

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Natural Rubber (NR)

The principal source of NR today is *Heavea Brasiliensis*, which is a native of the tropic rain forest of the Amazon Brazil. Most of the world's NR comes today from South East Asia, mainly Thailand, Malaysia and Indonesia [22]. *Heavea Brasiliensis*, the commercial rubber tree, is a tall tree, growing naturally up to forty meters (130 feet) and living for one hundred years or more. *Heavea Brasiliensis* requires temperatures of 20-30°C, at least 2,000 mm of rainfall per year, and high atmospheric humidity [23]. This naturally occurring polymer is known chemically as *cis*-1,4-polyisoprene (Figure 2.1)

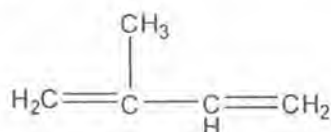


Figure 2.1 Isoprene structure

The possibility that the NR molecule might contain a mixture of *cis*- and *trans*- groups was considered to be unlikely because such a mixed polymer would have an irregular structure and be unable to crystallize in the manner of NR. Infrared studies have indeed shown that NR was at least 97% *cis*-1,4-polyisoprene and the other were 1,2-structure and 3,4-structure as shown in Figure 2.2 [24].

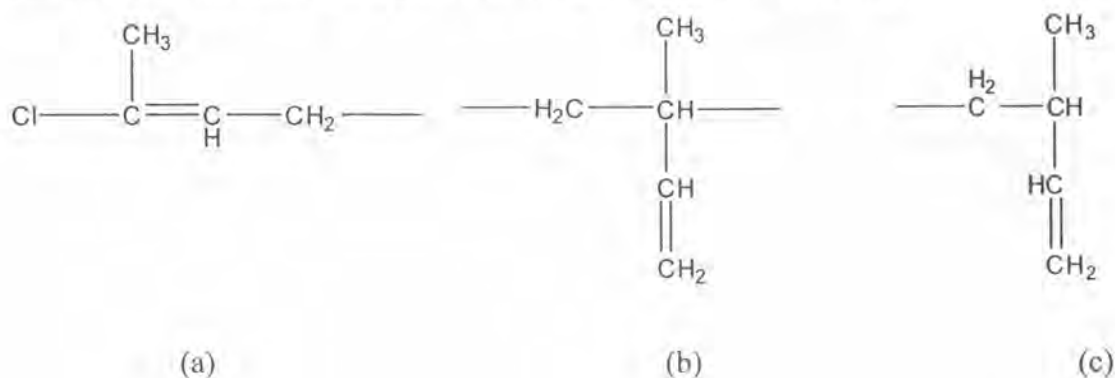


Figure 2.2 Structure of polyisoprene isomers: a) 1,4-polyisoprene b) 1,2-polyisoprene
c) 3,4-polyisoprene

NR in their original state is suitable for engineering applications since it is hard and brittle at low temperature, and soft at high temperature. When the raw rubber is mixed with filler, sulfur, and other ingredients and vulcanized, it becomes strong and hard. Therefore, NR can be used for many industrial applications in wider temperature ranges. Besides tire production, NR in vulcanized form is used as rubber goods such as mechanical goods, hoses, sole, linings to avoid corrosion in chemical processes, gaskets, etc.

2.2 Vulcanization

2.2.1 Definition of Vulcanization [25]

Vulcanization is a process generally applied to rubbery or elastomeric materials. These materials forcibly retract to their approximately original shape after a rather large mechanically imposed deformation. Vulcanization can be defined as a process which increases the retractile force and reduces the amount of permanent deformation remaining after removal of the deforming force. Thus, vulcanization increases elasticity while it decreases plasticity. It is generally accomplished by the formation of a crosslinked molecular network as illustrate in Figure 2.3.

According to the retractile force to resist a deformation is proportional to the number of network supporting polymer chains per unit volume of elastomer. A supporting polymer chain is a linear polymer molecular segment between network junctures. An increase in the number of junctures or crosslinks gives an increase in the number of supporting chains. In an unvulcanized linear high polymer (above its melting point), only molecular chain entanglements constitute junctures. Vulcanization, thus, is a process of chemically producing network junctures by the insertion of crosslinks between polymer chains. A crosslink may be a group of sulfur atoms in a short chain, a single sulfur atom, a carbon to carbon bond, a polyvalent organic radical, an ionic cluster, or a polyvalent metal ion. The process is usually carried out by heating the rubber, mixed with vulcanizing agents, in a mold under pressure.

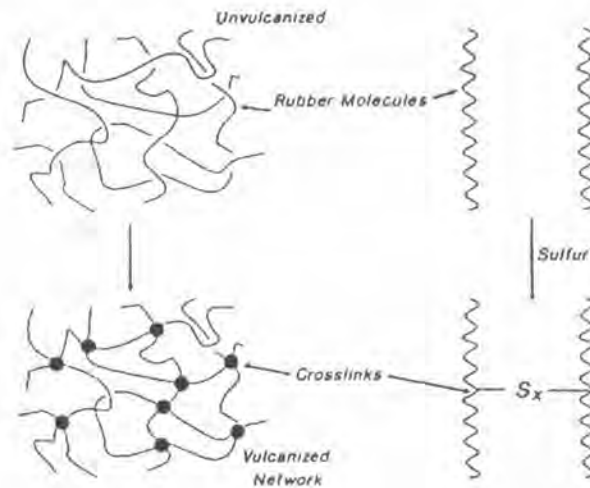


Figure 2.3 The formation of a crosslinked molecular network [25].

2.2.2 Description of Curing Parameters [26]

A cure curve in Figure 2.4 provides an information on scorch safety or cure induction time, cure rate, state of cure, optimum cure time when modulus no longer increases significantly, and the tendency of the compound to degrade upon overcure as follow.

Scorch is a premature vulcanization in which the stock becomes partly vulcanized before the product is in its final form and ready for vulcanization. It reduces the plastic properties of the compound so that it can no longer be processed. Scorching is a result of both the temperature reached during processing and an amount of time the compound is exposed to elevated temperatures. This period of time before vulcanization is generally referred to as a “scorch time”. It is important that vulcanization dose not start until the processing is complete.

Rate of cure is the rate at which crosslinking and the development of the stiffness (modulus) of the compound occur after the scorch point. As the compound is heated past the scorch point, the properties of the compound change from a soft to a tough elastic material. During the curing step, crosslinks are introduced, which connect the long polymer chains of the rubber together. As more crosslinks are introduced, the polymer chains become more firmly connected and the stiffness or modulus of the compound increases. The rate of cure is an important vulcanization parameter since it in part determines the time the compound must be cured.

State of cure is a general term used to indicate the development of property of the rubber as cure progresses. As the crosslinking or vulcanization proceeds, the modulus of the compound increases to various “states of cure”. Technically, the most important state is the so-called “optimum”. Since all properties imparted by vulcanization do not occur at the same level of cure, the state of optimizing may not be the best for other properties.

Cure time is the time required during the vulcanization step for the compounded rubber to reach the desired state of cure.

Overcure is the cure time which is longer than optimum. Overcure may be of two types. In one type, the stock continues to harden, the modulus rises, and tensile and elongation fall. In other cases, including most NR compounds, reversion occurs with overcure and the modulus and tensile strength decreases.

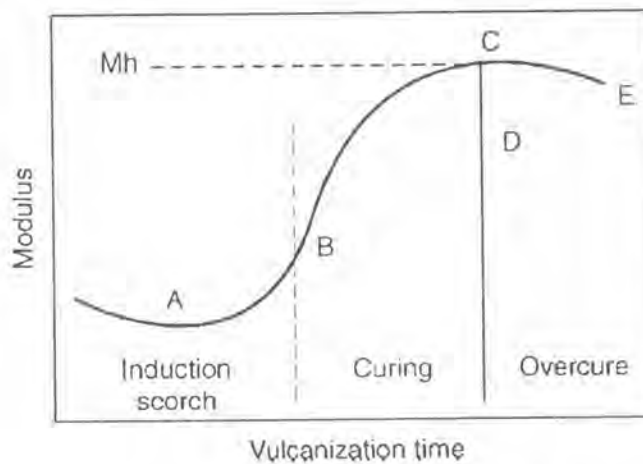


Figure 2.4 Cure curve from oscillating disk rheometer where A represents scorch safety, B cure rate, C state of cure, D optimum cure, and E reversion.

2.2.3 Effects of Vulcanization on Vulcanizate Properties [27]

Vulcanization causes profound changes at the molecular level. The long rubber molecules become linked together with junctures (crosslinks) spaced along the polymeric chains. As a result of this network formation, the rubber becomes essentially insoluble in any solvent, and it cannot be processed by any means which requires it to flow, e.g., in a mixer, in an extruder, on a mill, on a calender, or during shaping, forming, or molding. Thus, it is essential that vulcanization occur only after

the rubber article is in its final form. Major effects of vulcanization properties are illustrated by the idealization of Figure 2.5. It should be noted that static modulus increases with vulcanization to a greater extent than does the dynamic modulus. Hysteresis is reduced with increasing crosslink formation. Tear strength, fatigue life, and toughness are related to the breaking energy. Values of these properties increase with small amounts of crosslinking, but they are reduced by further crosslink formation. It should be noted that the properties given in Figure 2.5 are not functions only of crosslink density. They are also affected by the type of crosslink, the type of polymer, and type and amount of filler, etc.

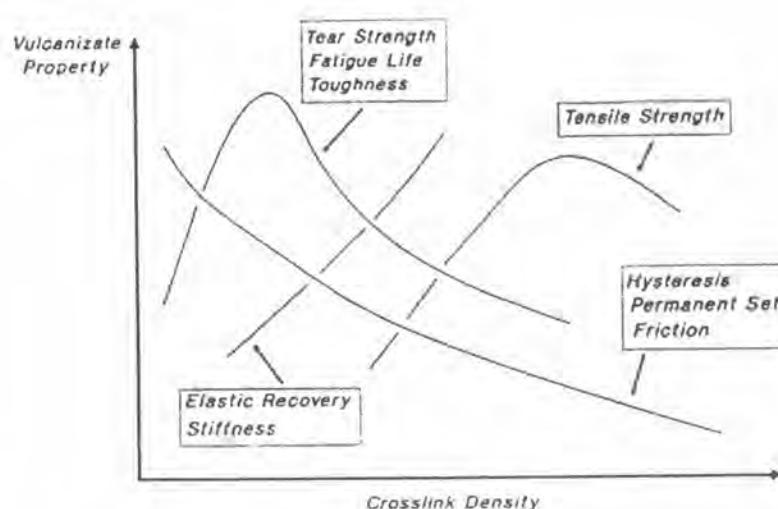
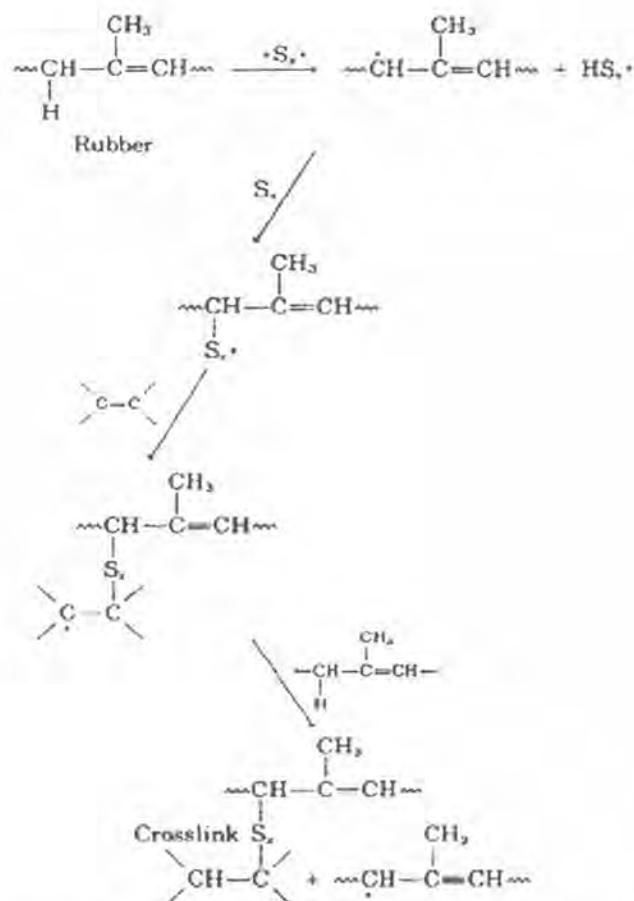


Figure 2.5 Vulcanizate properties as a function of the extent of vulcanization [27].

2.2.4 Sulfur Vulcanization [27]

Initially, vulcanization was accomplished by using elemental sulfur at a concentration of 8 parts per 100 parts of rubber (phr). It required 5 hours at 140°C. The addition of zinc oxide reduced the time to 3 hours. The use of accelerators in concentrations as low as 0.5 phr has since reduced the time to as short as 1 to 3 minutes. As a result, elastomer vulcanization by sulfur without accelerator is no longer of much commercial significance. Even though unaccelerated sulfur vulcanization is not of commercial significance, its chemistry has been the object of much research and study. The chemistry of unaccelerated vulcanization is controversial. Many slow reactions occur over the long period of vulcanization. Some

investigators have felt that the mechanisms involved free radicals as shown in scheme 2.1.



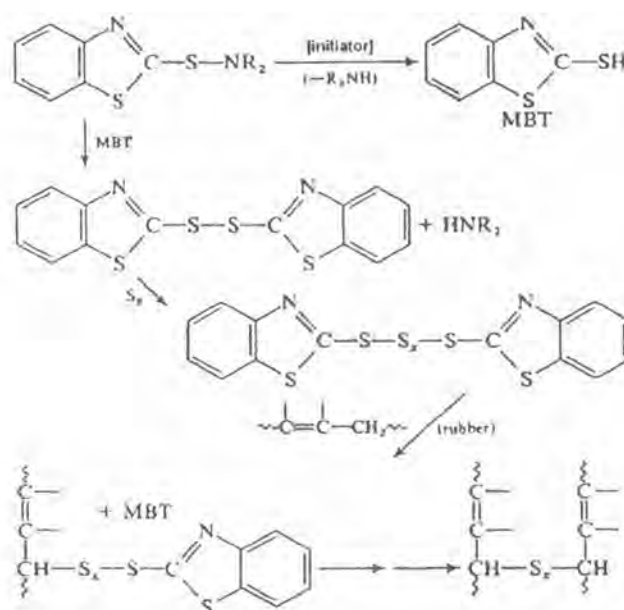
Scheme 2.1 Vulcanization of natural rubber crosslinking via free radicals [27].

2.2.5 Accelerated Sulfur Vulcanization [27]

Vulcanization by heating with sulfur alone is a very inefficient process with approximately 40-50 sulfur atoms incorporated into the polymer per crosslink. Sulfur is wasted by the formation of long polysulfide crosslinks, vicinal crosslinks, and intramolecular cyclic sulfide structures. Commercial sulfur vulcanizations are carried out in the presence of various additives, referred to as accelerators, which greatly increase the rate and efficiency of the process.

The most used accelerators are sulfonamide derivatives of 2-mercaptobenzothiazole (MBT). Actually, the use of accelerators alone as illustrate in scheme 2.2 usually gives only small increases in crosslinking efficiency. Maximum efficiency is achieved by using accelerators together with a metal oxide and fatty acid. The latter substances are referred to as the activator. Zinc oxide and stearic acid are

the most commonly used. The fatty acid solubilizes the zinc oxide by forming the zinc carboxylate salt. Vulcanization is achieved in minutes using the accelerator–activator combination compared to hours for sulfur alone. Analysis of the crosslinked product showed a large decrease in the extent of the wastage reactions. The crosslinking efficiency in some systems is increased to slightly less than two sulfur atoms per crosslink. Most of the crosslinks are monosulfide or disulfide with very little vicinal or cyclic sulfide units.



Scheme 2.2 Acceleration of natural rubber vulcanization [27].

Accelerators can be classified chemically and functionally. The principal chemical classes of accelerators in commercial use today are listed in Table 2.1. Functionally, these compounds are typically classified as primary or secondary accelerators (including ultra-accelerators, or “ultras”). Compounds classified as primary accelerators usually provide considerable scorch delay, medium-to-fast cure rates, and good modulus development. Compounds classified as secondary accelerators usually produce scorch, very fast curing stocks.

Table 2.1 Accelerator classes [28]

Class	Response speed	Acronyms
Aldehyde-amine	Slow	-
Guanidines	Medium	DPG, DOTG
Thiazoles	Semi-fast	MBT, MBTS
Sulfenamides	Fast, delayed action	CBS, TBBS, MBS, DCBS
Dithiophosphates	Fast	ZBPD
Thiurams	Very fast	TMTD, TMTM, TETD
dithiocarbamates	Very fast	ZDMC, ZDBC

2.3 Reinforcement of Rubbers

2.3.1 The Reinforcement Concept [29]

Rubber is generally reinforced by short fibers, carbon black and silica. The concept of reinforcement relates basically to composites built from two or more structural elements or components of different mechanical characteristics whereby the strength of these elements is imparted to the composite and combined with the set of favorable properties of the other component. A pure gum vulcanizate of general purpose SBR has a tensile strength of no more than 2.2 MPa but, by mixing in 50 phr of a reinforcing black, this value can easily be raised to 25 MPa as shown in Figure 2.6. Therefore, the best definition is probably: reinforcing filler is a filler that improves the modulus and failure properties (tensile strength, tear resistance, and abrasion resistance) of the final vulcanizate.

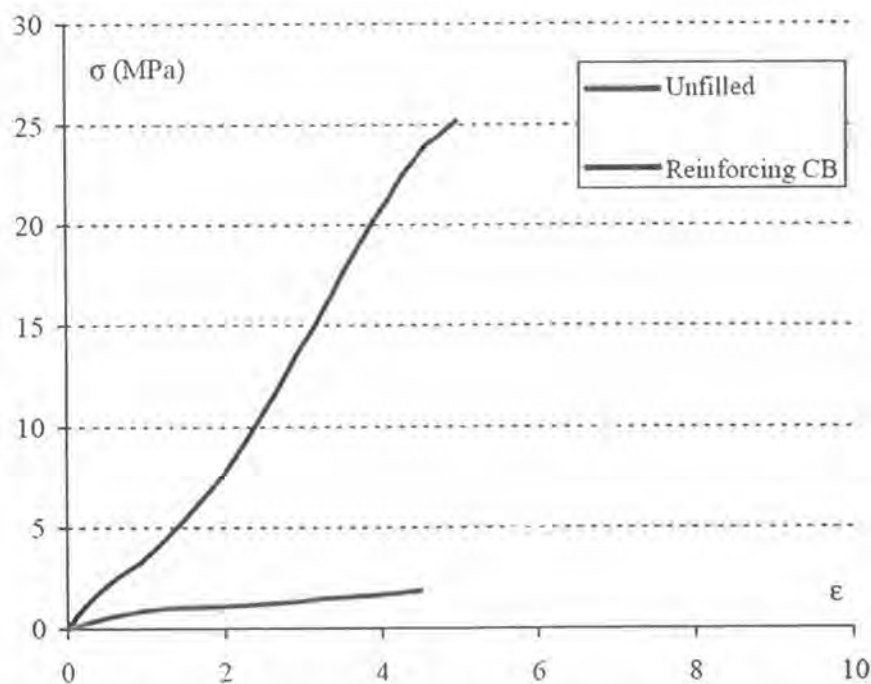


Figure 2.6 Stress-strain curves of pure gum vulcanizate and pure gum vulcanizate reinforced by carbon black [29].

2.3.2 Factors Affecting Filler Reinforcement [30]

The reinforcement of elastomers by fillers has been studied in depth in numerous investigations and it is generally accepted that this phenomenon is dependent, to a large extent, on polymer properties, filler properties and processing. Generally, the primary filler factors influencing elastomer reinforcement are:

2.3.2.1 Particle Size

If the size of the filler particle greatly exceeds the elastomer inter-chain distance, it introduces an area of localized stress. This can contribute to the rupture of elastomer chain on flexing or stretching. Filler with particle size greater than $10\ \mu\text{m}$ is therefore generally avoided because they can reduce performance rather than reinforce or extend. Filler with particle sizes between $1,000\text{-}10,000\ \mu\text{m}$ is used primarily as diluents and usually has no significant effect on rubber properties. Semi-reinforcing filler, which range from $0.1\text{-}1\ \mu\text{m}$ improves strength and modulus properties. The truly reinforcing filler, which range from $0.01\text{-}0.1\ \mu\text{m}$, significantly improves rubber properties.

2.3.2.2 Surface Area

Filler must make intimate contact with the elastomer chains if it is going to contribute to reinforcement. Filler that has a high surface area has more contact area available and therefore has a higher potential to reinforce the rubber chains. The shape of the particle is also important. Particles with a planar shape have more surface area available for contacting the rubber than spherical particles with an equivalent average particle diameter. Particles of carbon black or precipitated silica are generally spherical, but their aggregates are anisometric and are considerably smaller than the particles of clay, which have planar-shaped particle. Surface area for rubber-grade carbon blacks vary from 6 to 250 m²/g. Most reinforcing precipitated silica vary from 125 to 200 m²/g and typical hard clay ranges vary from 20 to 25 m²/g.

2.3.2.3 Structure

The shape of an individual particle of reinforcing filler is less important than the filler's effective shape once dispersed in an elastomer. The blacks and precipitated inorganic used for reinforcement have generally round primary particles but function as anisometric (needle-like) aggregates.

2.3.2.4 Surface Activity

A filler can offer high surface area and high structure, but still provide relatively poor reinforcement if it has low specific surface activity. The specific activity of the filler surface per cm² of filler-elastomer interface is determined by the physical and chemical nature of the filler surface in relation to that of the elastomer. Nonpolar fillers are best suited to nonpolar elastomers; polar fillers work best in polar elastomers. Beyond this general chemical compatibility is the potential for reaction between the elastomer and active sites in the filler surfaces.

2.3.3 Measurement of Reinforcement in Rubber Vulcanizates [31]

Reinforcement effects in vulcanizates containing active fillers are generally measured by the resistance to abrasion, tearing, cut growth, flex cracking and tensile fracture. These are all failure phenomena which appear to involve, in complex ways, the common process of rupture propagation through the rubber. A widely used method to assess the relative ability of fillers to reinforce rubber as shown in Figure 2.7 which demonstrates the “optimum loading concept” of filler. As can be seen the reinforcement conveyed to a rubber by a reinforcing filler increases initially until a maximum is reached after which dilution effects predominate and the strength of the rubber composite reduces. Fillers can be compared for their relative performances in any rubber polymer on this basis.

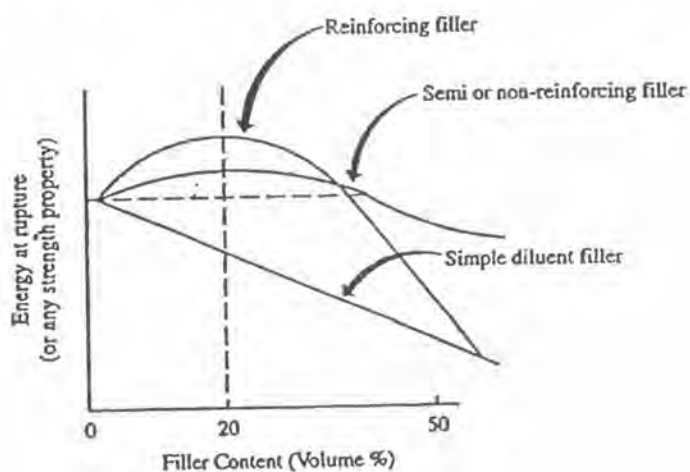


Figure 2.7 The optimum loading concept [31].

2.4 Type of filler

2.4.1 Silica [32]

In this research, silica was used as the reinforcing filler. Silicon dioxide or silica is particularly the main component of the crust of the earth. Combined with the oxides of magnesium, aluminum, calcium, and iron, it forms the silicate minerals in our rocks and soil. The general formula of silica is $\text{SiO}_2 \cdot x\text{H}_2\text{O}$. Due to its properties such as chemical resistance, high thermal and mechanical stability, silica is thus widely used as reinforcing filler in rubber. There are essentially two types of silica commonly used as reinforcing filler.

2.4.1.1 Type of Silica

a) Precipitated Silica

Silica used as reinforcing fillers is mainly obtained by precipitation. The process basically consists in the preparation of a silica glass by alkaline fusion of pure sand and an alkaline salt. Then this glass is solubilized in water at high temperature and acid precipitated. The silica suspension obtained is then filtered, washed, and dried. In order to obtain reinforcing silica, much care must be taken in precipitation recipes (to obtain small rigid objects) and drying conditions (to maintain high dispersibility).

b) Fumed Silica

Fumed silica is obtained by high temperature oxydecomposition of SiH_4 , or other methyl hydride precursors (SiHMe_3 , SiH_2Me_2) Coming out of the furnace, fumed silica are obtained in a fluffy form, and because of their high temperature of formation, they present a very stable morphology and few surface silanols compared to precipitation silica. This confers a high dispersibility and reactivity to fumed silicas but, because of their higher price, they are rarely used in the rubber industry.



The structure of silica shows in Figure 2.8 contains siloxane bond (Si-O-Si) and silanol group (Si-OH). The latter can be divided into three types: vicinal, germinal and isolated silanol. Vicinal or H-bonded or associated silanols are Si-OH groups. Germinal silanols are silanediols groups. An isolated silanol includes an OH group located at a distance sufficiently far from neighboring hydroxyl groups to prevent hydrogen bonding as shown in Figure 2.9.

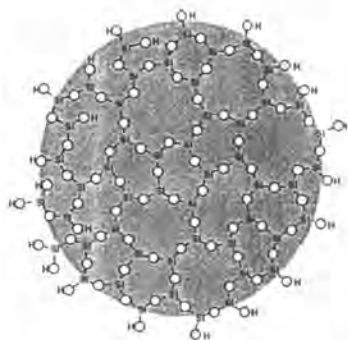


Figure 2.8 Structure of silica particle [25].

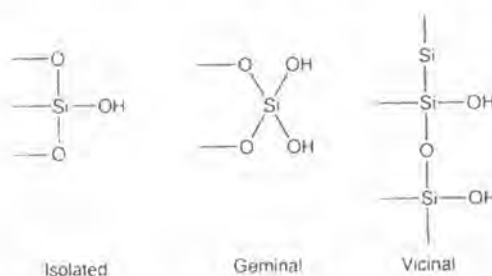


Figure 2.9 Typical silanol groups on silica [25].

The dispersion and the distribution of silica are generally recognized to be determined by the state of aggregation and agglomeration, which are schematically shown in Figure 2.10. Aggregates are three-dimensional clusters of ultimate particles, covalently bonded to one another via siloxane bonds. Aggregates can physically agglomerate though intermolecular hydrogen bonding of surface silanol groups of one aggregate to a silanol group of other aggregate.

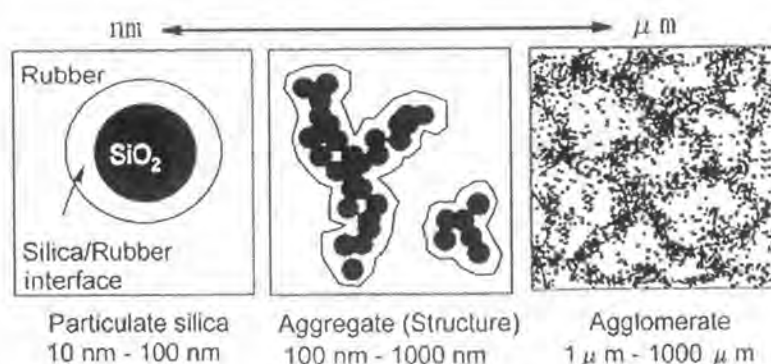


Figure 2.10 Silica particles in NR matrix [33].

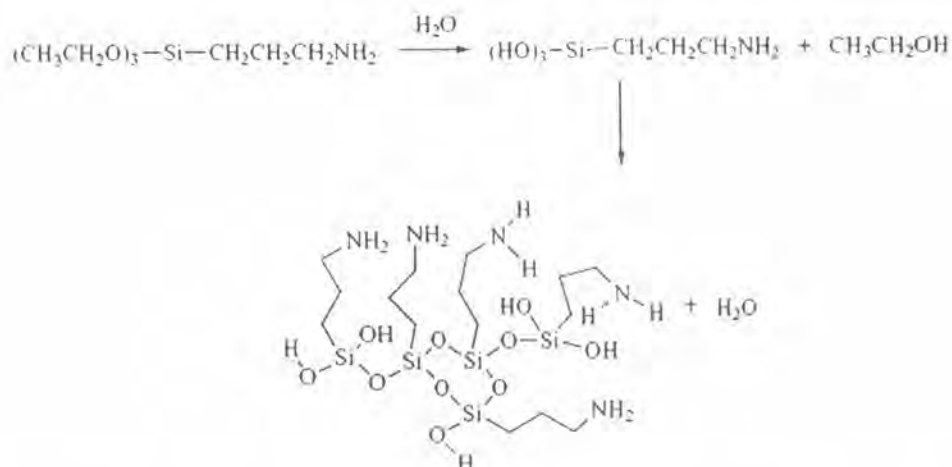
2.4.1.2 Silane Coupling Agent [25]

The term silane coupling agent generally applies to silicon-containing species capable of forming chemical linkages between dissimilar materials, especially in reinforced polymer composites. The materials to be linked are often organic polymers and inorganic fillers, though silane coupling agents can also be useful with other kinds of fillers and polymers. Small amounts of silane coupling agents, used at an interface, can greatly improve the mechanical properties of composite materials.

Silane coupling agents generally have hydrolyzable and organofunctional ends. The general structure of the coupling agents can be represented as

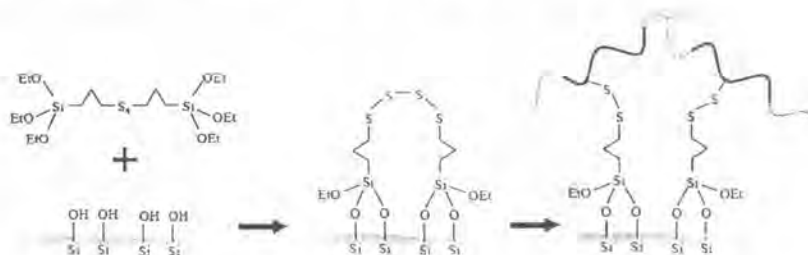


where the X represents the hydrolyzable groups that are typically chloro, ethoxy, or methoxy groups. The organo, R, group can have a variety of functionalities chosen to meet the requirements of the polymer. The first step in the application of a silane coupling agent is the hydrolysis of the X groups. Generally water is required and the by-products are HCl or alcohol. Following hydrolysis, and in some cases competing with it, is the condensation of the silanols with other silanols or surface species. This typically occurs with the loss of water as illustrate in Scheme 2.3.



Scheme 2.3 Idealized representation of the hydrolysis and condensation of 3-aminopropyltriethoxysilane (APS) [25].

The silane coupling agent reacted with the silanol groups on the surface of silica and compatible with the polymer. Additionally, coupling also can participate in the sulfur vulcanization to form chemical linkage with polymer. As a consequence, silane coupling agent could act as a bridge between silica and polymer to enhance the polymer-filler interaction as illustrate in Scheme 2.4.



Scheme 2.4 A complete coverage of silica surface by TESPT [25].

2.4.1.3 Sol-Gel Process [14]

The sol-gel process may be described as “formation of an oxide network through polycondensation reactions of a molecular precursor in a liquid”. A sol is a stable dispersion of colloidal particles or polymers in a solvent. The particles may be amorphous or crystalline. An aerosol is particles in a gas phase, while a sol is particles in a liquid. A gel consists of a three dimensional continuous network, which encloses a liquid phase. In a colloidal gel, the network is built from agglomeration of colloidal particles. In a polymer gel, the particles have a polymeric sub-structure made by aggregates of sub-colloidal particles. Generally, the sol particles may interact by van der waals forces or hydrogen bonds. A gel may also be formed from linking polymer chains. In most gel systems used for materials synthesis, the interactions are of a covalent nature and the gel process is irreversible. The gelation process may be reversible if other interactions are involved. Sol-gel synthesis may be used to prepare materials with a variety of shapes, such as porous structures, thin fibers, dense powders and thin films as illustrate in Figure 2.11.

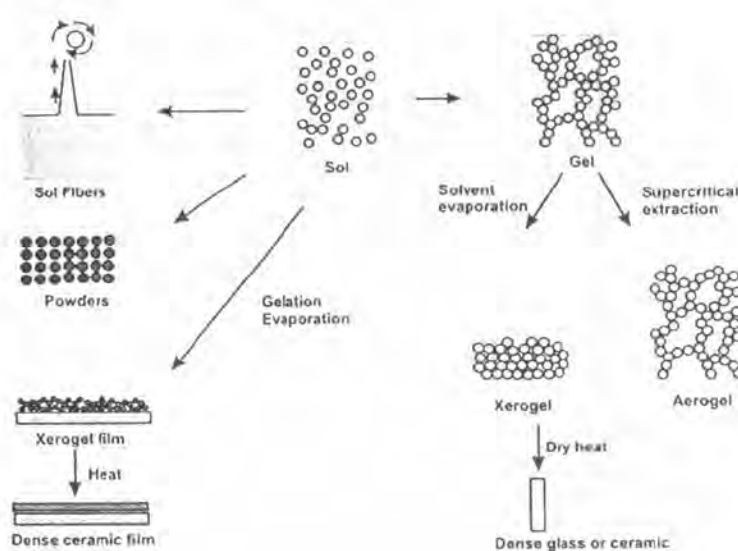


Figure 2.11 Sol-gel process options [26].

The sol-gel reaction takes place into two steps of hydrolysis and followed by the condensation reactions. Water and alcohol are the by-products of the sol-gel reaction as shown in Scheme 2.5. The mechanisms of sol-gel reaction in acidic and basic environment are different as illustrated in Scheme 2.6-7, respectively.

Hydrolysis:



Alcohol Condensation:



Water Condensation:



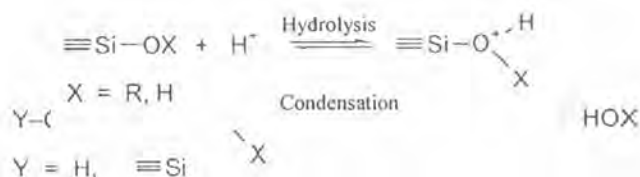
Over all reaction:



Scheme 2.5 Hydrolysis and condensation reactions of TEOS to form silica [14].

a) Reactions in Acidic Environments [14]

The oxygen atom in Si-OH or Si-OR is protonated and H-OH or H-OR are good leaving groups. The electron density are shifted from the Si atom, making it more accessible for reaction with water (hydrolysis)) or silanol (condensation).



Scheme 2.6 Chemical equation of the sol-gel reaction in acidic environment.

Hydrolysis reaction: X= R, Y= H, Condensation reaction: X= R or H, Y= Si≡

b) Reactions in Basic Environments [14]

Nucleophilic attack by OH^- or Si-O^- on the central Si atom. These species are formed by dissociation of water or Si-OH. The reactions are of SN_2 type where OH^- replaces OR^- (hydrolysis) or silanolate replaces OH^- or OR^- (condensation) and reaction are reversible.



Scheme 2.7 Chemical equation of the sol-gel reaction in basic environment.
Hydrolysis reaction: $\text{X} = \text{R}$, $\text{Y} = \text{H}$, Condensation reaction: $\text{X} = \text{R}$ or H ,
 $\text{Y} = \text{Si}\equiv$.

2.4.1.4 Parameters which Influence the Sol-Gel Process

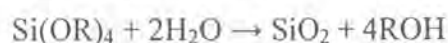
a) Types of Precursor

The stability and reactivity of the silicon alkoxides are influenced by a steric factor. Bulky ligands slow down the hydrolysis:



b) The Ratio between Alkoxide and Water (R_W)

The reaction states that a water ratio of $R_W = 2$ ($\text{OR}/\text{H}_2\text{O}$) is need to convert everything to SiO_2 . A water ratio of $R_W=1$ leads to complete hydrolysis but no condensation. Increasing the water content (i.e. lower R_W) will reduce condensation and reducing the water content increases the condensation.



c) Types of Catalyst Used [14]

The dependence of the reaction rate with pH is different for acid and base catalyzed systems as shown in Figure 2.12. The polymerization process is divided into three approximate pH domains: $\text{pH} < 2$, $\text{pH} 2-7$, and $\text{pH} > 7$. $\text{pH} 2$ appears as a boundary, since the point of zero charge (PZC), where the surface charge is zero, and the isoelectric point (IEP), where the electric mobility of the silica particles is zero, both are in the range $\text{pH} 1-3$. $\text{pH} 7$ appears as a boundary because both the silica solubility and dissolution rates are maximized at or above $\text{pH} 7$ and because the silica particles are appreciably ionized above $\text{pH} 7$ so that particle growth occurs without aggregation or gelation.

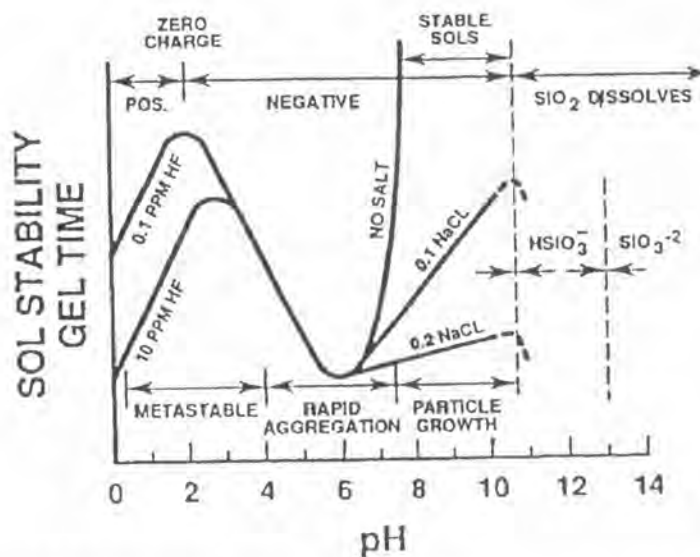


Figure 2.12 Effect of pH in the colloidal Silica- water system [14].

d) Types of Solvent

The polarity, dipolar moment, viscosity, protolytic/non protolytic properties are important for the reactions taking place. Polar solvents stabilize polar gels by hydrogen bonding. Non-polar solvents are better for systems which are not completely hydrolyzed. Solvents may be either protic or aprotic and may vary in their proarity. Depending of the pH, either protonated or deprotonated silanol are involved in the condensation mechanism. Because in protic solvents, hydrogen bond of nuclepphilic deprotonated silanols group and aprotic solvents retard base-catalyzed

condensation and promote acid catalyzed condensation. Aprotic solvents have the reverse effect.

2.4.1.5 Network Formation

During reaction, objects will grow, however, a gel may not form as the sol aggregates the viscosity will increase until a gel is formed. The sol-gel transition (gel-point) is reached when a continuous network is formed as shown in Figure 2.13. The gel-time is determined as the time when it is possible to turn the container upside-down. All fluid is kept in the gel, and the volume is maintained.

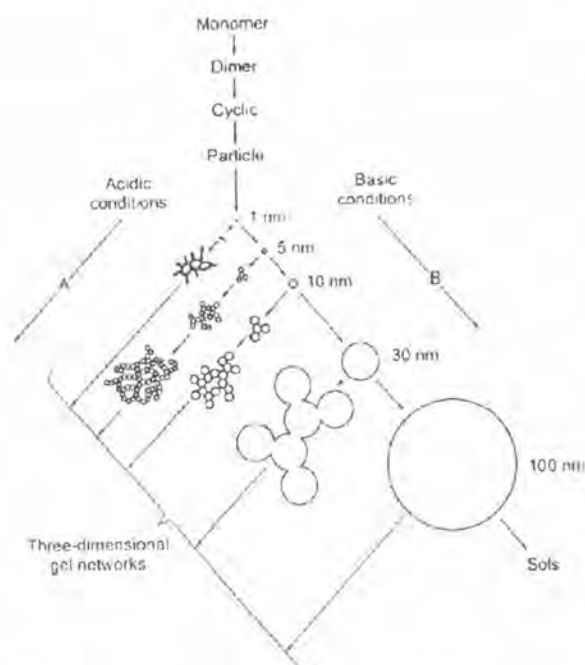


Figure 2.13 Structure development of silica gel [14].

2.4.2 Carbon Black [26]

2.4.1.1 Chemical Structure of Carbon Black

Carbon black is widely used as a reinforcing and coloring agent in compounding rubber, ink, paints, plastics, paper, and electrical conducting applications. Carbon black may contain 83 to 99% of carbon. Other chemicals including oxygen, hydrogen and heavy metals may be chemically combined in the crystallite structure or be present on the surface of carbon black. Relatively, large amounts of oxygen volatile yield carbon blacks that have a low pH or acidic in nature. Oxygen may be present in aldehyde, hydroxyl, carbonyl, quinone, hydroquinone, lactone and possibly chromene groupings as shown in Figure 2.14.

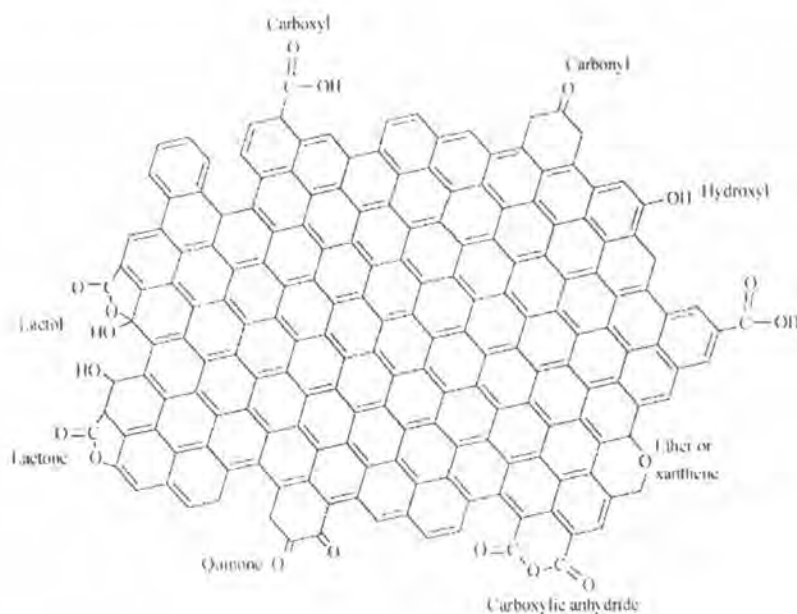


Figure 2.14 Surface chemistry of carbon black.

Although based solely on the element carbon like graphite and diamond, carbon black differs both chemically and physically from these purer and more crystalline forms of carbon. Electron microscopy shows carbon black particles of planar hexagonal nets of carbon black they are not large or extensive as in graphite. The layers are also farther apart, at about 3.5 Å, compares to 3.35 Å for graphite as demonstrated in Figure 2.15.

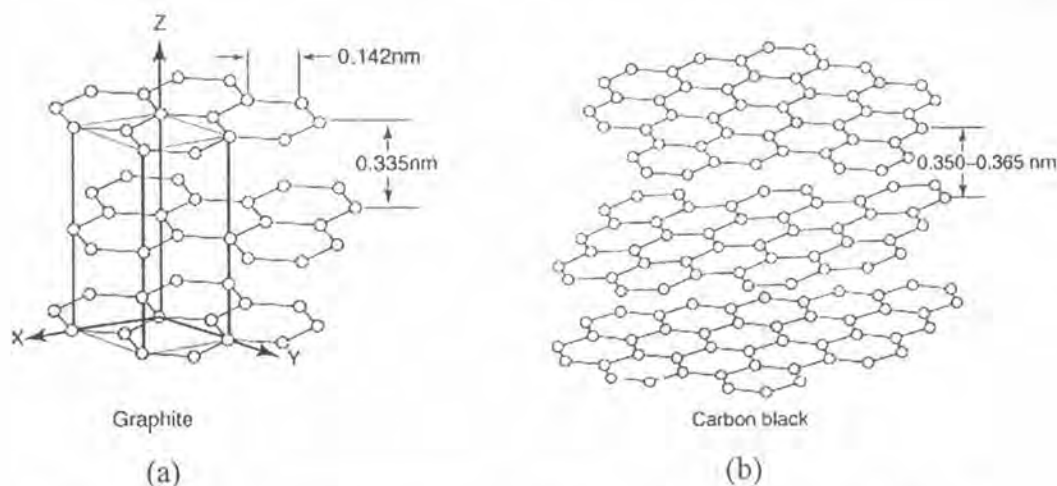


Figure 2.15 Atomic structure model: (a) graphite, and (b) carbon black

2.4.1.2 Applications of Carbon Black

U.S. consumption of carbon black in 2000 by various market sectors are shown in Table 2.2 About 89% of total consumption is in the rubber industry and 70% for tires. About 10% is consumed for other automotive products and 9% for rubber products unrelated to the automotive industry. The automotive industry accounts for 80% of consumption. Eleven percent of the black is for non rubber uses and its main applications are related to pigmentation, ultraviolet absorption, and electrical conductivity of other products such as plastics, coating, and inks.

Table 2.2 U.S. End-Use Consumption of Carbon Black in 2000 [34]

	Millions of metric tons	Percent of total
Automotive rubber used tire and tire products	1.17	70
Belts, hoses, and other automotive products	0.16	10
Industrial rubber products	0.16	9
Non rubber uses	0.18	11
Total	1.67	100

2.4.2 Calcium Carbonate [31]

Precipitated calcium carbonate is formed by dissolving limestone and precipitating CaCO_3 as very fine particles using carbon dioxide (Arogonite Process) or sodium carbonate (Solvay Process). Typical particle sizes range from 0.02 to 2 μm . Most commercially available precipitated calcium carbonate is spherical colloidal particles or aggregates consisting of a few spherical particles. Additional shapes and aggregates of varying morphology are possible and provide increased reinforcement.

Precipitated calcium carbonate is used as semireinforcing filler in shoe products and industrial polymer goods, particularly when resistance to alkali solutions is needed. The low moisture content and good reinforcement allow precipitated calcium carbonate to be used in wire and cable insulation applications. Typical calcium carbonate levels used in polymer compounds range from 20 to 300 phr.

2.5 Literature Reviews

Ikeda and Kohjiya [35] studied on the *in situ* formed silica particles in butadiene rubber (BR) vulcanizate by the sol-gel method. BR was sulfur cured, and the resultant crosslinked BR was subjected to soaking in TEOS at 30°C for 48 h. The swollen vulcanizates were kept in an aqueous solution of n-butyamine at 30°C for 24 h, followed by standing at 50°C for 72 h to conduct the *in situ* sol-gel reaction of TEOS. They were subjected to tensile and dynamic mechanical measurement, differential scanning calorimetry and transmission electron microscopic observation. The *in situ* formed silica was dispersed homogeneously in the rubber matrix. The size of *in situ* silica was influenced by the crosslinking density, probably because it was formed in the crosslinked rubber networks. Compared to the conventional silica-filled BR vulcanizate, which was prepared by mechanical mixing of the silica particles, the new vulcanizates with the *in situ* formed silica showed better mechanical properties.

Poh and NG [36] studied on effect of silane coupling agent on the Mooney scorch time of silica-filled natural rubber compound. Two types of silane coupling agents, γ -mercaptopropyltrimethoxysilane (A-189) and bis(triethoxysilylpropyl)-tetrasulphide (Si-69) of various loadings were used to study the effect of silane coupling agents on the scorch property of natural rubber. Results indicated that the Mooney scorch time and cure index decreased with increasing A-189, but increased

with increasing Si-69. The apparent activation energy for various loadings of silane coupling agents was determined and reported that when increased A-189 concentration, the value of E_a was decreased. On the contrary, as the concentration of Si-69 is increased, E_a also increases correspondingly.

Ono *et al.* [37] studied on the structure development in silica filled polyisoprene composites. They reported that the main mechanism of formation of bound rubber in this composite was considered to be a physical adsorption of rubber molecules on the silica surface. The amount of bound rubber is affected by the state of aggregation of silica particles which was function of particle size and amount of silanol groups on the particles. When the composites were annealed, the amount of bound rubber increased with increasing annealing temperature due to the development of chemical crosslinks in bound and free rubber phase.

Yoshikai *et al.* [21] studied on the silica reinforcement of synthetic diene rubber by sol-gel process in the latex. SBR and NBR were reinforced with silica by the sol-gel method of TEOS in latex. They found that the amount of TEOS added and molar ratio of TEOS to water ($[H_2O]/[TEOS]$) in the mixture were related the silica content in the compounds, particle size, and reinforcing behavior of silica. By the dispersion of the fine silica in the nanometer-order level, the tensile strength of the compound was drastically improved. Compounds with a high tensile strength had a high bound rubber fraction and a very strong interaction of the fine silica with rubber.

Kohjiya and Ikeda [6] studied on the sol-gel reaction of tetraethoxysilane in NR matrix to obtain NR/*in situ* silica mixtures. The NR sheet was soaked in TEOS after that swollen in catalyst solution. The mixtures were compounded with curing regents, and their viscosities were evaluated. The *in situ* silica afforded better compound than conventional silica or carbon black in term of processability and *in situ* silica with a coupling agent afforded the lowest viscosity compared not only with conventional silica but also with a carbon black (HAF). The cure time of *in situ* silica compound was shorter than conventional silica compound. Physical properties of the vulcanizates were also evaluated, and again *in situ* silica stock gave the best result. The *in situ* silica afforded a very low compression set and high rebound resilience equal to that of carbon black stock, different from the other silica stocks.

Ansarifar *et al.* [38] studied on the use of a silanised silica filler to reinforce and crosslink NR. They have reported that the availability of the coupling agent bis(3 triethoxysilylpropyl-)tetrasulphane (TESPT) has provided a better opportunity for

using synthetic silica to reinforce NR since TESPT chemically adheres silica to rubber and also prevents silica from interfering with the reaction mechanism of sulfur-cure. The silica surfaces were pretreated with TESPT and the filler was perfectly dispersed in the rubber. The effect of accelerator (CBS) and zinc oxide on cure of rubber were also studied and concluded the need for the accelerator depended on the amount of silica content in rubber.

Lopez *et al.* [39] studied on the use of mesoporous silica as a reinforcing agent in styrene-butadiene rubber (SBR) compounds. The filler-polymer interactions were compared with those exhibited when Ultrasil silica (VN3) was used. A silane coupling agent was added to improve filler dispersion and its influence on the bound-rubber formation was also investigated. The bound-rubber content was higher for the mesoporous silica and increased further for the sample containing silane. The increase was explained by chemical interactions between filler and rubber and penetration of the rubber chains into the mesopores. This result was confirmed by ^{13}C solid-state NMR, IR spectroscopy and differential scanning calorimetry. Dynamic mechanical thermal analysis showed higher storage modulus for the rubber filled with mesoporous silica.

Poompradub *et al.* [20] studied on the sol-gel reaction of *in situ* silica in NR matrix. The mechanical properties of conventional silica composites were studied comparing with the *in situ* silica composites. *n*-Hexylamine was used as the catalyst. The uses of *n*-hexylamine as the catalyst in sol-gel reaction generated high *in situ* silica content 71 phr. The mechanical properties of the *in situ* silica composite such as hysteresis loss and permanent set were much lower than those of the conventional silica composite and dispersed more homogeneously.

Rattanasom *et al.* [40] studied on the use of silica/CB blends in NR vulcanizates to enhance the mechanical and dynamic properties of NR (NR) vulcanizates. The reinforcement of NR with silica/CB hybrid filler at various ratios was studied in order to determine the optimum silica/CB ratio. The total hybrid filler content was 50 phr. The mechanical properties indicating the reinforcement of NR vulcanizates, such as tensile strength, tear strength, abrasion resistance, crack growth resistance, heat buildup resistance and rolling resistance, were determined. The results reveal that the vulcanizates containing 20 and 30 phr of silica in hybrid filler exhibit the better overall mechanical properties.

Tangpasuthadol *et al.* [17] studied on NR composites reinforced by silica generated inside the NR matrix. The silica particle was formed by a sol-gel process at 50°C of tetraethoxysilane (TEOS) mixed with NR latex. The results showed that the conversion of TEOS to silica was close to 100%, and the particles size was about 44 nm in diameter, determined by TEM. The silica particles scattered evenly in the rubber. A statistical analysis method “two-level factorial design” was used to study the influence of the amount of TEOS, ammonia, and gelation time on the mechanical properties of the composite. A composite having silica as high as 19% was prepared successfully. It was also found that the composite containing *in situ* silica had a shorter cure time and higher tensile modulus than the composite that was prepared by conventional mixing with silica powder.

Ikeda *et al.* [15] studied on the effect of amines on an *in situ* silica generation in NR and they reported that *n*-hexylamine, *n*-heptylamine and *n*-octylamine were found to increase the *in situ* silica content. Effect of amines type (primary, secondary and tertiary as the same molar mass) were compared. The results indicated that primary amine (*n*-hexylamine obtained higher amount of *in situ* silica than secondary (dipropylamine) and tertiary amine (triethylamine), respectively. The nanometer sized silica particles up to ca. 80 phr were generated *in situ* in the rubber matrix via a sol-gel reaction of tetraethoxysilane. Additionally, dispersion of the silica in the rubbery matrix was more homogeneous than that of commercial silica dispersed by a conventional mechanical mixing. In this *in situ* silica generation, the polarity and solubility in water of amine were influential factors for controlling the *in situ* silica content in the rubbery matrix.