

## CHAPTER II

### THEORY AND LITERATURE REVIEW

#### 2.1 Natural Rubber

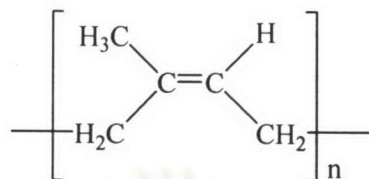
Natural rubber can be obtained from nearly five hundred different species of plants. The outstanding source is *Hevea Brasiliensis* from which comes the name Hevea rubber. Rubber is obtained from latex that exudes from the bark of the Hevea tree when it is cut [11]. Early explorers of South America found that natives, living in areas where the rubber tree grew, used latex, which had the capability of fabrication rubber goods such as water-proof clothing, water bottle, and shoes from latex [12]. Today rubber trees are grown in many regions of Africa, South America and mainly in Southeast Asia including Thailand, Indonesia, and Malaysia [13].

*Hevea 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. *Hevea Brasiliensis* requires temperatures of 20-30 °C, at least 2,000 mm of rainfall per year, and high atmospheric humidity.

##### 2.1.1 Natural Rubber Latex

Natural rubber latex is produced in special vessels outside the cambium layer of the *Hevea Brasiliensis* tree. The reason why the rubber tree makes rubber is still not known. One theory holds that it is a waste product of the tree. Latex, as from the tree, has a solid content of about 36%, a surface tension of 40.5 dyn/cm (30 °C) and a pH of 6. The polymer is primarily cis-1,4-polyisoprene (Fig. 2.1). Latex fresh from the tree is stabilized by naturally occurring proteins and phospholipids. It also contains other materials such as resins, sugars, mineral salts, and alkaloids. The protein stabilizer is very susceptible to bacterial action and would be destroyed within a few hours if ammonia were not immediately added. Soap-forming fatty acids are formed when the ammonia hydrolyzes the lipids. This ammonia soap then becomes the

primary stabilizer, displacing the adsorbed protein from the particle surface [14]. The composition of a typical field latex is presented in Table 2.1 [15].



**Figure 2.1 Cis-1,4-polyisoprene**

**Table 2.1** Composition of fresh *Hevea* latex

<b>Ingredient</b>	<b>Content (%w/w)</b>
Total solid content	36.0
Dry rubber	33.0
Proteinous substance	1.0-1.5
Resinous substance	1.0-2.5
Carbohydrates	1.0
Inorganic matter	Up to 1.0
Water	60

### 2.1.2 Concentrated Natural Rubber Latex [16]

“Field latex” or latex obtained directly from rubber trees has an average rubber content of 30 % by weight. This latex is not utilized in its original form due to its high water content and susceptibility to bacterial attack. The latex is usually preserved and concentrated, so that the end product is stable and contains 60 percent or more of rubber.

Latex concentrate usually made by a centrifugation-spinning at a high speed to separate a cream containing 60% rubber from a liquid part containing 5% rubber, from which dry skim rubber is made. A small amount of ammonia is added to the

latex, both on collection and before centrifugation, to prevent it from coagulation. Other methods to concentrate the latex are by evaporation and by adding a chemical, such as ammonium alginate.

Details of the preservation systems used in centrifuged concentrate are given in Table 2.2. The predominant products are the HA and LA-TZ types. The latex concentrate prepared by evaporation is usually stabilized by potassium hydroxide, while the creamed latex is normally preserved with 0.7 % ammonia.

**Table 2.2** Types of preservative system used in centrifuged NR latex concentrate

Preservative system	Abbreviation	Percent by weight
High ammonia	HA	0.7% ammonia
Low ammonia TZ	LA-TZ	0.2% ammonia, 0.025% zinc oxide, 0.025% tetramethylthiuram disulphide
Low ammonia pentachlorophenate	LA-SPP	0.2% ammonia, 0.2% sodium pentachlorophenate
Low ammonia boric acid	LA-BA	0.2% ammonia, 0.24% boric acid

Natural rubber latex concentrates are very highly specified materials and a large measure of international agreement has been achieved regarding acceptable limits for their basic properties. Table 2.3 summarizes the requirements of the International Standard Organization (ISO) specifications for various types of natural rubber latex concentrate.

**Table 2.3** ISO 2004 requirements for the centrifuged and cream concentrate latex

Characteristic	Centrifuged concentrate latex		Cream concentrate latex	
	HA	LA	HA	LA
Total solid content (%) (min)	61.5	61.5	66.0	66.0
Dry rubber content (%) (min)	60.0	60.0	64.0	64.0
Non-rubber solids (%) (max)	2.00	2.00	2.00	2.00
Alkalinity (as NH <sub>3</sub> ) (on latex)	0.6 (min)	0.29 (max)	0.55 (min)	0.35 (max)
Mechanical stability (s) (min)	650	650	650	650
Coagulum content (%) (max)	0.05	0.05	0.05	0.05
Copper content (mg.kg <sup>-1</sup> of solids) (max)	8	8	8	8
Manganese content (mg.kg <sup>-1</sup> of solids) (max)	8	8	8	8
Sludge content (%) (max)	0.10	0.10	0.10	0.10
Volatile fatty acid number (max)	0.20	0.20	0.20	0.20
Potassium hydroxide number (max)	1.0	1.0	1.0	1.0
Color on visual inspection	No pronounced blue or grey			
Odor after neutralization with boric acid	No pronounced odor of putrefaction			

HA = high-ammonia, LA = low ammonia

## 2.2 Fillers

### 2.2.1 Filler properties [17]

The characteristics that a filler will impart to a rubber compound are particle size, surface area, structure and surface activity.

Particle Size – If the size of the filler particle greatly *exceeds* the polymer inter-chain distance, it introduces an area of localized stress. This can contribute to the rupture of elastomer chain on flexing or stretching. Fillers with particle size greater than 10,000 nm (10  $\mu\text{m}$ ) are therefore generally avoided because they can reduce performance rather than reinforce or extend. Fillers with particle sizes between 1,000-10,000 nm (1-10  $\mu\text{m}$ ) are used primarily as diluents and usually have no significant effect on rubber properties. Semi-reinforcing fillers, which range from 100-1,000 nm (0.1-1  $\mu\text{m}$ ) improve strength and modulus properties. The truly reinforcing fillers, which range from 10-100 nm (0.01-0.1  $\mu\text{m}$ ) significantly improve rubber properties.

Carbon blacks and precipitated silicates and silica are available in various particle sizes that range from semi-reinforcing to highly reinforcing. They generally exist as structural agglomerates or aggregates rather than individual spherical particles.

Surface Area – A filler must make intimate contact with the elastomer chains if it is going to contribute to reinforcement. Fillers that have a high surface area have more contact area available and therefore have a higher potential to reinforce the rubber chains. The shape of the particle is also important. Particles with a planar shape have more surface 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  $\text{m}^2/\text{g}$ . Most reinforcing precipitated silica range from 125 to 200  $\text{m}^2/\text{g}$ ; a typical hard clay ranges from 20 to 25  $\text{m}^2/\text{g}$ .

Structure – The shape of an individual particle of reinforcing filler (e.g. carbon black or precipitated silica) is of less importance 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 acicular (needle-like) aggregates.

For reinforcing fillers which exist as aggregates rather than discrete particles, carbon black and silica in particular, a certain amount of structure that existed at manufacture is lost after compounding. The high shear forces encountered in rubber milling will break down the weaker aggregates and agglomerates of aggregates. The structure that exists in the rubber compound, the persistent structure, is what affects processability and properties.

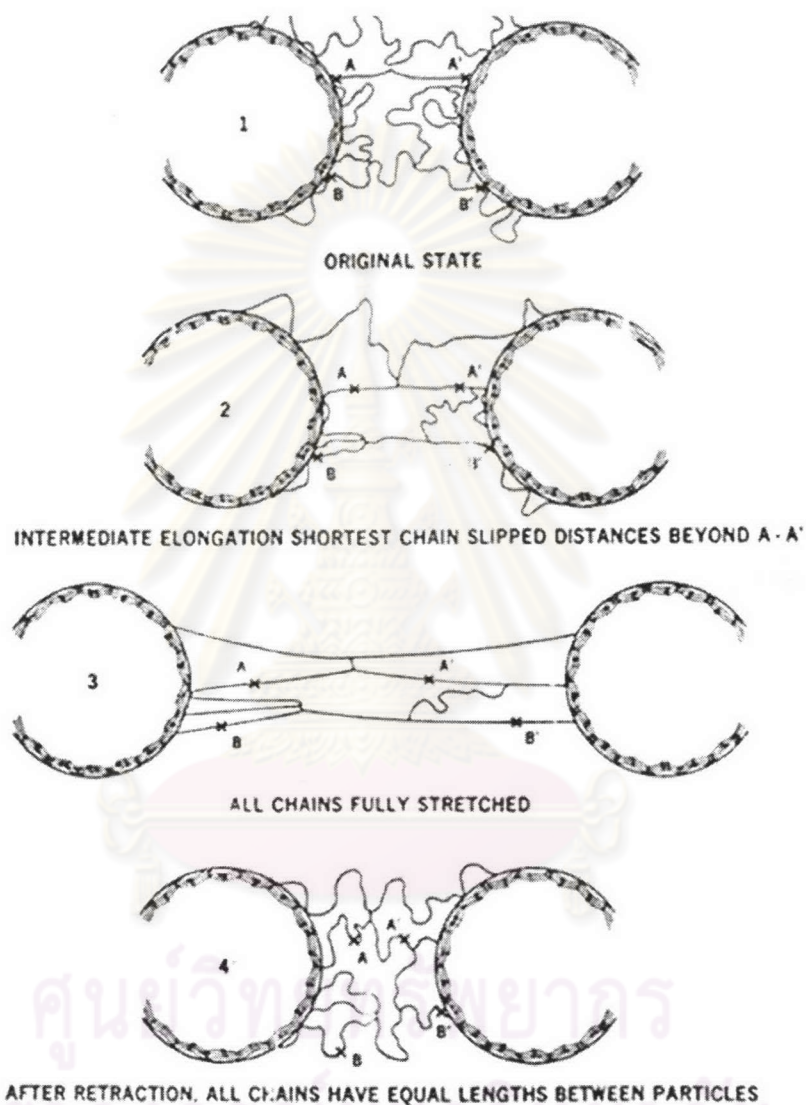
Surface Activity – a filler can offer high surface area and high structure, but still provide relatively poor reinforcement if it has low specific surface activity. The specific activity of the filler surface per  $\text{cm}^2$  of filler-elastomer interface is determined by the physical and chemical 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.

### **2.2.2 Reinforcement Concepts [18]**

Reinforcement basically relates to composites built from two or more structural elements or components of different mechanical characteristics. The strength of one of these elements is imparted to the composite. One typical example of reinforcement is that of concrete with embedded steel rods or cable where the high tensile strength of the steel is imparted to the concrete to give it increased flexural and impact strength. A strong bond must develop between the reinforcing materials and the embedding matrix in order to achieve a maximum reinforcing efficiency.

A very schematic picture of a slippage process when stress is applied to a polymer reinforced with carbon black is drawn in Fig. 2.2 [18]. Three chains of different lengths between the two carbon black particles in the direction of stress are displayed. As the stretching process proceeds from stage 1, the first chain slips at the points of connection A and A' until chain 2 is also stretched between B and B' (stage 2). Elongation continues until finally a stage 3 is reached in which all three chains are stretched to their maximum and share the imposed load. The homogenous stress distribution causes a high improvement in strength. In stage 4 the tension is relieved

and the test piece has retracted. There is now still a difference from the original situation (stage 1); due to the slippage does not have to be furnished as was the case originally.



**Figure 2.2** Molecule slippage model of a reinforcement mechanism [18].

### 2.2.3 Silica [19]

Addition of silica to a rubber compound offers a number of advantages such as improvement in tear strength, reduction in heat buildup and increase a compound adhesion in products such as tires. Two fundamental properties of silica influence its use in rubber compounds: ultimate particle size and the extent of hydration. Other

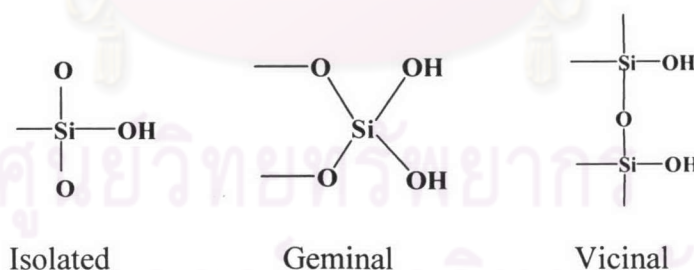
physical properties such as pH, chemical composition and oil absorption are of secondary importance.

Silica, when compared to carbon blacks of the same particle size does not provide the same level of reinforcement. Nevertheless the deficiency of silica largely disappears when *coupling agents* are used with silica. Wagner reported that addition of silica to a tread compound leads to a loss in tread wear, even though improvements in hysteresis and tear strength are obtained. But the tread wear loss can be corrected by the use of silane coupling agents [20].

The chemistry of silica is described as follows:

1. Silica is amorphous, consists of silicon and oxygen arranged in a tetrahedral structure of a three-dimensional lattice. Particle size ranges from 1 to 30 nm and surface area from 20 to 300 m<sup>2</sup>/g. There is no long-range crystal order, only short-range ordered domains in a random arrangement with neighboring domains.

2. Silanol types fall into three categories – isolated, geminal (two hydroxyl groups on the same silicon atom) and vicinal (two hydroxyl groups on adjacent silicon atoms) as illustrated in Figure 2.3.



**Figure 2.3** Typical silanol groups on silica.

3. Surface silanol concentration (silanol groups, Si-OH) influences the degree of surface hydration and acidity. The interaction between rubber and filler is affected by these sites. Also a high level of hydration can adversely affect final compound physical properties.

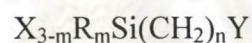
In general, silica produces relatively greater reinforcement in more polar elastomers such as NBR and CR than in non-polar polymers such as SBR and NR.



The lack of reinforcement properties of silica in NR and SBR can be corrected through the use of silane coupling agents. A coupling agent is the bifunctional molecule, capable of reacting chemically with both the silica and either directly or indirectly with the polymer via participation in the vulcanization reaction or sulfur crosslinking process.

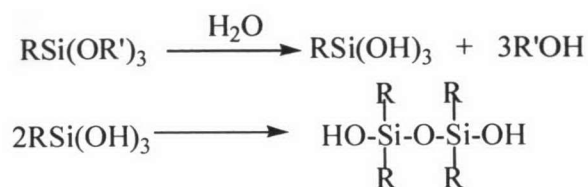
### 2.3 Silane Coupling Agents [19, 21, 22]

Silanes have been around for over 40 years but their early applications are more in adhesives and coatings. In rubber compounding, the first silane coupling agent was commercialized in 1971, bis-(3-triethoxysilyl propyl)tetrasulfide (TESPT) known as Si-69 (by Degussa). Silane coupling agents are bifunctional organosilanes which can be represented viz:



where X is a hydrolysable group, such as halogen, alkoxy or acetoxy groups, capable of forming strong covalent bonds with the hydroxyl groups on silica surfaces (or silanol groups), and Y is a functional group which itself is able to chemically react with the polymer either directly or through other chemicals. It may also be a chemical group able to develop a strong physical interaction with polymer chains. For the Y groups, important silane coupling agents include amino, epoxy, acrylate, vinyl and sulfur-containing groups such as mercapto, thiocyanate and polysulfide. The bifunctional silane coupling agents most often contain three ( $m=0$ ) X groups and the functional group Y is generally in the  $\gamma$  position ( $n=3$ ). Practically, when silica is incorporated in a hydrocarbon rubber, the most popular and effective coupling agents are  $\gamma$ -mercaptopropyltrimethoxysilane ( $\gamma$ -MPS), known as A189, and TESPT. In fact, as far as the commercialized coupling agents are concerned, TESPT is the most commonly used silane enabling silica to be applied to tire compounds-tread compounds in particular.

Upon contact with water, the following reactions take place.



The hydrolysis of trialkoxy groups takes place in a stepwise fashion to give the corresponding silanols, which ultimately condense to siloxanes.

## 2.4 Vulcanization Tests

### 2.4.1 Description of Curing Parameters [23]

**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 does 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, i.e., “the cure time”.

**State of Cure** In general, “state of cure” is a 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

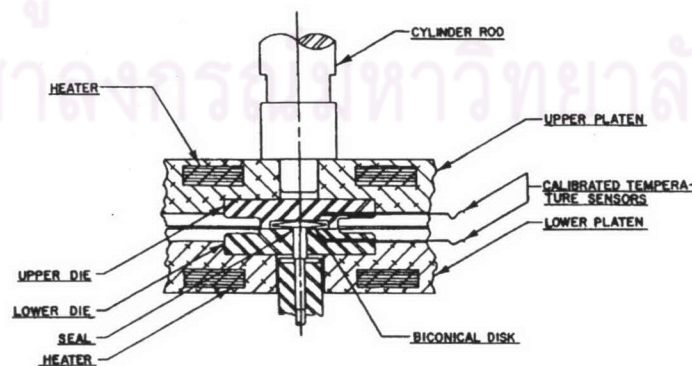
imparted by vulcanization do not occur at the same level of cure, the state of optimizing may not be the best for other properties.

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

**Overcure** A cure which is longer than optimum is an “overcure”. 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 natural rubber compounds, reversion occurs with overcure and the modulus and tensile strength decrease.

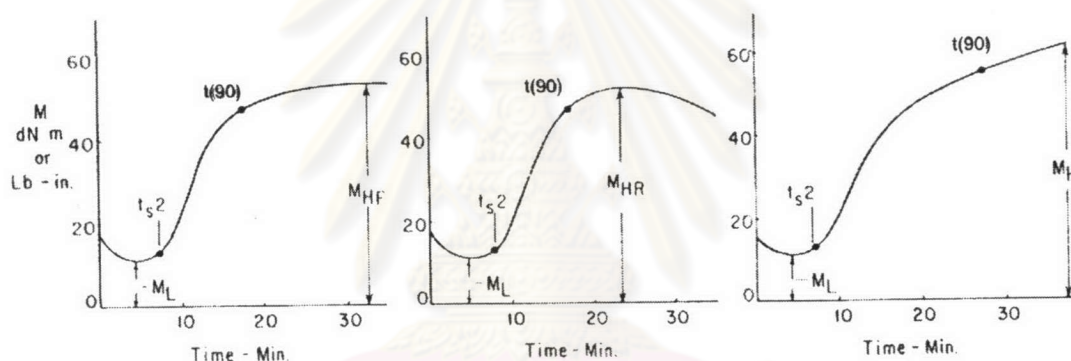
#### 2.4.2 Characterization of the Vulcanization Process [23-25]

The effects of compound variations on curing characteristics are important in compound development studies or a production control. Cure meter tests are ideally suited for use in both areas. Composition of the compound can be varied until the desired vulcanization characteristics are obtained. The most widely used cure meters are **oscillating disk rheometers** as shown in the Figure 2.4. To measure the vulcanization characteristics, the rubber is enclosed in a heated cavity. Embedded in the rubber is a metal disk which oscillates sinusoidally in its plane about its axis. Vulcanization is measured by the increase in the torque required to maintain a given amplitude of oscillation at a given temperature. The torque is proportional to a low-strain modulus of elasticity.



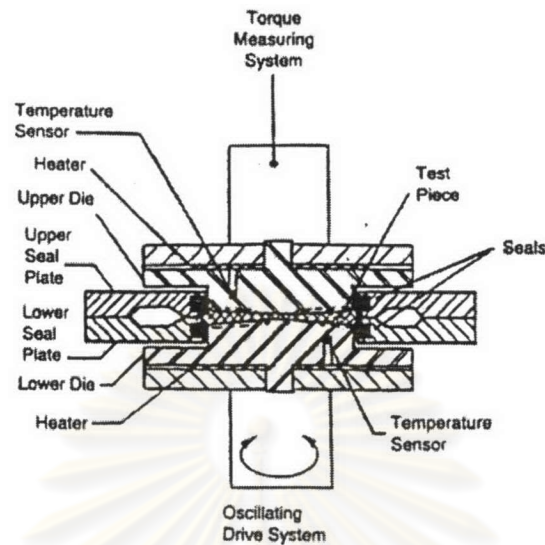
**Figure 2.4** Oscillating disk rheometers (source: ASTM D 2084-93, Fig. 2, p. 352).

Thus, it has been assumed that the increase in torque during vulcanization is proportional to the number of crosslinks formed per unit volume of rubber. The torque is plotted against time to give a so-called rheometer chart, rheograph, or cure curve. The cure curve obtained with a cure meter is a “fingerprint” of the compound’s vulcanization and processing character. The three different types of cure curve which can be obtained with different types of rubber compounds are shown in Figure 2.5. For example, some synthetic rubber compounds attain a constant or equilibrium torque level while most natural rubber compound exhibit reversion. The minimum torque ( $M_L$ ), maximum torque ( $M_{HF}$ ), scorch time ( $t_{s2}$ ) and time to 90% cure ( $t_c(90)$ ) are indicated.



**Figure 2.5** Type of cure curve. Left curve: cure to equilibrium torque. Middle curve: cure to a maximum torque with reversion. Right curve: cure to no equilibrium or maximum torque [23].

New versions of the cure meter have been introduced. The cavity is much smaller and there is no rotor. In this type of cure meter, one-half of the die is stationary and the other half oscillates. These instruments are called moving-die rheometers (e.g., the Monsanto MDR 2000) (Fig. 2.6). The sample is much smaller and heat transfer is faster. Also, because there is no rotor, the temperature of the cavity and sample can be changed more rapidly.



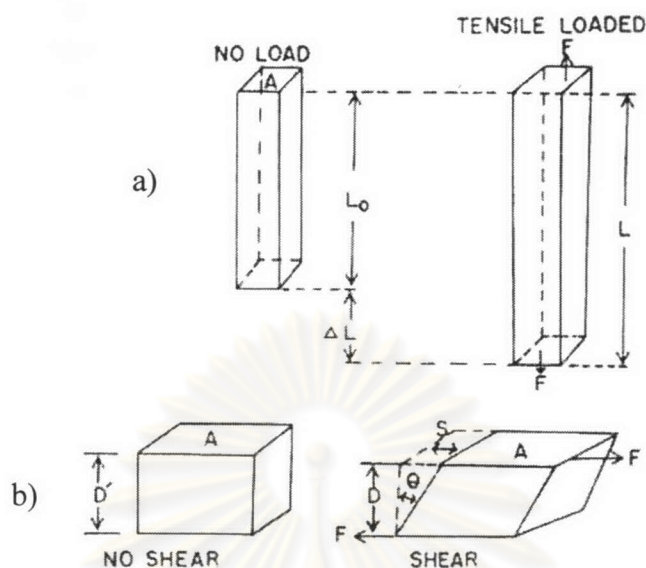
**Figure 2.6** Moving-die rheometers (source: ASTM D 5289-93a, Fig. 4 (a), p. 789).

## 2.5 Mechanical Testing

### 2.5.1 Stress-Strain Tests [25]

Physical testing of rubber often involves application of a force to a specimen and measurement of resultant deformation or application of a deformation and measurement of the required force. Two common modes of deformation, tensile and shear are shown in Figure 2.7.

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

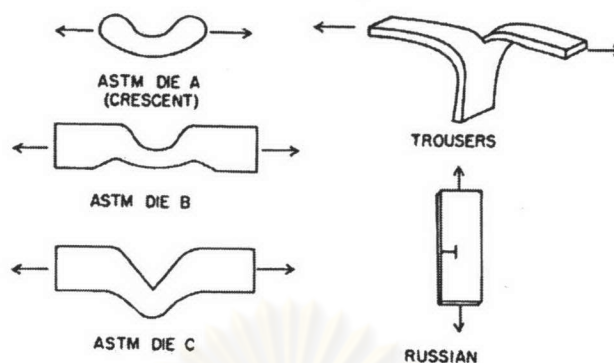


**Figure 2.7** a) Tensile stretching of a bar; b) Shear of a rectangular block.

### 2.5.2 Tear Tests [25]

Tear test results are strongly dependent on the type of specimen used, the rate of tearing, and the temperature. The method is useful only for laboratory comparisons and is not applicable for service evaluations, except when supplemented by additional tests, nor for use in purchase specifications.

Three types of tear specimens are classified by Buist: indirect tearing as in the trousers specimen (Fig. 2.8), tearing perpendicular to the direction of stretching as in the ASTM methods, and tearing in the direction of stretching as in the Russian test piece. Except in the ASTM die C specimen nicks of prescribed lengths are cut into the region of desired stress concentration.



**Figure 2.8** Types of tear specimens.

Tear test results are usually expressed as the pull in pounds required to tear a specimen one inch thick, but the required pull on specimens of the ASTM type is dependent on width as well as thickness. The results on such specimens should be called tear strength, whereas those on direct tearing method such as the trousers specimen should be called tear resistance.

### 2.5.3 Hardness [25]

Hardness, as applied to rubber, may be defined as the resistance to indentation under conditions which do not puncture the rubber. Hardness must be expressed in terms of instrument parameters rather than in basic units. The spring-loaded pocket durometer is the most common instrument for measuring hardness of elastomers. The shore durometer (ASTM D2240) in particular is generally used. In this instrument the scale runs from zero hardness for a liquid to 100 for a hard plane surface such as glass. The type A durometer is used for soft stocks, up to a reading of 90. Above 90 the type D durometer, having a different indenter shape and different stiffness spring, is used.

In ordinary SBR rubber compounds the hardness increases with increased cure. In natural rubber compounds the hardness increases to a maximum and then decreases because of reversion as the cure time is increased.

#### 2.5.4 Dynamic Mechanical Tests [25, 26]

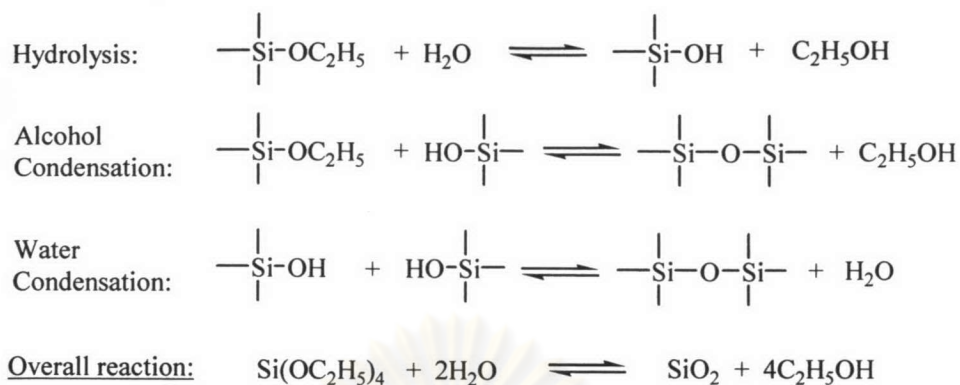
In most of its uses, rubber is subjected to relatively large deformations during which it absorbs mechanical energy, transforming it into heat energy. The deforming force is thus resisted by both elastic and damping forces. [*Damping* refers to the progressive reduction of vibrational amplitude in a free vibration system. Damping is a result of hysteresis, and the two terms are frequently used interchangeably]. The principal purpose of dynamic mechanical tests is to evaluate these forces.

Measurements by dynamic mechanical properties refer to any one of several methods where the sample undergoes repeated small-amplitude strains in a cyclic manner. Loss tangent ( $\tan \delta$ ) is the ratio of *Young's storage modulus* ( $E'$ ), a measure of the energy stored elastically, to *Young's loss modulus* ( $E''$ ), a measure of the energy lost as heat. The maxima on  $E''$  and  $\tan \delta$  are sometimes used as the definition of glass transition temperature ( $T_g$ ). The width of the transition and shifts in the peak temperature of  $E''$  or  $\tan \delta$  are sensitive guides to the exact state of the material, molecular mixing in blends.

#### 2.6 Sol-Gel Process [4]

The sol-gel technique is used to prepare inorganic glasses at low temperatures. A classic example is the reaction of tetraethoxysilane (TEOS) to give silica glass ( $\text{SiO}_2$ ). The reaction of TEOS takes place in two steps, hydrolysis and condensation, to produce  $\text{SiO}_2$  as shown in Figure 2.9.





**Figure 2.9** Hydrolysis and condensation reactions of TEOS to form silica.

## 2.7 Experimental Design- $2^k$ Factorial Design [27, 28]

Factorial designs are widely used in experiments involving several factors where it is necessary to study the joint effect of the factors on response. There are several special cases of the general factorial design that are important because they are widely used in research work and also because they form the basis of other designs of considerable practical value.

The most important of these special cases is that of  $k$  factors, each at only one two levels. These levels may be quantitative or may be qualitative such as the presence and absence of a factor, the high and low levels of a factor. A complete replicate of such a design requires  $2 \times 2 \times \dots \times 2 = 2^k$  observations and is called a  $2^k$  factorial design. It is particularly useful in the early stages of experimental work, when there are likely to be many factors to be investigated. It provides the smallest number of runs which  $k$  factors can be studied in a complete factorial design. Consequently, these designs are widely used in factor screening experiments. Because there are only two levels for each factor, we assume that the response is approximately linear over the range of the factor levels chosen.

Suppose that three factors, A, B and C, each at two levels, are of interest. The design is called a  $2^3$  factorial design. Using the “+” and “-” notation to represent the

high and low levels of the factors, the eight runs in the  $2^3$  design are listed in Table 2.4. This is called a *design matrix*. There are actually three different notations that are widely used for the runs in the  $2^k$  design. The first is the + and – notation, often called the *geometric notation*. The second notation uses 1 and 0 to denote high and low factor levels, respectively, instead of + and –. The final notation is the use of lowercase letter labels to identify the treatment combinations. These different notations are illustrated in Table 2.4 for the  $2^3$  design.

**Table 2.4** The design matrix and different notation for the  $2^3$  design

Run	A	B	C	A	B	C	labels
1	-	-	-	0	0	0	(1)
2	+	-	-	1	0	0	<i>a</i>
3	-	+	-	0	1	0	<i>b</i>
4	+	+	-	1	1	0	<i>ab</i>
5	-	-	+	0	0	1	<i>c</i>
6	+	-	+	1	0	1	<i>ac</i>
7	-	+	+	0	1	1	<i>bc</i>
8	+	+	+	1	1	1	<i>abc</i>

There are seven degrees of freedom between the eight treatment combinations in the  $2^3$  design. Three degrees of freedom are associated with the main effects of A, B and C. Four degrees of freedom are associated with interactions; one each with AB, AC and BC and one with ABC.

Next a value called ‘*effect*’ must be determined from the design matrix. The effect is the difference between average value of the *high* and the *low* levels of each factor.

$$Effect = \hat{y}_+ - \hat{y}_-$$

The effects are calculated by using the columns of contrast coefficients, illustrated in Table 2.5. The contrasts for the main effects are the sign used in the design matrix. These are applied to the responses and then divided by 4, since this is the number of comparison mode. Thus, to calculate the A effect:

$$A \text{ Effect} = \frac{-y_1 + y_2 - y_3 + y_4 - y_5 + y_6 - y_7 + y_8}{4}$$

The other main effects could be calculated in a similar manner. Note that each effect has four – signs and four + signs associated with it.

For an interaction effect, the AB effect is shown below.

$$AB \text{ Effect} = \frac{+y_1 - y_2 - y_3 + y_4 + y_5 - y_6 - y_7 + y_8}{4}$$

**Table 2.5** The columns of contrast coefficients for the  $2^3$  design

A	B	C	AB	AC	BC	ABC	CRF (y)
-	-	-	+	+	+	-	y <sub>1</sub>
+	-	-	-	-	+	+	y <sub>2</sub>
-	+	-	-	+	-	+	y <sub>3</sub>
+	+	-	+	-	-	-	y <sub>4</sub>
-	-	+	+	-	-	+	y <sub>5</sub>
+	-	+	-	+	-	-	y <sub>6</sub>
-	+	+	-	-	+	+	y <sub>7</sub>
+	+	+	+	+	+		y <sub>8</sub>

If replicate experiments are also performed, whose *standard errors* ( $E$ ) in the effect values are calculated.

$$E = \left( \frac{\sum V}{2N} \right)^{1/2}$$

Where  $V$  is the variance of replications and  $N$  is the number of experiments performed.

The standard error ( $E$ ) is used to determine which factor is likely to be important or significant. If the effect value is larger than the standard error, that effect has a significant influence on the tested property.

Detailed method for experimental design carried out in this research is shown in Experimental chapter.

## 2.8 Literature Reviews

In 2003, Brinke *et al.* [29] studied the mechanistic aspects of the reactions of sulfur built in the silane coupling agent vs elemental sulfur in the curing package on the dynamic mechanical properties of silica-filled tyre tread compounds. The compounds were mixed in three steps, the first two steps were done in internal mixer and the third mixing step was performed on the two-roll mill. The accelerators and sulfur were added in a two-roll mill step. They found that the interaction between the elemental sulfur and the coupling agents plays a crucial role throughout the processing history of silica-reinforced compounds. The sulfur not only acts as a crosslinking agent between rubber molecules during vulcanization, but is in a vigorous interaction with the coupling agent during mixing, the latter extending so far as to apply evenly to the coupling agents which have no built-in sulfur. The compounds with sulfur containing coupling agents are more prone to show effects of silica-rubber coupling, than those containing sulfur-free coupling agents.

In 2004, Sae-oui *et al.* [30] studied the reinforcement of NR by hydrated silica filling combined with TESPT. The rubber compounds were prepared using the internal mixer. They found that the addition of TESPT not only improves compound processability, but also enhances the mechanical properties, such as tensile strength, tear strength, abrasion resistance, hardness and compression set, and curing behaviors of the rubber vulcanizates. Due to TESPT improves filler dispersion, filler-rubber interaction and reduces the silanol groups on the silica surface. The dynamic mechanical properties of the NR-silica vulcanizates,  $E'$  increases noticeably with increasing TESPT content due to improved rubber-filler interaction and higher state of cure.  $\tan \delta$  decreases significantly with the addition of TESPT, is attributed to the improvement of both state of cure and filler dispersion leading to the reduction of filler-filler frictional losses. Heat build-up of the rubber vulcanizates with TESPT is lower than it without TESPT.

In 1998, Hashim *et al.* [2] prepared silica-reinforced SBR (styrene-butadiene rubber) by *in situ* silica filling combined with TESPT. The process began by sulfur-cure SBR with TESPT also added. To generate the silica *in situ*, Hashim soaked the sulfur-cured SBR in TEOS, followed by n-butylamine- a base catalyst. The sol-gel process was carried out 50°C for 72 h to complete *in situ* silica filling in the rubber. The results obtained from the dynamic mechanical analysis indicated that the rubber-silica bonds introduced by TESPT significantly decreased the damping and heat build up properties of vulcanizates. TESPT in the SBR compounds therefore acted as a co-curing agent which also affected the cure characteristics and improved the tensile properties of the silica-rubber vulcanizates. The very fine and homogeneous *in situ* silica particles in the SBR vulcanizate with TESPT is also considered to be one of the factors that gives an excellent reinforcement effect.

In the same year as Tanahashi *et al.* [7] studied reinforcement of NBR (acrylonitrile-butadiene rubber) by silica generated *in situ*. It was found that the amount of *in situ* silica introduced in the NBR vulcanizates was limited due to the high polarity of NBR. The  $\gamma$ -mercaptopropyl-trimethoxysilane ( $\gamma$ -MPS) was added in the preparation process of NBR vulcanizate and found to increase the conversion of

TEOS in the sol-gel reaction and resulted in the higher amount of *in situ* silica compared to the system without  $\gamma$ -MPS. The obtained silica was very fine and dispersed very homogeneously.

In 2000, Kohjiya and Ikeda [31] presented a review of the reinforcement of rubber by silica generated *in situ* that its effect was similar to the soaking method reported earlier by Hashim. This silica was found to be a good reinforcing agent for ENR (epoxidized NR), SBR, and BR in terms of tensile and dynamic mechanical properties. The particle size of *in situ* silica prepared in the presence of silane coupling agent as observed by TEM was mono-dispersed and smaller than that formed *in situ* but without the coupling agent. Thus, the mechanical properties were further improved.

In previous literatures, the sol-gel silica was generated in the rubber vulcanizates in which this technique restricts the thickness of the samples for the homogeneous filling of *in situ* silica. A few millimeter thicknesses of the vulcanizates were adequate for a swelling in TEOS before the reaction. The samples were immersed in the aqueous solution of the catalyst in order to conduct the sol-gel reaction of TEOS, and this procedure also limited the thickness for the sake of homogeneous reaction in the rubber matrix. Therefore, in 2001, Kohjiya *et al.* [32] prepared the *in situ* silica filling in the rubber matrix before vulcanization. The NR sheet of ca. 1 mm thickness was immersed in TEOS and aqueous solution of *n*-butylamine to follow the sol-gel reaction of TEOS. After that, the *in situ* silica-filled NR was compounding with ingredients for the sulfur vulcanization reaction on a two-roll mill and vulcanized at 150 °C in the compression mould. He found that fine and well-dispersed *in situ* silica particles were generated by the sol-gel reaction of TEOS in the rubber matrix before vulcanization and those did not much inhibit the crosslinking reaction of NR compound by sulfur, which suggested that the amount of silanol groups on the surface of *in situ* silica was lower than that of conventional silica and vulcanizates improved the mechanical properties. Since the filling of *in situ* silica was conducted before curing, this method is more useful as an industrially practical technique than the method in which the sol-gel reaction of TEOS was carried out in the rubber vulcanizates.

Upon detailed analysis of the literatures, the method to generate *in situ* silica-reinforced rubber has one limitation. The amount of silica formed was, however, limited by the degree of diffusion TEOS into rubber matrix. In 2002, Yoshikai *et al.* [9] reported a study on silica reinforcement of synthetic diene rubbers by a sol-gel process of TEOS in the latex. The TEOS was mixed directly into the latex of SBR and NBR (nitrile rubber). The sol-gel process of TEOS then proceeded in a mixture of latex, water and a catalyst. The silica content in the compounds, particle size and reinforcing behavior of silica were found to depend on the amount of TEOS added and the molar ratio of water to TEOS. The average particle size of silica was reported to be smaller than 100 nm. The tensile strength of SBR and NBR were over 25 MPa.

Until recently, Nuntivanich and Tangpasuthadol [10] studied silica reinforcement of NR starting from NR latex. Silica was formed *in situ* by a sol-gel process of tetraethoxysilane (TEOS) in the concentrated NR latex which has already contained 40% water and 0.7% NH<sub>3</sub>, two ingredients were needed for the sol-gel reaction. The conversion of TEOS to silica was close to 100%, and the particles size was about 44 nm in diameter. The silica particles were scattered evenly in the rubber matrix. A statistical analysis method, named '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. In this study, silica content as high as 19% was prepared successfully. It was also found that the composite containing *in situ* silica had a higher tensile modulus and tear strength than the composite prepared by conventionally mixing with silica powder.