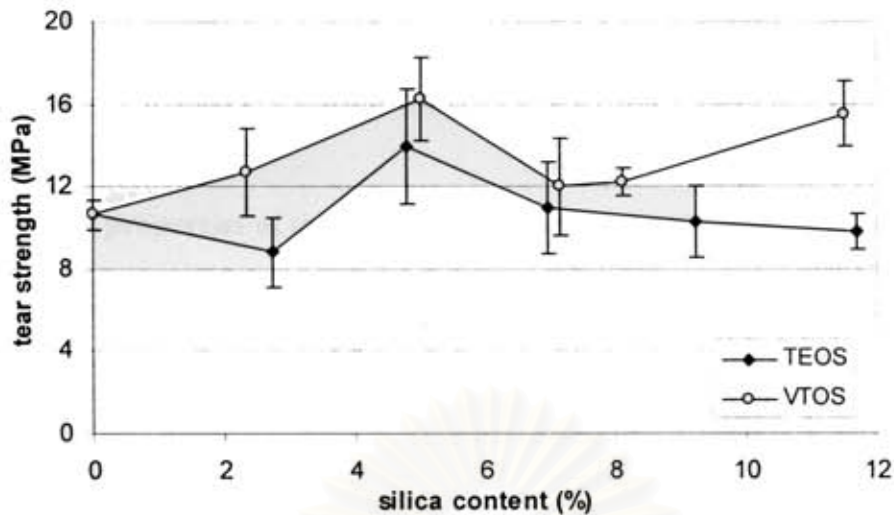


Figure 4.23 Changes in tear strength of the *in situ* silica/RVNR sheets as a function of silica content (Each data point was averaged from 3 sample sets.)

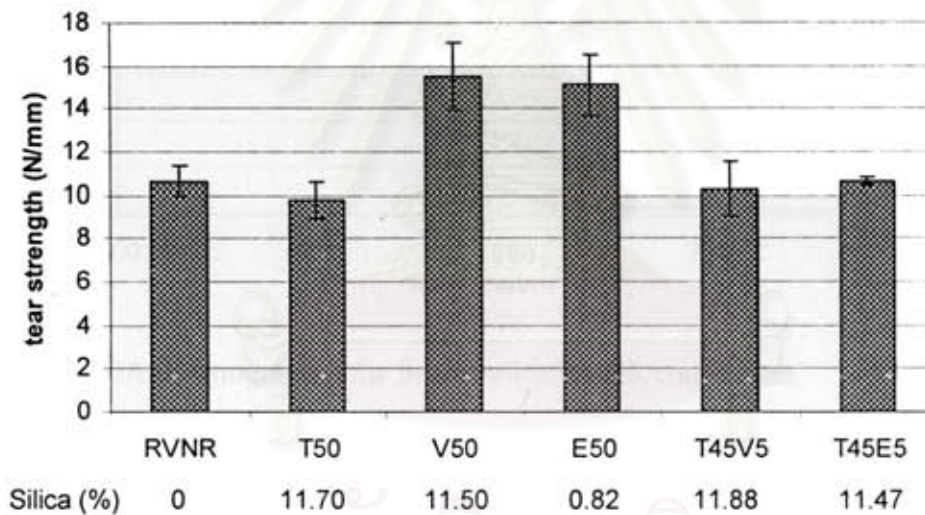


Figure 4.24 Changes in tear strength of the *in situ* silica/RVNR sheets as a function of silane type (Each data point was averaged from 3 sample sets.)

4.8 Relationship between chemical structure of silica and physical properties of rubber

According to the physical properties of the *in situ* silica/RVNR composites in section 4.7, the results suggest that the chemical structure of the silica was play importance role in the physical properties of the composites films. Q structure-the silicon atoms that

have without hydroxyl group, $\text{Si}(\text{O}-\text{Si})_4$ or one hydroxyl group, $(\text{Si}-\text{O})_{4-n}\text{Si}(\text{OH})_n$ effect on M300, hardness, and tension set while T structure-the silicon atom in which one bond is connected to the alkyl group, $(\text{Si}-\text{OR})_n(\text{Si}-\text{O})_{3-n}\text{Si}-\text{R}$ effects on tear strength.

4.9 Thermal properties of the *in situ* silica/RVNR composites

The thermal stability of the *in situ* silica/RVNR composites was studied by TGA in air. The TGA thermograms of RVNR and *in situ* silica filled RVNR composites are shown in Figure 4.25.

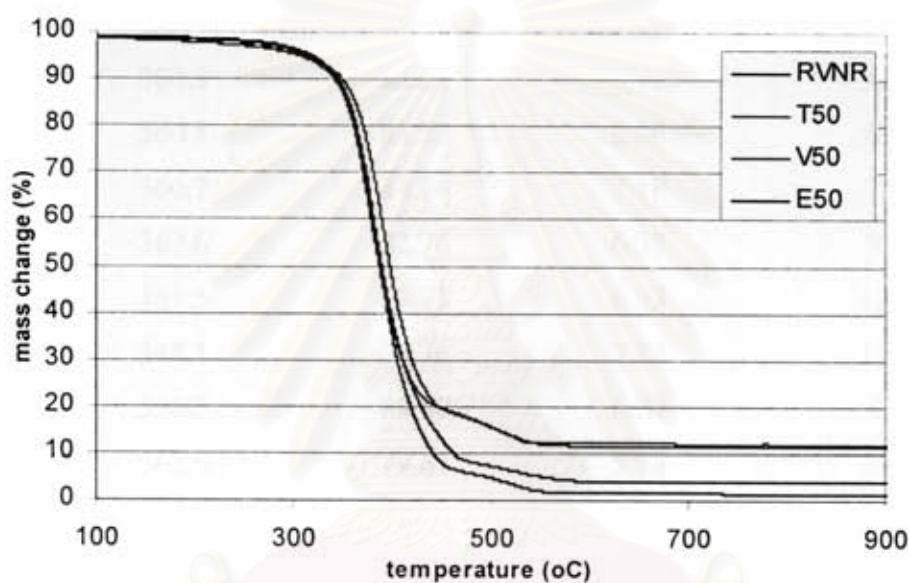


Figure 4.25 TGA thermogram of the *in situ* silica/RVNR composites

The onset temperature of decomposition was calculated from the TGA thermogram by extrapolating from the curve at the peak of degradation back to the initial weight of the composites. In Table 4.4, the onset temperature of most composites was shifted to higher temperature (about 5-8 °C) than those of the cured NR film. Moreover, the mass change (%) in temperature range of 105-460 °C decreased with increasing the silica content. This should be due to the aggregation of silica particles that restricted polymer chain mobility and diffusion of the decomposition products from the bulk polymer to gas phase [Peng, 2007]. In case of 'V50' and 'E50', the onset temperatures were lower than those of the pure NR. This might be due to the decomposition of the unreacted silane monomer which was trapped within the rubber matrix. Another interesting point was that the residual mass (%) of the composites at

900 °C was much greater than the pure NR due to the amount of the silica particles and increased with increasing silane loading. These results indicated the presence of silica in the composite with the amounts similar to the results obtained from furnace oven burning reported in Section 4.3.2.

Table 4.4 Onset temperature, mass change and residual mass of the *in situ* silica/RVNR composites

Sample	Onset temp. (°C)	Mass change (%)		Residual Mass (%)
		105-460 (°C)	460-600 (°C)	
RVNR	355.1	92.29	5.07	1.23
T10	363.3	88.28	6.12	4.36
T20	360.8	85.52	6.96	6.18
T30	360.7	84.14	7.18	7.43
T40	362.6	82.76	6.37	9.99
T50	361.5	80.33	6.53	12.01
V50	348.1	79.76	7.52	11.31
E50	350.3	88.60	6.24	4.15
T45E5	362.6	79.67	5.18	14.22
T45V5	360.6	80.41	5.90	13.28

CHAPTER V

CONCLUSION AND FUTURE DIRECTION

5.1 Conclusions

Radiation-vulcanized NR latex filled with *in situ* generated silica was prepared. The NR latex having 50% dry rubber content was irradiated under gamma rays with total radiation dose of 15 kGy. The pre-vulcanized latex was then mixed with alkoxysilanes, i.e. TEOS, VTOS and ETOS, as precursors for silica. The mixture was heated at 50 °C for 48 hours in order to initiate the formation of silica inside the rubber matrix by the sol-gel process of silanes. The silica content increased with increasing the silane loading, from 0-50 phr. However, the conversion of silane to silica is in the order TEOS (80%)>VTOS (60%)> ETOS (10%). The silica particles obtained from all silanes dispersed evenly in the rubber matrix. The silica generated from TEOS tended to agglomerate, but those from VTOS and ETOS which had alkyl groups on the particle surface, remained finely dispersed in the rubber matrix.

The swelling of silica-filled composites in toluene was found to decrease with increasing the silica content. Using the alkyltriethoxysilane did not significantly affect the swelling behavior in toluene. For water absorptivity, using the alkyltriethoxysilane with one vinyl group resulted in a reduction of water absorption.

The modulus at 300% elongation (M300), hardness and tension set of the *in-situ* silica/RVNR composites increased with increasing the amount of silica in the composites. The composites with silica generated from the mixed silanes, i.e. TEOS mixed with VTOS or ETOS, had higher M300 and tension set than the one with TEOS-generated silica. The tear strength did not change when increasing the silica content. It was however found that the uses of either VTOS or ETOS resulted in an increase of tear strength over the composites filled with TEOS-generated silica. It can conclude that Q structure-the silicon atoms that have without hydroxyl group, $\text{Si}(\text{O}-\text{Si})_4$ or one hydroxyl group, $(\text{Si}-\text{O})_{4-n}\text{Si}(\text{OH})_n$ effect on M300, hardness, and tension set while T structure-

the silicon atom in which one bond is connected to the alkyl group, $(\text{Si-OR})_n(\text{Si-O})_{3-n}\text{Si-R}$ effects on tear strength.

Thermal properties of the composites were measured by TGA. The onset temperatures of most of the composites were shifted to the higher temperatures by 5-8 °C in comparison with those of the pure NR film. Moreover, the mass change (%) in temperature range of 105-460 °C decreased with increasing silica content in the composites.

5.2 Future Directions

- Explore the use of other ratios of alkyltriethoxysilane and TEOS to prepare the composites with the aim to find the best formulation to effectively reinforce the composites.
- Develop a method for generation of silica inside the rubber latex having low dry rubber content (<50%DRC).
- Investigate in more detail about the effect of functional group on the silica particle surface on the mechanical properties of the composites.

REFERENCES

- Ansarifar, A., Azhar, A., Ibrahim, N., Shiah, S.F., and Lawton, J.M.D., **2005**, The use of a silanised silica filler to reinforce and crosslink natural rubber, *Int. J. adhes. adhes.*, vol. 25, 77-86.
- Bhowmick, A.K., Sengupta, R., Bandyopadhyay, A., Sabharval, S., and Chaki, T.K., **2005**, Polyamide-6,6/in situ silica hybrid nanocomposites by sol-gel technique:synthesis, characterization and properties, *Polymer*, vol. 46, 3343-3354.
- Bokobza, L., and Chauvin, J. P. **2005**, Reinforcement of natural rubber: use of *in-situ* generated silicas and nanofibres of sepiolite, *Polymer*, vol. 46, 4144-4151.
- Dafader, N.C., Haque, M.E., Akhtar, F., and Ahmad, M.U., **2006**, Study on grafting of different types of acrylic monomers onto natural rubber by γ -rays, *Radiat. Phys. Chem.*, vol. 75, 168-172.
- Gehman, S.D. and Auerbach, I., **1956**, Gamma-ray vulcanization of rubber, *Int. J. App. Radiat. Iso.*, vol. 1, 102-114.
- Han, Y.H., Taylor, A., Mantle, M.D., and Knowles, K.M., **2007**, Sol-gel-derived organic-inorganic hybrid material, *J. Non-Cryst Solids*, vol. 353, 313-320.
- Haque, M.E., Dafader, N.C., Akhtar, F., and Ahmad, M.U., **1996**, Radiation dose required for the vulcanization of natural rubber latex, *Radiat. Phys. Chem.*, vol. 48, 505-510.
- Hsiue, G.H., Chen, J.K., and Liu, Y.L., **2000**, Synthesis and characterization of nanocomposite of polyimide-silica hybrid from nonaqueous sol-gel process. *J. Appl. Polym. Sci.*, vol. 76, 1609-1618.
- Ikeda, Y., and Kohjiya, S., **1997**, *In situ* formed silica particles in rubber vulcanizate by the sol-gel method, *Polymer*, vol. 38, 4417-4423.

- Ikeda, Y., Tanaka, A., and Kohjiya, S., **1997**, Reinforcement of styrene-butadiene rubber vulcanizate by *in situ* silica prepared by the sol-gel reaction of tetraethoxysilane, *J. Mater. Chem.*, vol. 7, 455-458.
- Ikeda, Y., Kohjiya, S., Murakami, K., Iio, S., and Tanahashi, T., **2001**, In situ filling of silica onto "Green" natural rubber by the sol-gel process, *Rubber Chem. Technol.*, vol. 74, 16-27.
- Jai, X., Li, Y., Cheng, Q., Zhang, S., and Zhang, B., **2007**, Preparation and properties of poly(vinyl alcohol)/silica nanocomposites derived from copolymerization of vinyl silica nanoparticles and vinyl acetate, *Eur. Polym. J.*, vol. 43, 1123-1131.
- Kohjiya, S. and Ikeda, Y., **2000**, Reinforcement of general purpose grade rubbers by silica generate *in situ*, *Rubber Chem. Technol.*, vol. 73, 534-550.
- Kohjiya, S. and Ikeda, Y., **2000**, Reinforcement of natural rubber by silica generated *in situ*, *Proc. Japan Acad.*, vol. 76, 29-34.
- Loy, D.A., Baugher, B.M., Baugher, C.R., Schneider, D.A., and Rahimian, K., **2000**, Substituent effects on the Sol-Gel chemistry of organotrialkoxysilanes, *Chem. Mater.*, vol. 12, 3624-3632.
- Makuuchi, K., **2003**, An Introduction to Radiation Valcanization of Natural rubber latex, T.R.I. Global Co., Ltd., Bangkok.
- Mark, J.E., Abou-Hussein, R., Sen, T.Z., and Kloczkowski, A., **2005**, Some simulation on filler reinforcement in elastomers, *Polymer*, vol. 46, 8894-8904.
- Morton, M., **1973**, Rubber technology 2nd edition, Van Nostrand Reinhold, New York, pp.114-150.
- Nuntivanich, D., **2003**, Silica reinforcement of natural rubber by sol-gel process in latex. Master's Thesis, Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University.

- Peng, Z., Kong, L.X., Li, S.D., Chen, Y. and Huang, M.F., **2007**, Self-assembled natural rubber/silica nanocomposites: Its preparation and characterization, *Compos. Sci. Technol*, Article in press.
- Rankin, S.E. and Tan, B., **2006**, Study of effects of progressive change in alkoxy silane structure on sol-gel reactivity, *J. Phys. Chem.*, vol. 110, 22353-22364.
- Sae-oui, P., Sirisinha, C., Wantana, T. and Hatthapanit, K., **2007**, Influence of silica loading on the mechanical properties and resistance to oil and thermal aging of CR/NR blends, *J. Appl. Polym. Sci.*, vol.104, 3478-3483.
- Siramanon, J., **2005**, Reinforcement of natural rubber by silica generated from sol-gel process of silanes in latex, Master's Thesis, Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University.
- Sombatsompop, N., Wimolmala, E. and Markpin, T., **2007**, Fly-ash particles and precipitated silica as fillers in rubber. II. Effect of silica content and Si69-Treatment in natural rubber/styrene-butadiene rubber vulcanizates, *J. Appl. Polym. Sci.*, vol. 104, 3396-3405.
- Thiangchanya, A., Siri-upathum, C., Na-ranong, N., and Sonsuk, M., **2003**, Improvement of RVNRL film properties by adding fumed silica and hydroxyl apatite, *Songklanarin Journal of Science and Technology*, vol. 25, 53-61.
- Zhonghai, C and Makuuchi, K. **1989**, N-butyl acrylate as a sensitizer of radiation vulcanization of natural rubber latex, *Proceeding International Symposium of Radiation Vulcanization of Natural Latex*, JAERI-M Japan, 326.



APPENDIX

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Table A-1 Water absorption (%) of the *in situ* silica/RVNR composites

sample	1	2	3	Average \pm SD
RVNR	5.6311	9.4889	7.3662	7.50 \pm 1.93
T50	6.0345	6.8393	6.2209	6.36 \pm 0.42
V50	2.2745	2.2732	2.3772	2.31 \pm 0.06
E50	6.2701	4.7349	6.9815	6.00 \pm 1.15
T45V5	5.2571	6.0895	5.6502	5.67 \pm 0.42
T45E5	6.9771	6.7978	6.5675	6.78 \pm 0.21

Table A-2 Hardness (shore A) of the *in situ* silica/RVNR composites

sample	1	2	3	4	5	Average \pm SD
RVNR	29	29	29	29	28	28.8 \pm 0.4
T10	31	31	31	31	31	31.0 \pm 0.0
T20	35	35	35	35	34	34.8 \pm 0.4
T30	35	36	36	36	36	35.8 \pm 0.4
T40	38	38	39	38	38	38.2 \pm 0.4
T50	40	40	39	39	40	39.6 \pm 0.5
V50	36	37	37	37	36	36.6 \pm 0.5
E50	27	27	26	28	27	27.0 \pm 0.7

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Table A-3 The stress of the *in situ* silica/RVNR composites at various elongation

sample	Stress (MPa)			
	50%elongation	100%elongation	300%elongation	500%elongation
RVNR	0.417 ± 0.012	0.547 ± 0.012	1.053 ± 0.012	2.843 ± 0.177
T10	0.482 ± 0.013	0.630 ± 0.020	1.280 ± 0.032	3.474 ± 0.091
T20	0.564 ± 0.023	0.746 ± 0.038	1.760 ± 0.055	5.528 ± 0.246
T30	0.602 ± 0.008	0.804 ± 0.025	2.192 ± 0.016	7.328 ± 0.249
T40	0.628 ± 0.008	0.884 ± 0.028	2.630 ± 0.048	8.660 ± 0.278
T50	0.658 ± 0.015	0.930 ± 0.046	2.932 ± 0.091	9.644 ± 0.234
V10	0.440 ± 0.025	0.580 ± 0.044	1.270 ± 0.115	3.856 ± 0.288
V20	0.476 ± 0.005	0.636 ± 0.024	1.548 ± 0.059	4.330 ± 0.059
V30	0.508 ± 0.019	0.690 ± 0.021	1.756 ± 0.083	4.834 ± 0.334
V40	0.528 ± 0.011	0.736 ± 0.031	1.858 ± 0.117	5.298 ± 0.319
V50	0.598 ± 0.013	0.812 ± 0.016	2.278 ± 0.102	6.336 ± 0.410
E10	0.442 ± 0.004	0.590 ± 0.012	1.292 ± 0.030	4.416 ± 0.523
E20	0.444 ± 0.005	0.602 ± 0.013	1.298 ± 0.031	4.364 ± 0.172
E30	0.436 ± 0.013	0.566 ± 0.005	1.252 ± 0.015	4.088 ± 0.472
E40	0.420 ± 0.007	0.568 ± 0.008	1.244 ± 0.028	3.938 ± 0.109
E50	0.432 ± 0.019	0.582 ± 0.016	1.314 ± 0.025	4.204 ± 0.333
T5V45	1.015 ± 0.009	1.350 ± 0.042	3.682 ± 0.093	9.908 ± 0.130
T45V5	0.802 ± 0.013	1.166 ± 0.033	4.002 ± 0.119	N/A
T15E35	0.682 ± 0.008	0.950 ± 0.045	2.612 ± 0.113	9.254 ± 0.391
T25E25	0.794 ± 0.009	1.132 ± 0.039	3.448 ± 0.065	10.635 ± 0.106
T35E15	0.744 ± 0.005	1.090 ± 0.042	3.298 ± 0.143	10.688 ± 0.827
T45E5	0.754 ± 0.018	1.060 ± 0.027	3.806 ± 0.088	N/A

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Table A-4 Tension set (%) of the *in situ* silica/RVNR composites

sample	1	2	3	Average ± SD
T10	3.03	4.28	4.56	3.96 ± 0.81
T20	4.73	4.10	3.33	4.05 ± 0.70
T30	4.21	5.73	3.64	4.53 ± 1.08
T40	4.61	6.13	5.12	5.29 ± 0.77
T50	4.52	6.38	5.12	5.34 ± 0.95
V30	4.77	3.39	3.43	3.86 ± 0.79
V50	4.29	4.06	3.50	4.16 ± 0.72
E50	2.34	2.75	2.39	2.49 ± 0.22
T45V5	5.21	5.37	5.92	5.50 ± 0.37
T45E5	5.27	5.26	5.97	5.50 ± 0.41

Table A-5 The tear strength (MPa) of the *in situ* silica/RVNR composites

sample	1	2	3	Average ± SD
RVNR	10.53	9.99	11.40	10.64 ± 0.70
T10	8.25	7.46	10.69	8.80 ± 1.68
T20	10.94	14.59	16.31	13.95 ± 2.74
T30	10.30	13.38	9.16	10.95 ± 2.18
T40	8.98	9.57	12.24	10.26 ± 1.74
T50	8.93	10.64	9.80	9.79 ± 0.86
V10	14.84	10.63	12.67	12.71 ± 2.10
V20	15.89	14.38	18.39	16.22 ± 2.02
V30	9.31	13.13	13.50	11.98 ± 2.32
V40	12.39	11.51	12.80	12.24 ± 0.66
V50	14.83	17.31	14.45	15.53 ± 1.55
E50	14.97	13.71	16.60	15.09 ± 1.44
T35V15	10.99	11.13	11.95	11.36 ± 0.52
T45V5	9.50	9.56	11.69	10.25 ± 1.24
T35E15	11.40	11.90	12.34	11.90 ± 0.43
T45V5	10.41	10.80	10.64	10.62 ± 0.20

Table A-6 TGA analysis of the *in situ* silica/RVNR composites

sample	Mass change (%)				Total mass change (%)	Residual Mass (%)	Total mass (%)
	RT-105 (°C)	105-460(°C)	460-600(°C)	600-900(°C)			
RVNR	0.79	92.29	5.07	0.42	98.57	1.23	99.8
T10	1.00	88.28	6.12	0.07	95.47	4.36	99.83
T20	1.29	85.52	6.96	0.07	93.84	6.18	100.02
T30	1.15	84.14	7.18	0.14	92.61	7.43	100.04
T40	0.59	82.76	6.37	0.11	89.83	9.99	99.82
T50	0.92	80.33	6.53	0.09	87.87	12.01	99.88
V50	1.17	79.76	7.52	0.20	88.65	11.31	99.96
E50	0.74	88.60	6.24	0.03	95.61	4.15	99.76
T45E5	0.73	79.67	5.18	0.13	85.71	14.22	99.93
T45V5	0.27	80.41	5.90	0.01	86.59	13.28	99.87



สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

VITAE

Name: Miss Kamolchat Charungchitaree

Date of birth: May 12th, 1982

Address: 4/11 Moo 9 Raminthra Road, Tharang, Bangkok, Bangkok 10230.

Educational background:

2000-2003 B.Sc. Chulalongkorn University, Bangkok, Thailand

2004-2007 M.Sc. Petrochemistry and Polymer Science Program,
Chulalongkorn University, Bangkok, Thailand

Presentation

16-17 Mar 2006 : Oral presentation on 14th Congress on Faculty of Science,
Chulalongkorn University, Thailand

10-12 Oct 2006 : Oral presentation on The 32nd Congress on Science &
Technology (STT32), Thailand

12-14 Dec 2006 : Poster presentation on The 2nd Mathematics and Physical
Science Graduate Conference (2nd MPSGC), Singapore

10-11 May 2007 : Oral presentation on The 1st Polymer Graduate Conference
of Thailand, Thailand

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย