Chapter 1

INTRODUCTION

Abstract

The importance of vulcanisation of elastomers, major types and mechanism of action has been reviewed in this introductory chapter. Attention has been made to investigate accelerated and non-accelerated vulcanisation. Possible mechanisms by which the reaction is taking place are discussed. The role of accelerators, activators and fillers has been described. The different types of crosslinks and importance of each type on the specific properties of the resulting vulcanisates etc. are discussed. Various aspects of vulcanisation like model compound vulcanisation, nitrosamine generation are discussed. The importance of binary accelerators and possible mechanism of their action have been mentioned. The method of double network formation, which is useful for the improvement in properties, is also described. The different methods for characterisation of networks and estimating crosslink densities are well explained.
In modern times, rubber owing to its unique properties has gained increasing prominence as an essential industrial raw material. Raw rubber is an entanglement of high molecular weight hydrocarbon chains. For rubber to become truly useful, its chains must be permanently linked together to increase the strength. One of the common ways to achieve high performance rubber is vulcanisation, by which the linear macromolecules are crosslinked into three-dimensional networks [1]. Ever since the initial discovery of Charles Good Year and Thomas Hancock that small quantities of sulphur used at the time of vulcanisation can yield best quality rubber of extra strength, researchers have been fascinated by the infinite possibilities in this field. The vulcanised articles give service performance superior to that of unvulcanised articles. Vulcanisation is the technique of transforming rubber, by some suitable treatment, from a plastic substance of very low strength and breaking elongation to a resilient highly elastic material of considerable strength and not so sensitive to temperature changes. The discovery that rubber can be vulcanised or cured by heating it with sulphur was a technological accomplishment of major importance. As our present study summarises the processing, curing and vulcanisate properties of different elastomers and their blends a detailed description of rubber compounding ingredients, different vulcanisation systems, their mechanisms etc. are described.

At the molecular level, vulcanisation causes profound chemical changes. The long molecules become linked in crosslinks spaced along the polymeric chains. As a result of this network formation, the rubber becomes essentially insoluble in solvents and cannot be processed by any means that requires it to flow. Thus vulcanisation should only occur after the rubber article is in its final form. Vulcanisation increases elasticity while it decreases plasticity. It should be noted that the modulus increases with vulcanisation.
Tear strength, fatigue life and toughness are increased as crosslinking proceeds and then reduced.

Important characteristics related to the vulcanisation process are the time taken before crosslinking starts, the rate of crosslink formation and the extent of crosslinking at the end of the process. There must be sufficient delay or scorch resistance to permit mixing, shaping and flowing in the mould. Then the formation of crosslinks should be rapid and the extent of crosslinking must be controlled. Natural rubber and most of the unsaturated synthetic rubbers can also be vulcanised by a wide variety of non sulphurated agents including organic peroxides, quinones and their oximes and imines, poly nitrobenzenes, biz-azodicarboxylic esters and by means of high energy radiations. Polychloroprene rubbers are usually vulcanised by metallic oxide like MgO along with other ingredients. Non-olefinic polymers generally require non-sulphurated agents or high energy radiations for effective vulcanisation. The most common vulcanising agent for diene rubbers is sulphur. A vast amount of technical literature is available for sulphur vulcanisation of rubber. Depending on the application, either soluble or insoluble sulphur is used. Insoluble sulphur is polymeric, gives 60-95% CS₂ soluble fraction and does not bloom to the surface like soluble sulphur. For the preparation of vulcanisates of normal hardness 0.25 to 3 phr sulphur may be used.

The use of elastomers as a material for finished products dates back to the 1830's. Vulcanisation is basically the process of introducing crosslinks between hydrocarbon chains. According to the definition of American Society for Testing and Materials (ASTM), ‘Vulcanisation is a chemical process in which the long chains of the rubber molecules become crosslinked by reactions with the vulcanising agent to form three dimensional structures’. This reaction
Chapter I

transforms the soft, weak, plastic-like material into a strong elastic product. The rubber loses its tackiness, becoming insoluble in solvents and more resistant to deterioration, normally caused by heat, light and ageing processes.

Vulcanisation is usually effected by heating the mechanically plasticized rubber with sulphur and other ingredients. Before vulcanisation the mixing of rubber with other ingredients (compounding) is done. The main objectives of compounding are to facilitate processing, to achieve the required balance in vulcanisate properties and produce durability. The various ingredients generally added to rubber during compounding include processing aids, accelerators and activators, fillers, antidegradants etc. Vulcanisation of rubber with sulphur alone is a slow process and requires several hours or even days to acquire optimum curing depending on the nature of rubber and the temperature of vulcanisation. This gives rise to vulcanisates of only very low physical properties. Moreover, they have a strong tendency to revert and their resistance to ageing is very poor and sulphur blooming occurs. Hence vulcanisation with sulphur alone is of no technological importance. The low crosslink density, which is obtained when sulphur is used alone, is mainly due to the fact that multivalent polysulphidic bridges, cyclic sulphides and vicinal bridge links are formed. Sulphur, which exists as \( S_8 \) ring, requires a large amount of activating energy to split. This process of activation occurs at high temperature and can be promoted by accelerators.

Sulphur alone was the vulcanising agent up to the discovery of organic accelerators in the early part of 20\(^{th}\) century. It was quickly realised that the use of accelerators gave improved properties and significantly reduced the required cure times. The first accelerators were amine-based compounds, with other classes of accelerators following quickly. Other compounds used in
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vulcanisation in addition to sulphur and accelerators are zinc oxide and saturated fatty acids such as stearic acid. These materials are termed as activators. Rubber formulations can also include fillers such as silica and carbon black and compounds such as stabilisers and antioxidants.

1.1. Methods of Vulcanisation

The formation of network structure is one of the essential conditions for generating the elastomeric properties. Sulphur vulcanisation is the most widely used curing technique for rubbers, preferably for unsaturated ones. The other curing methods include peroxide, resin, moisture, urethane, metal oxide and radiation crosslinking [2].

1.1.1. Peroxide Vulcanisation

A wide variety of peroxides are used to crosslink most type of elastomers. The crosslinks formed by peroxides are purely carbon-carbon linkages. The importance of peroxides is their ability to crosslink saturated elastomers such as low-density polyethylene, ethylene-propylene rubber, silicone rubber etc., which cannot be crosslinked with other types of vulcanising agents. The advantages and disadvantages of peroxide crosslinking are given in Table 1.1.

In addition to the disadvantages described in Table 1.1, there are several other important limitations for peroxide crosslinking of rubbers. One of them is that antioxidants can react with peroxide generated radicals and can result in reduced crosslinking efficiency [3]. Another potential problem is that carbon-centered radicals can react with oxygen. This reaction will produce hydroperoxides and can lead to tacky, unvulcanised surfaces. The mechanism for peroxide crosslinking is shown in Scheme 1.1.
Table 1.1 Advantages and disadvantages of peroxide crosslinking [4]

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simple compounding</td>
<td>Expensive crosslinking agent</td>
</tr>
<tr>
<td>Good heat ageing resistance</td>
<td>Low mechanical strength</td>
</tr>
<tr>
<td>Low tension set and strain</td>
<td>Higher curing time</td>
</tr>
<tr>
<td>No mould contamination</td>
<td>Difficult hot-air cure</td>
</tr>
<tr>
<td>Transparent rubbers possible</td>
<td>Need secondary cure of high temperature</td>
</tr>
</tbody>
</table>

Scheme 1.1. Mechanism of peroxide crosslinking (P-H saturated or unsaturated elastomer)[2]

The crosslinking reaction involves the homolytic decomposition of the peroxide to produce alkoxy radicals followed by hydrogen atom abstraction.
Studies with model compounds indicate that the hydrocarbon radicals predominantly undergo coupling rather than disproportionation. The coupling reaction forms crosslink between polymer chains. For polydiene elastomers experimental evidence indicates that the primary radical formed by peroxide decomposition abstracts a hydrogen atom from a carbon alpha to the double bond. In the case of natural rubber the methyl group is also reactive towards hydrogen atom abstraction.

1.1.2. Resin Crosslinking

Resin crosslinking was discovered around 1940's. It has been used for curing unsaturated rubbers. Resin curing systems are extensively used with butyl rubber for high temperature applications. Resin cures are slower than accelerated sulphur cures and high temperatures are required, and they can be activated only by zinc oxide and halogen atoms. The resin has got adhering capacity. Low molecular weight resin molecules diffuse into rubber and thereby stiffen the rubber.

The phenol-resin crosslinking of butyl rubber is accelerated by adding benzocarbonium ions to the double bond, forming a cyclic coumarone structure or a non-cyclic compound as illustrated in the Scheme 1.2. Crosslinking is considered to proceed via a mechanism such that a coumarone ring is produced by a Diels-Alder (4+2) cyclo-addition reaction of quinomethine. Compared to butyl rubber the resin crosslinking rates of EPDM and nitrile rubber are low. Volintu et al. [5] have reported the crosslinking of nitrile rubber with p-octyl phenol formaldehyde resin.
1.1.3. Silane Crosslinking

This type of crosslinking is also called moisture crosslinking. Alkoxy silane compounds are used as crosslinking agents together with water. The silanes carry functional groups, which are likely to react with rubbers. The moisture crosslinking of polyethylene using vinyl silane is shown in Scheme 1.3. The crosslinking reaction includes two steps; (1) the reaction of a silane compound with a polymer (grafting) and (2) the condensation of the silanol groups produced by hydrolysis of the alkoxy silyl groups. This process was used for EPR for the cable industry [6]. The major advantage of this type of cure is the applicability at relatively low temperature.
1.1.4. **Metal Oxide Crosslinking**

Chloroprene rubbers are generally vulcanised by the action of metal oxides [7,8]. The primary crosslinking agent is zinc oxide, which is used along with magnesium oxide. Lead oxides are sometime used when low water absorption is required. The reaction is thought to involve the vinyl group of the elastomer, which is the result of 1, 2 polymerisation. Two routes have been proposed for the curing. One requires the incorporation of zinc atoms into the crosslink [Scheme 1.4]; the other leads to ether crosslinks [Scheme 1.5].
Scheme 1.4. Mechanism of crosslinking in 1,2-poly chloroprene involving incorporation of Zn atom [7]

Scheme 1.5. Mechanism showing crosslinking in 1,2-poly chloroprene through the formation of ether crosslinks [8]
1.1.5. **Radiation Induced Crosslinking**

The most recent type of crosslinking is the radiation-induced crosslinking. This includes electron beam crosslinking, photo-crosslinking, microwave crosslinking, ultrasonic crosslinking etc. Radiation induced crosslinking is a physically induced chemical reaction, which is easier and preferable for continuous curing technologies, and thus it has some potential for the future. The radiation dose required for rubber differs. Radiation crosslinking of different rubbers are reported [9-11]. Upon irradiation free radicals are formed in rubber molecules. The free radicals can combine to form crosslinks as in the case with peroxide crosslinking. In radiation crosslinking of rubbers, kneaded rubber is placed in an aluminium die and is pressed at 100-200°C for 5-10 minutes. It is then allowed to cool under pressure and then exposed to radiation. The use of sensitisers can reduce the required dose and radiation time. Halogen compounds, nitrous oxide, sulphur monochloride and bases like amine, ammonia etc are used as sensitisers [12]. Radiation vulcanisation for NR latex, SBR and functional monomers have been reported [13].

1.1.6. **High Temperature Crosslinking**

This type of crosslinking is also called high velocity crosslinking and is carried out over a temperature range of 170-230°C. However it is often associated with reversion. Chen and coworkers [14] have shown that the phenomenon of reversion seems to appear when two competing reactions occur during vulcanisation. These two reactions are crosslinking and desulphuration. Morrison and Porter [15] confirmed that the observed reduction in vulcanisate properties is caused by two reactions proceeding in parallel, i.e. desulphuration and decomposition. Loo [16] has demonstrated that as the cure temperature rises, the
crosslink density drops and the degree of reversion increases. A constant level of crosslinking is observed beyond the optimum cure time at temperatures above 160°C. Temperature is thus a major factor than the duration of vulcanisation in determining the degree of crosslinking. Loss of properties at elevated temperatures could be avoided by two ways (1) optimisation of the accelerator/sulphur ratio and (2) use of an accelerator, which is less sensitive to increased temperatures.

1.1.7. Dynamic Vulcanisation

Dynamic vulcanisation is the process of vulcanising the elastomer during the melt-mixing process, with a non-vulcanisable molten thermoplastic. One of the most interesting applications of accelerated sulphur vulcanisation is in the preparation of thermoplastic elastomers by dynamic vulcanisation.

In this process, small rubber droplets are vulcanised to give vulcanised rubber particles with stable domain morphology which are then dispersed in the molten thermoplastic polymer to allow the blend to be fabricated into finished products in thermoplastic processing equipment. The diameters of the elastomer particles are reported to be in the 1-2 µm range. Various blends of EPDM with polypropylene were dynamically vulcanised with accelerated vulcanising systems consisting of sulphur, zinc oxide, stearic acid, tetramethyl thiuram disulphide and benzothiazyl disulphide [17]. Peroxides are also used for dynamic vulcanisation.

Recently, new vulcanising agents were introduced for dynamic crosslinking of elastomer blends [18]. They were found to be efficient in crosslinking and impart good mechanical properties to the resulting vulcanisates.
1.1.8. Sulphur Vulcanisation

Rubber vulcanisation by sulphur, without any accelerators takes several hours and is no longer of commercial importance. With the use of accelerators, optimum curing can now be achieved in periods as short as 2-5 minutes. Accelerated sulphur vulcanisation is suitable not only for natural rubber (NR) and its synthetic counterpart isoprene rubber (IR) but also for other synthetic rubbers such as polybutadiene rubber (BR), styrene butadiene rubber (SBR), nitrile rubber (NBR), butyl rubber (IIR) and ethylene-propylene-diene rubber (EPDM). Sulphur vulcanisation can be divided into two categories; unaccelerated and accelerated sulphur vulcanisation. Unaccelerated formulations typically consist of sulphur, zinc oxide and a fatty acid while accelerated formulations include an accelerator in the system. A sub category of accelerated sulphur vulcanisation is sulphur free systems, which are also referred to as sulphur donor systems. In these systems the sulphur needed for network formation is supplied by the accelerator, which functions both as an accelerator and sulphur donor. It should be noted that while un-accelerated sulphur systems are no longer of commercial significance, they are of interest as a starting point to the understanding of accelerated sulphur vulcanisation systems.

1.2. Unaccelerated Sulphur Vulcanisation

Unaccelerated sulphur vulcanisation, which is also referred to as ‘sulphur only’ vulcanisation is the oldest form of vulcanisation practices. Sulphur only vulcanisation chemistry involves many reactions that either do not occur or, to much lesser extent in accelerated systems. These reactions range from double bond migration, isomerisation and saturation to chain cleavage, cyclisation and formation of vicinal crosslinks [19,20]. Information
about sulphur only vulcanisation has been derived from model compound reactions and subsequent analysis of these materials. Shelton and Mc Donnel [21] used radical scavengers to evaluate vulcanisation mechanisms. From their studies they concluded that unaccelerated sulphur vulcanisation is a polar process. Another approach, which was used by Blokh [22] involved electron paramagnetic resonance studies. Based on the absence of a radical signal in the EPR studies, Blokh also concluded that unaccelerated sulphur vulcanisation proceeds via polar mechanism.

A major cause of disagreement on the mechanism of unaccelerated sulphur vulcanisation arises from the possible reactions of elemental sulphur. The S₈ ring is capable of undergoing homolytic (radical) and heterolytic (polar) ring opening reactions. The mechanism by which the vulcanisation occurs is still open for debate. The free radical sulphurisation tells the formation of sulphur radicals via homolytic scission of the octet sulphur ring as shown in Scheme 1.6. The sulphur radical abstracts a proton from the rubber to form a carbon radical on the elastomer. The elastomer radical opens the S₈ ring to form a rubber bound sulphur radical capable of forming crosslink structures. The polar mechanism is given in Scheme 1.7. The key step in the polar mechanism is the formation of the three- membered sulphur-carbon charged ring. A major source for the uncertainty has arisen from the intractable nature of the cured vulcanisate. Cured elastomers are insoluble; this eliminates most analytical techniques for examining polymeric structures. To avoid these problems several methods have been used; including model compound [23-25], electron spin resonance (ESR) [26], chemical probes [27,28], radical scavengers [21], solid state C¹³ NMR [29-34] and analysis of the extra net work materials [35].
Scheme 1.6. Proposed radical mechanism for unaccelerated sulphur vulcanisation [36]
The chemical probe work has allowed characterisation and quantification of the number of mono, di and poly sulphidic crosslinks. The model compound work has been useful in providing information for mechanistic studies by allowing comparison of products predicted by a mechanism to the products obtained from model compound work [37].

Electron spin resonance and radical scavenger work have been used to examine whether radical processes are active during vulcanisation with various formulations and elastomers. Solid-state NMR work has been used to elucidate the products of vulcanisation. Analysis of extra network materials has provided insights into the nature of the vulcanisation chemistry by analysis of content of various intermediates as cure progresses [38].

Scheme 1.7. Proposed polar mechanism for unaccelerated sulphur vulcanisation [36]
1.3. **Accelerators**

Substances that are added in small amounts during compounding to accelerate the vulcanisation reaction and to improve the physical and service properties of the finished products are called accelerators. These substances can reduce the cure time from days or hours to minutes or seconds at the vulcanisation temperature. The decrease in vulcanisation time is of tremendous economic importance because of increased turnover and consequent reduction in cost of production. Further, the amount of sulphur required can be reduced considerably in presence of an accelerator. Generally 0.1 to 3 phr is sufficient to give a vulcanisate of desired properties.

The first accelerators were inorganic compounds. Among the basic salts and metals oxides, which are or have been widely used as accelerators, litharge, lime magnesium oxide and zinc oxide are the most important ones. Organic vulcanisation accelerators were first utilised in the rubber industry in the beginning of the 20th century [39-45]. Oenslager [40] in 1906 introduced the organic bases aniline and thiocarbanilide as accelerators in rubber compounds to improve the quality of low grade rubber and to accelerate the rate of vulcanisation. Thus organic bases were the first vulcanisation accelerators of rubber [46-48]. Other accelerators such as diphenyl guanidine (DPG) diorthotolyl guanidine [49-50] (DOTG) and hexamethylene tetramine (HEXA) came in to use around 1910 and were a great relief for the people in the rubber industry because of their relative non-toxic character compared to the former ones.

Dithiocarbamates and xanthates were widely used as accelerators. Because of their instability, fast reactivity and poor processing safety they are generally used in low temperature processing and curing and in accelerator
combinations. Sebrell et al. [51-53] and Bruni et al. [54] discovered independently that 2-mercapto benzothiazole, its homologues, its disulphides [55, 56] and its metal salts are very effective accelerators, which yields vulcanisates of improved physical properties. 2, 2’ dithiobenzothiazole (MBTS) was developed to give greater scorch safety at the use of fine furnace blacks. Delayed action accelerators like sulphenamide type (eg. Benzothiazyl derivative of sulphenamide) were developed for long processing safety and satisfactory cure rates. Attempts to modify the extraordinary fast ammonium dithiocarbamates resulted in the zinc dialkyl dithiocarbamates. Further efforts to substitute the mercaptan sulphur in dithiocarbamate resulted in tetra alkyl thiuram disulphides like tetra methyl thiuram disulphide (TMTD), tetra methyl thiuram mono sulphides (TMTM) and thiuram tetra disulphides [57-59]. They are used as ultra accelerators and vulcanising agent itself. All of these products are currently used in a large scale as accelerators. Thus the discovery of various types of accelerators which differ in their effects on the rate of scorching, ageing etc. of rubber compounds and on the structure of the resultant vulcanisates which determines the ultimate property have revolutionised the rubber industry. Based on the nature of curing and chemical nature, accelerators are classified into several groups. The generalised classification is shown in Table 1.2.

1.4. Role of Activators

The rate of vulcanisation can be increased by the addition of metallic oxides, which function as activators. Activators enable an accelerator to exercise its maximum effect. Organic accelerators usually require the presence of organic acid or inorganic activators. ZnO is probably the most important inorganic activator but magnesium and lead oxides also find use. Fatty acids (eg. stearic acid) are used as coactivators. Polyalcohols (eg. ethylene glycol) and amino alcohols are used to counteract the retarding effect of white fillers.
Table 1.2. Principal classes of accelerators used in the sulphur vulcanisation of elastomers [59]

<table>
<thead>
<tr>
<th>Compound</th>
<th>Property</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Thiazoles</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-mercaptobenzothiazole (MBT)</td>
<td>Semi-ultra accelerator, scorhy</td>
<td><img src="image" alt="2-mercaptobenzothiazole" /></td>
</tr>
<tr>
<td>2-2' dithiobenzothiazole (MBTS)</td>
<td>Delayed action semi ultra accelerator</td>
<td><img src="image" alt="2-2' dithiobenzothiazole" /></td>
</tr>
<tr>
<td><strong>Sulphenamides</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-cyclohexyl benzothiazole 2- sulphenamide (CBS)</td>
<td>Semi ultra accelerator, delayed action</td>
<td><img src="image" alt="N-cyclohexyl benzothiazole 2-sulphenamide" /></td>
</tr>
<tr>
<td>N-t-butyl benzothiazole 2-sulphenamide (TBBS)</td>
<td>Delayed action</td>
<td><img src="image" alt="N-t-butyl benzothiazole 2-sulphenamide" /></td>
</tr>
<tr>
<td>2-morpholinothio benzothiazole (MBS)</td>
<td>Delayed action</td>
<td><img src="image" alt="2-morpholinothio benzothiazole" /></td>
</tr>
<tr>
<td>N-dicyclohexyl benzothiazole 2-sulphenamide (DCBS)</td>
<td>Delayed action, fast accelerator</td>
<td><img src="image" alt="N-dicyclohexyl benzothiazole 2-sulphenamide" /></td>
</tr>
<tr>
<td><strong>Thiurams</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tetramethyl thiuram monosulphide (TMTM)</td>
<td>Ultra accelerator</td>
<td><img src="image" alt="Tetramethyl thiuram monosulphide" /></td>
</tr>
<tr>
<td>Compound</td>
<td>Type</td>
<td>Formula</td>
</tr>
<tr>
<td>----------------------------------</td>
<td>----------------------------------------------------------------------</td>
<td>------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Tetramethyl thiuram disulphide</td>
<td>Ultra accelerator, vulcanising agent</td>
<td><img src="" alt="Structure" /></td>
</tr>
<tr>
<td>Zinc diethyl dithiocarbamate (ZDEC)</td>
<td>Ultra accelerator</td>
<td><img src="" alt="Structure" /></td>
</tr>
<tr>
<td>Zinc isopropyl xanthate (ZIX)</td>
<td>Ultra accelerator, low temperature curing</td>
<td><img src="" alt="Structure" /></td>
</tr>
<tr>
<td>Sodium isopropyl xanthate (SIX)</td>
<td>Water soluble ultra accelerator for latex work</td>
<td><img src="" alt="Structure" /></td>
</tr>
<tr>
<td>Diphenyl guanidine</td>
<td>Medium accelerator used along with other accelerators</td>
<td><img src="" alt="Structure" /></td>
</tr>
<tr>
<td>Di-orthotolyl guanidine</td>
<td>Medium accelerator</td>
<td><img src="" alt="Structure" /></td>
</tr>
</tbody>
</table>
A combination of ZnO and a long chain fatty acid like stearic acid, which is used as a co-activator form an ideal activator system [60]. ZnO can also function as a filler to reduce cost and it was found to have reinforcing effect and was later found to reduce the curing time [61]. The function of fatty acid activators such as stearic acid, is to solubilise the zinc oxide, a secondary effect is an increase in the amount of zinc sulphide produced. The zinc salts of fatty acids, which are a type of surfactant, also solubilise insoluble accelerators to form the actual catalyst. A general scheme of accelerated sulphur vulcanisation that demonstrates the role of zinc oxide, in conjunction with fatty acids is shown in Scheme 1.8.[62]. Duchacek [63] noted that the increasing the zinc oxide concentration increased the rate of extent of crosslinking up to a certain zinc oxide concentration; this concentration is believed to be the minimum level of zinc oxide needed to completely convert the accelerator to the zinc-accelerator-sulphur complex. He also noted that the optimum zinc oxide content to minimise reversion was slightly greater than this minimum. Coran [64] also noted that the induction time had a dependence on the zinc oxide concentration in excess of that required for formation of the accelerator-zinc complex. This suggests that zinc exerts an influence beyond inclusion in the accelerator complexes.

Physical properties of vulcanisates depend on the type of crosslink and the extent to which they are formed. When some of the properties depend fully on degree of crosslinking some depend partly on crosslinking. A brief outline of properties and their dependence on the degree of crosslinking is given in Table 1.3.
Recently research work on safe accelerators has gained a lot of interest [65-68]. Some of the accelerators are reported to be unsafe due to the formation of carcinogenic compounds such as nitrosamines. It is reported that accelerators derived from secondary amines are usually evolving nitrosamines [65]. Avoidance of unfavorable conditions, elimination of secondary amine containing accelerators and elimination of formed nitrosamines are the various possibilities of reducing nitrosamine formation [67]. Nitrosamine can be generated during the processing stage of rubber. The faster the amine is produced from cure or the earlier it is produced in the process cycle, the
greater the opportunity for nitrosamine formation [68]. This makes the synthesis of safe accelerators a field of great interest.

**Table 1.3.** Influence of degree of crosslinking on physical properties [15]

<table>
<thead>
<tr>
<th>Property</th>
<th>Change with increase in degree of crosslinking</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Properties dependent only on degree of crosslinking</em></td>
<td></td>
</tr>
<tr>
<td>Stiffness</td>
<td>Increase</td>
</tr>
<tr>
<td>Hardness</td>
<td>Increase</td>
</tr>
<tr>
<td><em>Properties partly dependent on degree of crosslinking</em></td>
<td></td>
</tr>
<tr>
<td>Breaking elongation</td>
<td>Decrease</td>
</tr>
<tr>
<td>Resilience</td>
<td>Increase</td>
</tr>
<tr>
<td>Heat build up</td>
<td>Decrease</td>
</tr>
<tr>
<td>Solvent swelling</td>
<td>Decrease</td>
</tr>
<tr>
<td>Creep, Stress relaxation</td>
<td>Decrease</td>
</tr>
<tr>
<td>Set</td>
<td>Decrease</td>
</tr>
<tr>
<td>Abrasion resistance</td>
<td>Increase</td>
</tr>
<tr>
<td>Fatigue cracking</td>
<td>Increase</td>
</tr>
<tr>
<td>Low temperature crystallisation</td>
<td>Decrease in rate</td>
</tr>
<tr>
<td>Tensile strength/ tear strength</td>
<td>Increase then decrease</td>
</tr>
</tbody>
</table>
1.5. Sulphur Donor Systems

Apart from using free sulphur as a crosslinking agent other materials which could donate sulphur to the system are used for curing. Tetramethyl thiuram disulphide is found to act as a crosslinking agent in the absence of sulphur. It is not known whether the reaction involves the intermediate formation of elemental sulphur or whether the disulphide itself is the active agent. It appears that under cure conditions and in the presence of zinc oxide, two thirds of the thiuram disulphide invariably appears eventually as the zinc dithiocarbamate.

The network structures of sulphurless systems are similar to those obtained from accelerated sulphur systems discussed in the preceding section. It has been suggested that thiuram disulphides function during cure by decomposition to yield active sulphur and ZDC, which together constitute an accelerated sulphur system. In the past the opinion has been that TMTD vulcanises via the intermediate formation of TMTM and active sulphur [69] and later the reverse has been suggested [70] i.e., TMTM vulcanises in the presence of sulphur via the intermediate formation of TMTD.

Another approach for sulphur donor vulcanisation was the use of model compounds. This study by Gregg and Lattimer [23] used the cyclic tetramer shown in Figure 1.1 to model cis-polybutadiene. Their conclusions were similar to previous findings. They elaborated about an ionic mechanism involved in the process.
Another technique for analysis of sulphurless vulcanisation has been the use of DSC coupled with chemical probe/equilibrium swelling [71]. The results of this work indicated that zinc oxide dramatically increases the efficiency of vulcanisation, but is not required for sulphurisation. The advantage of sulphurless cure using TMTD is that the vulcanisates have low sulphur content and excellent ageing properties. Further more the curing is more efficient than the normal efficient vulcanisation (EV).

### 1.6. Influence of Fillers

Fillers of many types are added to rubber compounds to extend the range of physical properties, to reduce the cost of the compound, to modify the processing properties and to influence the chemical resistance of the
compound. In addition, fillers can pigment a compound, impart conductivity to it and influence its ageing characteristics. A reinforcing filler can be defined as a filler that improves modulus, tensile strength, tear strength and abrasion resistance. The effect of a particulate filler on rubber depends on factors like the particle size, the chemical nature of the particle surface, structure of the particles and porosity. The fillers are primarily classified as carbon blacks and non-black fillers. Silicas are generally more porous than carbon black, and thus silica gives higher viscosity compounds at equal volume loadings.

Carbon black is of the following grades depending on the manufacturing process. Channel blacks are manufactured by burning natural gas in small flames and particles get deposited on cooled channels. Furnace blacks are obtained by burnings natural gas or oil in a controlled supply of air in furnaces. Lamp black and thermal black are obtained by burning oil or natural gas. Acetylene black is produced from acetylene gas by exothermic reactions. Furnace blacks are more reinforcing in NR as compared to all other grades. This is mainly due to its fine particle size and high structure. The finer the particle size the more will be the reinforcing properties. Silicas are reinforcing white fillers that can be produced by two processes, precipitation and combustion methods. The precipitation process yields filler with a particle size of 10 – 40 nm. Silica can give tensile and tear strength equivalent to those obtainable from carbon black, but the resilience, set and abrasion resistance are generally inferior. Hot tear strength is superior to that obtainable with carbon black. Diethylene glycol, triethanolamine or silane coupling agents are required to eliminate the cure retarding effect of silica fillers. White clay based fillers are useful compounding ingredients in rubber. They can be divided into hard and soft. The hard clays can be classed as semi-reinforcing fillers due to their smaller size. Contrary to most types of synthetic rubbers,
natural rubber (NR) does not require the use of fillers to obtain high tensile strength by virtue of its higher stress crystallisation. However, the use of fillers is necessary in order to achieve the level and range of properties that are required for technical reasons. Reinforcing fillers enhance the already high tensile properties of gum natural rubber and they improve in particular the abrasion and tear resistance. It must be stated that hardly any filler will enhance all properties to the same optimal degree. The reinforcing effect of active filler as well as the dosage required could be quite different for different elastomers. The amount and type of fillers required in different rubbers or their blends are also different. For example, the activity of fillers in SBR, BR and NBR is often quite more pronounced because of their lack of strain crystallisation than in NR and partially also in polychloroprene rubber (CR) [72]. The variation in the effectiveness of NR and synthetic rubbers with regard to fillers can be explained with the theory of over stressed molecules [73-74].

1.7. Antioxidants / Antiozonants

Elastomers undergo ageing and deterioration that are characteristic of their structure and the environment in which they are used. Major degradation of rubber is due to oxygen and ozone attack. It is therefore, necessary to incorporate antioxidants and antiozonants in rubber compounds. Antioxidants can be divided into staining and non-staining. Amines are usually staining in nature. Phenyl β naphthyl amine (PBN) is one of the commonly used antioxidants, but causes staining. So PBN can only be used in black or dark coloured compounds. Phenols are non-staining antioxidants. Styrenated phenols, though non-staining in character possess less antioxidant property than amines. Antiozonants are more relevant to diene rubbers and related
polymers having unsaturation. Wax and some p-phenylene diamine derivatives are also useful in this regard.

1.8. Binary Accelerator Systems

Unaccelerated or sulphur only vulcanisation while alleviating many of the disadvantages of uncrosslinked elastomers, does not provide an optimum product. Vulcanisation with sulphur but without accelerators is an extremely slow process. Relatively large amount of sulphur and long vulcanisation time are necessary and the vulcanisates are not of high quality. They have strong tendency to revert and their resistance to ageing is poor. A problem of sulphur blooming is also found to occur. Vulcanisation with sulphur alone is therefore of no technological importance. The yield of crosslinked polymer is low when sulphur is used alone, which may be due to the formation of multivalent polysulphidic bridges, cyclic sulphidic and vicinal bridge links. It is known that several reactions by different mechanisms (of a radical or ionic nature) may take place simultaneously or consecutively during vulcanisation. These reactions range from double bond migration, isomerisation, chain cleavage, cyclisation and formation of vicinal crosslinks. [75–82]. Several techniques including the use of radical scavengers and electron paramagnetic resonance (EPR) analysis have been used to study the reaction mechanism involved in sulphur only vulcanisation.

Rubber vulcanisation reaction can be effectively accelerated by the combined action of two or more accelerators. Mixed in the proper proportions, these accelerator combinations can lead to significant improvement in curing behaviour and mechanical properties and pre-vulcanisation can be prevented [83]. The binary systems are increasingly used because of several factors including a desire to optimise the end-use properties and better control of processing safety. Such systems generally possess an increased activity over
that obtained with the individual components. A binary accelerator system refers to the use of two accelerators in a given formulation. The accelerator present at a reasonably high level is called primary accelerator and that present in smaller amounts is called the secondary accelerator. The binary system usually gives a faster cure rate than either of the accelerators used alone due to synergistic effect. Some of the more widely used accelerators for binary systems are given in the work of Layer [84]. The synergistic behaviour of different binary systems has been studied by several authors [85–87]. Many amines such as diphenyl guanidine (DPG) are used in combination with other accelerators like MBT or sulphenamides to activate the vulcanisation reaction. Some other binary accelerator systems used in rubber consist of benzothiazole and thiocarbamate or benzothiazole and thiuram systems [88-89].

In spite of the wide practice of using binary systems, the mechanism of the joint action of the accelerators has not been well studied. There are many approaches to analyse the vulcanisation behaviour of binary accelerators. The method used by Layer to illustrate this effect is to measure mechanical or physical properties as a function of accelerator ratio. The results obtained in this method suggest the formation of specific complexes. Minotaya et al [90] and Aoe and Yokosima [91] explained the increase in activity arising from the use of two accelerators by the formation of a salt-like complex which is more active than either alone. Dogadkin and collaborators [92] investigated different combinations of most generally used accelerators and classified them into three groups.

1. Systems with synergistically active accelerators

2. Systems with a pair of accelerators in which the activity of the pair does not exceed the activity of the most active accelerator.

The active complex formed depends on the molar ratio of accelerators [93]. This does not explain all the facts exhibited by the combined accelerator systems.

The use of certain coactivators in delayed action sulphur vulcanisation had been reported [94]. Thiourea (TU) and its derivatives are popular in the mixed accelerator systems in rubber vulcanisation. Some compounds in this class are diphenyl thiourea, sym-di-o-tolyl thiourea, N, N’-dimethyl thiourea, N–butyl-thiourea, diethylene thiourea etc. Chloroprene rubber (CR) has been crosslinked on an industrial scale with TU systems. The reaction of thiourea in diene rubber is peculiar. For example, in NR the accelerator MBTS gives no crosslinking by itself, even if it is heavily dosed. If, however, substituted or un-substituted thiourea is used simultaneously very rapid vulcanisation is obtained at normal temperature [95]. The vulcanisates have reasonably high tensile strength and good resistance to ageing. Thiourea accelerates TMTD/ZnO vulcanisation [96]. In this case the trithiocarbamate formed is a source of thiuram polysulphides. In the initial steps of vulcanisation, characterised by an induction period and fast crosslinking, mainly ionic reactions take place. This is in accordance with theories of Bateman and Moore [75]. In the next steps, characterised by degradation and slow crosslinking, mainly radical reactions occur. Support for this view derives from the influence of thiourea which is known not only as secondary accelerator of thiuram vulcanisation but also as radical scavenger [97]. When thiourea is used alone, no trace of crosslinking is seen indicating that this is a perfect example of synergistic behaviour. A number of studies have been reported in the literature on the acceleration activity of thiourea and its
chemical reactions involved when a binary accelerator system is used in rubber vulcanisation vary with the systems used and the elastomers involved. The exact mechanism of the crosslinking processes is not still understood clearly. It has been proved that accelerators in which sulphur is covalently linked to another sulphur, carbon or nitrogen are of the delayed action type, displaying little activity around 100°C. This is due to the inherent stability of their sulphur bonds. Some accelerators among them are the disulphide (XSSX) and sulphenamide (XSNR₂) accelerators of the benzthiazyl series like MBTS and CBS, and the monosulphide (XSX) and disulphide (XSSX) accelerators of the dithiocarbamyl series. The acceleration characteristics of these sulphur-bearing accelerators depend partly on the nature of the group X and partly on the mode of attachment of the functional sulphur atom to other atomic groupings in the molecule.

According to Dogadkin and Shershnev [103] the differences in the points of view regarding the mechanism of vulcanisation are so much a matter of approach to the interpretation of experimental factors, as the fact that for such a complicated phenomenon as vulcanisation, it is improper to support a single mechanism. Even though the use of sulphur alone in rubber vulcanisation is typically ineffective requiring 45-55 sulphur atoms per crosslink and tends to produce a large proportion of intramolecular (cyclic) crosslinks, such ineffective crosslink structures are of interest in the understanding of complex nature of vulcanisation reactions. Spectroscopic studies of unaccelerated sulphur vulcanisation point to the formation of polysulphidic, monosulphidic and also cyclic sulphidic linkages [104].
The synergistic activity of two or more different accelerators arise from the interaction of the accelerators to form new intermediate compounds which again actively take part in the vulcanisation reaction leading to enhancement of crosslink density and the rate of vulcanisation reaction [105]. The majority of the studies on elastomeric vulcanisation have been focused on the sulphur crosslinking of natural rubber. Further investigations [106-119] with binary accelerator systems have provided more valuable information regarding the mechanism of their action.

A novel probable mechanism for the synergistic activity of o-p- and m-DTBs is given in scheme 1.9. MBS reacts with ZnO to form benzothiazyl zinc salt.

\[
m[X'\text{X}+\text{ZnO}] \rightarrow \frac{m}{2} \left[ (X')_2\text{Zn} + (X'O)_2\text{Zn} \right] \quad \text{(1.1)}
\]

where \(m > 2\) and

\[
X = \begin{array}{c}
\text{N} \\
\text{C} \\
\text{S}
\end{array} \quad X' = \begin{array}{c}
\text{N} \\
\text{O}
\end{array}
\]

Benzothiazyl Zinc salt reacts with elemental sulphur to form zinc per thio salt II.

\[
S_8 + (X')_2\text{Zn} \rightarrow XS_{\text{a}} \text{Zn} \quad \text{(1.2)}
\]
DTB reacts with MBS to form polysulphides III

\[ \text{III} \]

Compound III stabilises by proton shift to ZnO and simultaneous elimination of perthioanion IV

\[ \text{IV} \]

Trisulphide V (XS}_3X) can be formed by the reaction between perthioanion and MBS.

\[ \text{V} \]

Disulphide (VI) X SS X can be formed by the reaction between MBS and ZnO which is a slow process.

\[ \text{VI} \]
Participation of disulphides VI and trisulphides V in processes similar to equations 1.5, 1.6 and 1.7 lead to the formation of higher polysulphides.

In the presence of o-p and m-DTBs, SX' bond fission in MBS is accelerated, providing an easier and faster route for the formation of polysulphide XSmX.

The polysulphide XSmX and zinc perthio salt react with Rubber hydrocarbon RH to form a rubber bound intermediate RSmX

\[
\text{RH} + \text{XSS}_a \text{ZnS}_b \text{SX} \rightarrow \text{X S}_a \text{R} + \text{ZnS} + \text{HS}_b \text{X} \quad \text{......... (1.8a)}
\]

\[
\text{RH} + 2 \text{X Sm X} \xrightarrow{\text{ZnO}} \text{RSmX} + \text{ZnS} + \text{XS}_{m-1}^H \quad \text{.........(1.8b)}
\]

\[
\text{RH} + \text{RSmX} \xrightarrow{\text{ZnO}} \text{RS}_{m-1} \text{R} + \frac{1}{2} \left[ \text{Zn(SX)}_2 + \text{H}_2\text{O} \right] \quad \text{.......(1.8c)}
\]

Scheme 1.9. Reaction mechanism of DTB with MBS

1.9. Accelerated Sulphur Vulcanisation

By far the common vulcanisation systems used in industrial applications are the accelerated sulphur formulations. The accelerated sulphur systems can be classified into single and binary accelerator combinations. Almost all accelerators need metal oxides for the development of their full activity. Zinc oxide is being used as the best additive. The mechanism under which accelerated sulphur vulcanisation occurs is a function of the class of accelerators/activators. The proposed radical mechanism of accelerated sulphur vulcanisation is shown in Scheme 1.10. The intermediate cleaves to form persulphuryl radicals, which then abstract protons. The rubber radical reacts with another intermediate to form a rubber-bound intermediate. Two
rubber bound intermediates then form the actual cross-link. Maturity of the network occurs through sulphur exchange reactions. Isomerisation, which is widely observed in vulcanisation [75], occurs through alkyl radical.

\[
\begin{align*}
\text{XSSxZnSxSX} & \rightarrow \text{XSSx} + \text{XSxZn}\bullet \\
\text{XSSx} + \text{RH} & \rightarrow \text{XSSxH} + \text{R}\bullet \\
\text{R}\bullet + \text{XSSxZnSxSX} & \rightarrow \text{RSyX} + \text{XSx-y} \\
\text{RSxX} + \text{RsyX} & \rightarrow \text{RSxR} + \text{XSyX}
\end{align*}
\]

**Scheme 1.10.** Radical mechanism of accelerated sulphur vulcanisation [2]

As the rate of vulcanisation is directly related to productivity, it is desirable to increase the rate by raising temperature. However at higher temperature the effectiveness of sulphur cross-links is lower with a sacrifice of the physical properties caused by the dissociation of sulphur bonds and rubber chains. Thus the reactivity was controlled by additional amounts of sulphur and accelerator instead of raising temperature. The increase of sulphur addition leads to increase in crosslink density and the proportion of polysulphidic linkage, causing a decrease in the stability on ageing. With the increase of accelerators the effectiveness of sulphur vulcanisation having mono and disulphidic linkages is improved to give stability on ageing [116]. The sulphur level determines the overall extension of sulphurisation, while the accelerator concentration determines the efficiency of the formulation [36].

Various structures formed in sulphur vulcanised natural rubber is shown in Scheme 1.11.
Layer [117] used the unique approach of ‘vulcanisate recurring’ to probe the role of sulphur and accelerators in the curing and reversion process. The author has concluded that sulphur determines the overall amount of reaction, but the accelerator determines the length of sulphur chains. Layer and P. J. Nieuwenhuizen et al proposed that the key step in the curing reaction was the sulphur exchange reaction [117,118].

Model compound vulcanisation (MCV) is the vulcanisation of a low molecular weight model for the rubber polymer. It is a prime research technique applied to gain information about the chemistry of vulcanisation. The compound selected for MCV should contain at least one allylic hydrogen, since crosslink formation involves the substitution of allylic hydrogen for a sulphur link [119].
The objective of an MCV study is to obtain information regarding the chemistry of the repeating rubber unit, to elucidate the structure of the crosslinked products that are produced during vulcanisation and to study the reactions of curatives in a rubber like environment. Ultimately this knowledge would furnish information about the mechanism of the vulcanisation reactions [39,120,121].

![Figure 1.2. Typical rheograph showing different stages on curing](image)

A typical cure curve obtained from rheometer is shown in the Figure 1.2. The initial portion of the curve is called the induction or scorch period where much of the accelerator chemistry involves. As time goes on torque increases and attains a maximum value. This point indicates the maximum torque. The time required to attain 90% of the maximum torque is termed as the optimum cure time ($T_{90}$) where as the time required to attain 10% of the maximum torque is termed as the scorch time ($T_{10}$). After attaining a maximum torque the crosslinks formed will be shortened or destroyed. This behaviour is different for different compounds and the type of curing.
Depending on the accelerator/sulphur ratio desulphuration or decomposition may occur. An outline of the mechanism is shown in Scheme 1.12. Depending on the type and nature of vulcanisation the cure curves exhibit different nature. After attaining the maximum torque, it may increase further (marching), or decrease (reversion), or levels off (Figure 1.3).

The choice of the accelerator in the process of sulphur vulcanisation determines the kind of network structure and consequently, leads to the specific material properties [122,123]. The chosen accelerator affects the cure rate and scorch safety, as well as the numerosity and the average length of the formed crosslinks. Both the number and the length of the crosslinks have an influence on physical properties of rubber. Monosulphidic crosslinks are regarded as being unable to exchange,
rearrange or break to relieve mechanical stresses without cleaving main chains. Polysulphidic crosslinks on the other hand are able to rearrange under stress, through breaking and reforming and this is partly associated with high mechanical strength. Also, changes during service are determined in considerable measure by the strength of the crosslinks. Shorter mono and disulphide crosslinks contain thermally stronger C-S-C and C-S-S-C bonds, which are associated with superior thermal and oxidative stabilities. Studies have been undertaken on network characterisation of natural rubber vulcanisates [124].

Based on the amount of accelerator and sulphur present, the vulcanisation systems are classified into conventional (CV), semi-efficient (semi-EV) and efficient (EV). The amount of accelerator and sulphur present in these systems are given in Table 1.4.

**Table 1.4.** Composition of conventional, semi EV and EV cure systems [88]

<table>
<thead>
<tr>
<th>Type of system</th>
<th>Sulphur (phr)</th>
<th>Accelerator (phr)</th>
<th>A/S ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional</td>
<td>2.0-3.5</td>
<td>1.2--0.4</td>
<td>0.1-0.6</td>
</tr>
<tr>
<td>Semi EV</td>
<td>1.0-1.7</td>
<td>2.5-1.2</td>
<td>0.7-2.5</td>
</tr>
<tr>
<td>EV</td>
<td>0.4-0.8</td>
<td>5.0-2.0</td>
<td>2.5-12</td>
</tr>
</tbody>
</table>
Scheme 1.12. Generalised mechanism of vulcanisation [17]
The properties of the resultant vulcanisates are given in Table 1.6. As seen from the mechanism of vulcanisation given by earlier researchers [3,125] the active sulphurating agent is the zinc perthio mercaptide complex. The concentration of this complex determines the type of crosslinks formed. As the CV system has got greater amount of sulphur compared to the accelerator the possibility of forming more polysulphidic linkages is higher for CV system. As the concentration of accelerator increases two reactions viz., desulphuration or decomposition may occur. Desulphuration results in mono and disulphidic linkages while decomposition leads to cyclic sulphides and conjugated dienes etc. When the temperature is increased the polysulphidic linkages break into mono and disulphidic linkages. This explains the reversion shown at higher temperatures. This leads to low strength and modulus. Properties like compression set and thermal stability are better for EV systems. This is primarily due to the lower amount of polysulphidic linkage in the EV system.

The general nature and amount of crosslinks present in an efficient vulcanising system and conventional system is given in Figures 1.4 and 1.5 respectively. It is seen that the amount of monosulphidic linkages is a maximum in the efficient system and it increases initially and decreases with cure time. At the same time amount of polysulphidic and disulphidic linkages decreases with time. The final network formed after the desulphuration and decomposition reactions will be highly crosslinked with mainly monosulphidic bonds and there will be relatively few modifications of the cyclic sulphide or conjugated triene type [3]. Such a network is termed efficiently crosslinked.
Figure 1.4. Features of NR vulcanisate produced by an efficient crosslinking system [3].

Figure 1.5. Features of NR vulcanisate produced by a conventional crosslinking system [3].

On the other hand desulphuration process proceeds slowly as in the case of the compound depicted in Figure 1.5. Here the amount of polysulphidic
linkages is higher. 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 polysulphidic and hence will be liable to further decomposition. These networks are said to be inefficiently crosslinked.

**Table 1.5.** Vulcanisates structure and properties of the different sulphur curing systems [123].

<table>
<thead>
<tr>
<th>Properties</th>
<th>CV</th>
<th>Semi EV</th>
<th>EV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly and disulphidic crosslinks (%)</td>
<td>95</td>
<td>50</td>
<td>20</td>
</tr>
<tr>
<td>Monosulphidic crosslinks (%)</td>
<td>5</td>
<td>50</td>
<td>80</td>
</tr>
<tr>
<td>Cyclic sulphide concentration</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Low temperature crystallisation resistance</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heat ageing resistance</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reversion resistance</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Compression set 22 hours at 70 °C (%)</td>
<td>30</td>
<td>20</td>
<td>10</td>
</tr>
</tbody>
</table>

Now-a-days binary accelerators are widely used in industry. They are becoming increasingly popular due to the fact that such mixed systems (1) permit Vulcanisation to be carried out at lower temperature in lesser time (2) produce vulcanisate with superior physical and mechanical properties compared to those of a stock cured with a single accelerator.
Though a great deal of work has been done on elucidating the mechanism of vulcanisation by single accelerators, little attention has been paid so far to the chemistry of vulcanisation with binary accelerator systems. Dogadkin and co-workers [125] and Skinner and Watson [126, 127] investigated a number of popular accelerator combinations and found mutual activation with many of them.

Depending on the experimental results obtained in the vulcanisation with various combinations of most generally used accelerators, Dogadkin and co-workers [128] classified the various binary accelerators into the following three different groups.

1. **Systems with synergistically active accelerators**

   This group consists of disulphides or mercaptans with nitrogen containing organic bases and disulphides eg. MBTS TMTD/MBT with MBS/CBS etc.

2. **Systems in which the mutual activity of the pair does not exceed the activity of the most active accelerator used and**

   This group consists of sulphenamides with nitrogen containing organic bases

3. **Systems with an additive action of the accelerators.**

   They include sulphenamides in combination with TMTD and those containing combination of accelerators belonging to the same class.

   Based on these observations Dogadkin and coworkers [128] suggested that in the initial stage of vulcanisation, the accelerators interact with one another to form an active complex, which then disintegrate with the formation
of active free radicals responsible for initiating the interaction of rubber with sulphur. Though the above classification of binary accelerator systems is very useful, the mechanism suggested cannot explain all the facts exhibited by the mixed accelerator systems. The schematic representation of the action of binary accelerator proposed by Dogadkin is shown in Scheme 1.13. But it could not fully explain all the observed properties shown by binary accelerator vulcanisation. Studies are going on in search of more details about the mechanism of acceleration performed by binary systems.

Scheme 1.13. Schematic representation of the action of binary accelerators

Thiourea and its derivatives have been used as accelerators in dry rubber and lattices. In the works of Aprem et al. [111] dithiobiurets were synthesised and compared. It was found that cure reaction becomes faster upon the use of DTB. DTB could be effectively used as a binary accelerator with sulphenamides. A mechanism has been proposed for the cure acceleration by DTB based on its nucleophilic nature. The optimum concentration of DTB is found to be between 0.5-1.0phr in the EV system and 0.4-0.6phr in the CV system for NR vulcanisation. Double networks prepared with DTB show an increased strength and modulus. Susamma et al. [66] have used amidino thiourea as a binary accelerator. In these studies attempts have been made to optimise the amount of the new accelerator based on the physical properties of the resulting vulcanisates. The nucleophilic nature of thiourea and its derivatives is suggested as responsible for the cure activating nature of those binary accelerators. Binary accelerators and fillers are
expected to improve the cure rate by improving the crosslinking in rubber[129-134]. This could be responsible for the improvement in mechanical properties.

1.10. Concept of Double Networks

Natural rubber (NR) is essentially composed of cis-1,4 polyisoprene whose stereoregularity allows its crystallisation at low temperature. One of the common ways to achieve high performance rubber is vulcanisation, by which the linear macromolecules are crosslinked into three-dimensional networks [135]. Various types of chemical modifications have been performed to increase the useful properties of the NR [136]. An important modification to NR is preparation of double networked natural rubber. Double network elastomers are very recent form of rubber modifications prepared from previously cross linked natural rubber or styrene-butadiene copolymer by curing under strain. This new technology imparts superior mechanical and failure properties to elastomers [137-138]. The “double network structure” can be readily implemented in conventional rubbers using existing processing techniques. Initial isotropic crosslinking will be followed with a deformation induced by simple tension under which the second stage curing is done. The ratio of rubber length after the double network formation and initial-stage curing is referred to as residual strain. Infact, a double network rubber sample owns two different states of strain in the relaxed situation. A given residual strain can be realised through different combinations of strain and crosslinking proportions, between the two networks. Double network in rubber is a relatively new concept. It is of great significance in view of the engineering applications of rubber such as automotive suspensions, engine mounts, building mounts etc. Therefore a better understanding of this new concept in elastomers is highly important in order to achieve improvement in
product performance. Double networking in rubbers offer a method for obtaining superior mechanical properties, in that they may allow circumvention of the usual compromise between stiffness and strength.

Many studies have been carried out on double networks [139-141], including their use in evaluating the contribution of trapped entanglements to rubber elasticity. The modulus and strength of materials with flexible chain polymers can be increased by orientation and crystallisation of the polymer chains. In plastics and fibers, molecular chain orientation is maintained after processing as the chains are frozen by glassy state or crystallisation. On the other hand, in rubbers, orientation produced during simple processing will decay after processing.

Double network rubber is prepared by the further crosslinking of an already crosslinked rubber in a stretch - deformed state. The deformation employed is simple tension, which results in a rubber with final length greater than the initial, isotropic crosslinking. The ratio of these lengths is referred to as residual strain. A desired residual strain can be achieved with different combinations of strain and crosslinking apportionment between the two networks.

Double networks contain, interpenetrating segments belonging to both networks. This orientation gives rise to enhanced anisotropy [139-141] to the rubber. The modulus of a double network rubber will differ from the modulus of the corresponding isotropic elastomer. The equilibrium modulus is high at higher residual strains. Mechanical and optical properties of double network rubbers have been studied by Mott and Roland [142]. The properties of an elastomeric network depend not only on the density of junctions but also on the distribution and
orientation of the chains when the junctions are formed. Double networks can also arise spontaneously through chain scission [143], strain-induced crystallisation [144-146] or by the presence of reinforcing fillers. The strain-induced crystallisation of natural rubber imparts superior strength to it. In this context, it is desirable to explore the conditions, which would enrich the mechanical and swelling properties of the sample.

1.11. Characterization of networks

Network structure of ordinary rubber vulcanisates is too complex to be elucidated. The network structure of a vulcanised rubber could not be related directly to its macroscopic properties. Different methods are available for characterisation of rubber networks. The important methods are (1) swelling method (2) freezing point depression method (3) dynamic mechanical analysis (4) stress-strain method and (5) NMR measurements.

Swelling of vulcanisates in solvents has been proved to be an effective method to determine the chemical crosslink density. Flory-Rehner theory [147] is used for the determination of molecular weight between crosslinks. Flory Rehner equation can be applied to the results of swelling of rubber in suitable solvents.

\[-\ln(1-V_r) + V_r + \chi V_r^{\frac{3}{2}} = \left[\frac{\rho V_s (V_r)^{1/3}}{M_c}\right]\]  

where $V_r$ is the equilibrium volume fraction of rubber in swollen gel, $\rho$ the density of rubber, $\chi$ an interaction constant characteristic of rubber and swelling liquid and $V_s$ the molar volume of the swelling liquid [148]. Treatment of the vulcanisates with different thiols [149] cleaves the mono, di and polysulphidic crosslinks preferentially. This helps to find the relative proportion of crosslinks. It has long been known that an anomalous freezing
point depression of the swelling solvent in swollen gels was observed and that the magnitude of the depression was closely related to the degree of crosslinking and or the structure of swollen gels [150]. The stress-strain behaviour of rubber like networks are influenced both by contributions of constraints caused by the uncrossability of the network chains. Using theoretical results based on the tube approach to polymer melts and networks [151], a well-founded separation of crosslink and constraint contributions to the stress-strain behaviour can be achieved and a reliable method for the evaluation of the network parameters can be developed. The Mooney equation [152] is used for calculating the crosslink density from stress-strain data. It was then modified by Rivlin and Saunders [153].

\[
\sigma = \frac{\rho R T A_0}{M_c} \left\{ \frac{1}{\lambda} - \frac{1}{\lambda^2} \right\} \quad \text{(1.10)}
\]

where 'σ' is the force to extend a sample of cross-sectional area 'A₀' to extension ratio 'λ', 'ρ' is the density, 'R' is the gas constant and 'T' is the absolute temperature.

Dynamic mechanical measurement is used to estimate the entanglement density of the rubber vulcanizates. The modulus of the rubbery plateau region is a direct measure of the entanglement density. According to the statistical theory of rubber elasticity, the crosslink density for a tetra functional network can be calculated according to the equation,

\[
v = \frac{E'}{6dRT} \quad \text{........................(1.11)}
\]

where E' is the storage modulus in the rubbery plateau region, 'd' is the density of the vulcanisate, 'R' is the gas constant and 'T' is the absolute temperature.
A recent promising approach to direct analysis of the crosslink structure and distribution in sulphur vulcanisates was the application of solid state C\(^{13}\) NMR spectroscopy [75,154,155]. In a work on unaccelerated sulphur vulcanisation, a number of signals were also assigned to monosulphidic crosslinks on the basis of calculated chemical shifts of proposed structures [156]. Chemical shifts differences between disulphidic and trisulphidic crosslinks are of the order of 0.1 ppm. Crosslinking results in broadening of the peaks. Recent studies [157, 158] have shown that C\(^{13}\) high-resolution solid state NMR spectroscopy is a valuable method to analyse the formation of polysulphidic and monosulphidic crosslinks at various sites on the monomer unit in NR.

1.12. Scope and Objectives of the Work

As delineated from the previous discussions, studies on vulcanisation, which leads to, the mechanism of the curing process is a hot topic of elastomer research. Despite the ongoing work, little effort is being made in order to elucidate the mechanism of curing with accelerator combinations. Several opinions do exist regarding the pathways of the curing process. Model compound vulcanisation and structural analysis of the adducts formed by the interaction of additives have helped to go further into the discrepancies prevailing in the complex process going on in the vulcanisation process.

Recently vulcanisation using thiourea derivatives have gained interest in the fields of elastomer research. Studies have been reported [110-112] regarding the nucleophilic activity of thiourea based compounds. They have been tried as secondary accelerators in rubber vulcanisation. Aprem et al. [111] compared the accelerating capability of various dithiobiurets in elastomers. They used dithiobiurets as a secondary accelerator. However no systematic efforts have been
done to evaluate the accelerating capacity of the 1-phenyl5-tolyl -2, 4-dithiobiuret.
The chemical reactions involved when a binary accelerator system is used in
rubber vulcanisation vary with the systems used and the elastomers involved.
But the exact mechanism of the crosslinking processes is not still understood
clearly. If has been proved that accelerators in which sulphur is covalently
linked to another sulphur, carbon or nitrogen are of the delayed action type,
displaying little activity around 100ºC. This is due to the inherent stability of
their sulphur bonds. Some accelerators among them are the disulphide (XSSX)
and sulphenamide (XSNR₂) accelerators of the benzothiazyl series like MBTS
and CBS, and the monosulphide (XSX) and disulphide (XSSX) accelerators of
the dithiocarbamyl series. The acceleration characteristics of these sulphur –
bearing accelerators depend partly on the nature of the group X and partly on
the mode of attachment of the functional sulphur atom to other atomic
groupings in the molecule.

In the first part of this study we tried 1-phenyl 5-ortho, para and meta
tolyl 2,4 dithiobiurets in different binary systems with MBS /CBS/DCBS as
primary accelerators in NR gum compounds and compared their properties
with mixes containing control formulations. A detailed investigation of these
mixes was made with special reference to cure characteristics, physical
properties and network structure. There is found to be appreciable reduction in
optimum cure time of the different experimental mixes. Their physical
properties are also found to be encouraging. The effect of this secondary
accelerator on filled systems was also studied. For this, mixes were prepared
using different fillers like carbon black, precipitated silica. The cure
characteristics, mechanical properties and the network structure of the filled
systems were also investigated.
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Based on the encouraging results obtained in the study of the synergistic activity of DTB along with CBS, DCBS or MBS in the sulphur vulcanisation of natural rubber, we thought it worthwhile to try this secondary accelerator in the vulcanisation studies of a synthetic rubber also. It is to be noted that the mechanism of rubber vulcanisation depends on the type of elastomer also. Many differences are encountered in the compounding and vulcanisation of NR and synthetic rubbers. In this context we selected styrene butadiene rubber for this investigation. SBR, a general-purpose diene rubber has lower green strength and lower gum tensile strength by virtue of lesser stress crystallisation. In order to improve these properties different fillers are incorporated in SBR compounds. Different compositions of DTB were tried in different SBR mixes using standard recipes and reference formulations were also studied. The effect of changes in concentration of DTB on the different cure characteristics is investigated. Mechanical properties like tensile strength, elongation at break, tear strength, etc. were evaluated and compared with control mixes. In order to correlate the variations in the physical properties of the various Vulcanisates the total crosslink density values were also estimated using the equilibrium swelling method.

All the known elastomers do not exhibit all the properties desired and may have shortcomings in one or more properties. Therefore to obtain the right compromise in properties elastomers are often blended with others during processing. Theoretically, blends of chemically dissimilar i.e. immiscible elastomers can attain a wider variation in properties than blends of miscible and thus chemically similar elastomers. Most blends of elastomers are immiscible, because mixing is endothermic and the entropic contribution is small because of high molecular weight. Based on the results obtained with natural rubber and styrene butadiene rubber, we thought of investigating
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different blend systems of these elastomers using the DTB as a secondary accelerator. NR and SBR being general-purpose rubbers can be usefully blended if the fundamental differences and similarities between them are recognised. In this study the effect of binary systems containing different concentrations of DTB as secondary accelerator in the vulcanisation of a 50-50 NR-SBR blend is investigated. Both gum and filled mixes are evaluated with regard to the various processing, curing and vulcanisate properties. Necessary control formulations were also prepared for comparison of these properties.

The vulcanisation of NR latex at low vulcanisation temperatures using disulphide and sulphenamide type accelerators is not possible. The compounding of NR latex is in principle similar to that of dry rubber. There are two major differences. First, as latex compounds are mixed at room temperature, highly active vulcanisation systems can be used, which enable vulcanisation to be performed at temperatures below 100°C. In dry rubber, such systems are difficult or impossible because the heat developed in mixing causes premature vulcanisation or scorch. Secondly, the reinforcing action of fillers, which is of major importance in dry rubber, is not obtainable in normally processed latex compounds. In our study also DTB was tried as secondary accelerator in natural rubber latex with primary accelerators like TMTD, ZDC at 120°C. The curing characteristics of the different mixes were investigated at these two temperatures. Mechanical properties like tensile strength and tear strength of the latex vulcanisate films were also evaluated. Chemical characterisation of the vulcanisate samples was carried out using the equilibrium swelling method.

The work embodied in this thesis focuses on the synthesis and
characterization of 1-phenyl 5-(ortho, para and meta) tolyl 2, 4-dithiobiuret (DTB) and the use of it as a binary accelerator with sulphenamides in the vulcanisation of rubbers. The investigation carried out on the effect of DTB as a binary accelerator in natural rubber, styrene butadiene rubber and their blends are addressed to evaluate the curing behaviour, mechanical properties, net work characteristics and dynamic mechanical properties. The important objectives of the thesis are listed below.

1.12.1. Influence of DTB/MBS binary accelerator system in NR

Studies have been done on processing characteristics, mechanical properties and network characteristics of MBS/DTB cured NR vulcanisates. The effect of fillers like carbon black and silica on the technological properties of rubber vulcanisates was also investigated. Dynamic mechanical analysis was performed to study the effect of DTB on crosslinking and the damping behaviour.

1.12.2. Influence of DTB/CBS binary system in NR

The effect of DTB as a secondary accelerator with CBS in NR was carried out. Studies have been done on the cure characteristics, cure kinetics, mechanical properties, dynamic mechanical properties and network characterisation of the vulcanisates.

1.12.3. Effect of DTB/DCBS binary system on NR

DTB was used as a secondary accelerator with dicyclohexyl benzothiazole sulphenamide (DCBS) in natural rubber. The efficient and conventional curing systems were taken in this study. The purpose of the study was to find an optimum concentration for the new binary accelerator system. Studies have been done on mechanical properties, chemical characterisation, dynamic mechanical behaviour etc.
1.12.4. DTB as a binary accelerator in SBR

Since SBR is also a general-purpose rubber, studies have been extended to SBR vulcanisation using DTB. Owing to its lower unsaturation, greater amount of accelerator is required in SBR vulcanisation. DTB has been added to SBR and the curing behaviour along with the technical properties has been analysed.

1.12.5. Technological properties of NR/SBR blends cured with DTB

The influence of DTB as a secondary accelerator in the curing behaviour, mechanical properties and network characteristics of NR/SBR blends has been studied in this section.

1.12.6. Influence of DTB/TMTD, DTB/ZDC of binary accelerator systems in NR latex

The influence of DTB as a secondary accelerator in the curing behaviour, mechanical properties and network characteristics has been studied in this section.

1.12.7. Double network formation in natural rubber

The introduction of double networks was expected to impart better mechanical properties to elastomers. The influence of the binary accelerator systems developed on the double network formation in NR became an area of interest. The influence of the extent of orientation of the chains and residual extension ratios were tried in order to get a clear idea of the factors influencing the formation and stability of these networks.
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