

ผลของสารตัวเติมผสมซิลิกา/คาร์บอนแบล็กต่อสมบัติเชิงกลและสถานะยานวิทยาของยางสไตรีนบิวทา

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EFFECTS OF SILICA/CARBON BLACK HYBRID FILLER ON MECHANICAL
PROPERTIES AND MORPHOLOGY OF STYRENE BUTADIENE
RUBBER/ACRYLONITRILE BUTADIENE RUBBER BLENDS



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EFFECTS OF SILICA/CARBON BLACK HYBRID
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จันทร์สมร มะเอียด : ผลของสารตัวเติมผสมซิลิกา/คาร์บอนแบล็กต่อสมบัติเชิงกล และสัณฐานวิทยาของยางสไตรีนบิวทาไดอีน/ยางอะครีโลไนไตรล์บิวทาไดอีน เบลนด์ (EFFECTS OF SILICA/CARBON BLACK HYBRID FILLER ON MECHANICAL PROPERTIES AND MORPHOLOGY OF STYRENE BUTADIENE RUBBER/ACRYLONITRILE BUTADIENE RUBBER BLENDS).
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คาร์บอนแบล็กและซิลิกาเป็นสารตัวเติมเสริมแรงสำหรับยาง เนื่องจากสารตัวเติมแต่ละชนิดจะมีข้อดีหลายอย่าง การใช้สารตัวเติมผสมซิลิกาและคาร์บอนแบล็กสามารถเพิ่มสมบัติเชิงกล สมบัติทางไดนามิกส์ การทนทานต่อน้ำมัน และความต้านทานต่อแรงอัด อย่างไรก็ตาม สัดส่วนที่เหมาะสมของสารตัวเติมผสมซิลิกา/คาร์บอนแบล็กที่ให้สมบัติสูงสุดจำเป็นต้องศึกษา การศึกษาในงานวิจัยนี้ศึกษาผลของสารตัวเติมผสมซิลิกา/คาร์บอนแบล็กต่อสมบัติเชิงกลของยางเบลนด์ SBR/NBR แปรสัดส่วนเบลนด์ของยาง SBR/NBR ปริมาณของสารตัวเติม และ สัดส่วนของสารตัวเติมผสมซิลิกา/คาร์บอนแบล็ก ระบบวัลคาร์ไนเซชันเป็นระบบร่วมของ ซัลเฟอร์และไดควิมิวเปอร์ออกไซด์ เพื่อปรับปรุงแรงยึดเหนี่ยวระหว่างซิลิกาและยางด้วยสาร ควบคู่ไซเลน 3 ชนิด คือ แกมมาเมอร์แคปโทโพรพิลเมทอกซีไซเลน แกมมาไกลซิโดกซีโพรพิลโพรเมทอกซีไซเลน และไวนิลทริส-2-เมทอกซีเอทอกซีไซเลน การวิเคราะห์ผลของสารตัวเติมซิลิกา/คาร์บอนแบล็กและสารควบคู่ไซเลนต่อสมบัติความต้านทานต่อแรงดึง โมดูลัสและความต้านทานต่อแรงอัด พบว่ายางเบลนด์ (SBR/NBR=30/70) ที่ปริมาณสารตัวเติมผสมซิลิกา/คาร์บอนแบล็ก 50 ส่วนต่อหนึ่งร้อยส่วนของยาง ที่ดัดแปลงด้วยสารควบคู่ไซเลน แกมมาเมอร์แคปโทโพรพิลเมทอกซีไซเลน แกมมาไกลซิโดกซีโพรพิลโพรเมทอกซีไซเลน และไวนิลทริส-2-เมทอกซีเอทอกซีไซเลน แสดงสมบัติเชิงกล การทนทานต่อน้ำมัน และความต้านทานต่อแรงอัดที่ดี สามารถนำไปใช้เป็นโอริงที่มีสมบัติการทนทานต่อน้ำมันเครื่องยนตร์ระดับปานกลาง (น้ำมันเอสทีเอ็ม เบอร์ 1 และน้ำมันเบรค)

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ สาขาวิชาปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ สาขาวิชาปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์
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Carbon black (CB) and silica have been used as the reinforcement fillers of rubber composites. As the each filler possesses its own advantages, the use of silica/CB blends could increase the mechanical, dynamic properties, oil resistance and compression set. However, the appropriate silica/CB ratio giving rise to the optimum properties needs to be study. In this work, the effect of silica/CB hybrid filler on mechanical properties of SBR/NBR blends were studied and the variables are blending ratio of SBR/NBR blends, filler content and ratio of silica/CB hybrid filler. The combination of sulfur and dicumylperoxide as vulcanizing systems was employed. To improve interaction between silica and rubber matrix, 3 types of silane coupling agent, γ -mercaptopropylmethoxysilane, γ -glycidoxypropyltrimethoxysilane and vinyl-*tris*-(2-methoxyethoxy) silane were used. The effects of silica/CB hybrid filler and coupling agent in rubber compound on tensile strength, modulus, and compression set and oil resistance were analyzed. This rubber blends (SBR/NBR=30/70) with 50 phr of silica/CB hybrid filler modified with γ -mercaptopropyltrimethoxysilane, γ -glycidoxypropylmethoxysilane, vinyl-*tris*-(2-methoxyethoxy) silane exhibited good mechanical properties oil resistance and compression set and could be used as o-ring for motor oil medium resistance (ASTM oil no.1 and brake fluid).

Field of Study : Petrochemistry and polymer science

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ศูนย์วิทยทรัพยากร
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CONTENTS

	PAGE
ABSTRACT (THAI)	iv
ABSTRACT (ENGLISH).....	v
ACKNOWLEDGEMENTS	vi
CONTENTS.....	vii
LIST OF TABLES.....	x
LIST OF FIGURES.....	xii
LIST OF ABBREVIATIONS.....	xv
CHAPTER I INTRODUCTION.....	1
1.1 The Purpose of the research work.....	1
1.2 Objective of the Research Work.....	2
1.3 Scope of the Research Work.....	2
CHAPTER II THEORY AND LITERATURE REVIEWS.....	4
2.1 Elastomers.....	4
2.1.1 Styrene butadiene rubber (SBR).....	5
2.1.2 Acrylonitrile butadiene rubber (Nitrile rubber;NBR).....	6
2.2 Theory of Vulcanization.....	8
2.2.1 Vulcanization of Specific Elastomer.....	8
2.2.2 Influence of Crosslink Type and Density.....	9
2.2.3 Sulfur Vulcanization Systems.....	11
2.2.4 Peroxide Vulcanization System.....	14
2.3 Elastomer blends.....	17
2.4 Fillers.....	17
2.4.1 Carbon Blacks.....	17
2.4.2 Silicas.....	19
2.5 Surface Treatment.....	21
2.6 Literatures review.....	23

CHAPTER III EXPERIMENTAL.....	27
3.1 Raw Materials.....	27
3.2 Instruments.....	28
3.3 Procedures.....	28
3.3.1 Compounding and Cure Assessment.....	28
3.3.2 Preparation of SBR/NBR blends.....	29
3.3.3 Preparation of total silica/CB hybrid filler content of SBR/NBR blends.....	29
3.3.4 Vulcanization Process.....	29
3.4 Testing.....	33
3.4.1 Determination of Cure Characteristics.....	33
3.4.2 Tensile Properties.....	33
3.4.3 Hardness Measurement.....	34
3.4.4 Compression Set.....	34
3.4.5 Thermal Aging Properties.....	35
3.4.6 Measurement of Swelling Behaviour (Oil resistance).....	35
3.4.7 Determination of Specific Gravity.....	36
3.4.8 Elastic retraction test at low temperature (TR test).....	36
3.4.9 Scanning Electron Microscopy (SEM).....	38
CHAPTER IV RESULTS AND DISCUSSIONS.....	39
4.1 Cure characteristics.....	39
4.2 Mechanical properties.....	42
4.2.1 Tensile Properties.....	42
4.2.2 Hardness.....	48
4.2.3 Compression set.....	49
4.3 Thermal Aging Properties.....	51
4.4 Swelling.....	56
4.5 Low Temperature Properties.....	61
4.6 Morphology.....	64

	PAGE
CHAPTER V CONCLUSIONS AND FUTURE WORK	69
5.1 Conclusion.....	69
5.2 Future Work.....	70
REFERENCES.....	71
APPENDICES.....	74
APPENDIX A.....	75
APPENDIX B	77
APPENDIX C.....	79
VITAE	89



ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

LIST OF TABLES

TABLE	PAGE
2.1 NBR properties – relationship to acrylonitrile content.....	7
2.2 Crosslink bond energies.....	10
2.3 Category of accelerator groups and their relative curing speeds.....	12
2.4 Composition of conventional, semi-EV and EV vulcanization syste.....	12
2.5 Vulcanizate structure and properties of three sulfur-curing systems.....	13
2.6 Peroxide for curing elastomers.....	14
2.7 Advantages and disadvantages of peroxide crosslink.....	15
2.8 Relative crosslinking efficiencies of various polymers with DCP.....	15
2.9 Carbon black classification.....	19
2.10 Silica typical properties.....	20
3.1 Rubber and chemicals used in this study.....	27
3.2 Instruments used in this study.....	28
3.3 Formulation of SBR/NBR blends.....	30
3.4 Formulation of rubber compound with various silica/carbon black hybrid fillers and silane coupling agents.....	30
4.1 Effect of blending ratios of SBR/NBR blends on cure characteristics at different curing temperature.....	40
4.2 Effect of silica/CB hybrid filler content and silane coupling agent types of SBR/NBR blends on cure characteristics at different curing temperatur.....	41
4.3 Effect of blending ratios of SBR/NBR blends on mechanical properties.....	44
4.4 Effect of silica/CB hybrid filler content and silane coupling agents on mechanical properties of SBR/NBR blend.....	46
4.5 Effect of blending ratios of SBR/NBR blends on properties retention after thermal aging at 100°C x 70.....	52
4.6 Effect of silica/CB hybrid filler content and silane coupling agents of SBR/NBR blends on properties retention after thermal aging at 100°C x 70h.....	53
4.7 Effect of blend ratios on percentage of change in properties of SBR/NBR Blends after immersion in oil.....	57

TABLE	PAGE
4.8 Effect of silica/CB hybrid filler content and silane coupling agents of SBR/NBR blends on percentage of change in properties after immersion in oil.....	58
4.9 Effect of hybrid filler content with silane coupling agent types of SBR/NBR blends on elastic retraction at low temperature (TR).....	62
A-1 Elastomer properties.....	75
A-2 Carbon black properties.....	75
A-3 Silica properties.....	75
A-4 Silane coupling agent properties.....	76
A-5 Specification and typical properties of ASTM oils.....	76
C-1 Mechanical properties of SBR/NBR vulcanizates according to ASTM D412...79	79
C-2 Mechanical properties of silica/CB filled SBR/NBR vulcanizates and silane coupling agents according to ASTM D412.....	80
C-3 Compression set property of SBR/NBR vulcanizates according to ASTM D395 method B.....	81
C-4 Compression set property of silica/CB filled SBR/NBR vulcanizates and silane coupling agents according to ASTM D395 method B.....	82
C-5 Change in volume of SBR/NBR vulcanizates after immersion in ASTM oil no.1 and ASTM oil no.3 at 100°C x 70h according to ASTM D471.....	83
C-6 Change in volume of SBR/NBR vulcanizates after immersion in Brake fluid and Fuel C at 25°C x 70h according to ASTM D471.....	84
C-7 Change in volume of silica/CB filled SBR/NBR vulcanizates and silane coupling agents vulcanizates after immersion in ASTM oil no.1 andmASTM oil no.3 at 100°C x 70h according to ASTM D471.....	85
C-8 Change in volume of silica/CB filled SBR/NBR vulcanizates and silane coupling agents vulcanizates after immersion in Brake fluid and Fuel C at 25°C x 70h according to ASTM D471.....	87

LIST OF FIGURES

FIGURE	PAGE
2.1 Structure of styrene butadiene rubber.....	6
2.2 Structure of acrylonitrile butadiene rubber.....	7
2.3 Vulcanizates properties and crosslink density.....	10
2.4 Generalized structure in sulfur-vulcanized nature rubber.....	13
2.5 Scheme peroxide crosslinking mechanism. P-H = saturated or unsaturated elastomer.....	16
2.6 Silica surface group: siloxane (-Si-O-Si-) and isolated, vicinal, and germinal silanols (-Si-O-H).....	20
2.7 Structure of silane coupling agents.....	22
2.8 Illustration of silane coupling of polymer to silicate surface.....	23
3.1 The overall schematic experimental process for preparing SBR/NBR blends.....	31
3.2 The overall schematic experimental process for preparing SBR/NBR blends filled with silica/CB hybrid filler and silane coupling agents.....	32
3.3 Dumbbell (Die C) shape sample for tensile property testing.....	33
3.4 Compression set device.....	35
3.5 Example of testing apparatus for elastic retraction at low temperature.....	37
3.6 Shape and dimensions of test piece.....	37
3.7 Example of percentage retraction versus temperature curve.....	38
4.1 Structure and reaction of silane coupling agent on silica surface and polymer for; (a) structure of vinyl-tris(2-methoxyethoxy)silane, (b) structure of γ -glycidoxypopyltrimethoxysilane, (c) structure of γ -mercaptopopyltrimethoxysilane (d) reaction of silane coupling agent with silica surface.....	43
4.2 Effect of blending ratios of SBR/NBR blends on; (a) tensile strength, (b) elongation at break and (c) 100% modulus.....	45
4.3 Effect of silica/CB hybrid filler content and silane coupling agents of SBR/NBR blends on; (a) tensile strength, (b) elongation at break and (c) 100% modulus.....	47

FIGURE	PAGE
4.4 Hardness property for; (a) effect of blending ratios of SBR/NBR blends, (b) effect of silica/CB hybrid filler content with silane coupling agents of SBR/NBR blends.....	48
4.5 Compression set for; (a) effect of blending ratios of SBR/NBR blends, (b) effect of silica/CB hybrid filler content with silane coupling agents of SBR/NBR blends.....	50
4.6 Effect of blending ratios of SBR/NBR blends on; (a) tensile strength retention, (b) elongation at break retention, (c) 100% modulus retention and (d) hardness retention after thermal aging.....	54
4.7 Effect of silica/CB hybrid filler content and silane coupling agents of SBR/NBR blends on; (a) tensile strength retention and (b) elongation at break retention (c) 100% modulus retention and (d) hardness retention.....	55
4.8 Schematic representation of rubber swelling.....	57
4.9 Effect of blending ratios of SBR/NBR blends on percentage of change in volume after immersion in oil; (a) ASTM oil No.1, (b) Brake fluid (c) ASTM oil No.3 and (d) Fuel C.....	59
4.10 Effect of silica/CB hybrid filler content and silane coupling agents of SBR/NBR blends on percentage of change in volume after immersion in oil; (a) ASTM oil No.1, (b) Brake fluid, (c) ASTM oil No.3 and (d) Fuel C.....	60
4.11 Effect of silica/CB hybrid filler content and silane coupling agents of SBR/NBR blends on elastic retraction; (a) without silane agent, (b) γ -mercaptopropyltrimethoxysilane, (c) γ -glycidoxypropylmethoxysilane and (d) vinyl-tris-(2-methoxyethoxy)silane.....	63
4.12 SEM photomicrographs of the fracture surface of silica/CB hybrid filler filled SBR/NBR blends and without silane coupling agent: (a) 30 phr of hybrid filler, (b) 40 phr of hybrid filler and (c) 50 phr of hybrid filler.....	65
4.13 SEM photomicrographs of the fracture surface of silica/CB hybrid filler content 30 phr and silane coupling agent types of SBR/NBR blends: (a) without silane, (b) γ -mercaptopropyltrimethoxysilane, (c) γ -glycidoxypropylmethoxysilane and (d) vinyl-tris-(2-methoxyethoxy)silane.....	66

FIGURE	PAGE
4.14 SEM photomicrographs of the fracture surface of silica/CB hybrid filler content 40 phr and silane coupling agent types of SBR/NBR blends: (a) without silane, (b) γ -mercaptopropyltrimethoxysilane, (c) γ -glycidoxy-propylmethoxysilane and (d) vinyl-tris-(2-methoxyethoxy)silane.....	67
4.15 SEM photomicrographs of the fracture surface of silica/CB hybrid filler content 50 phr with silane coupling agent types of SBR/NBR blends: (a) without silane, (b) γ -mercaptopropyltrimethoxysilane, (c) γ -glycidoxy-propylmethoxysilane and (d) vinyl-tris-(2-methoxyethoxy)silane.....	68
B-1 Cure curves of rubber compound with different blend ratios for; (a) 180°C and (b) 190°C.....	77
B-2 Cure curves of silica/CB filled rubber compound and silane coupling agent types for; (a) 180°C and (b) 190°C.....	78

LIST OF ABBREVIATIONS

$^{\circ}\text{C}$:	Degree Celsius
g	:	gram
kg	:	Kilogram
mg	:	Milligram
MW	:	Molecular Weight
μm	:	Micrometer
%wt	:	Percent by weight
avg	:	Average
nm	:	Nanometer
phr	:	Part per hundred rubber
ASTM	:	The American Society for Testing and Material
CBS	:	N-Cyclohexyl-2-benzothiazolesulfenamide
DCP	:	Dicumyl peroxide
TR-10	:	10 percentage of elastic retraction
TR-30	:	30 percentage of elastic retraction
TR-50	:	50 percentage of elastic retraction
TR-70	:	70 percentage of elastic retraction

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CHAPTER I

INTRODUCTION

1.1 The Purpose of the Research Work

The rubber blends are frequently used in the rubber industry to obtain best compromise in compound physical properties, processability and cost. A blend can offer a set of properties that can give the potential of application area not possible with either of the polymers comprising the blend [1]. Styrene butadiene rubber (SBR) has good mechanical properties. It has good abrasion resistance, greater ozone resistance and greater weatherability than natural rubber does. But its oil resistance is very poor. On the other hand, nitrile rubber (NBR) has good solvent resistance but its mechanical properties are poor compared with that of SBR [2].

One of the most important modification for the rubber blends is the reinforcement of the rubber by rigid entries. Reinforcement is primarily the enhancement of strength and strength-related properties, abrasion resistance, hardness, and modulus. In most applications, carbon black (CB) and silica have been used as the main reinforcing fillers that increase the usefulness of rubber [3]. Carbon black has very good compatibility with rubber. However, particle surface of silica have hydrophilic silanol groups, which results in strong filler-filler interaction by hydrogen bonds. Hence, silica dispersion is worse than carbon black dispersion in rubber compounds [4]. Therefore, surface treatments are need to improve the reinforcement of the composites.

Conventional methods used to modify the surface of silicas are largely suggested in terms of thermal, chemical, electrochemical, and coupling agent treatment. Among term, silane coupling agents have been used in the rubber industry to improve the performance of silica in rubber compounds. A silane coupling agent contains functional groups that can react with the rubber and the silica. In this way, the rubber-silica adhesion is increased and consequently the reinforcing effect of the silicas is added [5].

1.2 Objective of the Research Work

Study the effects of silica/carbon black (CB) hybrid filler content and silane coupling agent of SBR/NBR (30/70) blends. The mechanical properties, thermal aging stability, morphology, oil resistance and compression set were investigated for automotive application (seal and O-ring products).

1.3 Scope of the Research Work

The SBR/NBR blends were prepared at various blend ratios at 100/0, 70/30, 50/50, 30/70 and 0/100 (wt %). The silica/CB hybrid fillers loading (General semi-reinforcement; G-N550, and precipitated silica; Nisil ER) were varied at ratios of 15/15, 20/20 and 25/25 phr with three types of silane coupling agents. (M; γ -mercaptopropylmethoxysilane, G; γ -glycidoxypropyltrimethoxysilane, V; vinyl-*tris*-(2-methoxyethoxy) silane) and combination of sulfur and dicumyl peroxide as vulcanizing systems. The effects of silica/CB hybrid filler content and silane coupling agent on properties of SBR/NBR blends were investigated.

The experimental procedures were carried out as follows:

1. Survey literatures and study the research work.
2. Prepare SBR/NBR blends by using a two-roll mixing mill at various blending ratios (100/0, 70/30, 50/50, 30/70 and 0/100 wt %).
3. Prepare SBR/NBR (30/70) compounds by using an internal mixer (kneader) at various silica/CB hybrid filler content (Nisil ER/G-N550; 15/15, 20/20 and 25/25 phr) with three types of silane coupling agent.
4. Study cure characteristics of SBR/NBR blends by using moving die rheometer at temperature 180⁰C and 190⁰C.
5. Prepare vulcanizates by compression molding at 180⁰C and 120 kg/cm².
6. Investigate mechanical properties such as tensile properties, hardness and compression set of the vulcanizates.
7. Investigate thermal aging properties of the vulcanizates.
8. Investigate oil resistance properties of the vulcanizates.
9. Investigate morphology of the vulcanizates by using Scanning Electron Microscopy (SEM) technique.

10. Investigate low temperature properties of the vulcanizates by using Tension Retraction (TR) technique.
11. Summarize the results.



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CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Elastomers [6]

An elastomer is a polymer with the property of viscoelasticity (colloquially "elasticity"), generally having notably low Young's modulus and high yield strain compared with other materials. The term, which is derived from *elastic polymer*, is often used interchangeably with the term rubber, although the latter is preferred when referring to vulcanisates. Each of the monomers which link to form the polymer is usually made of carbon, hydrogen, oxygen and/or silicon. Elastomers are amorphous polymers existing above their glass transition temperature, so that considerable segmental motion is possible. At ambient temperatures, rubbers are thus relatively soft ($E \sim 3\text{MPa}$) and deformable. Their primary uses are for seals, adhesives and molded flexible parts.

Elastomers are usually thermosets (requiring vulcanization) but may also be thermoplastic. The long polymer chains cross-link during curing, i.e., vulcanizing. The molecular structure of elastomers can be imagined as a 'spaghetti and meatball' structure, with the meatballs signifying cross-links. The elasticity is derived from the ability of the long chains to reconfigure themselves to distribute an applied stress. The covalent cross-linkages ensure that the elastomer will return to its original configuration when the stress is removed. As a result of this extreme flexibility, elastomers can reversibly extend from 5-700%, depending on the specific material. Without the cross-linkages or with short, uneasily reconfigured chains, the applied stress would result in a permanent deformation.

Temperature effects are also present in the demonstrated elasticity of a polymer. Elastomers that have cooled to a glassy or crystalline phase will have less mobile chains, and consequentially less elasticity, than those manipulated at temperatures higher than the glass transition temperature of the polymer.

2.1.1 Styrene Butadiene Rubber (SBR) [7], [8]

Emulsion polymerized styrene-butadiene rubber (E-SBR) is one of the most widely used polymers in the world today. In the 1930's, the first emulsion polymerized SBR known as Buna S was prepared by I. G. Farbenindustrie in Germany. The U. S. Government in 1940 established the Rubber Reserve Company to start a stockpile of natural rubber and a synthetic rubber program. These programs were expanded when the United States entered World War II. The synthetic rubber efforts were initially focused on a hot polymerized (41° C) E-SBR. Production of a 23.5% styrene and 76.5% butadiene copolymer began in 1942. Cold polymerized E-SBR (5°C), that has significantly better physical properties than hot polymerized SBR, was developed in 1947.

The styrene content of most emulsion SBR varies from 0% to 50%. The percent styrene of most commercially available grades of E-SBR is 23.5%. In the cold polymerized E-SBRs, the butadiene component has, on average, about 9% cis-1,4, 54.5% trans-1,4, and 13% of vinyl-1,2 structure. At a 23.5% bound styrene level, the glass transition temperature, T_g of SBR is about -50°C . As the styrene content in the SBR increases, the glass transition temperature also increases. Rubbers with very low T_g values are characterized by a high resilience and good abrasion resistance, but have poor wet traction. By contrast, those rubbers with high T_g , as, for instance, SBR 1721, exhibit a low resilience and poor abrasion resistance with an excellent wet traction.

E-SBR is commercially available in Mooney viscosities ranging from 30 to about 120 (ML1+4@125C). Lower Mooney viscosity E-SBR grades band more easily on the mill, incorporate fillers and oil more readily, show less heat generation during mixing, are calendered more easily, shrink less, give higher extrusion rates and have superior extrudate appearance than the higher Mooney viscosity grades. On the other hand, the high Mooney viscosity SBR's have better green strength, less porosity in the vulcanizate, and accept higher filler and oil loadings.

As the molecular weight of the SBR increases, the vulcanizate resilience and the mechanical properties, particularly tensile strength and compression set, improve. The processability of SBR improves as its molecular weight distribution broadens. Formation of high molecular weight fractions with the increase in the average molecular weight can however, prevent improvements in the processability. This is

due to the fact that the tendency for gel formation also increases at higher molecular weights. Figure 2.1 shows structure of styrene butadiene rubber.

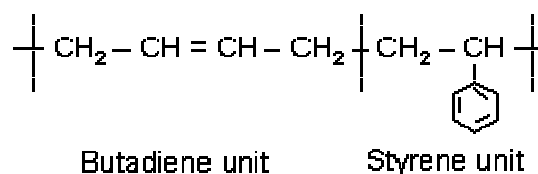


Figure 2.1 Structure of styrene butadiene rubber [7].

E-SBR is predominantly used for the production of car and light truck tires. For heavy truck and high speed tires, E-SBR is practically not used at all, because of the higher dynamic heat build-up, in comparison with NR, IR, or BR. Other applications for E-SBR are belting, molded rubber goods, shoe soling, cable insulation and jacketing, hose, roll coverings, pharmaceutical, surgical, and sanitary products, food packaging, etc[8].

2.1.2 Acrylonitrile Butadiene Rubber (Nitrile rubber; NBR) [9], [10]

NBR is produced in an emulsion polymerization system. The water, emulsifier/soap, monomers (butadiene and acrylonitrile), radical generating activator, and other ingredients are introduced into the polymerization vessels. The emulsion process yields a polymer latex that is coagulated using various materials (e.g. calcium chloride, aluminum sulfate) to form crumb rubber that is dried and compressed into bales. Some specialty products are packaged in the crumb form. NBR producers vary polymerization temperatures to make "hot" and "cold" polymers. Acrylonitrile (ACN) and butadiene (BD) ratios are varied for specific oil and fuel resistance and low temperature requirements. ACN content is one of two primary criteria defining each specific NBR grade.

The ACN level (about 18 to 51%), by reason of polarity, determines several basic properties, such as oil and solvent resistance low-temperature flexibility/glass transition temperature, and abrasion resistance. The elastic behavior of NBR vulcanizates is poor as the concentration of bound acrylonitrile in the NBR increases, but at the same time the copolymer is more thermoplastic, which is advantageous

regarding the processibility compounds [9]. Specialty NBR polymers which contain a third monomer (e.g. divinyl benzene, methacrylic acid) are also offered. Some NBR elastomers are hydrogenated to reduce the chemical reactivity of the polymer backbone, significantly improving heat resistance. Each modification contributes uniquely different properties [10].

Beside of, NBR has low permeability to gases, depending on its acrylonitrile content. The high polarity of NBR also influences its compatibility with certain compounding ingredients, and non-polar rubbers such as SBR and BR. Figure 2.2 shows structure of acrylonitrile butadiene rubber. Table 2.1 summarizes most of the common properties for conventional NBR polymers. The direction of the arrows signifies an increase/improvement in the values.

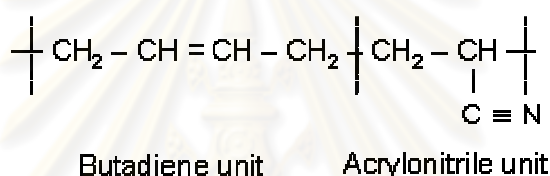


Figure 2.2 Structure of acrylonitrile butadiene rubber [9].

Table 2.1 NBR properties – relationship to acrylonitrile content [9]

<u>NBR with Lower Acrylonitrile Content</u>		<u>NBR with Higher Acrylonitrile Content</u>
	Processability	→
	Cure Rate w/Sulfur Cure System	→
	Oil/Fuel Resistance	→
	Compatibility w/Polar Polymers	→
	Air/Gas Impermeability	→
	Tensile Strength	→
	Abrasion Resistance	→
	Heat-Aging	→
←	Cure Rate w/Peroxide Cure System	
←	Compression Set	
←	Resilience	
←	Hysteresis	
←	Low Temperature Flexibility	

2.2 Theory of Vulcanization [11].

A practical rubber product is developed by incorporating crosslinks which chemically tie together the independent elastomer chains. This process is generally referred to as vulcanization and a better understanding can be developed by considering the following statements:

1. Much of our understanding of polymer chemistry is based upon the very basic assumption that the reactivity of a given group is unaffected by the size of the molecule of which it forms a part.
2. The essential requirement for a substance to be rubbery is that it consists of long, flexible chain-like molecules. The molecules themselves must therefore have a 'backbone' of many noncollinear single valence bonds, about which rapid rotation is possible as a result of thermal agitation.
3. It is now well established that the stress in a deformed (elastomeric) network originates within the chains of the network.
4. According to the theory of rubber elasticity (Flory), the retractive force resisting a deformation is proportional to the number of network supporting chains per unit volume of elastomer. A supporting chain is a segment of polymer backbone between network junctures (crosslinks). An increase in the number of junctures gives us an increase in the number of supporting chains.

2.2.1 Vulcanization of Specific Elastomers [11]

Vulcanization, the process of cross-linking elastomers, occurs by a chemical process initiated through some form of energy input. It occurs between two statistically favorable reactive sites. Such sites are available through one or more of the following conditions:

- **Inherent;** Double bonds in diene-containing elastomers.
- **Specific;** Double bonds pendant to the polymer backbone from cure-site monomers (EPDM, etc.).
- **Chemically induced;** Reactive sites left by the abstraction of backbone hydrogen or halogen atoms.

The sites are coupled to each other by covalent bonding via one or more of the following mechanisms:

1. Carbon-carbon bonds through the backbone.
2. Insertion of difunctional curatives such as sulfur between reactive sites.
3. Insertion of di- and multifunctional monomers such as acrylates, phenolics, or triazines between reactive sites.

In truly vulcanization, the most widely used group of elastomers consists of those containing a diene site for crosslinking, i.e.; Natural rubber (NR) and Polyisoprene (IR), Butadiene rubber (BR), Styrene-butadiene rubber (SBR), Isobutene-isoprene rubber (Butyl, IIR), and Nitrile-butadiene rubber (NBR), which are crosslinked by using sulfur as a vulcanizing agent.

2.2.2 Influence of Crosslink Type and Density [11]

Crosslinks create a profound effect on the mechanical properties of a vulcanized elastomer. The effect can be summarized by considering first the crosslink density, and then the individual crosslink type. Crosslink density or crosslink concentration of a network is described by Funke in terms of:

Mean molecular weight (M_c): Average mass of a polymer chain which connects two adjacent crosslinks.

Crosslink density: Moles of crosslinked basic units per weight unit of the crosslinked polymer.

Degree of crosslinking: Moles of crosslinked basic units per total moles of basic units.

Crosslinking index: Crosslinked basic units per primary (linear) macromolecules.

Figure 2.3 shows that the static modulus increases with vulcanization to a greater extent than the dynamic modulus. The dynamic modulus is a comprise of viscous and elastic responses, whereas the static modulus is a measure of the elastic component alone. Vulcanization, then, causes a tranfer from viscous or plastic behavior to elasticity.

The effect of crosslink type is explained by the covalent bond strengths of the various crosslinks, measured in kJ/mole (Table 2.2). The chemical bond of carbon-

carbon is created by free-radical mechanism, which can be created by a peroxide vulcanizing agent or by high energy radiation. The sulfur crosslinks are improved as previously outlined. The monosulfidic crosslinks are created by sulfur donor (such as, thiuram disulfide or morpholine disulfide). The disulfidic and polysulfidic crosslinks are created by varying ratio of sulfur-accelerator.

However, the subsequent formation of crosslinks depends on each of rubber types and vulcanization system, which is appropriate for application. Such as, a tire tread subject to a range of mechanical abuse would be dictating the use of polysulfidic crosslinks at a minimum density (high molecular weight). Seal, specifically O- ring, are under compression set over a broad temperature range. The conditions of these would dictate thermally stable crosslinks (carbon-carbon, carbon-sulfur-carbon) at a high density (low molecular weight). Motor mounts would logically require a density somewhere between these two.

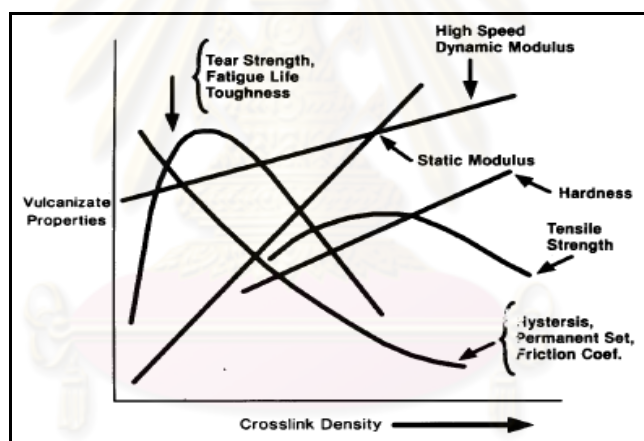


Figure 2.3 Vulcanizates properties and crosslink density [11].

Table 2.2 Crosslink bond energies [11]

Linkage Type	Bond Energy (kJ mole ⁻¹)
—C—C—	351
—C—S—C—	285
—C—S—S—C—	267
—C—S _x —C—	<267

2.2.3 Sulfur Vulcanization Systems [12]

Many reagents which are associated with the sulfur vulcanization is associated with polydienes, e.g. natural rubber, have been developed. These reagents are categorized into vulcanization agents, accelerators, activators, retarders, and pre-vulcanization inhibitors. Vulcanization agents consist of elemental sulfur (insoluble sulfur, colloidal sulfur) or an organic sulfur donor such as tetramethylthiuram disulfide (TMTD) or 4,4'-dithiobismorpholine (DTDM). The most important categories of accelerators are those based on sulfenamides, benzothiazoles, guanadines, and dithiocarbamic acid. The category of these accelerators, in terms of their chemical composition and speed of vulcanization, is shown in Table 2.3. Activators (sometimes called secondary accelerators) may be used to potentiate accelerators. Useful activators include metal oxides (usually zinc oxide), fatty acids, and nitrogen-containing bases. Retarders and prevulcanization inhibitors are added to obtain longer processing times by avoiding premature vulcanization (scorch). Retarders include acidic compounds (phthalic anhydride, salicylic and benzoic acids) and nitroso compounds. The most widely used prevulcanization inhibitor is N-cyclohexylthiophthalimide (CTP).

Rubber vulcanization by sulfur with no accelerators takes several hours and is not appropriate for commercial. With the use of accelerators, optimum curing can now be completed in periods as short as 2-5 min. Accelerated sulfur vulcanization is suitable for not only natural rubber (NR) and its synthetic rubber (IR), but also for other synthetic rubbers such as poly-butadiene rubber (BR), styrene-butadiene rubber (SBR), nitrile rubber (NBR), butyl rubber (IIR), and ethylene-propylene-diene rubber (EPDM).

Sulfur vulcanization systems are classified as conventional, semi-efficient (semi-EV), and efficient (EV), based on the level of sulfur and the ratio of accelerator to sulfur, as shown in Table 2.4. EV systems use low or even zero (with a sulfur donor) levels of sulfur and a relatively high level of accelerators. As shown in Table 2.5, the resultant vulcanizate efficiently utilizes sulfur to form networks in which the crosslinks are mainly monosulfidic, and which exhibit a low degree of main-chain modifications. The use of EV systems in natural rubber reduces or eliminates

reversion, except at very high curing temperatures. Thus, the resulting vulcanizates exhibits a high resistance to thermal and oxidative ageing.

The structures of sulfur-vulcanized rubbers have been determined by spectroscopic analyses such as IR, UV, ESR, and Raman⁴⁹⁻⁵¹ and by chemical methods. Figure 2.4 shows the structures of sulfur-vulcanization. These include cyclic sulfide units, pendant side groups (R may be an accelerator group), isomerized double bonds, and conjugated unsaturated bonds, in addition to a variety of sulfur crosslinking units.

Table 2.3 Category of accelerator groups and their relative curing speeds [12]

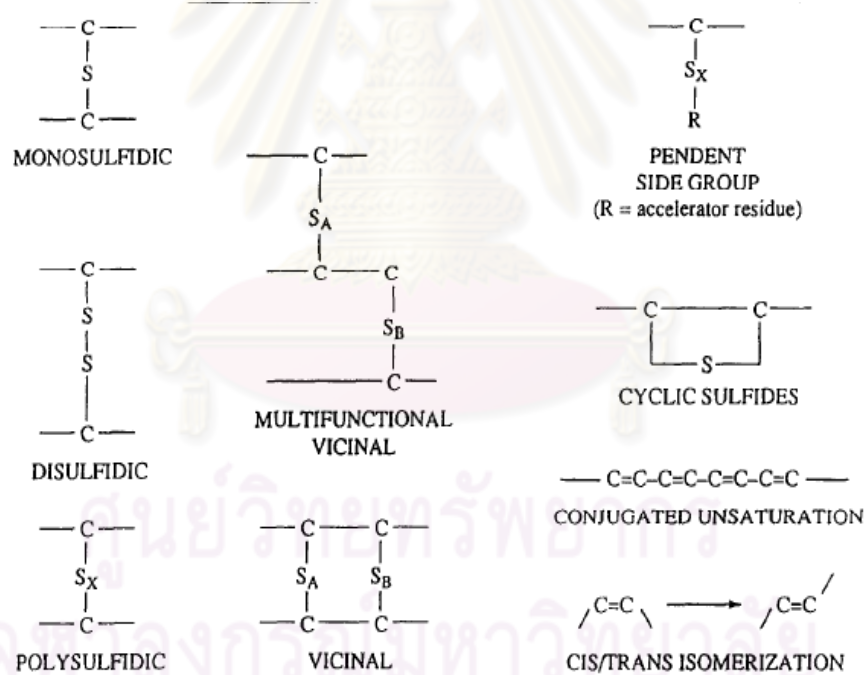
Type	Abbreviations	Relative curing speed
Guanidines	DPG	Slow
Dithiocarbamates	ZDBC	Very fast
Thiurams	TMTD, TMTM, DPTTS	Very fast
Thioureas	ETU	Fast
Thiophosphates	DIPDIS	Semi-fast
Thiazoles	MBT, MBTS, ZMBT	Moderate
Sulfenamides	CBS, MBS	Fast

Table 2.4 Composition of conventional, semi-EV and EV vulcanization system [12]

Type	Sulfur (S, phr)	Accelerator (A, phr)	A/S ratio
Conventional	2.0 – 3.5	1.0 – 0.4	0.1 – 0.6
Semi-EV	1.0 – 1.7	2.5 – 1.2	0.7 – 2.5
EV	0.4 – 0.8	5.0 – 2.0	2.5 – 1.2

Table 2.5 Vulcanizate structure and properties of three sulfur-curing systems [12]

Properties	Conventional	Semi-EV	EV
Poly- and disulfide crosslinks (%)	95	50	20
Monosulfidic crosslinks (%)	5	50	80
Cyclic sulfidic concentration	high	medium	low
Low-temperature crystallization resistance	high	medium	low
Heat-ageing resistance	low	medium	high
Reversion resistance	low	medium	high
Compression set, 22 h at 70°C (%)	30	20	10

**Figure 2.4** Generalized structure in sulfur-vulcanized nature rubber [12].

2.2.4 Peroxide Vulcanization System [12], [13]

Peroxides can be used to crosslink for the most elastomers. The importance of peroxide is half-life for vulcanizing. The commercially available peroxides and their 10 h half-life temperatures are shown in Table 2.6. In general, the diacyl peroxides are useful for the crosslinking of silicone elastomers, whereas the ketal and diakyl peroxides are used primarily for diene and ethylene-propylene elastomers. Compared with sulfur vulcanization, crosslinking by peroxides is a relatively simple process. The advantages and disadvantages of peroxide crosslinking are summarized in Table 2.7.

Beside of, the important of peroxide vulcanization is the relative crosslinking efficiency of some rubbers. Table 2.8 shows the relative crosslinking efficiency of some rubbers cured with dicumyl peroxide (DCP).

Table 2.6 Peroxide for curing elastomers [12].

Peroxide types	Examples	10 h Half-life (10°C)*
Diacyl peroxide		20 – 70
	Dibenzoyl peroxide	73
	Di(2,4-dichlorobenzoyl) peroxide	54
<i>t</i> -Alkyl peroxyesters		49 – 107
	<i>t</i> -Butyl perbenzoate	105
Di-(<i>t</i> -alkyl peroxy) ketals		92 – 115
	1,1-Di- <i>t</i> -butyl peroxy-3,3,5-trimethylcyclohexane	96
Di-alkyl peroxides	Di- <i>t</i> -butyl peroxide	128
	Di-cumyl peroxide	115
	2,5-Dimethyl-2,5-di-(<i>t</i> -butyl peroxy)hexane	119

*The temperature at which the peroxide has a half-life of 10 h

Table 2.7 Advantages and disadvantages of peroxide crosslink [12]

Advantages	Disadvantages
Short crosslinking time	Expensive crosslinking agent
Simple compounding	Low mechanical strength (TB, flex resistance)
Good heat-aging resistance	Crosslinking inhibited for kind of compounding ingredient
Less tension set and strain	Difficult hot-air cure
No mold contamination	Need secondary, cure of high temperature long time
Transparent rubbers possible	

Table 2.8 Relative crosslinking efficiencies of various polymers with DCP [12]

Polymers	Crosslinking efficiency
SBR	12.5
BR	10.5
NR	1.0
NBR	1.0
CR	0.5
RE	1.0
IIR	0

Networks formed from peroxide vulcanization typically have good heat aging stability and low compression set. These qualities are a direct manifestation of the chemical composition of the covalent crosslinks formed. Synergistic use of multifunctional coagents can improve upon these properties by increasing the crosslink density of the network and by altering the crosslink composition. Greater adhesion to polar substrates and better balance of heat-aged and dynamic properties result from a judicious choice of coagent [13].

The mechanism of peroxide crosslinking is shown in Figure 2.5. The crosslinking reactions include the homolytic decomposition of the peroxide to produce alkoxy radicals [Eq.(1)] followed by hydrogen-atom removal [Eq.(2)]. The hydrocarbon radicals undergo coupling [Eq.(3)] rather than disproportionate [Eq.(4)]. The cross-linking reaction forms coupling between polymer chains. For polydiene elastomers, experimental evidence indicates that the primary radical formed by peroxide decomposition eliminates a hydrogen atom from a carbon alpha to the double bond [Eq.(5)]. In natural rubber, the methyl group is also reactive towards hydrogen-atom abstraction [Eq.(6)].

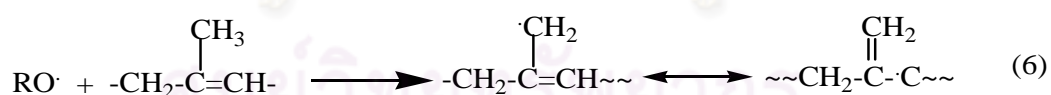
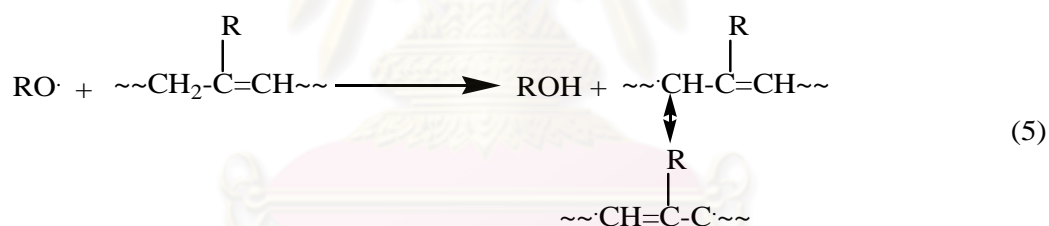
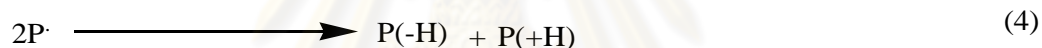


Figure 2.5 Scheme of peroxide crosslinking mechanism. P-H = saturated or unsaturated elastomer [12].

2.3 Elastomer Blends [14]

Rubbers are often blended with one another, or copolymerized with another in the polymerization stage. The blends are expected to have better properties and price than, the individual components hence giving technical and economic advantage. For example, the addition of small amounts of a selected synthetic rubber to another may improve such properties as oil and ozone resistance, or improve processing behavior.

Blends in emulsion and in solution synthetic rubbers polymerized often give processing difficulties due to their differences in Mooney viscosities and curing characteristics. In this case the final properties of the blend will be inferior to levels attainable with the individual rubbers. Properties adversely affected by non-compatible rubber blends include tensile strength, permanent set, low temperature behavior and co-vulcanizability. Reactivity differences in the blended phases, and/or diffusion of vulcanizing agents (which are generally polar) from the less polar to the more polar phase, may mean that consistency of blending may be difficult to achieve under factory conditions. In adequate co-vulcanization then leads to unfavorable mechanical properties, such as low tensile strength and poor dynamic behavior. This is also true when blending different grades of the same synthetic rubbers which have different Mooney viscosities and curing characteristics.

2.4 Fillers

The fillers are primarily classified as carbon blacks and light colored filler. Among the light colored fillers chemical position is primary the basic for classification. For example, one can list colloidal silica, calcium-and aluminium silicate, alumina gel, kaoline, silica, talcum, calcium carbonate, metal oxide, like zinc oxide and metal carbonates.

2.4.1 Carbon Blacks [8], [15]

The application of carbon black in rubber compounds is over a hundred years old. The incomplete combustion of hydrocarbons or the thermal cracking is processed for producing carbon blacks.

According to the production process, the carbon blacks are classified as follows; F = Furnace Black, C = Channel Blacks and T = Thermal Blacks. Furnace black is today the most important of them. Channel blacks have practically disappeared for the runner industry. Thermal blacks have in recent years been replaced by suitable furnace blacks because of economic and ecological factors, often with suitable changes in recipes. Reasons are increase in price of natural gas and costly air pollution control installations [8].

Carbon black structure gives rise to reinforcing effects and therefore the aggregate is the smallest form of a given carbon black grade well dispersed in an elastomer that will still keep all the reinforcing capabilities of the filler. The reinforcing character of carbon black grades is accordingly related to both size of the elementary particle and the structure of aggregate essentially, whilst certain singular flow properties of filled rubber compounds can be shown to depend also parameters. The ASTM classification of carbon black reflects the importance of carbon black structure, as shown in Table 2.9. All carbon blacks are graded with respect to a four-character code, i.e. N χ yz, where N stands for 'normal curing', meaning that the filler does not interfere much with vulcanization chemistry and χ yz are three digits describing the reinforcing character. The first digit χ was referring to the average typical size of elementary particle in ASTM D1765-86, and is now inversely proportional to average specific area, according to the most recent version of standard, ASTM D1765-96. The two digits yz form a number that describes the structure of the aggregate; whilst no rules are given in the standard how to assign the yz digits to a given black, it is generally agreed that the higher yz, the more intricate the aggregate and hence its reinforcing character, for instance N340 is a more reinforcing grade than N237, whilst their elementary particles have essentially the same diameter, in the 26 – 30 nm. A low structure black may have less than 20 elementary particles per aggregate, though a high structure one may consist of aggregates with up to 200 particles.

Table 2.9 Carbon black classification [15]

Classification N _{xyz}	ASTM D1675-86	ASTM D1765-96
χ	Average (elementary) particles size (nm)	N ₂ average specific area (m ² /g)
0	1 – 10	>150
1	11 – 19	121 – 150
2	20 – 25	100 – 120
3	26 – 30	70 – 99
4	31 – 39	50 – 69
5	40 – 48	40 – 49
6	49 – 60	33 – 39
7	61 – 100	21 – 32
8	101 – 200	11 – 20
9	201 – 500	0 – 10

2.4.2 Silicas [8], [15], [16]

The highly active, light colored fillers are, chemically, silicas (silicic acids). They can be manufactured by two methods: Solution process or pyrogenic process (fumed silica). Those most important for the rubber industries are made by precipitation: Alkali silicate solutions are acidified under controlled conditions. The precipitate silicic acid (silica) is washed and dried. Depending on the condition during highest activity is pure silica with large specific surfaces.

In the preparation of colloidal silica by the pyrogenic process, silicone tetrachloride is reacted at high temperature with hydrogen and oxygen;



The reaction products are quenched immediately after coming out of the burner. One obtains very finely divided silica that is important as filler for example for Q. For the normal types of rubber, fumed silica is too active and too expensive.

Amorphous silica consists of ultimate particles of the inorganic polymer (SiO₂)_n, where a silicon atom is covalently bonded in a tetrahedral arrangement to four oxygen atoms. Each of the four oxygen atoms is covalently bonded to at least one silicon atom

to form either a siloxane (-Si-O-Si-) or a silanol (-Si-O-H) functionality. Surface silanol groups can be isolated from one another such that hydrogen bonding between the silanols cannot occur, vicinal to one another, promoting the formation of intramolecular hydrogen bonding, or geminal to one another, where two silanol groups are bonded to the same silicon atom (see Fig. 2.6).

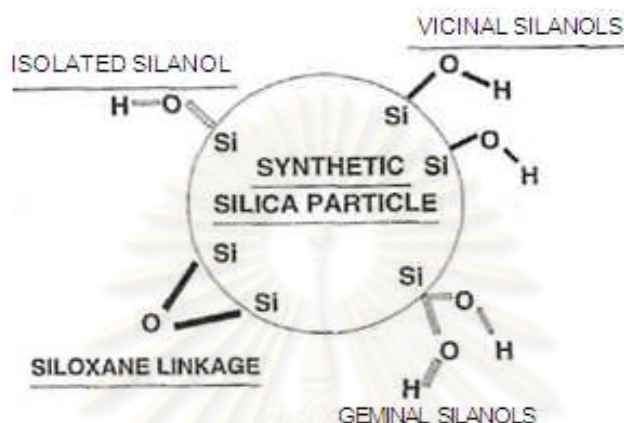


Figure 2.6 Silica surface group: siloxane (-Si-O-Si-) and isolated, vicinal, and geminal silanols (-Si-O-H) [16].

Particulate silicas are made by precipitation from aqueous solution. The physical and chemical properties of precipitated silicas can vary according to the manufacturing process. Reinforcement and control of suspension pH, temperature, and salt content can change the ultimate particle and aggregate sizes of silicas precipitated from solution. The surface area, as determined by nitrogen or CTAB adsorption, is a function of the ultimate particle size. Ultimate particles can range from 5 to 50 nm in diameter (see Table 2.10) [15].

Table 2.10 Silica typical properties [15]

Property	Fumed silica	Precipitated silica
N ₂ (BET) surf. Area (m ² /g)	50 – 380	140 – 250
Elementary particle diameter (nm)	7 – 40	15 – 100
DBP adsorption (ml/100g)	200 – 280	175 – 285
CTAB ads. surf. area (m ² /g)	160 – 220	110 – 200
pH (4% suspension in H ₂ O)	3.6 – 4.5	6.0 – 9.0

Aggregates are three-dimensional clusters of ultimate particles, covalently bonded to one another via siloxane bonds, and range in size up to 500 nm in diameter. Aggregates can physically agglomerate through intermolecular hydrogen bonding of surface silanol groups of one aggregate to a silanol group of another aggregate, yielding structure up to approximately 100 μm in diameter. The median agglomerate particle size is generally 20 to 50 μm in diameter, but can be reduced by milling to approximately 1 μm . Precipitated silica is prepared from an alkaline metal silicate solution, such as sodium silicate in a ratio of approximately 2.5 to 3.3 SiO_2 : Na, but using lower concentrations of silicate than is used in silica gel preparation. In the absence of a coagulant, silica is not precipitated from solution at any pH value, but is precipitated by adding acid to sodium silicate to reduce the pH value of the hot suspension to 9 to 10, where the concentration of sodium ion exceeds approximately 0.3 N. Sulfuric acids is normally used to neutralize sodium silicate and precipitate silica.

Because of its small particle size and complex aggregate structure precipitated silica imparts the highest degree of reinforcement to elastomer compounds among all of the non-black particulate fillers. This superior reinforcement is employed in a variety of rubber compounds for shoe soles, industrial rubber goods, and tires. Precipitated silica is used in shoe soles for its resistance to wear and to tearing, its non-scuffing characteristics, and to obtain compounds with light color, or even transparent materials. Precipitated silica is used to improve the tear strength, resistance to flex fatigue (cracking, cut-growth), and heat aging of a wide variety of manufactured rubber goods, including conveyor and power transmission belts, hoses, motor and dock mounts, and bumper pads. Rubber rolls that are produced with precipitated silica for the abrasion resistance, stiffness, and non-marking characteristics, are used in paper processing and the dehulling of grains, particularly rice [8].

2.5 Surface Treatment [16]

Carbon black remains the particulate filler of choice for rubber articles because the inherent reinforcing effect of the non-black fillers in hydrocarbon elastomers is not comparable. This primarily results from the nonbonded interactions established between the particulate filler and polymer functionalities. Surface chemistry plays an important role in the interaction of the non-black fillers and the polymer with

contributions ranging from electrostatic interactions to covalent bonding to the polymer backbone. However, surface chemistry also strongly affects the interaction of the non-black filler with other chemicals in the rubber compound, particularly active metal oxides, curatives, and antidegradants.

Both surface morphology and surface chemistry play an important role in the interaction of filler with coupling agents. For example, the dipole-induced dipole interactions between polar groups, such as siloxane and silanol, on the surface of silicas with non-polar groups (methyl, alkenyl, aryl) of hydrocarbon elastomers are weak compared to the dipole-dipole interactions resulting from hydrogen bonding between surface silanol groups in silica aggregates. In addition, the dispersive forces between a nonpolar molecule and silica are low, while those between a nonpolar molecule and carbon black are high. Thus, materials that improve the compatibility between hydrocarbon elastomers and mineral fillers are of considerable interest.

Organosilane coupling agents have been successfully utilized to further increase the physical properties of a number of non-black fillers including calcium silicate, clays, mica, silica, and talc. Clays pretreated with amino-functional or mercapto-functional silanes, and silicas pretreated with the mercapto-functional or tetrasulfide-containing (TESPT) silanes are commercially available (see Fig. 2.7). A manual of commercial couplants to promote adhesion between polymers and various substrates is available. The reaction of a bifunctional organosilane with a silica or silicate particulate filler involves the hydro-phobation of the alkoxy group of the silane with a surface silanol group of the silica or silicate, followed by reaction of the sulfur-containing function of the silane with an olefin group of the elastomer to afford a covalently bonded structure (see Fig. 2.8).

$\text{HS-CH}_2\text{-CH}_2\text{-CH}_2\text{-Si(-O-CH}_3\text{)}_3$ 3-Mercaptopropyltrimethoxysilane (A-189)

$\text{H}_2\text{N-CH}_2\text{-CH}_2\text{-CH}_2\text{-Si(-O-CH}_2\text{-CH}_3\text{)}_3$ 3-Aminopropyltriethoxysilane (A-1100)

$[\text{S-S-CH}_2\text{-CH}_2\text{-CH}_2\text{Si(-O-CH}_2\text{-CH}_3\text{)}_3]_2$ Bis(3-triethoxysilylpropyl)tetrasulfide (Si-69)

Figure 2.7 Structure of silane coupling agents [16].

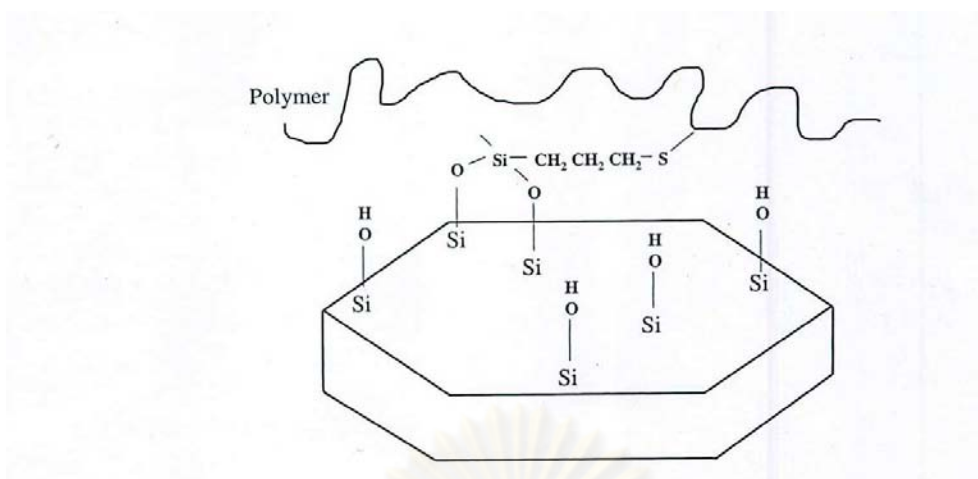


Figure 2.8 Illustration of silane coupling of polymer to silicate surface [16].

2.6 Literatures Review

Rattanasom *et al.* [3] studied the reinforcement of natural rubber with silica/carbon black hybrid filler. In this research, reinforcement of NR with silica/CB hybrid filler at various ratios was studied in order to determine the optimum silica/CB ratio. The total hybrid filler content was 50 phr. The mechanical properties indicating the reinforcement of NR vulcanizates, such as tensile strength, tear strength, abrasion resistance, crack growth resistance, heat buildup resistance and rolling resistance, were determined. The results reveal that the vulcanizates containing 20 and 30 phr of silica in hybrid filler exhibit the better overall mechanical properties.

Yatsuyanagi *et al.* [17] studied the effect of secondary structure of fillers on the mechanical properties of silica filled styrene butadiene rubber (SBR). A study carried out on the mechanical properties of silica-filled SBR systems in relation to secondary structure formed by silica particles in the systems, which was controlled by a surface chemistry of silica particles and by a strain applied to the samples. The breakdown of the secondary structure was successfully detected by transmission electron microscopy (TEM) observations when the strain was applied to silica filled vulcanizates. The degree of breakdown was more prominent in the larger agglomerates of which the size was controlled by the number of silanol group per unit surface area of silica particles. The initial modulus of the filled vulcanizates increased with increase in the size of agglomerate. On the other hand, at a higher strain, the

modulus decreased with the increase strain. The decrease was more prominent in the filled vulcanizates, which had a larger size of network structure. The reduction of modulus by the strain was closely related to the reduction of entrapped rubber phase, in addition to the breakdown of secondary structure of silica particles as suggested by Payne.

Suzuki *et al.* [18] studied the effect of rubber/filler interaction on deformation behavior on silica filled SBR systems. The rubber/filler interactions were controlled by the modification of silica surface using several kinds of silane coupling agents. Information on the chain scission was obtained by the electron spin resonance (ESR) measurements. The combination of ESR results and stress–strain data revealed that, at a given strain, the tensile stress increased with increasing the interfacial interactions between rubber molecules and silica surface, and simultaneously the chain scission became remarkable.

Ansarifar *et al.* [19] studied the use of silanised silica filler to reinforce and crosslink natural rubber. The coupling agent bis(3-triethoxysilylpropyl-)tetrasulphane (TESPT) has provided a better opportunity for using synthetic silicas to reinforce natural rubber. TESPT chemically adheres silica to rubber and also prevents silica from interfering with the reaction mechanism of sulphur-cure. Some rubber compounds were prepared by mixing a large amount of precipitated amorphous white silica with natural rubber. The silica surfaces were pretreated with TESPT and the filler was perfectly dispersed in the rubber. The rubber was cured primarily by using sulphur in TESPT and the cure was optimised by adding a sulphenamide accelerator and zinc oxide to the rubber. The need for the accelerator depended on the amount of silica incorporated into the rubber.

Hexiang *et al.* [20] studied the effect of nitrile rubber on properties of silica-filled natural rubber compounds. The effect of nitrile rubber (NBR) on the properties of silica-filled natural rubber (NR) compounds was studied in the presence of a new silane coupling agent, 3-octanoylthio-1-propyltriethoxysilane (NXT). The properties of silica-filled NR compounds were improved by adding NBR. The torque at equilibrium of compounds decreased with increasing NBR content. The dispersion of silica was improved by adding NBR. The scorch time and optimum cure time became shorter with increasing NBR content. The crosslink density of silica-filled NR vulcanizates also increased with increasing NBR content. The modulus and hardness

of NR vulcanizates were increased by adding NBR. The wet traction of the NR vulcanizates containing NBR was better than that without NBR, but rolling resistance of the vulcanizates containing NBR was worse than that without NBR.

Mastafar *et al* [21] studied the effect of carbon black loading on the swelling and compression set behavior of styrene butadiene rubber (SBR) and nitrile rubber (NBR) compound. The obtained results of five different compositions for SBR and NBR with 0, 20, 30, 50 and 70 phr of CB were compared. The swelling percentage decreases with increasing CB loading for both SBR and NBR filled compounds. At a similar CB loading, CB-filled NBR vulcanizates showed alower swelling percentage than did CB-filled SBR vulcanizates. The lower swelling percentage is due to better crosslinking density of NBR filled compounds than SBR filled compounds. The compression set value increases with increasing CB loading for both SBR and NBR filled compounds. The best chosen material for seal in motor oil medium is NBR loaded with 50 phr CB which have a reasonable value of swelling percentage and compression set value.

Rahiman *et al* [2] studied the cure characteristics and mechanical properties of styrene-butadiene rubber/acrylonitrile butadiene rubber blends (SBR/NBR). Blends of styrene butadiene rubber (SBR) and acrylonitrile-butadiene rubber (NBR) were prepared. Sulfur, dicumyl peroxide (DCP) and a combination of sulfur and DCP were used as vulcanizing agents. Cure and scorch times increase with the increase in SBR content. Among the different vulcanizing systems, the scorch safety is highest for the sulfur system and lowest for the DCP-cured system. Optimum cure time is maximum for pure SBR compound. Cure time decreases with the increase of NBR content in the blend. Torque is comparatively high for the DCP-cured system. Blends prepared by using sulfur as the vulcanizing agent showed comparatively better mechanical properties. Tensile and tear strengths showed synergism for the blends containing 60% SBR. A relatively co-continuous morphology was observed for 60:40 SBR/NBR (S60) blends, and this composition showed better properties.

Ramesan *et al* [1] studied the cure and mechanical properties of blends of natural rubber with dichlorocarbene modified styrene-butadiene rubber (DCSBR) and chloroprene rubber (CR). This study focused on the comparative evaluation of cure characteristics and mechanical properties of blends of natural rubber with dichlorocarbene modified styrene-butadiene rubber and chloroprene rubber with

different blend composition. The Mooney scorch time t_5 of CR was longer than that of NR and DCSBR. The lower t_5 of NR/DCSBR blend was due to the activation of adjacent double bond by the dichlorocarbene group. Positive deviation of tensile modulus and hardness indicate that the higher synergism occurred in NR/DCSBR than NR/CR blends. In all the blend system the thermal, flame, oil and ozone resistance was decreased with increase in concentration of NR and also NR/DCSBR blend exhibited better of these properties than that of NR/CR. After oil immersion the mechanical properties such as modulus and hardness decreases progressively with increasing NR content, compared to NR/CR blend DCSBR containing blend showed good oil resistance properties.



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CHAPTER III

EXPERIMENTAL

3.1 Raw Materials

Table 3.1 Rubber and chemicals used in this study

Chemicals	Function	Commercial name	Supplier
SBR	Rubber	NIPOL SBR1502	Zeon Corporation
NBR	Rubber	NIPOL DN2850	Zeon Corporation
Carbon black	Filler	G-N550	Thai Carbon Product Co., Ltd
Silica	Filler	NIPSIL ER	Tosoh Silica Corporation
ZnO	Activator	ZnO White Seal	Seido Chemical Industry Co., Ltd.
Stearic acid	Activator	Stearic acid	Miyoshi Oil & Fat Co., Ltd.
TMQ	Antioxidant	Antage RD-G	Kawaguchi Chemical Industry
CBS	Accelerator	Nocceler CZ-G	Ouchi Shinko Chemical Industry
Mercapto-Silane	Coupling agent	KBM-803	Shin-Etsu Chemical Co., Ltd
Vinyl-Silane	Coupling agent	A-171NT	Momentive Performance Materials
Epoxy-Silane	Coupling agent	A-187	Momentive Performance Materials
Peroxide	Vulcanizing agent	Percumyl D	P.T. NOF MAS Chemical
Sulfur	Vulcanizing agent	Sulfur	Tsurumi Chemical Industry Co., Ltd
Isooctane	Cleaning solvent	Isooctane	Merk Co., Ltd
ASTM oil no.1	ASTM oil#1	SONOCO	Japan Sun Oil Co., Ltd
ASTM oil no.3	ASTM oil#3	SONOCO	Japan Sun Oil Co., Ltd
Toluene	Solvent	Toluene	Merk Co., Ltd

3.2 Instruments

Table 3.2 Instruments used in this study.

Instruments	Manufacturer
Internal mixer	Moriyama machinery, Japan
Two roll mill mixer 10"	Moriyama machinery, Japan
Rheometer	RLR-3 model, Toyoseiki, Japan
Compression machine	NOK machinery, Japan
Tensile testing machine	Stereograph model, Toyoseiki, Japan
Mooney viscometer	SMV-300 model, Shimadzu, Japan
Auto-Specific Gravity Tester	Densimeter model, Toyoseiki, Japan
Hardness tester	Durometer hardness type A, Asker, Japan
Gear oven	Toyoseiki, Japan
Test tube aging tester	No.273, Toyoseiki, Japan
Scanning electron microscopy	JSM-6510LA, Jeol, Japan
Tension retraction tester	TRL107SLCS, Yasuda, Japan

3.3 Procedures

3.3.1 Compounding and Cure Assessment

SBR/NBR blends were prepared at ratios of 100/0, 70/30, 50/50, 30/70 and 0/100 (wt %). Silica/carbon black hybrid filler content (Precipitated silica; Nipsil ER and Semi reinforcing furnace; G-N550) were prepared at ratios of 15/15, 20/20 and 25/25 (wt %). The three types of silane coupling agent (γ -mercaptopropyltrimethoxysilane, γ -glycidoxypropyltrimethoxysilane and vinyl-tris-(2-methoxyethoxy) silane were used at 2% of silica content and used combination of sulfur and peroxide for vulcanizing systems. The formulations of the blends are given in Tables 3.3 and 3.4.

3.3.2 Preparation of SBR/NBR Blends.

The rubbers were masticated for 5 min and then activator, antioxidant, accelerator additives such as zinc oxide (5 phr), stearic acid (1 phr) and antioxidant (2 phr) were added. The rubber compound was mixed by cut-and-fold technique on the two-roll mill for 10 min until the surface of compound was smooth. The compound was mixed with accelerators (co-agent) and vulcanizing agents for 5 min. The sheet of rubber compound was kept at room temperature (25 °C) for 24 h before cure assessment using Rotor Less Die Rheometer (RLR-3) at 180 °C and 190 °C to determine the cure characteristic according to ASTM D2084-200.

3.3.3 Preparation of SBR/NBR Blends Filled with Silica/CB Hybrid Filler

Nipol SBR 1502 (30 phr) and NBR Nipol DN2850 (70 phr) were put into an internal mixer (Kneader mixer) and masticated under 60 rpm at 60 °C for 1 min, then silica/carbon black (15/15, 20/20 and 25/25 wt%) and coupling agent (2% of silica) were mixed with masticated SBR/NBR blends under 60 rpm at 100 °C for 2 min. Then, zinc oxide, stearic acid and antioxidant were mixed with rubber compounds at 100 °C for 2 min. Finally, the sulfur, accelerator and peroxide were added to the masterbatch at 50 °C for 5 min by two roll mill.

3.3.4 Vulcanization Process

Rubber sheets of approximately 4 mm of thickness were vulcanized in hydraulic compression mold preheated at 180 °C for 30 min and then followed by compressing at 120 kgf/cm² of pressure for the respective cure time (t_{c90}) obtained from the RLR-3.

The summarized procedure for preparation of SBR/NBR compound, SBR/NBR filled with silica/carbon black hybrid fillers are shown in Figures 3.1 and 3.2.

Table 3.3 Formulation of SBR/NBR blends

Ingredients*	Composition, phr (part per hundred rubber)				
	SBR	N30	N50	N70	NBR
Nipol SBR1502	100	70	50	30	0
NBR Nipol DN2850	0	30	50	70	100
Stearic acid	1	1	1	1	1
Zinc Oxide	5	5	5	5	5
TMQ	2	2	2	2	2
CBS	1.0	1.0	1.0	1.0	1.0
Sulfur	0.8	0.8	0.8	0.8	0.8
DCP	3.5	3.5	3.5	3.5	3.5

TMQ; Poly (1, 2-dihydro-2, 2, 4-trimethylquinoline), CBS; N-Cyclohexyl-2 benzothiazolesulfenamide, DCP; Dicumyl peroxide

Table 3.4 Formulation of rubber compound with various silica/carbon black hybrid fillers and silane coupling agents.

Ingredients*	Composition, phr											
	R30	R40	R50	R30M	R40M	R50M	R30G	R40G	R50G	R30V	R40V	R50V
SBR	30	30	30	30	30	30	30	30	30	30	30	30
NBR	70	70	70	70	70	70	70	70	70	70	70	70
Nipsil ER	15	20	25	15	20	25	15	20	25	15	20	25
G-N550	15	20	25	15	20	25	15	20	25	15	20	25
Silane (M*,G*,V*)	-	-	-	0.3	0.4	0.5	0.3	0.4	0.5	0.3	0.4	0.5

M*; γ - mercaptopropylmethoxysilane , G*; γ - glycidoxypropyltrimethoxysilane, V*; vinyl-*tris*-(2-methoxyethoxy) silane(used silane 2% of silica). Other ingredients*; stearic acid=1.0 phr, zinc oxide=5.0 phr, TMQ=2.0 phr, CBS=1.0 phr, sulfur=0.8 phr and DCP=3.5 phr

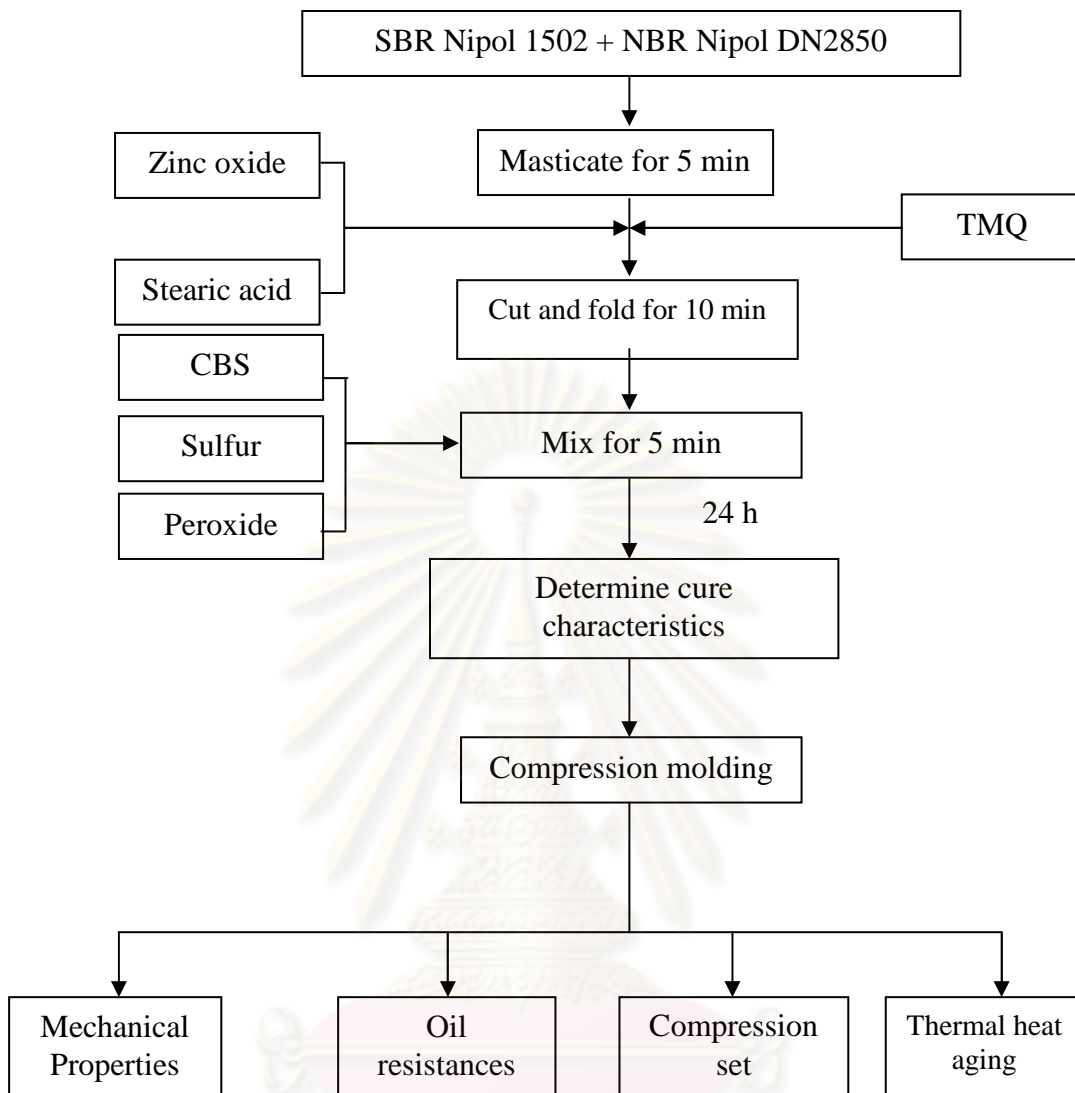


Figure 3.1 The overall schematic experimental process for preparing SBR/NBR blends.

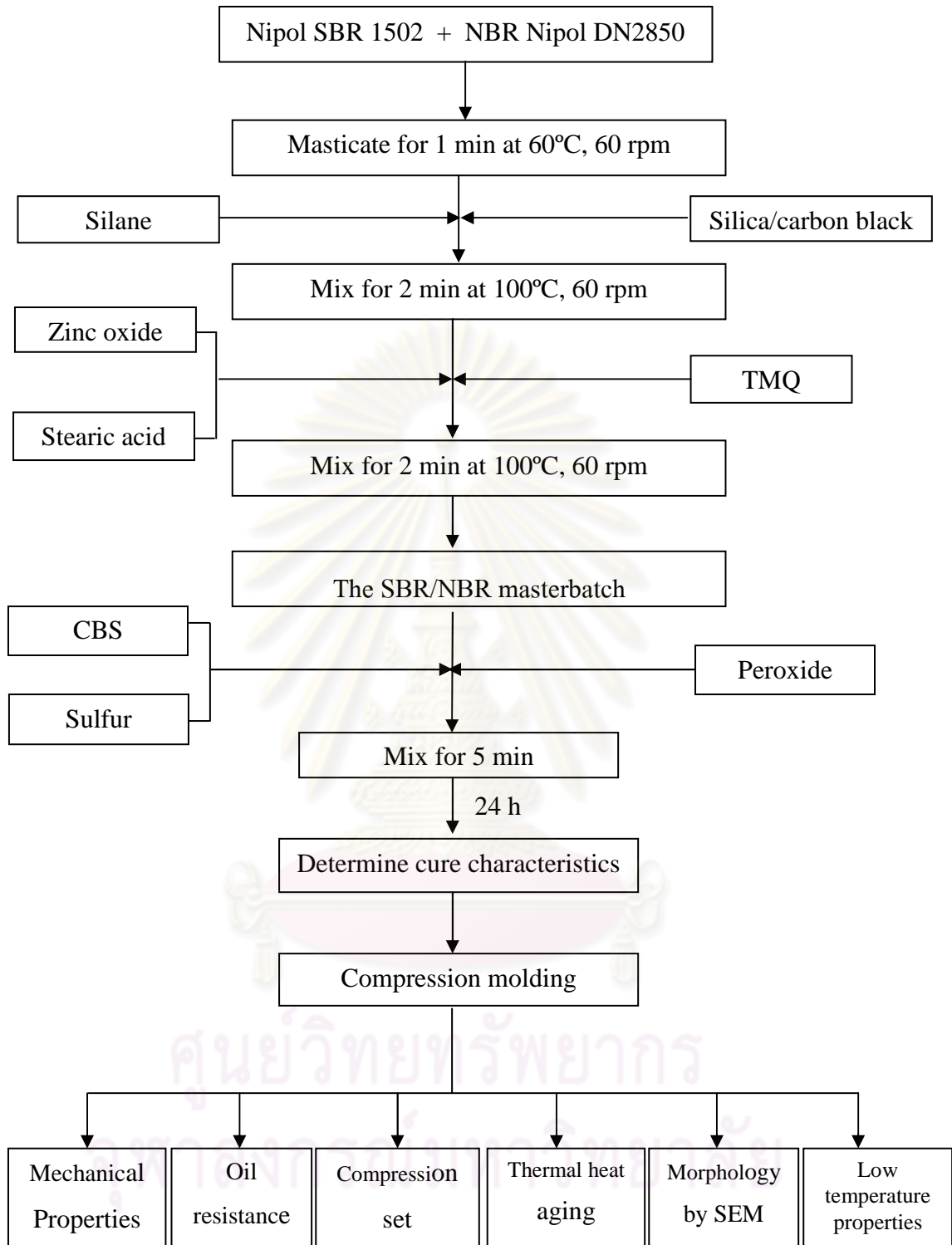


Figure 3.2 The overall schematic experimental process for preparing SBR/NBR blends filled with silica/CB hybrid filler and silane coupling agents.

3.4 Testing

3.4.1 Determination of Cure Characteristics

A Rotor Less Die rheometer, RLR-3 model, was used to obtain the torque-time curve at 180 °C and 190 °C with 1 amplitude.

- M_L - Minimum torque, lbf-in
- M_H -Highest torque, lbf-in attained during specified period of time when plateau or maximum torque is obtained.
- Scorch time (ts_1) in minute is the time taken for a two unit rise above the minimum torque.
- Cure time (tc_{90}) in minute is the time taken for attaining 90% of the maximum torque.

3.4.2 Tensile Properties

The vulcanizates were prepared by curing at 180°C for optimum cure time. Dumbbell samples were cut from molded sheet with a die cutter (Die C) (Figure 3.3). The samples were tested using Autograph tensile testing machine at crosshead speed of 500 mm/min, according to ASTM D412. Three samples were used in each case to obtain the median and standard deviation values. The tensile strength (T.S.), tensile stress at 100 % elongation (M_{100}) and elongation at break (E.B.) were recorded directly at the end of each test.

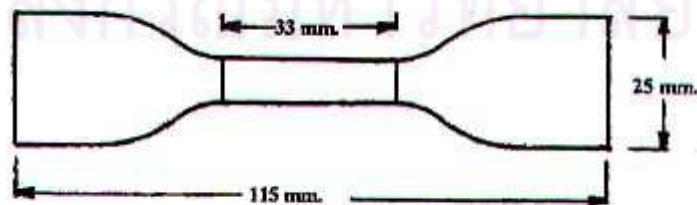


Figure 3.3 Dumbbell (Die C) shape sample for tensile property testing.

3.4.3 Hardness Measurement

The test was conducted following ASTM D2240 using a hardness tester, model durometer A. The thickness of test sample was at least 6 mm. The samples were flat and parallel over a sufficient area to permit the pressure foot to contact the sample. The samples were placed on a hard and horizontal surface. The pressure was held on a vertical position with the point of the indentation at least 12 mm from any edge of the sample. The pressure was applied to the sample by the constant load standard for hardness tester model CL-150 series. After the pressure foot was contact with the sample, the hardness value was read scale 3 sec after the specified time. Every sample was tested 3 different points. The median and standard variations of hardness values were reported.

3.4.4 Compression Set

Compression set testing is used to determine the ability of elastomeric materials to maintain elastic properties after prolonged compressive stress. The test measures the somewhat permanent deformation of the sample after it has been exposed to compressive stress for a set time period. This test is particularly useful for applications in which elastomers would be in a constant pressure/release state.

The compression set value was performed on standard test sample of cylindrical shape of 25 ± 0.1 mm diameter and 12 ± 0.5 mm thickness vulcanized by compression molding method. The test sample was be placed between the plates of the compression device with the spacers on each side of it, allowing sufficient clearance for bulging of the rubber when compressed as shown in Fig. 3.5. The bolts was be tightened so that the plates are drawn together uniformly until they were in contact with the spacers. The percentage of the compression employed was 25% of the original thickness. The samples were analyzed by keeping the samples in oven at 100°C for 70 h according to ASTM D 395 Method B. Thereafter, the samples were cooled at room temperature for 30 min before testing.

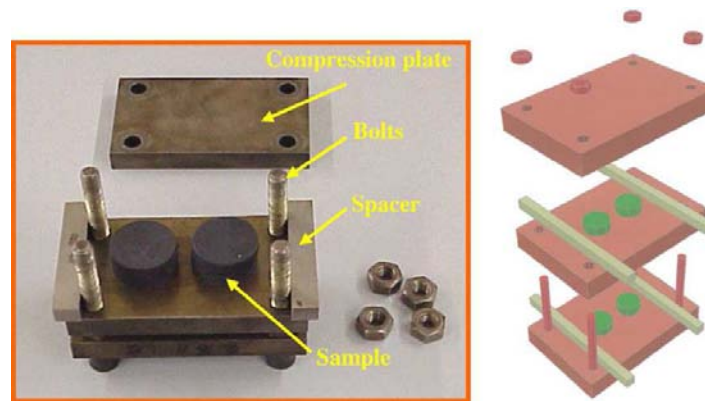


Figure 3.4 Compression set device [21].

3.4.5 Thermal Aging Properties

The samples were cut as a dumbbell shape using a die C according to the standard method ASTM D 412. The resistance to thermal aging of the samples was analyzed by keeping the samples in an air circulating oven operated at 100°C for 70 h according to ASTM D 573. Thereafter, the samples were cooled at room temperature for at least 16 h before testing. The properties retention, hardness, 100% modulus, tensile strength and elongation at break were calculated by following Eq. 3.1.

$$\% \text{ Retention} = \frac{\text{Properties after aging}}{\text{Properties before aging}} \times 100 \quad (3.1)$$

3.4.6 Measurement of Swelling Behaviour (Oil Resistance)

Swelling test was performed on 30 x 5 x 2 mm cut sample from the compression-molded rubber disk by the immersion method in motor oil such as, ASTM oil no. #1 and ASTM oil no. 3 at 100°C for 70 h, Brake fluid and Fuel C at 25° for 70 h according to ASTM D 471. Thereafter, the test samples were taken out, quickly dipped in acetone and blotted lightly with filter paper to remove excess oil from the surface. The variations of apparent percentage of change in hardness, volume were calculated by Eqs. 3.2 and 3.3.

$$\Delta H = H_i - H_0 \quad (3.2)$$

where: ΔH = Hardness change after immersion, units,
 H_0 = Original hardness before immersion, units and
 H_i = Hardness after immersion, units.

$$\Delta V = 100 \times \frac{[(M_3 - M_4) - (M_1 - M_2)]}{(M_1 - M_2)} \quad (3.3)$$

where: ΔV = Change in volume, %
 M_1 = Weight in the air before immersion, g
 M_2 = Weight in the water before immersion, g
 M_3 = Weight in the air after immersion, g
 M_4 = Weight in the water after immersions, g

3.4.7 Determination of Specific Gravity

The specific gravity of vulcanized rubbers was determined by using Electronic Densimeter (Auto-Specific Gravity tester, model Densimeter, Toyoseki). The determination of (relative) density value was based on the density of water at 23°C: 1g/cm³ per electronic densimeter instruction manual.

3.4.8 Elastic Retraction Test at Low Temperature (TR test) [22]

This test is carried out for measuring the elastic retraction of vulcanized rubber which was first frozen at low temperature after being elongation and then was raised up its temperature, and then for comparison and easy estimation of the crystallization tendency and viscoelasticity property at low temperature. Fig.3.5 shows an example of testing apparatus. The shape and dimensions of a test piece, as shown in Fig.3.6, is letter "I" type, both ends have 6.5mm side square for being clamped, parallel part measures 2.0 ± 0.2 mm in width, 100.0 ± 0.2 mm or 50.0 ± 0.2 mm in length, and thickness is 2.0 ± 0.2 mm.

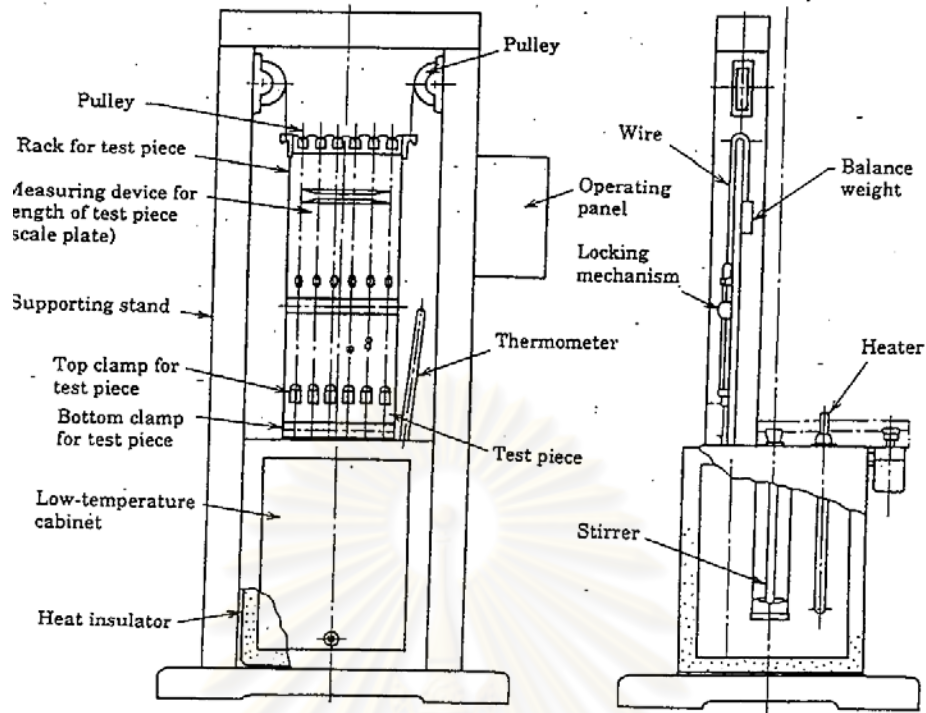


Figure 3.5 Example of testing apparatus for elastic retraction at low temperature [22].

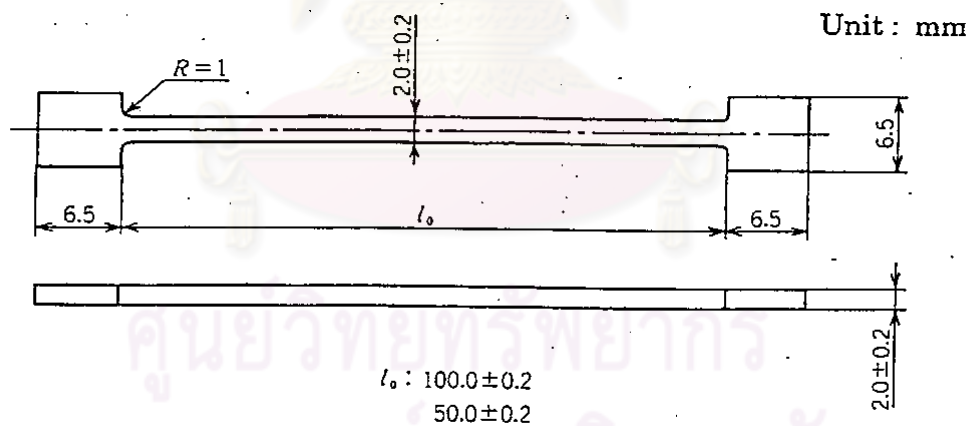


Figure 3.6 Shape and dimensions of test piece [22].

Test conditions according to JIS K6261, the samples were elongated of half original length, temperature for setting -70°C to 20°C and heating rate $1^{\circ}\text{C}/\text{min}$. Fig 3.7 shows the relation between the percentage retractions given at each point and measured temperatures, to prepare the percentage retraction versus temperature curve. The results report TR-10, TR-30, TR-50 and TR-70.

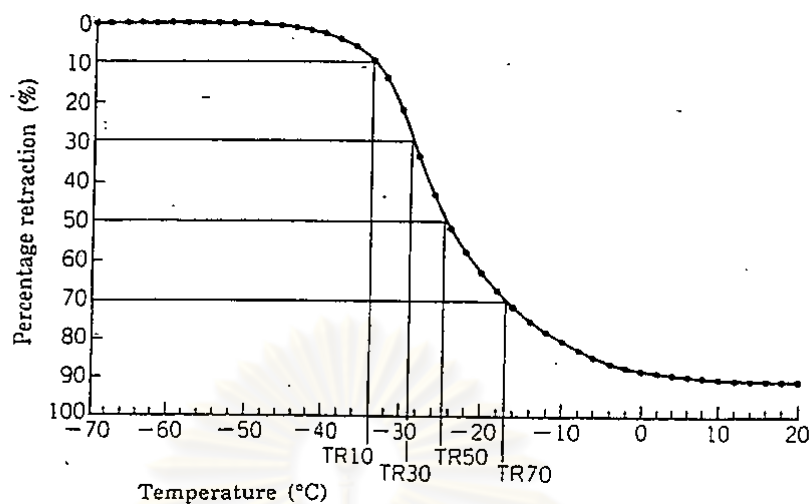


Figure 3.7 Example of percentage retraction versus temperature curve [22].

3.4.9 Morphological Study by Scanning Electron Microscopy (SEM)

The morphology of blends was studied using a JEOL model JSM- 6510LA scanning electron microscopy operated at 15 kV. The samples were cryogenically fractured under liquid nitrogen. The samples were taken a treatment with gold before observation.

ศูนย์วิทยทรัพยากร
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CHAPTER IV

RESULTS AND DISCUSSIONS

4.1 Cure characteristics

The cure characteristics of uncured SBR/NBR blends from the RLR-3 rheometer can be used to predict the blending performance. Minimum torque (M_L) is commonly considered as representative of the rubber elastic modulus [23]. Table 4.1 shows that at two different curing temperatures, the M_L values of SBR/NBR blends do not change with increasing NBR content (30-70 phr). This indicates that the incorporation of the NBR has improved the processability of the blend.

Table 4.2 shows that the M_L value of SBR/NBR blends filled with silica/carbon black (CB) hybrid filler filled silane coupling agents is higher than that of unfilled SBR/NBR (30/70) blends. It can be seen that the M_L value of SBR/NBR composites increased with increasing silica/CB hybrid filler content (30-50phr), indicating the increasing viscosities with hybrid filler content. At two curing temperature, 180°C and 190°C, the M_L value did not change indicating the good processability at these temperatures.

The maximum torque (M_H) generally correlates with durometer hardness and/or modulus [23]. Table 4.1 shows that at two different temperatures, the M_H value of SBR/NBR blends slightly increased with increasing NBR content (30-70 phr). This result illustrated that the incorporation of NBR increased the stiffness of the rubber blend. The maximum torque (M_H) of SBR/NBR composites is presented in Table 4.2, the M_H of SBR/NBR blends filled with silica/CB hybrid fillers of 50 phr were the highest. Moreover, the M_H of silica/CB-filled SBR/NBR blends increased when the silane coupling agent was added. This result shows that the incorporation of silica/CB hybrid fillers increased the stiffness of SBR/NBR composites.

Table 4.1 also presented the scorch time (t_{S1}) of the SBR/NBR blends at various blending ratios. The scorch time did not change when increasing NBR content was increased. The cure times (t_{c90}) of SBR/NBR blend are also presented in Table 4.1. The t_{c90} value was slightly affected by varying NBR content in the blend. Again, at same blend ratio, the t_{c90} value at 190°C was lower than that 180°C. This can be

explained that the tc_{90} value decreased as a result of the decreasing effect on double bond activation in the rubber blend, indicating enough thermal energy for activation energy of vulcanization and consequently the induction effect of NBR became less important.

The scorch time (ts_1) and cure time (tc_{90}) of silica/CB-filled SBR/NBR blends with silane coupling agents was lower than that without silane coupling agents. This is due to the adsorption of accelerator by silanol groups on the silica surface. Thus, the use of silane coupling agents could reduce the adsorption of accelerator on the silica surface, resulting the decrease in scorch time and cure time when silane coupling agent was added. Also, at same hybrids filler content, the tc_{90} value at 190°C is lower than that of 180°C.

Table 4.1 Effect of blending ratios of SBR/NBR blends on cure characteristics at different curing temperature.

Properties	Temp. (°C)	SBR	N30	N50	N70	NBR
Minimum torque (ML); lbf-in	180	0.75	0.77	0.73	0.73	0.74
	190	0.74	0.74	0.73	0.72	0.71
Maximum torque (MH); lbf-in	180	9.89	10.3	10.3	10.7	11.8
	190	9.44	9.57	10.1	10.4	11.2
Scorch time (ts_1); min	180	0.53	0.52	0.53	0.54	0.55
	190	0.41	0.41	0.41	0.41	0.43
Cure time (tc_{90}); min	180	3.08	2.82	2.65	2.53	3.11
	190	1.50	1.41	1.35	1.26	1.27

Table 4.2 Effect of silica/CB hybrid filler content and silane coupling agent types of SBR/NBR blends on cure characteristics at different curing temperature.

Properties	Temp. (°C)	N70	R30	R40	R50	R30M	R40M	R50M	R30G	R40G	R50G	R30V	R40V	R50V
Minimum torque (ML); lbf-in	180	0.73	2.04	2.45	3.36	2.02	2.74	3.19	2.00	2.69	3.54	2.02	2.74	3.19
	190	0.72	2.04	2.39	3.40	2.02	2.69	3.12	1.95	2.63	3.50	2.02	2.69	3.12
Maximum torque (MH); lbf-in	180	10.7	19.3	22.7	25.9	21.9	27.4	29.6	18.8	25.0	27.1	20.1	22.7	26.0
	190	10.4	18.3	21.3	25.0	20.5	24.8	27.7	17.9	21.5	24.2	18.3	21.4	25.1
Scorch time (ts ₁); min	180	0.54	0.75	0.73	0.67	0.76	0.69	0.65	0.76	0.70	0.67	0.76	0.70	0.67
	190	0.41	0.54	0.51	0.50	0.55	0.48	0.47	0.53	0.50	0.48	0.53	0.50	0.48
Cure time (tc ₉₀); min	180	2.53	2.63	2.92	2.75	2.61	2.90	2.67	2.69	3.05	2.90	2.83	2.68	2.62
	190	1.26	1.37	1.45	1.42	1.40	1.30	1.31	1.39	1.35	1.36	1.37	1.33	1.37

4.2 Mechanical properties

The mechanical properties of the SBR/NBR blends at various NBR contents (0, 30, 50, 70 and 100% w/w) were firstly investigated to find appropriate SBR/NBR blend ratio. Then, the mechanical properties of the silica/CB-filled SBR/NBR (30/70) blends with various silane coupling agent types [without silane, γ -mercaptopropyltrimethoxysilane (M), γ -glycidoxypropyltrimethoxysilane (G) and vinyl-tris-(2-methoxyethoxy)silane (V)] were explored. The 100% modulus (M100), tensile strength (T.S.), elongation at break (E.B.), hardness and compression set (C.S.) of the rubber composites are presented in Tables 4.3 – 4.4.

4.2.1 Tensile Properties

Table 4.3 and Figure 4.2 show the mechanical properties of SBR/NBR blends at various NBR contents. The 100% modulus, tensile strength and elongation at break of blends increased with increasing NBR content up to 70 phr and then slightly decreased when NBR content up to 100 phr. This indicated that the blend at NBR content of 70 phr exhibited the homogeneous phase of NBR and SBR. However, the mechanical properties of the blends were quit low because both SBR and NBR had the irregular molecular structure and did not crystallize. Thus, the reinforcing filler is required to achieve good mechanical properties. The appropriate fillers are carbon black and silica [24].

Effect of silica/CB hybrid filler content of SBR/NBR blends on mechanical properties is shown in Table 4.4 and Figure 4.3. The tensile strength and 100% modulus of SBR/NBR vulcanizates increased with increasing silica/CB hybrid filler content (30-50 phr) but elongation at break decreased. This can be explained that silica/CB filled rubber composites have multiphase systems depending on the mobility of the rubber molecule, the stiffness and toughness of the blends were improved due to the reinforcement effect of the composites [25]. It is also recognized that the increase in component with high surface free energy of the hybrid filler (silica/CB) is important for improving the degree of adhesion between the fillers and the rubber. The interaction between the rubber and hybrid filler surfaces are believed to be due to the hydrogen bonding or Van der Waal forces and the extent of interaction increases when the oxygen content on the filler surface increases [26].

For the effect of silane coupling agent, the mechanical properties of silica/CB-filled SBR/NBR vulcanizates with silane coupling agent was higher than that without silane coupling agent. This can be explained that the reaction took place between silane and the rubber blends when the silanol-blocking group was broken, resulting the increasing chemical bond between the rubber blends and silica as shown in Figure 4.1. The γ -mercaptopropylmethoxy silane, vinyl-tris-(2-methoxyethoxy)silane and γ -glycidoxypropyltrimethoxysilane were efficient silane coupling agent for silica/CB-filled SBR/NBR blends because reaction of the reactive organic group (mercapto, vinyl and epoxy) function of the silane with an olefin group of the elastomer could afford a covalently bonded structure.

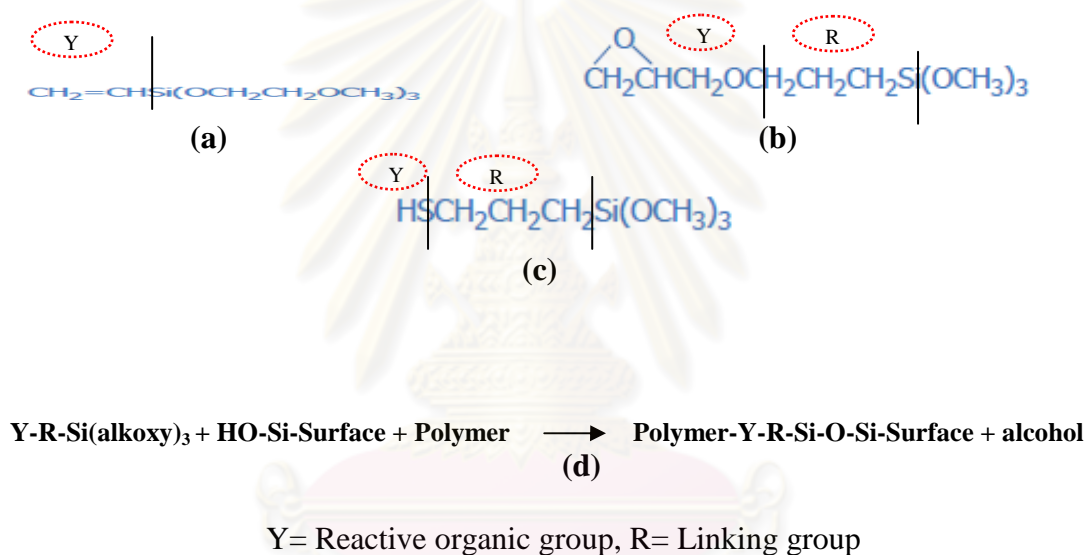


Figure 4.1 Structure and reaction of silane coupling agent on silica surface and polymer for; (a) vinyl-tris (2-methoxyethoxy)silane, (b) γ -glycidoxypropyltrimethoxysilane, (c) γ -mercaptopropyltrimethoxysilane (d) reaction of silane coupling agent with silica surface [27].

Table 4.3 Effect of blending ratios of SBR/NBR blends on mechanical properties.

Properties	SBR	N30	N50	N70	NBR
Tensile strength, MPa	2.10(0.25)	3.20(0.35)	4.50(0.30)	4.70(0.31)	2.60(0.31)
Elongation at break, %	246(15)	339(17)	420(11)	375(12)	260(13)
100% Modulus, MPa	0.72(0.07)	0.86(0.06)	0.84(0.05)	1.09(0.03)	1.07(0.03)
Hardness, shore A	43(0.6)	43(1.2)	44(1.0)	48(1.0)	49(1.0)
Compression set@ 100°Cx70h, %	44(2.3)	43(4.2)	40(4.9)	38(3.6)	41(1.5)

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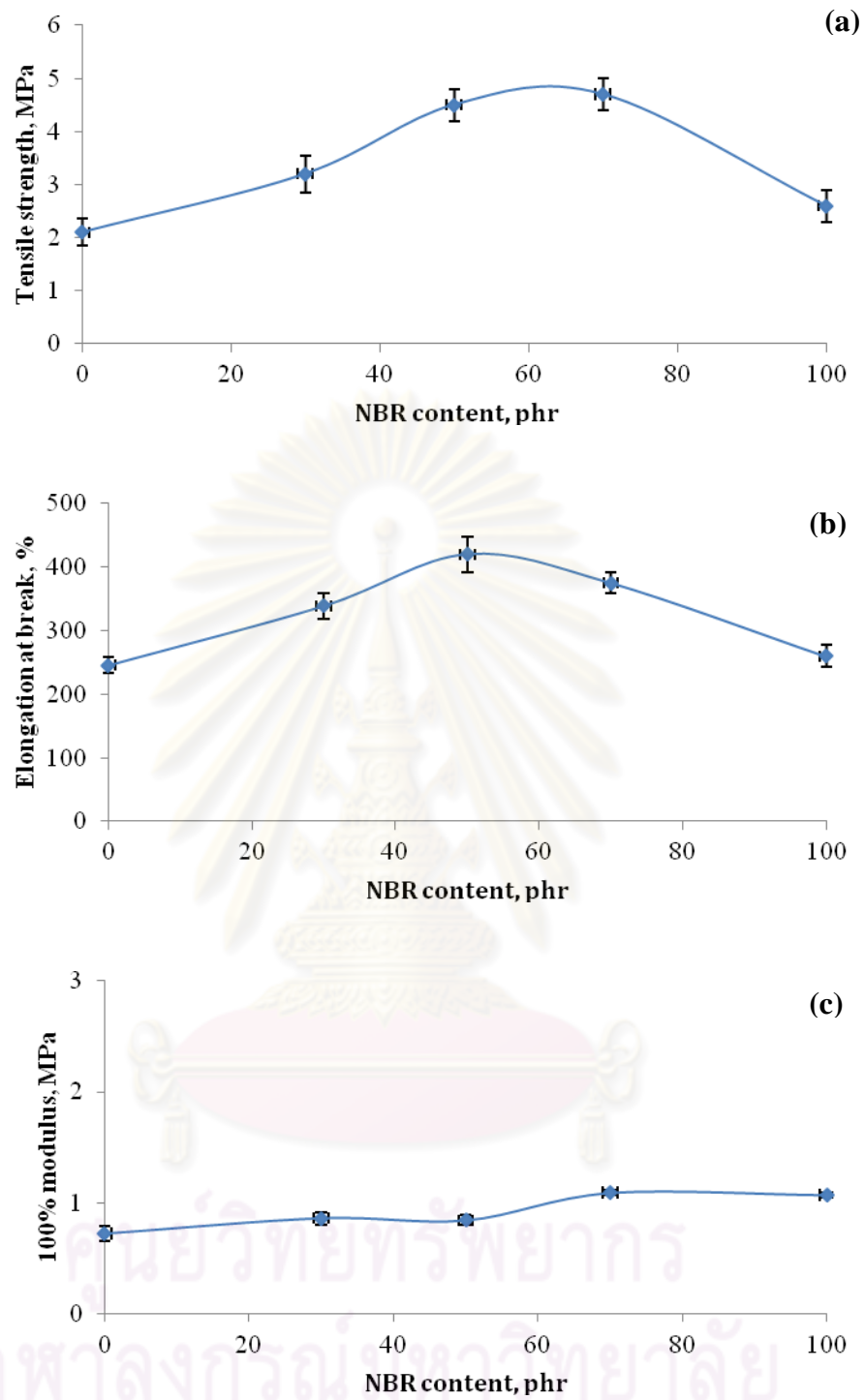


Figure 4.2 Effect of blending ratios of SBR/NBR blends on; (a) tensile strength, (b) elongation at break and (c) 100% modulus.

Table 4.4 Effect of silica/CB hybrid filler content and s ne coupling agents on mechanical properties of SBR/NBR blends.

Properties	N70	R30	R40	R50	R30M	R40M	R50M	R30G	R40G	R50G	R30V	R40V	R50V
Tensile strength, MPa	4.70 (0.31)	11.90 (0.22)	13.90 (0.38)	16.42 (1.24)	15.31 (0.43)	15.49 (0.51)	18.72 (0.19)	13.59 (0.43)	15.70 (0.59)	18.37 (0.22)	12.66 (0.92)	14.98 (0.20)	17.61 (0.82)
Elongation at break, %	375 (15)	296 (4)	275 (7)	290 (5)	334 (6)	345 (11)	338 (11)	326 (10)	319 (11)	283 (21)	332 (12)	379 (16)	300 (19)
100%Modulus, MPa	1.09 (0.07)	3.10 (0.13)	3.23 (0.15)	3.77 (0.14)	5.14 (0.18)	5.49 (0.16)	5.62 (0.13)	3.30 (0.11)	5.09 (0.17)	5.28 (0.15)	3.16 (0.11)	3.72 (0.12)	4.67 (0.34)
Hardness, shore A	48(1.0)	63(1.0)	67(1.5)	68(0.6)	70(1.0)	72(1.0)	74(1.0)	63(1.2)	69(0.6)	71(0.6)	64(0.6)	66(0.6)	70(0.6)
compression set @ 100°C x 70h, %	38(3.6)	36(2.9)	35(2.0)	33(1.4)	18(1.9)	17(1.6)	16(3.4)	26(1.2)	22(1.4)	19(0.9)	28(2.3)	23(1.2)	19(1.8)

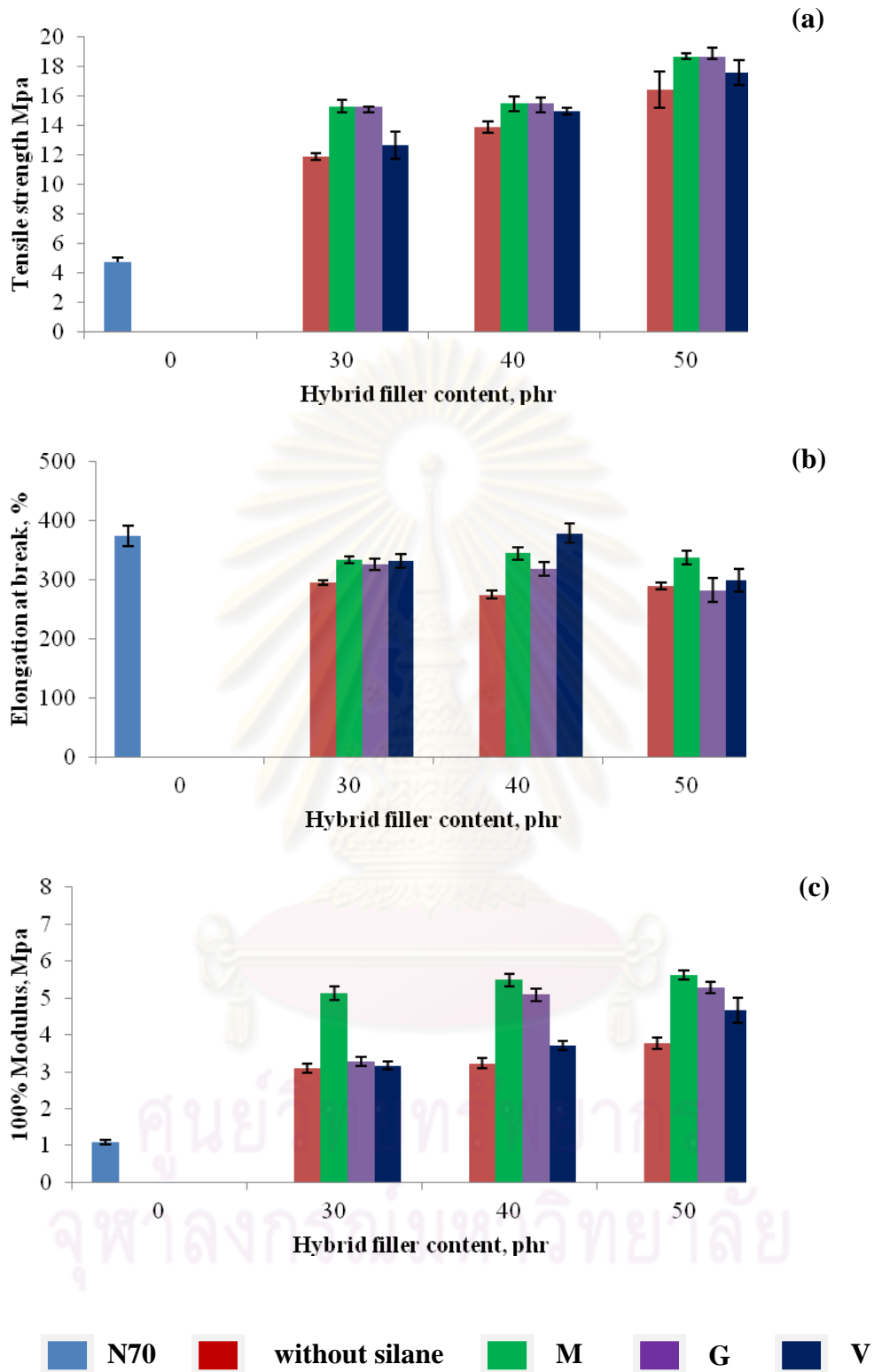


Figure 4.3 Effect of silica/CB hybrid filler content and silane coupling agents of SBR/NBR blends on; (a) tensile strength, (b) elongation at break and (c) 100% modulus.

4.2.2 Hardness

Hardness is typically measured as resistance to surface indentation under specific condition, so the force is supplied as a point of compression rather than area of tension. The effect of blending ratios on hardness of SBR/NBR blends is shown in Figure 4.4(a). The hardness increased with increasing NBR content, which can be attributed to the crosslink density after vulcanization. However, the gum of the blends (without hybrid filler) had low hardness while hardness increase noticeably when silica/CB hybrid filler was added to the SBR/NBR blends.

Effect of the silica/CB hybrid filler content and silane coupling agents on hardness of SBR/NBR blends is shown in Figure 4.4(b). The hardness increased with increasing silica/CB hybrid filler content up to 50 phr. The similar result was earlier reported by Rattanasom *et al* [28], the silica/CB-filled (50 phr) rubber vulcanizate exhibited the highest stiffness. The hardness of reinforced SBR/NBR vulcanizates with silane coupling agent was higher than that without silane coupling agent.

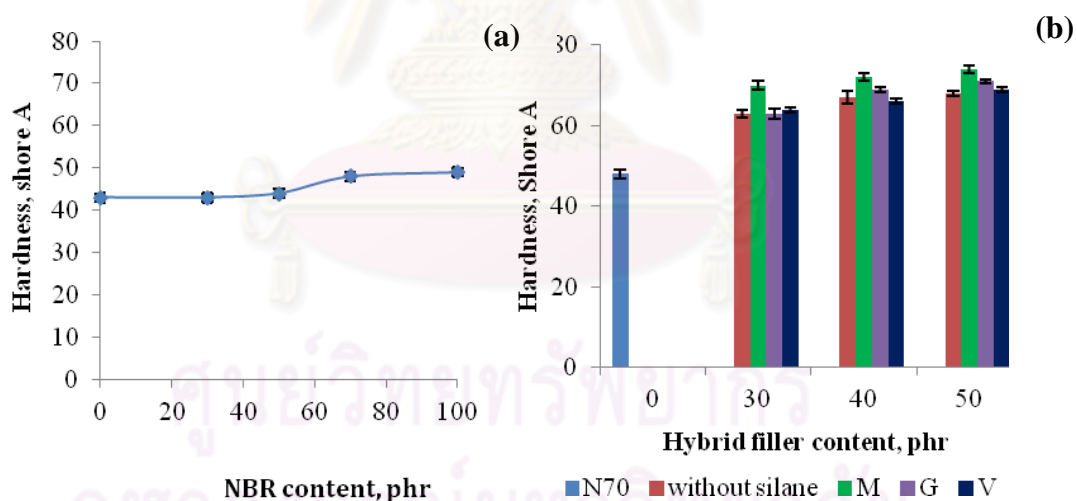


Figure 4.4 Hardness property for; (a) effect of blending ratios of SBR/NBR blends, (b) effect of silica/CB hybrid filler content with silane coupling agents of SBR/NBR blends.

4.2.3 Compression set

Compression set is the residual strain remaining on rubber after the removal of the force which produced the deformation. The compression set test is the most common set in the rubber industry. This test itself does not relate directly to rubber product performance conditions as do the stress relaxation and creep test. However, the compression set test is probably performed more often than stress relaxation or creep because compression set is relatively simple, making it ideal for quality control [16].

Figure 4.5(a) shows the effect of steady rate of SBR/NBR blends on the compression set performance at 100°C for 70h. The compression set of SBR/NBR vulcanizates decreased with increasing the NBR content up to 70 phr due to the crosslink density. From this figure, the compression set of pure gum (SBR/NBR; 30/70) was low and the compression set of SBR/NBR vulcanizates decreased with increasing silica/CB hybrid filler content, as shown in Figure 4.5(b). The compression set also decreased with increasing silica/CB hybrid filler and adding silane coupling agent. The compression set of the rubber blends was lower than that without silane coupling agent. This is due to the fact that when the hybrid filler loading increased, the crosslink density increased and the mobility of the rubber chains decreased, resulting in stiffness in the filled compound. This result was earlier reported by Mostafa *et al* [21].

The reinforced rubber vulcanizates modified by γ -mercaptopropyltrimethoxysilane had lower compression set than that by γ -glycidoxypropylmethoxysilane and vinyl-tris-(2-methoxyethoxy)silane. In addition, γ -mercaptopropyltrimethoxysilane with combination of sulfur-peroxide system was more efficient than the others silane coupling agent for SBR/NBR blends due to the high bond strength crosslinks (combination of C-C bonds and C-S_x-C bonds of vulcanizates). The higher bond strength of shorter crosslinks is important for the high temperature compression set and heat stability of the vulcanizates. The low value of x in C-S_x-C generally give better permanent set value [24].

The compression set (C.S.) of SBR/NBR vulcanizates filled with silica/CB hybrid filler and γ -mercaptopropyltrimethoxysilane is compared with previous works. The compression set of SBR/NBR vulcanizates filled with silica/CB hybrid filler and γ -mercaptopropyltrimethoxysilane (C.S. = 16–18%) was the same as NBR

vulcanizates filled with carbon black (C.S. = 16%), but was lower than NBR filled with silica (C.S. = 70%) [29]. This indicates that the SBR/NBR blend with silica/CB hybrid filler had the improved compression set which was higher than rubber blend filled with only silica.

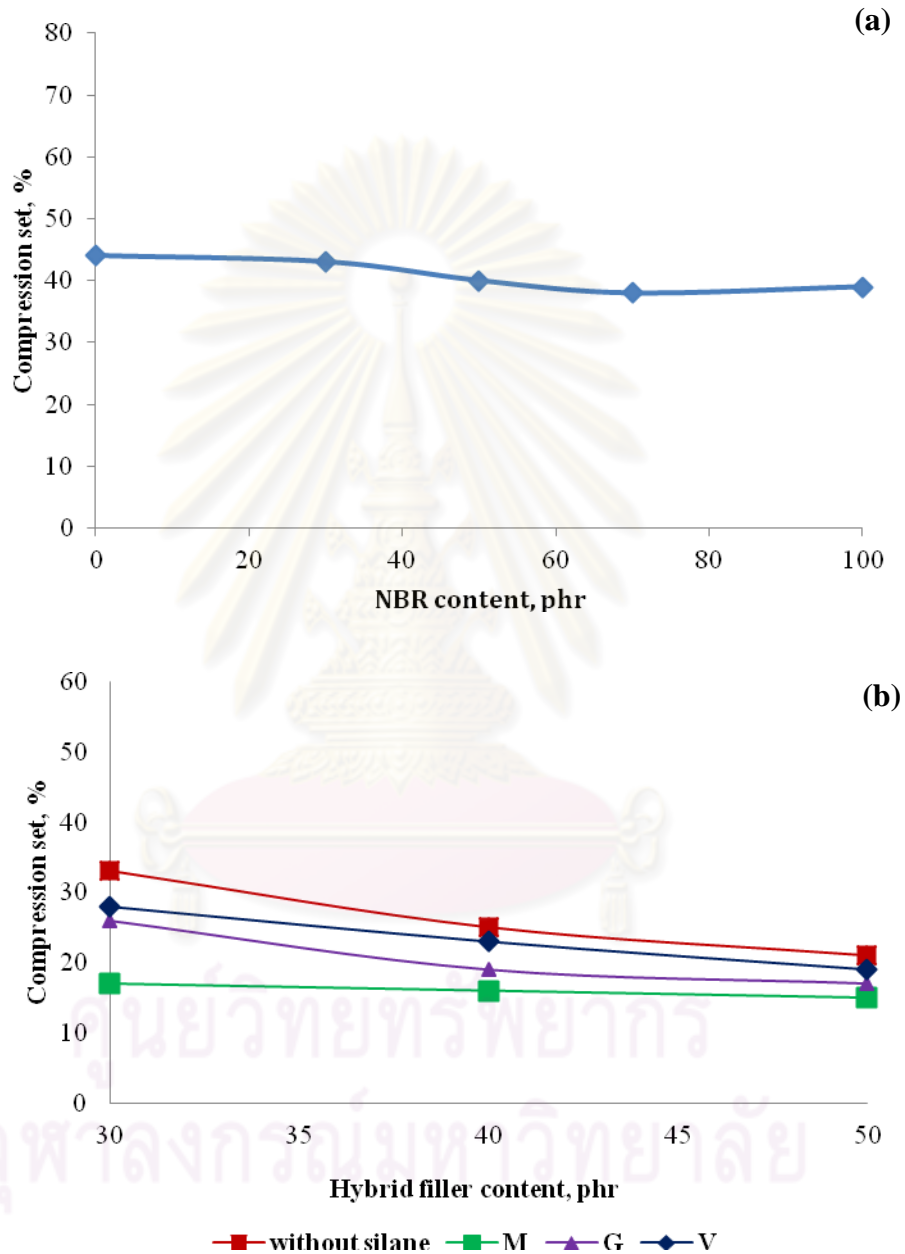


Figure 4.5 Compression set for; (a) effect of blending ratios of SBR/NBR blends, (b) effect of silica/CB hybrid filler content with silane coupling agents of SBR/NBR blends.

4.3 Thermal Aging Properties

The thermal resistance of the rubber vulcanizates is considered as an essential requirement for the long service life product. The percentage of retention in tensile strength, elongation at break, 100% modulus and hardness of SBR/NBR blends without filler and with hybrid filler with coupling agents as a result of aging at 100°C for 70 h are presented in Tables 4.5-4.6 and Figures 4.6–4.7.

From Figure 4.6 after aging the percent retention in tensile properties and hardness of the SBR/NBR blends vulcanizates increased with increasing NBR content. The results indicated that the degradation of polymer was affected by the substituents in the backbone especially NBR structure. A higher number of substituents usually decrease thermal stability while acrylonitrile groups in polymer backbone increase the thermal stability [30, 31]. For silica/CB filled the rubber compound filled after aging the hardness retention, 100% modulus retention and tensile strength retention was higher than that of without silica/CB hybrid filler. The elongation at break retention was lower because the rubber vulcanizates after aging increased the crosslink density due to the decrease in the mobility of the rubber chains.

Effect of silane coupling agent on the properties retention of the SBR/NBR vulcanizates with adding silane coupling agent was better than that without silane coupling agent as shown in Figure 4.7. It can be explained that the silane coupling agent introduced organic functional group onto silica surface, and the adhesion at interfaces between silica and rubber matrix was increased, resulting in improved thermal stability of the composites [32]. On the other hand, the vulcanizates with γ -mercaptopropyltrimethoxysilane, vinyl-tris-(2-methoxyethoxy)silane and γ -glycidoxypropyltrimethoxysilane modified filler were similar trends properties retention.

Table 4.5 Effect of blending ratios of SBR/NBR blends on properties retention after thermal aging at 100°C x 70h.

Retention	SBR	N30	N50	N70	NBR
Tensile strength retention, %	71.4	75.0	71.1	74.5	88.5
Elongation at break retention, %	89.5	85.5	93.8	93.9	96.2
100% Modulus retention, %	100.0	105.8	106.0	105.5	110.3
Hardness, %	102.3	104.7	104.5	106.3	106.1

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Table 4.6 Effect of silica/CB hybrid filler content and silane coupling agents of SBR/NBR blends on properties retention after thermal aging at 100°C x 70h.

Retention	N70	R30	R40	R50	R30M	R40M	R50M	R30G	R40G	R50G	R30V	R40V	R50V
Tensile strength retention, %	74.5	104.5	106.5	109.6	113.8	114.9	121.7	113.5	112.2	113.6	113.6	113.9	114.2
Elongation at break retention, %	93.9	89.0	94.5	94.8	92.8	95.1	95.0	91.4	93.4	95.1	91.9	90.2	93.7
100%Modulus retention, %	105.5	105.5	105.6	108.8	105.1	107.1	115.7	104.3	106.1	108.3	109.5	112.9	114.6
Hardness retention, %	106.3	106.3	107.5	107.4	107.1	106.9	108.1	106.3	107.2	107.0	106.3	107.6	107.2

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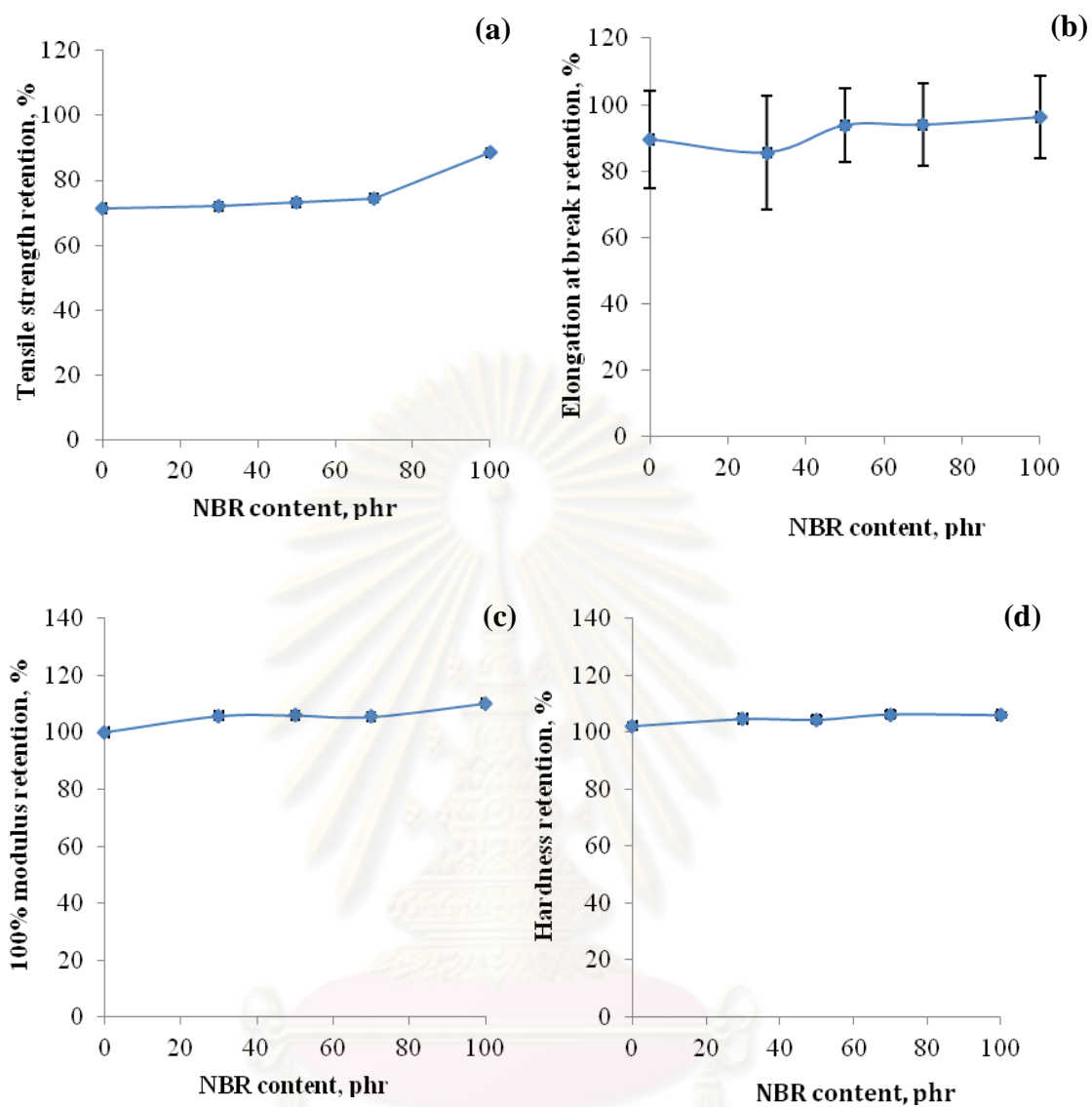


Figure 4.6 Effect of blending ratios of SBR/NBR blends on; (a) tensile strength retention, (b) elongation at break retention, (c) 100% modulus retention and (d) hardness retention after thermal aging.

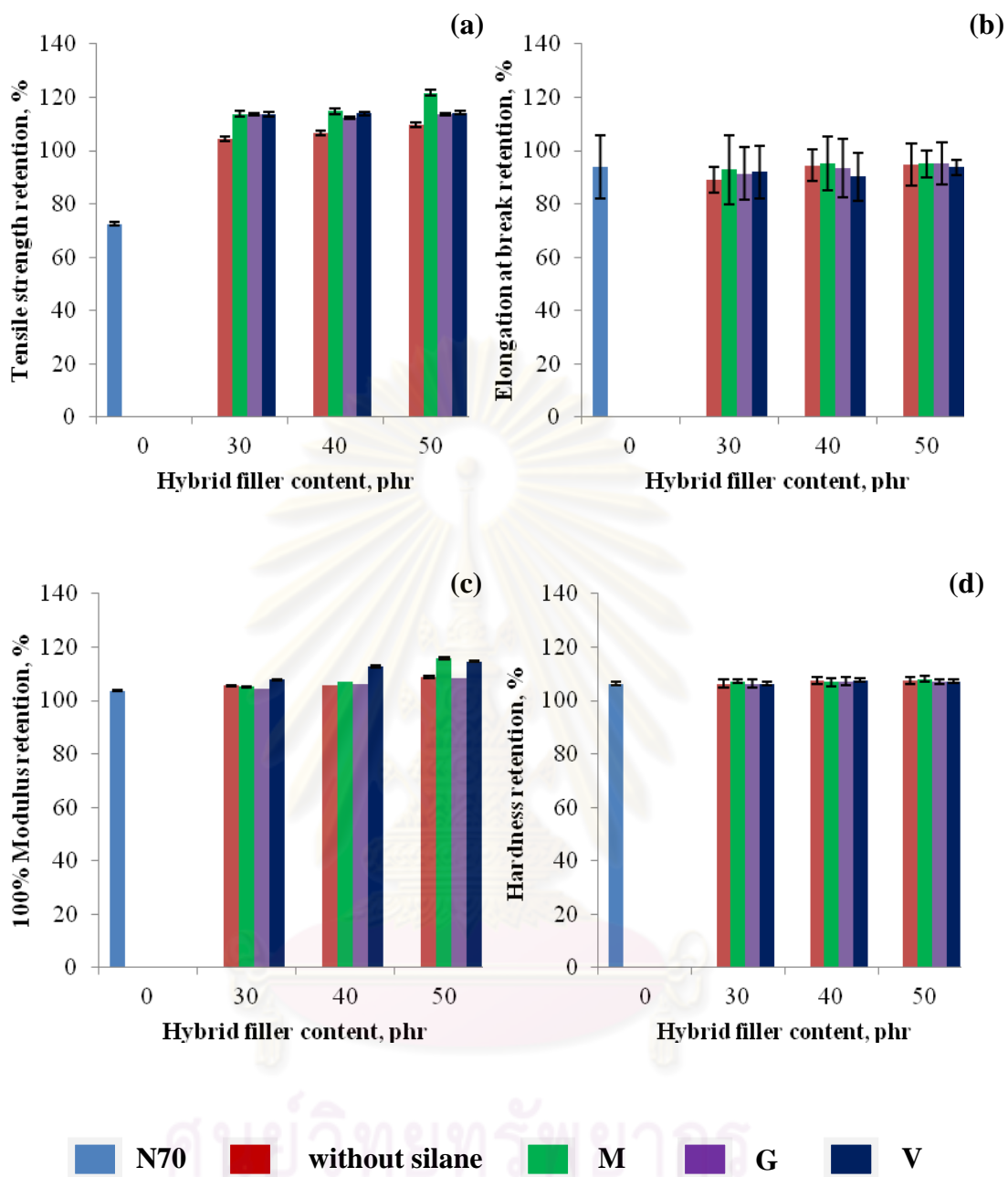


Figure 4.7 Effect of silica/CB hybrid filler content and silane coupling agents of SBR/NBR blends on; (a) tensile strength retention and (b) elongation at break retention (c) 100% modulus retention and (d) hardness retention after thermal aging.

4.4 Swelling

The percentage of change in hardness and volume after immersion in different oil types are presented in Table 4.7 and Figure 4.9. The swelling resistance of SBR/NBR blends vulcanizates increased with increasing NBR content because NBR with nitrile group ($=\text{CN}$) had good swell resistance in motor oil and fuel [20].

The effect of silica/CB hybrid filler content and silane coupling agents on swelling resistance of SBR/NBR vulcanizates are presented in Table 4.8 and Figure 4.10. The swelling resistance (volume change, %) of SBR/NBR blends vulcanizates increased with increasing silica/CB hybrid filler content and adding silane coupling agent. Thus, the hybrid filler could improve the swelling property by increasing swelling resistance. The increase in swelling resistance of the rubber blends with increasing hybrid filler (silica/CB) content could be explained as a consequence of the existing pressure involved between the rubber blends network and the oil which acts to expand or shrink the rubber blends network. The crosslink density in rubber compounds increased drastically with increasing hybrid filler content because of network elasticity contributions [21]. These crosslinks restrict extensibility of the rubber chains induced by swelling and make it more difficult for oil to diffusion into the gaps between rubber molecules and decrease the volume change percentage. From swelling phenomena of rubber compounds, the rubber with hybrid filler was in the collapsed state (Fig. 4.8b) under the oil rather than expanded state (Fig. 4.8c) [21]. Therefore, the swelling resistance increased with increasing of network. Finally, a high degree of swelling indicates that the rubber is not appropriate for use in that environment, thus, rubber filled with hybrid filler at 50 phr with silane coupling agents is practically preferable than without silane coupling agent. The SBR/NBR hybrid filler vulcanizates with hybrid filler modified γ -mercaptopropyltrimethoxysilane exhibited the minimum oil volume change (good swelling resistance).

The effect of oil types on swelling resistance of SBR/NBR vulcanizates was also evaluated. The oil resistance of SBR/NBR volume change in ASTM oil no.1, ASTM oil no.3, Brake fluid and Fuel C were 6.2 - 8.1, 41.5 - 50.2, 12.8 - 15.7 and 82.5 - 116.3, respectively. Therefore that the SBR/NBR vulcanizates had better oil resistance in ASTM oil no.1 and Brake fluid than in ASTM oil no.3 and Fuel C.

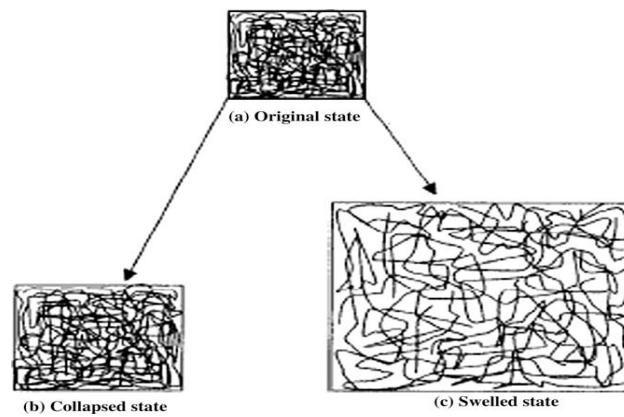


Figure 4.8 Schematic representation of rubber swelling [21].

Table 4.7 Effect of blend ratios on percentage of change in properties of SBR/NBR blends after immersion in oil.

Properties	SBR(N0)	N30	N50	N70	NBR(N100)
ASTM oil No.1@100°C x 70h					
Hardness change, HS	-16	-11	-13	-8	-5
Volume change, %	62.8	39.2	23.4	12.2	10.9
ASTM oil No.3@100°C x 70h					
Hardness change, HS	-22	-19	-21	-17	-13
Volume change, %	192.2	137.3	109.6	69.1	54.4
Brake fluid@25°C x 70h					
Hardness change, HS	-17	-16	-16	-14	-12
Volume change, %	50.0	23.3	21.2	18.8	13.2
Fuel C@25°C x 70h					
Hardness change, HS	-16	-16	-17	-16	-14
Volume change, %	225.7	201.1	176.1	137.1	89.1

Table 4.8 Effect of silica/CB hybrid filler content and silane coupling agents of SBR/NBR blends on percentage of change in properties after immersion in oil.

Properties	N70	R30	R40	R50	R30M	R40M	R50M	R30G	R40G	R50G	R30V	R40V	R50V
ASTM oil No.1@ 100°C x 70h													
Hardness change, HS	-8	-11	-10	-8	-6	-4	-8	-7	-7	-9	-7	-7	-6
Volume change, %	12.2	8.1	7.2	7.1	7.2	6.7	6.2	7.4	7.0	6.9	7.7	7.6	6.8
ASTM oil No.3@ 100°C x 70h													
Hardness change, HS	-17	-19	-21	-20	-18	-18	-21	-18	-19	-18	-18	-20	-19
Volume change, %	69.1	50.2	48.5	44.6	42.9	41.5	39.2	49.8	42.9	42.9	49.4	47.7	44.2
Brake Fluid@ 25°C x 70h													
Hardness change, HS	-14	-12	-14	-12	-11	-10	-11	-12	-11	-12	-12	-16	-16
Volume change, %	18.8	15.7	14.6	13.9	13.5	13.4	12.8	14.5	14.3	13.4	15.2	14.1	13.2
Fuel C@ 25°C x 70h													
Hardness change, HS	-16	-16	-18	-14	-14	-15	-15	-15	-19	-17	-14	-20	-20
Volume change, %	137.1	116.3	106.6	102.8	112.4	93.3	82.5	105.3	95.0	91.5	107.1	104.5	103.7

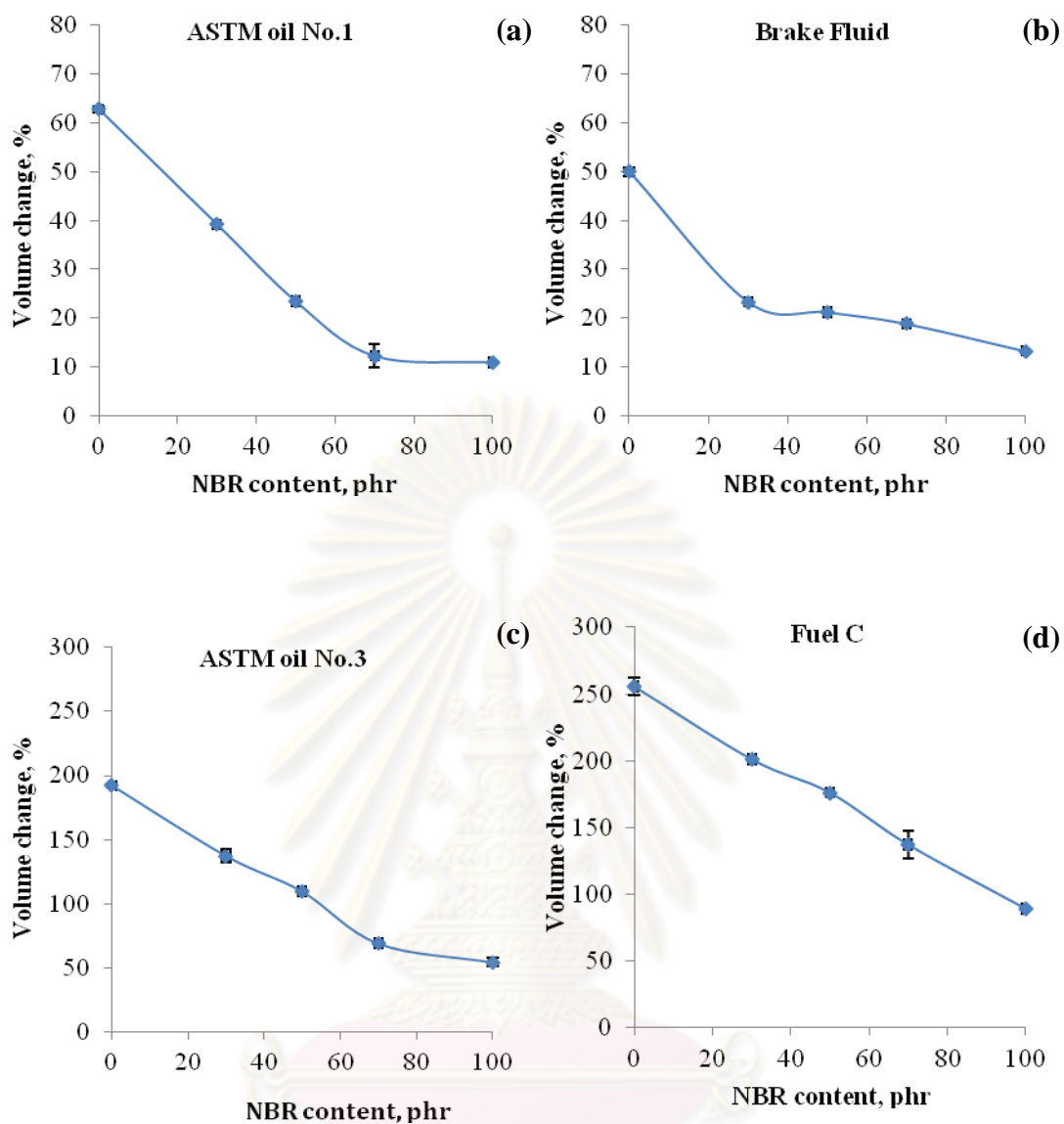


Figure 4.9 Effect of blending ratios of SBR/NBR blends on percentage of change in volume after immersion in oil; (a) ASTM oil No.1, (b) Brake fluid (c) ASTM oil No.3 and (d) Fuel C.

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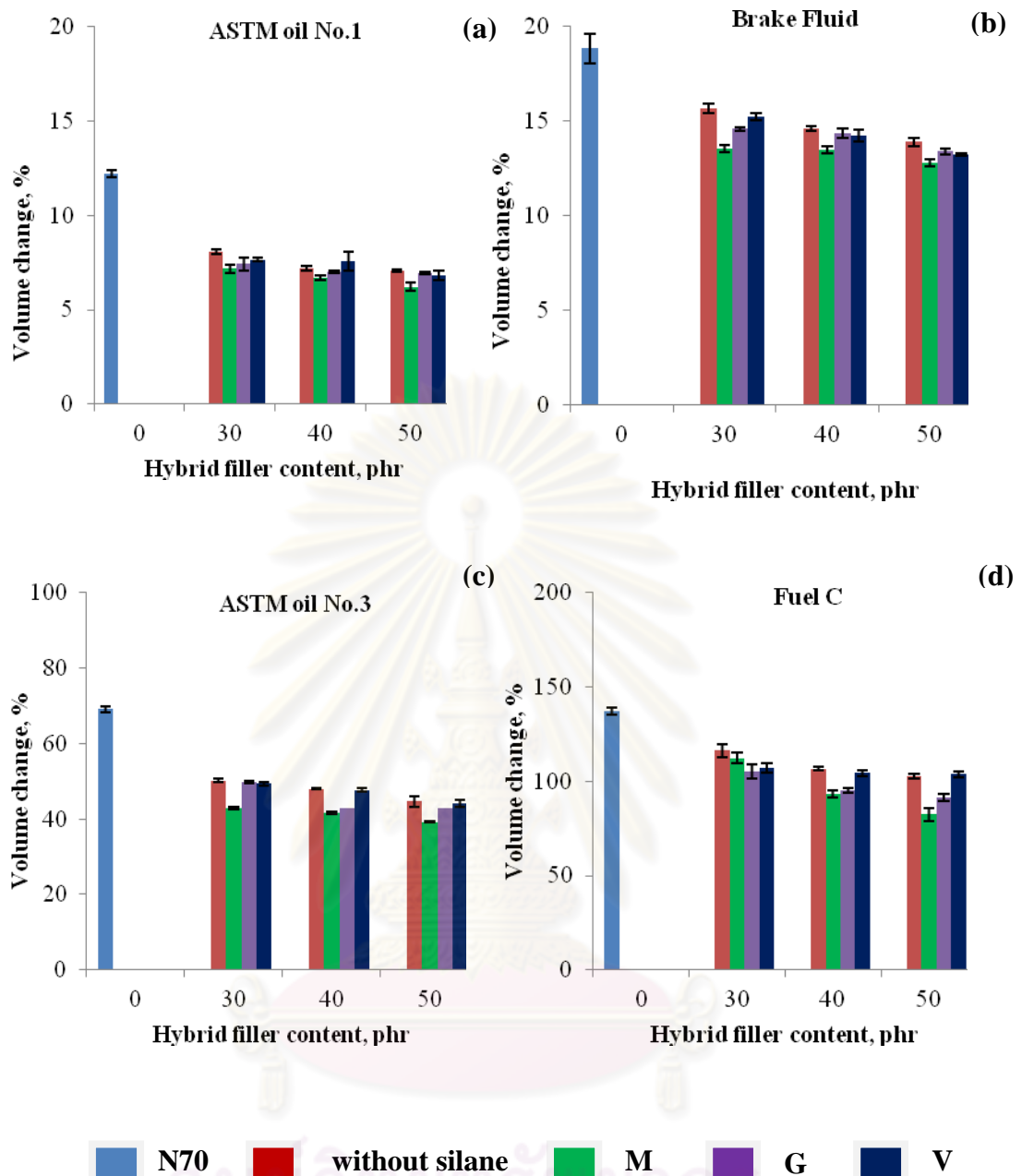


Figure 4.10 Effect of silica/CB hybrid filler content and silane coupling agents of SBR/NBR blends on percentage of change in volume after immersion in oil; (a) ASTM oil No.1, (b) Brake fluid, (c) ASTM oil No.3 and (d) Fuel C.

4.5 Low Temperature Properties

The chains of elastomer are able to move laterally and freely depending upon the thermodynamic state of the rubber. The low temperature test was carried out for measuring the elastic retraction of vulcanized rubber which was first frozen at low temperature after being elongation and then was raised up its temperature, and then for comparison and easy estimation of the crystallization tendency and viscoelasticity property at low temperature.

The low temperature properties were investigated by using TRL107SLCS, Yasuda machine with elongation mode in the range of temperature -70°C to 50°C with a heating rate $1^{\circ}\text{C}/\text{min}$. The rubber vulcanizates behaved as glassy at very low temperature because of lack of thermal kinetic energy. With an increased in temperature, the thermal energy increased the material's flexibility. The temperature for 10 percentage retraction was the glass transition (T_g) of the rubber vulcanizates because the temperature increased further, the percentage retraction increased, the rubber vulcanizates finally reached what has been called the rubbery plateau where normal rubber behavior is seen [15].

Table 4.9 and Figure 4.11 show the effect of hybrid filler, the temperature for 10 percentage retraction (or T_g) of the rubber vulcanizates with 30, 40 and 50 phr filler content and silane coupling agent was -33°C because the T_g of the rubber vulcanizates are greatly depended on the chemical structure of the base elastomer. The temperature for 30, 50 and 70 percentage retraction of the rubber vulcanizates (silica/CB filled 30, 40 and 50 phr) with silane coupling agent was -30 , -28 and -24°C respectively because low temperature properties of the rubber vulcanizates depend on structure of elastomer more than filler content and did not depend on silane coupling agent. Thus, these compounds could be applied at low temperature (minimum temperature -33.0°C).

Table 4.9 Effect of hybrid filler content with silane coupling agent types of SBR/NBR blends on elastic retraction at low temperature (TR).

Silane coupling agent types	Hybrid filler content, phr	Low temperature properties (°C)			
		TR-10	TR-30	TR-50	TR-70
without silane	30	-33.4	-30.4	-28.2	-24.9
	40	-33.3	-30.1	-28.0	-24.6
	50	-33.4	-30.0	-27.8	-24.8
γ -mercaptopropyltrimethoxysilane	30M	-33.3	-29.7	-27.6	-25.4
	40M	-33.3	-29.9	-27.8	-25.3
	50M	-33.2	-29.8	-27.2	-23.2
γ -glycidoxypropylmethoxysilane	30G	-33.6	-30.5	-28.4	-25.2
	40G	-33.1	-30.0	-27.9	-25.3
	50G	-33.3	-29.7	-27.4	-24.4
vinyl-tris-(2-methoxyethoxy)silane	30V	-33.1	-30.2	-28.0	-24.6
	40V	-33.5	-30.3	-28.1	-25.1
	50V	-32.8	-29.6	-27.9	-25.9

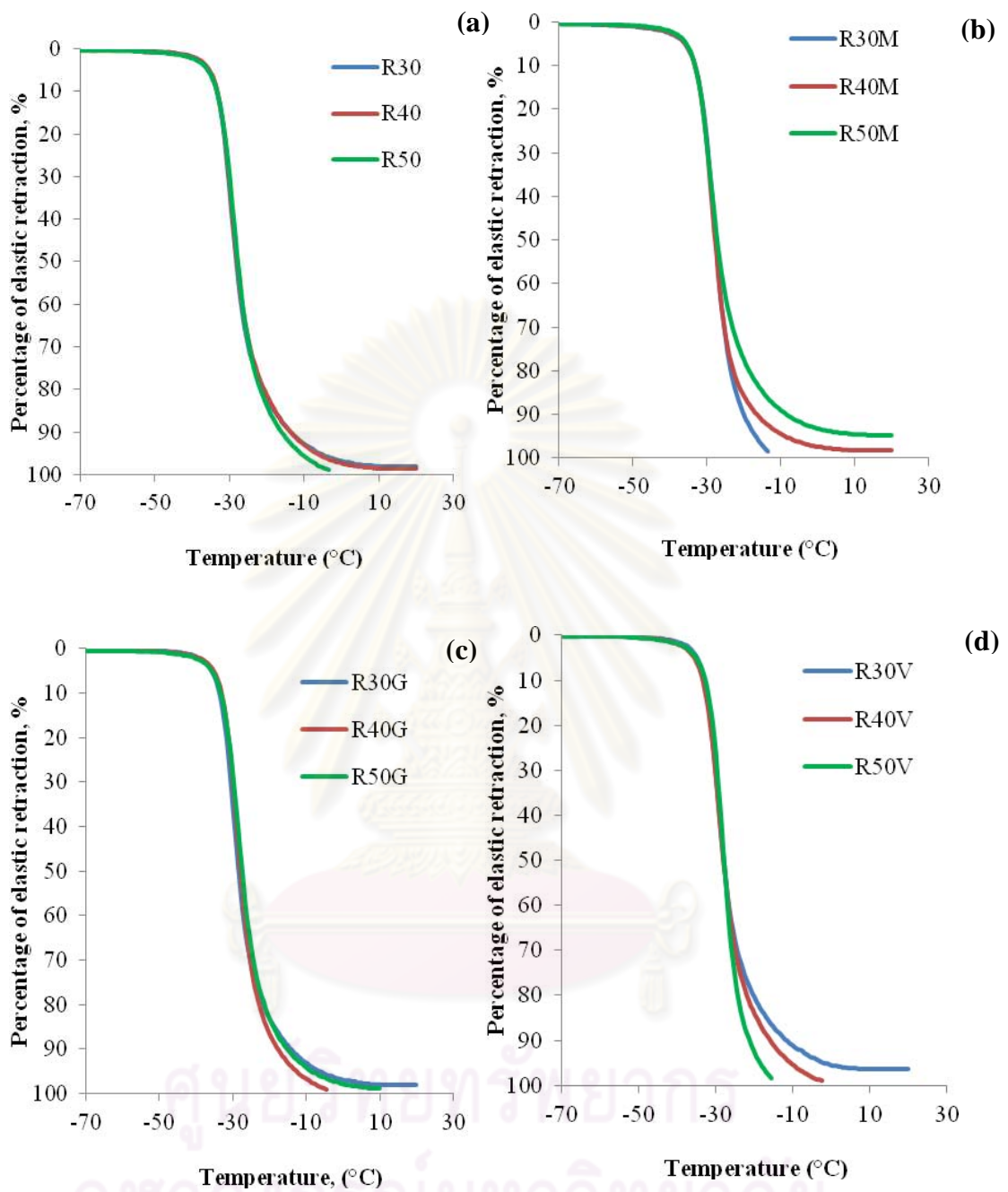


Figure 4.11 Effect of silica/CB hybrid filler content and silane coupling agents of SBR/NBR blends on elastic retraction; (a) without silane agent, (b) γ -mercaptopropyltrimethoxysilane, (c) γ -glycidoxypropylmethoxysilane and (d) vinyl-tris-(2-methoxyethoxy)silane.

4.6 Morphology

After coating with gold on the fracture surface of sample, the rubber phase in SBR/NBR could be identified as dark area in the SEM micrograph because their double bonds endowed the scattering capacity electrons. For 30/70; SBR/NBR blends, the SBR phase was dispersed in the continuous NBR matrix.

Compared the SEM micrograph of SBR/NBR blends with various silica/CB hybrid filler content and silane coupling agents, the extent of filler dispersion in the rubber vulcanizates with silane coupling agent was better than that without silane coupling agent. However, it could not be distinguished between silica and carbon black as shown in Figures 4.13–4.15.

Figures 4.12 (a)-(c) show the observed morphology of the silica/CB filled blends without silane coupling agent, the silica exhibited poor dispersion and was agglomerated in the rubber matrix. This phenomena affected the low tensile properties and swelling resistance of rubber vulcanizates [33]. The filler dispersion of the silica/CB filled SBR/NBR blends with γ -mercaptoproyltrimethoxysilane was better than that with γ -glycidoxypropylmethoxysilane and vinyl-tris-(2-methoxyethoxy)silane as shown in Figures 4.13-4.15. Thus, the morphology of SBR/NBR blends with the silica/CB hybrid filler and γ -mercaptoproyltrimethoxysilane supported good tensile properties, compression set and swelling resistance.

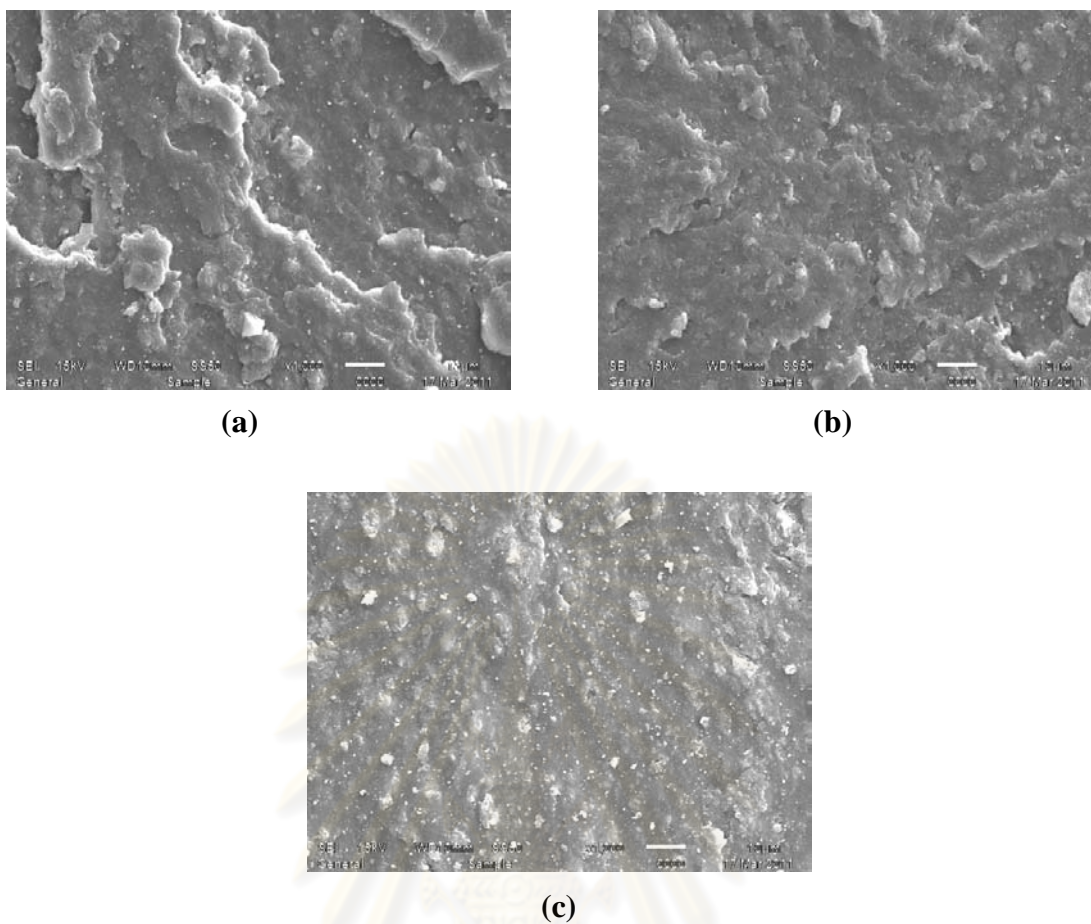


Figure 4.12 SEM photomicrographs of the fracture surface of silica/CB hybrid filler filled SBR/NBR blends and without silane coupling agent: (a) 30 phr of hybrid filler, (b) 40 phr of hybrid filler and (c) 50 phr of hybrid filler.

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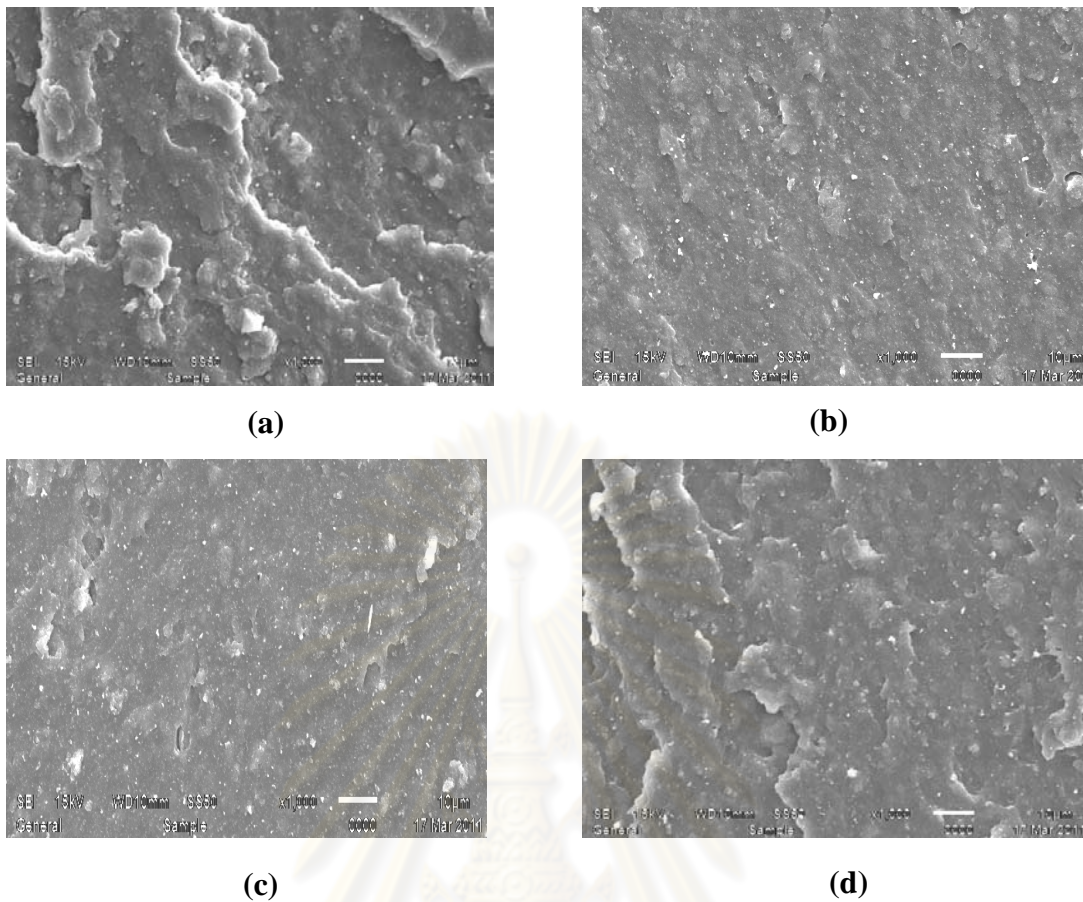


Figure 4.13 SEM photomicrographs of the fracture surface of silica/CB hybrid filler content 30 phr and silane coupling agent types of SBR/NBR blends: (a) without silane, (b) γ -mercaptopropyltrimethoxysilane, (c) γ -glycidoxypropylmethoxysilane and (d) vinyl-tris-(2-methoxyethoxy)silane.

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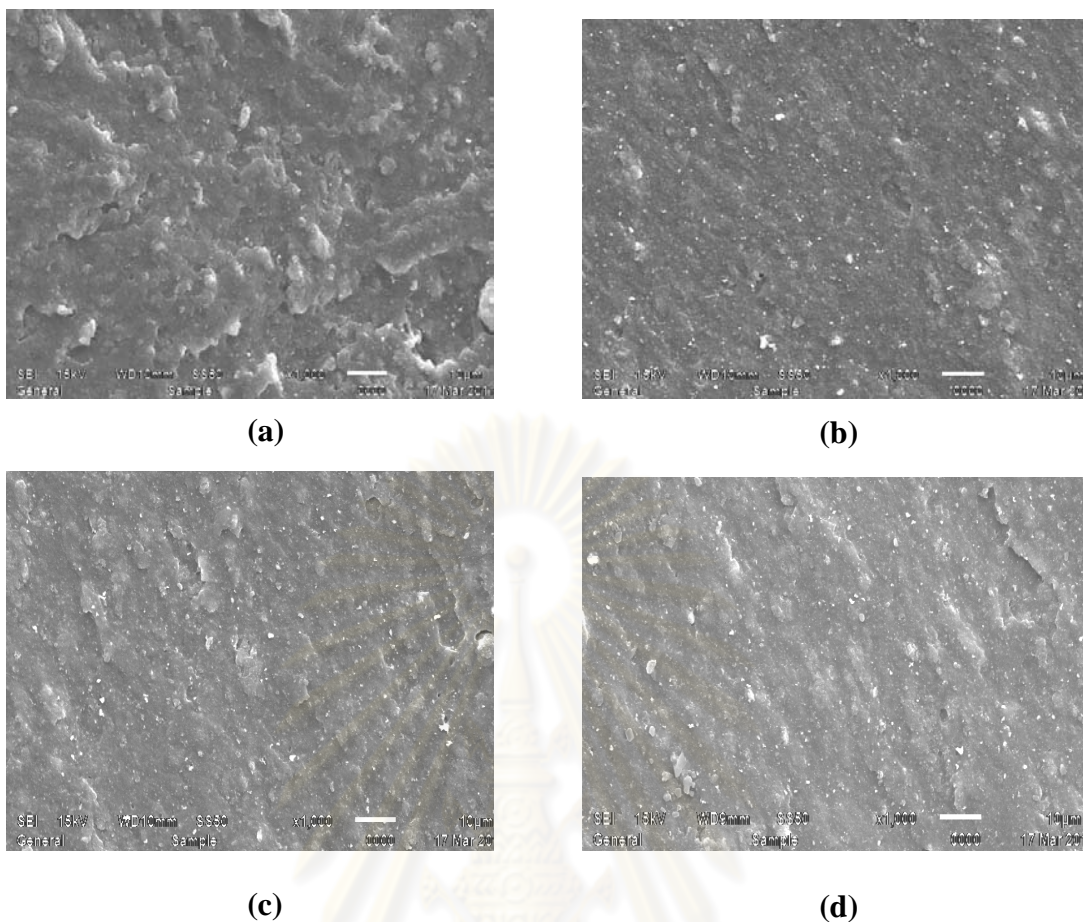


Figure 4.14 SEM photomicrographs of the fracture surface of silica/CB hybrid filler content 40 phr and silane coupling agent types of SBR/NBR blends: (a) without silane, (b) γ -mercaptopropyltrimethoxysilane, (c) γ -glycidoxypropylmethoxysilane and (d) vinyl-tris-(2-methoxyethoxy)silane.

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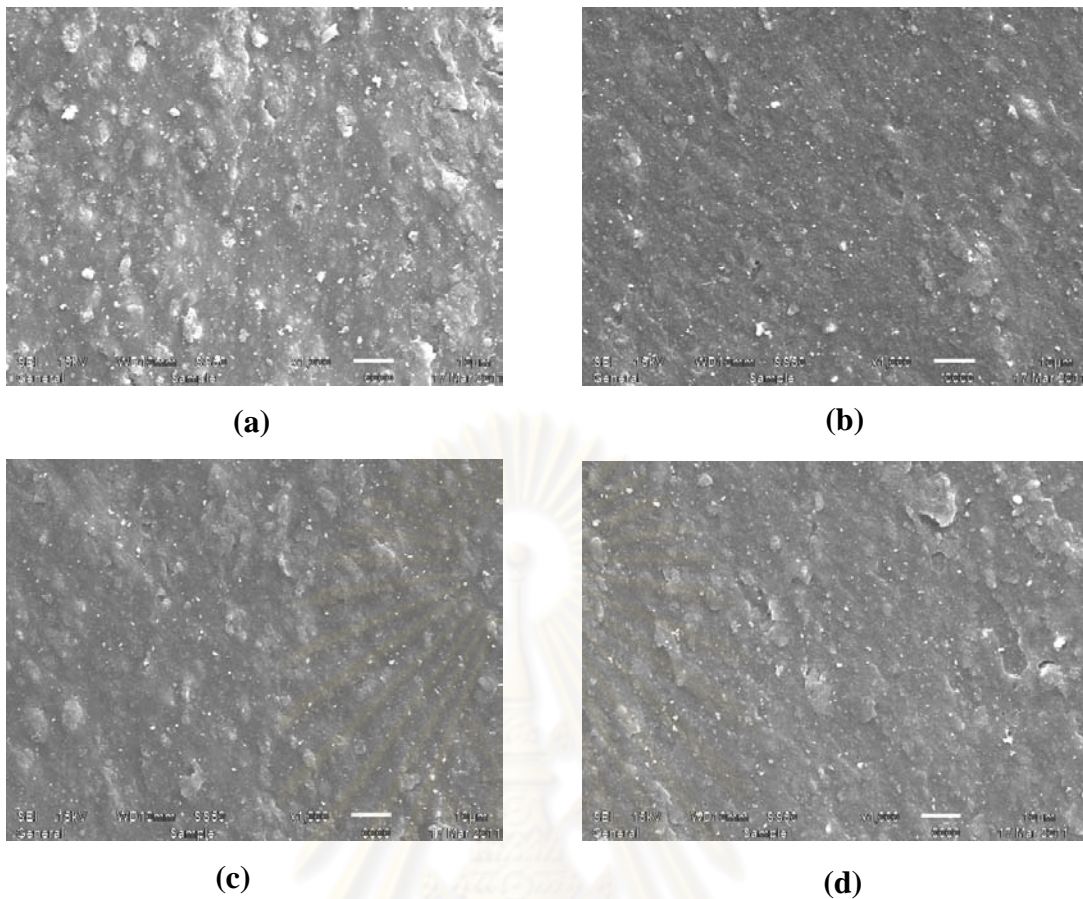


Figure 4.15 SEM photomicrographs of the fracture surface of silica/CB hybrid filler content 50 phr with silane coupling agent types of SBR/NBR blends: (a) without silane, (b) γ -mercaptopropyltrimethoxysilane, (c) γ -glycidoxypropylmethoxysilane and (d) vinyl-tris-(2-methoxyethoxy)silane.

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

CHAPTER V

CONCLUSIONS AND FUTURE WORK

5.1 Conclusions

The effects of silica/CB hybrid filler content on properties and morphology of SBR/NBR blends were studied. In this work, the appropriate blending ratio of SBR/NBR blends was investigated for good oil resistance and compression set resistance. Moreover, the silica/CB hybrid filler content and silane coupling agents on properties of SBR/NBR blends were investigated. The results were concluded as follows:

1. From the cure characteristics of SBR/NBR blends, the maximum torque increased with increasing NBR content. The SBR/ NBR (30/70) blend and with silica/CB hybrid filler content at 50 phr and γ - mercaptopropyltrimethoxysilane exhibited maximum torque. The cure temperature did not affect maximum torque but affected the cure time. The silane coupling agent had affected the cure characteristics.
2. The 100% modulus, tensile strength and elongation at break of SBR/NBR blend increased with an increase in NBR content to 70 phr . This rubber blends (SBR/NBR=30/70) with 50 phr silica/CB hybrid filler modified with γ - mercaptopropyltrimethoxysilane exhibited the higher 100%modulus and tensile strength and lower elongation at break than with γ -glycidoxypropylmethoxysilane, vinyl-tris-(2-methoxyethoxy)silane and without silane coupling agent.
3. The compression set of SBR/NBR blends decreased with increasing NBR content. The SBR/NBR blends filled with silica/CB hybrid filler (50 phr) modified with γ - mercaptopropyltrimethoxysilane, the compression set was better than that modified with γ -glycidoxypropylmethoxysilane, vinyl-tris-(2-methoxyethoxy)silane and without silane coupling agent.

4. The thermal aging and oil resistance properties of SBR/NBR blends increased with increasing NBR content. The SBR/NBR blends filled with 50 phr silica/CB hybrid filler modified with silane coupling agent was better than that without silane coupling agent.
5. The low temperature properties of SBR/NBR vulcanizates at various hybrid filler content and silane coupling agents were not significantly different. Thus, the silica/CB hybrid filler content and silane coupling agent did not affect the elasticity retraction properties (TR-10, TR-30, TR-50 and TR-70).
6. From morphology of silica/CB filled SBR/NBR blends, the extent of filler dispersion in the rubber vulcanizates with silane coupling agent was better than without silane coupling agent. The morphology of the blends with filler modified γ - mercaptopropyltrimethoxysilane show the continuous filler dispersion.
7. Thus, the rubber blend (SBR/NBR = 30/70) reinforced with 50 phr of silica/CB (25/25) hybrid filler modified with γ - mercaptopropylmethoxysilane exhibited the good mechanical properties, oil resistance and compression set and could be used as o-ring for motor oil medium resistance.

5.2 Future work

Future study work on the effect of other hybrid fillers such as carbon black-N330, calcium carbonate, magnesium silicate and clay on the properties of SBR/NBR blends should be performed.

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APPENDICES

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

APPENDIX A

Table A-1 Elastomer Properties

Elastomer	Characteristic		
	Bound ACN (%)	Bound Styrene (%)	Mooney viscosity [ML(1+4) 100°C]
Nipol DN2850 (NBR)	28 ± 1	-	49 ± 5
JSR SBR 1502 (SBR)	-	22.5 ± 1	50 ± 5

Table A-2 Carbon black properties

Characteristic	Unit	G-N550
Iodine No.	mg/g	43 ± 7
DBP No.	ml/100g	121 ± 7
Ash content	(%)	0.5 max
pH value	-	6.5 ± 1.5
Heat loss	(%)	2.0 max
Sieve residue: screen size 150µm	(%)	0.00020 max
Individual pellet hardness: avg 20 pellet		

Table A-3 Silica properties

Characteristic	Unit	Nipsil ER
Moisture	(%)	2.6
pH value	-	8.1
Lose weight	g/l	96
Specific surface area (BET)	m ² /g	117

Table A-4 Silane coupling agent properties

Characteristic	Unit	γ -mercaptopropyl-trimethoxysilane	γ -glycidoxypropyl-trimethoxysilane	vinyl- <i>tris</i> -(2-methoxyethoxy)silane
Appearance (color)	-	Colorless	Clear color	Clear color
Appearance (state)	-	Transparent liquid	Liquid	Liquid
Purity	(%)	99.0	95.6	96.6

Table A-5 Specification and typical properties of ASTM oils.

Characteristic	Unit	ASTM oil no.1	ASTM oil no.3
Aniline Point	(°C)	124 ± 1	70 ± 1
Kinematic Viscosity	(mm ² /s)	18.7 – 21.0(99°C)	31.9 – 34.1(38°C)
Gravity, 16°C	API	-	21.0 – 23.0
Viscosity-Gravity Constant	-	-	0.875 – 0.885
Flash point	(°C)	243 min	163 min
Naphthenics, C _N	(%)	-	40 min

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APPENDIX B

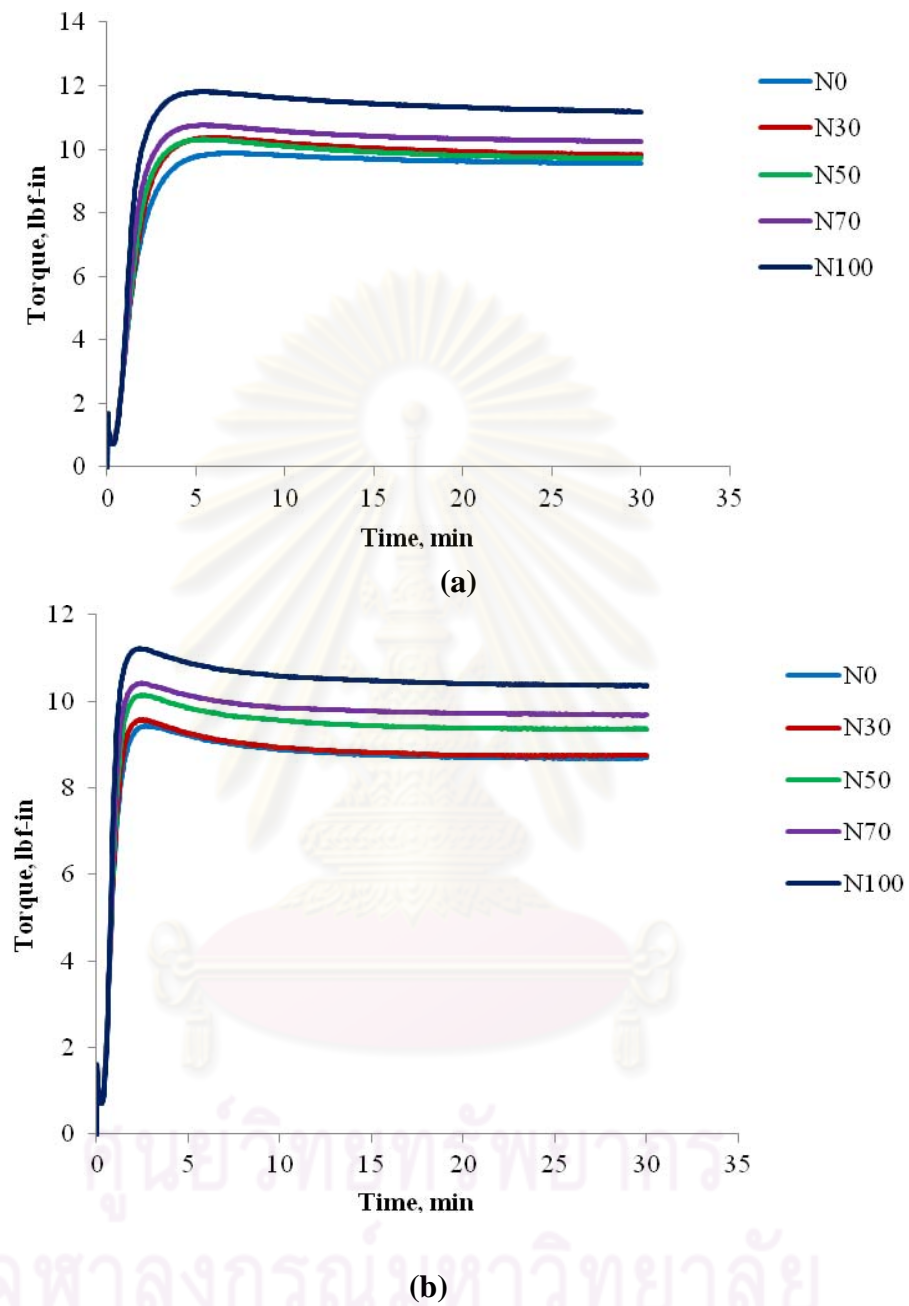


Figure B-1 Cure curves of rubber compounds with different blend ratios for; (a) 180°C and (b) 190°C.

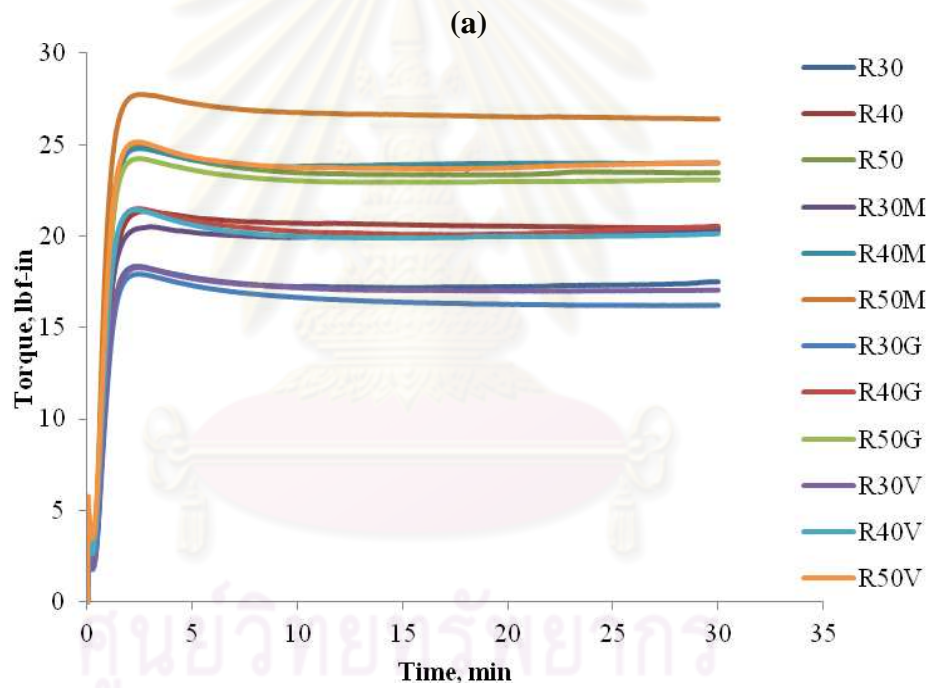
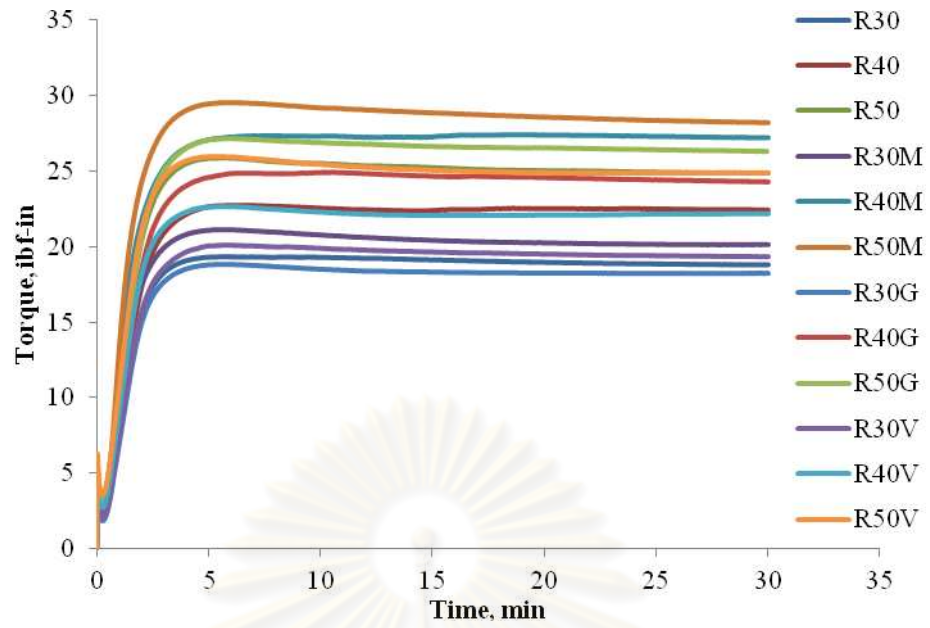


Figure B-2 Cure curves of silica/CB filled rubber compound and silane coupling agent types for; (a) 180°C and (b) 190°C

APPENDIC C

Table C-1 Mechanical properties of SBR/NBR vulcanizates according to ASTM D412.

Samples	No.	Hardness		100% Modulus		Tensile strength (MPa)		Elongation at break (%)		SG
		Before aging	After aging	Before aging	After aging	Before aging	After aging	Before aging	After aging	
SBR(N0)	1	43	45	0.69	0.72	1.90	1.50	255	220	0.984
	2	43	44	0.82	0.67	2.10	1.40	230	209	0.982
	3	44	44	0.72	0.83	2.40	1.80	246	238	0.983
	Median	43	44	0.72	0.72	2.10	1.50	246	220	0.983
	σ	0.6	1.0	0.07	0.08	0.25	0.21	13	15	0.001
N30	1	43	44	0.86	0.91	2.80	2.80	339	290	0.992
	2	43	45	0.94	0.89	3.20	2.40	310	295	0.990
	3	45	45	0.83	0.96	3.50	2.20	348	263	0.995
	Median	43	45	0.86	0.91	3.20	2.40	339	290	0.992
	σ	1.2	1.0	0.06	0.04	0.35	0.31	20	17	0.003
N50	1	44	46	0.88	0.89	4.80	3.40	420	380	0.999
	2	43	47	0.79	0.88	4.50	2.60	386	402	1.001
	3	45	46	0.84	1.01	4.20	3.20	440	394	0.998
	Median	44	46	0.84	0.89	4.50	3.20	420	394	0.999
	σ	1.0	0.6	0.05	0.07	0.30	0.42	27	11	0.002
N70	1	47	49	1.09	1.11	4.30	3.40	375	370	1.004
	2	46	49	1.10	1.15	4.70	3.50	358	352	1.001
	3	47	48	1.05	1.24	4.90	3.70	391	346	0.999
	Median	46	49	1.09	1.15	4.70	3.50	375	352	1.001
	σ	1.0	0.6	0.03	0.07	0.31	0.15	17	12	0.003
NBR (N100)	1	49	52	1.07	1.18	2.80	2.40	260	250	1.012
	2	49	53	1.09	1.11	2.60	2.30	249	237	1.009
	3	51	51	1.04	1.23	2.20	2.10	283	262	1.014
	Median	49	52	1.07	1.18	2.60	2.30	260	250	1.012
	σ	1.0	1.0	0.03	0.06	0.31	0.15	17	13	0.003

Table C-2 Mechanical properties of silica/CB filled SBR/NBR vulcanizates and silane coupling agents according to ASTM D412.

Samples	n	Hardness		100% Modulus		Tensile strength (MPa)		Elongation at break (%)		SG
		Before aging	After aging	Before aging	After aging	Before aging	After aging	Before aging	After aging	
R30	1	63	67	2.95	3.30	11.61	12.43	290	265	1.116
	2	64	69	3.10	3.24	12.03	12.10	296	258	1.118
	3	62	66	3.21	3.27	11.90	13.89	288	255	1.114
	Median	63	67	3.10	3.27	11.90	12.43	290	258	1.116
	σ	1.0	1.5	0.13	0.03	0.22	0.95	4.2	5.1	0.002
R40	1	66	72	3.32	3.32	13.91	14.27	267	256	1.125
	2	69	70	3.23	3.46	13.24	14.80	281	269	1.123
	3	67	72	3.03	3.41	13.90	15.61	275	260	1.120
	Median	67	72	3.23	3.41	13.90	14.80	275	260	1.123
	σ	1.5	1.2	0.15	0.07	0.38	0.67	7.02	6.66	0.003
R50	1	68	73	3.99	4.05	16.42	17.51	290	264	1.126
	2	68	73	3.72	4.10	16.81	18.10	288	279	1.121
	3	69	71	3.77	4.52	14.49	18.00	298	275	1.120
	Median	68	73	3.77	4.10	16.42	18.00	290	275	1.121
	σ	0.6	1.2	0.14	0.26	1.24	0.32	5.29	7.8	0.003
R30M	1	71	74	5.14	5.32	15.63	17.42	341	310	1.117
	2	69	75	5.00	5.40	15.31	16.90	329	300	1.119
	3	70	75	5.36	5.49	14.78	17.42	334	325	1.115
	Median	70	75	5.14	5.40	15.31	17.42	334	310	1.117
	σ	1.0	0.6	0.18	0.09	0.43	0.30	6.03	12.6	0.002
R40M	1	72	77	5.72	5.88	15.49	17.80	361	328	1.148
	2	73	78	5.49	5.92	16.28	18.11	345	334	1.142
	3	71	75	5.42	5.80	15.32	17.35	340	314	1.152
	Median	72	77	5.49	5.88	15.49	17.80	345	328	1.148
	σ	1.0	1.5	0.16	0.06	0.51	0.38	11.0	10.3	0.005
R50M	1	75	79	5.75	6.20	18.51	21.06	338	321	1.176
	2	73	81	5.62	6.50	18.88	23.11	351	316	1.172
	3	74	80	5.49	6.90	18.72	22.79	330	326	1.168
	Median	74	80	5.62	6.50	18.72	22.79	338	321	1.172
	σ	1.0	1.0	0.13	0.35	0.19	1.10	10.6	5.00	0.004
R30G	1	63	67	3.13	3.48	13.47	14.59	320	286	1.110
	2	65	66	3.28	3.35	14.26	15.42	339	298	1.119
	3	63	69	3.35	3.42	13.59	15.89	326	306	1.117
	Median	63	67	3.28	3.42	13.59	15.42	326	298	1.117
	σ	1.2	1.5	0.11	0.07	0.43	0.66	9.71	10.1	0.005
R40G	1	69	72	4.88	5.50	14.78	18.18	301	281	1.142
	2	69	74	5.21	5.30	15.87	17.62	319	298	1.139
	3	70	75	5.09	5.40	15.70	17.20	321	301	1.149
	Median	69	74	5.09	5.40	15.70	17.62	319	298	1.142
	σ	0.6	1.5	0.17	0.10	0.59	0.49	11.0	10.8	0.005
R50G	1	72	77	5.44	5.72	18.69	20.72	319	269	1.176
	2	71	75	5.28	5.68	18.28	20.86	280	281	1.169
	3	71	76	5.14	5.75	18.37	21.00	283	266	1.170
	Median	71	76	5.28	5.72	18.37	20.86	283	269	1.170
	σ	0.6	1.0	0.15	0.04	0.22	0.14	21.7	7.94	0.004
R30V	1	64	68	3.06	3.60	13.63	14.46	332	297	1.117
	2	63	67	3.01	3.3	11.79	14.38	327	316	1.119
	3	64	68	3.22	3.21	12.66	14.20	349	305	1.111
	Median	64	68	3.06	3.3	12.66	14.38	332	305	1.117
	σ	0.6	0.6	0.11	0.20	0.92	0.13	11.5	9.54	0.004
R40V	1	65	71	3.81	4.80	15.18	16.88	379	356	1.147
	2	66	71	3.59	3.9	14.79	17.29	365	342	1.152
	3	66	72	3.77	4.2	14.98	17.06	396	338	1.148
	Median	66	71	3.77	4.2	14.98	17.06	379	342	1.148
	σ	0.6	0.6	0.12	0.46	0.20	0.21	15.5	9.45	0.003
R50V	1	69	74	5.13	5.59	17.61	18.80	300	281	1.176
	2	69	75	4.67	5.21	18.30	20.11	332	285	1.174
	3	70	74	4.46	5.35	16.66	19.92	299	279	1.167
	Median	69	74	4.67	5.35	17.61	19.92	300	281	1.174
	σ	0.6	0.6	0.34	0.19	0.82	0.71	18.8	3.06	0.005

Table C-3 Compression set property of SBR/NBR vulcanizates according to ASTM D395 method B.

Samples	n	To	Ts	Tf	To-Ts	To-Tf	$\frac{[To-Tf]}{To-Ts} \times 100$	Median	σ
SBR(N0)	1	13.45	9.52	11.63	3.93	1.82	46.31	44.13	2.27
	2	13.44	9.52	11.71	3.92	1.73	44.13		
	3	13.47	9.52	11.82	3.95	1.65	41.77		
N30	1	13.26	9.52	11.48	3.74	1.78	47.59	40.68	4.20
	2	13.33	9.52	11.78	3.81	1.55	40.68		
	3	13.32	9.52	11.80	3.8	1.52	40.00		
N50	1	13.29	9.52	11.56	3.77	1.73	45.89	37.60	4.91
	2	13.11	9.52	11.76	3.59	1.35	37.60		
	3	13.15	9.52	11.80	3.63	1.35	37.19		
N70	1	12.98	9.52	11.52	3.46	1.46	42.20	37.80	3.63
	2	12.88	9.52	11.61	3.36	1.27	37.80		
	3	12.92	9.52	11.73	3.4	1.19	35.00		
NBR(N100)	1	13.16	9.52	11.70	3.64	1.46	40.11	39.22	1.51
	2	13.18	9.52	11.82	3.66	1.36	37.16		
	3	13.09	9.52	11.69	3.57	1.40	39.22		

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Table C-4 Compression set property of silica/CB filled SBR/NBR vulcanizates and silane coupling agents according to ASTM D395 method B.

Samples	n	To	Ts	Tf	To-Ts	To-Tf	$\frac{To-Tf}{To-Ts} \times 100$	Median	σ
R30	1	12.92	9.52	11.69	3.40	1.23	36.18	36.39	2.97
	2	12.84	9.52	11.53	3.32	1.31	39.46		
	3	12.89	9.52	11.76	3.37	1.13	33.53		
R40	1	12.79	9.52	11.93	3.27	0.86	26.30	24.50	2.04
	2	12.84	9.52	12.10	3.32	0.74	22.29		
	3	12.89	9.52	12.05	3.37	0.84	24.93		
R50	1	12.88	9.52	12.18	3.36	0.70	20.83	21.84	1.35
	2	12.90	9.52	12.11	3.38	0.79	23.37		
	3	12.90	9.52	12.18	3.38	0.72	21.30		
R30M	1	12.82	9.52	12.22	3.30	0.60	18.18	18.32	1.92
	2	12.82	9.52	12.15	3.30	0.67	20.30		
	3	12.80	9.52	12.26	3.28	0.54	16.46		
R40M	1	12.77	9.52	12.32	3.25	0.45	13.85	15.52	1.57
	2	12.82	9.52	12.30	3.30	0.52	15.76		
	3	12.82	9.52	12.26	3.30	0.56	16.97		
R50M	1	12.80	9.52	12.12	3.28	0.68	20.73	16.84	3.43
	2	12.80	9.52	12.29	3.28	0.51	15.55		
	3	12.82	9.52	12.35	3.30	0.47	14.24		
R30G	1	12.90	9.52	12.00	3.38	0.90	26.63	25.74	1.22
	2	12.95	9.52	12.05	3.43	0.90	26.24		
	3	12.97	9.52	12.13	3.45	0.84	24.35		
R40G	1	12.87	9.52	12.11	3.35	0.76	22.69	22.20	1.44
	2	12.95	9.52	12.15	3.43	0.80	23.32		
	3	12.97	9.52	12.26	3.45	0.71	20.58		
R50G	1	12.87	9.52	12.21	3.35	0.66	19.70	18.73	0.93
	2	12.95	9.52	12.31	3.43	0.64	18.66		
	3	12.94	9.52	12.33	3.42	0.61	17.84		
R30V	1	12.88	9.52	11.98	3.36	0.90	26.79	27.92	2.30
	2	12.89	9.52	11.86	3.37	1.03	30.56		
	3	12.89	9.52	12.00	3.37	0.89	26.41		
R40V	1	12.90	9.52	12.15	3.38	0.75	22.19	23.28	1.20
	2	12.94	9.52	12.10	3.42	0.84	24.56		
	3	12.90	9.52	12.12	3.38	0.78	23.08		
R50V	1	12.90	9.52	12.24	3.38	0.66	19.53	19.40	1.80
	2	12.77	9.52	12.20	3.25	0.57	17.54		
	3	12.88	9.52	12.17	3.36	0.71	21.13		

Table C-5 Change in volume of SBR/NBR vulcanizates after immersion in ASTM oil no.1 and ASTM oil no.3 at 100°C x 70h according to ASTM D471.

ASTM oil no.1 at 100°C x 70h

Samples	n	M1(gm)	M2(gm)	v(cc)	M3(gm)	M4(gm)	V(cc)	$\frac{V-v}{v} \times 100$	Median	σ
SBR(N0)	1	2.199	0.028	2.171	3.316	-0.219	3.535	62.828	62.805	0.705
	2	2.191	0.009	2.182	3.307	-0.219	3.526	61.595		
	3	2.194	0.019	2.175	3.321	-0.22	3.541	62.805		
N30	1	2.085	0.019	2.066	2.735	-0.126	2.861	38.480	39.194	2.320
	2	2.084	0.025	2.059	2.738	-0.128	2.866	39.194		
	3	2.096	0.080	2.016	2.752	-0.127	2.879	42.808		
N50	1	2.043	0.002	2.041	2.456	-0.073	2.529	23.910	23.443	0.289
	2	2.025	0.002	2.023	2.424	-0.072	2.496	23.381		
	3	2.041	0.002	2.039	2.445	-0.072	2.517	23.443		
N70	1	2.016	0.012	2.004	2.217	-0.032	2.249	12.226	12.226	0.180
	2	2.013	0.012	2.001	2.217	-0.031	2.248	12.344		
	3	2.022	0.012	2.010	2.219	-0.032	2.251	11.990		
NBR(N100)	1	2.184	0.016	2.168	2.378	-0.027	2.405	10.932	10.932	0.650
	2	2.171	0.016	2.155	2.357	-0.028	2.385	10.673		
	3	2.157	0.015	2.142	2.368	-0.029	2.397	11.905		

ASTM oil no.3 at 100°C x 70h

Samples	n	M1(gm)	M2(gm)	v(cc)	M3(gm)	M4(gm)	V(cc)	$\frac{V-v}{v} \times 100$	Med.	σ
SBR (N0)	1	2.193	0.042	2.151	6.038	-0.224	6.262	191.120	192.230	1.705
	2	2.206	0.031	2.175	6.243	-0.113	6.356	192.230		
	3	2.199	0.03	2.169	6.279	-0.108	6.387	194.467		
N30	1	2.088	0.011	2.077	4.61	-0.247	4.857	133.847	137.331	5.066
	2	2.069	0.011	2.058	4.777	-0.241	5.018	143.829		
	3	2.087	0.011	2.076	4.678	-0.249	4.927	137.331		
N50	1	2.056	0.019	2.037	4.11	-0.185	4.295	110.849	109.619	0.938
	2	2.051	0.003	2.048	4.109	-0.184	4.293	109.619		
	3	2.066	0.001	2.065	4.131	-0.185	4.316	109.007		
N70	1	2.023	0.012	2.011	3.281	-0.095	3.376	67.877	69.094	0.705
	2	2.024	0.011	2.013	3.306	-0.098	3.404	69.101		
	3	2.031	0.012	2.019	3.318	-0.096	3.414	69.094		
NBR(N100)	1	2.248	0.090	2.158	3.249	-0.083	3.332	54.402	54.424	2.975
	2	2.241	0.072	2.169	3.389	-0.072	3.461	59.567		
	3	2.25	0.080	2.17	3.291	-0.06	3.351	54.424		

Table C-6 Change in volume of SBR/NBR vulcanizates after immersion in Brake fluid and Fuel C at 25°C x 70h according to ASTM D471.

Brake fluid at 25°C x 70h

Samples	n	M1(gm)	M2(gm)	v(cc)	M3(gm)	M4(gm)	V(cc)	$\frac{V-v}{v} \times 100$	Med.	σ
SBR(N0)	1	2.092	0.018	2.074	3.316	0.232	3.084	48.698	50.000	0.945
	2	2.071	0.029	2.042	3.307	0.244	3.063	50.000		
	3	2.084	0.030	2.054	3.321	0.229	3.092	50.536		
N30	1	2.065	0.022	2.043	2.735	0.215	2.52	23.348	23.348	0.232
	2	2.059	0.028	2.031	2.738	0.229	2.509	23.535		
	3	2.066	0.042	2.024	2.752	0.261	2.491	23.073		
N50	1	2.053	0.014	2.039	2.756	0.194	2.562	25.650	21.164	3.044
	2	2.045	0.018	2.027	2.664	0.208	2.456	21.164		
	3	2.06	0.029	2.031	2.645	0.211	2.434	19.842		
N70	1	2.026	0.022	2.004	2.517	0.142	2.375	18.513	18.756	0.763
	2	2.033	0.032	2.001	2.521	0.121	2.400	19.940		
	3	2.022	0.012	2.010	2.419	0.032	2.387	18.756		
NBR(N100)	1	2.204	0.016	2.188	2.428	0.011	2.417	10.466	13.179	2.165
	2	2.181	0.026	2.155	2.457	0.018	2.439	13.179		
	3	2.158	0.015	2.143	2.468	0.009	2.459	14.746		

Fuel C at 25°C x 70h

Samples	n	M1(gm)	M2(gm)	v(cc)	M3(gm)	M4(gm)	V(cc)	$\frac{V-v}{v} \times 100$	Med.	σ
SBR(N0)	1	2.13	-0.029	2.159	6.434	-1.246	7.680	255.720	255.720	6.710
	2	2.135	-0.029	2.164	6.644	-1.07	7.714	256.470		
	3	2.158	-0.029	2.187	6.503	-1.031	7.534	244.490		
N30	1	2.083	-0.011	2.094	5.543	-0.761	6.304	201.051	201.051	9.966
	2	2.07	-0.011	2.081	5.486	-0.821	6.307	203.075		
	3	2.086	-0.012	2.098	5.452	-0.525	5.977	184.890		
N50	1	2.047	0.000	2.047	4.983	-0.608	5.591	173.131	176.090	5.347
	2	2.087	0.000	2.087	5.07	-0.692	5.762	176.090		
	3	2.061	-0.001	2.062	5.104	-0.742	5.846	183.511		
N70	1	2.029	0.011	2.018	4.253	-0.531	4.784	137.066	137.066	2.043
	2	2.035	0.011	2.024	4.237	-0.55	4.787	136.512		
	3	2.041	0.011	2.03	4.319	-0.559	4.878	140.296		
NBR(N100)	1	2.186	0.031	2.155	3.73	-0.314	4.044	87.657	89.076	1.307
	2	2.156	0.029	2.127	3.731	-0.316	4.047	90.268		
	3	2.172	0.030	2.142	3.734	-0.316	4.05	89.076		

Table C-7 Change in volume of silica/CB filled SBR/NBR vulcanizates and silane coupling agents vulcanizates after immersion in ASTM oil no.1 and ASTM oil no.3 at 100°C x 70h according to ASTM D471.

ASTM oil no.1 at 100°C x 70h

Samples	n	M1(gm)	M2(gm)	v(cc)	M3(gm)	M4(gm)	V(cc)	$\frac{V-v}{v} \times 100$	Med.	σ
R30	1	2.231	0.239	1.992	2.361	0.208	2.153	8.082	8.082	0.095
	2	2.241	0.241	2.000	2.369	0.209	2.160	8.000		
	3	2.216	0.238	1.978	2.346	0.206	2.140	8.190		
R40	1	2.556	0.328	2.228	2.686	0.295	2.391	7.316	7.194	0.110
	2	2.583	0.331	2.252	2.712	0.298	2.414	7.194		
	3	2.618	0.335	2.283	2.747	0.302	2.445	7.096		
R50	1	2.656	0.404	2.252	2.783	0.372	2.411	7.060	7.099	0.062
	2	2.676	0.408	2.268	2.804	0.375	2.429	7.099		
	3	2.562	0.390	2.172	2.686	0.358	2.328	7.182		
R30M	1	2.456	0.376	2.080	2.567	0.345	2.222	6.827	7.177	0.213
	2	2.440	0.374	2.066	2.557	0.342	2.215	7.212		
	3	2.452	0.376	2.076	2.569	0.344	2.225	7.177		
R40M	1	2.359	0.313	2.046	2.468	0.285	2.183	6.696	6.696	0.115
	2	2.415	0.320	2.095	2.527	0.291	2.236	6.730		
	3	2.406	0.319	2.087	2.513	0.290	2.223	6.517		
R50M	1	2.466	0.377	2.089	2.575	0.349	2.226	6.558	6.215	0.217
	2	2.508	0.384	2.124	2.611	0.355	2.256	6.215		
	3	2.531	0.387	2.144	2.635	0.359	2.276	6.157		
R30G	1	2.383	0.254	2.129	2.519	0.224	2.295	7.797	7.433	0.326
	2	2.395	0.254	2.141	2.518	0.224	2.294	7.146		
	3	2.454	0.261	2.193	2.585	0.229	2.356	7.433		
R40G	1	2.329	0.308	2.021	2.441	0.279	2.162	6.977	7.001	0.045
	2	2.321	0.307	2.014	2.433	0.278	2.155	7.001		
	3	2.317	0.307	2.010	2.429	0.277	2.152	7.065		
R50G	1	2.419	0.370	2.049	2.534	0.341	2.193	7.028	6.972	0.061
	2	2.421	0.370	2.051	2.535	0.341	2.194	6.972		
	3	2.427	0.371	2.056	2.540	0.342	2.198	6.907		
R30V	1	2.482	0.325	2.157	2.614	0.292	2.322	7.650	7.650	0.096
	2	2.507	0.329	2.178	2.638	0.295	2.343	7.576		
	3	2.386	0.313	2.073	2.515	0.281	2.234	7.767		
R40V	1	2.338	0.249	2.089	2.448	0.217	2.231	6.798	7.587	0.477
	2	2.377	0.255	2.122	2.505	0.222	2.283	7.587		
	3	2.384	0.255	2.129	2.514	0.222	2.292	7.656		
R50V	1	2.399	0.259	2.140	2.513	0.229	2.284	6.729	6.823	0.262
	2	2.345	0.254	2.091	2.466	0.224	2.242	7.221		
	3	2.349	0.253	2.096	2.462	0.223	2.239	6.823		

Table C-7 (Continued)

ASTM oil no.3 at 100°C x 70h

Sample s	n	M1(gm)	M2(gm)	v(cc)	M3(gm)	M4(gm))	V(cc)	$\frac{V-v}{v} \times 100$	Med.	σ
R30	1	2.364	0.253	2.111	3.341	0.170	3.171	50.213	50.213	0.475
	2	2.329	0.249	2.080	3.304	0.167	3.137	50.817		
	3	2.353	0.250	2.103	3.319	0.167	3.152	49.881		
R40	1	2.468	0.315	2.153	3.425	0.232	3.193	48.305	48.018	0.220
	2	2.487	0.317	2.170	3.446	0.234	3.212	48.018		
	3	2.505	0.320	2.185	3.467	0.236	3.231	47.872		
R50	1	2.349	0.254	2.095	3.204	0.180	3.024	44.344	44.615	1.489
	2	2.410	0.259	2.151	3.348	0.185	3.163	47.048		
	3	2.413	0.259	2.154	3.299	0.184	3.115	44.615		
R30M	1	2.407	0.368	2.039	3.216	0.298	2.918	43.109	42.933	0.228
	2	2.438	0.372	2.066	3.253	0.300	2.953	42.933		
	3	2.443	0.373	2.070	3.255	0.302	2.953	42.657		
R40M	1	2.363	0.312	2.051	3.147	0.248	2.899	41.346	41.646	0.178
	2	2.413	0.320	2.093	3.215	0.250	2.965	41.663		
	3	2.352	0.311	2.041	3.135	0.244	2.891	41.646		
R50M	1	2.469	0.379	2.090	3.218	0.313	2.905	38.995	39.188	0.152
	2	2.444	0.375	2.069	3.191	0.309	2.882	39.294		
	3	2.415	0.371	2.044	3.151	0.306	2.845	39.188		
R30G	1	2.238	0.239	1.999	3.148	0.161	2.987	49.425	49.824	0.238
	2	2.226	0.239	1.987	3.137	0.160	2.977	49.824		
	3	2.206	0.236	1.970	3.110	0.158	2.952	49.848		
R40G	1	2.314	0.305	2.009	3.112	0.238	2.874	43.056	42.893	0.101
	2	2.327	0.307	2.020	3.125	0.239	2.886	42.871		
	3	2.326	0.307	2.019	3.123	0.238	2.885	42.893		
R50G	1	2.419	0.369	2.050	3.231	0.299	2.932	43.024	42.891	0.094
	2	2.458	0.376	2.082	3.278	0.303	2.975	42.891		
	3	2.489	0.379	2.110	3.322	0.308	3.014	42.844		
R30V	1	2.378	0.254	2.124	3.360	0.171	3.189	50.141	49.373	0.451
	2	2.313	0.248	2.065	3.251	0.167	3.084	49.346		
	3	2.322	0.248	2.074	3.266	0.168	3.098	49.373		
R40V	1	2.422	0.317	2.105	3.333	0.239	3.094	46.983	47.728	0.492
	2	2.507	0.328	2.179	3.462	0.243	3.219	47.728		
	3	2.424	0.316	2.108	3.353	0.235	3.118	47.913		
R50V	1	2.722	0.415	2.307	3.668	0.333	3.335	44.560	44.202	0.978
	2	2.732	0.412	2.320	3.644	0.333	3.311	42.716		
	3	2.755	0.418	2.337	3.706	0.336	3.370	44.202		

Table C-8 Change in volume of silica/CB filled SBR/NBR vulcanizates and silane coupling agents vulcanizates after immersion in Brake fluid and Fuel C at 25°C x 70h according to ASTM D471.

Brake fluid at 25°C x 70h

Samples	n	M1(gm)	M2(gm)	v(cc)	M3(gm)	M4(gm)	V(cc)	$\frac{V-v}{v} \times 100$	Med.	σ
R30	1	2.255	0.243	2.012	2.573	0.252	2.321	15.358	15.702	0.247
	2	2.270	0.243	2.027	2.600	0.252	2.348	15.836		
	3	2.283	0.245	2.038	2.611	0.253	2.358	15.702		
R40	1	2.261	0.299	1.962	2.557	0.307	2.250	14.679	14.640	0.143
	2	2.274	0.300	1.974	2.572	0.309	2.263	14.640		
	3	2.293	0.302	1.991	2.589	0.311	2.278	14.415		
R50	1	2.426	0.318	2.108	2.728	0.326	2.402	13.947	13.947	0.211
	2	2.423	0.318	2.105	2.726	0.326	2.400	14.014		
	3	2.518	0.330	2.188	2.823	0.337	2.486	13.620		
R30M	1	2.319	0.356	1.963	2.596	0.364	2.232	13.704	13.542	0.208
	2	2.337	0.358	1.979	2.613	0.366	2.247	13.542		
	3	2.354	0.360	1.994	2.629	0.370	2.259	13.290		
R40M	1	2.346	0.312	2.034	2.626	0.320	2.306	13.373	13.373	0.191
	2	2.334	0.310	2.024	2.618	0.318	2.300	13.636		
	3	2.355	0.312	2.043	2.634	0.320	2.314	13.265		
R50M	1	2.582	0.394	2.188	2.870	0.401	2.469	12.843	12.843	0.195
	2	2.550	0.387	2.163	2.839	0.396	2.443	12.945		
	3	2.637	0.401	2.236	2.926	0.409	2.517	12.567		
R30G	1	2.434	0.312	2.122	2.750	0.321	2.429	14.467	14.467	0.089
	2	2.421	0.310	2.111	2.737	0.319	2.418	14.543		
	3	2.451	0.314	2.137	2.766	0.322	2.444	14.366		
R40G	1	2.398	0.257	2.141	2.720	0.267	2.453	14.573	14.273	0.237
	2	2.468	0.263	2.205	2.788	0.272	2.516	14.104		
	3	2.463	0.263	2.200	2.785	0.271	2.514	14.273		
R50G	1	2.463	0.376	2.087	2.747	0.384	2.363	13.225	13.359	0.141
	2	2.439	0.373	2.066	2.722	0.380	2.342	13.359		
	3	2.404	0.368	2.036	2.685	0.374	2.311	13.507		
R30V	1	2.281	0.245	2.036	2.595	0.253	2.342	15.029	15.180	0.200
	2	2.258	0.242	2.016	2.577	0.250	2.327	15.427		
	3	2.236	0.240	1.996	2.548	0.249	2.299	15.180		
R40V	1	2.413	0.261	2.152	2.721	0.269	2.452	13.941	14.078	0.320
	2	2.389	0.258	2.131	2.698	0.267	2.431	14.078		
	3	2.358	0.255	2.103	2.675	0.266	2.409	14.551		
R50V	1	2.555	0.390	2.165	2.847	0.398	2.449	13.118	13.197	0.077
	2	2.540	0.388	2.152	2.831	0.395	2.436	13.197		
	3	2.579	0.394	2.185	2.877	0.402	2.475	13.272		

Table C-8 (Continue)Fuel C at 25°C x 70h

Sample s	n	M1(gm)	M2(gm)	v(cc)	M3(gm)	M4(gm)	V(cc)	$\frac{V-v}{v} \times 100$	Median	σ
R30	1	2.249	0.298	1.951	4.107	-0.206	4.313	121.066	116.344	3.372
	2	2.296	0.301	1.995	4.082	-0.198	4.280	114.536		
	3	2.263	0.299	1.964	4.060	-0.189	4.249	116.344		
R40	1	2.540	0.325	2.215	4.436	-0.141	4.577	106.637	106.637	0.901
	2	2.522	0.332	2.190	4.396	-0.137	4.533	106.986		
	3	2.497	0.319	2.178	4.340	-0.131	4.471	105.280		
R50	1	2.617	0.397	2.220	4.340	-0.215	4.555	105.180	102.816	1.392
	2	2.595	0.394	2.201	4.260	-0.202	4.462	102.726		
	3	2.637	0.400	2.237	4.331	-0.206	4.537	102.816		
R30M	1	2.382	0.315	2.067	4.274	-0.034	4.308	108.418	112.427	2.671
	2	2.369	0.314	2.055	4.353	-0.034	4.387	113.479		
	3	2.357	0.313	2.044	4.314	-0.028	4.342	112.427		
R40M	1	2.348	0.360	1.988	3.873	-0.005	3.878	95.070	93.252	1.886
	2	2.327	0.356	1.971	3.808	-0.001	3.809	93.252		
	3	2.308	0.354	1.954	3.744	0.006	3.738	91.300		
R50M	1	2.539	0.389	2.150	3.960	-0.067	4.027	87.302	82.498	3.368
	2	2.589	0.395	2.194	3.941	-0.063	4.004	82.498		
	3	2.588	0.394	2.194	3.909	-0.058	3.967	80.811		
R30G	1	2.412	0.257	2.155	4.395	-0.034	4.429	105.522	105.288	3.998
	2	2.434	0.259	2.175	4.297	-0.020	4.317	98.483		
	3	2.392	0.255	2.137	4.367	-0.020	4.387	105.288		
R40G	1	2.424	0.372	2.052	4.395	-0.013	4.012	95.517	95.024	1.112
	2	2.421	0.371	2.050	4.297	-0.009	3.998	95.024		
	3	2.428	0.370	2.058	4.367	-0.003	3.980	93.392		
R50G	1	2.275	0.244	2.031	3.808	-0.082	3.890	91.531	91.531	2.005
	2	2.284	0.245	2.039	3.849	-0.078	3.927	92.594		
	3	2.291	0.244	2.047	3.791	-0.072	3.863	88.715		
R30V	1	2.268	0.242	2.026	4.041	-0.166	4.207	107.651	107.143	2.315
	2	2.242	0.240	2.002	3.992	-0.155	4.147	107.143		
	3	2.298	0.246	2.052	4.023	-0.151	4.174	103.411		
R40V	1	2.498	0.327	2.171	4.361	-0.131	4.492	106.909	104.507	1.618
	2	2.474	0.322	2.152	4.278	-0.123	4.401	104.507		
	3	2.404	0.315	2.089	4.145	-0.113	4.258	103.830		
R50V	1	2.331	0.252	2.079	4.074	-0.202	4.276	105.676	103.742	1.468
	2	2.327	0.252	2.075	4.012	-0.196	4.208	102.795		
	3	2.365	0.254	2.111	4.106	-0.195	4.301	103.742		

VITAE

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