

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Natural Rubber[4,5]

Natural rubber, on which the technology of the industry was built, is obtained by the coagulation of the milky aqueous dispersion of rubber—called latex— produced by the tree *Hevea brasiliensis*.

The *Hevea brasiliensis* tree is the main source of natural rubber and its existence in the Amazon basin was first reported by Charles de la Condamine to the french Academy in 1736. He described to them the native methods of obtaining rubber from this tree and also methods that were used to convert it into useful products.

As methods were discovered of preserving and transporting the latex from the tropical areas, in which the trees grow, to the USA and Europe, a separate technology for the manufacture of products direct from latex developed during the 1920s. The several methods of concentrating the latex, by heat, by creaming, centrifugally or chemically, and later by electrodecantation, encouraged these developments because less water was transported and because higher solids content increased still further its

advantage over solutions of rubber in organic solvents for some manufacturing operations.

2.2 Production of Natural Rubber in Thailand[6]

The data from Customs Department shown that in 1997, Thailand exported 1,919,429 metric tons of rubber and the total value exported 57,447 millions Baht. Thailand exports the different types of rubber, for example, ribbed smoked sheet rubber, block rubber, crepe rubber, concentrated latex, air dried sheet rubber and others rubber. About the rubber products, Thailand exported 24,789 millions Baht. The total quantity and value of natural rubber exports is shown in Table 2.1.

Table 2.1 Total quantity and value of natural rubber exports.

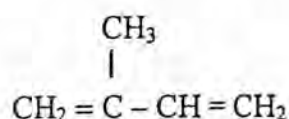
Year	Quantity (metric tons)	Value (millions of Baht)
1993	1,492,794	29.181
1994	1,711,648	41,821
1995	1,747,269	61,261
1996	1,922,042	63,370
1997	1,919,429	57,447

Source: Customs Department, 1998

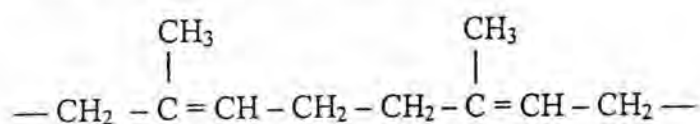
2.3 Properties of Natural Rubber[7]

First recorded analysis of natural rubber was performed by Faraday. He reported it to be composed of hydrogen and carbon in the ratio expressed by C_5H_8 as early as 1826. Williams found in 1860 by destructive distillation that isoprene was the building unit of natural rubber. Tilden also reported that the probable structure of rubber was 2-methyl-1,3 butadiene. That is, one double bond unit existed for each C_5H_8 group. Bouchardat recognized in 1879 that isoprene could be polymerized into natural rubber.

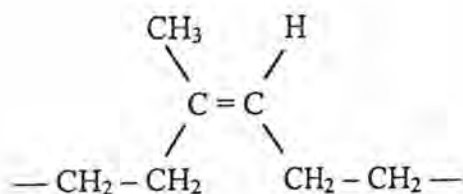
Isoprene was found to have the formula C_5H_8 which structure is as follows



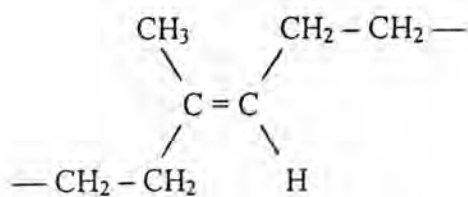
Natural rubber is a polymer, in which all the isoprene units are linked together at carbon atom 1 and 4 in a head-to-tail arrangement, and in which all or nearly the repeating units possess the "cis" configuration.



Head - to - tail arrangement



cis - polyisoprene

*trans* - polyisoprene

2.3.1 Composition[8]

Commercial raw natural rubber has a small, but highly important number of nonrubber constituents. These may comprise as much as 5-8% of the total composition. Most important are the natural occurring antioxidants and activators of cure, represented by the proteins, sugars, and fatty acids. Typical composition is shown in Table 2.2.

Table 2.2 Analysis of representative natural rubber.

Ingredient	Ave. %	Range %
Moisture	0.5	0.3-1.0
Acetone Extract	2.5	1.5-4.5
Protein	2.5	2.0-3.0
Ash	0.3	0.2-0.5
Rubber Hydrocarbon	94.2	-
Total	100.0	-

Trace elements present include potassium, magnesium, and phosphorus, as well as copper, manganese, and iron. Although usually present only to the extent of 2-3 parts per million, the latter are important as catalysts to promote the oxidation of vulcanized rubber. Amounts higher than 8-10 parts per million are not tolerated.

Outlines in detail the complex variety of chemical substances present in the dry rubber and latex is shown in Table 2.3.

Table 2.3 Approximate concentrations of nonrubber constituents in centrifuged latex concentrates.

Constituent	Percentage by weight of latex
Fatty acid soaps(e.g., ammonium oleate)	0.5
Sterols and sterol esters	0.5
Proteins	0.8
Quebrachitol	0.3
Choline	0.1
Glycerophosphate	0.1
Water-soluble carboxylic acid salts (acetate,citrate,etc.)	0.3
Amino acids and polypeptides	0.2
Inorganic salts (ammonium and potassium carbonate and phosphate, etc.)	0.2

2.3.2 Physical Properties

Physical properties of natural rubber may vary slightly due to the nonrubber constituents present and to the degree of crystallinity. When natural rubber is held below 10 °C, crystallization occurs, resulting in a change of density from 0.92 to about 0.95. Listed in Table 2.4 are some average physical properties.

Table 2.4 Some physical properties of natural rubber

Properties	Value
Density	0.92
Refractive index (20°C)	1.52
Coefficient of cubical expansion	0.62 /°C
Cohesive energy density	63.7 cal./c.c.
Heat of combustion	10,700 cal./g
Thermal conductivity	0.32 cal./sec/cm ² /°C
Dielectric constant	0.33 2.37
Power factor (1,000 cycles)	0.15-0.2*
Volume resistivity	10 ¹⁵ ohms/c.c.
Dielectric strength	1,000 volts/mil

*The power factor is reduced to 0.0015 and the resistivity substantially increased in deproteinized rubber.

2.4 Contents of Rubber Compounds[9]

Natural rubber, and with a few exceptions the many synthetic polymers commercially available, are unsaturated; that is, they contain double bonds which provide sites for the vulcanization reaction. The polymers are mostly linear or branched, but some also contain (either intentionally or unintentionally) minor amounts of gel (crosslinked particles) prior to vulcanization. This can have a profound effect on processing properties. The following substances are also included in rubber compounds.

2.4.1 Reinforcing Fillers[10,11]

Most rubber compounds that are intended to develop a reasonable tensile strength, abrasion, and tear resistance will contain up to 50 phr or more of a reinforcing filler, nearly always a carbon black. The use of carbon black in rubbers is quite different than in plastics, where it is strictly a pigment and limited to much lower loadings.

Carbon blacks are not simply carbon. Basic blacks have hydroxyl groups at the particle surfaces and acid blacks have carboxylic acid functionality. It has been shown that the rubber polymer forms strong secondary and primary covalent bonds with the carbon black, which accounts for its reinforcing ability. A wide variety of carbon blacks is available. In addition to chemical functionality, they differ in such factors as particle size, degree of aggregation, and surface area, and different types of rubber polymers require particular kinds of black for optimum reinforcement.

Carbon blacks are essentially elemental carbon and are composed of aggregated particles. The particles are partly graphitic in structure and are of colloidal dimensions. The carbon atoms in the particle are in layer planes which, by parallel alignment and overlapping, give the particles their semi-graphitic nature. The outer layers are more graphitic than those in the centre. The carbon black particle is shown in Figure 2.1. The particles range in size from 10 nm to 400 nm in diameter, the smaller ones being less graphitic.

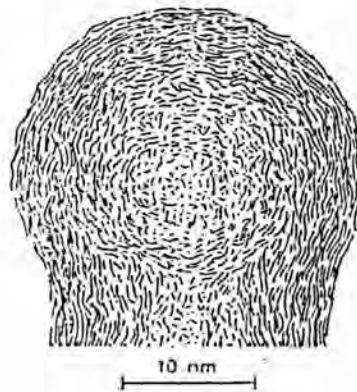


Figure 2.1 Concentric layer orientation of carbon black particle

Carbon blacks are produced by converting either liquid or gaseous hydrocarbons to elemental carbon and hydrogen by partial combustion or thermal decomposition. Table 2.5 summarises the various manufacturing processes which have been since the introduction of carbon black and indicates the types of products which can be obtained from them.

Table 2.5 Carbon black manufacturing process and products

Process	Year introduced	Raw material	Method	Temperature (°C)	Yield of available carbon (%)	Product
Lamp	About 1850	Oil, coal tar	Partial combustion in shallow pans	-	20-60	Particles of broadly distributed sizes (ave. 100 nm) High structure
Channel	1915	Natural gas	Many small flames impinging on a cool surface	1100	0.5-5	Small particle size (9-30 nm) Low structure High oxidation-slow curing in rubber
Gas furnace	1922	Natural gas	Partial combustion in large, refractory furnace	1200	30-40	Medium particle size (50-87 nm) Low structure
Thermal	1922	Natural gas	Thermal cracking on heated refractory brick checkerwork	1300	40-50	Large particle size (120-500 nm) Low structure
Acetylene		Acetylene gas	Exothermic decomposition of acetylene gas	900		Medium particle size (50-60 nm) more graphitic Very high structure
Oil furnace	1943	Oil, coal tar	Partial combustion in refractory furnace	1200-1600	45-80	High structure Wide range of particle size(14-90 nm)

The naming of the different types of carbon blacks has developed over many years with no logical basis; manufacturers have arbitrarily given new products new type names as well as trade names. The system proposed in 1967 in ASTM D1765 has been adopted world-wide, the International Standards Organization having decided, in 1980, to use this system. This ASTM system consists of one letter followed by three numerals.

The letter indicates rate of cure, N and S being used for normal and slow respectively.

The first numeral give the surface area of carbon black as measured by iodine adsorption. Here, some attempt has been made to relate the proposed system to the type name system, e.g., 1 = SAF, 2 = ISAF, 3 = HAF.

The remaining two numerals are selected arbitrarily, but one rule applies. In the case of a black with a standard level of structure, the second numeral is always a repeat of the first numeral and the last is zero, e.g. SAF = N-110 and ISAF = N-220.

2.4.2 Fillers

As with plastics, the function of fillers in rubber is mainly to reduce the cost of the compound. Most rubber fillers are finely divided inorganics such as CaCO_3 . The addition of such high-modulus fillers raises the modulus (stiffens the compound), and too much will cause a loss of rubbery properties, all other things being equal. Carbon blacks sometimes perform as fillers as well as reinforcing agents in rubber compounds.

2.4.3 Extending Oils

Hydrocarbon oils are often used in rubber compounds. Their function is twofold. First, they plasticize the polymer, making it softer and easier to process. This is particularly important with very high molecular weight polymers. Second, since they are usually cheaper than the rubber polymer, they act like fillers in reducing the cost of the compound. Extending oils are available in various degrees of aromaticity, and the properties of the compound depend on the type of oil in relation to the polymer as well as oil level.

Carbon black and extending oils have opposite effects on the modulus of a rubber compound. One trick for producing low-cost compounds from synthetic polymers is to polymerize to higher-than-normal molecular weight. The modulus is cut down by the addition of an extending oil and then brought back up to the desired level by the addition of large amounts of black.

2.4.4 Vulcanizing or Curing Systems[12,13]

The function of these is to crosslink the polymer. The most common curing systems are based on sulfur. While sulfur alone will cure unsaturated rubbers with heating, the process is slow and inefficient in its use of the sulfur. The mechanisms of sulfur curing are not well understood, but are thought to include (among other things) the formation of sulfide or disulfide links between chains and the abstraction of protons from adjacent chains to form H_2S , with the chains crosslinking at the remaining unshared electrons.

To control the time and/or temperature required for vulcanization and improve the properties of the vulcanizate, accelerators are generally used. These are usually complex sulfur-containing organic compounds, often of proprietary composition.

Accelerator activators are used to increase the vulcanization rate by activating the accelerator so that it performs more effectively. It is believed that they react in some manner to form intermediate complexes with the accelerators. Accelerator activators are grouped as follows:

- i) Inorganic compounds (mainly metal oxides) used include zinc oxide, magnesium oxide, alkali carbonates, and hydroxides. Zinc oxide is the most common and it is generally used in combination with a fatty acid to form a rubber-soluble soap in the rubber matrix.
- ii) Organic acids are normally used in combination with metal oxides; they are generally high molecular weight monobasic or mixtures of the following types: stearic, oleic, lauric, palmitic, and myristic acids, and hydrogenated oils from palm, castor, fish, and linseed oils.
- iii) Alkaline substances will increase the pH of a rubber compound and in most instances increase the cure rate. As a rule of thumb, in the majority of recipes, any material which makes the compound more basic will increase the cure rate since acidic materials tend to retard the effect of accelerators. Typical examples of these ingredients include ammonia, amines, salts of amines with weak acids, and reclaim rubbers made by the alkali process.

2.4.5 Antioxidants or Stabilizers

These are particularly important with natural rubber and the many synthetic rubber that contain a major proportion of butadiene or isoprene. These polymers are highly unsaturated and the double bonds are extremely susceptible to attack by oxygen and ozone, resulting in embrittlement, cracking, and general degradation. Since the degradation reactions take place by free-radical mechanisms, antioxidants are compounds that scavenge free radicals.

2.4.6 Pigments

Where great mechanical strength is not required, and thus carbon black not used, rubbers can be colored with pigments as can plastics.

2.5 Latex Compounding[10]

It is a basic principle of compounding to minimize the number of additives used to achieve the desired processing behaviour and product properties. In general most latex compounds require three classes of additive:

- a) stabilizers to ensure adequate processing stability.
- b) vulcanizing agents to effect crosslinking of the rubber.
- c) protective agents to ensure adequate service life.

In addition some compounds, depending on the nature of the process or on

the end use, may require gelling agents, foaming agents, thickeners, flame proofing agents, pigments, fillers, extenders, and tackifying resins.

2.6 Vulcanization[14]

Elastomers are one of the oldest and widely polymers known to man, which accounts for their use in a variety of applications. Originally natural rubber was used uncured, but suffered from drastic softening in warm weather and highly increased rigidity in cold weather. The first significant elastomeric technology advancement was the simultaneous discovery in England and the United States that addition of sulfur to rubber, followed by heating, leads to an improvement in the properties. This was the first vulcanization system, and was discovered by Goodyear in the U.S. and Hancock in England.

This form of 'sulfur-only' vulcanization, while alleviating many of the disadvantages of uncrosslinked elastomers, does not provide an optimum product. Around 1910 it was discovered by Oenslanger in Germany that the addition of aniline to a rubber/sulfur formulation greatly increase the rate of vulcanization and improved the final vulcanizate properties. It was quickly discovered that a wide variety of amines functioned similarly. These amines were the first accelerators for vulcanization.

Presently there are a wide range of accelerator systems available for elastomers, providing a range of cure rates, scorch times and final properties. These accelerators include the thiurams, sulfenamides, mercaptobenzothiazoles, amines and more recently sulfenimides; several common accelerators are show

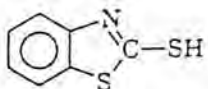
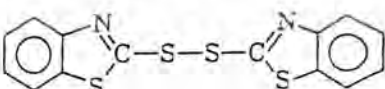
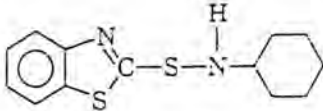
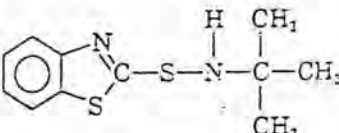
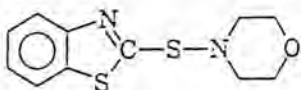
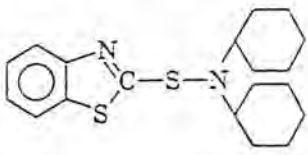
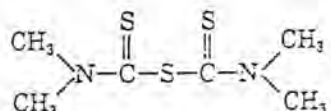
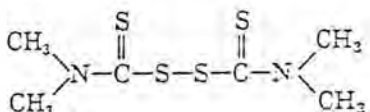
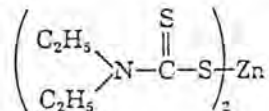
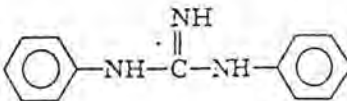
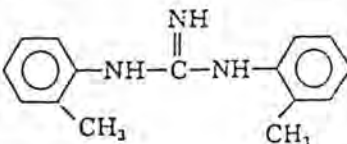
in Table 2.6. Additionally, there are combination systems (i.e., thiuram sulfenamides) also available. The variety of accelerators accounts for the wide applicability of elastomers to material applications. Also of increasing utility are binary accelerator systems, which utilize two or more accelerators in a synergistic manner. Mixed in the proper proportions, binary systems can lead to significant improvement in curing behavior and mechanical properties.

2.6.1 Theory of Sulfur Vulcanization[15]

In fact the chemistry of sulfur vulcanization is so complex that it is only within the few years that a coherent theoretical treatment has been possible. Even today, only the main stages are proven and there is still much to be learned about the effect of additives of various types.

This complex reaction is an excellent example of the combined efforts of physical and organic chemists. It starts with measurement in 1910-1912, of the rate of the sulfur reaction, followed by the examination of the apparent loss of unsaturation by rubber in 1938-1945. The use of methyl iodide as a 'chemical probe' increased knowledge of the crosslinking reactions further. These latter workers used 'model olefines' of low molecular weight to follow crosslinking reactions. These model substances were easier to handle than vulcanized rubber and enabled intelligent guesses to be made as to the nature of the crosslinks themselves.

Table 2.6 Several common accelerators used in sulfur vulcanization

Compound	Abbreviation	Structure
<i>Benzothiazoles</i>		
2-mercaptobenzothiazole	MBT	
2,2'-dithiobisbenzothiazole	MBTS	
<i>Benzothiazolesulfenamides</i>		
<i>N</i> -cyclohexylbenzothiazole-2-sulfenamide	CBS	
<i>N</i> - <i>t</i> -butylbenzothiazole-2-sulfenamide	TBBS	
2-morpholinothiobenzothiazole	MBS	
<i>N</i> -dicyclohexylbenzothiazole-2-sulfenamide	DCBS	
<i>Dithiocarbamates</i>		
tetramethylthiuram monosulfide	TMTM	
tetramethylthiuram disulfide	TMTD	
zinc diethyldithiocarbamate	ZDEC	
<i>Anilines</i>		
diphenylguanidine	DPG	
di- <i>o</i> -tolylguanidine	DOTG	

Sulfur is combined in the vulcanized network in a number of ways as show in Figure 2.2.

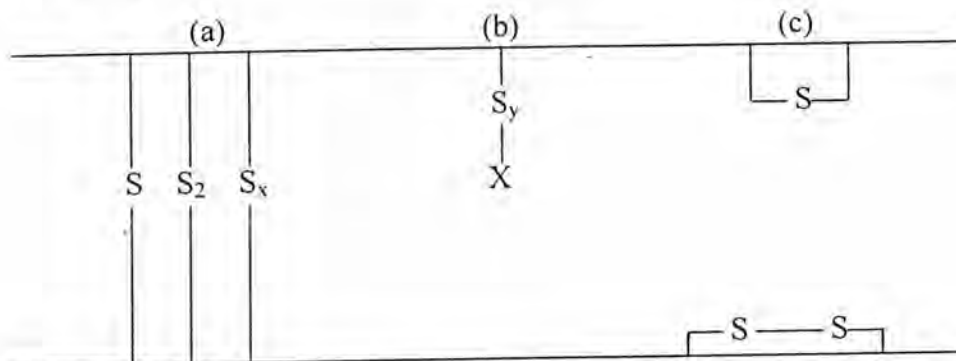
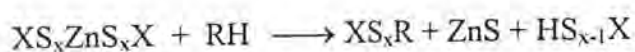


Figure 2.2 Structural features of vulcanized network

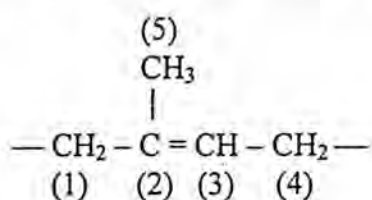
As crosslinks, it may be present as monosulfide, disulfide, or polysulfide show in Figure 2.2(a), but it may also be present as pendent sulfides show in Figure 2.2(b), or cyclic monosulfides and disulfides show in Figure 2.2 (C).

2.6.2 Mechanisms of Sulfur Vulcanization[5]

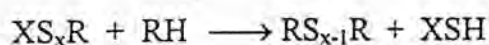
The initial step in vulcanization seem to be the reaction of sulfur with the zinc salt of the accelerator to give a zinc perthio-salt XS_xZnS_xX , where X is a group derived from the accelerator (e.g. thiocarbamate or benzthiazyl groups). This salt reacts with the rubber hydrocarbon RH to give a rubber-bound intermediate



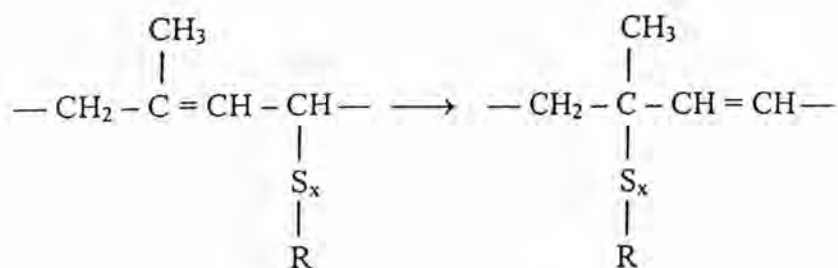
and a perthio-accelerator group which, with further zinc oxide will form a zinc perthio-salt of lower sulfur content; this may, nevertheless again be an active sulfurating agent, forming intermediates $HS_{x-1}R$. In this way each molecule of accelerator gives rise to a series of intermediates of varying 'degree of polysulfidity'. The hydrogen atom which is removed is likely to be attached to a methylene group in the α -position to the double bond, i.e. in natural rubber the hydrogen atoms at positions 4 and 5 are the most labile in this type of reaction.



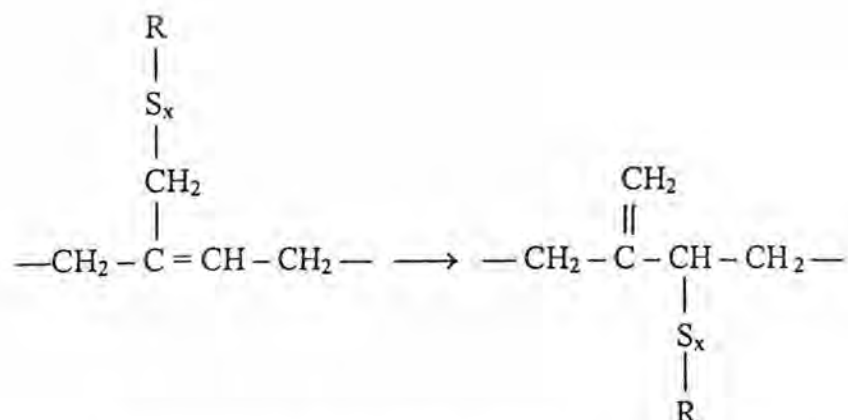
The intermediate XS_xR then reacts with a molecule of rubber hydrocarbon RH to give a crosslink, and more accelerator is regenerated:



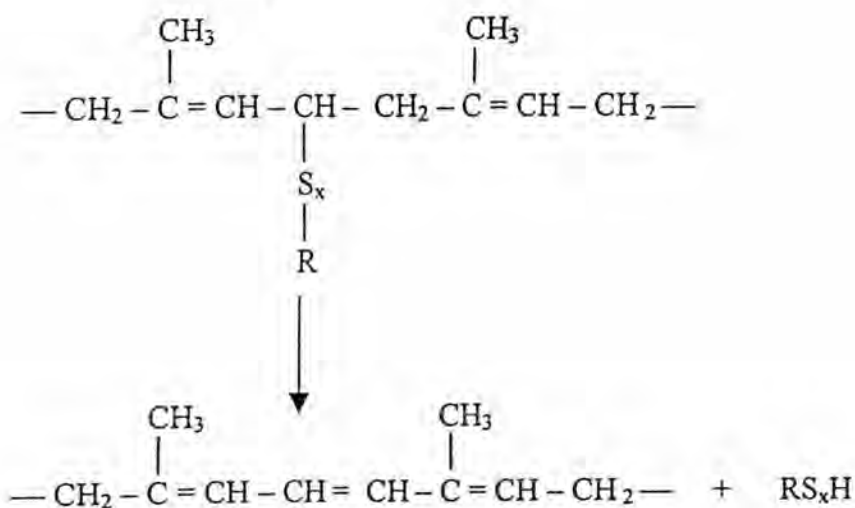
Even this is not the whole story, for, on further heating, the degree of polysulfidity of the crosslink declines. This process is catalysed by XS_xZnS_xX and can result in additional crosslinks. It is also evident that the crosslinks which were initially at positions 4 and 5 undergo an allylic shift, with the result that new configurations appear:



and



At the same time, disappearance of crosslinks of the disulfide and polysulfide type occurs, with formation of conjugated trienes:



This destruction of crosslinks is apparently associated with the formation of the cyclic sulfides (Figure 2.2 (C)), but this has not been investigated in detail.

A consideration of the above reactions leads to the conclusion that, if desulfuration proceeds rapidly, the final vulcanized network will be highly crosslinked with mainly monosulfidic bonds and there will be relatively few modifications of the cyclic sulfide or conjugated triene type: such a network is termed “efficiently crosslinked”. If on the other hand, desulfuration proceeds slowly, there will be opportunities for thermal decomposition, leading to reversion or loss of crosslinks and to networks containing modifications: further, the crosslinks which do survive will be di- or poly- sulfidic and hence will be liable to further decomposition. These networks are inefficiently crosslinked.

An overall scheme of vulcanization is shown in Figure 2.2. This scheme summarizes the key steps of the accelerated sulfur vulcanization reactions.

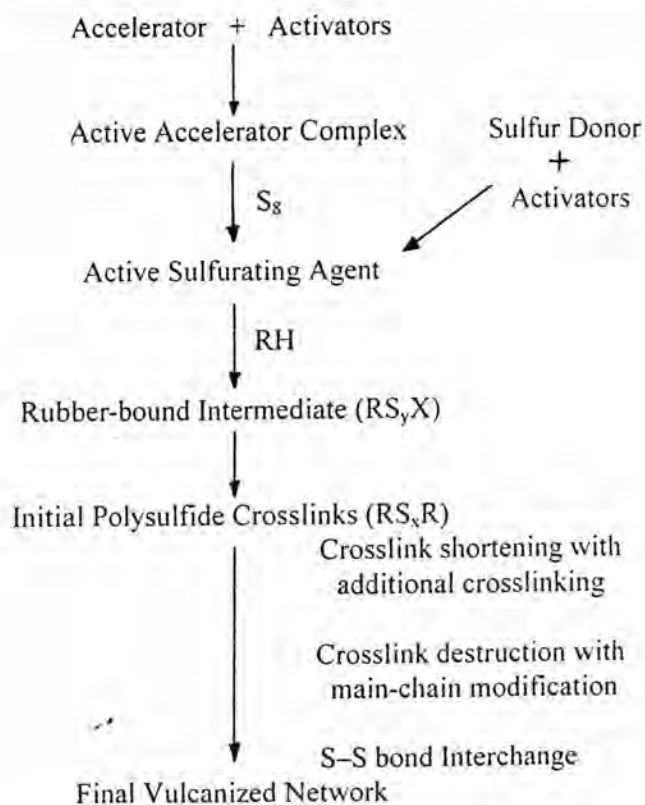


Figure 2.3 Generalized mechanism of vulcanization; R = rubber chain, H = allylic proton, and X = accelerator residue

2.6.3 State of cure[12]

A typical cure curve is shown schematically in Figure 2.4. This simulated curemeter trace illustrates the three main regions of cure (labeled I–III). The first region is the scorch delay period or induction period, in which the majority of the accelerator chemistry takes place. The second period is the crosslinking period, in which the initial network structures are formed and the accelerator intermediates are consumed. The final stage is the overcure, or reversion period, during which maturation and resulting property deterioration occurs.

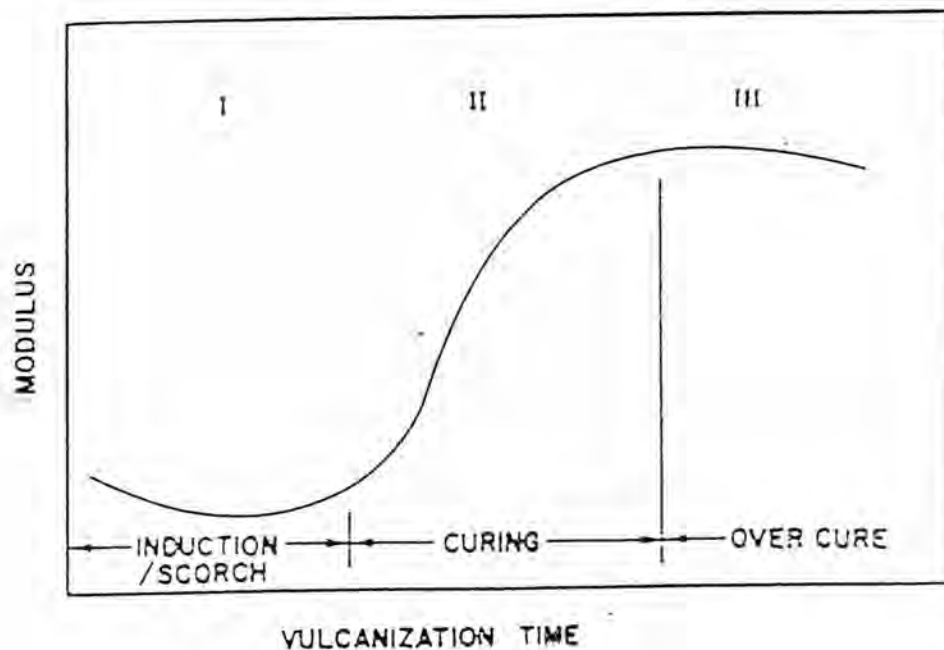


Figure 2.4 Typical cure curve illustrating the three main regions of vulcanization: scorch delay(I), crosslinking(II), and reversion(III)

2.7 Literature Review

J.V.Hallum and H.V.Drushe[16] studied the organic nature of carbon black surfaces. Evidence is presented for the existence of quinone groups and aromatic hydroxyl groups on the surface of carbon black particles. This evidence is based largely upon polarographic analyses of slurries of carbon blacks. A mechanism for the chemical interaction of carbon blacks with elastomers is proposed on the basis of these functional groups.

S.Bhoumick and S.Banerjee[17] studied on MBT-accelerated sulfur vulcanization of natural rubber reinforced with carbon black. The mechanism of thiazole-accelerated sulfur vulcanization of rubber has been reported to be both free radical and polar. Because the effect of fillers on vulcanization reaction has not been studied in detail then crosslinking of different mixes containing sulfur and in the presence of 2-mercaptobenzothiazole (MBT) were studied. All the mixes contained carbon black. The compound formulation of their work that used to compare the properties with this research are given below:

- Natural rubber	100	parts
- Carbon black	10	phr.
- MBT	1	phr.
- Sulfur	1	phr.
- Zinc oxide	5	phr.
- Stearic acid	3	phr.

The physical properties of this vulcanized sheet are shown in Table 2.7.

Table 2.7 The physical properties of vulcanized sheets from S.Bhoumick and S.Banerjee's work

Properties*	results
Modulus 200% (kg/cm ²)	4.79
Elongation (%)	810
Tensile strength (kg/cm ²)	57.99
Hardness (shore A)	19.0
Resilience (%)	47.55

* cure time was 10 min

M.R.Krejsa[12] had reviewed and summarised the present understanding of the fundamental science and chemistry of rubber vulcanization. For the purpose of this review, two general categories of sulfur vulcanization—unaccelerated and accelerated— were considered. Unaccelerated sulfur formulations consisted of rubber and sulfur, while accelerated systems contained rubber, accelerator and sulfur. In addition, zinc oxide and stearic acid were often included in both types of systems. There were also accelerator systems in which elemental sulfur was not present; instead, the accelerator provided the sulfur for vulcanization. These sulfurless systems were generally referred to as sulfur donor formulations. The ultimate goal of understanding vulcanization chemistry is to be able to tailor formulations to produce desired mechanical and chemical properties.

A.Y.Coran and J.B.Donnet[18,19] studied the dispersion of carbon black in rubber. The work was focused on methodology for reproducibly mixing carbon black with rubber in the laboratory, and reproducibility, but rapidly and easily estimating the degree of dispersion of carbon black into the rubber as a function of mixing time. A small-scale (70 g batch size) laboratory mixing procedure for studying the dispersion of carbon black in rubber has been developed. Laboratory internal mixer was used. The method was characterized in that after the mastication of the pure polymer, a portion of the rubber was removed from the mixer (to make room for the carbon black). The carbon black was then added and after the carbon black was taken into the mixer, the rubber which had been removed was added back. There was little or no unmixed powder at the end of a mixing run.

Meaningful estimates of the degree of dispersion could be easily obtained by using a simple, improved method for preparing surfaces of carbon black filled rubber vulcanizates for dark-field optical microscopic examination. The method could even be adapted to the preparation of surfaces of unvulcanized stocks and masterbatches. Dispersion ratings as determined by the present method correlated very well with ultimate tensile strength values obtained by using a specially designed highly elongated test specimen.

W.M.Hess[2] had reviewed the methods of pigment dispersion analysis. This paper reviewed many of procedures to characterize pigment dispersion. The main emphasis was on the analysis of elastomeric compounds containing carbon black. The characteristics of dispersions had been divided into three categories:

(1) agglomeration (2) microdispersion (networking) and (3) polymer-phase distribution. Optical analysed were preferred for rubber compounds containing high loadings of carbon black. This research used this method to characterize carbon black dispersions. The other procedures of this paper were very helpful and the scanning electron microscope was also used in this research.