REINFORCEMENT OF NATURAL RUBBER AND EPOXIDIZED NATURAL RUBBERS WITH AMINE-TREATED SILICA

by

INDRA SURYA

Thesis submitted in fulfilment of the

requirements for the degree

of Master of Science

May 2002

DEDICATION

This work is dedicated to the persons who I love very much;

My beloved parents,	**Roslaini Nasution**
	Muhammad Akram Dalimunthe
My beloved wife,	**Yulia Kalsum**
My dearest children,	**Ikhwan Indrawan Dalimunthe (Iwa)**
	Annisa Riftah Andreani Dalimunthe (Ica)
	Muhammad Khatami Dalimunthe (Amy)
	Nurul Izza Dalimunthe (Izza)

ACKNOWLEDGEMENTS

My utmost gratitude goes to my friendly supervisor, Associate Professor Dr. Azanam S.Hashim, for his advice, guidance, and assistance both academically and personally throughout the project. My gratitude also goes to Associate Professor Dr. Poh Beng Teik, my second supervisor, for his tireless patience and efforts in correcting this manuscript word by word.

I would also want to thank the Dean of the School of Industrial Technology, Associate Professor Dr. Wan Rosli Wan Daud, and both the Deputy Dean, Associate Professor Dr. Rozman Hj. Din, and Dr. Karim Alias, and to all the administrative staff for their academic assistance. My thanks go to all lectures in the Polymer Division for their academic assistance. Thank you to all laboratory assistants for their assistance and co - operation in the laboratories, especially, Mr. Segaran a/l. N.B. Dorai, Md. Zandar Md. Saman. Thanks are especially due to Mr. Patchamuthu a/l. Ramasamy for being of tremendous helps with the high magnification electron microscopy studies.

I would like to express my sincere gratitude to all my colleagues in School of Industrial Technology for their help and advice, especially, Susantha, Hao, Puspa, Hariharan. Last but not the least, I would like to express my sincere gratitude to all my "Medan Group" colleagues; Lilis Sukeksi, Suryadiansyah/Salmah, Hamidah Harahap, Maulida Lubis, Halimah, my nephew Didi Salahuddinsyah.

Finally, I would like to express my regards to my beloved parents, Roslaini Nasution and Muhammad Akram Dalimunthe, for their love, concern and moral support. My beloved wife, Yulia Kalsum and my dearest children, Iwa, Ica, Amy and Izza, for their sacrifices and loves.

TABLE OF CONTENTS

CHAPTER 2: MATERIALS AND EXPERIMENTAL PROCEDURE 37

CHAPTER 3: RESULTS AND DISCUSSION 48

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
BS	British Standard
CV	Conventional Vulcanization
DPG	Diphenyl guanidine
EB	Elongation at break
ENR	Epoxidized Natural Rubber
EPDM	Ethylene Propylene 1,4 Hexadiene Terpolymer
EV	Efficient Vulcanization
HAF	High Abrasion Furnace
IPPD	N-Isopropyl-N'-phenyl-p-phenylene diamine
MBS	2-(Morpholinothio) benzothiazolesulfenamide
MBTS	Mercapto benzothiazolyl disulfide
MDR	Moving Die Rheometer
Mmax	the rheometer maximum torque
Mmin	the rheometer minimum torque
MPa	Mega Pascal
NR	Natural Rubber
ODR	Oscilating Disk Rheometer
phr.	Parts per hundred rubber
ppi.	Pound per inch
RE	Reinforcing Efficiency
rev.	Revolution

SBR	Styrene Butadiene Rubber
Semi-EV	Semi Efficient Vulcanization
SMR	Standard Malaysian Rubber
TEOS	Tetraethyl orthosilicate
TESPT	Bis(3-triethoxysilylpropyl)tetrasulfide
Tg	Glass transition temperature
TS	Tensile strength
ZnO	Zinc oxide

PENGUKUHAN GETAH ASLI DAN GETAH ASLI TEREPOKSIDA DENGAN SILIKA TERAWAT AMINA

ABSTRAK

Pengkajian mengenai kesesuaian penggunaan silika terawat amina untuk pengukuhan getah-getah SMR-L, ENR 25 dan ENR 50 telah dilakukan. Silika terawat amina disediakan melalui proses perawatan amina, dimana silika normal dirawat didalam larutan butilamina dengan pH yang tertentu.

Kajian yang terperinci dilakukan untuk membandingkan kesan pengukuhan silika terawat amina dengan kesan-kesan pengukuhan daripada silika normal dengan TESPT, silika normal sahaja, dan hitam karbon keatas sifat-sifat tensil, mekanikal, dan penuaan daripada getah-getah tersebut. Silika terawat amina didapati memberikan waktu pematangan yang lebih pendek jika dibandingkan dengan silika dengan TESPT, dan silika sahaja, dan mendekati waktu pematangan vulkanisat berpengisi hitam karbon. Kajian ini pula mendapati, silika terawat amina apabila disebatikan dengan getah SMR-L, menunjukkan sifat-sifat tensil, mekanikal, dan penuaan yang lebih baik jika dibandingkan dengan pengisi-pengisi lain. Apabila disebatikan dengan getah-getah ENR, silika terawat amina menunjukkan sifat tensil, rintangan lelasan dan penuaan yang lebih baik jika dibandingkan dengan silika dengan TESPT, dan silika sahaja, dan didapati sifat-sifat diatas yang kurang baik berbanding dengan hitam karbon.

Kajian mengenai keberkesanan pengukuhan pengisi-pengisi keatas getah-getah itu menunjukkan bahawa keberkesanan yang lebih tinggi daripada silika terawat amina adalah disebabkan oleh saiz partikal yang lebih kecil dan penyebaran yang lebih merata didalam vulkanisat getah-getah itu jika dibandingkan dengan silika normal.

REINFORCEMENT OF NATURAL RUBBER AND EPOXIDIZED NATURAL RUBBERS WITH AMINE-TREATED SILICA

ABSTRACT

The feasibility study of utilising amine-treated silica on reinforcement of SMR-L, ENR 25 and ENR 50 by using semi-efficient (semi-EV) system was carried out. The amine-treated silica was prepared by treating normal silica filler in a butylamine solution with a certain pH.

An investigation was carried out to compare the reinforcement effect of amine-treated silica with that of normal silica with and without the addition of bis (triethoxysilylpropyl)tetrasulphide or TESPT, and with that of carbon black (HAF 330) on cure characteristics and properties of those rubbers. It was found that amine-treated silica gave shorter cure time than normal silica with and without the addition of TESPT, and closer cure time to carbon black.

It was also found that amine-treated silica showed better tensile strength, mechanical and ageing properties than other fillers, when compounded with SMR-L. On ENRs, amine-treated silica caused better tensile properties, abrasion and ageing resistances than normal silica with and without the addition of TESPT, and a little poorer in those properties than carbon black.

Investigation on reinforcing efficiencies of those fillers on the rubbers found that the higher reinforcing efficiency of amine-treated silica is attributed to smaller particle-size and better dispersion of amine-treated silica in the rubbers phases when compared with normal silica with and without TESPT.

1.0. INTRODUCTION.

1.1. Introduction to filler reinforcement.

Generally, the definition of filler reinforcement is the enhancement of mechanical properties, such as stiffness, tensile strength, tear and abrasion resistances, of the rubber products resulting from the incorporation of a filler.

A practical definition of reinforcement is the enhancement in service life of rubber articles. Rubber articles fail in numerous ways, one of the most important being rupture failure accelerated by fatigue processes, such as occurs during the wear of a tire tread. The enhancement in road wear resistance of tire tread resulting from the use of particulate filler in rubber is the most important example of filler reinforcement (Mullins, 1963).

1.2. Reinforcement concepts.

Fillers are usually used to enhance the mechanical properties of rubber vulcanizates such as tensile strength (TS), resistance to abrasion, tearing and flexing or cheapen the cost of product. However, fillers also affect the viscoelastic properties and stiffness of rubber compound.

Based on their reinforcing effect on rubber properties, fillers can be divided into three groups: reinforcing, semi, and non-reinforcing fillers. Reinforcing filler is used to improve tensile strength, modulus, resistance to abrasion, tearing and flexing. Carbon blacks and silicas are the most popular reinforcing fillers for rubbers (Bueche, 1965; Horn, 1971). Non-reinforcing filler is used to cheapen the cost of a product and improve the processability. It also increases hardness, reduces tensile and tear strengths, resistance to abrasion, and also resilience. Clays, calcium carbonate, barium sulfate, etc. are classified as non-reinforcing filler for rubbers (Horn, 1971; Thorn & Robinson, 1994).

The most important feature of rubber reinforcement by fillers is the size of the filler particles (Kraus, 1965). Based on their particle-sizes, Hepburn (1984) has classified fillers into four groups, as shown in Table 1.1.

Table 1.1. Particle-sizes for rubber reinforcement. (Hepburn, 1984).

No.	Particle-sizes	Reinforcing Effects
1	Particle > 5,000 nm	Degrade rubber
2	Particle between 1,000 - 5,000 nm	Have little effect on strength hence large volumes can be used with little degradation of rubber.
3	Particle < 1,000 nm	Reinforce
4	Particle < 100 nm	"Real reinforcing agents"

Some theories of rubber reinforcement have been accepted to elucidate the mechanism of filler reinforcement and described as follows;

(a). Hydrodynamics theories of Smallwood and Guth.

One of the most obvious changes which occurs when filler is dispersed in rubber is a stiffening, as expressed by the equation, (Guth, 1945):

$$E = Eo\,(1 + 2.5\,\phi + 1.41\,\phi^2) \qquad (1.1)$$

where:

E = Young's modulus of filled vulcanizate at low extension in the linear region.

Eo = Young's modulus of gum vulcanizate.

ϕ = Volume fraction of filler.

Equation (1.1) is suitable for non-reinforcing filler such as calcium carbonate, or clays. However, for semi - reinforcing filler (fine thermal black) the equation (1.1) fitted the data for up to volume fraction 0.3. For high reinforcing filler, this equation is not suitable, therefore, the shape factor (f) must be used and the equation is modified as follows:

$$E = Eo\,(1 + 0.67\,f\phi + 1.41\,f^2\phi^2) \qquad (1.2)$$

in which:

f = the shape factor, defined as the ratio of length over diameter of shaped particles. For examples, with carbon black type HAF, f = 6 (Boonstra, 1971). The equation gives good agreement with experimental values.

(b).Strain - amplification theory of Mullins (Boonstra, 1971).

The modulus or stiffness is related to crosslink density by the well-known formula of the kinetic theory of elasticity, in its simplest form:

$$\sigma = v\,k\,T\,(\alpha - 1/\alpha^2) \qquad (1.3)$$

where: σ = the stress / modulus

α = the extension ratio.

v = the crosslink density of rubber vulcanizate.

$k\,T$ = the Boltzmann constant and the absolute temperature.

According to the equation, the modulus or stiffness at a certain extension ratio and at a given temperature can only be increased by increasing "v" the crosslink density. The addition of a reinforcing filler increases modulus, so its effect is the same as an increase in crosslink density.

(c).Blanchard and Parkinson mechanisms.

Reinforcing fillers can cause important changes in the nature of the rubber network. These changes involve the formation of weak and strong linkages between segments and particle surface sites. It was concluded that the strong rubber - filler linkages were most important in characterising reinforcing properties. Since most of the weak linkages were broken at low strains, their effect on reinforcing properties was considered to be small. Morever, the surface character of the filler will determine the number of strong rubber - filler bonds, both high surface area and high surface activity should lead to good reinforcing effect (Dannenberg, 1975).

(d).Bueche's interparticle chain breakage mechanism.

Bueche (1965) has proposed a mechanism of stress softening and reinforcement based on the simple concept of the breakage of network chains, or their attachments to adjacent filler particles during extension. Firstly, at small elongations, the shorter chains will rupture. Since the stress on a chain before rupture is large, it contributes greatly to the stiffness (modulus). Chain broken on the first stretch will not be able to affect stiffness on the second stretch and softening (Mullins effect) will occur. The breakage of a single chain between particles causes the stiffness/the stress to be distributed which is attached to the filler particles, in another word, filler particles act as a load distributor.

(e). Molecular slippage mechanism.

Houwink (1965) has proposed a mechanism of reinforcement which explains the complex mechanical properties of reinforced vulcanizates. Under stress, the surface-adsorbed network segments move relative to the surface, accommodating the imposed stress and preventing molecular rupture. Because of this slippage process, the stress is redistributed to neighbouring molecules. The stress redistribution results in molecular alignment and increased strength. Firstly, this process absorbs strain energy and then dissipates it by slippage a frictional heat, in this way, acts as a source of hysteresis.

1.2.1. Degree of reinforcement.

The degree of reinforcement provided by fillers depends on a number of variables, the most important of which is the development of a large rubber - filler interaction. The interaction is dependent on the following factors (Boonstra, 1973);

1. The surface area of the filler particles. This is directly related to the particle size. The lower the particle-size, the higher the surface area, the higher is the degree of reinforcement. The effect of filler particle-size on rubber properties is shown in Table 1.2.
2. The chemical and physical natures of the particle surface and of the rubber. Elastomer of a polar nature such as neoprene, nitrile rubber, etc. will interact strongly with filler surface having dipole such as OH and COOH groups or chlorine atoms (Boonstra, 1973)
3. Geometrical factors, are
    a. The "structure" or shape of the filler. The particles are bound together in aggregates. This aggregation is called primary structure. Secondary structure is

the agglomeration of aggregates due to Van der Waals forces. The effect of structure on rubber properties is shown in Table 1.2.

b. The porosity of the filler. Silicas are generally more porous than carbon blacks, thus silicas give higher viscosity compounds at equal volume loading, and also will absorb accelerators, and make them less effective than a nonporous filler would (Barlow, 1988).

Table 1.2. Effect of filler particle-size and structure on rubber properties. (Bhakuni, *et al.*, 1989).

Properties	Decreasing particle-size constant structure	Increasing structure constant particle-size
Hardness	Increases	Increases
Tensile strength	Increases	Variable
Modulus	Unaffected	Increases
Elongation	Unaffected	Decreases
Resilience	Decreases	Unaffected
Dispersibility	Decreases	Increases
Green strength	Unaffected	Increases
Extrusion shrinkage and Die swell	Unaffected	Decreases

The degree of reinforcement provided by a filler relatively can be measured through its reinforcing efficiency, which in its simplest form is given by equation (Hashim, *et al.*, 1998):

$$\text{Reinforcing efficiency} = (M_{100f} - M_{100g}) / M_{100g} \qquad (1.4.)$$

in which:

M_{100f} : modulus at elongation 100% of filled vulcanizate

M_{100g} : modulus at elongation 100% of gum vulcanizate

The reinforcing efficiency also can be calculated by using the equation (1.2.) in terms of (E - Eo)/Eo.

Based on the cure characteristics data of a rubber vulcanizate, which is provided by rheograph, reinforcing efficiency can also be calculated by using equation:

$$\text{Reinforcing efficiency} = (M_f - M_g) / M_g \qquad (1.5.)$$

in which:

M_f : value of Mmax - Mmin of filled vulcanizate

M_g : value of Mmax - Mmin of gum vulcanizate

High reinforcing efficiency means high rubber - filler interaction, which is influenced by the degree of filler dispersion. Better filler dispersion would provide greater surface area for rubber - filler interaction.

The degree of dispersion of filler in the rubber phase is expressed by the equation (1.6.) (Lee, 1979; Pal & De, 1982),

$$L = \eta_r - m_r \qquad \ldots\ldots\ldots (1.6.)$$

in which:

η_r : M min,f / M min,g

m_r : M max,f / M max,g

M min,f : the minimum torque of the filled vulcanizate

M min,g : the minimum torque of the gum/unfilled vulcanizate

M max,f : the maximum torque of the filled vulcanizate

M max,g : the maximum torque of the gum/unfilled vulcanizate.

The lower the value of L at particular loading, the better is the dispersion of the filler in the rubber vulcanizate.

1.3. Silica as a reinforcing filler.

Silica can be classified, according to its nature, as natural or synthetic (Nunes, *et al.*, 2000). Natural silica is not reinforcing and has been used only to cheapen cost. The synthetic ones are reinforcing and nowadays have comparable particle-sizes to carbon blacks.

At the surface, synthetic silicas end in siloxane groups (Si - O - Si) and one of the several forms of silanol groups (Si-OH). All synthetic silicas are amorphous and have a SiOH type chemical composition. Silicas can also be classified, according to the production method, into three groups; pyrogenic silica, obtained by high temperature processes (thermal or electric), silica gel, and precipitated silica. Silica obtained by high temperature process is costly whereas silica obtained by precipitation process is cheaper and has been more frequently used as reinforcing filler.

Each particle of synthetic silica is composed of four different layers (Boonstra, *et al.*, 1975; Wason, 1987). The first one is a random polymer formed by SiO_2 units completely involved by silanol groups (second layer). Water molecules strongly hydrogen-bonded to the silanol groups form the third layer. At the outer part of the fourth layer, water physically adsorbed is found and can be removed by heating at 105 °C. Water hydrogen-bonded to silanol groups can be eliminated at temperatures in the range 105 – 200 °C. The hydrogen-bonded silanol can be progressively removed by heating at temperature in the range 200 - 600 °C. The isolated silanol groups are thermally very stable, their loss coinciding with slow silica sintering after several hours of heat treatment at 1000 °C.

Addition of synthetic silica to some polymers results in changes in their mechanical and rheological properties, which are related to particle-size and density of silanol groups at its surface (Boonstra, *et al.*, 1975).

1.3.1. Introduction to silica reinforcement.

Besides carbon blacks, silicas of varying forms and particles-sizes have been widely used as reinforcing fillers in rubber industry today. In general, the properties of silica-reinforced rubbers are usually inferior to those of carbon blacks, even when they are of comparable size (Pinter & Mc.Gill, 1978). This is attributed to apparent dissimilarity of surface chemistry of both of them. Each type of filler produces useful rubber properties as a result of its specific surface chemistry. However, due to the polar nature and relatively inert nature of its surface, silica provides a unique combination of tear strength, abrasion and ageing resistances, and also adhesion properties (Wagner, 1981; Fetterman, 1986).

The main application of silica is in products where black colour is not a requirement e.g. shoe soles (Davies, 1994). It is also used, in combination with carbon black, in chipping and cut-resistance tyres for earthmovers and mining vehicles.

In order to use silica as a reinforcing agent effectively in the rubber industry, two basic features associated with silica in rubber must first be well understood. Those features are the influence of silica on rubber vulcanization, and the silica - rubber interaction.

1.3.1.1. The influence of silica on rubber vulcanization.

Due to the presence of numerous silanol groups on its surface, silica is a highly polar material and can readily interact with zinc oxide during curing. Figure 1.1. illustrates how silica interacts with stearic acid solubilized zinc. The silica bound zinc unable to activate the accelerator. Consequently, zinc activity is reduced and the sulphur reaction is retarded.

$$ZnO + 2\,C_{17}H_{35}COOH \longrightarrow Zn(OCOC_{17}H_{35})_2 + H_2O$$

Zinc oxide Stearic acid Stearic acid solubilized zinc Water

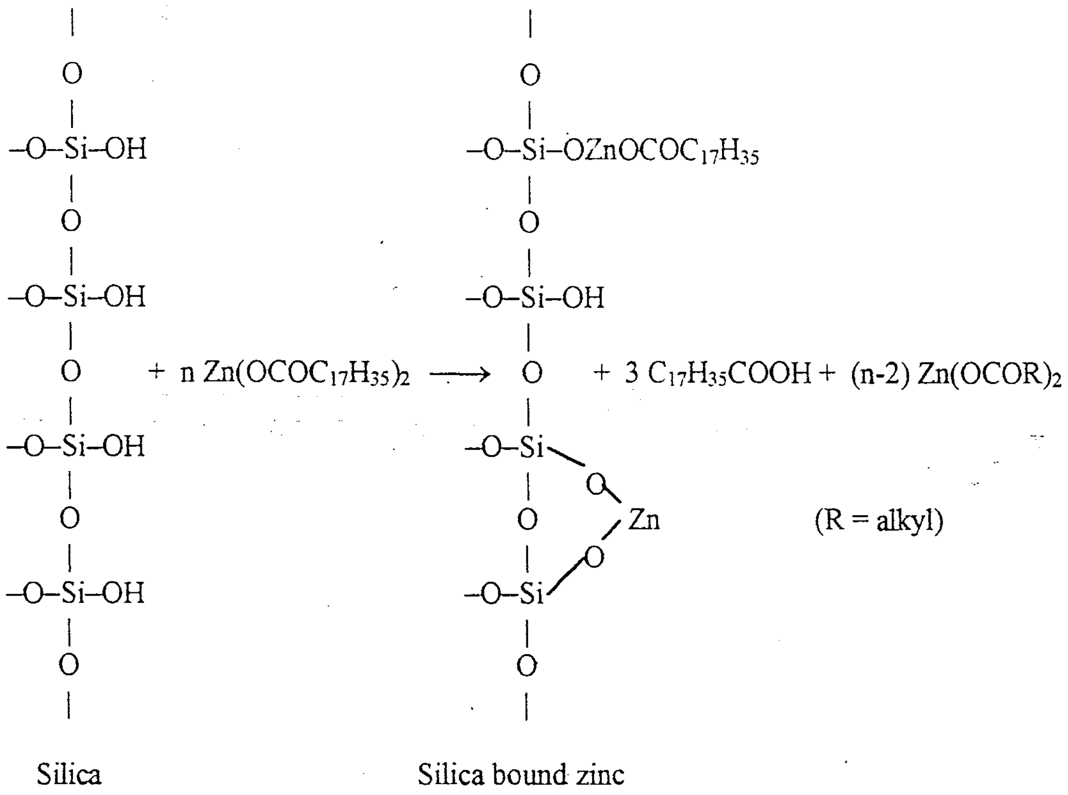


Figure 1.1. Soluble zinc/silica reaction (Mukhopadhyay & De, 1979).

Studying the influence of silica on cure characteristics of rubbers, Fetterman (1973, 1984, 1986) concluded that the effect upon cure retardation is directly proportional to the total surface area of silica present and the functionality of sulfur is dependent on both the particle-size and the total content of silica. Other workers (Dannenberg, 1981; Wagner, 1981) have reported similar observations.

In order to understand better the practical aspects of using silica in rubber reinforcement, it is important to review some basic features that are associated with silica in rubber as illustrated in Table 1.3.

Table 1.3. Effect of Hi - Sils (silicas) on rubber properties without Adjustments. (Wagner, 1981).

Hi-Sil^R EP (HS-400), phr.	20	40	60	80	--	--	--
Hi-Sil 233 (HS-200), phr.	--	--	--	--	20	40	60
ML-4 (100 °C)	14	17	20	27	16	32	91
ODR at 150 °C							
Scorch, min.	2.5	2.5	3.5	9.0	3.0	4.5	5.5
90% Cure, min.	8.0	9.0	10.0	15.0	9.0	19.0	41.0
300% Modulus, psi	590	840	1100	1310	580	610	710
Tensile strength, psi	3350	3260	3000	2840	3640	3480	3200
Elongation, %	590	570	540	500	640	680	600
Hardness (A)	50	60	65	70	55	65	78
Tear (Die A), ppi	260	360	460	500	330	510	480
Goodrich Heat Build-up, °C	11	12	18	52	13	43	57

Formulation - SMR-L, 100; Hi-Sil as indicated; ZnO, 5; stearic acid, 1; oil, 10; antioxidant, 3; wax, 1.5; sulphur, 2.5; MBTS, 0.8; DPG, 1.25.

From the data shown, it can be observed that cure time increases as the loading increases. The trend becomes more pronounced with Hi-Sil 233, which is more reinforcing and greater available surface than Hi-Sil^R EP (Wagner, 1981).

According to Bachmann *et al.* (1959), the higher the surface area of the filler, the greater is the power in absorbing accelerator. This absorption may be due to the existence of pores in the individual particles, or even of inter-particle capillaries. Generally, the pores are too small to allow rubber molecules to penetrate, and consequently do not contribute to reinforcement.

In order to use silica in a rubber recipe, the cure retardation phenomenon must be recognized and overcome. Adjustment of the curative system is a requirement, because besides the type of rubbers, curative system also affects the cure characteristics. This can be done either by increasing accelerator, addition of glycol or amine, or both (Fetterman, 1986). Amine, being one of accelerator activators is an alkaline substance, which will increase the pH of rubber compound and increase the cure rate (Long, 1985), while one slight disadvantage of using glycol is a reduction in the scorch time (Stephens, 1973).

1.3.1.2. The silica - rubber interaction.

Carbon black will react with sulfur during vulcanization and form sulfur bonds that link the rubber chains and also tie the carbon black on the rubber. This is filler - rubber crosslinking, another type of crosslink to rubber system, and defined as coupling bonds (Fetterman, 1984, 1986).

In marked contrast to the hydrocarbon functionality of carbon black, silica does not react with sulfur, and due to its hydrophilic silanol groups that are relatively incompatible with hydrocarbon rubbers, such as NR, thus, coupling bonds will not be formed.

1.3.2. Silica reinforcement on Natural Rubber (NR).

The surface properties of silica cause several difficulties in using it as reinforcing filler, particularly in hydrocarbon rubbers such as NR, SBR. The surface of silica is highly polar and hydrophilic due to the presence of numerous silanol groups. These silanol groups are relatively incompatible with NR, and interaction between them is weak. On the other hand, the silica particles tend to interact with each other to form aggregates. Since the silica - NR interaction is weaker than the silica-silica interaction; the results are the formation of large agglomerates, poor dispersion of silica.

Due to the nature of its surface properties, silica has a low level of surface activity for rubber bonding which results in small amounts of effectively immobilized rubber. Because of this factor, a silica reinforced NR has a poorer modulus than a carbon black-reinforced one.

Table 1.4. Comparison of black and silica-filled vulcanizates* of Natural Rubber. (Gelling, 1986).

Filler Properties	Black	Silica
Hardness (IRHD)	65	69
Modulus at 300% (MPa)	11.9	5.8
Tensile strength (MPa)	29.4	23.2
Elongation at break (%)	495	720
Akron abrasion (mm^3/500 rev.)	21	63
Compression set (%)	18	32
Ring fatigue (0-100%)Kcs.	70	51

* 50 phr. silica or N330 black in semi-EV formulation (S 1.5 phr. / MBS 1.5 phr.) cured to optimum at 150 °C.

Studying the effect of carbon black and silica on the properties of NR, as illustrated in Table 1.4. Gelling (1986) found that due to the dissimilarity of the surface chemistry of silica and carbon black, marked differences in NR vulcanizate properties, such as modulus and mechanical properties were observed. Poorer modulus and abrasion resistance of the silica-reinforced NR seem to be ascribed to a factor of poorer surface activity.

Modulus is a well-recognized criterion of filler reinforcement. High modulus performance of filled vulcanizates results in high rupture energy. Compared to carbon black, generally, silica reinforced rubbers have poorer modulus, even when they are of comparable size (Pinter & Mc. Gill, 1978). This means that silica has lower reinforcing efficiency than carbon black. Puspa (1999), as illustrated in Table 1.5 found that due to its lower reinforcing efficiency, silica-filled SBR vulcanizate gives poorer tensile and mechanical properties than carbon black. She concluded that due to the dissimilarity of their surface chemistry, silica has different reinforcing effect than carbon black. The lower reinforcing effect of silica is attributed to the weaker bonds and interaction of silica with SBR, which resulted in difficult and poorer dispersion of silica in the SBR phases.

Table 1.5. Tensile properties of filled-vulcanizates* of Styrene Butadiene Rubber. Puspa (1999).

Filler Properties	Silica (Vulcasil S)	Carbon black (HAF 330)
Tensile properties		
M100, MPa	0.61	0.84
Tensile strength, MPa	5.46	13.33
Elongation at break, %	942	686
Mechanical properties		
Tear strength, N/mm	42	48
Hardness, Shore A	42	65
Abrasion, cm^3/1000 rev.	0.72	0.55
Reinforcing efficiency, RE	0.36	0.87
Degree of dispersion, L	2.245	0.155

*Recipe: 100.0 phr. SBR, 4.0 phr. Zinc oxide, 2.0 phr. Stearic acid, 1.5 phr. IPPD, 1.0 phr. CBS, 2.0 phr. Sulfur, 30.0 phr. Filler.

In order to overcome these deficiencies of silica, coupling agents are used with silica in the reinforcement of hydrocarbon rubbers. The most efficient one presently known is organosilane (Plueddemann, 1982).

1.3.2.1. Organosilanes as coupling agents.

Organosilanes are utilized to improve silica - rubber interaction of the silica-filled rubbers and consequently enhance the reinforcing effect of the silica (Gelling & Porter, 1988). Organosilanes are reactive additives, and usually utilized in a small quantity, less than 2 phr. (Dannenberg, 1981; Hewitt, 1981; Ismail, 2000). The organosilanes will modify the surface of silica (Lautenschlaenger & Edward, 1980). The modified silica provides a chemically active surface that can participate in vulcanization, providing coupling bonds between organosilane and both the silica and the rubber phases (Ranney & Pagano, 1971; Wagner, 1974). There is much evidence confirming the existence of such bonds (Gent, 1974; Goerl, 1997). In all these cases marked improvement in rubber properties was noted, as illustrated in Table 1.6 (Wagner, 1971; Fetterman, 1973; Wagner, 1976; Dannenberg, 1981; Nasir *et al.*, 1988; Nasir *et al.*, 1989).

Table 1.6. Effect of coupling agent A189* addition on properties of silica-filled Natural Rubber compound (50 phr.) (Dannenberg, 1981)

	Precipitated silica (control)	Precipitated silica (1.0 phr A189)	Carbon black (N285)
t_{90} (min.)	22	16.5	13.3
300% modulus (MPa)	4.6	9.7	23.1
Tensile strength (MPa)	28.2	33.2	28.8
Elongation (%)	700	640	400
Shore hardness (A)	65	65	73
Tear, Die C (N/mm)	69	96	71
Set at break (%)	50	50	30
Goodrich flexometer, ΔT (C)	36.1	19.4	21.7
Permanent set (%)	23	8.4	6.2

*A189 — Union Carbide, Inc., (δ - mercaptopropyltrimethoxysilane)

Observing the data in Table 1.4, there is a significant improvement in tensile, tear and modulus by the addition of mercaptosilane (A189). Compared to N285 carbon black compound, the silica with A189 compound had higher tensile and tear strengths, but with a substantially lower modulus value. According to Dannenberg (1981), this remarkable improvement in properties can be attributed to the ability of the organosilane to correct a number of inherent deficiencies of silica including,

1. the cure retarding effect of acidic silanol groups by converting them to mercaptopropylsiloxy groups
2. the difficult dispersion of hydrophilic silica by providing a more hydrophobic silica which is more compatible with hydrocarbon rubber
3. the low interaction and weak bonding by providing a chemically active surface that readily forms silica-silane-rubber coupling bonds. Any enhancement in silica-rubber interaction consequently reduces secondary filler structures, a characteristic phenomenon of silica - rubber systems.

One of the most widely used organosilanes is Bis(3-triethoxysilypropyl) tetrasulfide or TESPT or Si 69. According to Goerl, *et al.* (1997), the triethoxysilyl groups of TESPT can react with silanol groups on the silica surface during compounding with loss of ethanol, as illustrated in Figure 1.2.

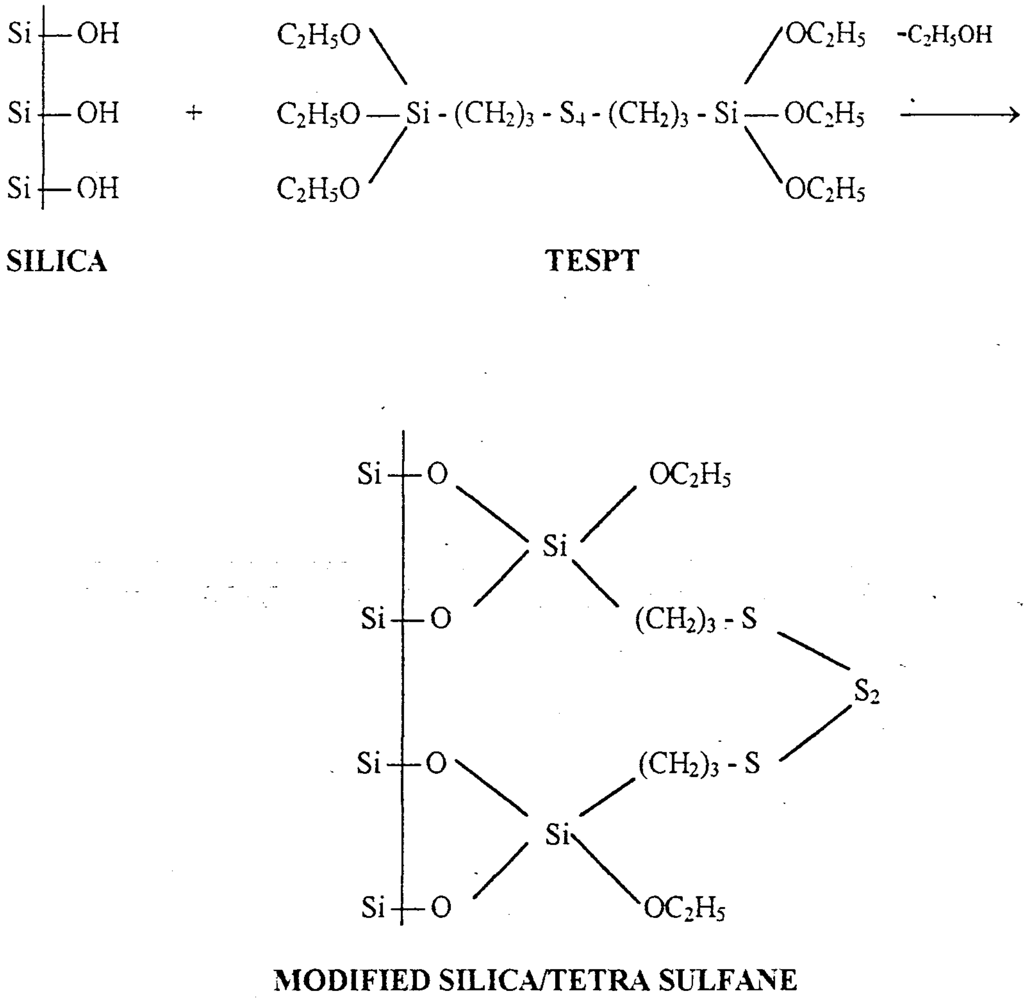


Figure 1.2. Modification reaction of silica with TESPT (Wolff, 1982).

During vulcanization, the rubber-reactive group of the TESPT (e.g. tetrasulfane) tends to form silica - TESPT - rubber networks/bonds.

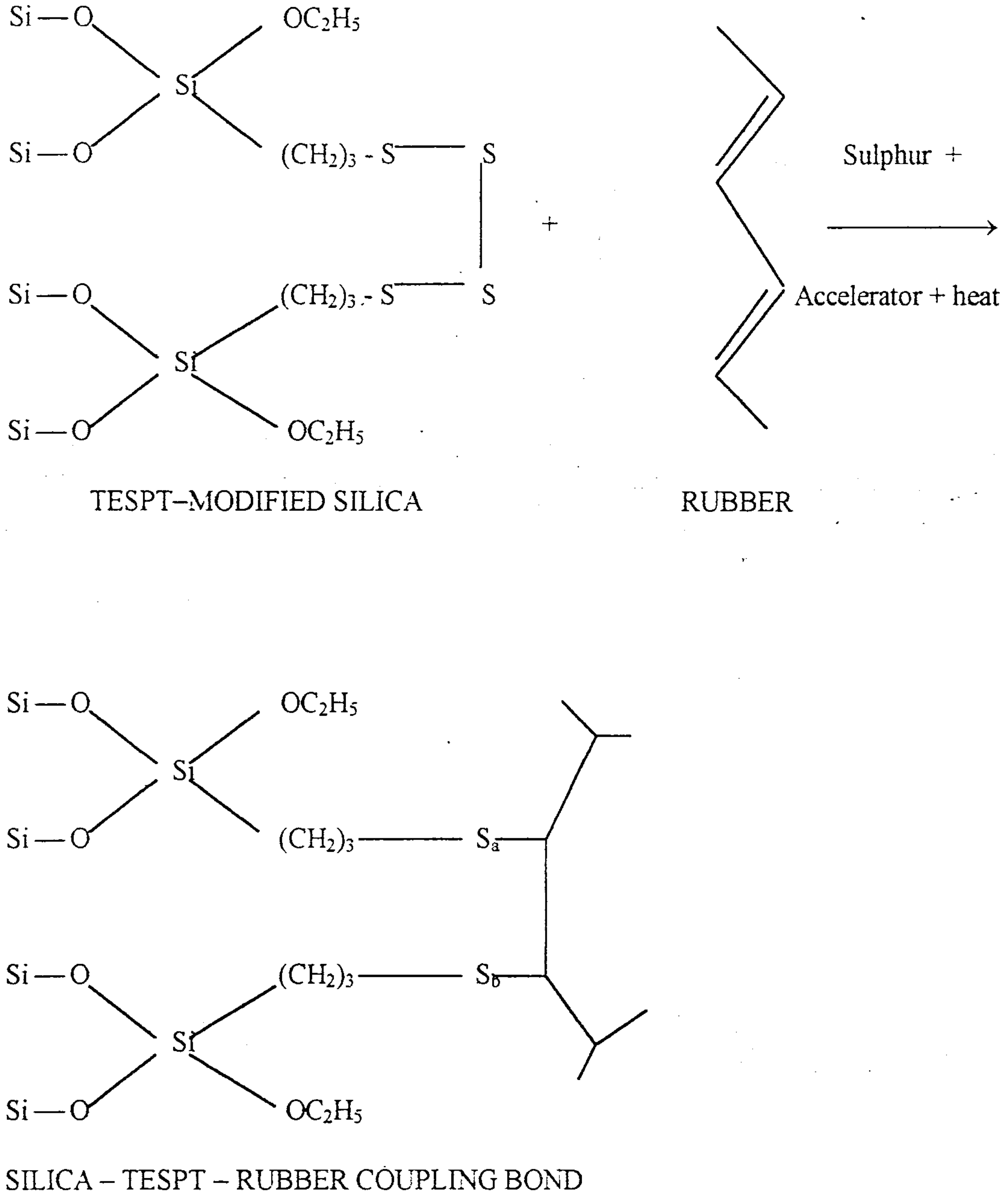


Figure 1.3. The formation of silica-TESPT-rubber coupling bond. (Ismail, 2000).

Observing the reaction between tetrasulfane and rubber in Figure 1.3, it is clearly seen that the sulfur bridge of TESPT reacts with the allylic hydrogens or the double bonds of the rubber to form sulfur crosslinks. This reaction mechanism is similar to the sulfur crosslinking mechanism. So TESPT can be considered as a part of cure system, and since it contains sulfur, therefore, it should also be treated as a co-curing or curative agent when sulfur cure systems are used.

Table 1.7. Recipes and properties of SBR mixes and gum vulcanizates. (Hashim, *et al.*, 1998).

Sample code	F1	F2	F3	F4
Ingredients, phr.				
SBR	100.0	100.0	100.0	100.0
Zinc oxide	5.0	5.0	5.0	5.0
Stearic acid	1.5	1.5	1.5	1.5
MSA[a]	0.5	1.0	0.5	1.0
Sulfur	0.5	1.0	0.5	1.0
TESPT[b]	---	---	5.0	5.0
Properties				
(Mmax-Mmin), kgf.cm	2.46	5.46	5.75	8.25
t_{90}, min	43	35	40	32
Kapp, kgf.cm/min	0.11	0.58	0.26	0.74
M100, MPa	0.51	0.69	0.74	0.90
Tensile strength, MPa	2.03	2.05	3.34	2.32
Elongation at break, %	1240	615	725	420

a N-oxydiethylene-2-benzothiazolyl sulfenamide.

b Bis(3-triethoxysilylpropyl)tetrasulfide.

Hashim, *et al.* (1998), reported the use of TESPT as a co-curing agent on SBR compounds. They compared the recipes without TESPT with the recipes with TESPT and found that TESPT affects the cure characteristics and the tensile properties of SBR gum rubber. As illustrated in Table 1.7, recipes F1 and F2 are without TESPT, while recipes F3 and F4 are with TESPT. By comparing recipes F1 with F3 and F2 with F4, it can be observed that TESPT-contained recipes have shorter t_{90} and significantly higher Kapp and value of (Mmax-Mmin). It is obviously attributed to the acting of TESPT as a co-curing agent during curing process which subsequently increases the degree of cure, the tensile moduli, and the tensile strength.

Their further study on the effect of TESPT on silica-filled vulcanizates of SBR, as illustrated in Table 1.8, also found that TESPT is a co curing agent, which obviously affects the cure characteristics and mechanical and tensile properties of the silica-filled SBR vulcanizates. Except for t_{90}, the scorch time and the torque are reduced and increased, by about a factor of two. TESPT produced a stiffer and stronger vulcanizate with slightly reduced tear strength but a much better abrasion resistance.

Table 1.8. Recipes for conventional silica-filled vulcanizates with TESPT. (Hashim, *et al.*, 1998).

Sample code	RS1	RS2
Ingredients, phr.		
SBR	100.0	100.0
Zinc oxide	5.0	5.0
Stearic acid	2.0	2.0
IPPD[a]	2.0	2.0
MBTS[b]	1.5	1.5
Sulfur	1.5	1.5
TESPT[c]	--	5.0
Silica (VN-3)	30.0	30.0
Properties		
Scorch time, min	16.5	8.1
(Mmax-Mmin), dNm	7.0	16.7
t_{90}, min	50	50
Kapp. dNM/min	0.14	5.32
M100, MPa	0.97	2.37
Tensile strength, MPa	9.4	12.7
Elongation at break, %	860	410
Relative tear strength	1.0	0.81
Abrasion, g/125 rev	0.36	0.19

[a] N-phenyl-N'-isopropyl-p-phenylenediamine.

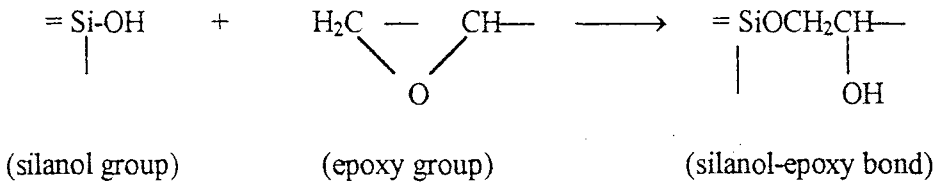
[b] dibenzothiazyldisulfide

[c] Bis(3-triethoxysilylpropyl)tetrasulfide.

1.3.3. Silica reinforcement of Epoxidized NR.

Epoxidized NR (ENR) is a chemically modified form of NR (cis-1.4-polyisoprene), in which some of the unsaturation is converted into epoxide groups, which are randomly distributed along the NR chains. ENR can be crosslinked through residual unsaturation using standard sulphur formulation or by a peroxide. It was found that vulcanization characteristics of ENR 25 and ENR 50 are similar to those of NR (Gelling & Morrison, 1985; Baker, *et al.*, 1985) with an exception that the onset crosslinking occurs earlier i.e. shorter scorch delay. ENR 25 and ENR 50 can strain crystallize (Gelling, 1988), which is reflected by their gum vulcanizates properties. The tensile strengths of ENR 25 and ENR 50 are comparable to that of NR.

However, unlike NR, Epoxidized NR has the ability to be reinforced with silica in the absence of organosilane. High tensile properties comparable to N330 carbon black reinforcement could be obtained (Gelling, 1986). This is clearly the unique ability of ENR that may be due to the interaction of the epoxy groups of ENRs with the silanol groups of silica, as illustrated in Figure 1.4.



(silanol group) (epoxy group) (silanol-epoxy bond)

Figure 1.4. Chemical reaction of silanol group with epoxy group. (Hashim & Kohjiya, 1993).