CHAPTER II

THEORETICAL 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 [3]. 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 waterproof clothing, water bottle, and shoes from latex [4]. Today rubber trees are grown in many regions of Africa, South America and mainly in Southeast Asia including Thailand, Indonesia, and Malaysia [1].

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. This naturally occurring polymer is primarily cis-1,4-polyisoprene.

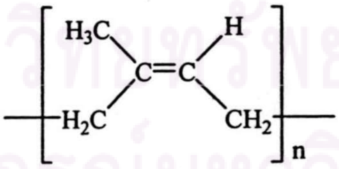


Figure 2.1 Cis-1,4-polyisoprene

2.1.1 Natural Rubber Latex [5]

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. However, the mechanism by which the tree makes rubber has now been fairly well determined. Latex as it 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. 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 composition of typical field latex is presented in Table 2.1.

Table 2.1 Composition of fresh *Hevea* latex [6]

Ingredient	Content (%w/w)
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

2.1.2 Concentrated Natural Rubber Latex [7]

"Field latex" or latex obtained directly from rubber trees has 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 solution is to preserve and concentrate it, so that the end product is stable and contains 60 percent or more of rubber.

Latex concentrate usually made by centrifugation-spinning at high speed to separate a cream containing 60% rubber from a liquid 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. Another concentrate made by evaporation, evaporated latex concentrated, has a higher rubber content and so slightly different properties. Finally, there is creamed latex concentrate: the field latex is mixed with a chemical, such as ammoniam alginate, which makes the rubber particles rise to the top of the liquid, like cream, when left to stand for several weeks. All latex concentrate are chemically treated to prevent coagulation.

Details of the preservation systems used in centrifuged concentrate are given in Table 2.2, the predominant latices are the HA and LA-TZ types. Latex concentrate prepared by evaporation is usually stabilized by potassium hydroxide, while creamed latex is normally preserved with 0.7 percent 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 summarized the requirements of the International Standard Organization (ISO) specifications for various types of natural rubber latex concentrate.

Table 2.3 ISO 2004 requirements for 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_3) (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^{-1} of solids) (max)	8	8	8	8
Manganese content (mg.kg^{-1} 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			

2.1.3 Natural Rubber Grades [8]

The American Society for Testing and Materials (ASTM) describes six basic grades of coagulated technically specified natural rubber which is processed and compacted into 34-kg blocks (Table 2.4). These six general grades of technically specified natural rubber are defined in more details by the respective producing countries. Standard Malaysian Rubber (SMR), Standard Indonesian Rubber (SIR), and Thai Technical Rubber (TTR) expand the large of rubber available.

Table 2.4 Specifications for technically grade natural rubber

Property	**Rubber Grade**					
	L	**CV**	**5**	**10**	**20**	**50**
Dirt (%maximum)	0.050	0.050	0.050	0.100	0.200	0.500
Ash (% maximum)	0.60	0.60	0.60	0.750	1.00	1.50
Volatile matter (%)	0.80	0.80	0.80	0.80	0.80	0.80
Nitrogen (%)	0.60	0.60	0.60	0.60	0.60	0.60
Plasticity	30	-	30	30	30	30
Plasticity retention index	60	60	60	50	40	30
Color index	6.0	-	-	-	-	-
Mooney Viscosity	-	60	-	-	-	-

Smoke Sheet [10]

The largest single type of dry rubber is the ribbed smoked sheet (RSS), and recently air dried sheet (ADS). Ribbed smoked sheet is made from whole-field latex. It is diluted to about 15% solids and then coagulated with dilute formic acid. Coagulation usually takes place overnight. The coagulum is then passed through successive two-roll mills, which squeeze much of the water out. The last pair of the rollers has ribs that impart a ribbed appearance to the sheet and increase the surface area, to expedite drying. The sheets from the last mill are draped on poles, supported by a framework, which is wheeled into the smokehouse. Here, the rubber is dried, very much like clothes on a line, for 2-4 days at 40-55°C. Losing its water, the white sheet turns to yellow-brown color in the smokehouse and has a distinctive smoky smell The rubber now has less than 1% moisture and is more fungus-resistant due to fungicides in the wood smoke.

Standard Thai Rubber (STR) [9]

The production process is not much different from that for smoked sheet up to and including the coagulation stage. Then it is passed through a two-roll mills and mechanically torn into crumbs. These are then dried in sieved-bottom trays by passing them through air circulating tunnel driers at 100°C. The dried crumb rubber is then compressed into 33.33 kg bales, which have a standard size of 66×33×18 cm, wrapped in thin polyethylene film, and packed into crates containing 1 metric ton. The processing materials of the various STR grades are shown in Table 2.5.

Table 2.5 Processing materials of STR grades

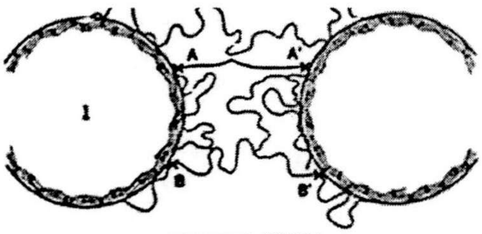
Grade	Processing Materials
STR XL, STR 5L	Whole field latex bulked and formic acid coagulated under strictly controlled conditions.
STR 5	Either whole fresh coagulum or unsmoked sheet (USS) or blend of them subjected to further crumb processing.
STR 10, STR 20	Field grade materials based on unsmoked sheet, lump, scarp, green crepe or mixture.

2.2 Filler Reinforcement System [5]

2.2.1 Reinforcement Concepts

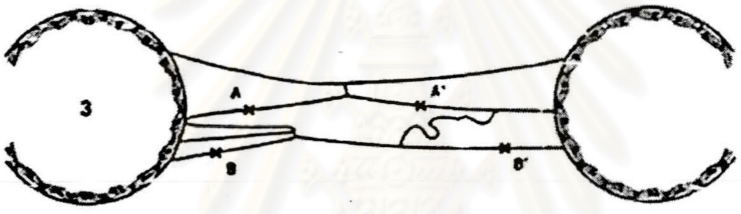
Reinforcement basically relates to composites built from two or more structural elements or components of different mechanical characteristics. The strength of one of these elements is imparted to the composite. One typical example of reinforcement is that of concrete with embedded steel rods or cable 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.

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. Three chains of different lengths between 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.

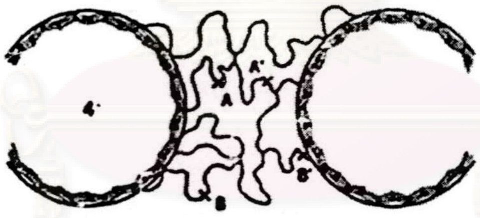


ORIGINAL STATE

INTERMEDIATE ELONGATION SHORTEST CHAIN SLIPPED DISTANCES BEYOND A - A'



ALL CHAINS FULLY STRETCHED



AFTER RETRACTION, ALL CHAINS HAVE EQUAL LENGTHS BETWEEN PARTICLES

Figure 2.2 Molecule slippage model of reinforcement mechanism [5].

2.2.2 Effect of Particle Size on Elastomer Reinforcement

Modulus and tensile strength of the composite are very much dependent on the particle size of the filler. Small particles have a much greater effect than coarse ones. Particle size is directly related to the reciprocal of surface area per gram of filler; thus the effect of smaller particles actually reflects their greater extent of interface between polymer and solid material.

The reduction in properties at higher loading is a dilution effect, general to all fillers, merely due to a diminishing volume fraction of polymer in the composite. If the volume percentage of filler becomes so high that there is not enough rubber matrix to hold the filler particles together, strength approaches zero. Before this stage of loading is reached, the compound attains a level of stiffness where it becomes brittle and, at the normal rate of testing (e.g. 50 cm per minute) such a brittle compound would show poor strength. The place of the maximum is also dependent on the particle size of the filler.

A summary of the main influence of each of the four filler characteristics is given below:

1) Smaller particle size (larger external surface area)
   Results: higher tensile strength, higher hysteresis, higher abrasion resistance, higher electrical conductivity for carbon blacks, higher Mooney viscosity. Minor effects on: extrusion shrinkage and modulus.

2) Increase in surface activity (physical adsorption)
   Results: higher modulus at higher extension (300% up), higher abrasion resistance, higher adsorptive properties, higher "bound rubber", lower hysteresis

3) Increase in persistent structure and anisometry
   Results: lower extrusion shrinkage, higher modulus and medium extension (up to 300%), higher Mooney viscosity, higher hysteresis, longer incorporation time. Better dispersion, low electrical resistivity for carbon blacks. This property particularly is interrelated with surface activity; structure changes on fillers without surface activity (graphitized black) show the effects indicated above only rather faintly. When a filler's surface activity is high (and constant), variations in its structure have the greatest effect on its rubber properties.

4) Porosity
   Results: higher viscosity, lower electrical resistivity for carbon blacks.

2.3 Description of Curing Parameters [5]

Scorch is 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 result of both the temperature reached during processing and amount of time the compound is exposed to elevated temperatures. This period of time before vulcanization is generally referred to as "scorch time". It is important that vulcanization dose not start until 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 required for use. 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 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". Overcures 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 Characterization of the Vulcanization Process

The effects of compound variations on curing characteristics are important in compound development studies or production control. Cure meter tests are ideally suited for use in both these areas. In composition of the compound can be varied until the desired vulcanization characteristics are obtained. The effect of compound changes on viscosity and scorch can be determined from the early portion of the cure curve, while from the latter portion, the effect on rate of vulcanization and the modulus of the cured compound can be measured. The cure curve obtained with a cure meter is a "fingerprint" of the compound's vulcanization and processing character. Many properties are obtainable from the data; the most common being minimum and maximum stiffness, scorch time, cure time to 90% or 95% of maximum stiffness, and a cure rate index.

2.4.1 Rheometer [8]

The most widely used cure meters are oscillating disk rheometers. 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. 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 automatically plotted against time to give a so-called rheometer chart, rheograph, or cure curve. The tree different types of cure curve (Figure 2.3) which can be obtained with different types of rubber compounds. 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. Also obtainable are initial viscosity at zero time, minimum viscosity, and reversion (time after M_{HF} to reach 98% of M_{HF}).

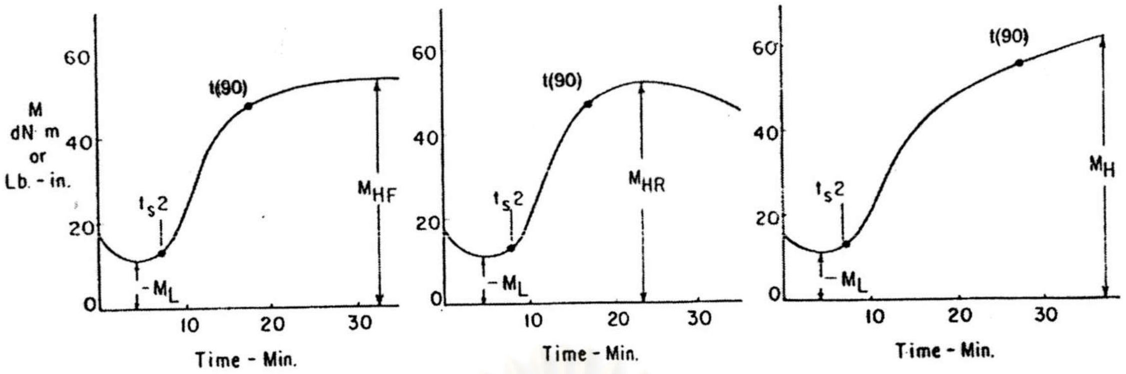


Figure 2.3 Type of cure curve. Left curve: cure to equilibrium torque. Middle curve: cure to a maximum torque with reversion. Right curve: cure to no equilibrium or maximum torque.

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 (Fig.2.4). 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.

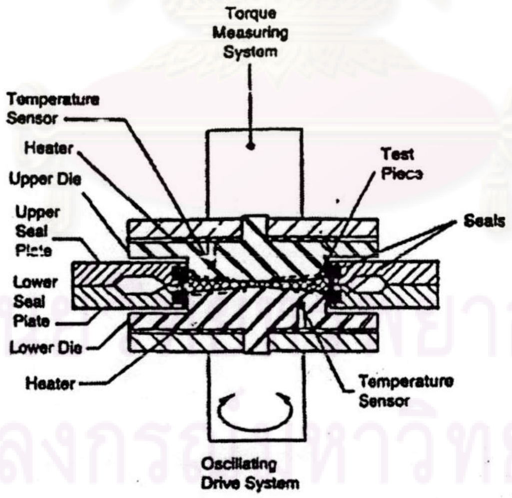


Figure 2.4 Moving-die rheometers

2.4.2 Rotating Disk Viscometer

The shearing action is performed by disk rotating in shallow cylindrical cavity filled with the rubber under test, as shown in Figure 2.5. The rubber is squeezed into the cavity under considerable pressure. The surface of the disk and the dies which form the cavity are grooved to avoid slippage. The test specimen consists of two pieces which completely fill the test chamber.

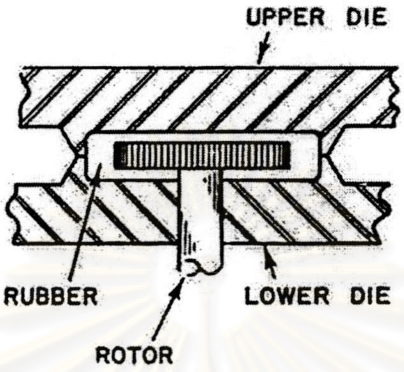


Figure 2.5 Mooney chamber and rotor.

2.5 Tests for Mechanical Properties

2.5.1 Stress-Strain Tests

Physical testing of rubber often involves application of a force to 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 2.6. Stress is the force per unit cross sectional area (F/A for either tensile or tear deformation). Strain is the deformation per unit original length ($\Delta L/L$) in tensile tests or deformation per unit distance between the contacting surfaces in shear tests. Stress is usually expressed in unit of newton per square meter (N/m^2).

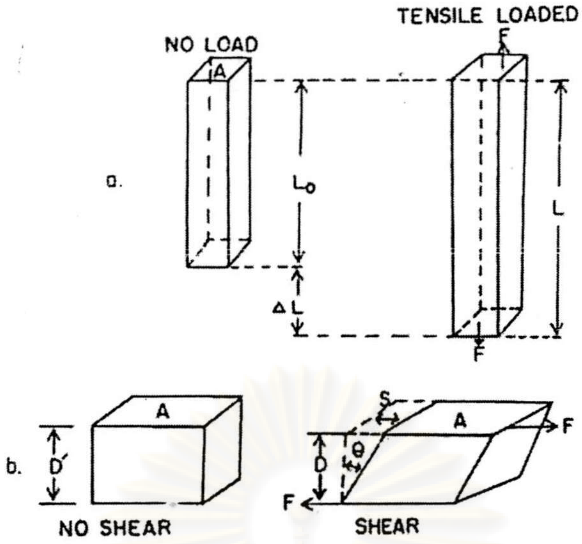


Figure 2.6 a) Tensile stretching of a bar; b) Shear of a rectangular block.

2.5.2 Tear Test

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 (Figure 2.7), 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.

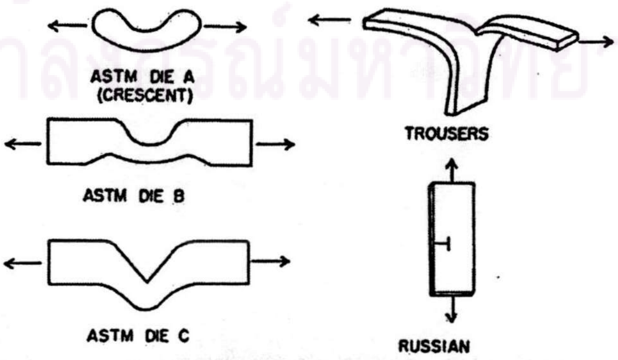
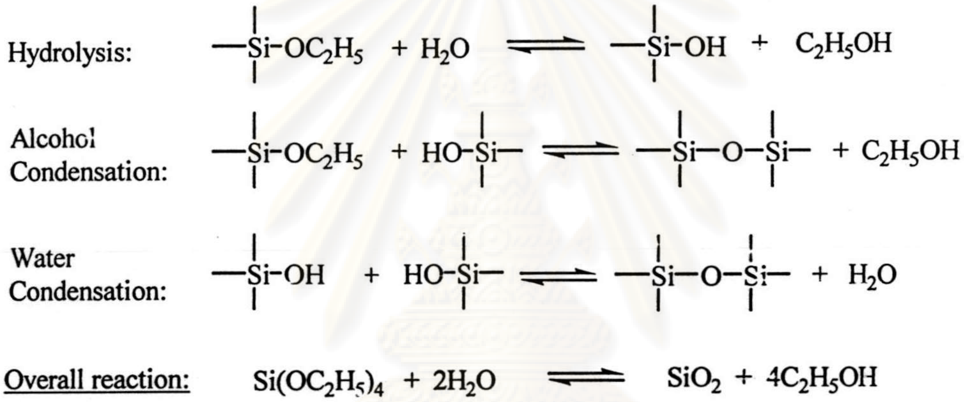


Figure 2.7 Types of tear specimens

Rate of stretching in the ASTM method is 20 inches per minute. An increase in rate would normally decrease the tearing energy for SBR rubbers but give a more complicated effect in natural rubber. In theory, a portion at least of tire wear is a result of high speed tear, such a test has been considered for evaluation of abrasion resistance.

2.6 Sol-gel Process

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 (SiO_2). The reaction of TEOS takes place in two steps, hydrolysis and condensation, to produce SiO_2 as shown in Fig. 2.8.



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

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

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

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

Figure 2.8 Hydrolysis and condensation reaction of TEOS to form silica.

Sol-gel process in polymers

Recently, a sol-gel process of TEOS was applied to prepare silica for reinforcing many types of rubbers; e.g. natural rubber [13], synthetic rubber [14, 15, 16, 17, 18]. The thin sheet rubbers were swollen in TEOS, followed by soaking in acid or base catalyst to follow the sol-gel reaction of TEOS. Then the samples were subjected to heating after removal from the catalyst solution. The drying of the samples was conducted for several day. The *in situ* silica-filled rubbers were obtained.

From work of Ikeda Y., et al.[18] studied effect of catalyst on *in situ* silica reinforcement of SBR found that the base catalyst (n-butylamine) was a good catalyst for *in situ* silica filling of the SBR vulcanizate. Therefore, the ammonia was in the latex work as catalyst in this work.

Mooney viscosity, ML_{1+3} (121°C), of NR-*in situ* were smaller than that of NR-mix of in situ filling of silica onto green natural rubber by the sol-gel process[13]. Moreover, the scorch time of NR-*in situ* was shorter compared with that of the NR-mix.

The disadvantages of the swelling method are long time-consuming and uncontrollable TEOS content in the solid rubber. A solution to this problem is to directly add TEOS in the polymer latex. This method was successfully implemented in a number of reports for silica-reinforced SBR [19], poly(butyl methacrylate) [20], polyacrylamide [21], and polyimide [22]. From the work reported on the synthetic rubber composite [19], the ratio of water and TEOS in the latex mixture controlled the size of silica particles. The size reached a nanometer-order level, leading to a drastic increase of tensile strength of the composite.

2.7 Experimental Design-2^k Factorial Design [11,12]

Factorial designs are most efficient for the study of the effects of two or more factors in relatively few experiments as compared to the one-factor-at-a-time technique. The one-factor-at-a-time technique, varying one factor while keeping the other factors at a constant level, is tedious when a large number of factors have to be investigated, whereas statistically based experimental designs are more efficient approach to deal with a large number of variables. Moreover, if there are statistical interactions between factors, that is where the effect of one factor is dependent on the value of another factor, then this information will not be obtained using the one-factor-at-a-time technique.

Factorial designs allow one to study a large number of variables simultaneously, while a large amount of information is obtained with a reduced experimental effort. The clarification of experimental kinetics is an iterative process involving seven steps. These steps are recognition of and statement of the problem, choice of factors and levels, selection of a response variable, choice of experimental design, performing the experiment, data analysis, and conclusions. Within the choice of experimental design, it is always necessary to maintain a balance between statistical accuracy and cost.

A factorial design assumes that the factors are fixed, the designs are completely randomized, and the usual normality assumptions are satisfied. The 2^k design 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. Detailed method for experimental design carried out in this research is shown in Experimental Chapter.