CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Natural Rubber

Natural rubber is obtained from the milky secretion (latex) of various plants, but the only important commercial source of natural rubber (sometimes called Pará rubber) is the tree *Hevea brasiliensis.*

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

Latex, is normally called 'field' latex, 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 highly linear cis-1,4-polyisoprene (Fig. 2.1) of about 5 x 10^5 g/mol. The colloids stable the presence of protein adsorptions at the surface of the rubber particles. These adsorbed proteins are in the anionic state so that the rubber particles carry negative charges on their surfaces [13].

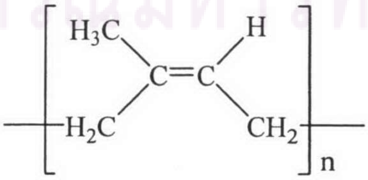


Figure 2.1 *Cis*-1,4-polyisoprene

Field latex can be concentrated by using a centrifuge to obtain 60% dry rubber content. The composition of a typical field latex is presented in Table 2.1. Details of the preservation systems used in centrifuged concentration are given in Table 2.2 [14].

Table 2.1 Composition of fresh *Hevea* latex.

Ingredient	**Content (%by weight)**
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

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

Designation	**Abbreviation**	**Preservative system (%by weight)**
High or full ammonia	HA	0.7% ammonia
Low ammonia TZ	LA-TZ	0.2% ammonia, 0.025% zinc oxide, 0.025% tetramethylthiuram disulphide
Low ammonia pentachlorphenate	LA-SPP	0.2% ammonia, 0.2% sodium pentachlorphenate
Low ammonia boric acid	LA-BA	0.2% ammonia, 0.24% boric acid

2.2 Fillers for Rubbers

Fillers may be of two types, reinforcing and non-reinforcing. Common reinforcing fillers are silica and carbon black. The latter are the most widely used in automotive tires to improve wear characteristics such as abrasion resistance. Non-reinforcing fillers, such as calcium carbonate, may provide color or opacity or may merely lower the price of the final product [13].

2.2.1 Filler properties

The characteristics that a filler will impart to a rubber compound are particle size, surface area, structure and surface activity [15].

<u>Particle Size</u>– 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 μm) 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 μm) 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 μm) improve strength and modulus properties. The truly reinforcing fillers, which range from 10-100 nm (0.01-0.1 μm), significantly improve rubber properties.

Carbon blacks and precipitated 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.

<u>Surface Area</u>– 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 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 m^2/g. Most reinforcing precipitated silica range from 125 to 200 m^2/g; a typical hard clay ranges from 20 to 25 m^2/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 discreet 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 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 Reinforcing fillers

Natural rubber has a certain degree of self-reinforcement, since it crystallizes on elongation. The thermoplastic elastomers also gain by the presence of hard blocks. However, nearly all elastomeric materials have some type of reinforcing filler.

The reinforcing fillers, with dimensions in the order of 10 to 20 nm, form a variety of physical and chemical bonds with the polymer chains. Tensile and tear strength are increased, and the modulus is raised. The reinforcement can be understood through chain slippage mechanisms (see Fig. 2.2). The filler permits local chain segment motion but restricts actual flow [13].

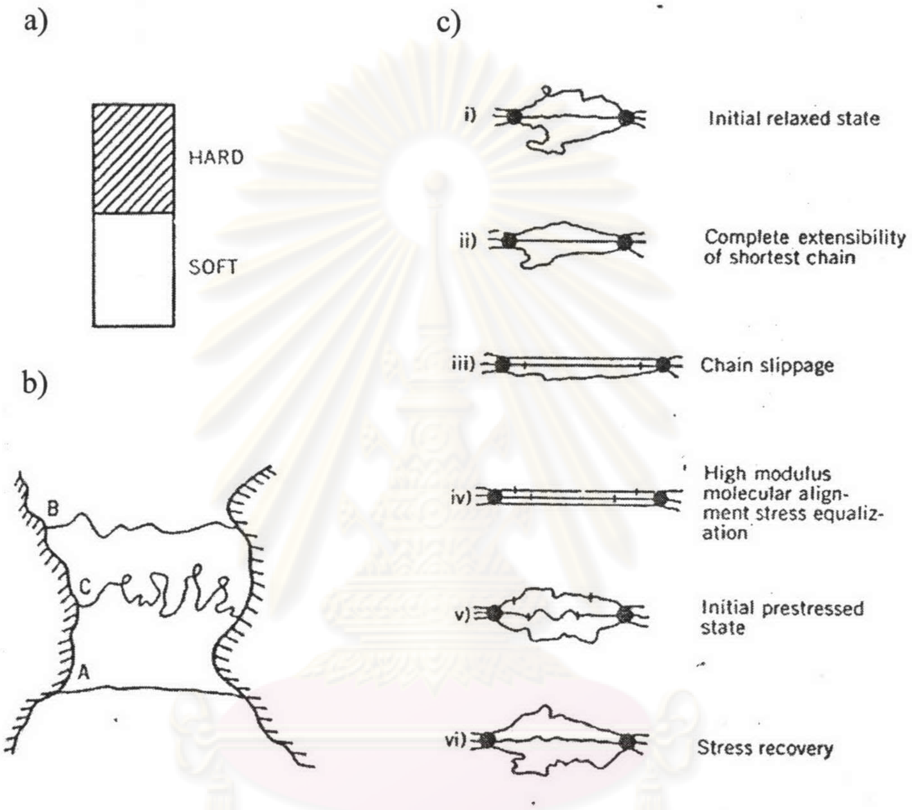


Figure 2.2 Mechanisms of reinforcement of elastomers by carbon black: (a) Takayanagi model approach; (b) on stretching, some chains (A) will become taut before others (B, C); (c) chain slippage on filler surface maintains polymer-filler bonds [13]

2.2.3 Silica

Amorphous silica consists of ultimate particles of the inorganic silicon dioxide $(SiO_2)_n$, where a silicon atom is covalently bonded in a tetrahedral arrangement to four oxygen atoms. Each of the four oxygen atoms is covalently bonded to either one silicon atom forming a siloxane (-Si-O-Si-) or to a hydrogen forming a silanol (-Si-O-H) functionality (Fig. 2.3).

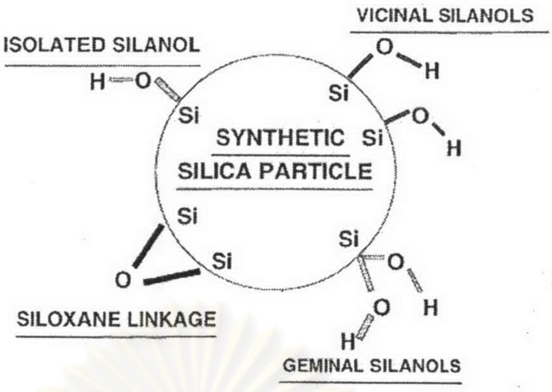


Figure 2.3 Silica surface groups: siloxane (-Si-O-Si-) and isolated, vicinal, and geminal silanols (-Si-O-H) [16]

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 Fig. 2.4 [17].

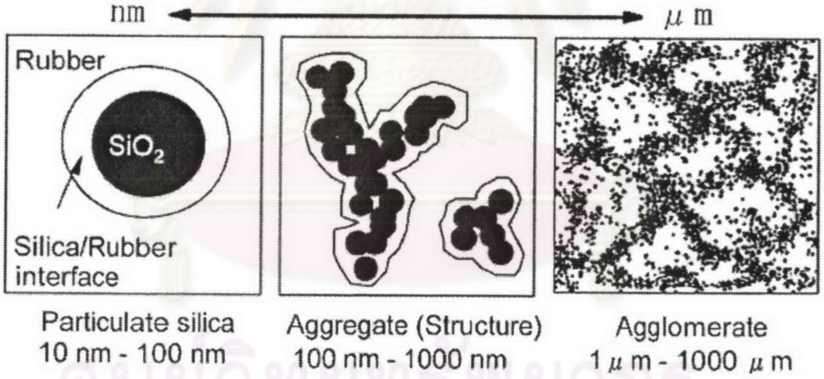


Figure 2.4 Silica particle and its morphology in rubber matrix [17]

Aggregates are three-dimensional clusters of ultimate particles, covalently bonded to one another via siloxane bonds. Aggregates can physically agglomerate through intermolecular hydrogen bonding of surface silanol groups of one aggregate to a silanol group of other aggregate.

Because of its small particle size and complex aggregate structure, precipitated silica imparts the highest degree of reinforcement to elastomer compounds among all of the non-black particulate fillers. This superior reinforcement is employed in a variety of rubber compounds for shoe soles, industrial rubber goods, and tires [18].

2.2.4 Organotrialkoxysilane

Trialkoxysilanes R-Si(OR′)$_3$ with an organic substituent R are suitable precursors of organic-inorganic hybrid materials due to their ability to readily undergo hydrolysis and condensation reactions via the three alkoxy groups. The sol-gel polymerization of trialkoxysilanes involving hydrolysis and condensation results in the formation of polysilsesquioxane products (scheme 2.1).

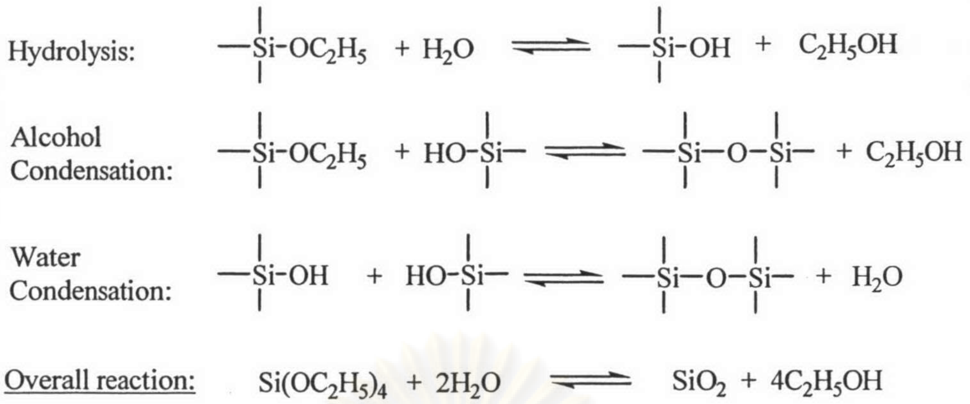
$$\mathrm{n\ R{-}Si(OR')_3} \quad + \quad \mathrm{1.5n\ H_2O} \xrightarrow{\mathrm{H^+\ or\ OH^-}} \left[\mathrm{R{-}SiO_{1.5}}\right]_n \quad + \quad \mathrm{3n\ R'OH}$$

Scheme 2.1 Hydrolysis and condensation of trialkoxysilanes to give polysilsesquioxane [19]

The polymers are composed of a monomer repeat unit, ($RSiO_{1.5}$), with a single silicon atom attached to other repeat units in the polymer through up to three siloxane bonds. The remaining substituent is an organic group attached to the silicon through a silicon-carbon single bond [19]. The formation of interaction or chemical bonds between the inorganic and organic components is expected to be of great importance in guarantee a durable chemical junction between the two incompatible phases.

2.3 Sol-Gel process

The sol-gel process involves the hydrolysis of a reactive, multifunctional inorganic monomer. A reaction is the acid- or base-catalyzed hydrolysis of tetraethoxysilane (TEOS) (Scheme 2.2). This compound can be hydrolyzed in solution to silicic acid [$Si(OH)_4$], a monomer that will condense rapidly to a cross-linked matrix and ultimately to silica.



Hydrolysis: $$-\mathrm{Si}-OC_2H_5 + H_2O \rightleftharpoons -\mathrm{Si}-OH + C_2H_5OH$$

Alcohol Condensation: $$-\mathrm{Si}-OC_2H_5 + HO-\mathrm{Si}- \rightleftharpoons -\mathrm{Si}-O-\mathrm{Si}- + C_2H_5OH$$

Water Condensation: $$-\mathrm{Si}-OH + HO-\mathrm{Si}- \rightleftharpoons -\mathrm{Si}-O-\mathrm{Si}- + H_2O$$

Overall reaction: $$Si(OC_2H_5)_4 + 2H_2O \rightleftharpoons SiO_2 + 4C_2H_5OH$$

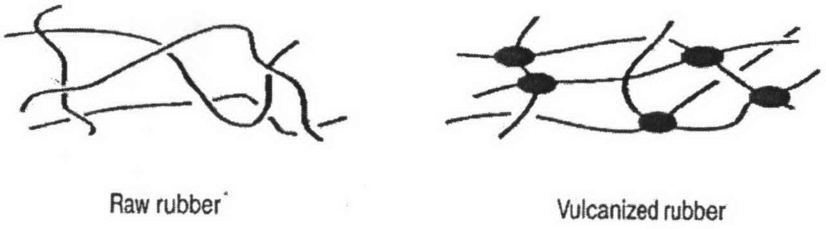
Scheme 2.2 Hydrolysis and condensation reaction of TEOS to form silica

In practice, the hydrolysis is carried out in ethanol solvent under controlled conditions that allow the solution (sol) to form a formable loosely cross-linked matrix (gel). This, after molding into a prescribed shape, is heated to remove the remaining water and alcohol and convert the matrix to a heavily cross-linked ceramic with a composition similar to that of silica. The method is also applicable to the alkoxides of titanium, aluminum, and many other elements. The main drawback of this process is that a considerable contraction of volume occurs during the final condensation steps.

The sol-gel process is widely used to produce high-performance ceramics. The advantages are the possibility of using low temperatures, the high purity of the products, the control of structure (at the nanometer level), and the relative ease of forming ceramics alloys [16].

2.4 Vulcanization

Vulcanization (or curing) is a chemical process designed to reduce the effects of temperature, or solvents on the properties of a rubber compound and to create useful mechanical properties. This is most often accomplished by heating with vulcanizing agents, such as elemental sulfur, organic peroxides, organic resins, metal oxides, or urethane. This process converts a viscous entanglement of long chain molecules into a three dimensional elastic network, as shown in Fig. 2.5 [20].



Raw rubber

Vulcanized rubber

Figure 2.5 Crosslinking [20]

Sulfur is by far the most widely used vulcanizing agent in conjunction with activators (metal oxides and fatty acids) and organic accelerators. These are used primarily with general purpose rubbers such as natural rubber (NR), styrene butadiene rubber (SBR), and polybutadiene rubber (BR)—all of which contain unsaturation (double bonds) as opposed to basically saturated rubbers (e.g., butyl, EPDM, etc.). Sulfur donors are used to replace part or all of the elemental sulfur to improve thermal and oxidative aging resistance. They may also be used to reduce the possibility of sulfur bloom and to modify curing and processing characteristics. Two chemicals; tetramethylthiuram disulfide (TMTD) and dithiodimorpholine (DTDM), have been developed over the years to function as sulfur donors to be used in combination with sulfur. They are used to provide significantly improved heat and aging resistance plus reduced heat build-up, in many cases [20].

2.4.1 Description of Curing Parameters

The related terms of vulcanization process are described as follows [21];

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, i.e., "the cure time".

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 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

Oscillating disk rheometers (Fig. 2.6) are widely used to measure the curing behavior of rubber compounds, by following the change in torque as the curing reaction proceeds. A rotor is embedded in the rubber sample, which is confined in a die cavity under pressure, and controlled at a predetermined temperature. The sample is subjected to an oscillatory shearing action of constant amplitude, and the torque required to oscillate the rotor is measured. Since the rotor is straining the sample, the torque values are directly related to the shear modulus of the rubber.

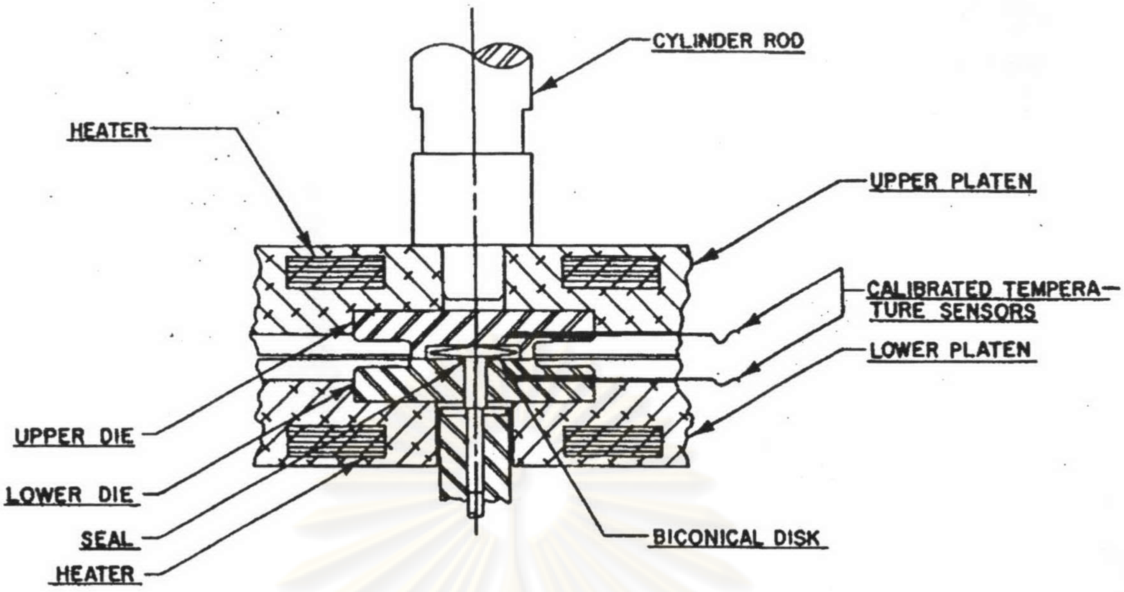


Figure 2.6 Oscillating disk rheometers (source: ASTM D 2084-93, Fig. 2, p. 352)

Typical curves from an oscillating rheometer are shown in Fig. 2.7 [17]. Most rubbers provide one of the three general shapes. The middle curve is typical of most natural rubber compounds, exhibiting reversion.

The values read from the curves are:

M_L	minimum torque in Nm or lbf·in
M_{HF}	maximum torque where curve plateaus in Nm or lbf·in
M_{HR}	maximum torque of reverting curve in Nm or lbf·in
M_H	highest torque attained during specified period when no plateau or maximum torque is obtained in Nm or lbf·in
t_{s1}	minutes to 1 lbf·in rise above ML – used with 1° arc
t_{s2}	minutes to 1 lbf·in rise above ML – used with 3° arc
t_x	minutes to x% of torque increase, t_x = minutes to $x \cdot M_H/100$
t'_x	minutes to x% of torque increase, t'_x = minutes to $M_L + x(M_H - M_L)/100$

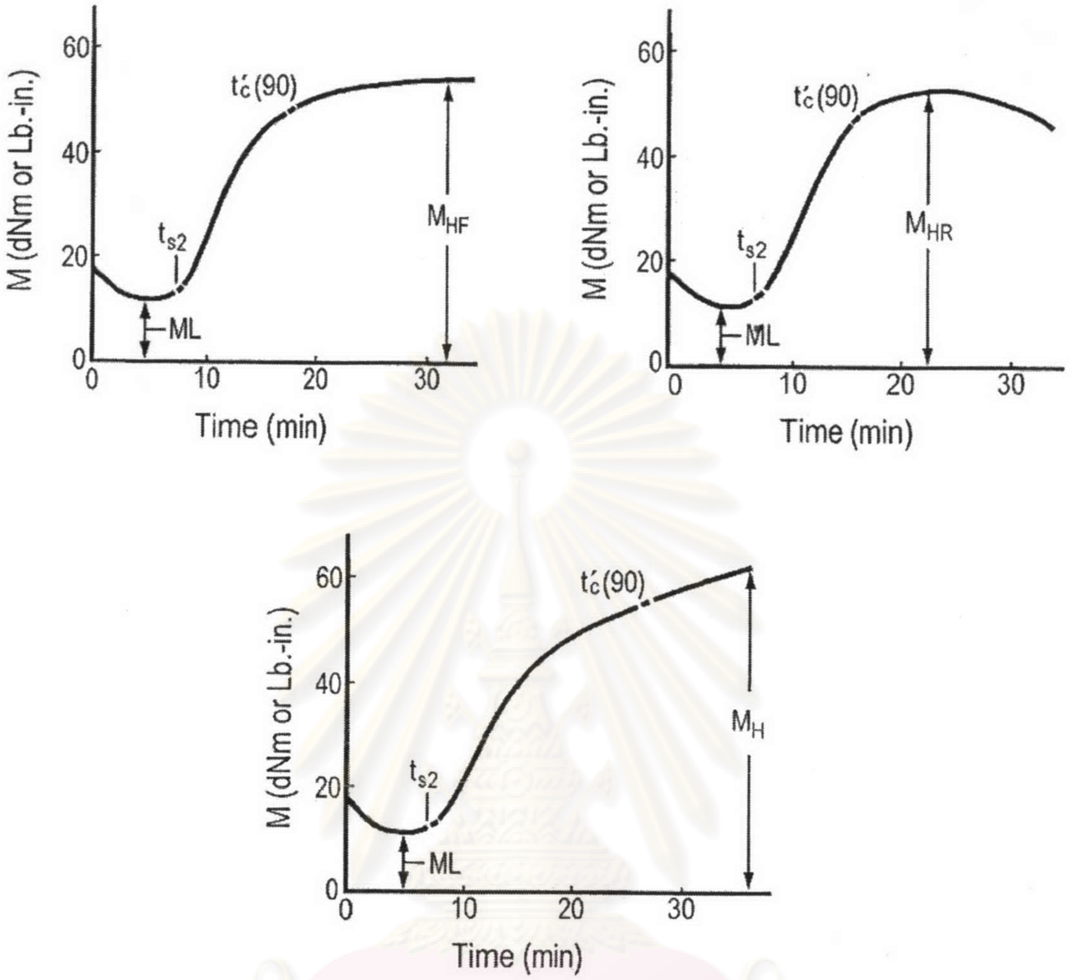


Figure 2.7 Typical curves from an ODR [22]

Curemeters are used widely to test finished compound prior to the shaping and curing stage. They will detect changes in curing characteristics readily. They are also widely used in developing formulations. Changes, which affect viscosity and scorch, are reflected in the first portion of the curve, and the effect on rate of cure and the modulus of the resulting vulcanizate can be seen in the latter portion of the curve.

A new version of the cure meter, called ‘moving-die rheometer’, has been introduced (e.g., the Monsanto MDR 2000) (Fig. 2.8). 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. 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.

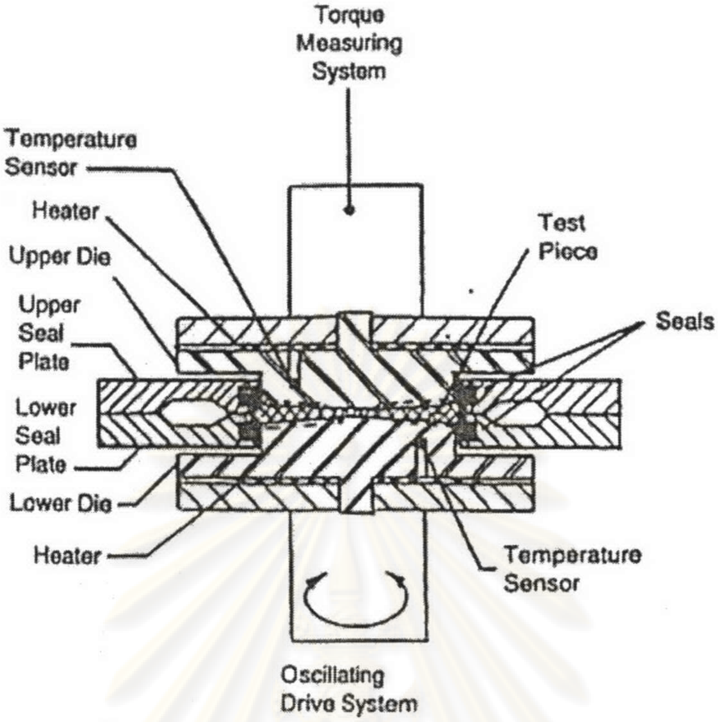


Figure 2.8 Moving-die rheometers (source: ASTM D 5289-93a, Fig. 4 (a), p. 789)

2.5 Mechanical Testing

Mechanical tests provide the only method to obtain engineering-type evaluations of new polymers. Such tests are performed routinely in materials laboratories and in industrial research laboratories. Because most of the tests result in destruction of the sample, and because such tests do not have a high degree of reproducibility, multiple tests on similar samples are needed before valid results can be obtained [23].

2.5.1 Tensile Stress-Strain

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. In practice, stress-strain experiments are often carried out on a flat sample that has been shaped into the form shown Figure 2.9.

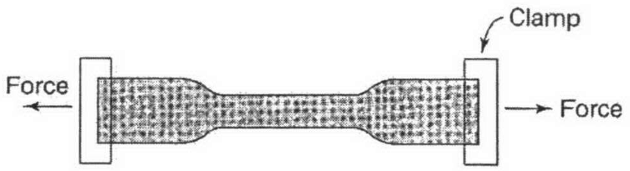


Figure 2.9 Typical shape of a flat polymer sample used for stress-strain test [16]

Two common modes of deformation, tensile and shear are shown in Figure 2.10. 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 [24].

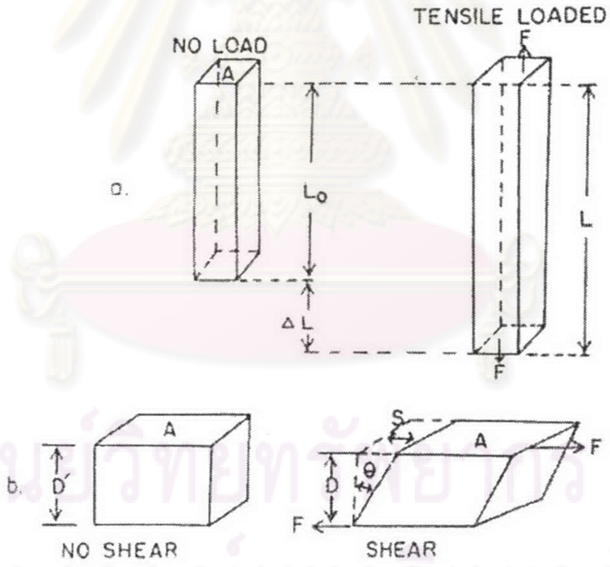


Figure 2.10 a) Tensile stretching of a bar; b) Shear of a rectangular block [24]

2.5.2 Tear resistance

High stress concentration on a rubber product applied at a cut or defect area during service can lead to the propagation of a tear or rupture. Different rubber vulcanizates show different resistance to tear. Tear characteristics for a compound can be related to the compound's crosslink density and state of cure, as well as filler type and loadings. The force to initiate a tear is quite different from the forced required to propagate a tear. Various tear tests place a deliberate flaw in a rubber specimen to try to relate to the tear propagating force [25].

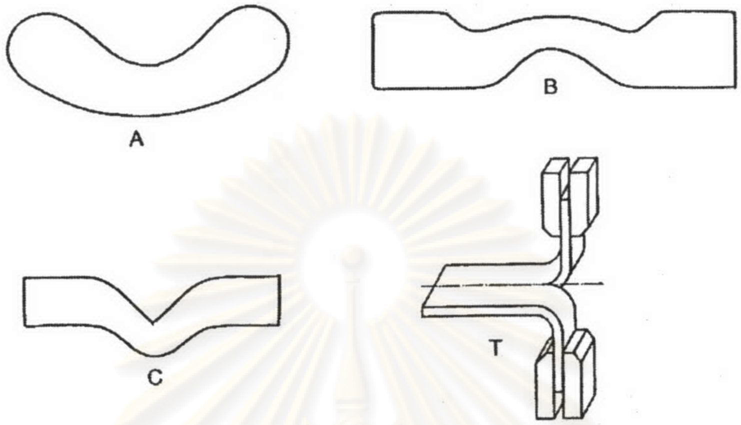


Figure 2.11 Shaping of standard tear specimens, A, B, C, and T [25]

Figure 2.11 shows the shapes of some commonly used tear test pieces which are described in ASTM D624. Die B is a crescent-shaped test piece with large ends for better gripping in a tensile tester. This specimen is nicked with a razor blade to a specified depth to help initiate a tear. The Die C test piece has an angle to help initiate a tear and does not necessarily require a cut nick. The Die T Trouser tear specimen is separated by a shear force from the tension applied in opposite directions to each leg at right angles to the plane of the test piece. The tear strength (T_s) is reported as kilonewton·meter^{-1} of thickness from the formula:

$$T_s = F / d$$

where F = maximum force (in N), for dies B and C, and the median or mean for die T (trouser), and d = test piece thickness in mm.

In accordance with fracture mechanics, tearing energy theoretically is a basic material property that is truly independent of the cut geometry and geometry of the rubber specimen. Most standard tear tests do not measure tearing energy. A modified Trouser tear comes closed to relating to true tearing energy; however, features such as the width of the cut and variations in cut geometry, among others, can greatly affect accuracy of results.

2.5.3 Hardness

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 indentor shape and different stiffness spring, is used [24].

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 Abrasion Resistance

Abrasion tests use an abradant to be applied to the surface of a rubber specimen. Tested compounds are usually compared on a "volume loss" basis which is calculated from the weight loss and density of the compound. Abrasion test results are known to be variable; therefore, it is important to control and standardize the abradant used in the test. It is also required to relate the test results to a standard reference vulcanizate [25].

ISO 4649 refers to the DIN Abrader, so called because it is based on the German standard. The rubber test piece with a holder traverses a rotating cylinder covered with the specified abradant paper. By allowing the sample holder to move the test piece across the drum as it rotates, there is less chance of rubber buildup on the abradant paper. This method is used extensively in Europe.

2.6 Swelling

When a polymer in contact with a solvent, diffusion takes place in both directions, the polymer into the solvent, and vice versa. However, the rate of diffusion of the solvent, being a small molecule, is much faster. A cross-linked polymer only swells, reaching an equilibrium degree of swelling. There are also some polymers, particularly with high melting temperatures or strong internal secondary bonds, which cannot be dissolved without degradation [13].

Two of the most widely recognized effects of reinforcing fillers are changes in the mechanical properties of the composites and their swelling. A reinforced vulcanized rubber possesses a substantial increase in stiffness (modulus) and a reduction in the extent to which the vulcanizate will swell in a rubber solvent. Both of these effects can also be achieved quantitatively by increasing the degree of crosslinking of the rubber. Reinforcing fillers such as carbon black interact strongly with unsaturated hydrocarbon rubbers during milling or during mastication in an internal mixer. The amount of rubber which remains associated with the filler when the mixture is subsequently immersed in a rubber solvent ('bound rubber') is often used as a measure of this interaction (The quantity of bound rubber normally increases on storage or heating of the rubber-filler 'mix'). Thus, the rubber is adsorbed on the filler surface and this alters the stress-strain properties and reduces the extent of swelling in a solvent. Since stress-strain and equilibrium volume swelling measurements are the principal means of assessing crosslink density, it becomes very difficult to measure crosslink density when a reinforcing filler is present in the rubber because the effects of crosslinks cannot be readily distinguished from the effects of rubber-filler interaction.

2.7 Literature Reviews

2.7.1 Sol-Gel Process of TEOS

In 2000, Kohjiya *et al.* [26] 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 *in situ* silica-filled NR 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. However, this method has one limitation to generate *in situ* silica-reinforced rubber by the degree of diffusion TEOS into rubber matrix.

In 2002, Yoshikai *et al.* [27] 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.

For sol-gel process of ethoxysilane in NR latex, Nuntivanich and Tangpasuthadol [11] studied silica reinforcement of NR by a sol-gel process of tetraethoxysilane (TEOS) in the commercial-grade concentrated NR latex which has already contained 40% water and 0.7% NH_3. These 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. 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.

Until 2005, Niyompanich and Tangpasuthadol [12] studied the effect of silane coupling agent, bis-(3-triethoxysilylpropyl)tetrasulfide (TESPT), on *in situ* silica reinforcement of natural rubber. TEOS in combination of TESPT were mixed with rubber latex and followed by heating at 50°C to activate the sol-gel process of both silanes. The *in situ* generated silica particles were well dispersed in the NR matrix. The addition of TESPT reduced both scorch time (ts_2) and optimum cure time (t_{90}). Furthermore, from 'two-level factorial design', tensile modulus at 300% elongation, tear strength and hardness of the composites were significantly affected by the amount of TEOS and TESPT added. *In situ* silica-filled NR vulcanizate having high mechanical properties was obtained by adding a large amount of TEOS and TESPT contents up to 50 and 5 phr, respectively.

2.7.2 Sol-Gel Process of Organotrialkoxysilanes

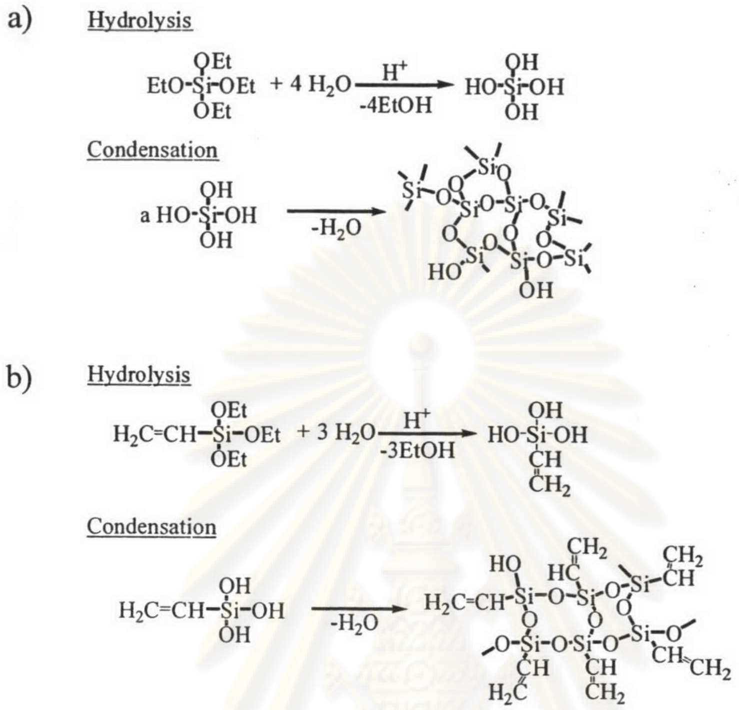
In 2000, Loy et al. [19] examined the sol-gel chemistry of organotrialkoxysilanes having different organic groups with methoxide or ethoxide substituents on silicon, at varying monomer concentrations, and under acidic, neutral, and the basic conditions. Polysilsesquioxane gels were prepared by the sol-gel polymerization of organotrialkoxysilane. They found that the large substituent group of organotrialkoxysilane led to the formation of oligomers and polymers in the form of oils and resins. Formation of gels from organotrialkoxysilane is significantly hindered by phase separation of oligomeric or polymeric silsesquioxanes and, to lesser extent, by sterically bulky organic substituents.

2.7.3 Modification of Silica Surfaces by Sol-Gel Process

In 1999, Hsiue et al. [8] prepared polyimide-silica (PI-SiO_2) hybrids with silica particles at a nanometer scale. Polyimide-silica hybrids were obtained using the nonaqueous sol-gel process by polycondensation of phenyltriethoxysilane (PTEOS) in a poly(amic acid) solution. PTEOS and poly(amic acid) react in a flask with tetrahydrofuran (THF) as a solvent. The mixture was then stirred for about 24 h until the reaction solution became homogeneous. They found that PTEOS introduced phenyl groups into the final formed silica network, to increase the compatibility between the organic polyimide and the inorganic silica network. Since the resulting polyimide-silica hybrids are transparent while containing a high silica content of 45%. The increasing of the silica contents in the hybrid, promotes the compatibility of polyimide and silica, and, consequently, brings about some benefits in improving their physical and mechanical properties.

In 2003, Bauer et al. [9] studied the reinforcement of polyacrylate nanocomposites by acid catalyzed grafting of organotrialkoxysilanes onto the surface of silica nanoparticles. To overcome the problem of incompatibility of acrylates with a high content of silica, the surface composition of the nanoparticles has to be altered from hydrophilic to organophilic. Three organotrialkoxysilanes [methacryloxypropyltrimethoxysilane (MEMO), vinyltrimethoxysilane (VTMO), and *n*-propyltrimethoxysilane (PTMO)] were grafted onto the surface of silica nanoparticles. They found that after radiation curing the polyacrylate nanocomposite films showed a higher scratch and abrasion resistance as well as improved viscoelastic properties in comparison to the neat polyacrylate.

In the same year, Wahab et al. [28] studied the effect of the polysilsesquioxane on the microstructure, interfacial interaction, and properties of the polyimide (PI) based on hybrid films. New hybrid composite films of polyimide and poly(vinylsilsesquioxane) (PVSSQ) were produced with the use of vinyltriethoxysilane. Thermal stability and DMTA results suggested the stronger interaction as well as better interfacial interaction between the PI and PVSSQ rather than that between PI and tetraethoxysilane (TEOS). The interfacial interaction between the PI and PVSSQ has led to the improved mechanical properties of the hybrid composites.



Scheme 2.3 a) hydrolysis and condensation reactions of TEOS
b) hydrolysis and condensation reactions of VTOS [24]

In 2005, Chen et al. [10] studied the silica nanoparticles with different surface properties by modification of colloidal silica particles with different silane coupling agents such as methyltriethoxysilane, octyltriethoxysilanr, vinyltriethoxysilane and methacryloxypropyltrimethoxysilane. Compared with the unmodified nanosilica particles, the abrasion resistance of polyurethane coats could be further improved through modification of silica particles with these silane coupling agent molecules.