

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 *Anacardium Occidentale* [2, 3]

2.1.1 The Cashew Tree

The cashew tree, *Anacardium occidentale* Linn., is a native plant of Brazil, the tree grows in the coastal areas of Asia and Africa. It is now found widely in other parts of tropical South and Central America. The generic name, *Anacardium*, is bestowed upon it because it describes the heart-like shape of the nut. The specific name, *occidentale*, is used because the nut come from the Western Americas.

The cashew plant is a jungle or semi-jungle tree by nature. The tree, which is an evergreen, naturally grows up to 12 metres in height and has a spread of 25 metres. It is readily recognized by its light colored foliage. The yellow-green leaves, revealing distinct veins, are elliptic in shape and approximately 4 to 6 inches in length and 2 to 3 inches in width. They feel leathery to the touch.

2.1.2 Cashew apple and Cashew nut

The cashew nut is attached to the bottom of the cashew apple, with the size of 2 to 4 inches in length and 1.5 to 2 inches in width. It has a waxy yellow, red or orange skin. Broadly conical or pear-likes in shape, it is called a cashew “pear” or cashew “apple”.



Figure 2.1 A picture of cashew apple and cashew nut. Reproduced from [4].

The whole cashew nut is from 2.5 to 4 cm long; 1.9 to 2.2 cm broad at the base; and 1.3 to 1.6 cm thick at the stem-end. It is gray brown and shapes more like the kidney than the heart from which its generic name is derived. The shell is about 0.3 cm thick, having a soft leathery outer skin and a thin hard inner skin. Between these skin is the honeycomb structure containing the phenolic material populary called “Cashew Nut Shell Liquid (CNSL)”. Inside the shell is the kernel wrapped in a thin brown skin, known as the testa.

The nut thus consists of the kernel (20-25%), the shell liquid (20-25%), and the testa (2%), the rest being the shell.

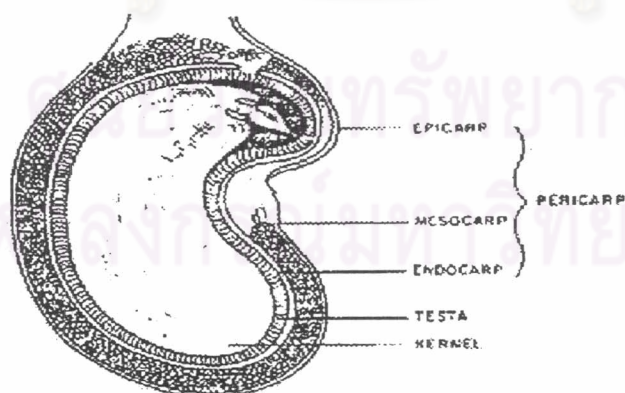


Figure 2.2 A cross section of a cashew nut. Reproduced from [5].

2.1.3 Cashew Nut Shell Liquid

2.1.3.1 Introduction [6]

Cashew nut shell liquid (CNSL) occurs as a reddish brown viscous liquid in the soft honeycomb structure of the shell of cashew nut and is reported to occur in the fresh shell to the extent 15 to 20 and 20 to 30 percent by weight for African nuts and Indian nuts, respectively. CNSL is extremely caustic and a strong vesicating agent.

2.1.3.2 Extraction of CNSL [7]

In the production of cashew kernels for edible purposes, CNSL is extracted from the outer shell of the cashew nuts before they are decorticated in order that the kernels may be removed without becoming contaminated by the liquid. There are three main methods which have been suggested for obtaining this liquid:

1. Hot oil bath method

This is the most common method of commercial extraction. The raw nuts are passed through a bath of hot CNSL (180-200°C) itself, when the outer part of the shell bursts open and releases CNSL (50% recovery). Another 20% could be extracted by passing the spent shells through an expeller and the rest by solvent extraction techniques.

2. Expeller method

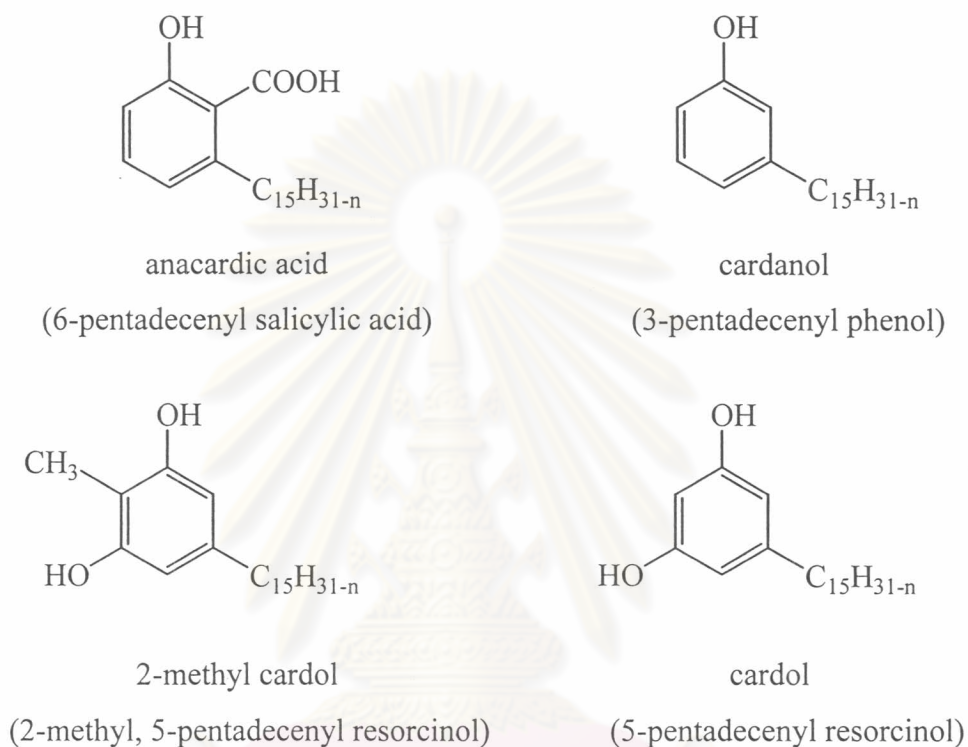
Some factories have introduced manually operated cutting machines in which shells of lightly roasted nuts are cut, keeping the dernel intact. The shells are then fed to an expeller to recover 90% of the oil.

3. Kiln method

The nuts are shelled after sun drying or after drum roasting. The liquid obtained is, however, crude and contaminated.

CNSL, extracted with low boiling petroleum ether, contains about 90% anacardic acid and about 10% cardol. CNSL, on distillation, gives the pale yellow phenolic derivative cardanol. Natural CNSL contains 80.9% anacardic acid, 10-15%

cardol and small amounts of other materials, notably the 2-methyl derivative of cardol. The chemical structures of major compounds in natural CNSL are shown in Figure 2.3. The side chains exist in saturated ($n = 0$), monoene ($n = 2$), diene ($n = 4$) and triene ($n = 6$) forms with cis configuration [8-11].



Where $n = 0, 2, 4$ or 6

Figure 2.3 Chemical structures of major compounds in natural CNSL.

In the roasting process, some polymerization as well as decarboxylation occurs, because of the highly unsaturated nature of CNSL. Thus, a typical product could contain polymer (20-25%), cardanol (60-65%), cardol (10-12%) and other minor components. The characteristics of cardanol and IS specification for CNSL are given in Tables 2.1 and 2.2, respectively [7, 12-13].

Table 2.1 Characteristics of Cardanol [7]

Characteristics	
Boiling point, °C	228-235 (3.4 mm Hg)
Color (Livibond, 1 cm cell) (freshly distilled)	Red (1.0-3.0) Yellow (1.5-3.5)
Viscosity, 30 °C (cP)	40-60
Specific gravity 30/30 °C	0.93-0.95
Ash content	negligible
Volatile loss, % by wt (max)	2.0
Acid value	1.9-2.0
Iodine value (Wij's method)	210-220
Hydroxyl value	180-200

Table 2.2 IS Specifications* for Cashew Nut Shell Liquid [7]

Characteristics	Requirement
Specific gravity 30/30 °C	0.950 to 0.970
Viscosity at 30 °C, cP (max)	550
Moisture, % by wt (max)	1.0
Matter insoluble in toluene, % by wt (max)	1.0
Loss in wt on heating, % by wt (max)	2.0
Ash, % by wt (max)	1.0
Iodine value (max)	
a) Wij's method	250
b) Catalytic method	375
Polymerization	
a) Time, min (max)	4
b) Viscosity at 30 °C, cP (max)	30
c) Viscosity after acid washing at 30 °C, cP (min)	200

*IS 840: 1964

2.1.3.3 Uses and Applications [5, 7]

The CNSL is an undesirable by-product of the cashew kernel industry. This is an effective replacement of source and expensive petrochemicals. CNSL is described often as a versatile industrial raw material. It has wide application in the manufacture of numerous industrial products.

The CNSL is second only to the cashew kernel or nutmeat in economic importance. In its natural state, it serves as a protection to the kernel against insect attack. If used in combination with kerosene or diesel oil, it is an effective insecticide against mosquito larvae. Made into a varnish it is a preservation of wooden floors and fine carved woods, protecting them from insect destruction. For many years, fishermen have used the liquid to waterproof and preserve their fishnets, fishing lines and boats.

With recent advances in chemical technology, the CNSL is finding many new industrial applications. It is used commercially as a phenolic raw material for the manufacture of certain resins and plastics. In particular, it is used as a friction modifier in the manufacture of brakelinings and clutch facings. It have the property of absorbing the heat generated by friction in the braking action while retaining their braking efficiency longer. Apart from low 'fade' characteristics, cashew-based friction materials again give a much quieter braking action and also are more efficient for 'cold wear'. These materials are ideal for use in low speed automobiles where the temperature generated does not exceed 250 °C. It is also used in rubber compounds, where it acts as reinforcing fillers, which tensile strength, hardness and abrasion-resistance are improved. The resins from CNSL are used in laminating for papers, cloths and glass fibers, or impregnating materials where oil or acid resistance is required. Other uses include the manufacture of lacquers, paints, printing inks, electrical insulation material, an anti-corrosive for metals, water proofing compounds and adhesives.

2.2 Vulcanization [14, 15]

The uncured rubber must be transformed from a soft, tacky, stretchy substance into tough, hard tread that will resist abrasion and provide excellent mileage and traction.

Treatment of rubber is to give its certain qualities, e.g., strength, elasticity, and resistance to solvent, and render it impervious to moderate heat and cold. Chemically, the process involves the formation of cross-linkages between the polymer chains of the rubber's molecules. In 1839, vulcanization was accomplished usually by a process invented by Charles Goodyear, involving a combination with sulfur and heating. Mr. Goodyear stumbled upon a way to harden molded rubber without losing its flexibility. In 1846, Alexander Parkes developed a method of cold vulcanization (treating rubber with a bath or vapors of a sulfur compound). Rubber for almost all ordinary purposes is vulcanized; exceptions are rubber cement, crepe-rubber soles, and adhesive tapes. There are many vulcanization methods, the compound is usually placed in molds and subjected to heat and pressure. The heat may be applied directly by steam, by steam-heated molds, by hot air, or by hot water. Vulcanization can also be accomplished with certain peroxides, gamma radiation, and several other organic compounds. The finished product is not sticky like raw rubber, does not harden with cold or soften much except with great heat, is elastic, springing back into shape when deformed instead of remaining deformed as unvulcanized rubber does, is highly resistant to abrasion and to gasoline and most chemicals, and is a good insulator against electricity and heat.

2.2.1 Theory of Vulcanization [14, 16]

The vulcanization is a chemical process to link the polymer structure. The name vulcanization is used for a linking procedure, during which the macromolecules of the rubber are linked to each other over linking bridges. This linking can take place with the help of vulcanization agents. During vulcanization, the following changes occur.

Firstly, the long chains of the rubber molecules become crosslinked by reaction with the vulcanization agent to form three-dimensional structures. This reaction transforms the soft, weak plastic-like material into a strong elastic product.

Secondly, the rubber loses its tackiness and becomes insoluble in solvents and is more resistant to deterioration normally caused by heat, light, and aging processes.

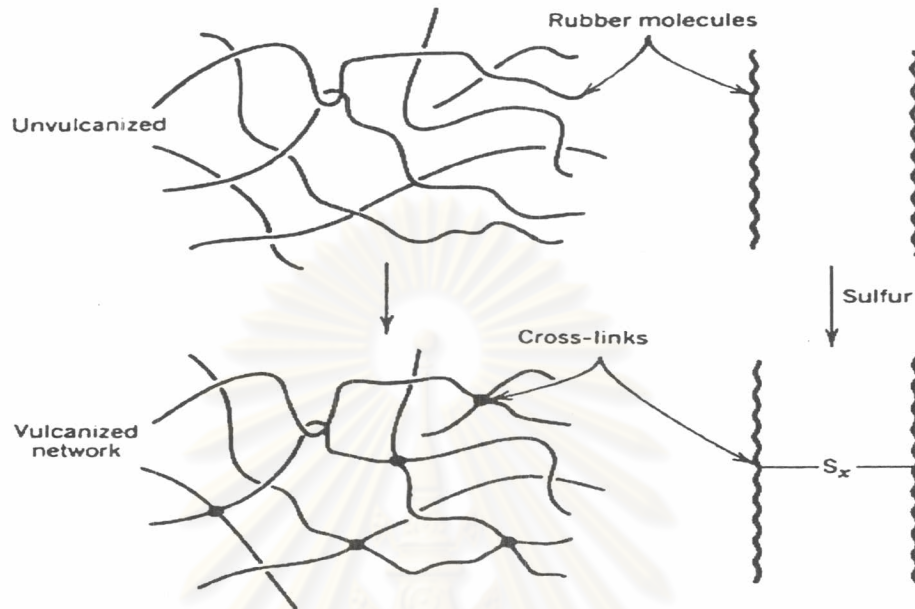


Figure 2.4 Network of sulfur vulcanization. Reproduced from [14].

The properties of the vulcanized rubber, or vulcanizate, depends on the nature and distribution of the crosslinks, the crosslink density, non-crosslink modifications introduced along the polymer chain, and extra-network material, that is the unattached residual reaction products of the vulcanizing system.

2.2.2 Degree of Vulcanization or Crosslink Density [17]

The number of crosslinks formed depends on the amount of vulcanizing agent, its activity and the reaction time. In sulfur vulcanization, the most commonly used, various types of crosslink are forms depending on the quantity and activity of other additives, particularly accelerators. Sulfur can be combined in the vulcanization network in a number of ways between monosulfide to polysulfide, but it also presents as pendent sulfides, or cyclic sulfur structure as shown in Figure 2.5

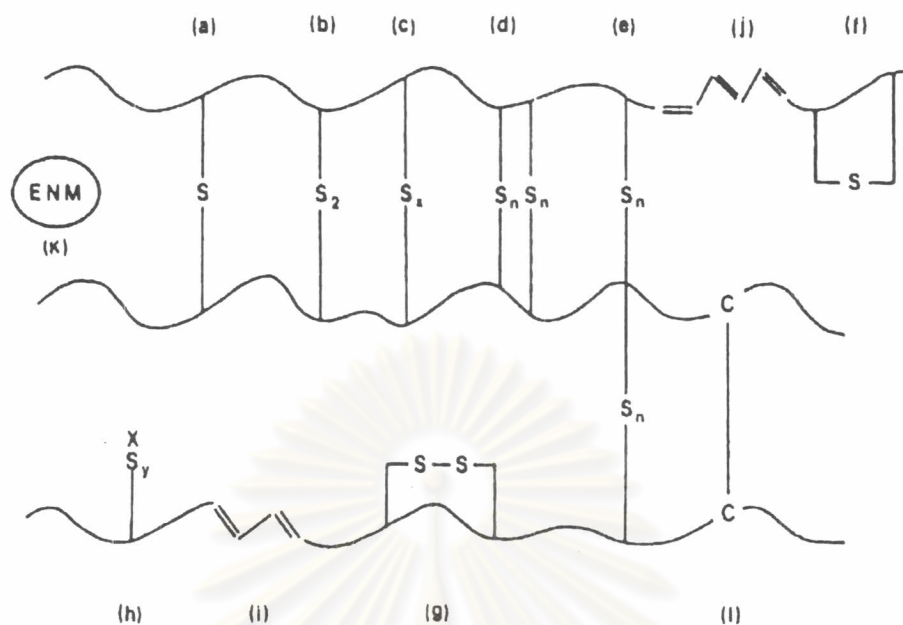
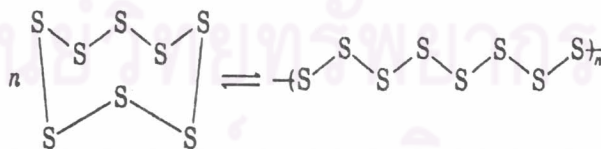


Figure 2.5 Network structure. a) monosulfide crosslink C-S-C; b) disulfide crosslink C-S-S-C; c) polysulfide crosslink C-S_x-C ($3 \leq x < 6$); d) parallel vicinal crosslink C-S_n-C ($n = 1$ to 6); e) crosslinks attached to common or adjacent carbon atoms; f) intra-chain cyclic monosulfide; g) intra-chain cyclic disulfide; h) pendent sulfidic group terminated by accelerator fragment (X); i) conjugated diene; j) conjugated triene; k) extra-network material; l) carbon-carbon crosslink. Reproduced from [18].

2.2.3 Mechanism of Sulfur Vulcanization [15, 19]

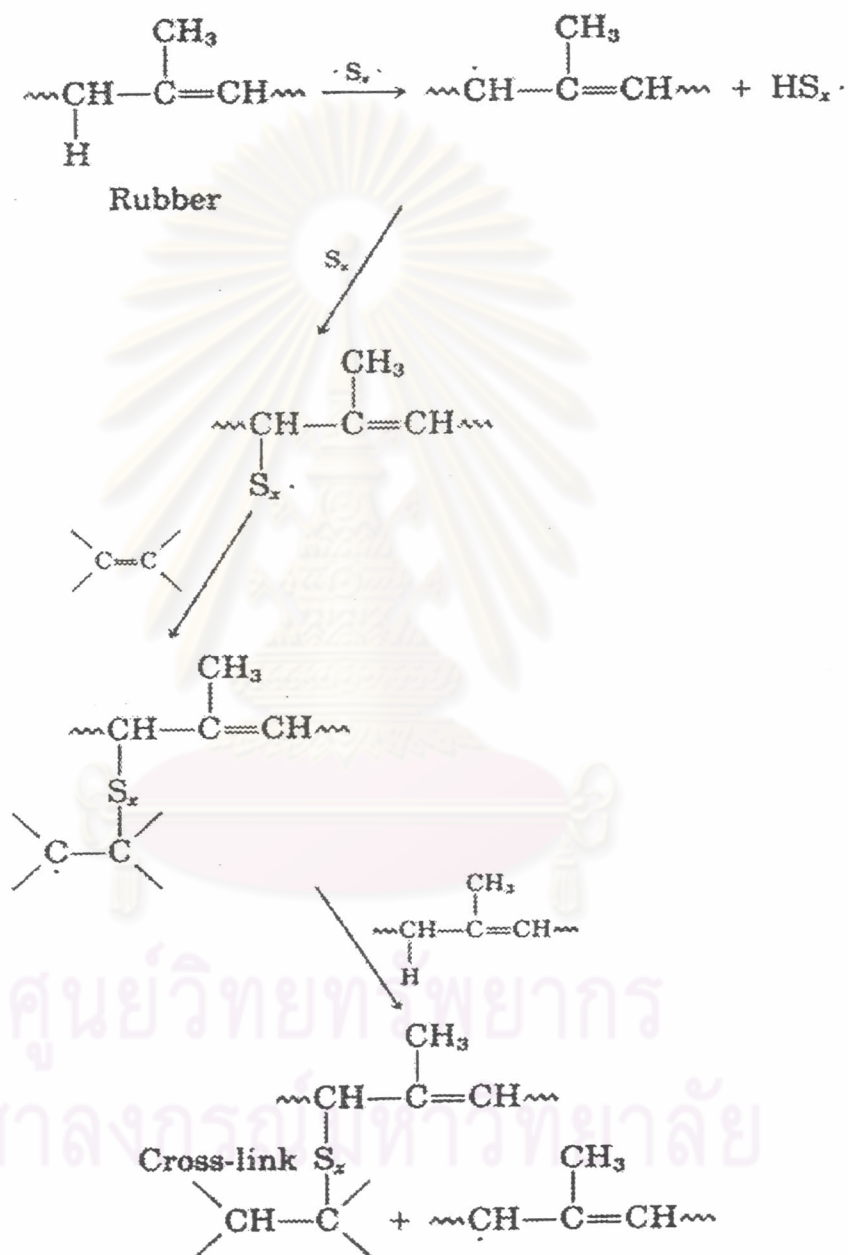
The initial step of vulcanization seems to be the splitting of a sulfur ring. It can crosslink or vulcanize directly even at room temperature.



Scheme 2.1 Splitting of sulfur ring. Reproduced from [19].

After being activated by ring splitting, the sulfur is able to react with an accelerator, zinc oxide and also with reactive sites on the rubber molecule, whether these are α -methylene groups, double bonds, or other sites, in such a way that no intermolecular crosslinks are formed initially.

With sulfur vulcanization, the vulcanization structures formed are of great importance to crosslink yield; moreover, the structures formed in accelerator-free vulcanization are many different types. To begin with, therefore, the chemical mechanism of unaccelerated sulfur vulcanization will be considered in some details.



Scheme 2.2 Unaccelerated vulcanization by sulfur, free radical mechanism.

Reproduced from [14].

2.2.4 Vulcanization Systems [17]

The vulcanizing system is the combination of sulfur with accelerators needed to convert the rubber compound from an essentially plastic state to a shaped elastomer thermoset. The system is added to the rubber polymer during mixing and remains inactive during subsequent processing and fabrication operations. Vulcanization then takes place, usually by the application of heat to activate the system. Crosslinks are inserted between adjacent polymer chains to form a three dimension network, which prevents further flow. The vulcanizing system determines the type and concentration of crosslinks.

Sulfur is used in combination with one or more accelerators and an activator system comprising zinc oxide and a fatty acid (normally stearic acid). Part or all of the sulfur may be replaced by a sulfur donor. In the presence of a vulcanization accelerator, the average number of sulfur atoms per crosslink is decreased. The proportion of sulfur and accelerator and the range of E values of each system are shown in Table 2.3.

Table 2.3 Classification of sulfur vulcanization system [20]

System	Sulfur concentration (phr)	Accelerator concentration (phr)	Approximate range of E values obtained
EV	0.3-1.0	6.0-2.0	1.5-4
Semi-EV	1.0-2.0	2.5-1.0	4-8
Conventional	2.0-3.5	1.0-0.5	10-25
Very inefficient	3.5-10	0.5-0	25-100

2.2.5 Vulcanization Methods [18]

Systems for vulcanizing rubber are divided into five different methods i.e. vulcanization in the press, open cure, vulcanization in water, vulcanization in lead and continuous vulcanization. Each method can be subdivided into minor methods such as the vulcanization in water, which can be used for very large articles, can be carried out in two

ways, i.e. vulcanization under atmospheric pressure and under pressure. Almost all rubber products are vulcanized by one or more of these.

For this research, the vulcanization of thick-walled articles, a type of vulcanization in the press was chosen because it is the simplest method. The size of the mold, the type of press, the mold material and other factors greatly affect the curing time and temperature. The higher the mold, the more efficiently the protection of the loss of heat.

2.3 Vulcanizing Agents [18]

Vulcanizing agents are substances which bring about the actual crosslinking process. The most important ones are sulfur, sulfur donors, selenium, tellurium, peroxides, and metallic oxides.

2.3.1 Sulfur and Related Elements

2.3.1.1 Sulfur for Vulcanization

The most important vulcanizing agent for rubber is elementary sulfur, which is marketed in a ground form as sulfur for vulcanization. Sulfur suitable for vulcanizing has to be at least 99.5% pure and it must not contain more than 0.5% of ash.

The solubility of sulfur varies from polymer to polymer. Whereas sulfur dissolves relatively easily in natural rubber at room temperature. The solubility of sulfur increases as the temperature of the rubber rises. The proportion of sulfur soluble at a high mixing temperature which exceeds the proportion soluble at room temperature tends, once the products have cooled, to crystallize out of the over-saturated solution, the crystals being formed either inside or on the surface of the products. The rate of crystallization depends on the over-saturation of the compound and on the rate of diffusion of the sulfur in the polymer. The fact that blooming thus depends on the over-saturation of the compound means that the mixing temperature, which governs the amount of sulfur dissolved, is very important.

To prevent blooming in unvulcanized rubber compounds (which would make bonding or welding difficult), the sulfur is incorporated at the lowest possible temperature.

a) Insoluble Sulfur

Another way of preventing sulfur blooming is to use a special modified sulfur known as “insoluble sulfur”. The insoluble sulfur available on the market contains about 65-95% of material which is insoluble in carbon disulfide. Insoluble sulfur in carbon disulfide is also insoluble in rubber, and therefore has no tendency to bloom.

However, insoluble sulfur is not stable. Instead it changes into the normal soluble form, which is again capable of blooming, doing so very slowly at room temperature, faster when the temperature is raised. Insoluble sulfur, therefore, has to be stored at the lowest possible temperature. In the course of compounding and processing, care should be taken to keep the temperatures low and thus to prevent transformation into the stable, soluble form.

Attempts have been made to stabilize insoluble sulfur against conversion into the stable form, e.g. by adding a small amount of chloride, bromine, iodine, sulfur monochloride, or of a terpene, which have been found to reduce the rate of transformation.

When insoluble sulfur is properly dispersed in the rubber compound its use (instead of normal soluble sulfur) causes practically no change in the course of vulcanization or in the properties of the vulcanizates. However, its insolubility sometimes makes uniform dispersion difficult.

b) Colloidal Sulfur

Normal vulcanization sulfur is very difficult to disperse because of its coarse particles and it is therefore not at all easy to incorporate it uniformly in latex. To ensure uniform incorporation and prevent sedimentation in latex mixes it is advisable to use colloidal mill or by precipitation form colloidal sulfur solutions.

As colloidal sulfur tends to recrystallize in the course of storage, the grades available on the market contain additives which prevent particle enlargement. Humidity and dispersing agents have proved particularly suitable for prevention recrystallization.

Table 2.4 Physical properties of sulfur [18]

Physical properties	
Apparent Color	Yellow; impurities may cause color to be yellow shades of green, gray and red
Odor	Pure sulfur is odorless, but traces of hydrocarbon impurity may impart an oily and/or rotten egg odor; + FAINT ODOR
Boiling Point	444.6°C
Melting Point	112.8 to 120°C
Molecular Weight	32.06
Density	112.400 lb/cu ft at 255 deg F
Hardness	1.5 to 2.5
Sensitivity Data	May cause irritation of skin, mucous membranes. May cause irritation to eye. If spilled on clothing and allowed to remain, may cause smarting and reddening of the skin.

2.3.1.2 Selenium and Tellurium [14, 18]

Occasionally selenium and tellurium, which are close to sulfur in the periodic system, are used analogously to sulfur for the vulcanization of rubber. Their action is somewhat less powerful than that of sulfur. In some cases small amounts of selenium or tellurium are used as additives to sulfur or to sulfur-liberating accelerators. The proportion of sulfur can then be considerably reduced. Vulcanizates produced in this way are characterized by particularly good heat resistance in steam and hot air and by a high modulus. The difference between sulfur, selenium and tellurium are illustrated in Table 2.5.

Table 2.5 Comparison of Elemental Vulcanization Agents [14]

	Sulfur	Selenium	Tellurium
Atomic weight	32.06	78.96	127.61
Appearance	Yellow powder	Metallic powder	Metallic powder
Specific gravity	2.07	4.80	6.24
Melting Point (°C)	112.8-119	217.4	449.8
Price (\$/lb)	0.17	16.00	25.00

2.3.2 Sulfur-Bearing Chemicals

Sulfur-bearing chemicals, accelerators, and similar compounds can be used as a source of sulfur for the vulcanization of natural rubber. The sulfur-bearing compounds used decompose at the vulcanization temperature and release radicals which combine with the chains to form crosslinkings.

2.3.3 Nonsulfur Vulcanization

Most nonsulfur vulcanization agents belong to one of three groups: (1) metal oxides, (2) difunctional compounds, or (3) peroxides. Each will be discussed here separately.

2.3.3.1 Metal Oxides

Carboxylated nitrile, butadiene, and styrene-butadiene rubbers may be crosslinked by the reaction of zinc oxide with the carboxylated groups on the polymer chains. This involves the formation of zinc salts of the carboxylate groups. Other metal oxides are also capable of reacting in the same manner.

Polychloroprenes (neoprenes) are also vulcanized by reactions with metal oxides, zinc oxide being normally used. Chlorosulfonated polyethylene (Hapalon) is also crosslinked in the same general way. Litharge (PbO), litharge/magnesia (MgO), and magnesia/pentaerythritol combinations are used.

2.3.3.2 Difunctional Compounds

Certain difunctional compounds form crosslinks with rubbers by reacting to bridge polymer chains into networks. Epoxy resins are used with nitrile, quinone dioximes with butyl, and diamines or dithio compounds with fluororubbers.

2.3.3.3 Peroxides

Organic peroxides are used to vulcanize rubbers that are saturated or do not contain any reactive group capable of forming crosslinks. This type of vulcanization agent does not enter into the polymer chains but produces radicals which form carbon-to-carbon linkages with adjacent polymer chains.



The peroxide crosslinking has the following advantages:

- 1) Better heat stability
- 2) Better reversion resistance
- 3) Lower high temperature compression set
- 4) Absence of sulfur avoids corrosion in cable metals

Peroxide initiates crosslinking through a free radical reaction. In essence, thermally liberated peroxy radical abstracts labile hydrogen from the polymer chain and then crosslinking is effected by the combination of two adjacent polymer free radicals. In practice, the reaction is more complicated because coagents are often used with the peroxide to enable a reduction in peroxide levels and improved processing safety.

2.4 Sulfur Donors [18]

A sulfur donor used decompose at the vulcanization temperature and release radicals, which combine with the chains to form crosslinks. Consequently, this form of vulcanization produces products, which resist aging processes at elevated temperatures much more efficiently than those produced with normal curing systems.

However, due to the large amounts of the sulfur donors used, these systems are more expensive than normal sulfur cured.

Theoretically, total sulfur content can be given from sulfur donors to incorporate with the molecules of rubbers, however, usually only active sulfur becomes activated. Practically, this means that the equivalent quantities of sulfur donors that are required in order to obtain the same crosslink density are calculated by the active sulfur content. Weight percentage of total sulfur and active sulfur content of commercial sulfur donors are shown in Table 2.6.

Table 2.6 Total sulfur content and active sulfur content of commercial sulfur donors [18]

	Total sulfur (wt%)	Active sulfur (wt%)
DTDM	27.1	13.6*
CLD	22.2	11.1*
MBSS	22.5	11.3*
DPTT	33.3	16.6**
OTOS	12.9	12.9*
TMTD	26.6	13.3*

*Refers to one available S atom (monosulfidic structure)

**Refers to one available S atom (disulfidic structure)

A sulfur donor can be prepared from many organic compounds and sulfur. For this research, cardanol polysulfide (CPS) used as a sulfur donor type vulcanizing agent is synthesized from cardanol and elemental sulfur.

2.5 Vulcanization Stages [1]

The way in which the vulcanization time affects the tensile stress of rubber compounds at a given elongation shows that vulcanization consists of several reaction phases: the scorch or onset of vulcanization, undervulcanization, optimum vulcanization, and overvulcanization. The various stages are shown in Figure 2.6.

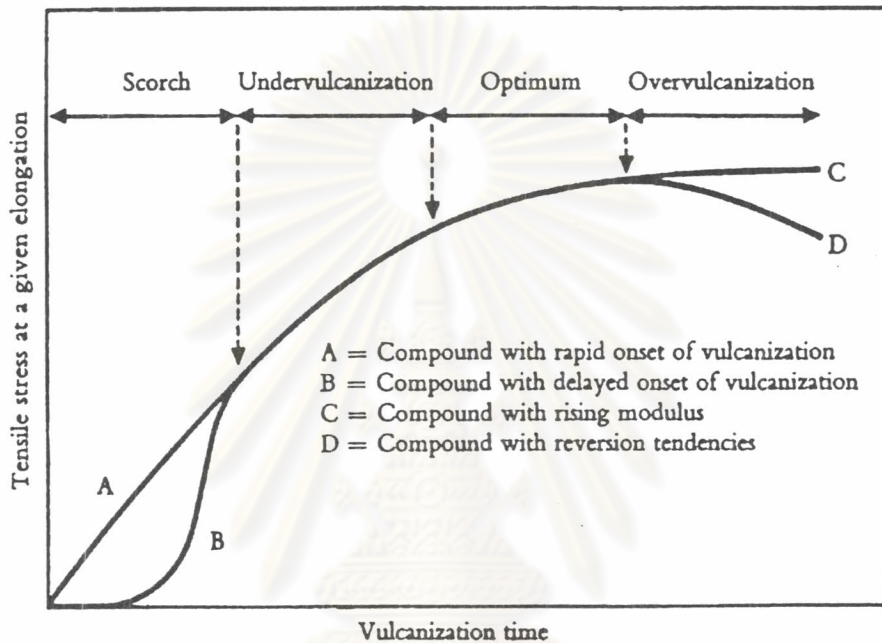


Figure 2.6 Vulcanization stages. Reproduced from [1].

2.5.1 Onset of Vulcanization

This is the point of time at which the compound first begins to stiffen, thus becoming incapable of flowing thermoplastically; in the case of a press cure it is the point of time at which the compound ceases to flow in the mold. Depending on the vulcanization auxiliaries chosen, it may occur early or late.

2.5.2 Undervulcanization

This is the stage between the onset of vulcanization and the vulcanization optimum. It is the stage at which the tensile stress still increases very much with the vulcanization time. As the degree of crosslinking is still small at this stage, most of the

properties required in a rubber article are still so little evident that a highly undervulcanized article is of no technical value.

2.5.3 Vulcanization Optimum

In most cases goods have to be vulcanized to a fairly high degree of crosslinking. Within the range of tensile stresses which is designated the vulcanization optimum, the manufacturer (depending on the requirements which the rubber articles have to fulfill) will aim to get either a relatively low tensile stress of a relatively high degree of vulcanization. Not all the properties are optimal at a given degree of vulcanization.

2.5.4 Plateau and Overvulcanization

In the case of natural rubber, when the vulcanization optimum is exceeded the crosslinking is reversed at a rate which depends on the chosen vulcanization system and this “reversion” causes the mechanical properties to suffer.

2.5.5 Postvulcanization

In connection with overvulcanization mention should also be made of postvulcanization which even though it occurs during prolonged storage, e.g. at room temperature.

Whilst the modulus curve is rising rapidly, vulcanization is occurring. ‘Cure time’ can therefore be defined as the sum of the scorch time and the vulcanization time, although the definition of ‘optimum cure’ time is not so simple. In the first place, distinction must be made between a full cure, such might be required for experimental process, and the ‘technological optimum’ which would be given under production conditions. Under factory and laboratory conditions, it has paramount importance to measure this quantity with the minimum of time and effect whilst the rubber is actually curing. It is possible to put the uncured stock into a hot mold, transfer to the press, and heat for the required time at the temperature of cure by a machine which automatically records the result in a convention form as shown in Figure 2.7.

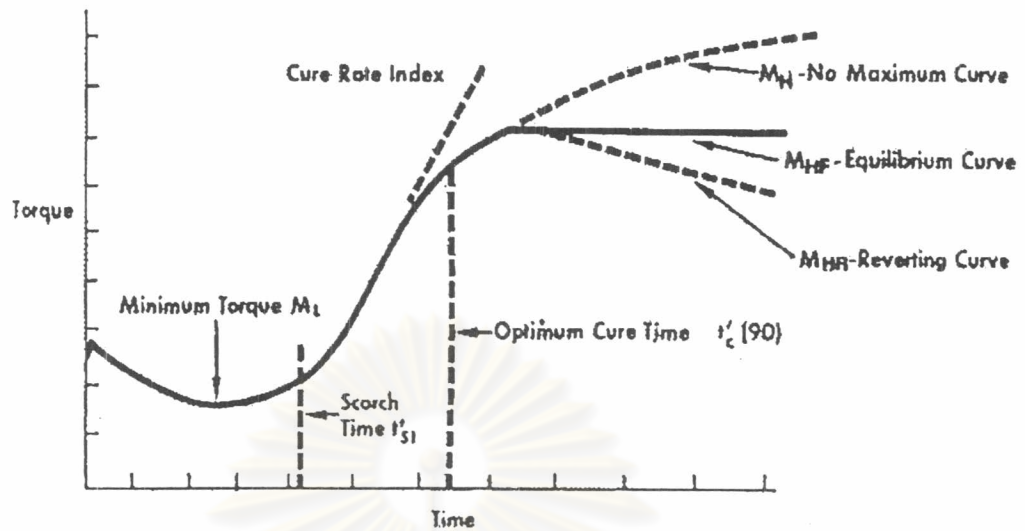


Figure 2.7 Rheograph. Reproduced from [18].

From Figure 2.7, a plot of the torque against time gives a so-called rheometer chart, rheograph, or cure curve.

2.6 Processing Technique [14]

For rubber mixing processed, the most widely used equipments are internal mixer, banbury, brabender mixer and two-roll mill.

The objective of the mixing process is to produce a compound with its ingredients sufficiently and thoroughly incorporated and dispersed so that it will process easily in the subsequent forming operations. Also, it is necessary for cure efficiency and to develop the necessary properties for end-use; allwith the minimum expenditure of machine time and energy.

A banbury and two-roll mill are selected for mixing natural rubber and additives for this research. First, the natural rubber and common additives were mixed by banbury except vulcanization ingredients (sulfur, accelerator and sulfur donor), called non-productive compounds. Then it was mixed with vulcanization ingredients by two-roll mill, which usually heated at 70 °C. Thus, the long time of mixing should be avoided because scorching may occur.

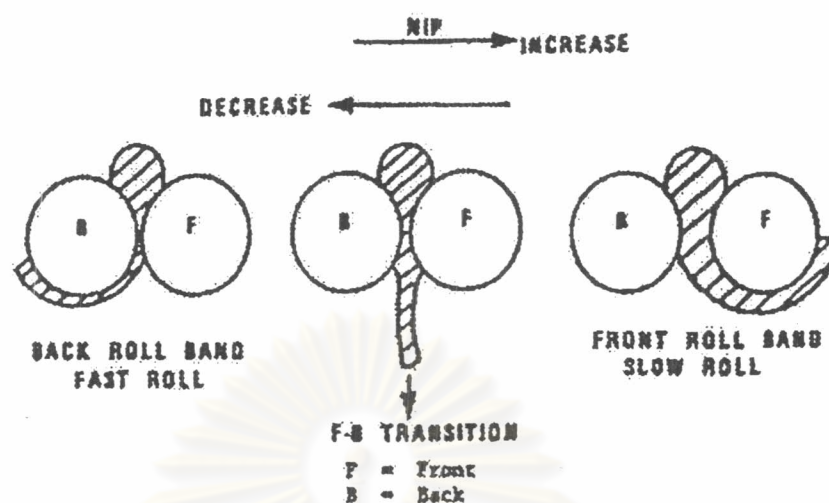


Figure 2.8 Behavior of rubber on the two-roll mill. Reproduced from [13].

2.7 Literature Reviews

Sulfur donors have been used as vulcanizing agents for a long time. One of the oldest sulfur donors is sulfur dichloride, which was discovered in 1846. It makes vulcanization of thin natural rubber articles possible at room temperature or better at slightly elevated temperatures (cold temperature). It was of little importance because of poor aging properties of vulcanizates. Afterwards, sulfur dichloride was improved by use incorporation with organic compounds to be transformed into sulfur bearing compounds. One important organic compound is alkyl phenol.

Para-tertiary amyl phenol disulfide, the most popular phenol sulfide resin, has been used as a vulcanizing agent for the improvement properties of rubber. It was prepared from para-tertiary amyl phenol and disulfur dichloride or sulfur dichloride known as Vultac[®]. There have been reported on developments for using alkyl phenol sulfide as a vulcanizing agent in many ways as shown below:

In 1947, W. M. George et al. [21] studied the treatment of butadiene polymerizates, including polymerizates of various butadiene derivatives and vulcanization of the butadiene polymerizate with the material added to impart tack and with such other materials as are desired for incorporation in the ultimate product. Phenol

sulfides were found to be valuable as primary vulcanizing agents in the treatment of synthetic elastomers. The phenol sulfides which are preferred for practice of the invention are the tertiary alkyl phenol sulfides that they may be obtained by reacting sulfur monochloride with a tertiary alkyl phenol. The sulfur contained in the phenol sulfide apparently enters into the vulcanization reaction, and in cases in which large amounts of sulfur are made available for use in vulcanization through the phenol sulfide, in addition to the quantities of sulfur normally used in the vulcanization. When, however, it was recognized that the phenol sulfide served as a primary vulcanizing agent, and the quantity of sulfur separately incorporated in the mixture to be vulcanized is correspondingly reduced or eliminated to take account of the sulfur available from the phenol sulfide, it was found that these factors of tear resistance upon aging, elongation at break and heat embrittlement are actually improved by inclusion of the phenol sulfide as compared to products obtained by vulcanizing operations in which the phenol sulfide was omitted.

Then 1976, E. N. Robert [22] improved process for preparing chlorobutyl rubber compositions employs para-tertiary butyl phenol disulfide as curing agent. Para-tertiary butyl phenol disulfide was produced by the reaction of para-tertiary butyl phenol with sulfur monochloride. The reaction was carried out using an approximately 11:10 mole ratio of phenol to monochloride. It has a sulfur content in excess of about 27 wt% and a softening point not less than 80 °C. Unlike other commercially employed alkyl phenol sulfides, para-tertiary butyl phenol disulfide is a solid substance, which is a non-tacky brittle solid and does not deteriorate as by coalescing under normal storage conditions.

In 1976, M. R. Le [23] synthesized friable tertiary amyl phenol sulfides as vulcanizing agents, by reacting tertiary amyl phenol with sulfur monochloride at a mole ratio of 0.7 to 0.95 of the phenol to one mole of sulfur monochloride. The alkyl phenol was introduced to a reactor in a molten condition or else it is introduced as a solid and then melted or at least partially melted before sulfur monochloride addition is started. The hot liquid reaction product was then flaked on a cooled surface. The use of tertiary amyl phenol sulfide as a sulfur donor in the vulcanization of rubber is facilitated by its ease of shipping and handling in a flaked form.

In 1999, N. Rabindra et al. [24] studied the anti-reversion coagent and sulfide resin of vulcanization of rubber. This invention was related to the vulcanization process which is carried out in the presence of an anti-reversion coagent and a sulfide resin and the use of an anti-reversion coagent in combination with sulfide resin in a process for the vulcanization of rubber. The anti-reversion coagent comprised at least two groups selected from citraconimide and/or itaconimide groups. The resulting vulcanized rubbers have significantly improved mechanical and heat resistance properties.

For the last related literature, in 2000, M. Radeemada [25] synthesized cardanol polysulfide (CPS) as a sulfur donor type vulcanizing agent which was obtained from the reaction of decarboxylated cashew nut shell liquid and elemental sulfur. It has a sulfur content about 30 wt%. The CPS was mixed with natural rubber and common additives by a two-roll mill. The resulting vulcanized rubbers improved basic mechanical properties and reduced the reversion of rubber compounds.



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