

**STUDIES ON NEW BINARY ACCELERATOR
SYSTEMS IN RUBBER VULCANISATION**

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**COCHIN UNIVERSITY OF
SCIENCE AND TECHNOLOGY**

By

SUSAMMA. A. P.

*in partial fulfillment of the requirements
for the award of the degree of*

DOCTOR OF PHILOSOPHY

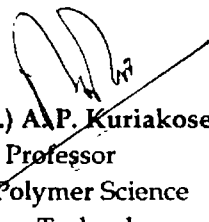
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CERTIFICATE

This is to certify that the thesis entitled "Studies on New Binary Accelerator Systems in Rubber Vulcanisation" is an authentic record of the research work carried out by Ms. Susamma. A. P. under my supervision and guidance in the Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Kochi, and no part of this thesis has been presented for any other degree from any other institution.

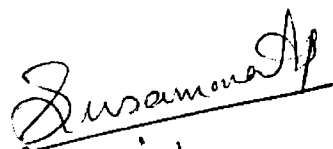


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Declaration

I hereby declare that the thesis entitled "Studies on New Binary Accelerator Systems in Rubber Vulcanisation" is the original work carried out by me under the supervision of Prof. (Dr.) A. P. Kuriakose, Professor Emeritus, Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Kochi, and no part of this thesis has been presented for any other degree from any other institution.

A handwritten signature in black ink, reading "Susamma A. P.", written over a horizontal line.

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Chapter 1

INTRODUCTION

Owing to its unique properties rubber has gained importance as an essential industrial raw material. But to be practically useful, all rubbers will have to undergo the process of vulcanisation. Originally natural rubber was used uncured (unvulcanised), but it suffered from drastic softening in warm water 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 sulphur to rubber followed by heating, leads to an improvement in the properties. This was the first vulcanisation system, discovered by Goodyear in U. S and Hancock in England¹. Vulcanisation is the process of conversion of rubber by any treatment, from a plastic substance of very low strength and breaking elongation to a resilient highly elastic material of considerable strength. From the chemical point of view vulcanisation is the process whereby the flexible, discrete rubber chains are joined together by

crosslinking reactions giving a three dimensional network. The transformation of raw rubber with limited practical application to an indispensable commodity of modern life is due to the discovery of this vulcanisation process. An understanding of the formation, structure and stability of the vulcanisate is therefore important. Studies on the chemistry of vulcanisation play a central role in the efforts to achieve better product performance from natural and synthetic rubbers. Understanding the network structure of the cured elastomers is important. The empirical relationship between the degree and type of crosslinks and the end use properties are to be established. These provide rubber technologists with a realistic picture of molecular framework of vulcanisates from which relation between physical properties and chemical constitution can be deduced.

Before vulcanisation the process known as compounding is carried out for any rubber product manufacture. Incorporation of ingredients into the virgin polymer is carried out in this process. Compounding of elastomers involves milling down the raw rubber into pliable sheets and then incorporation of compounding ingredients into it. The various ingredients generally added to rubber during compounding include processing aids, vulcanising agents, accelerators, activators, fillers, antidegradants and a variety of other materials. The main objectives of compounding are, to facilitate processing and fabrication, to achieve the required balance in vulcanisate properties and provide durability, all at lowest possible cost². The practical aspect of compounding varies from rubber to rubber whether it is saturated or unsaturated, natural or synthetic etc. Compounding of dry elastomers is done either in a two-roll rubber mill or in a Banbury internal mixing mill. There is much difference in compounding of natural rubber, synthetic rubbers or rubber blends. Synthetic rubbers are slower curing³ than natural rubber and so the quantity of the compounding ingredients will be different for different rubbers. Also it is seen that synthetic rubbers have more scorch safety than natural rubber. Further, natural rubber is more stress crystallisable than synthetic rubbers and the gum vulcanisates have good strength where as reinforcing fillers are essential for imparting strength to synthetic rubber vulcanisates. Both natural and synthetic rubbers require

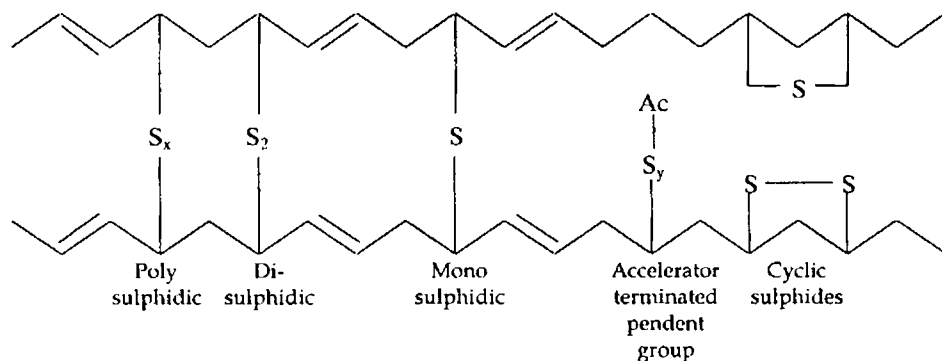
mastication before compounding, but for synthetic rubbers mastication requires longer time.

Our study involves the investigations on different systems of vulcanisation of elastomers or their blends using new binary accelerator combinations. In this context we thought it worthwhile to deal in some detail on the use of vulcanising agents, accelerators, fillers etc. in rubber vulcanisation.

1.1 VULCANISING (CURING) AGENTS

Substances that bring about the actual crosslinking process are called vulcanising agents. Numerous and varied vulcanising agents are now used in rubber industry. In addition to sulphur they include various organic peroxides, quinones, metal oxides, bifunctional oligomers, resins, amine derivatives etc. Vulcanisation can also be achieved by using high-energy radiation without any vulcanisation chemicals. The crosslinks formed by peroxides are purely carbon-carbon linkages. The importance of peroxides is their ability to cross link saturated elastomers such as ethylene propylene rubber, silicone rubber etc. which cannot be cross-linked by other vulcanising agents. Chloroprene rubbers are generally vulcanised by the action of metal oxides along with other chemicals. Sulphur and nonsulphur systems have advantages and disadvantages of their own, but sulphur systems still remain versatile. There are several advantages for sulphur as the vulcanising agent viz. (1) higher flexibility during compounding, (2) easier adjustment of the balance between the vulcanisation stages, (3) possibility of air heating, (4) possibility to control the length of the crosslinks, (5) better mechanical properties to the vulcanisates and (6) economic reasons^{4,5}. However compared to peroxide curing, sulphur systems show lower heat and reversion resistance, higher compression set and higher possibility of corrosion in cable metals. Vulcanisation reaction is determined in large measure by the type of vulcanising agents (curatives), the type of process, temperature, and time of cure. The number of crosslinks formed, also referred to as degree of vulcanisation or state of cure, has an influence on the elastic and other properties of the vulcanisate. Therefore the type of vulcanisation process is the important connecting link between the raw material and the finished product.

Vulcanisation of rubber with sulphur alone is a very slow process and it takes several hours or even days to reach optimum cure depending on the temperature of vulcanisation and the nature of rubber used. The vulcanisates formed are of very low physical strength and mechanical properties also. Further they have a strong tendency for reversion and their resistance to ageing is poor. The use of sulphur alone is ineffective and requires 45 to 55 sulphur atoms per crosslink and tends to produce a large portion of intramolecular (cyclic) crosslinks⁶. Sulphur bloom is also very common. Vulcanisation with sulphur alone is therefore of no technological importance at all. A major breakthrough came with the discovery of organic nitrogen compounds known as accelerators. Bases like aniline, thiocarbanilide etc. were the first organic vulcanisation accelerators of rubber. Now a large number of compounds have been suggested as vulcanisation accelerators. In the vulcanisation network sulphur is combined in a number of ways. In the form of crosslinks it remains as monosulphide, disulphide or polysulphide. It may also be present as pendent sulphides or cyclic monosulphides or disulphides as shown:



The accelerator sulphur ratio determines the efficiency by which sulphur is converted into crosslinks, the nature of crosslinks and the extent of main chain modification. Depending on the sulphur accelerator ratio the sulphur vulcanising systems can be categorised as: (a) the conventional or high sulphur vulcanisation system (CV) where sulphur is added in the range of 2-3.5 parts per hundred rubber (phr.) and the accelerator in the range 1- 0.4 phr. (b) the efficient vulcanising (EV) system where sulphur is added in the range of 0.3-0.8 phr. and accelerator in the range of 6.0-2.5 phr. and (c) the semi efficient (SEV) system where sulphur is added in the range 1-1.8 phr. and accelerator in the range 2.5-1 phr⁷. As

the CV system has got greater amount of sulphur compared to the accelerator the possibility of polysulphidic linkage formation is higher. At higher temperatures the polysulphidic linkage may break to mono and disulphidic. This explains the reversion at higher temperatures, which leads to low strength and modulus. Properties like compression set and thermal stability are better for EV systems primarily due to the lower amount of polysulphidic linkages.

1.2 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 used in rubber vulcanisation were in fact inorganic compounds. Magnesium oxide, litharge and zinc oxide were the most widely used among them. A major breakthrough came with the discovery of organic nitrogen compounds acting as accelerators for the vulcanisation process. An intense search for the vulcanisation accelerators started around 1906 by Oenslager⁸. He introduced organic base aniline as accelerator into rubber compounds to improve the quality of low-grade rubber and to accelerate the vulcanisation reaction. Though aniline was proved to be a powerful accelerator, it was unacceptable because of its toxic nature. A number of aniline derivatives were then investigated. Among these thiocarbanilide was found to be effective in combination with zinc oxide. Later several other organic compounds were shown to have accelerating activity and majority of them was nitrogen containing organic bases^{9,10}. First, it was believed that it is the basicity of these substances rather than the chemical constitution that is responsible for the accelerator activity. Later it was established that the activity of organic bases is not proportional to their basicity¹¹⁻¹². With the discovery of nitrogen free accelerators like zinc alkyl xanthate¹³ and zinc thiophenols¹⁴ the theory that the element nitrogen was responsible for the accelerator activity was rejected. A large variety of accelerators were developed during the first two

decades of the 20th century. By this time dithiocarbamates and alkyl xanthates were widely used as accelerators. In the early 1920's it was discovered that thiocarbanilide reacts with sulphur to yield 2-mercaptobenzothiazole. This and its derivatives are still the most important accelerators used in rubber industry, particularly because they impart outstanding properties to the vulcanisates. Sebrell et al.¹⁵⁻¹⁷ and Bruni et al.¹⁸ discovered independently that 2 mercaptobenzothiazole and its homologues, its disulphide and its metal salts are very effective accelerators and these yield vulcanisates of improved physical properties¹⁹⁻²¹. A reaction product of amines from beet molasses with CS₂ was introduced by Molony²², which was later identified as tetramethylthiuram disulphide (TMTD). Around 1920 it was discovered that thiuramdisulphides enable vulcanisation to proceed without sulphur. Investigations in the field of accelerators aimed at development of those, which reacted slowly and safely at the processing temperature but rapidly at the vulcanisation temperature resulted in the introduction of dibenzothiazyl disulphide (MBTS) which gave greater scorch safety at higher processing temperatures. Later more delayed action and yet fast curing vulcanisation systems were made possible from thiazole derivatives of sulphenamides. Thiocarbamyl sulphenamides are reported to be more productive than the corresponding benzothiazole derivative, due to the combined scorch delay of sulphenamides and the fast acceleration activity of thiocarbamate both being present in their structure²³. With the discovery of ultra accelerators vulcanisation can be achieved even at room temperature²⁴. Thus there are different classes of compounds, which can serve as accelerators in sulphur vulcanisation. Following table shows main classes of organic compounds that are commercially useful either as primary or secondary accelerators in sulphur vulcanisation of diene rubbers.

Class	Speed	Examples
Thiourea derivatives	Slow	DPTU, DBTU
Guanidines	Medium	DPG, DOTG
Benzothiazoles	Semi fast	MBT, MBTS
Sulphenamides, Sulphenimides	Fast, delayed action	CBS, TBBS, MBS
Dithiophosphates, Xanthates	Fast	ZDBP
Thiurams	Very fast	TMTD, TMTM, TETD
Dithiocarbamates	Very fast	ZDC, ABDC

Noting the structure of these vulcanisation accelerators a feature common is some form of a tautomerisable double bond and many of them contain the $\text{-N}=\overset{\text{|}}{\text{C}}\text{-S-H}$ functionality. The time to the onset of cure varies with the class of the accelerator used. Usually a long delay period before the onset of sulphur crosslinking occurs with sulphenamide and sulphenimide accelerators. Prior to crosslinking reaction, it is the role of accelerators to react with elemental sulphur, metal oxide and/or the rubber. Accelerators offer many advantages such as lowering the cure temperature and shortening of the cure time, thus reducing thermal and oxidative degradation. Also, optimum physical properties could also be obtained with lower sulphur content.

1.3 ACCELERATOR ACTIVATORS

In order to achieve the full potential of vulcanisation accelerators it is necessary to use organic or inorganic 'activators'. Inorganic activators are metallic oxides such as ZnO, PbO, MgO etc. Zinc oxide is the most important of these additives. Originally ZnO was used as an extender for cost reduction, and then it was found to have a reinforcing effect and was later found to reduce vulcanisation time²⁵. Usually an activator system, a combination of zinc oxide and a long chain fatty acid such as stearic acid that act as a co-activator is used. Generally it can be stated that increasing the pH leads to activation of the vulcanisation. The basic activators mentioned lead to improved strength properties of the vulcanisates and come to a shortening of the vulcanisation time. Better processing and improvement in dispersion of fillers and other chemicals can also be achieved by the use of fatty acids and fatty acid salts as co-activators. 5 phr. zinc oxide with 1-3 phr. stearic acid is the commonly accepted combination²⁶.

1.4 FILLERS

Fillers are usually inorganic powders of small particle size incorporated during compounding for various purposes like improvement in strength, cheapening the product etc. Choice of the type and amount of the fillers to be used depends on the hardness, tensile strength and other properties required in the product. Some fillers are incorporated primarily

to reinforce the product and they are termed as reinforcing fillers. Carbon blacks, silicas, silicates etc. are in this class. Others are included mainly to cheapen and stiffen the final product. China clay, barytes etc. come under this type. Reinforcement by filler is the enhancement of one or more properties of an elastomer by the incorporation of that filler, thus making it more suitable for a given application²⁷⁻²⁸. It is generally agreed that strong links exist between rubber chain and reinforcing filler particles²⁹⁻³¹. The effect of filler on rubber vulcanisates depends on its physical properties such as particle size, surface area, surface reactivity, electrical charge on the particle and chemical properties such as pH and reactivity with accelerators. Reinforcing fillers substantially improves the mechanical and dynamic properties of the rubber. As the filler dose increases the properties increase progressively and then decreases. This also depends on the type of filler and rubber used.

The most common and effective reinforcing filler is carbon black. There are varieties of blacks characterised by the particle size, method of manufacture etc. They are essentially elemental carbon and are composed of aggregated particles. During vulcanisation carbon blacks enter into chemical reaction with sulphur, accelerator etc. participating in the formation of vulcanised network. Thus the filler will influence the degree of crosslinking also. Carbon black also interacts with the unsaturated hydrocarbon rubbers during milling and the rubber is adsorbed on to the filler. This alters the stress - strain properties and reduces the extend of swelling of the product in solvents³². Porter reported that the crosslink density of a black reinforced vulcanisation system increased by about 25% compared to the corresponding unfilled ones³³. Carbon black generally increases the rate of vulcanisation and improves the reversion resistance³⁴. However, carbon blacks can be used in dark coloured products only.

Precipitated silica is the best non-black reinforcing filler so far developed, and come closer to carbon black in its reinforcing properties. They have particle size as fine as that of carbon black and have an extremely reactive surface. Precipitated silica is highly adsorptive, and hence in formulations containing them, it is necessary to use more than the normal quantity of accelerator or a combination of accelerator system, which is more reactive. Proper choice of the accelerator and activator are done to

obtain appropriate scorch and cure times in silica and silicate filled mixes. One distinct advantage imparted by silica to many rubbers is the increased resistance to air ageing at elevated temperature³⁵. In our studies we used both carbon black and precipitated silica as reinforcing fillers.

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)³⁶. The variation in the effectiveness of NR and synthetic rubbers with regard to fillers can be explained with the theory of overstressed molecules³⁷⁻³⁹. Other compounding ingredients that are not dealt with in detail here include antidegradents and other special additives.

1.5 MECHANISM OF RUBBER VULCANISATION

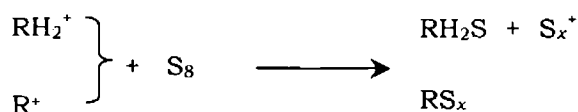
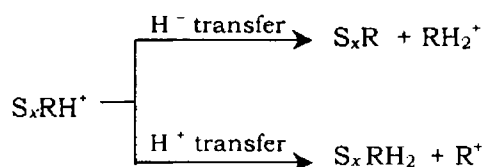
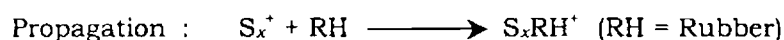
Vulcanisation is the crosslinking process that prevents permanent deformation under load and ensures elastic recovery on removal of the load on the product. Since vulcanisation was first discovered, a major focus on elastomer systems has been to characterise the network structures formed. Complex mechanisms are involved in vulcanisation processes rather than a simple chemical reaction. A series of consecutive and competing reactions occur during the sulphuration of rubber under vulcanising conditions and hence no single mechanism can be appropriate. Further, the network structures are complex and rich in types of structure. Many of the traditional analytical techniques are not useful, as the concentration of the chemically modified structures induced by the vulcanisation is extremely low. Even then many approaches have been

attempted in an effort to relate the chemical microstructure to the physical properties of both raw and cured elastomers. NMR spectroscopy is one of the powerful spectroscopic methods used to directly evaluate the chemical structures of polymeric materials⁴⁰. Solid state C-13 NMR has also been widely applied for the characterisation of vulcanised rubber systems⁴¹⁻⁴³.

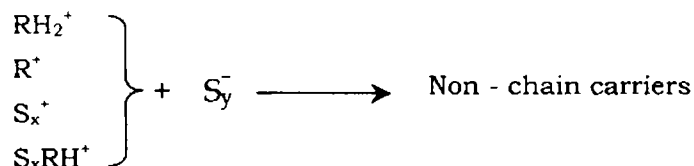
For the study of reaction mechanism, sulphur vulcanisation reactions can be broadly classified into two, the unaccelerated and the accelerated types. Unaccelerated sulphur formulation consists of rubber and sulphur while the accelerated systems contain rubber, accelerator and sulphur. In addition to this, both the types include zinc oxide - stearic acid activator system also. There are also accelerator systems in which elemental sulphur is not present instead; the accelerator provides sulphur for vulcanisation. This sulphur free vulcanisation can also be referred to as sulphur donor systems. The most widely used accelerator in this type is tetra methyl thiuram disulphide (TMTD), although other accelerators such as 4-morpholinyl 2-benzothiazyl disulphide (MBDS) are also used. If a full understanding of the relationship between vulcanisation chemistry and network structure is possible, one can tailor formulations to produce the desired mechanical and chemical properties.

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 technical 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 crosslinks⁴⁴⁻⁵¹. 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. According to Shelton and McDonel⁵² the unaccelerated sulphur vulcanisation is a polar process. Blokh also concluded from his EPR studies that unaccelerated sulphur vulcanisation proceeds through a polar mechanism⁵³. There is the possibility for a free radical mechanism for sulphuration where sulphur radicals are formed via a homolytic fission of the S₈ ring. Although a radical process would explain certain experimental results, the general agreement is that a polar mechanism operates during the sulphur only vulcanisation. A general version allowing for either proton or hydride transfer for the unaccelerated vulcanisation can be represented as:



Termination:



According to Dogadkin and Shershnev⁵⁴ 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

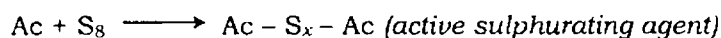
vulcanisation is typically ineffective requiring 45-55 sulphur atoms per crosslink and tends to produce a large proportion of intramolecular (cyclic) crosslinks, such ineffective crosslink structures are of interest in the understanding of complex nature of vulcanisation reactions. Spectroscopic studies of unaccelerated sulphur vulcanisation point to the formation of polysulphidic, monosulphidic and also cyclic sulphidic linkages⁵⁵.

1.5.1 Accelerated Sulphur Vulcanisation

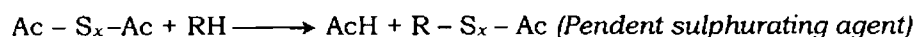
By far the common vulcanisation systems used in industrial applications are the accelerated sulphur formulations. The accelerated sulphur systems can be classified into single and binary accelerator combinations. Almost all accelerators need metal oxides for the development of their full activity. Zinc 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.

A generally accepted scheme of the reactions is as follows^{47,56,57} :

- ❖ Accelerator (Ac) and activator interacting with sulphur to form the active sulphurating agent.



- ❖ The rubber chains interact with the sulphurating agent to form polysulphidic pendant groups terminated by accelerator groups.

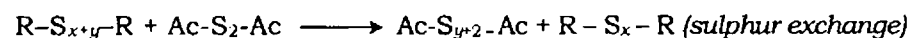
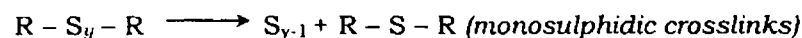
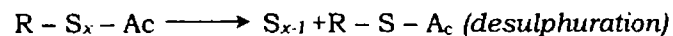
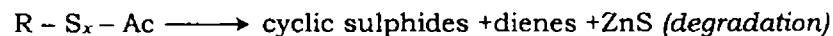


Where RH is the rubber chain.

- ❖ Polysulphidic crosslinks are formed.



- ❖ Network maturing and competing side reactions and thermal decomposition leads to the following reactions

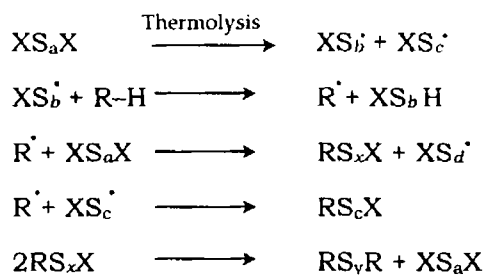


There are at least three competing reactions (cross linking, desulphuration and degradation) that occur during the cure and network maturing period.

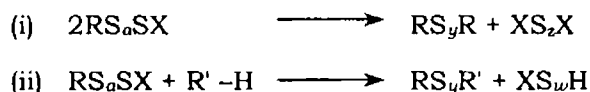
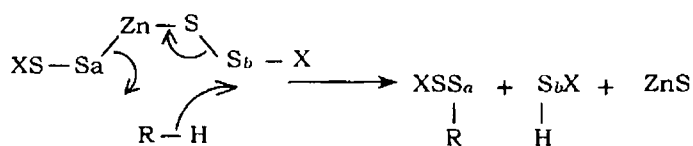
The first step is the formation of active sulphurating agent. The accelerator and activator first interact to form a species, which then reacts with sulphur to form active sulphurating agent⁵⁸⁻⁶⁰. The active sulphurating agent reacts directly with the rubber molecule to give a rubber bound pendent group. In this pendent group a fragment derived from the accelerator or sulphur donor is linked through two or more sulphur atoms to the rubber chains. These form crosslinks either by direct reaction with another rubber molecule or by disproportionation with a second pendent group of a neighbouring rubber chain. Polysulphide crosslinks formed undergo further transformation by two competing reactions, desulphuration or decomposition. Progressive shortening of the polysulphide producing finally monosulphide links by desulphuration. Then a number of competing reactions, which are termed network maturing lead to the final crosslinked structure. The ultimate network structure formed depends on the temperature, accelerator types and concentration. The ratio of types of crosslinks formed (poly, di or mono sulphidic) depends on the ratio of sulphur to accelerator in the formulation. Changes may continue to occur in the network structure, especially if the vulcanisate is in service under elevated temperature, after the formal vulcanisation is over. Layer⁶¹ proposed that sulphur determines the overall amount of reaction but the accelerator determines the length of the sulphur chains. Although mechanism of accelerated vulcanisation has been extensively studied, there is still much disagreement to its exact mechanism. Craig⁶², Dogadkin^{63,64}, Bevilacqua⁶⁵, Scheele^{66,67}, Blokh⁶⁸ Tsurugi and Fukuda⁶⁹ all have advanced free radical mechanism to explain the results of accelerated sulphur vulcanisation, where as Bateman⁴⁴ Porter⁷⁰ and Allen et al.⁷¹ suggested polar mechanism as a logical extension of their proposed mechanism for unaccelerated sulphur vulcanisation. On the other hand Shelton and McDonel⁵² and Coran⁷² proposed mechanisms involving both freeradical and ionic species.

In radical mechanism of accelerated sulphur vulcanisation the accelerator cleaves to form persulphenyl radicals, which then abstract protons. The rubber radical reacts with another intermediate to form

rubber bound intermediates. Two such rubber bound intermediates then form the actual crosslink.



The proposed polar mechanism is as shown.



The active sulphurating agent is assumed to be the zinc accelerator perthiolate complex. The co ordination of electron donating ligands to the zinc atom will increase the electron density on the sulphur atom of the perthiolate groups. In the transition state C-S bond formation will be enhanced by the increased nucleophilicity of the XSS_a group while C-H bond fission will be limited by the reduced electrophilicity of the XS_b group, which increases the SN₂ character of the process. The rubber bound pendent group RS_aSX is converted to crosslinks by the process (i) or (ii).

1.5.2 Binary Accelerator Systems

A binary accelerator system refers to the use of two or more accelerators in a given formulation. The use of such systems finds wide technological applications. One of the motivations for the use of binary systems is the synergistic behaviour of accelerator combinations in that the final properties are better than those produced by either accelerator separately⁷³⁻⁷⁵. These systems are widely used in industry and are

becoming increasingly popular due to the fact that such mixed systems provide better acceleration, better control of processing safety and improvement in physical and chemical properties of the vulcanisates. Though the practice of using binary accelerators is quite old, the mechanism of the combined action of these accelerators are not studied adequately and only recently scientists began to fully probe the complicated mechanism of binary systems.

Accelerator present at a relatively higher concentration is called primary and that present in smaller amounts is called secondary accelerator. A lot of binary systems have been developed for practical applications⁷⁶. These include thiuram disulphides, sulphenamides, benzothiazyl disulphides, some derivatives of piperidine, pyrrole, piperazine, phthalamides etc. Amines like diphenyl guanidine (DPG) are used in combination with other accelerators such as MBT or sulphenamides to activate the vulcanisation reaction. Usual binary systems consist of thiocarbamate derivatives and benzothiozoles. Thiuram systems generally show very little scorch safety. In order to increase scorch delay period, often sulphenamides and MBT are added^{77,78}. Thiourea and its derivatives are also known to be good secondary accelerators in rubber vulcanisation⁷⁹⁻⁸¹.

Even though a good deal of work has been reported to elucidate the mechanism of vulcanisation by single accelerator, little attention has been paid to the chemistry of vulcanisation of binary systems. Higher accelerating action of binary system is assumed to be through the formation of either a eutectic mixture or salt forming compound having greater chemical reactivity and better solubility⁸²⁻⁸³. Dogadkin and collaborators⁸⁴⁻⁸⁶ investigated a number of popular accelerator combinations and found mutual activation with many of them. Based on the experimental observations in the vulcanisation by using various combinations of accelerators, they classified the various binary systems into three different groups.

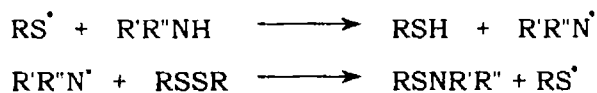
1. Systems, which show synergism.
2. Systems with a pair of accelerators in which the mutual activity of the pair does not exceed the activity of the most activated accelerator.

3. Systems with only additive action of accelerators.

The first group consists of disulphides (eg: MBTS, TMTD etc.) or mercaptans (eg: MBT) with nitrogen containing organic bases or disulphides with sulphenamides. Sulphenamides with nitrogen containing organic bases belong to the second group. The third type exhibiting additional effect include systems containing sulphenamides (and some disulphides) with TMTD and those containing combinations of the same chemical class. In the case of systems with mutual activity such as MBTS with DPG or CBS, the reaction between the accelerators were observed higher under vulcanisation conditions than when they are reacted alone⁸⁴. It was suggested that in the initial stage of vulcanisation, the accelerators interact with one another to form an active complex⁸⁶. This complex then disintegrates with the formation of active free radicals responsible for initiating the interaction of rubber with sulphur.



The reaction is believed to propagate as follows:



RSH and RSNR'R'' are considered as highly active accelerators.

The accelerator activity of sulphur bearing accelerators (XSSX, XSX etc.) depends partly on the nature of X and partly on the mode of attachment of the functional sulphur to other atomic grouping in accelerator molecule. In a report by Moore et.al⁸¹, which presented the investigations on the TMTD-TU binary accelerator systems, a novel probable mechanism for the synergistic activity of TU was suggested. This theory recognises the importance of the polysulphidic intermediates (I) formed during the vulcanisation process, which subsequently reacts with the rubber chain to yield further intermideates (II). These intermideates finally react to yield sulphurated crosslinks.

