ผลของซิลิกาต่อยางเติมคาร์บอนแบล็กสำหรับคอมพาวด์หน้ายาง

นายประสิทธิ์ อยู่คง

EFFECT OF SILICA ON CARBON BLACK FILLED RUBBER
FOR TREAD COMPOUND
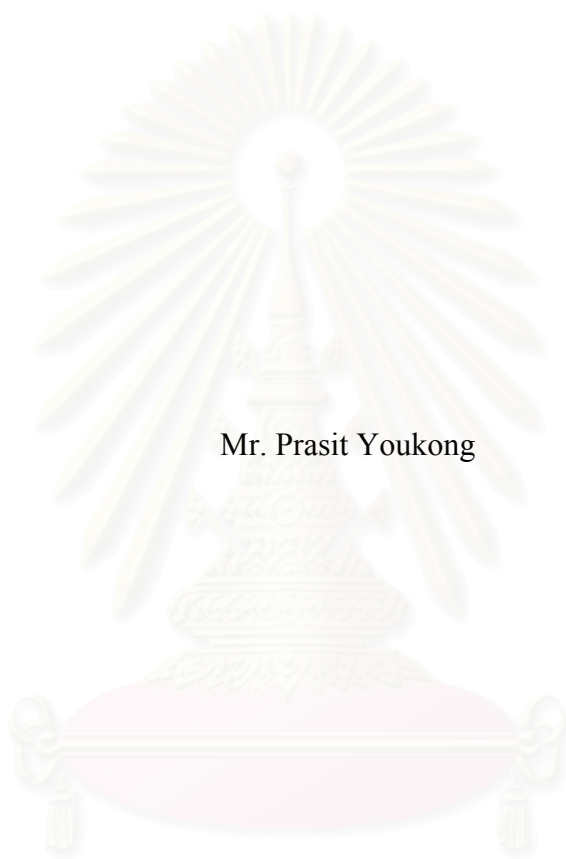
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Thesis Title   **:** Effect of Silica on Carbon Black Filled Rubber for Tread Compound.

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คอมพาวด์หน้ายางจากยางผสมของยางธรรมชาติกับ ยางสไตรีนบิวทาไดอีน ในอัตราส่วน
ต่างๆกัน (100:0, 80:20, 70:30, 60:40, 30:70, 20:80) เตรียมได้จากวิธีการบดผสมร้อน ซิลิกา
และคาร์บอนแบล็กเป็นสารเสริมแรงที่อัตราส่วนต่างๆ (5:0, 4:1, 3:2, 2:3, 1:4, 0:5) คิดเป็นน้ำ
หนัก 30 เปอร์เซ็นต์ของน้ำหนักเติมในคอมพาวด์ทั้งหมด การศึกษาสมบัติทางกายภาพที่สำคัญต่อ
คอมพาวด์หน้ายาง พบว่าการเพิ่มปริมาณซิลิกามีผลทำให้ความยืดหยุ่นของคอมพาวด์มีค่าเพิ่มขึ้น
และค่าความร้อนที่เกิดขึ้นในคอมพาวด์ลดลง ดังนั้นทำให้ ความต้านทานการหมุนของยางลดลง
และรถยนต์มีการใช้เชื้อเพลิงที่ลดลง อย่างไรก็ตามสมบัติความต้านทานแรงดึง ความต้านทานการ
ฉีกขาด ความต้านทานการสึกหรอ และค่าความแข็งมีค่าลดลง สามารถทำให้อายุการใช้งานของ
ยางสั้นลง

ในงานวิจัยได้ทำการศึกษาผลของปริมาณยางสไตรีนบิวทาไดอีน ต่อสมบัติทางกายภาพ
ของคอมพาวด์ เมื่อปริมาณยาง สไตรีนบิวทาไดอีนเพิ่มขึ้น มีผลทำให้ค่าความยืดหยุ่น ความความ
ต้านทานการฉีกขาดลดลง ค่าความร้อนที่เกิดขึ้นในคอมพาวด์เพิ่มขึ้น ยิ่งกว่านั้นปฏิกิริยา
วัลคาไนเซชัน ใช้เวลานานขึ้น

สาขาวิชา...ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์...   ลายมือชื่อนิสิต....…..………………........
ปีการศึกษา...2546…………........................   ลายมือชื่ออาจารย์ที่ปรึกษา………...…..........

Tread compounds from rubber blends with different natural rubber and styrene butadiene rubber ratio (100:0, 80:20, 70:30, 60:40, 30:70, 20:80) were prepared by melt-mixing process. The silica and carbon black mixture as reinforcing filler at different proportions (5:0, 4:1, 3:2, 2:3, 1:4, 0:5) was 30%wt blended in rubber compounds. The important physical properties for tread compound were investigated. As silica content increased, the % resilience increased and heat build up in the compound decreased. Thus, the lower rolling resistance and the reduction of fuel consumption could be obtained. However, the tensile strength, tear resistance, abrasion resistance and hardness decreased, they could also decrease the tire life.

The effects of styrene butadiene rubber content on the physical properties of the compounds were also studied in this work. As SBR content increased, % resilience and tear resistance decreased and heat build up increased. Moreover, the vulcanization reaction takes longer time.

Field of study ..Petrochemistry and Polymer Science.. Student's signature……….….

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ACKNOWLEDGEMENTS

CONTENTS

CONTENTS (continued)

CONTENTS (continued)

LIST OF TABLES

LIST OF TABLES (continued)

LIST OF TABLES (continued)

LIST OF TABLES (continued)

LIST OF FIGURES

LIST OF FIGURES (continued)

LIST OF ABBREVIATIONS

ASTM	=	American Standard of Testing Material
Avg.	=	Average
BR	=	Butadiene Rubber
BS	=	British Standard
DPG	=	Diphenyl guanidine
ECETSI	=	2-(3, 4-epoxycyclo-hexyl)-ethyltrimethoxysilane
GPTSI	=	3-glycidoxypropyl-trimethoxysilane
HAF	=	High Abrasion Furnace
IPPD	=	N-isopropyl-N-phenyl-P-phenylene diamine
ISO	=	International Organization for Standardization
K	=	Kelvin
MBTS	=	Mercaptobenzothiazyl disulphide
M_c	=	Number average molecular weight
MFA	=	Multifunctional agent
NR	=	Natural rubber
ODR	=	Oscillating Dish Rheometer
6PPD	=	6-Piperidine pentamethylene dithiocarbamate
SBR	=	Styrene Butadiene Rubber
Tg	=	Glass Transition Temperature
TBBS	=	N- tertbutyl-2-benzthiazole sulphenamide
TESPT	=	Bis (Triethoxy-silylpropyl) tetrasulphide
ZnO	=	Zinc oxide

CHAPTER I

INTRODUCTION

1.1 Reinforcing Filler in Tread Compound

Although tires can be classified into two main types, solid tire and pneumatic tire, the latter is more important than the first one because the pneumatic tire can give higher desired performances to the customer.

There is no doubt that the pneumatic tire has long been used in the automotive industry and subsequent industries, a lot of development have been made on this type of tire in order to accommodate demands of the customer. Nowadays, the pneumatic tire can be found in many models, depending mainly on the carcass construction e.g. radial tire or diagonal (or bias) tire, steel or fabric belted tire, as well as tube or tubeless tire [1]. Making good pneumatic tires requires not only the combination of both technology and manpower, but also the considerable skills and experiences of the working people in the factory.

Tread is the largest gum part used to make a pneumatic tire, thus most of the tire weight is consumed by the tread. The tread is not only the wearing surface of the tire but it also servers as a protection of the carcass against the abrasive surface of the road. Therefore, many attempts have been made to find superior performances tread compound. So far thousands of formula has been patented [2]. Most compounds used for tire's treads are usually based on polymer or elastomer blends with high level of reinforcing filler [3]. The rubber blends are used because only one elastomer cannot fulfill the optimum mechanical requirement of the tread.

It is well known that the blend of styrene-butadiene rubber (SBR) and butadiene rubber (BR) widely used for the tread of the passenger car tire. This two-elastomer combination is believed to yield the optimum properties of the tread [4]. But in truck tire, tread compounds based on natural rubber (NR) because of the high resilience and low hysteresis properties of the NR.

Though carbon black is commonly used as the reinforcing filler, but recently the use of silica system in tread compound is becoming an interesting topic in tire industry.

For example, the green tire concept by Michelin Tire Company [5] has been claimed that 5 % reduction in fuel consumption of the car can be achieved. The claimed tread is based on silica filled compound and this type of tire is now in production. Besides, silica was used due to the fact that it offers an improvement in tear strength, a reduction in heat build-up and an increase in tackiness of the compound when compared to only carbon black filled compound.

There are wide studies about the phenomenon of reinforcing filler in tires, but no complete reason can be given. Anyhow, this can be said that the reinforcement happened between elastomer and filler. Another important factor for the reinforcement is chemical component of surface area and filler's structure. Bonding between elastomer's molecule and sensitivity for reaction of elastomer's molecule would affect interaction between filler and elastomer. Due to this reason, each filler would reinforce each tire differently. From the past studies, SBR and silica are used to increase performance of tread compound's production for cars, but tread compound's production for truck still rarely uses these. Therefore, the work on the formulation of tread compound based on NR, SBR and silica is of interest. The effect of ratio of NR and SBR and silica content on modulus, tensile and heat build up was investigated.

1.2 Objectives of the Research Work

The objectives of this work fall into the following categories:
1. To study the appropriate formulation of NR, SBR, silica and carbon black in tread compound for truck tire.
2. To study the physical properties of the tread compounds.

1.3 Scope of the Research Work

The effects of silica and SBR on properties of the tread compound related to the tire performances were investigated.

1. Use 2 roll mill to mix tread compounds. The ratios of elastomer NR: SBR at ratio 100:0, 80:20, 70:30, 60:40, 30:70 and 20:80 was varied. In each ratio of NR: SBR, the silica and carbon black are used as reinforcing agent at ratio of 5:0, 4:1, 3:2, 2:3, 1:4 and 0:5 (reinforcing agent's weight is about 30 % of the compound's weight). The other ingredients are silane coupling agent (8%wt of silane based on the silica), ZnO of 4 phr, Stearic acid of 2 phr, 6PPD of 2 phr, DPG of 0.5 phr, TBBS of 1.6 phr and sulfur of 1 phr.

2. The properties of the compounds were determined as follows:
    -   Modulus (ASTM D638).
    -   Tensile strength (ASTM D412-87)
    -   Hardness (ASTM D2240-97)
    -   Tear strength (ASTM D624-8)
    -   % Resilience (BS.903 part A8)
    -   Heat build up
    -   Abrasion resistance (BS 903 part A9)

CHAPTER II

BACKGROUND AND LITERATURE REVIEW

2.1 Compound Design for Tire Tread [2, 6-10]

Like other rubber compounding, the compounding design for tire tread is generally based on following four reasons. The first reason is to incorporate the rubber and appropriate ancillary ingredients necessary for vulcanization. The second reason is to adjust the principal properties i.e. mechanical properties, abrasion resistance, etc., of the vulcanized product to the values required. The third reason is to adjust rheological properties of the compound in order to be easily processed. The fourth reason is to optimize the cost of the compound and the service life of the vulcanized products in order to achieve a commercially accepted commodity.

In general, compound ingredients of a recipe are expressed as parts per 100 parts of rubber. The ingredients may be classified due to their characteristics and functions as shown.

Rubber or polymers

Curing agents

Accelerators

Accelerator activators

Fillers

Antioxidant and antiozonants

Processing aids or softeners

Other special additives

Basically, the nature of the principal polymer is of prime importance in determining a compound characteristic. However, an elastomer will not be able to exhibit its advantageous characteristics unless its cross-linking process or vulcanization occurs. The properties of a rubber article depend not on the raw material and compounding but also the degree of vulcanization.

The vulcanization agents are vital in the basic processing which imparts the necessary elasticity. Although many vulcanizing agents have been discovered, sulphur is still the most popular, being utilized in rubber industry. Activators and accelerators modify the chemical action either before or during the vulcanization process. Besides,

choice of the proper acceleration depends on the type of rubber hydrocarbon and the final properties of the rubber required.

Fillers are used either as extenders to reduce cost in cheap rubber goods or as reinforcing agents to improve rubber properties.

Most rubber is generally susceptible to chemical attack because of its unsaturated organic characteristic, which often react with other chemical reagents. Even atmospheric oxygen attacks rubber, causing it to become hard and brittle. Ozone attacks it more rapidly. Therefore anti-oxidants and anti-ozonants are used to preserve the desirable properties of rubber during aging and in service.

The plasticizers and softeners are used not only to aid processing by reducing the time and temperatures involved and dispersion of the other compounding ingredients, but also to make the finished rubber tougher, more wear resistant and superior in wet-grip properties. Other specific additives, which can be found in rubber industry, are peptisers, pigments, tackifiers, coupling agents, etc., and more recently being developed it is multifunctional agent (MFA).

It is obvious that a compound can be formulated into innumerable recipes. Therefore the selection of material has to be very careful. Consequently, good understanding both the chemical and physical properties of materials is of great importance for the compounder.

2.2   Elastomers [7, 8, 11]

There are hundreds of commercially graded elastomers available. These elastomers are mainly synthetic. However, natural rubber is the prototype of all elastomers since it is the first rubber that was commercially used. Due to many reasons, the large numbers of developments have been made on synthetic elastomers rather than natural rubber. So far, a lot of successful achievements have been made to complete the synthetic elastomer with the natural rubber, and in some cases, the synthetic one is superior to natural one.

In general, the molecule of rubber is a long hydrocarbon chain composed of many repeating units, each of which normally has, at least, one reactive site. The reactive sites or functional groups can be double bond, hydroxyl group, halide group, amine group, etc., which can react with other substances i.e. curing agents. These sites

are the most important for the rubber that they can cause the vulcanization and degradation to occur. In the case of vulcanization, the rubber becomes tough, strengthened and hard, while it turns to a soft, sticky or brittle material in the case of degradation.

The length of the molecule is several thousand times the cross section. Along the chain, the links are able to move laterally and freely depending upon the thermodynamic state of the rubber, thus many conformations of the molecule could be possible to happen. Statistically, at a constant temperature, there is one most probable distance between the ends of the chains or between any two points along the chain. If the chains are very long, they become tangled and thus they can not slide by each other easily. It is these entropy and entanglement effects that explain the elastic recovery of raw rubber.

It is well understood that all elastomer has glass transition temperature (T_g) below ambient temperature and some elastomers can crystallize on stretching but some cannot. The ability to form crystallites when stretched is dependent on the intensity of the interchain forces, which is related to chemical structure and regularity of the rubber molecules. The elastomers with high regularity and strong interchain forces have high tendency to crystallize.

Generally, the elastomers which do not have ability to crystallize on stretching exhibit inferior tensile strength. This is why SBRs, which have high irregularity, cannot be used as pure gum product like NR, thus always requiring some reinforcing agents.

Although many rubbers have been studied to formulate a compound for tire tread, only three classes of them, NR, SBR and BR have been used in the tire industry.

2.2.1 Natural Rubber (NR) [12]

Any review of the major of the major rubbers fittingly starts with natural rubber. It was the first rubber and was unique until the development of polysulfide rubber about 1927. It supplies about one-third of the world demand for elastomers and is the one by which others are judged. Again it was Charles Goodyear and Thomas Hancock's experiments with natural rubber, sulfur, and heat that led to the discovery of vulcanization and was the birth as were of compounding.

Chemically, natural rubber is cis-1, 4-polyisoprene. A linear, long chain polymer with repeating isoprene units (C_5H_8). The molecular repeating unit structure of natural rubber is illustrated below.

$$-(CH_2-C=CH-CH_2)_n$$

(CH₃)

Small group
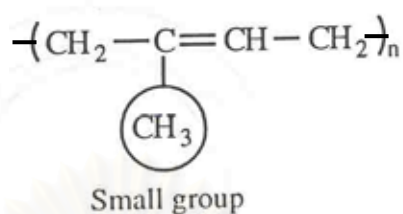
Figure 2.1 Natural rubber

Because of its structure, which is of remarkable regularity, NR is a crystallisable elastomer, especially on stretching. This effect renders high gum tensile strength to NR.

There are several grades of NR commercially available. Most grades mainly on the purity and final form of the elastomer.

Table 2.1 Typical analysis of natural rubber [2]

Component	%
Moisture	0.6
Acetone extract	2.9
Protein (calculated from nitrogen)	2.8
Ash	0.4
Rubber hydrocarbon	93.3
	100.0

2.2.2 Styrene Butadiene Rubber (SBR) [11]

SBRs are random copolymers of styrene and butadiene monomers where the butadiene can be present in cis-l,4-, trans-l,4- and 1,2-addition forms thus generally having the structure;

$$-\left(CH_2-CH=CH-CH_2\right)_n \left(CH_2-CH\right)_m$$

phenyl — Large group
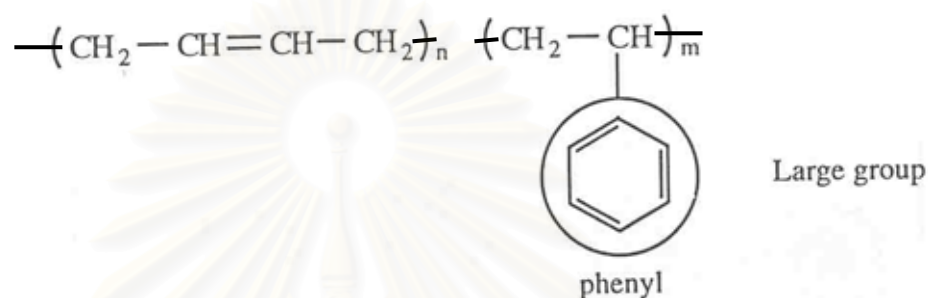
Figure 2.2 Styrene butadiene rubber

They were first developed during World War I as a substitute for NR. These materials can be produced by a solution polymerization or by an emulsion process. Since the solution SBRs have high tendency to form block co-polymers, the properties are thus more likely to be thermoplastic than rubbery and they also require high energy to process. However, some solution SBRs produced by a special catalyst can be made and used in tire tread compound in conjunction with silica-coupling agent. The performance of the tread is reported to be better than those compounded with carbon black alone.

It was soon realized that a new class of fillers was required which resulted in the development of Furnace blacks capable of giving properties equivalent to and in some cases superior to those of NR (i.e. abrasion and skid resistance). However, SBRs still suffers some disadvantages in comparison with NR e.g. much higher heat build-up, low green strength, and low hot tear. SBRs can be used to replace NR because they are fundamentally similar materials of similar cost. NR however is subject to many factors and thus is variable in its cost comparison with SBR. The greater price stability of SBR makes production planning/costing easier. Therefore the final choice between SBR and NR may not depend on properties or processing but availability,

cost and supplier relationships. However, grades containing 30-50% are used in high hysteresis tire, which have improved grip due to greater trade contact. Negative aspects include harder steering and greater fuel consumption. Cold SBR is preferred where high levels of mechanical properties are required, particularly abrasion resistance.

Table 2.2 "Mutual" SBR recipe. [12]

Component	Parts by Weight
Styrene	25
Butadiene	75
Water	180
Fatty acid soap	5
Lauryl mercaptan	0.50
Potassium persulfate	0.30
	285.80

Note: SBR is used here, but early publications used the term GR-S for government rubber styrene. That term is now obsolete.

2.3   Vulcanization [12]

The ASTM definition fro vulcanization reads as follows: "An irreversible process during which a rubber compound through a change in its chemical structure (for example, cross-linking) becomes less plastic and more resistant to swelling by organic liquids while elastic properties are conferred, improved, or extended over a greater range of temperature." This change can be brought about by a variety of agents including irradiation. Since this last method at present requires expensive equipment and works best on thin rubber section, this section will deal only with the conventional vulcanization materials. Again the terms curing and vulcanizing will be used interchangeably.

There are four curing agents or systems in widespread use. They are:

1. Sulfur system
2. Peroxides
3. Urethane cross linkers
4. Metallic oxides (used in vulcanizing neoprene only)

By far the most common vulcanizing methods are those dependent on sulfur. Practically all rubber products are vulcanized by one or more of six methods. There are:

1. Press curing (including injection and transfer molding)
2. Open steam curing
3. Lead press curing
4. Fluidized bed curing
5. Salt bath curing

Before considering specific vulcanizing agents two aspects of the curing process should be touched on. A common problem in rubber goods factories is scorch-that tendency of a compound to start curing before it is the right form and right place to be cured. There is a vicious circle here: for cost reasons the quicker the compound can be cured and at the lowest temperature the better, yet compounding to this aim alone means more stock will be rejected because of scorch. Apart from careful compounding scorch is lessened by mixing, storing, and processing the stock at the lowest temperature possible (yet breaking down and dispersing ingredients satisfactorily). So that heat history is at a minimum master batches of sulfur and accelerators added at the end of the mixing cycle helps. Stocks should be cooled after mixing and not held for long times on warm-up mills prior to extruding or calendering.

Another point to be remembered is that few rubber goods items are fully cured when made. By fully cured is meant that state when hardness is at a maximum, modulus is fully developed, and further curing might result in reversion, e.g., with natural rubber stocks. The reasons for not going to a full cure is that rubber properties develop at different rates as curing progresses. For example, tear resistance usually peaks before tensile strength as does abrasion. On the other hand, swelling resistance is greatest when a compound is fully cured. So if top tear resistance is wanted the best product cure might be what would be considered an under cure. Again the curing may

be finished in service giving a longer life. For example, steam hose tubes are made wit some under cure as the curing will be completed in service.

2.3.1 Theory of Sulfur Vulcanization [14]

Sulfur vulcanization has been treated in an essentially empirical manner, and in fact the chemistry of sulfur vulcanization is so complex that it is only within the last few years that a coherent theoretical treatment has been possible. Even today, only the main stages are proven and there is still much to be learned about the effect of additives of various types.

Figure 2.3 Structural features of vulcanisate network [14]

Sulfur is combined in the vulcanization network in a number of ways (Fig. 2.3), as enumerated by Porter (1969). As crosslink, it may be present as monosulphide, disulphides (Fig. 2.3a), but it may also be present as pendant sulphides (Fig. 2.3b), or cyclic monosulphides and disulphides (Fig. 2.3c). An estimate of the number of sulphur atoms for each crosslinks formed has been made: an unaccelerated rubber-sulfur vulcanisate may give a figure of 40-45, whilst in conventional accelerated sulfur vulcanisates this "inefficiency" figure may drop to 10-50. Special "efficient" vulcanizing systems can reduce it still further to 4 or 5, but for even lower values, so-called "non-sulfur" vulcanization systems must be used.

By the use of chemical probes, the relative amounts of mono-, di-, and poly-sulphide material can be assessed, and by measuring the degree of cross-linking as well, the pendant and intramolecular sulfur can be estimated. From this information

and the amounts of nitrogen and sulfur combined with the rubber at various stages of vulcanization, it is possible to deduce the general course of the vulcanization reaction.

The initial step in vulcanization seems to be the reaction of sulfur with the zinc salt of the accelerator to give a zinc perthio-salt XS_xZnS_xX, where X is a group derived from the accelerator (e.g. thiocarbamate or benzthiazyl groups). This salt reacts with the rubber hydrocarbon RH to give a rubber bond intermediate

$$XS_xZnS_x + RH \longrightarrow XS_xR + ZnS + HS_{x-1}X \qquad (1)$$

and a perthio-accelerator group which, with further zinc oxide will form a zinc perthio-salt of lower sulfur content; this may, nevertheless again be an active sulphurating agent, forming intermediates XS_x-1R. In this way each molecule of accelerator gives rise to a series of intermediates of varying "degrees of polysulphidity". The hydrogen atom which is removed is likely to be attached to a methylene group in the alpha-position to the double bond, i.e. in natural rubber the hydrogen atoms at positions 4 and 5 are the most labile in this type of reaction.
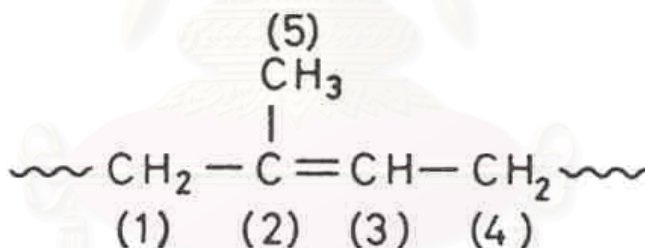
Figure 2.4 Position of hydrogen atoms in natural rubber [14]

The intermediate XS_xR then reacts with a molecule of rubber hydrocarbon RH to give a crosslinks declines. This process is catalyzed by XS_xZnS_xX and can result in additional crosslinks. It is also evident that the crosslinks which were initially at positions 4 and 5 undergo an allylic shift, with the result that new configurations appear:
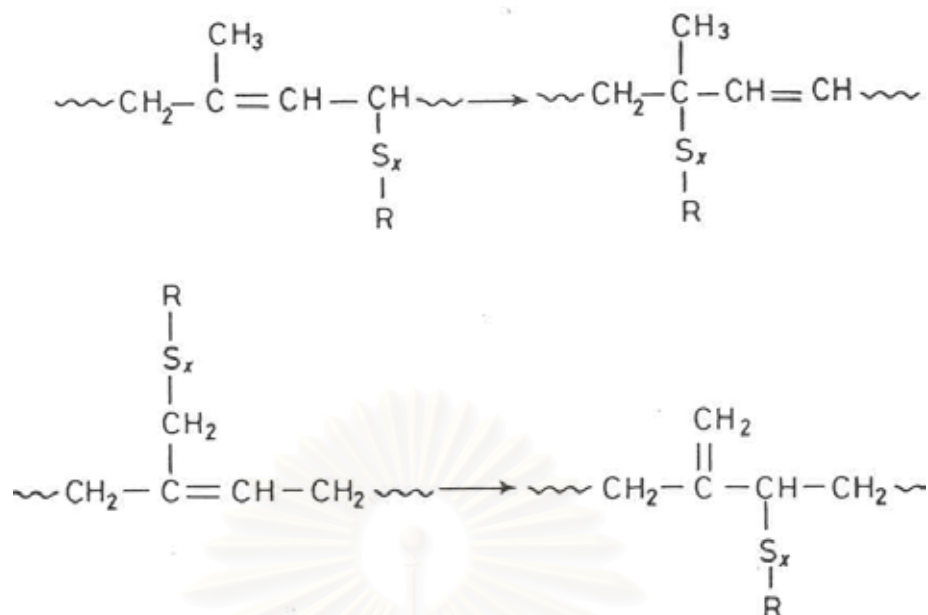
Figure 2.5 The crosslinks which were initially at positions 4 and 5. [14]

At the same time, disappearance of crosslinks of the disulphide and polysulphide type occurs, with formation of conjugated trienes:
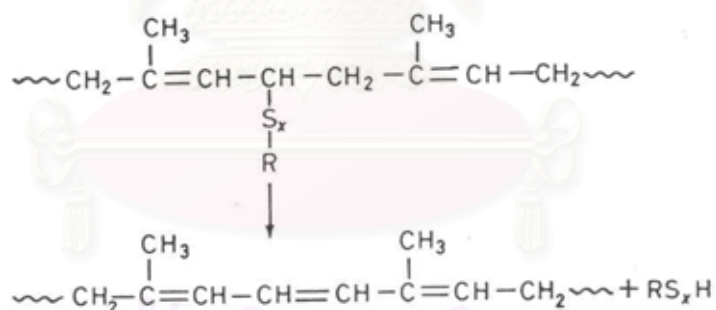
Figure 2.6 Formation of conjugated trienes. [14]

This destruction of crosslinks is apparently associated with the formation of the cyclic sulphides (Fig. 2.3c), but this has not been investigated in detail.

A consideration of the above reactions leads to the conclusion that, if desulphuration proceeds rapidly as in the case of the mix depicted in Fig. 2.7, the final network will be highly crosslinked with mainly monosulphidic bonds, and there will be relatively few modifications of the cyclic sulphide or conjugated triene type: such a network is termed "efficiently crosslinked".

If on the other hand, desulphuration proceeds slowly as in the case of the compound depicted in Fig. 2.8, there will be opportunities for thermal decomposition, leading to reversion or loss of crosslinks and to network containing modifications: further, the crosslinks which do survive will be di- or poly-sulphidic and hence will be liable to further decomposition. These networks are inefficiently crosslinked.
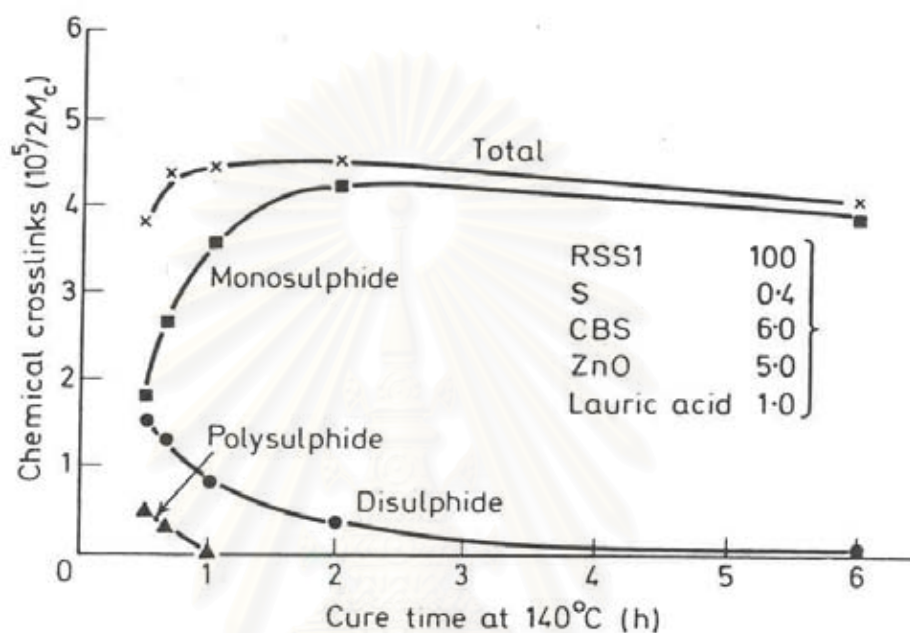
Figure 2.7 Features of NR vulcanisate produced by an efficient crosslinking system (M_c = number average molecular weight between crosslinks). From Moore, courtesy NRPRA [14].

Examination of a system containing HAF black shows that the remarks made above for a pure gum, generally hold for a natural rubber compound containing active black (Porter, 1969). The presence of HAF black increases the overall rate of reaction of the rubber and sulphur, and promotes the desulphuration reaction, thus leading to increased crosslink efficiency.
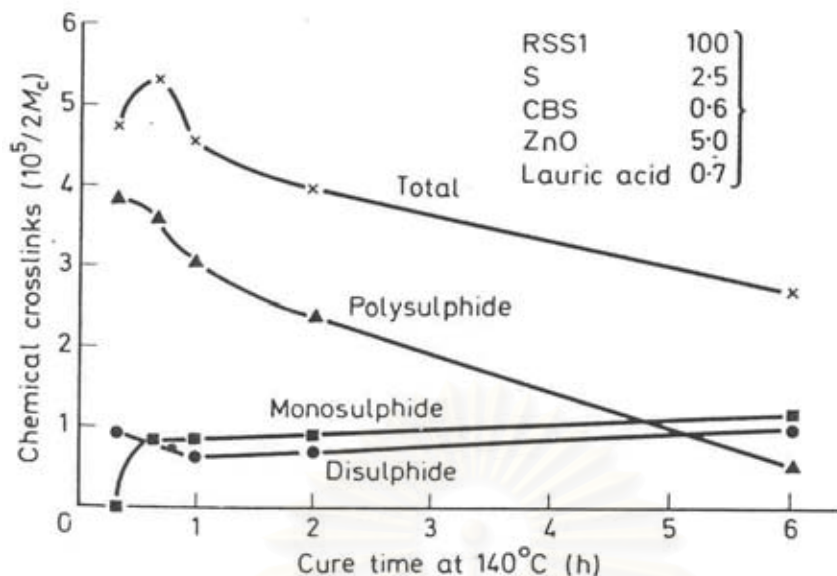
Figure 2.8 Features of NR vulcanization produced by a conventional crosslinking system (M_c = number average molecular weight between crosslinks). From Moore (1964), courtesy NRPRA [14].

2.3.2   Cure Characteristics

The vulcanization is a chemical reaction and generally considered as a first-order reaction. The shape of the cure curve is an important aspect in the consideration of practical vulcanization. An interesting property of a rubber is plotted against the vulcanization time at a specific temperature and a determination has to be made in order to find the optimum time for the property required. There is no precise definition for the optimum cure because it is a matter of individual choice. Three typical shapes of cure, marching, plateau and reversion cures can be encountered as shown in **Figure 2.9**
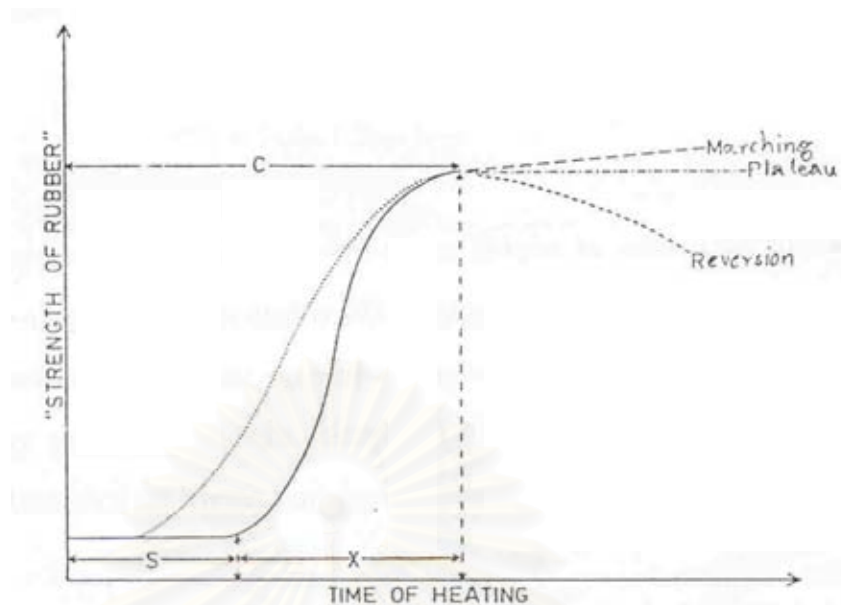
Figure 2.9 Typical cure curves [8]

From the cure graph, it is however possible to describe the state of cure whether the vulcanisate is under-cure, good, optimum, etc. For tread compound, the plateau cure is preferable since the tread is the thickest part and always subjected to heat for a longer time than other parts of the tire during curing process.

2.4   Fillers

Fillers are mostly in forms of both powders and compacted powders, they can be termed reinforcing and non-reinforcing, and also fall into black and non-black types. Within such types of fillers, subdivision can also be made for a particular purpose. However, the most popular filler used in tire tread compound is carbon black, since it, incidentally acting as an ultra-violet filter, gives added strength and resistance to wear. If non-black reinforcement is required, the pure silicas are capable of very good physical properties.

2.4.1 Carbon Blacks

Technology of carbon black is well documented and can be found in most of rubber books and literature. In general, the properties of a carbon black filled compound can be varied due to the surface area, particle size and structure level or aggregate size of the carbon black employed. High surface area, small particle size renders higher levels of reinforcement as reflected in tensile strength and resistance to abrasion and tearing. However, higher hysteresis and poorer dynamic performance are the imparted drawbacks. Higher structure or aggregate size gives improved extrusion behavior, high stock viscosity, improved green strength and higher modulus values.

2.4.2 Silica

Silica was used in rubber compound due to that it offers an improvement in tear strength, a reduction in heat buildup and an increase in tackiness of the compound when comparing to only carbon filled compound, though the resistance to abrasion may little be lowered. The use of silica in the tire industry has long been limited to three types of compounds.

a) Off-the-road tread compounds containing 10 to 15 phr of silica-blended with carbon black to improve tear properties.

b) Textile and steel cord bonding compounds containing 15 phr of silica blended with carbon black-often N326-in combination with resorcinol/formaldehyde systems.

c) Side wall compounds containing 10 phr of silica-blended with carbon black to improve heat buildup due flexing.

However, with the introduction of bi-functional organosilanes or coupling agents as reinforcing agents and appropriate modifications of the curing system, the reinforcing mechanism of silicas can be controlled by chemical means, thus improving the abrasion resistance and other properties required for tire tread. Besides, a combination of carbon black and silica-coupling agent system can provide an improved compromise with higher performance level than when using carbon black alone.

2.5   Antidegradants

It is well known that products based on natural and synthetic olefin rubbers are sensitive to attack by oxygen or ozone, due to the scattering of double bonds in the matrix; even a small amount of unsaturation can inspire a dramatic effect on the properties of the rubber because of oxidative or ozonised influences, especially that of the product being subject to damping. The effects manifest itself as a softening or embrittling of the rubber, thus giving reduced physical properties. Exposure to oxygen or ozone, i.e. air, for a period of time results in an adsorption of the oxygen or ozone into the cured rubber surface and the subsequent chain reaction gives rise to the gradual breakdown of the rubber. Therefore anti-oxidants and anti-ozonants have been developed and they are essential for almost every rubber product based on natural and synthetic olefin rubbers. Essentially an antioxidant or anti-ozonant breaks the chain reaction resulting from attack by oxygen or ozone. Practically, antioxidants and anti-ozonants can be found in three classes. Those are secondary amine, phenolic and phosphite groups. The amine groups are strong protective agents but discolor and stain to various degrees. However, for tread compound, this types of anti-degradants are commonly used e.g. IPPD, 6PPD, etc.

2.6   Processing Aids

There are several types of processing aids commercially available in many forms e.g. oil, wax, solid, etc. A processing aid may play one or more of the following list;

a) Helps to speed up the rate of polymer breakdown and also control the degree of breakdown.

b) Helps to disperse the other compounding ingredients. For mixing operations, softness is of great importance.

c) Helps to reduce nerve within the compound, and also shrinkage during subsequent processing.

d) Can impart building tack to the compound. Tack is very useful properties which permits the assembling of different rubber pieces into a composite article. The synthetic rubbers, particularly the butadiene types, are themselves deficient in tack, so that the use of tackifier becomes of major importance. However, the changes in

physical properties i.e. hardness, modulus, elongation, etc., could happen due to the use of processing aids.

e) Improves the stability of compound processing, especially in the compound preparation (blanking) and molding areas. In calendering and extrusion, where close dimensional tolerance is mandatory, it may be desirable to use low viscosity compound. However, the stock should be fairly hard or stiff enough to assist the following processes e.g. shaping and curing. Since tread compounds are very highly filled, a large amount of processing aid is required to assist the filler dispersion and to improve the properties to a certain extent. The processing aids used for tread compound are commonly an aromatic oils and waxes.

2.7 Special Additives

Other additives that can be found in the rubber industry are chemical blowing agents, stiffening agents, coloring agents, multifunctional additives, coupling agents etc. However, for a tread tire compound filled with silica, a coupling agent is required to improve the final properties, especially the abrasion resistance.

2.7.1 Coupling Agents for Silicas

In recent years much attention has focused on the use of coupling agents which serve to link two phases, especially between filler phase and rubber phase. However, the principal coupling agents presently used are based on organic siloxanes which possess functionally active end groups. One group is considered to bond to a hydroxy active surface of silica whilst the other organic group is selected to bond to a particular rubber. This type of bifunctional organosilanes is considered as reinforcing agents for filler-rubber interaction.

2.8   The Principle of Reinforcement with Carbon Black and Silica [5]

2.8.1   Introduction

It is rather difficult to define a precise meaning of reinforcement obtained by a filler. However, in the tire tread context, it is probably pertinent to give the credit to a filler that yields an improvement in abrasion resistance, tear resistance, tensile strength and stiffness of the vulcanisate because these all are required for tread performance. To technologists, the phenomena of a vulcanisate property under deformation that are of interest can be placed in three groups. Firstly, at strains of 10% or less, often below 1%, the elastomer is found to be truly elastic, at least, over a period of 3-30 min. No creep occurs and the original length is recovered on removal of the stress. Secondly, at higher strains, the material is not elastic and the original length is not recovered on removal of the stress i.e. there is considerable hysteresis. Furthermore, stress softening occurs, i.e. the second and subsequent stress-strain cycles are very different from the first, showing a reducing modulus but tending to approach a limit. On standing or after certain treatments, a return towards the original stress- strain takes place. Thirdly, there is the frequency effect in the determination of modulus at very low strains. The dynamic modulus may well be two or three times that of the static modulus. All these phenomenon lead to a seeking of explanation. Many attempts have been made but only a certain explanations have been well accepted. However, the direction which future research in reinforcing filler technology will follow will be the concept of filler-elastomer interactions. This will provide the most potential to enhance compound performance. For example, Le Bras [15] showed that carboxyl, phenolic, quinone, and other functional groups on the carbon black surface react with the polymer and provided evidence that chemical crosslinks exist between these materials in vulcanisates. It was reported that Ayala and co-workers [16] determined a rubber-filler interaction parameter directly from vulcanisate measurements by using the slope of the stress-strain curve, which relates to the black-polymer interaction and to the ratio of dynamic modulus at 1 and 25% strain amplitude as the measurement of filler-filler interaction. This interaction parameter emphasizes the contribution of carbon black-polymer interactions corresponding to the physical phenomena associated with networking. The values obtained provided a

good measure of black-polymer interaction for SBR and NR. By using an organosilane-coupling agent, Wolff and Gorl [17] found that the quantity of bound organosilane correlates with carbon black particle surface area and level of oxygen-containing functional groups and the reaction yielded a reduction of compound hysteresis.

2.8.2 Effects between Filler and Elastomer

Effects in vulcanisates containing active fillers are commonly measured by the resistance to abrasion, tearing, cut growth, flexing cracking and tensile fracture. These are all failure phenomena which appear to interact in complex ways. In general, preferable reinforcing filler should have both a small particle size, a chemically active surface and a surface which is both porous and very irregular in shape to maximize surface area of contact between rubber and filler. In the case of carbon blacks, structure and surface area can be varied over a wide range. This is also possible in the case of precipitated and pyrogenic silicas, although tile latter are much too expensive to be used as rubber-grade fillers. The various effects, for example, are illustrated in Figure 2.10

2.8.3 Influencing Factors of Silica and Carbon Black on Reinforcement

In general, the filler reinforcement factors of both silica and carbon black can be grouped into three types. Those are the extensity which is related to the surface area i.e. particle size, the intensity which is related to the surface chemistry or the surface energy, and the geometry which is related to the shape and porosity of the particles. For example, furnace carbon black consists of irregular chainlike, branched aggregates of nodular sub-units which are called particles. These particles are firmly fused together. The smallest discrete entity existing in rubber is the aggregate. The extent of inter-nodular fusion is termed "structure". There are carboxyl, phenolic, quinones, and other functional groups found on the carbon black surface. In the case of amorphous silica, it consists of silicon and oxygen arranged in the tetrahedral structure of a three-dimensional lattice. Particle size ranges from 1 to 30 nm and surface area from 20 to 300 m^2/g. There is no long-range crystal order, only short-range ordered domains in a random arrangement with neighboring domains. The

surface silanol concentration (silanol groups -Si-OH) influences the degree of surface hydration. The Silanol types fall into three types, isolated, geminal and vicinal as illustrated.
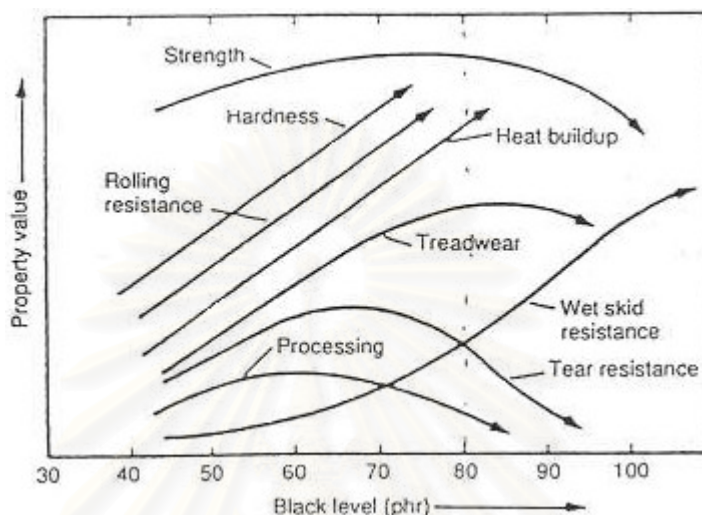
Figure 2.**10**   Effects of carbon loading on compound properties [5].

In addition, the surface acidity of the silica controlled by the hydroxyl groups on the surface of the silica can influence peroxide vulcanization, although in sulphur curing there is no significant effect. The rubber-filler interaction is affected by these sites. The surface hydration caused by water vapor absorption is also affected by surface silanol concentration. High levels of hydration can adversely affect final compound properties. Due to the different chemical properties of carbon blacks and silicas, Wolff used this fact to develop a technique, the so-called inverse gas-chromatography, for evaluating the surface energy of the fillers. The surface energy is composed of a dispersive component and a specific component. The dispersive component is a measure of rubber-filler interaction, mainly observed in the range of medium and large deformations. The specific component is a measure of filler-filler interaction, predominantly observed in the range of small deformations. The measurement of surface energy finally permits a clear distinction to be made between carbon blacks and silicas on the basis of their respective surface activities. The presence of surface activity was believed to be a prerequisite for the structure and surface area of a filler to become effective factors in rubber reinforcement. Since

silicas have high specific surface energy, they tend to interact with themselves, rather than the rubber. It is this differential which is overcome through the use of coupling agent i.e. TESPT. Besides, the covalent bonds formed between silica and rubbers constitute the strongest form of rubber-filler interaction and should lead to considerable improvements in the vulcanisate properties which are affected by this type of interaction.

2.8.4 Mechanism of Reinforcement

In order to explain the mechanism of reinforcement, many different concepts had been developed. One of the them was the assumption that a chemical bonding of rubber and filler or the so-called filler-rubber interaction takes place either during the compounding process or during vulcanization. This concept was based on the fact that reactive functional groups are found on the carbon black and bound rubber or rubber gel of un-vulcanized rubber always exists. Nowadays, the mechanism of reinforcement is still being extensively investigated. However, some mechanisms widely accepted are given here.

2.8.5 Reinforcement in Silica-Reinforcing Agent System

According to Wolff [18] using TESPT and an MBTS curing system, the mechanism of reinforcement in silica-reinforcing agent system is proposed into two main steps. Firstly, the silanisation reaction in which coupling agent reacts with silica, and secondly, the formation of crosslinks between the modified silica and polymer. The silanisation of the TESPT and silica surface can occur quite readily and it is a time-temperature dependent reaction for each elastomer system. Since three types of functional silanol groups exist on the silica surfaces, isolated hydroxyl groups, geminal groups and vicinal groups, the silica-silane intermediate can be shown in Figure.2.11
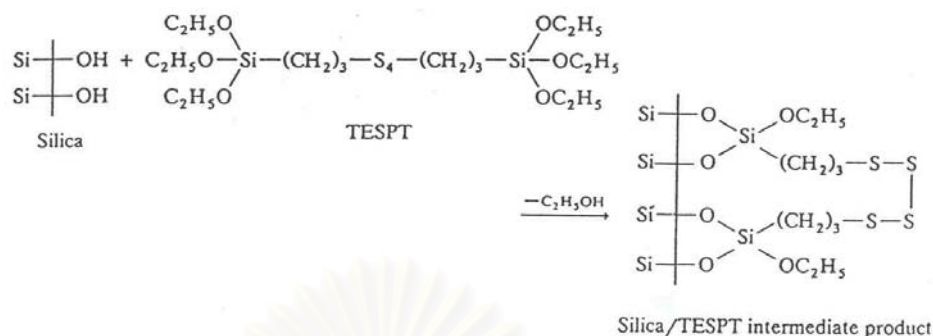
Figure 2.11 Silica-silane intermediate [5]

The filler/silane intermediate can then react with the allyl position of unsaturated sites on the polymer chain through the chemical route shown in Figure 2.12.

The TESPT/silica intermediate is present instead of sulphur. The mercaptobenzothiazyl disulphide (MBTS) react with the tetrasulfane group, thus forming 2 moles the polysulphide. The silica particle is on one side and the mercaptobenzthiazolyl on the other. This polysulphidic pendant group on the silica surface will undergo crosslink formation with the polymer in much the same way as occurs in rubber-bound intermediates that convert to crosslinks, thus releasing MBT and forming the rubber-silica bond.

The rubber-to-filler bonds, where the reinforcing agent is in between, are formed as a result of the reaction, thus constituting a chemical link between the filler and the rubber network as shown in Figure 2.13.
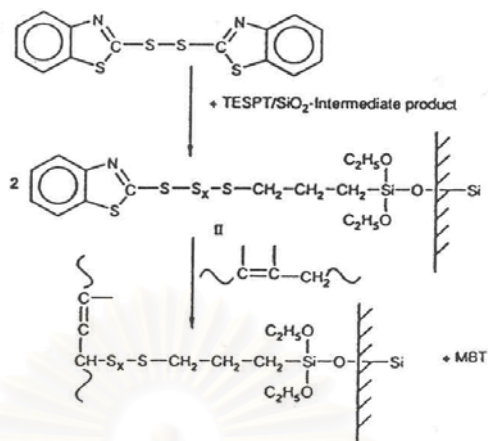
Figure 2.12 Chemical route of filler/silane intermediate with rubber [5]
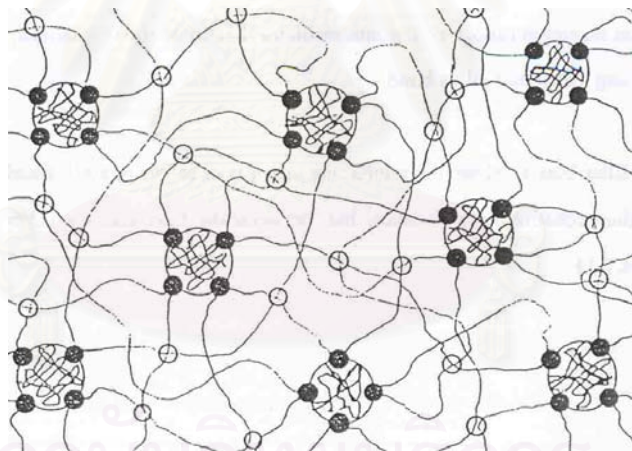
Figure 2.13 Schematic diagram of rubber – TESPT – filler network [5]

2.9   Literature Review

Hayashi et al. [19] studied the effect of filler on compatibility of natural rubber (NR). It has already been reported that styrene-butadiene rubber (SBR) with more than 15 % styrene content, Butadiene Rubber (BR) with less than 60 wt % vinyl content, and Isoprene Rubber (IR) with more than 20 wt% 3,4- microstructure are incompatible with NR. In this study, it was found that compatibility of SBR/NR reinforced with carbon black is different from that of with white carbon (silica), and that the compatibility is closely related to microstructure of SBR. It was found for the first time that compatibility is changed by filler.

Takino et al. [20] studied the effect of processing additives on carbon black dispersion and grip property of high-performance tire tread-compound. From this investigation, it could consider that good wettability toward the carbon black surface was necessary for processing additives in order to improve carbon black dispersion. The function of the processing additive was thought to enhance the surface lubrication of carbon black for disagglomeration in the early step of mixing. Consequently, it was found that tread compounds with improved carbon black dispersion had a remarkable effect on tire dry-grip properties at high temperature.

Choi [21] studied the filler-polymer interaction in both silica and carbon black-filled styrene-butadiene rubber compound. Difference in the filler-polymer interactions of the styrene, cis-1,4-, trans-1,4-, and 1,2-units were investigated. The filler-polymer interactions of the butadiene units were found to be stronger than that of the styrene unit. The interactions of the cis-1,4- and trans-1,4-units were stronger with carbon black than with silica, whereas the 1,2-unit interacted more strongly with silica than with carbon black.

Ezawa et al. [22] studied the rubber composition for tire tread and pneumatic tire. There was disclosed a rubber composition for a tire tread which comprises 100 parts by weight of a rubber component comprising a diene-based synthetic rubber or a mixture of a diene-based synthetic rubber and natural rubber and containing at least 20% by weight of a styrene-butadiene rubber; 5 to 50 parts by weight of aluminum hydroxide powders; and at least 5 parts by weight of silica powders, wherein the total amount of the silica and aluminum is in range of 40 to 80 parts by weight. The above rubber composition, when made into a tire tread, can maintain favorable low fuel

consumption properties and low wear resistance, and besides can impart the tire with greatly improved gripping properties on wet road surfaces particularly at a low temperature.

Park et al. [23] studied the filler-elastomer interaction. In this work, the surface and mechanical interfacial properties of silicas treated with H_3PO_4, KOH, and C_8H_{10} are investigated. It was found that the development of surface functional groups leads to a significant physical change in silica surfaces, such as, microstructures and surface free energy parameters. This treatment is possibly suitable for silica surfaces to be incorporated in a hydrocarbon rubber matrix, resulting in improving the tearing energy of the resulting composites.

Labauze et al. [24] studied the silica-filled elastomer composition which can be used for tires. A tire having a reduced resistance to rolling, characterized by the fact that it has a tread comprising 10 to 100 parts by weight of a sulfur-vulcanizable rubber composition comprising silica as reinforcing filler. However the use of silica raises difficulties in working due to silica/silica interactions which tend in raw state to cause an agglomeration of the silica particles before and even after mixing and thus to increase the consistency of the rubber compositions, and in any event to make the working more difficult than the working of carbon black.

Ajay et al. [25] studied the effect of silane coupling agent on the chemorheological behavior of epoxidised natural rubber filled with precipitated silica. The extent of interaction between the rubber and the filler depends on the extrusion time, the volume fraction of the filler, the shear rate and the addition of the silane coupling agent. It is also evident that addition of the silane coupling agent causes decrease in the activation energy of the chemical interaction between ENR and silica and increase in the tensile strength, modulus and elongation at break.

Matsuo et al. [26] studied the rubber composition for tire sidewall and tire. In the present invention, each of the precipitated silica and carbon black has function as reinforcement for tire. Further, dispersibility of the precipitated silica is improved by using the silane coupling agent and wear resistance of tire to be obtained is ensured. It was also noted that the increasing of the coupling effect of the silica with the diene rubber could improve the dispersibility of the silica into the diene rubber.

Ansarifar et al. [27] studied the use of synthetic silica fillers to improve tire service life. The mooney viscosities of the compounds containing 30 and 60 pphr silica decrease to their minimum levels when 1.5 and 7 pphr silane, respectively, are added. The optimum cure times for compounds containing 30 and 60 pphr silica shorten to their lowest values, when 4 and 7 pphr silane, respectively, are mixed. The cure rate of the mixes containing 30 and 60 pphr silica accelerates to a maximum after 4 and 7 pphr silane respectively, are introduced. In summery, when precipitated silica is used to reinforce natural rubber compounds, it is essential to add silane to improve processing properties. To optimize these attributes, the right combinations of silane and silica will be required. This is essentially decided by the amount of silica in the rubber.

Cochet P. [28] studied the high-performance precipitated silicas for winter tire tread. The design of the tread pattern with deep and specific strips is one of the major parameters, as is the use of highly dispersible silica which can form soft compound covering a wide range of temperatures. By the use of low specific surface area silica, it is possible to achieve a good balance in final properties, together with easier processing.

CHAPTER III

EXPERIMENTAL

3.1 Raw Materials

Table 3.1 Rubber and chemicals used in this study

Chemicals		Commercial name	Supplier
NR	(Rubber)	Natural rubber	Thai Hua Co., Ltd.
SBR	(Rubber)	SBR 1500	BST Elastomer Co., Ltd.
Silica	(Reinforcing filler)	Ultrasil	United Silica Siam
Silane coupling	(Coupling agent)	X50S	Degussa
Carbon black	(Reinforcing filler)	N330	TCP
ZnO	(Accelerator)	ZnO	Metoxide Thai
Steric acid	(Activator)	Sinar Far	SOCI
6PPD	(Antioxidant)	Flexone 7P	Crompton
Wax	(Antiozonant)	Parane B8	Total
DPG	(Activator)	DPG	Flexys
TBBS	(Accelerator)	Santocure TBBS	Flexys
Sulfur	(Vulcanizing agent)	Sulphur powder	Utids Chemical

3.2 Instruments

1) Two roll mill mixer
2) Compression mold   : Wabash, Charernchai Karnchang factory, Thailand
3) Rheometer   : Techpro, Model Rheotech, USA
4) Tensile testing machine : Lloyd LR5K, England
5) Hardness tester   : Shore A, Instron MFG, England
6) Akron abrader
7) Rebound resilience Tripsometer
8) Flexometer

3.3 Procedure

As we all know that internal mixer gives better homogeneity than the external mixer, nevertheless in this experiment a variety of recipe was used so that the mixing time could not be fixed. If the mixing time is too short, it gives the non-homogenous compound. On the other hand, if the mixing time is too long, some properties might drop. So that 2-roll mill was selected to use as a mixer in this experiment. It is easier to monitor the homogeneity of the compound and to control the final temperature of the mixing to prevent pre-vulcanization occur in mixing process.

The schematic diagram of rubber compound preparation is shown in Figure 3.1. The mixing roll temperature of 2-roll mill was kept constant at 35 ^{o}C. The rubber blend was fed to the front roll, masticated for 1 min., blended with the chemical ingredients (except accelerator and sulfur) until the compound was homogenized. For the final step mixing, the sulfur and accelerator were fed into the compound and blended for 1 min., then sheeted the compound to get thickness 6 mm. and cooled down by cold water to prevent the reaction occurring. Finally, the compound was determined the vulcanization time by ODR at 423 K, and prepared the standard specimens for mechanical testing according to the ASTM test method.
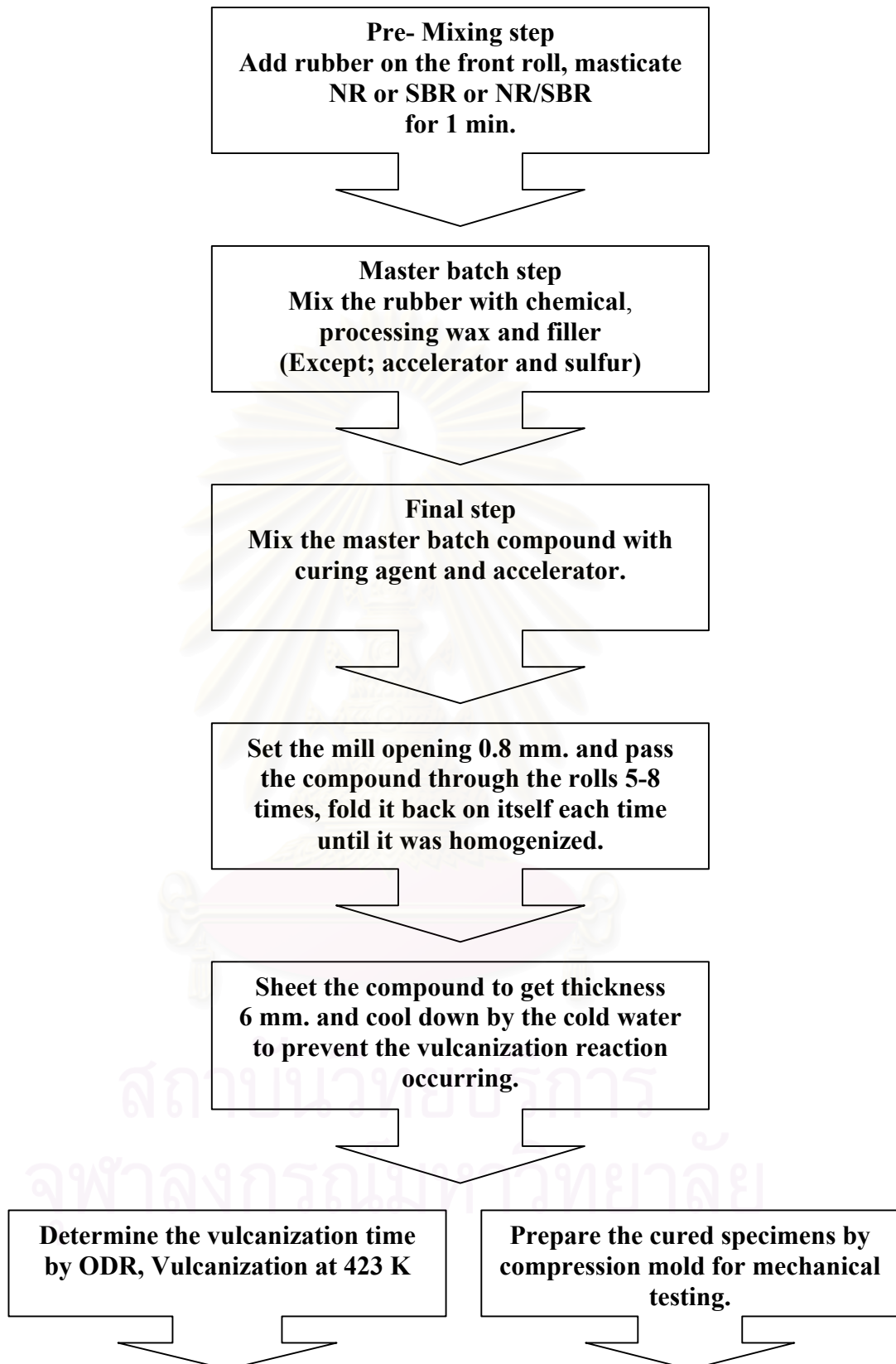
Figure 3.1 The schematic diagram for rubber compound preparation.

3.4 Formulation of the Compounds in the Experiments

In this experiment, the following formulations are used,

Table 3.2 Silica properties.

Characteristic	unit	tolerance
CTAB adsorption	m^2/g	147-187
Loss at 100-105 ^{o}C	%	3.8-7.0
Density	g/cm^3	2
pH at 5%		5.3-7.3
Specific surface BET	m^2/g	150-200
Loss at 1000 ^{o}C	%	8.0-12.0

Table 3.3 Carbon black properties.

Characteristic	unit	tolerance
DBP absorption	ml/100g	95-109
Iodine adsorption	mg/g	76-88
Sieve reject 45 μ	ppm	≤ 500
Sieve reject 500 μ	ppm	≤ 10
Loss at 125 ^{o}C	%	≤ 1.5
Surface BET	m^2/g	73-85

Table 3.4 Ingredients for all compounds.

Ingredient		Composition, phr (part per hundred rubber)
ZnO	(accelerator)	4
Stearic acid	(activator)	2
6PPD	(antioxidant)	2
Wax	(antiozonant)	2
DPG	(activator)	0.5
TBBS	(accelerator)	1.6
Sulfur	(vulcanizing agent)	1

Table 3.5 Group 1: NR/ SBR = 100/0

Ingredient*	Compound, phr					
	Compound 1/1	Compound 1/2	Compound 1/3	Compound 1/4	Compound 1/5	Compound 1/6
NR	100	100	100	100	100	100
Silica	50	40	30	20	10	0
Silane	4	3.2	2.4	1.6	0.8	0
Carbon black	0	10	20	30	40	50

* Other chemical ingredients according to Table 3.4

Table 3.6 Group 2: NR/ SBR = 80/20

Ingredient*	Compound, phr					
	Compound 2/1	Compound 2/2	Compound 2/3	Compound 2/4	Compound 2/5	Compound 2/6
NR	80	80	80	80	80	80
SBR	20	20	20	20	20	20
Silica	50	40	30	20	10	0
Silane	4	3.2	2.4	1.6	0.8	0
Carbon black	0	10	20	30	40	50

* Other chemical ingredients according to Table 3.4

Table 3.7 Group 3: NR/ SBR = 70/30

Ingredient*	Compound, phr					
	Compound 3/1	Compound 3/2	Compound 3/3	Compound 3/4	Compound 3/5	Compound 3/6
NR	70	70	70	70	70	70
SBR	30	30	30	30	30	30
Silica	50	40	30	20	10	0
Silane	4	3.2	2.4	1.6	0.8	0
Carbon black	0	10	20	30	40	50

* Other chemical ingredients according to Table 3.4

Table 3.8 Group 4: NR/ SBR = 60/40

Ingredient*	Compound, phr					
	Compound 4/1	Compound 4/2	Compound 4/3	Compound 4/4	Compound 4/5	Compound 4/6
NR	60	60	60	60	60	60
SBR	40	40	40	40	40	40
Silica	50	40	30	20	10	0
Silane	4	3.2	2.4	1.6	0.8	0
Carbon black	0	10	20	30	40	50

* Other chemical ingredients according to Table 3.4

Table 3.9 Group 5: NR/ SBR = 30/70

Ingredient	Compound, phr					
	Compound 5/1	Compound 5/2	Compound 5/3	Compound 5/4	Compound 5/5	Compound 5/6
NR	30	30	30	30	30	30
SBR	70	70	70	70	70	70
Silica	50	40	30	20	10	0
Silane	4	3.2	2.4	1.6	0.8	0
Carbon black	0	10	20	30	40	50

* Other chemical ingredients according to Table 3.4

Table 3.10 Group 6: NR/ SBR = 20/80

Ingredient*	phr					
	Compound 6/1	Compound 6/2	Compound 6/3	Compound 6/4	Compound 6/5	Compound 6/6
NR	20	20	20	20	20	20
SBR	80	80	80	80	80	80
Silica	50	40	30	20	10	0
Silane	4	3.2	2.4	1.6	0.8	0
Carbon black	0	10	20	30	40	50

* Other chemical ingredients according to Table 3.4

3.5 Mechanical Testing

Mechanical properties of the vulcanized rubbers, i.e., tensile strength, hardness, tear resistance were measured according to ASTM and ISO test methods.

3.5.1 Tensile Properties

Tensile strength, tensile modulus and elongation at break of specimen were measured in a universal testing machine (Lloyd LR5K). Dumbbell specimen is required according to ASTM D 412-87 (Figure 3.2). The specimens were placed in the grips at a specified grip separation and pulled until failure. Six specimens were required for each measurement. The test speed was 400 mm min^{-1} for measuring strength and elongation, and 1 mm min^{-1} for measuring modulus.
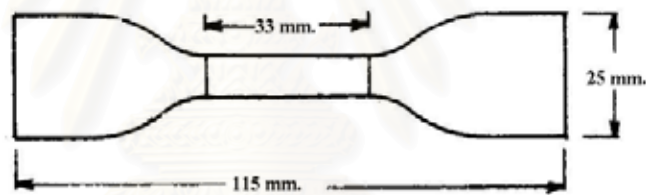
Figure 3.2 Dumbbell shape specimen for tensile property testing

The tensile strength and % elongation at break were determined from Eq. 3.1 and 3.2

$$\text{Tensile strength (MPa)} = \frac{\text{Force at rupture (N)}}{\text{Cross-section area (m}^2)} \tag{3.1}$$

$$\% \text{ Elongation at break (\%)} = \frac{(\text{Length at rupture-original length}) \times 100}{\text{Original length}} \tag{3.2}$$

3.5.2 Hardness Measurement

The test specimen shall be at least 3 mm in thickness. The lateral dimensions of the specimen shall be sufficient to permit measurements at least 12 mm from any edge. The specimen shall be flat and parallel over a sufficient area to permit the pressure foot to contact the specimen.

The specimen was placed on a hard and horizontal surface. The pressure was held on a vertical position with the point of the indentor at least 12 mm from any edge of the specimen. The pressure was applied to the specimen. After the pressure foot was in firm contact with the specimen, the scale reading was taken within 30 s. One measurement was made in 3 samples and the average of these measurements was used as the hardness value.

3.5.3 Tear Resistance

The specimen was die cut to the appropriate shape (Die C) from a sheet (see Figure 3.3), according to ASTM D 624-81. The specimen was then placed in the grips of the testing machine and pulled at a rate of 500 mm min^{-1} until rupture. The resistance was measured in Newtons. The tear strength was determined from Eq. 3.3

$$\text{Tear strength (MPa)} = \frac{\text{maximum force (N)}}{\text{Thickness of specimen (mm.)}} \quad (3.3)$$
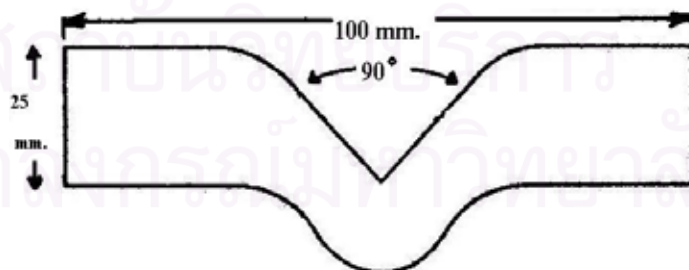
Figure 3.3 Angle shaped specimen for tear resistance testing

3.5.4 Abrasion Resistance

The abrasion resistance of rubber samples was measured by following the BS 903: Part A9. A typical laboratory machine is the Akron abrader. On this machine, the test wheel is driven against a grinding wheel at a slip angle. This ensures a greater loss of rubber per unit time. This slip angle represents condition that exists when we round a corner. The loss in weight of the rubber wheel or sometime the volume loss for a fixed number of revolutions of the grinding wheel is a measure of the abrasion resistance of the rubber.

Table 3.11 Approximate Running – In and Test Run

Approximate Running – In and Test Run		
Volume less in 500 – Revolution Trial Run (ml)	Revolution (Addition to Trial Run)	
	Running - In	Test Run
Above 0.05, not above 0.10	4000	1000
Above 0.10, not above 0.20	2000	500
Above 0.20, not above 0.40	750	250
Above 0.40	500	125

3.5.5 Resilience

The Resilience of rubber sample was measured by following the BS.903 part A8 and using equipment: Wallace Dunlop Tripsometer. Before the measurement, the sample was reheated for 5 min., then checked the sample 6 times for warming. The pendulum of the tripsometer was allowed to strike a fixed rubber sample and the rebound height was measured. The rebound height as a percentage of the original height is the resilience of the rubber. The measurement was repeated 3 times and the average of % rebound was calculated.

3.5.6 Cure Characteristics

The cure characteristics of compound rubber were investigated for determining the condition of rubber vulcanization. The specimen was cut into 0.03 m in diameter and 13×10^{-2} m in thickness, it was then placed on the top of the oscillating disc before closing the die. The specimen was heated at 150 $^{\circ}$C until it reached the optimum cure or 90% cross-linked time.

3.5.7 Heat Build Up

Heat build up of the rubber compound is measured using the Flexometer. Here, a cylindrical test sample is repeatedly deformed and the temperature rise measured using thermocouples. The measurement was repeated 3 times and the average of temperature increase was calculated and used to determine the heat build up of the compound.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Vulcanization Characteristics

The oscillating disk rheometer (ODR) was utilized to determine the vulcanization time (TC90) and maximum torque of compound rubbers. The condition was kept constant at temperature of 423 K, the testing time of 20 min and the rotational amplitude of 3°, according to ASTM D2084-95. The compound rubbers were tested under pressure in the die cavity located in the electrically heated plates. Torque plotted versus time is proportional to the stiffness or shear modulus of the rubber. The stiffness (torque) - time curve is shown in Figure 4.1.
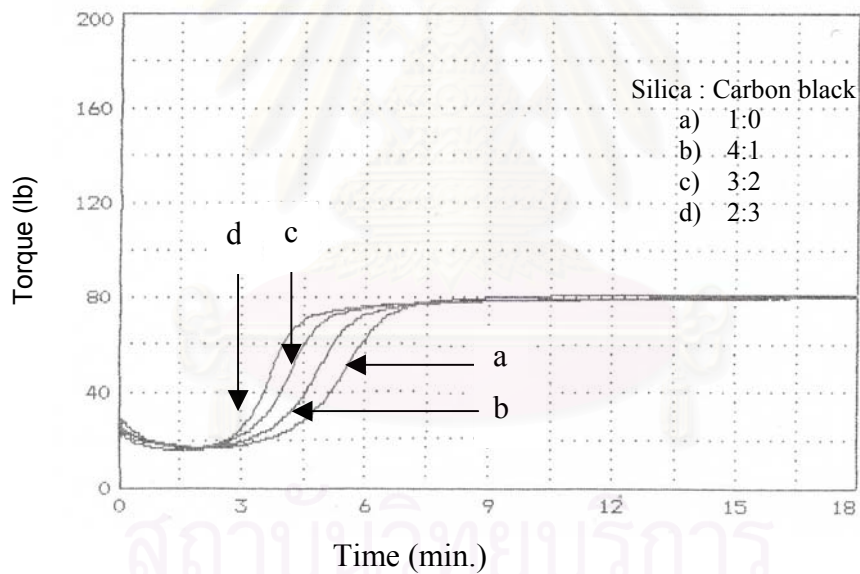
Figure 4.1 Stiffness (torque) - time curve for compound at NR : SBR of 80:20 and silica : carbon black ratio of 1:0, 4:1, 3:2 and 2:3 (filler content = 30 phr).
Test at 423 K.

4.1.1 Maximum Torque

The maximum torque of the torque-time curve is one of the indicators that used to explain the vulcanization characteristic and cross link density. In these experiments, the maximum torque of the compounds at various silica/carbon black and NR/SBR ratios were investigated as shown in the Table 4.1, Figure 4.2a and 4.2 b.

In this study, the maximum torque of the compounds decreased with increasing silica content for all NR/SBR ratios. It can be explained by the specific characteristics of silica. Silica composes of functional group of hydroxy (- OH) which is typically reactive to the accelerator in the tread compound formulas, so during the mixing process, accelerator could initiate the chemical reactions with silica [29]. Therefore, the efficiency of accelerator decreased, the crosslink density in the rubber matrix decreased and also the maximum torque was reduced.

From Figures 4.2a and 4.2b, the NR/SBR ratio does not affect the maximum torque of the compound.

Table 4.1 Maximum torque for various ratios of silica: carbon black and NR: SBR.

Silica: Carbon black Ratio*	Maximum torque, lb					
	NR : SBR					
	100:0	80:20	70:30	60:40	30:70	20:80
1:0	75.0	68.5	71.3	72.5	75.1	75.7
4:1	78.5	75.0	79.9	75.5	75.7	78.7
3:2	85.4	81.2	77.0	78.0	81.8	78.3
2:3	78.4	80.0	79.3	79.9	80.0	80.6
1:4	86.1	79.7	80.4	77.6	78.1	74.8
0:1	87.2	80.2	81.4	81.2	87.3	84.0

 * Filler content = 30 phr.
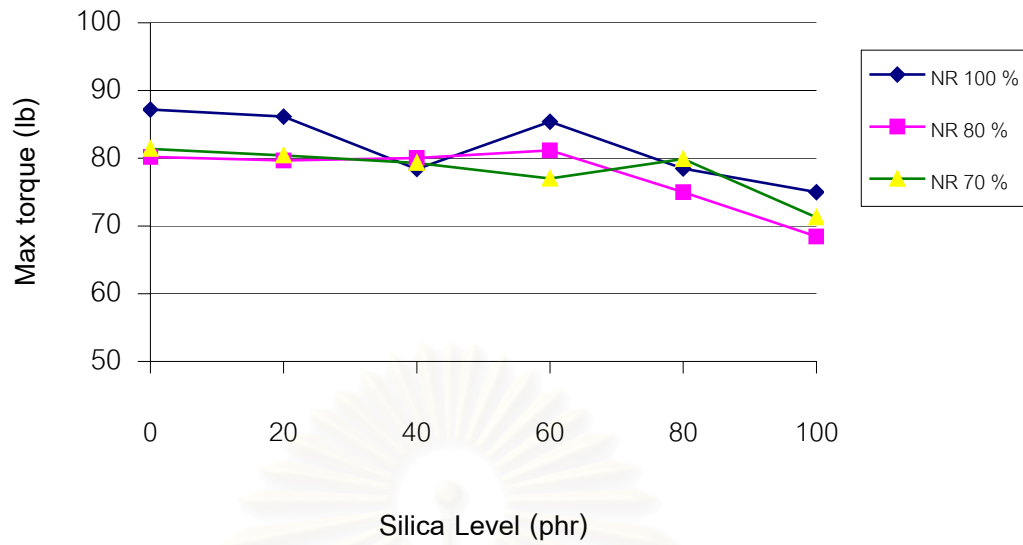
(a)
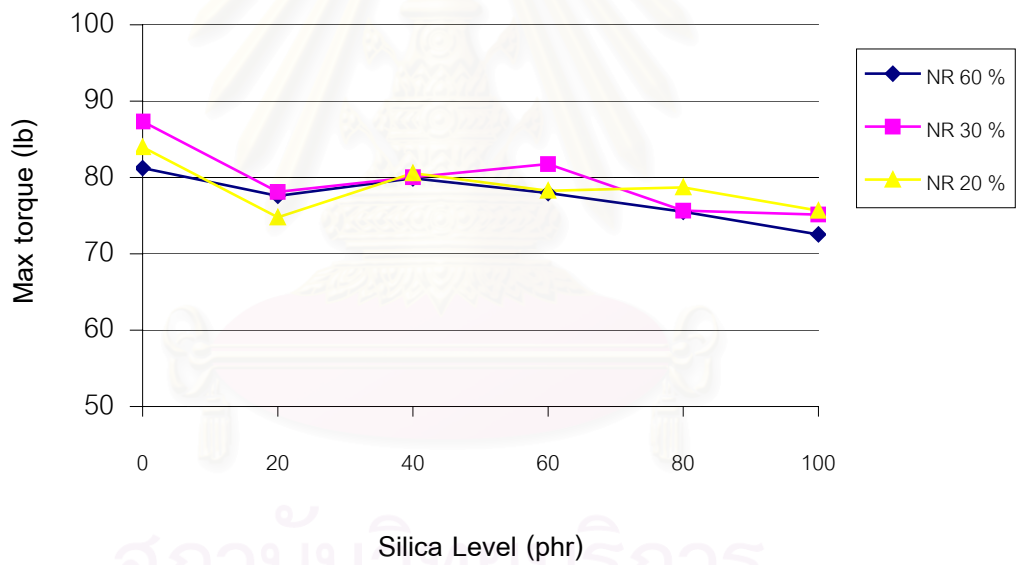
(b)

Figure 4.2 Effect of silica concentration on the maximum torque of tread compounds.
(a) 100 %, 80% and 70% NR   (b) 60%, 30% and 20% NR

4.1.2 TC90

The effect of silica on the vulcanization time was studied by measuring the TC 90, which is indicator of vulcanization time when the torque reaches 90 % of the maximum torque. Table 4.2, Figures 4.3a and 4.3b show the TC90 of the tread compounds as a function of silica content and NR content.

The results show an increase in TC90 as the silica loading is increased. It was found that silica could be easily reacted with the accelerator in the compound during mixing process. Thus, the efficiency and the amount of accelerator were reduced and it caused the slower vulcanization reaction (or higher T90).

Moreover, some investigators found that the dispersion of sulfur was good in NR when compared to SBR. So, the sulfur could generate the crosslinks in the NR compound faster than that in SBR. Figure 4.3b showed that TC90 of 20:80 NR/SBR blend is higher than that of 30:70 and 100:0 NR/SBR blend. Thus, the compound with high NR content could be cured faster.

Table 4.2 TC90 for various ratios of silica: carbon black and NR: SBR.

| Silica: Carbon black | TC90, min. | | | | | |
| Ratio* | NR : SBR | | | | | |
	100:0	80:20	70:30	60:40	30:70	20:80
1:0	7.6	12.6	13.0	10.3	9.1	15.4
4:1	7.8	10.0	8.9	7.1	8.4	12.9
3:2	6.2	7.7	8.2	7.1	8.2	11.1
2:3	6.2	7.0	6.4	6.6	8.0	10.1
1:4	5.1	6.2	6.6	5.6	8.6	10.5
0:1	5.0	5.8	6.3	6.4	8.1	9.3

* Filler content = 30 phr.
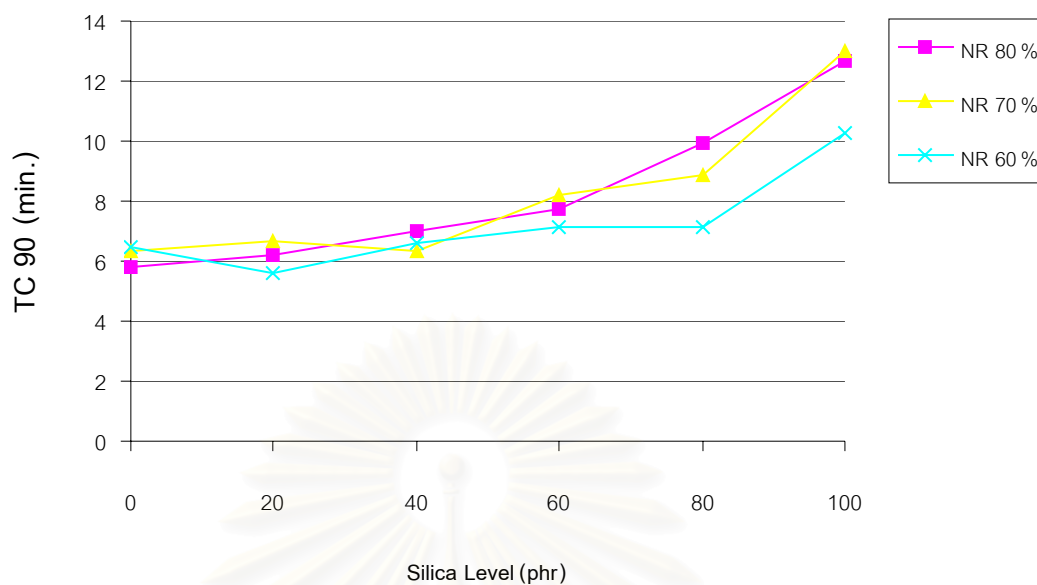
(a)
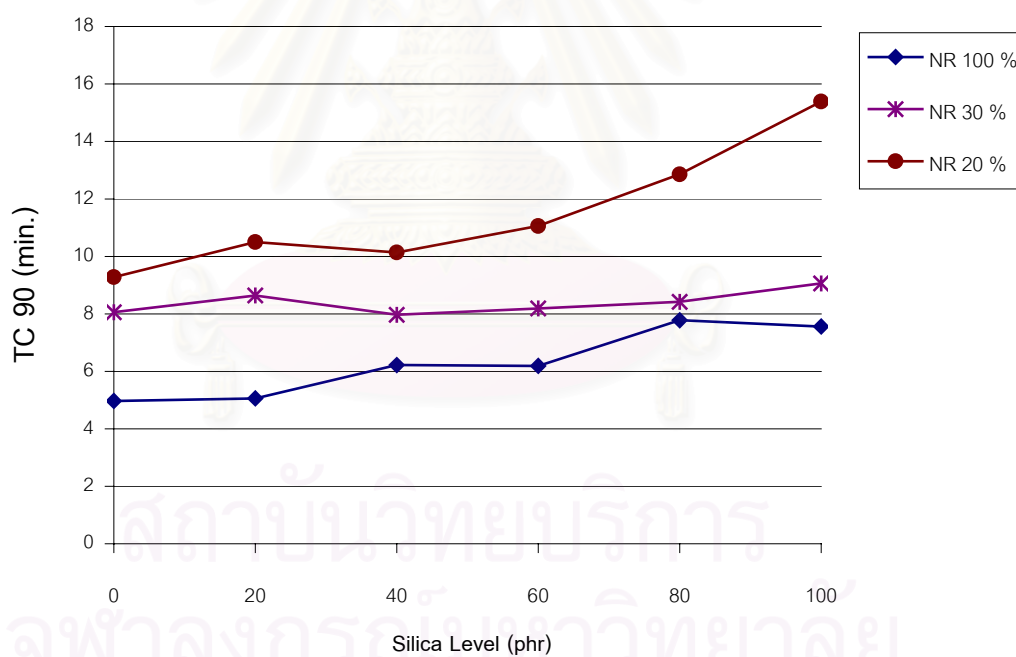
(b)

Figure 4.3 Effect of silica concentration on the TC90 of tread compounds
(a) 80 %, 70% and 60% NR   (b) 100%, 30% and 20% NR

4.2 Heat Build Up

4.2.1 Effect of Silica Concentration on Heat Build Up

The heat build up in compound comes from the transformation of the external energy to heat energy or hysteresis phenomenon. In this study, the heat build up (temperature) was measured by the flaxometer. The temperature increase of the tread compounds as a function of silica concentration were measured (Table 4.3). The effect of silica concentration on temperature of tread compound is shown in Figure 4.4.

From Figure 4.4, the temperature increase raised when the silica content decreased and heat build up (temperature increase) decreased with increasing NR content.

Thus, the replacing of carbon black with silica caused the reduction of heat build up in the compound.

It is accepted that elastomer chains have a natural affinity with carbon black. Consequently, the molecules forming these chains spontaneously attached themselves to the surface of the carbon black without the need for a coupling agent. However, the bonds thus created between the filler and the chain are low-energy bonds, which means that the elastomer chain will slip over the filler, especially when subjected to forces at low frequency. This molecular slippage leads to the energy losses in the form of heat (Figure 4.5).

Unlike carbon black, silica does not interact naturally with the elastomer chains. The silane (a coupling agent) must therefore be added to create a chemical bond between the silica and the elastomer. In this case, the creation of high-energy bonds ensures that when low-frequency forces are applied, molecular slippage is much more limited. Energy losses at low frequencies are therefore lower for a compound with silica filler, which explains the lower heat build up (Figure 4.6).
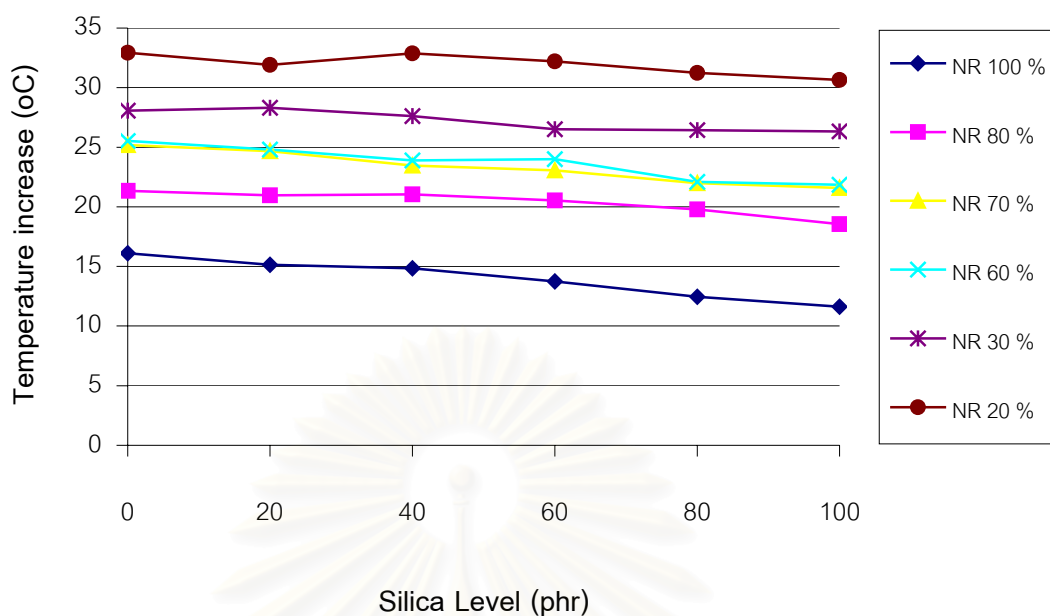
Figure 4.4 Effect of silica concentration and NR/SBR ratio on the temperature increase of tread compounds

Table 4.3 Heat build up for various ratios of silica: carbon black and NR: SBR.

Silica: Carbon black	Heat build up, ^{o}C					
Ratio*	NR : SBR					
	100:0	80:20	70:30	60:40	30:70	20:80
1:0	11.6	18.5	21.6	21.9	26.3	30.7
4:1	12.5	19.8	22.0	22.1	26.5	31.2
3:2	13.7	20.5	23.1	24.0	26.5	32.2
2:3	14.8	21.0	23.5	23.9	27.6	32.9
1:4	15.1	21.0	24.7	24.8	28.3	31.9
0:1	16.1	21.3	25.2	25.5	28.1	32.9

* Filler content = 30 phr.
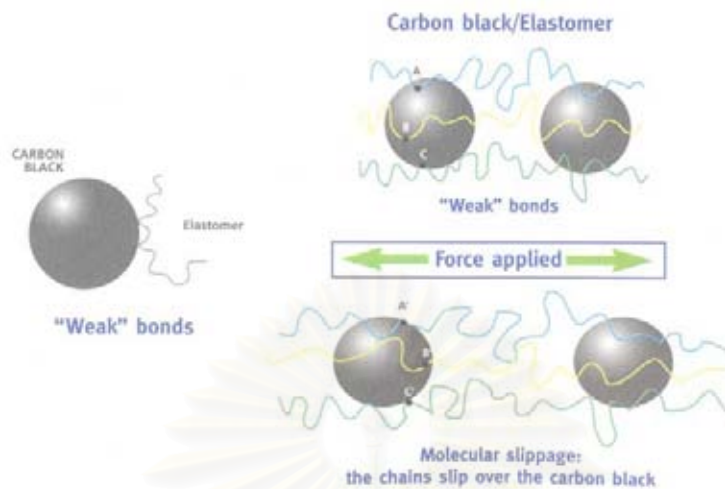
Figure 4.5 Molecular slippage of the carbon black filled elastomer.
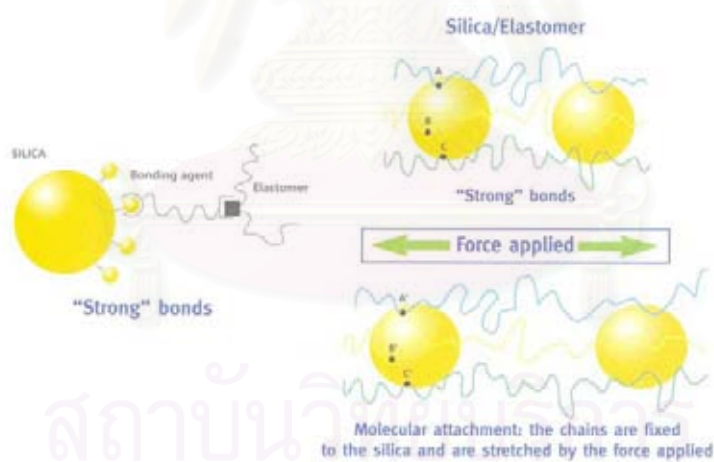
Figure 4.6 Molecular slippage of the silica filled elastomer.

4.2.2 Effect of SBR Concentration on Heat Build Up

Figure 4.7 shows the relation of the heat build up (temperature increase) and SBR content. The increasing SBR content in the compounds made heat build up increased, It can be explained that the SBR molecule is smaller than NR molecule and possibly form weak crosslinking in the compound. For the compound with high SBR content, the smaller molecules could move easier and have the better ability to absorb the mechanical forces during the testing, so the kinetic energy could be more converted to heat energy.
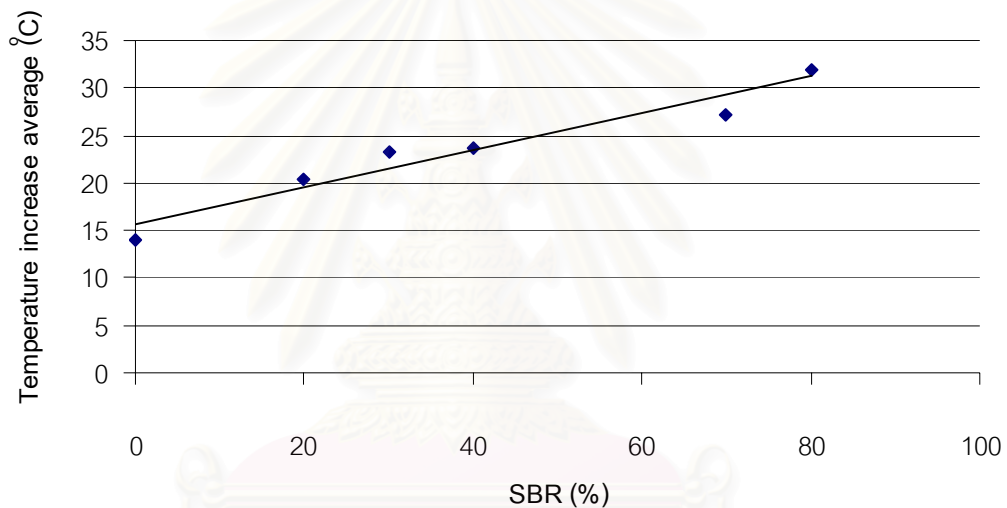
Figure 4.7 Effect of SBR concentration on the temperature increase of tread compounds

4.3 Abrasion Resistance

Abrasion resistance is a destructive test that measure the resistance to failure and it is an obvious property of the tire tread which is designed as a wearing part to the road surface. In this study, the abrasion resistance was measured from the volume loss of the compound after applying the external force. Table 4.4 and Figure 4.8 show the volume loss of the tread compounds as a function of silica and SBR content.

The results showed that increasing silica content in the compound caused the higher volume loss (low abrasion resistance) of the compounds. The reduction in abrasion resistance may be due to the high polarity of silica, which is easily aggregated itself to form a domain that like a foreign. This makes the worse dispersion in compound matrix and reduced the reinforcement in the compound when compared to carbon black reinforcement. The silica could also absorb the accelerator during the mixing process that caused less crosslinking, so the volume loss of the compound with silica was higher than that with carbon black.

Table 4.4 Volume loss, for various ratios of silica: carbon black and NR: SBR.

Silica: Carbon black Ratio*	Volume loss/1000 rounds, cm^3					
	NR : SBR					
	100:0	80:20	70:30	60:40	30:70	20:80
1:0	0.02	0.44	0.42	0.40	0.38	0.46
4:1	0.33	0.29	0.38	0.38	0.34	0.38
3:2	0.28	0.04	0.37	0.32	0.27	0.31
2:3	0.04	0.05	0.25	0.23	0.25	0.26
1:4	0.06	0.04	0.15	0.12	0.24	0.21
0:1	0.03	0.04	0.14	0.13	0.20	0.15

* Filler content = 30 phr.
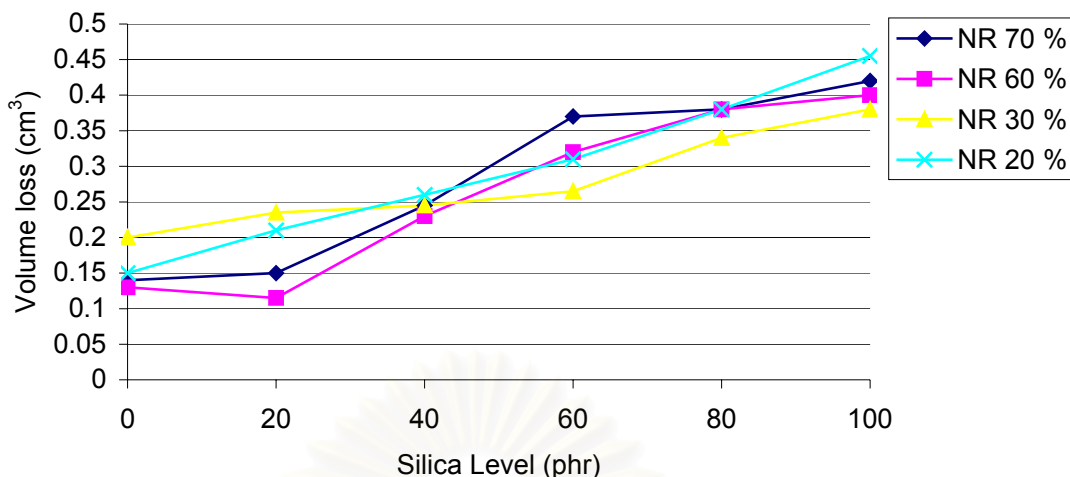
Figure 4.8 Effect of silica concentration on the volume loss of tread compounds

4.4 % Resilience

4.4.1 Effect of Silica Concentration on % Resilience

In this study, the effects of silica reinforcement on % resilience of tread compounds were studied. Table 4.5 and Figure 4.9 show % resilience as a function of silica content. It was found that % resilience is related to heat build up value, compound with high % resilience tends to generate low heat build up. The % resilience of compound increased with increasing silica content. This could be explained similarly to heat build up effect, the interaction force between silica and elastomer made low molecular slippage and made the compound absorbed less external energy than that of carbon black, so the % resilience was higher.

Table 4.5 % Resilience for various ratios of silica: carbon black and NR: SBR.

Silica: Carbon black Ratio*	% Resilience					
	NR : SBR					
	100:0	80:20	70:30	60:40	30:70	20:80
1:0	66.7	57.2	55.3	53.4	47.6	48.1
4:1	65.7	56.3	56.1	52.2	46.4	47.1
3:2	65.1	55.3	55.0	53.3	44.6	45.7
2:3	64.8	56.2	54.8	52.8	44.3	45.2
1:4	63.2	55.3	51.9	52.4	44.2	44.2
0:1	62.5	55.1	51.8	49.4	42.4	43.8

* Filler content = 30 phr.
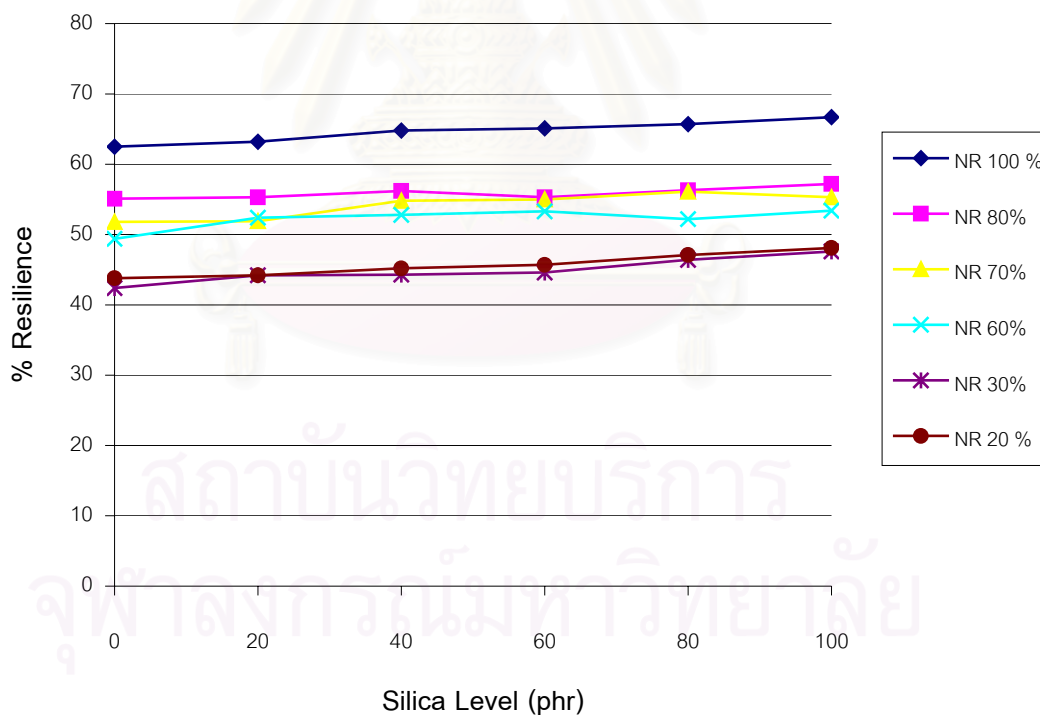
Figure 4.9 Effect of silica concentration on the % Resilience of tread compounds

4.4.2 Effect of SBR Concentration on % Resilience

Figure 4.10 shows % resilience as a function of SBR content in the NR/SBR blend compounds. The % resilience of compound with high NR content (low SBR content) had high % resilience because NR could generate more crosslinking than SBR. The NR molecules are larger than SBR molecule so NR compound has a better force resistance and lower energy absorption than SBR.
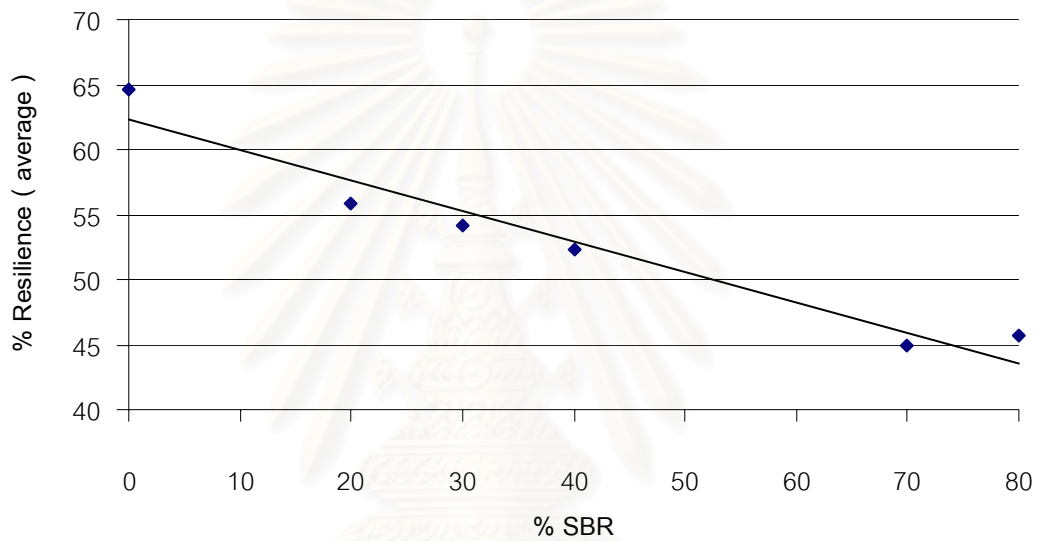
Figure 4.10 Effect of SBR concentration on the % Resilience of tread compounds

4.5 Tear Resistance (maximum strength)

The tear resistance indicated the maximum strength of the tread compound. The maximum strength data of the tread compounds as a function of silica and SBR content are shown in Table 4.6, Figures 4.11a and 4.11b.

It was found that there was no significant difference between silica and carbon black as a reinforcing filler in the tread compounds. This is may be due to the non-homogeneous dispersion of silica and carbon blend in the compounds. However the tear resistance of NR increased with an increase in NR content. This may explain that NR tends to have higher crosslinking density than that of SBR because diffusion rate of sulfur into NR matrix was higher than that of SBR.

Table 4.6 Maximum strength for various ratios of silica: carbon black and NR: SBR.

Silica: Carbon black Ratio*	Maximum strength, N/mm.					
	NR : SBR					
	100:0	80:20	70:30	60:40	30:70	20:80
1:0	62.9	90.5	84.3	74.4	54.6	56.7
4:1	108.4	110.0	103.7	90.4	56.6	59.5
3:2	99.3	109.2	97.3	67.6	51.0	59.5
2:3	106.0	105.8	84.8	58.9	57.3	62.9
1:4	82.3	110.6	95.4	60.2	55.3	62.1
0:1	67.1	103.9	77.8	58.8	57.2	59.0

* Filler content = 30 phr.
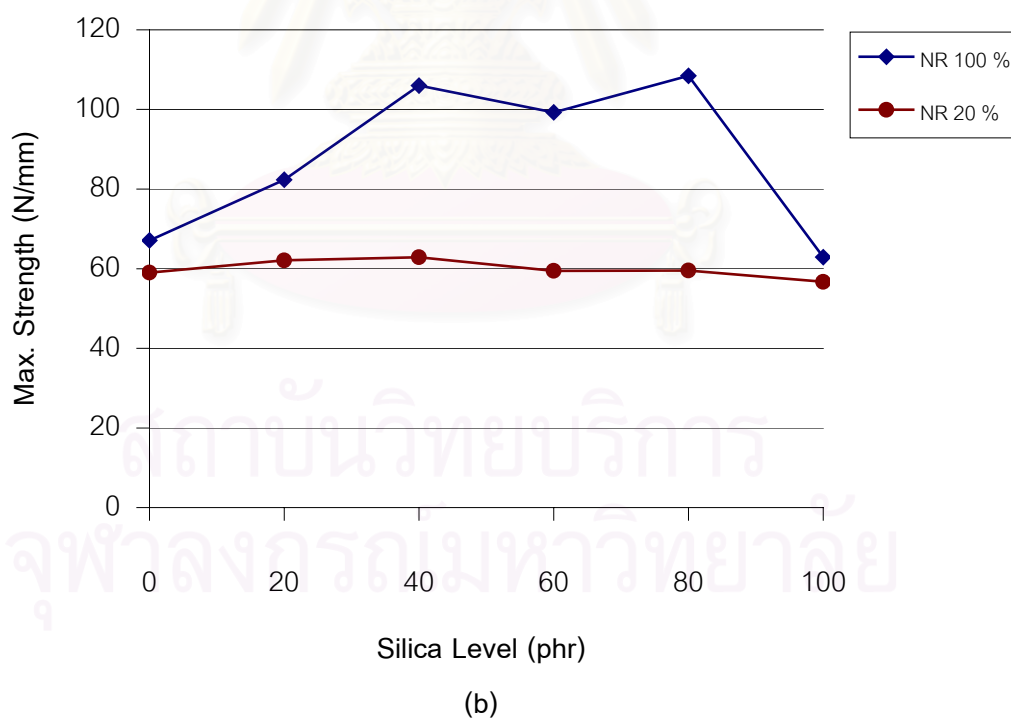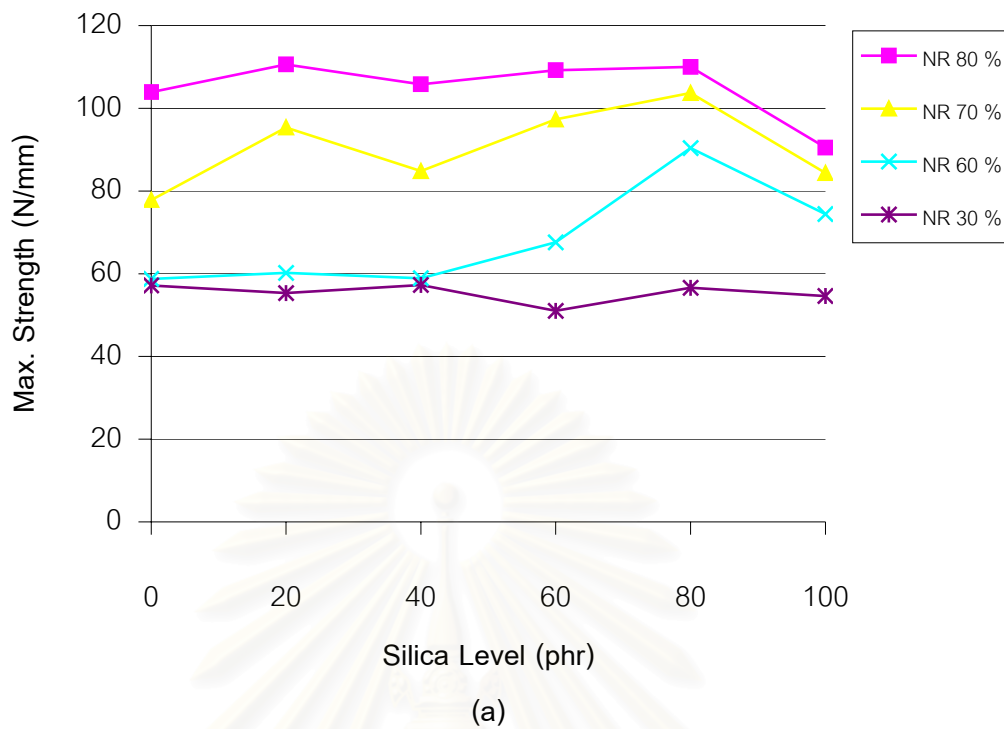
Figure 4.11 Effect of silica concentration on the maximum strength of tread compounds   (a) 80 %, 70%, 60% and 30% NR   (b) 100% and 20% NR

4.6 Tensile Strength

The stress at 300 % modulus as a function of silica and SBR content are shown in Table 4.7 and Figure 4.12.

It can be seen that an increase in the silica content tends to decrease the modulus and tensile strength. The strength of the compound depends on many factors but the most two importances are the effect of crosslink density and the reinforcement of the filler. Silica has high specific surface energy and low dispersive surface energy thus it tends to form filler to filler interactions rather than filler to rubber interactions. This can be the main reason in this experiment that the strength of the compound with high silica content was lower than that with high content.

Table 4.7 Stress at 300 % modulus for various ratios of silica: carbon black and NR: SBR.

Silica: Carbon black Ratio*	Stress at 300% modulus, MPa				
	NR : SBR				
	80:20	70:30	60:40	30:70	20:80
1:0	5.5	6.7	6.5	6.5	4.9
4:1	6.5	7.3	8.7	6.6	6.6
3:2	9.5	6.7	9.3	8.2	7.2
2:3	10.9	9.8	9.9	8.5	7.2
1:4	10.9	12.3	11.6	9.4	9.6
0:1	11.0	12.0	12.2	9.3	9.5

* Filler content = 30 phr.

(a)

(b)
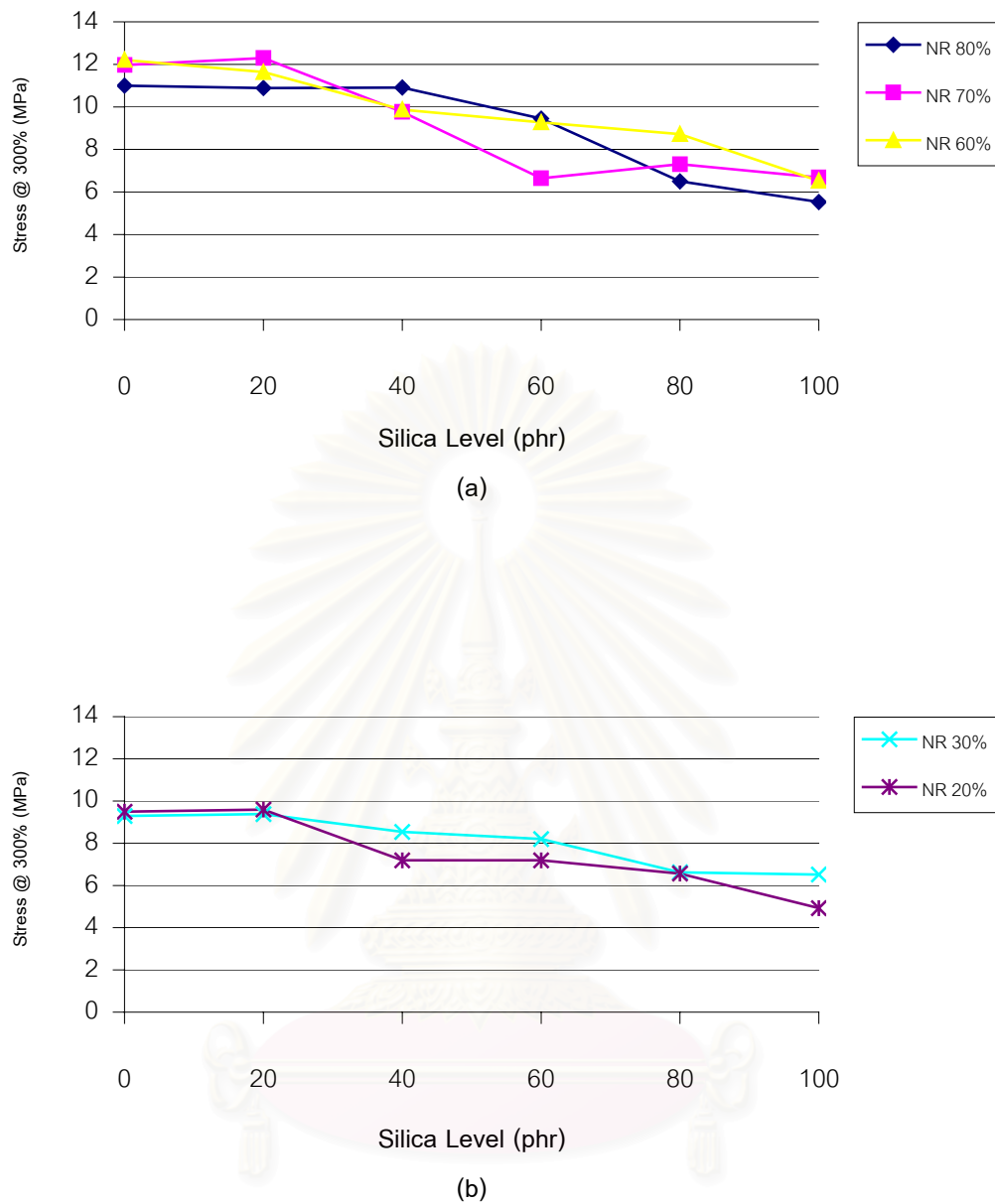
Figure 4.12 Effect of silica concentration on the stress @ 300% modulus of tread compounds.   (a) 80%, 70% and 60% NR   (b) 30% and 20% NR

4.7 Hardness

The hardness of the tread compounds as a function of silica and SBR content are shown in Table 4.8, Figures 4.13a and 4.13b

The hardness of compound was decreased with increasing silica content in compound. In general hardness increased with crosslink density and reinforcement of the filler. The hardness decreased because of the lower dispersion of silica and silica aggregation in the compound. The lower filler reinforcement in the compound is also due to the reaction between silica and accelerator during mixing process which could make the reduction of crosslink density. So, the compounds with silica reinforcement could be easily deformed compared to the carbon black reinforcement and it caused lower hardness.

Table 4.8 Hardness for various ratios of silica: carbon black and NR: SBR

Silica: Carbon black Ratio*	Hardness					
	NR : SBR					
	100:0	80:20	70:30	60:40	30:70	20:80
1:0	70.6	60.0	58.2	59.0	61.6	57.9
4:1	59.8	60.2	59.7	59.7	61.0	59.2
3:2	60.1	60.5	60.1	59.2	60.8	59.4
2:3	61.2	60.2	60.2	59.1	60.8	61.6
1:4	61.2	61.4	60.6	59.9	60.9	62.4
0:1	60.9	61.7	62.3	59.5	61.3	63.7

* Filler content = 30 phr.
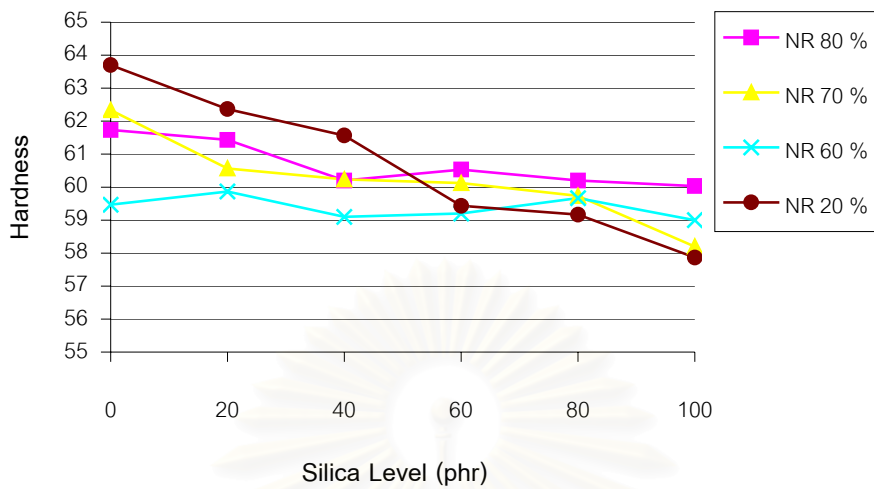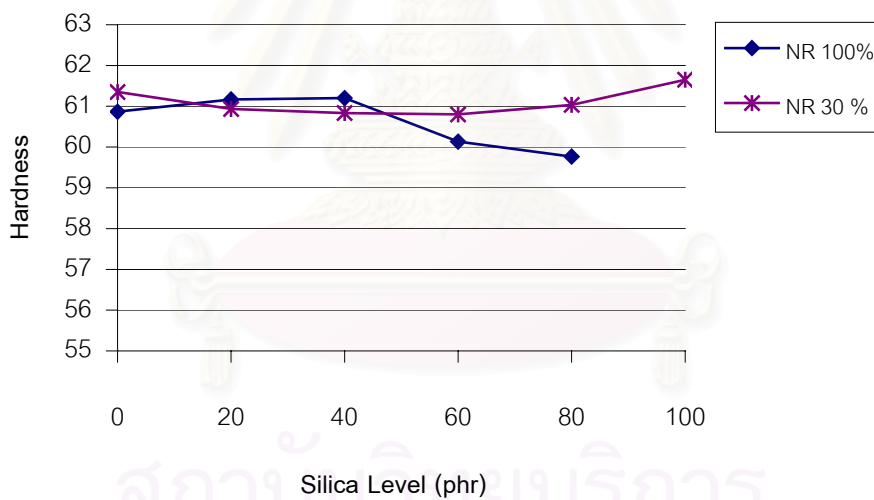
Figure 4.13 Effect of silica concentration on hardness of tread compounds
(a) 80 %, 70%, 60% and 20% NR   (b) 100% and 30% NR

CHAPTER V

CONCLUSION AND SUGGESTION

5.1 Conclusion

In the study, silica was used to replace carbon black as reinforcing agent in the tread compound NR/SBR blend for truck tire. The results showed that

- Increasing silica content in the tread compound could reduce the heat build up [29].
- Increasing silica content in the tread compound could increase the % resilience [29].
- Increasing SBR content in the tread compound gives higher heat build up and lower % resilience.
- Increasing SBR content gives the slower vulcanization reaction.

For the tread with silica reinforcement, a low rolling resistance and lower fuel consumption would be expected [22, 24, 26]. However, silica reinforcement could not be used successfully in the truck tire industry because it gives lower tensile strength, lower tear strength, lower hardness and lower abrasion resistance which could affect to the lower endurance and shorter life time of the tire.

Thus, the use of silica as reinforcing filler needs to be further investigated for understanding the phenomenon to improve the vulcanization efficiency and homogeneity of the reinforcing agent. Thus the appropriated properties of the tread compound could be obtained.

5.2   Suggestion

Further study for the improvement of the vulcanization efficiency and filler dispersion should be concerned with following aspects:

-   Study of specific mixing technique or sequence of the ingredient loading that can increase homogeneity of silica and crosslink density in tread compound.

-   Develop silane coupling agent (ex. TESPT, GPTSI, ECETSI, etc) to improve its efficiency, to reduce the aggregation of silica and to increase the dispersion of silica in tread compound.

-   The mechanical properties testing and determination of crosslink structure by

    IR spectra analysis are necessary to verify the final properties of the compound.

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APPENDICES

Appendix A

Table A1 The stress at 300% modulus of tread compounds prepared from
NR/SBR blend (100:0 w/w) as a function of silica content.

Silica : Carbon black	Stress @ 300 %						
Ratio	Sample no.						Avg.
	1	2	3	4	5	6	
1 : 0							
4 : 1	10.4	9.6	9.5	8.3	10.5	9.6	9.7
3 : 2	11.1	11.8	11.0	10.9	10.5	10.7	11.0
2 : 3	13.3	14.2	15.6	13.3	12.5	13.8	13.8
1 : 4	15.6	16.2	18.1	15.4	16.8	18.2	16.7
0 : 1	18.7	19.4	18.7	17.2	16.6	18.7	18.2

Table A2 The stress at 300% modulus of tread compounds prepared from
NR/SBR blend (80:20 w/w) as a function of silica content.

Silica : Carbon black	Stress @ 300 %						
Ratio	Sample no.						Avg.
	1	2	3	4	5	6	
1 : 0	5.4	5.3	5.7	5.7	5.2	5.9	5.5
4 : 1	6.7	5.8	6.3	6.4	6.1	7.7	6.5
3 : 2	9.3	9.0	9.0	8.0	12.5	9.0	9.5
2 : 3	11.0	10.8	10.6	10.9	10.7	11.6	10.9
1 : 4	11.7	12.4	10.1	10.8	11.5	10.3	10.9
0 : 1	12.0	9.7	10.9	11.7	11.7	9.9	11.0

Table A3 The stress at 300% modulus of tread compounds prepared from
NR/SBR blend (70:30 w/w) as a function of silica content.

Silica : Carbon black	Stress @ 300 %						
Ratio	Sample no.						Avg.
	1	2	3	4	5	6	
1 : 0	7.1	7.4	6.1	6.1	6.6	5.7	6.7
4 : 1	7.2	6.7	8.7	7.2	8	6.2	7.3
3 : 2	6.4	6.2	6.4	6.5	7.2	7.2	6.7
2 : 3	9.5	8.6	10.3	10.7	8.7	10.9	9.8
1 : 4	12.6	12.7	12.8	11.6	10.8	13.4	12.3
0 : 1	12.2	11.3	12.0	10.9	12.6	12.8	12.0

Table A4 The stress at 300% modulus of tread compounds prepared from
NR/SBR blend (60:40 w/w) as a function of silica content.

Silica : Carbon black Ratio	Stress @ 300 %						
	Sample no.						Avg.
	1	2	3	4	5	6	
1 : 0	6.8	6.8	6.2	6.6	6.6	6.1	6.5
4 : 1	8.9	8.5	8.7	8.1	9.0	9.1	8.7
3 : 2	9.1	9.5	9.8	8.6	9.6	9.0	9.3
2 : 3	10.8	10.0	8.6	9.6	10.2	10.1	9.9
1 : 4	12.3	12.2	10.8	10.6	12.2	11.8	11.6
0 : 1	10.5	12.9	12.2	13.1	11.1	13.5	12.2

Table A5 The stress at 300% modulus of tread compounds prepared from
NR/SBR blend (30:70 w/w) as a function of silica content.

Silica : Carbon black Ratio	Stress @ 300 %						
	Sample no.						Avg.
	1	2	3	4	5	6	
1 : 0	6.6	6.6	6.7	6.7	6.1	6.5	6.5
4 : 1	5.7	6.8	7.3	7.1	6.5	6.4	6.6
3 : 2	8.1	7.6	8.2	9.3	8.3	7.8	8.2
2 : 3	8.4	8.2	9.3	7.9	8.8	8.5	8.5
1 : 4	7.2	9.9	9.4	10.5	9.9	9.5	9.4
0 : 1	9.0	8.1	10.3	9.6	9.4	9.5	9.3

Table A6 The stress at 300% modulus of tread compounds prepared from
NR/SBR blend (20:80 w/w) as a function of silica content.

Silica : Carbon black Ratio	Stress @ 300 %						
	Sample no.						Avg.
	1	2	3	4	5	6	
1 : 0	4.7	5.2	4.7	5.2	4.8	5.1	4.9
4 : 1	6.3	6.5	6.2	6.4	6.9	7.1	6.6
3 : 2	7.6	7.5	6.6	6.5	6.8	8.2	7.2
2 : 3	6.5	7.1	6.7	7.3	7.4	9.0	7.3
1 : 4	10.8	9.0	9.5	8.3	9.8	10.1	9.6
0 : 1	8.2	10.0	10.5	10.0	9.5	8.9	9.5

Appendix B

Table B1 Loss volume of tread compounds prepared from NR/SBR blend
(100:0 w/w) as a function of silica content.

Silica : Carbon black Ratio	Loss volume (cm^3) /1000 rounds					Avg.
	Test run (round)					
	1000	2000	3000	4000	5000	
1 : 0	0.02	0.03	0.01	0.02	0.02	0.02
4 : 1	0.35	0.33	0.35	0.31	0.33	0.33
3 : 2	0.29	0.27	0.29	0.26	0.27	0.28
2 : 3	0.04	0.05	0.04	0.03	0.05	0.04
1 : 4	0.05	0.06	0.06	0.05	0.06	0.06
0 : 1	0.03	0.04	0.04	0.02	0.04	0.03

Table B2 Loss volume of tread compounds prepared from NR/SBR blend
(80:20 w/w) as a function of silica content.

Silica : Carbon black Ratio	Loss volume (cm^3) /1000 rounds					Avg.
	Test run (round)					
	1000	2000	3000	4000	5000	
1 : 0	0.43	0.46	0.43	0.45	0.45	0.44
4 : 1	0.33	0.32	0.24	0.23	0.35	0.29
3 : 2	0.06	0.03	0.04	0.05	0.02	0.04
2 : 3	0.06	0.04	0.06	0.03	0.08	0.05
1 : 4	0.03	0.04	0.04	0.06	0.04	0.04
0 : 1	0.03	0.06	0.03	0.05	0.02	0.04

Table B3 Loss volume of tread compounds prepared from NR/SBR blend
(70:30 w/w) as a function of silica content.

Silica : Carbon black Ratio	Loss volume (cm^3) /1000 rounds					Avg.
	Test run (round)					
	1000	2000	3000	4000	5000	
1 : 0	0.39	0.42	0.44	0.42	0.42	0.42
4 : 1	0.34	0.38	0.36	0.39	0.41	0.38
3 : 2	0.36	0.38	0.37	0.38	0.37	0.37
2 : 3	0.27	0.25	0.27	0.25	0.23	0.25
1 : 4	0.16	0.14	0.22	0.09	0.15	0.15
0 : 1	0.13	0.14	0.13	0.15	0.14	0.14

Table B4 Loss volume of tread compounds prepared from NR/SBR blend (60:40 w/w) as a function of silica content.

Silica : Carbon black Ratio	Loss volume (cm^3) /1000 rounds					Avg.
	Test run (round)					
	1000	2000	3000	4000	5000	
1 : 0	0.38	0.46	0.34	0.39	0.44	0.40
4 : 1	0.36	0.40	0.37	0.35	0.41	0.38
3 : 2	0.33	0.30	0.34	0.32	0.30	0.32
2 : 3	0.21	0.25	0.22	0.24	0.25	0.23
1 : 4	0.10	0.13	0.15	0.11	0.13	0.12
0 : 1	0.13	0.13	0.15	0.11	0.15	0.13

Table B5 Loss volume of tread compounds prepared from NR/SBR blend (30:70 w/w) as a function of silica content.

Silica : Carbon black Ratio	Loss volume (cm^3) /1000 rounds					Avg.
	Test run (round)					
	1000	2000	3000	4000	5000	
1 : 0	0.38	0.33	0.38	0.40	0.37	0.38
4 : 1	0.34	0.33	0.35	0.32	0.34	0.34
3 : 2	0.23	0.29	0.25	0.27	0.33	0.27
2 : 3	0.27	0.25	0.26	0.25	0.22	0.25
1 : 4	0.23	0.25	0.24	0.24	0.22	0.24
0 : 1	0.20	0.16	0.20	0.21	0.24	0.20

Table B6 Loss volume of tread compounds prepared from NR/SBR blend (20:80 w/w) as a function of silica content.

Silica : Carbon black Ratio	Loss volume (cm^3) /1000 rounds					Avg.
	Test run (round)					
	1000	2000	3000	4000	5000	
1 : 0	0.45	0.48	0.46	0.48	0.45	0.46
4 : 1	0.36	0.39	0.36	0.39	0.39	0.38
3 : 2	0.29	0.31	0.34	0.29	0.32	0.31
2 : 3	0.31	0.24	0.26	0.23	0.24	0.26
1 : 4	0.20	0.22	0.21	0.22	0.19	0.21
0 : 1	0.15	0.17	0.14	0.13	0.15	0.15

Appendix C

Table C1 Heat build up of tread compounds prepared from NR/SBR blend
(100:0 w/w) as a function of silica content.

Silica : Carbon black Ratio	Temperature increase (^{o}C)			Avg.
	Sample no.			
	1	2	3	
1 : 0	10.5	12.0	12.4	11.6
4 : 1	12.3	14.6	10.6	12.5
3 : 2	16.4	13.0	11.8	13.7
2 : 3	16.8	13.2	14.5	14.8
1 : 4	14.4	14.5	16.5	15.1
0 : 1	14.6	15.0	18.7	16.1

Table C2 Heat build up of tread compounds prepared from NR/SBR blend
(80:20 w/w) as a function of silica content.

Silica : Carbon black Ratio	Temperature increase (^{o}C)			Avg.
	Sample no.			
	1	2	3	
1 : 0	15.6	19.4	20.5	18.5
4 : 1	20.2	19.9	19.3	19.8
3 : 2	19.9	21.3	20.4	20.5
2 : 3	22.5	21.6	18.9	21.0
1 : 4	20.3	23.0	19.7	21.0
0 : 1	21.1	19.2	23.7	21.3

Table C3 Heat build up of tread compounds prepared from NR/SBR blend
(70:30 w/w) as a function of silica content.

Silica : Carbon black Ratio	Temperature increase (^{o}C)			Avg.
	Sample no.			
	1	2	3	
1 : 0	20.3	23.2	21.3	21.6
4 : 1	23.4	19.9	22.7	22
3 : 2	26.9	19	23.4	23.1
2 : 3	24.6	23.7	22.2	23.5
1 : 4	26.4	21.9	25.7	24.7
0 : 1	28.8	23.4	23.3	25.2

Table C4 Heat build up of tread compounds prepared from NR/SBR blend
(60:40 w/w) as a function of silica content.

Silica : Carbon black Ratio	Temperature increase (^{o}C)			
	Sample no.			Avg.
	1	2	3	
1 : 0	13.3	27.3	25.1	21.9
4 : 1	21.6	22.1	25.2	22.1
3 : 2	23.3	25.0	24.0	24.0
2 : 3	20	27.9	23.8	23.9
1 : 4	27.7	25.3	21.4	24.8
0 : 1	25.5	20.8	30.3	25.5

Table C5 Heat build up of tread compounds prepared from NR/SBR blend
(30:70 w/w) as a function of silica content.

Silica : Carbon black Ratio	Temperature increase (^{o}C)			
	Sample no.			Avg.
	1	2	3	
1 : 0	23.7	25.5	29.7	26.3
4 : 1	29.1	25.7	24.7	26.5
3 : 2	26.1	27.8	25.6	26.5
2 : 3	28.2	27.8	26.8	27.6
1 : 4	30.1	28.6	26.3	28.3
0 : 1	26.4	28.9	29	28.1

Table C6 Heat build up of tread compounds prepared from NR/SBR blend
(20:80 w/w) as a function of silica content.

Silica : Carbon black Ratio	Temperature increase (^{o}C)			
	Sample no.			Avg.
	1	2	3	
1 : 0	35.5	29.5	27.1	30.7
4 : 1	32.1	32.8	28.7	31.2
3 : 2	33.8	29.5	33.3	32.2
2 : 3	29.3	36.2	33.1	32.9
1 : 4	32.8	33.4	29.5	31.9
0 : 1	34.1	30.7	33.9	32.9

Table D1 % Resilience of tread compounds prepared from NR/SBR blend
(100:0 w/w) as a function of silica content.

Silica : Carbon black Ratio	% Resilience			
	Constant of 3 consecutive impacts			Avg.
	Sample no.			
	1	2	3	
1 : 0	68.0	65.2	67.0	66.7
4 : 1	63.3	70	63.8	65.7
3 : 2	64.7	66.3	64.2	65.1
2 : 3	64.4	62.8	67.2	64.8
1 : 4	64.2	62.8	62.2	63.2
0 : 1	62.4	62.4	62.8	62.5

Table D2 % Resilience of tread compounds prepared from NR/SBR blend
(80:20 w/w) as a function of silica content.

Silica : Carbon black Ratio	% Resilience			
	Constant of 3 consecutive impacts			Avg.
	Sample no.			
	1	2	3	
1 : 0	67.5	51.8	52.3	57.2
4 : 1	55.6	55.7	57.6	56.3
3 : 2	52.3	56.4	57.2	55.3
2 : 3	54.7	55.3	58.6	56.2
1 : 4	53.9	58.2	53.8	55.3
0 : 1	53.8	54.3	57.2	55.1

Table D3 % Resilience of tread compounds prepared from NR/SBR blend
(70:30 w/w) as a function of silica content.

Silica : Carbon black Ratio	% Resilience			
	Constant of 3 consecutive impacts			Avg.
	Sample no.			
	1	2	3	
1 : 0	64.5	50.4	51	55.3
4 : 1	55.4	55.9	56.9	56.1
3 : 2	52.2	61.0	51.8	55.0
2 : 3	54.8	55.4	54.3	54.8
1 : 4	52.6	51.8	51.4	51.9
0 : 1	57.6	48.8	49	51.8

Table D4 % Resilience of tread compounds prepared from NR/SBR blend (60:40 w/w) as a function of silica content.

Silica : Carbon black Ratio	% Resilience			Avg.
	Constant of 3 consecutive impacts			
	Sample no.			
	1	2	3	
1 : 0	58.9	50.9	50.4	53.4
4 : 1	51.8	52.9	51.8	52.2
3 : 2	52.8	52.8	54.3	53.3
2 : 3	53.3	53.3	51.8	52.8
1 : 4	51.8	52.2	53.1	52.4
0 : 1	49.0	48.8	50.4	49.4

Table D5 % Resilience of tread compounds prepared from NR/SBR blend (30:70 w/w) as a function of silica content.

Silica : Carbon black Ratio	% Resilience			Avg.
	Constant of 3 consecutive impacts			
	Sample no.			
	1	2	3	
1 : 0	48.7	47.6	46.4	47.6
4 : 1	46.1	46.8	46.8	46.4
3 : 2	44.9	43.9	44.9	44.6
2 : 3	44.9	42.8	45.3	44.3
1 : 4	44.3	43.3	44.9	44.2
0 : 1	41.8	42.5	43.0	42.4

Table D6 % Resilience of tread compounds prepared from NR/SBR blend (20:80 w/w) as a function of silica content.

Silica : Carbon black Ratio	% Resilience			Avg.
	Constant of 3 consecutive impacts			
	Sample no.			
	1	2	3	
1 : 0	47.4	47.9	49.0	48.1
4 : 1	47.4	47.6	46.4	47.1
3 : 2	46.8	45.8	44.6	45.7
2 : 3	44.9	45.3	45.3	45.2
1 : 4	43.5	44.4	44.7	44.2
0 : 1	44.4	44.9	42.1	43.8

Appendix E

Table E1 Maximum strength of tread compounds prepared from NR/SBR blend
(100:0 w/w) as a function of silica content.

Silica : Carbon black Ratio	Maximum Strength (N/mm)						Avg.
	Sample no.						
	1	2	3	4	5	6	
1 : 0	62.9	62.0	61.3	65.2	63.0	63.2	62.9
4 : 1	-	-	-	103.9	114.8	100.4	108.4
3 : 2	100.8	97.2	103.7	98.5	106.9	88.5	99.3
2 : 3	140.8	107.3	104.7	107.8	100.6	75.0	106.0
1 : 4	100.8	54.5	78.2	81.2	66.9	112.5	82.3
0 : 1	54.9	51.4	84.4	68.3	57.6	86.1	67.1

Table E2 Maximum strength of tread compounds prepared from NR/SBR blend
(80:20 w/w) as a function of silica content.

Silica : Carbon black Ratio	Maximum Strength (N/mm)						Avg.
	Sample no.						
	1	2	3	4	5	6	
1 : 0	83.4	90.2	83.3	85.1	102.6	98.4	90.5
4 : 1	110.2	111.8	112.6	110.4	108.5	106.5	110.0
3 : 2	105.3	112.8	97.8	114.0	125.3	100.2	109.2
2 : 3	97.8	122.8	113.3	68.8	124.3	107.7	105.8
1 : 4	82.6	84.8	114.4	128.8	124.8	128.1	110.6
0 : 1	84.4	89.2	133.0	118.6	124.3	74.2	103.9

Table E3 Maximum strength of tread compounds prepared from NR/SBR blend
(70:30 w/w) as a function of silica content.

Silica : Carbon black Ratio	Maximum Strength (N/mm)						Avg.
	Sample no.						
	1	2	3	4	5	6	
1 : 0	72.4	107.9	95.8	91.8	76.0	62.1	84.3
4 : 1	104.5	109	110.3	102.5	109.3	86.8	103.7
3 : 2	98.2	95.2	98.5	99.3	97.4	95.2	97.3
2 : 3	93.5	69.7	-	107.5	-	68.6	84.8
1 : 4	106.1	57.6	82.0	107.0	115.0	104.4	95.4
0 : 1	67.5	72.8	65.1	94.4	109.5	57.8	77.8

Table E4 Maximum strength of tread compounds prepared from NR/SBR blend
(60:40 w/w) as a function of silica content.

Silica : Carbon black Ratio	Maximum Strength (N/mm)						Avg.
	Sample no.						
	1	2	3	4	5	6	
1 : 0	77.9	71.9	74.5	71.6	80.7	69.9	74.4
4 : 1	69.8	67.0	93.3	94.2	107.2	110.6	90.4
3 : 2	56.7	53.9	108.7	61.7	58.3	66.4	67.6
2 : 3	61.9	56.1	57.6	55.3	58.2	64.3	58.9
1 : 4	64.0	59.7	54.7	59.5	62.6	60.7	60.2
0 : 1	58.4	60.5	53.0	58.7	59.6	62.5	58.8

Table E5 Maximum strength of tread compounds prepared from NR/SBR blend
(30:70 w/w) as a function of silica content.

Silica : Carbon black Ratio	Maximum Strength (N/mm)						Avg.
	Sample no.						
	1	2	3	4	5	6	
1 : 0	52.9	50.6	58.8	56.3	53.4	55.8	54.6
4 : 1	59.9	54.3	59.2	55.8	55.4	55.2	56.6
3 : 2	50.9	57.1	26.8	61.3	52.5	57.7	51.0
2 : 3	56.5	57.9	63.7	59.8	57.6	48.2	57.3
1 : 4	54.8	37.0	58.0	59.7	61.3	61.2	55.3
0 : 1	58.9	58.9	56.8	56.0	59.5	52.9	57.2

Table E6 Maximum strength of tread compounds prepared from NR/SBR blend
(20:80 w/w) as a function of silica content.

Silica : Carbon black Ratio	Maximum Strength (N/mm)						Avg.
	Sample no.						
	1	2	3	4	5	6	
1 : 0	56.0	55.2	55.4	57.4	57.1	58.1	56.7
4 : 1	55.3	57.8	60.1	58.5	64.8	60.8	59.5
3 : 2	59.1	61.2	61.6	58.4	55.9	60.6	59.5
2 : 3	63.7	54.6	72.5	63.8	58.2	64.6	62.9
1 : 4	61.6	66.4	64.1	60.1	62.0	58.6	62.1
0 : 1	58.4	53.6	57.9	67.8	55.7	60.8	59.0

Appendix F

Table F1 Maximum torque and TC90 of tread compounds prepared from
NR/SBR blend (100:0, 80:20, 70:30, 60:40, 30:70 and 20:80 w/w)
as a function of silica content.

Sample code	NR: SBR ratio	Silica : Carbon black ratio	Max. Torq.	TC90
1/1	100 : 0	1 : 0	75.0	7.6
1/2	100 : 0	4 : 1	78.5	7.8
1/3	100 : 0	3 : 2	85.4	6.2
1/4	100 : 0	2 : 3	78.4	6.2
1/5	100 : 0	1 : 4	86.1	5.1
1/6	100 : 0	0 : 1	87.2	5.0
2/1	80 : 20	1 : 0	68.5	12.6
2/2	80 : 20	4 : 1	75.0	10.0
2/3	80 : 20	3 : 2	81.2	7.7
2/4	80 : 20	2 : 3	80.0	7.0
2/5	80 : 20	1 : 4	79.7	6.2
2/6	80 : 20	0 : 1	80.2	5.8
3/1	70 : 30	1 : 0	71.3	13.0
3/2	70 : 30	4 : 1	79.9	8.9
3/3	70 : 30	3 : 2	77.0	8.2
3/4	70 : 30	2 : 3	79.3	6.4
3/5	70 : 30	1 : 4	80.4	6.6
3/6	70 : 30	0 : 1	81.4	6.3
4/1	60 : 40	1 : 0	72.5	10.3
4/2	60 : 40	4 : 1	75.5	7.1
4/3	60 : 40	3 : 2	78.0	7.1
4/4	60 : 40	2 : 3	79.9	6.6
4/5	60 : 40	1 : 4	77.6	5.6
4/6	60 : 40	0 : 1	81.2	6.4
5/1	30 : 70	1 : 0	75.1	9.1
5/2	30 : 70	4 : 1	75.7	8.4
5/3	30 : 70	3 : 2	81.8	8.2
5/4	30 : 70	2 : 3	80.0	8.0
5/5	30 : 70	1 : 4	78.1	8.6
5/6	30 : 70	0 : 1	87.3	8.1
6/1	20 : 80	1 : 0	75.7	15.4
6/2	20 : 80	4 : 1	78.7	12.9
6/3	20 : 80	3 : 2	78.3	11.1
6/4	20 : 80	2 : 3	80.6	10.1
6/5	20 : 80	1 : 4	74.8	10.5
6/6	20 : 80	0 : 1	84.0	9.3

Appendix G

Table G1 Hardness of tread compounds prepared from NR/SBR blend
(100:0 w/w) as a function of silica content.

Silica : Carbon black Ratio	Hardness			
	Sample			Avg.
	1	2	3	
1 : 0	70.1	72.2	69.6	70.6
4 : 1	59.6	60.1	59.6	59.8
3 : 2	60.4	59.0	61.0	60.1
2 : 3	60.3	62.1	61.2	61.2
1 : 4	61.4	60.5	61.6	61.2
0 : 1	61.2	61.0	60.4	60.9

Table G2 Hardness of tread compounds prepared from NR/SBR blend
(80:20 w/w) as a function of silica content.

Silica : Carbon black Ratio	Hardness			
	Sample			Avg.
	1	2	3	
1 : 0	63.0	60.2	56.9	60.0
4 : 1	60.3	59.7	60.6	60.2
3 : 2	60.5	60.2	60.9	60.5
2 : 3	60.9	60.0	59.7	60.2
1 : 4	61.9	59.8	62.6	61.4
0 : 1	61.0	61.4	62.8	61.7

Table G3 Hardness of tread compounds prepared from NR/SBR blend
(70:30 w/w) as a function of silica content.

Silica : Carbon black Ratio	Hardness			
	Sample			Avg.
	1	2	3	
1 : 0	58.4	57.1	59.1	58.2
4 : 1	59.3	61.1	58.8	59.7
3 : 2	56.4	55.3	55.7	55.8
2 : 3	60.1	60.2	60.4	60.2
1 : 4	60.7	60.1	60.9	60.6
0 : 1	63.0	61.7	62.3	62.3

Table G4 Hardness of tread compounds prepared from NR/SBR blend
(60:40 w/w) as a function of silica content.

Silica : Carbon black Ratio	Hardness			
	Sample			Avg.
	1	2	3	
1 : 0	59.0	56.8	61.2	59.0
4 : 1	59.8	59.6	59.6	59.7
3 : 2	59.2	58.5	60.0	59.2
2 : 3	58.9	60.5	57.9	59.1
1 : 4	63.0	57.7	58.9	59.9
0 : 1	57.9	60.6	59.9	59.5

Table G5 Hardness of tread compounds prepared from NR/SBR blend
(30:70 w/w) as a function of silica content.

Silica : Carbon black Ratio	Hardness			
	Sample			Avg.
	1	2	3	
1 : 0	61.4	-	61.9	61.6
4 : 1	60.3	62.5	60.3	61.0
3 : 2	60.9	60.3	61.2	60.8
2 : 3	60.9	61.0	60.6	60.8
1 : 4	59.8	59.9	63.1	60.9
0 : 1	-	60.0	62.7	61.3

Table G6 Hardness of tread compounds prepared from NR/SBR blend
(20:80 w/w) as a function of silica content.

Silica : Carbon black Ratio	Hardness			
	Sample			Avg.
	1	2	3	
1 : 0	58.2	57.7	57.7	57.9
4 : 1	60.2	56.3	61.0	59.2
3 : 2	58.7	60.1	59.5	59.4
2 : 3	63.9	61.1	59.7	61.6
1 : 4	63.4	62.8	60.9	62.4
0 : 1	63.4	64.0	63.7	63.7

VITAE

Mr. Prasit Youkong was born on June 26, 1975, in Chiang Mai, Thailand. He received his Bachelor of Science degree in Industrial Chemistry, Chiang Mai University, in !997. Since 2000, he has been a graduate student under the Program of Petrochemistry and Polymer Science at Chulalongkorn University and completed his Master of Science degree in 2004.