STUDIES ON NEW BINARY ACCELERATOR SYSTEMS IN RUBBER VULCANISATION

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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.*

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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 England[1]. 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.

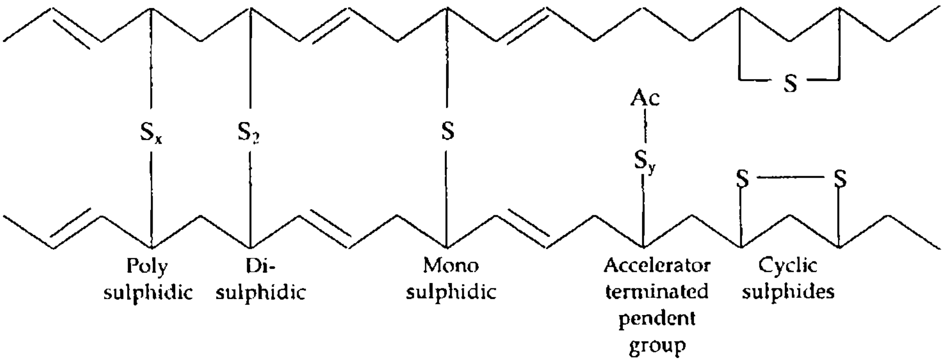
Before vulcanisation the process known as compounding is carried out for any rubber product manufacture. Incorporation of ingredients into the virgin polymer is carried out in this process. Compounding of elastomers involves milling down the raw rubber into pliable sheets and then incorporation of compounding ingredients into it. The various ingredients generally added to rubber during compounding include processing aids, vulcanising agents, accelerators, activators, fillers, antidegredants 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 cost[2]. 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 curing[3] 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) crosslinks[6]. 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 monsulphide, disulphide or polysulphide. It may also be present as pendent sulphides or cyclic monsulphides 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 phr[7]. 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 Oenslager[8]. 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 basicity[11-12]. With the discovery of nitrogen free accelerators like zinc alkyl xanthate[13] and zinc thiophenols[14] 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 properties[19-21]. A reaction product of amines from beet molasses with CS_2 was introduced by Molony[22], 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 structure[23]. With the discovery of ultra accelerators vulcanisation can be achieved even at room temperature[24]. 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 $-N=\overset{|}{C}-S-H$ 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 time[25]. 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 combination[26].

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 application[27-28]. It is generally agreed that strong links exist between rubber chain and reinforcing filler particles[29-31]. 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 solvents[32]. Porter reported that the crosslink density of a black reinforced vulcanisation system increased by about 25% compared to the corresponding unfilled ones[33]. Carbon black generally increases the rate of vulcanisation and improves the reversion resistance[34]. 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 temperature[35]. 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 over-stressed molecules[37-39]. Other compounding ingredients that are not dealt with in detail here include antidegredents 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 materials[40]. Solid state C-13 NMR has also been widely applied for the characterisation of vulcanised rubber systems[41-43].

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 crosslinks[44-51]. 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 McDonel[52] the unaccelerated sulphur vulcanisation is a polar process. Blokh also concluded from his EPR studies that unaccelerated sulphur vulcanisation proceeds through a polar mechanism[53]. There is the possibility for a free radical mechanism for sulphuration where sulphur radicals are formed via. a homolytic fission of the S_8 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:

Initiation $\quad S_8 \longrightarrow S_x^+ + S_y^-$

Propagation : $\quad S_x^+ + RH \longrightarrow S_xRH^+ \quad (RH = \text{Rubber})$

$$S_xRH^+ \left\{ \begin{array}{l} \xrightarrow{H^- \text{ transfer}} S_xR + RH_2^+ \\[2ex] \xrightarrow{H^+ \text{ transfer}} S_xRH_2 + R^+ \end{array} \right.$$

$$\left. \begin{array}{l} RH_2^+ \\[2ex] R^+ \end{array} \right\} + S_8 \longrightarrow \begin{array}{l} RH_2S + S_x^+ \\[2ex] RS_x \end{array}$$

Termination:

$$\left. \begin{array}{l} RH_2^+ \\ R^+ \\ S_x^+ \\ S_xRH^+ \end{array} \right\} + S_y^- \longrightarrow \text{Non - chain carriers}$$

According to Dogadkin and Shershnev[54] 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 polysuphidic, monosulphidic and also cyclic sulphidic linkages[55].

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.

  $Ac + S_8 \longrightarrow Ac - S_x - Ac$ *(active sulphurating agent)*

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

  $Ac - S_x - Ac + RH \longrightarrow AcH + R - S_x - Ac$ *(Pendent sulphurating agent)*

  Where RH is the rubber chain.

- Polysulphidic crosslinks are formed.

  $R - S_x - Ac + RH \longrightarrow AcH + R - S_x - R$ *(crosslinks)*

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

  $R - S_x - Ac \longrightarrow$ cyclic sulphides +dienes +ZnS *(degradation)*

  $R - S_x - Ac \longrightarrow S_{x-1} + R - S - A_c$ *(desulphuration)*

  $R - S_y - R \longrightarrow S_{y-1} + R - S - R$ *(monosulphidic crosslinks)*

  $R{-}S_{x+y}{-}R + Ac{-}S_2{-}Ac \longrightarrow Ac{-}S_{y+2}{-}Ac + R - S_x - R$ *(sulphur exchange)*

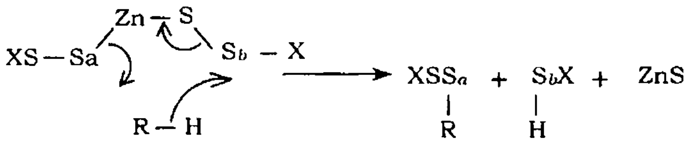
There are at least three competing reactions (cross linking, desulphuration and degradation) that occur during the cure and network maturing period.

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 agent[58-60]. 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. Layer[61] 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. Craig[62], Dogadkin[63,64], Bevilacqua[65], Scheele[66,67], Blokh[68] Tsurugi and Fukuda[69] all have advanced free radical mechanism to explain the results of accelerated sulphur vulcanisation, where as Bateman[44] Porter[70] 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 McDonel[52] and Coran[72] 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.

$$\begin{aligned}
&XS_aX &&\xrightarrow{\text{Thermolysis}} && XS_b^{\bullet} + XS_c^{\bullet}\\
&XS_b^{\bullet} + R\text{–}H &&\longrightarrow && R^{\bullet} + XS_bH\\
&R^{\bullet} + XS_aX &&\longrightarrow && RS_xX + XS_d^{\bullet}\\
&R^{\bullet} + XS_c^{\bullet} &&\longrightarrow && RS_cX\\
&2RS_xX &&\longrightarrow && RS_yR + XS_aX
\end{aligned}$$

The proposed polar mechanism is as shown.



$$\begin{aligned}
&\text{(i)}\quad 2RS_aSX &&\longrightarrow && RS_yR + XS_zX\\
&\text{(ii)}\quad RS_aSX + R'\text{–}H &&\longrightarrow && RS_yR' + XS_wH
\end{aligned}$$

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 SN_2 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 separately[73-75]. 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.

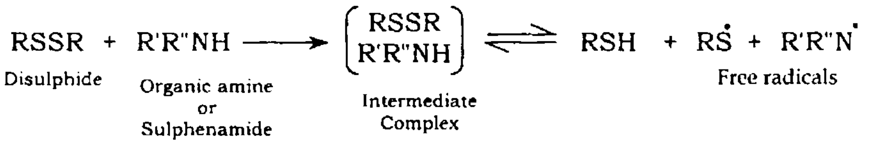
Accelerator present at a relatively higher concentration is called primary and that present in smaller amounts is called secondary accelerator. A lot of binary systems have been developed for practical applications[76]. These include thiuram disulphides, sulphenamides, benzothiazyl disulphides, some derivatives of piperidine, pyrrole, piperazine, phthalmides 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 vulcanisation[79-81].

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 solubility[82-83]. Dogadkin and collaborators[84-86] 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 alone[84]. It was suggested that in the initial stage of vulcanisation, the accelerators interact with one another to form an active complex[86]. This complex then disintegrates with the formation of active free radicals responsible for initiating the interaction of rubber with sulphur.



$$\underset{\text{Disulphide}}{RSSR} + \underset{\substack{\text{Organic amine}\\\text{or}\\\text{Sulphenamide}}}{R'R''NH} \longrightarrow \underset{\substack{\text{Intermediate}\\\text{Complex}}}{\begin{bmatrix} RSSR \\ R'R''NH \end{bmatrix}} \rightleftharpoons RSH + \underbrace{R\dot{S} + R'R''N^{\bullet}}_{\text{Free radicals}}$$

The reaction is believed to propagate as follows:

$$RS^{\bullet} + R'R''NH \longrightarrow RSH + R'R''N^{\bullet}$$

$$R'R''N^{\bullet} + RSSR \longrightarrow RSNR'R'' + RS^{\bullet}$$

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.al[81], 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 intermidiates (I) formed during the vulcanisation process, which subsequently reacts with the rubber chain to yeild further intermideates (II). These intermideates finally react to yeild sulphurated crosslinks.

The process is schematised as follows:

$$(m-1)\,\mathrm{XSSX} \xrightarrow{\mathrm{ZnO}} \underset{(\mathrm{I})}{\mathrm{XS_m\,X}} + \frac{(m-2)}{2}\,\{(\mathrm{XO})_2\mathrm{Zn} + (\mathrm{XS})_2\,\mathrm{Zn}\} \qquad (1)$$

$$\mathrm{RH} + \mathrm{XS}_m\mathrm{X} \xrightarrow{\mathrm{ZnO}} \underset{(\mathrm{II})}{\mathrm{RS}_{m-1}\,\mathrm{X}} + \frac{1}{2}\,\{(\mathrm{XS})_2\,\mathrm{Zn} + \mathrm{H_2O}\} \qquad (2a)$$

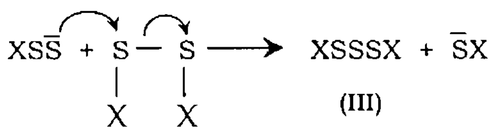
$$\mathrm{RH} + \mathrm{RS}_{m-1}\mathrm{X} \xrightarrow{\mathrm{ZnO}} \mathrm{RS}_{m-2}\,\mathrm{R} + \frac{1}{2}\,\{(\mathrm{XS})_2\,\mathrm{Zn}+\mathrm{H_2O}\} \qquad (2b)$$

Where X = Me$_2$N·C:S and RH= Rubber hydrocarbon.

Since the crosslinking reaction 2b follows from the products of the reaction 2a which itself requires the thiurarm polysulphides **(I)** produced in the reaction (1) it follows that any acceleration of the latter must also lead to a corresponding increase in overall vulcanisation rate. Studies on the basic oxyanion type nucleophiles suggests that oxygen atoms of ZnO prefer to attack the thiocarbamyl carbon atoms of TMTD causing the following polar substitution

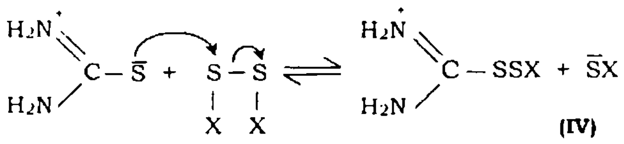
$$\mathrm{Zn^{++}} \ldots \mathrm{O^-}\ \mathrm{XSSX} \longrightarrow \mathrm{Zn^{++}} \ldots \bar{\mathrm{O}}\mathrm{X} + \bar{\mathrm{S}}\mathrm{SX} \qquad (3)$$

Reaction (3) yields a perthioanion (XS$\bar{\mathrm{S}}$) which will rapidly effect the heterolysis of S-S bond in another TMTD molecule to give the trisulphide **(III)**



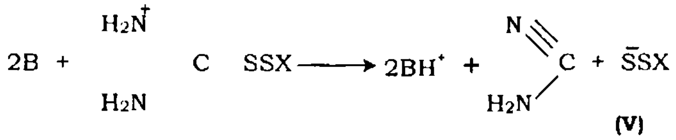
$$\mathrm{XS\bar{S}} + \underset{\mathrm{X}}{\mathrm{S}} - \underset{\mathrm{X}}{\mathrm{S}} \longrightarrow \underset{(\mathrm{III})}{\mathrm{XSSSX}} + \bar{\mathrm{S}}\mathrm{X} \qquad (4)$$

Participation of **(III)** in processes similar to (3) and (4) will lead to the formation of higher polysulphide of the type **I** (m ≥4). However when thiourea is present, it is assumed that it will interact with TMTD under the prevailing basic conditions providing an easier and faster route for the formation of polysulphide **(I)** replacing the slow processes (3) and (4) above. Thus addition of thiourea to TMTD causes acceleration in the production of polysulphide. The mechanism suggested is as follows. Thiourea will engage in a thioanion- disulphide interchange reaction of the type :



(5)

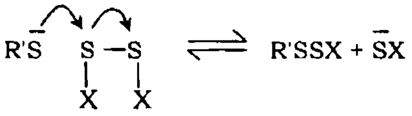
IV easily losses a proton to a suitable base B and rapidly decomposes to a pethioanion as in eqn.(6)



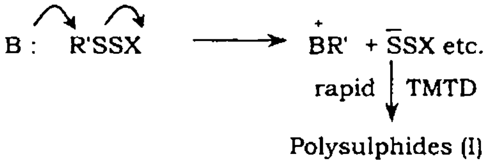
(6)

These perthioanions **(V)** are the precursors of the thiuram polysulphide **(I)** required in the ultimate crosslinking reaction.

On the basis of this theory it can be predicted that easy production of perthioanions $(X\bar{S}_x)$ and hence polysulphides **(I)** and a consequent acceleration of the vulcanisation in the NR-TMTD-ZnO system will result upon the addition of any thioanion $(R'\bar{S})$ where the group R' is more easily attacked by bases than X of TMTD. In general this suggestion can be written as follows:



$$R'\bar{S}\quad \underset{X}{S}-\underset{X}{S} \rightleftharpoons R'SSX + \bar{S}X \qquad (7)$$



$$B:\ R'SSX \longrightarrow \begin{array}{c} \overset{+}{B}R' + \bar{S}SX \text{ etc.} \\ \text{rapid} \Big\downarrow \text{TMTD} \\ \text{Polysulphides (I)} \end{array} \qquad (8)$$

The equation (7) being a reversible one is promoted by the removal of R'SSX by base and $\bar{S}X$ as $Zn\ (SX)_2$

Binary accelerator systems are of great importance because of their widespread use in the industry. Many other authors also investigated the technology of binary systems[87-91] and their conclusions also point to the formation of complex compounds. In binary accelerator systems also evidences are available for either polar or radical mechanism as in the case of single accelerator systems, even though no conclusive evidences have been reported.

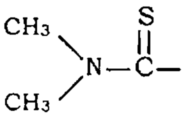
1.6. SCOPE AND OBJECTIVES OF THE PRESENT INVESTIGATION

Accelerators in which sulphur is covalently bonded to S, C or N are generally inactive at lower vulcanisation temperatures because of the inherent stability of their sulphur bonds. In his studies on the vulcanisation of natural rubber latex using a binary system consisting of TMTD and thiourea (TU), Philpott[92] suggested an ionic mechanism where the S-S bond in TMTD is cleaved by the nucleophile produced from thiourea as:

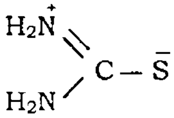
$$XSSX + \bar{Y} \longrightarrow XSY + X\bar{S}$$

where

X is

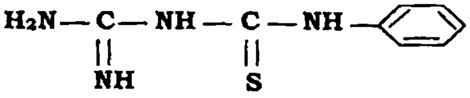


and $\bar{Y}$ is



Thiourea and its derivatives like ethylene thiourea, NN'-diphenyl thiourea, diethyl thiourea, sym-di-o-tolylthiourea etc. are reported to be effective secondary accelerators with TMTD or CBS especially in latex vulcanisation systems. In their capacity as accelerators these derivatives ensure a fast vulcanisation at comparatively lower temperature as reported by Philpott. Accelerators like MBTS or CBS when used alone does not give much crosslinking in diene rubbers but when used with thiourea rapid crosslinking occurs. Investigations were made in our laboratory[93-99] on binary systems containing derivatives of thiourea as secondary accelerators in the vulcanisation of different elastomers. The cure characteristics, especially the optimum cure time values in general, supported the fact that the more nucleophilic the compound the more is the accelerator activity. The results obtained were more or less in agreement with the suggestions made by Kempermann[100], Philpott[92] and Moore et al.[81]. However, the mechanism of reaction is also found to depend on type of elastomer used and the systems under review.

Based on the favourable results obtained in the above studies, we investigated an amidinothiourea derivative viz. N-amidino N'- phenyl thiourea [APT–(**A**)] as secondary accelerator in various binary systems using different elastomers and their blends. One of the aims of the study was to give further proof with regard to the theory of nucleophilic reaction mechanism or otherwise in such binary systems.



(A)

The activity of (**A**) as an accelerator was compared with that of TU in these binary systems. It may be noted that the presence of guanidinyl group of the amidinothiourea will enhance the polarisation of C= S bond and will be more nucleophilic than thiourea[101].

Many of the rubber compounding ingredients especially antioxidants and accelerators are reported to be toxic and there is much restriction in the use of these materials in rubber compounding[102-107]. Recently research work on safe accelerators has gained interest. Amidinophenyl thiourea is reported to be nontoxic and is used in many pharmaceutical applications[108,109]. This fact has also been taken into account in our investigations on these binary systems of rubber vulcanisation.

We first tried APT as a secondary accelerator along with TMTD/ MBTS/CBS as primary accelerator in NR gum compounds. Sulphur vulcanisation of natural rubber was carried out using standard compounding recipes and their properties were compared with control mixes containing thiourea as secondary accelerator and also different other binary combinations. Considering the fact that favourable cure characteristics were obtained in these systems, detailed investigations of these mixes were carried out. Tensile and other physical properties of the vulcanisates were studied and the network structures were estimated by using swelling studies. Although reasonable in physical strength, gum natural rubber vulcanisates are suitable only for very few commercial applications. In this context the effect of APT on filled natural rubber systems were also investigated. Considering the effectiveness of amidino phenyl thiourea in these various binary systems, the effect of change in concentration of APT on the cure characteristics of these systems was also investigated.

Rubber latex is a colloidal system and latex compounding is different from that of dry rubber[110]. Here the ingredients are added either as solutions or dispersions. There is no problem of scorching for latex systems and thus processing problems are less. But the stability of the compounded latex is to be considered. Usually ultra accelerators like dithiocarbamates and xanthates are used in latex processes. Philpott[92] studied several accelerator combinations such as TMTD, MBTS and CBS in various latex vulcanisation systems. The vulcanisation of latex using TMTD or CBS alone proceeds only at relatively higher temperature. At low temperatures (100°C or below) the reaction is very slow. Philpott showed that certain sulphur containing nucleophiles like thiourea, are able to activate vulcanisation by TMTD and CBS so that well cured vulcanisates may be prepared rapidly at or around 100°C. In our present study binary NR latex systems were prepared using TMTD and CBS as primary accelerators along with APT and latex films prepared were vulcanised at two different temperatures viz. 120 and 100°C. Various mixes were prepared with different concentrations of APT. The mixes requiring optimum concentrations of APT were studied in detail. Further the rheological behaviour of the compounded lattices were also investigated with a view to study the stability of the compounds in various systems at various temperatures.

It is to be noted that the mechanism of rubber vulcanisation depends on the type of elastomer used also[47]. Based on the favourable results obtained with NR we thought of trying APT in a synthetic rubber of the diene type viz. styrene butadiene rubber. SBR is slower curing than NR and needs either more accelerators or more active accelerator combinations. Scorch problems are less likely in SBR than in NR. Lack of crystallisation is responsible for the lower green strength and lower gum tensile strength of SBR. To overcome this type of behaviour incorporation of fine reinforcing fillers is necessary for synthetic rubbers. In our study also SBR vulcanisates were prepared with carbon black / precipitated silica as filler. Different mixes with varying concentrations of APT were tried in standard recipes in both gum and filled compounds. Gum formulations were prepared as investigations on reaction mechanisms are easier in such systems. The effect of change in concentration of APT on the cure characteristics was investigated and the results showed that as the concentration of the secondary accelerator increases the optimum cure time is seen to decrease accordingly. Considering the cure characteristics, practical cure systems with optimum concentration of APT have been developed for these SBR systems. Cure and vulcanisate properties of the experimental mixes were compared with those of control. To understand the variations in the physical properties of the various vulcanisates, chemical crosslinks were also estimated using the equilibrium swelling method.

Compounding, curing etc. of polar rubbers are different from other hydrocarbon rubbers[111-113]. The effectiveness of amidino phenyl thiourea in the compounding and vulcanisation of a typical polar rubber like polychloroprene is also tried in this study. Thiourea derivatives are popular in neoprene compounding. For example ethylene thiourea (NA22) is a common ingredient of compounding of this rubber. Metal oxides are also an important part of the curing system in CR. Considering the carbon backbone structure with double bonds, the possibility of sulphur crosslinking is also sometimes followed. In our studies we tried sulphur vulcanisation of Neoprene-W along with MgO and APT. TMTD-NA22 combination is used as control. Investigations were carried out to find out the effect of this amidinothiourea derivative on filled CR systems also. Carbon black and precipitated silica were used as fillers. It is also to be emphasised that conventional accelerator used in CR vulcanisation viz. ethylenethiourea (NA22) is reported to be toxic[114-116] while the amidinothiourea derivative is a non-toxic additive.

All rubbers have shortcomings in one or more properties. There are therefore technical reasons for blending, as it makes possible to obtain the right compromise in properties by blending different elastomers. The difficulties encountered in the processing and vulcanisation of some rubbers also emphasise the need for blending. Economic reasons can also be given for blending since appreciable price differences exist between different rubbers. For example, the resistance of polychloroprene to ozone is outstandingly good but its price is high and accordingly blending of CR with cheaper rubbers is normally beneficial for various applications. The mechanism of vulcanisation reaction in a single elastomer is bound to be different from that of a blend. In this context we attempted the use of APT as a secondary accelerator for the vulcanisation of NR-CR blends. A 50:50 blend of NR and CR was used and compounding ingredients were added after making a uniform mix of the elastomers. Microheterogenity may diminish when carbon black is added to the preblended elastomers[117]. Systems with varying concentrations of APT along with TMTD and other compounding ingredients were prepared in gum and carbon black filled blends. TMTD-TU and TMTD-NA22 binary combinations were taken as controls. Different cure characteristics and various physical properties of the experimental as well as control systems were investigated.

Chapter wise description of the above study is as given below:

Chapter 1 : General introduction on rubber vulcanisation and different accelerator systems.

Chapter 2 : Materials used and the various experimental procedures adopted in the present study.

Chapter 3:

Part A: Investigations on the effect of N- amidino N'- phenyl thiourea as a secondary accelerator in the sulphur vulcanisation of NR gum compounds.

Part B : Studies on the effect of APT in the vulcanisation of NR filled systems.

Chapter 4 : Investigations on the effect of APT as accelerator in NR latex systems.

Chapter 5:

Part A : Studies on the effect of the amidinothiourea derivative in binary systems for the vulcanisation of styrene butadiene rubber.

Part B : Studies on the effect of APT in the vulcanisation of SBR filled systems.

Chapter 6 : Effect of the amidino phenyl thiourea as an accelerator in the vulcanisation of polychloroprene rubber - gum and filled systems.

Chapter 7 : Investigations on the effect of APT in NR-CR blends.

Chapter 8 : Overall summary and conclusions of the present study.

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Chapter 2

EXPERIMENTAL TECHNIQUES

A detailed description of the experimental procedures adopted and the materials used in the present study is given in this chapter.

2.1.MATERIALS USED

2.1.1 Elastomers

2.1.1.A. Natural Rubber (NR)

Natural rubber confirming to ISNR-5 grade of Mooney viscosity (M_L 1+4, 100° C) equal to 85, used in the present study, is obtained from Rubber Research Institute of India, Kottayam. For a particular experiment rubber from the same lot has been used because the molecular weight, molecular distribution and non rubber constituents of natural rubber are known to be affected by clonal variation, season, use of yield stimulant and method of preparation[1,2]. Specification of the ISNR-5 grade rubber is given below.

Parameters	Limit
Dirt content, % by mass, max.	0.05
Volatile matter, % by mass, max.	1.00
Nitrogen, % by mass, max.	0.70
Ash, % by mass, max.	0.60
Initial plasticity, P_o, min.	30.00
Plasticity retention index	60.00

2.1.1.B. Natural Rubber Latex

High ammonia type 60% centrifuged natural rubber latex confirming to the specifications of the bureau of Indian standards, (BIS 5430-1981) used in this study. It was obtained from M/s Harrison Malayalam Ltd., Kochi. The properties of the latex used are given below.

Dry rubber content, % by mass	60.04
Total solid content, % by mass	61.05
Coagulum content, % by mass	00.03
Sludge content, % by mass	0.004
Alkalinity as ammonia, % by mass	00.73
KOH number	00.65
Mechanical stability time, sec	1075
Volatile fatty acid number	0.04
Copper content	Traces
Manganese content	Traces

2.1.1.C. Styrene Butadiene Rubber (SBR)

Styrene butadiene rubber used was Synaprene 1502 grade, obtained from Synthetics and Chemicals Ltd., Bareilly, U P, India. The Mooney viscosity (M_L, 1+4, 100° C) was 52. Other specifications are given below.

Volatile matter, % by mass	0.23
Ash, % by mass	0.24
Organic acid, %	5.53

Soap	Traces
Bound styrene	24.3

2.1.1.D. Chloroprene Rubber (CR)

Chloroprene rubber used in this study was W type (CR B 30) with Mooney viscosity [M_L (1+4), 100°C] 47. Du Pont, USA, supplied the rubber.

2.1.2 Other Ingredients

2.1.2.A. Zinc Oxide (activator)

Zinc oxide supplied by M/s Meta Zinc Ltd. Mumbai, was having the specifications given below.

Specific gravity	5.7
Zinc oxide content, (%)	98
Acidity (%) max.	0.4
Heat loss (2hrs. at 100°C) (%) max.	0.5

2.1.2.B. Stearic Acid (Co-activator)

Stearic acid was supplied by Godrej Soap (P) Ltd. Mumbai and had the following specifications.

Melting point	50-69°C
Acid number	185-210
Iodine number (max)	9.05
Specific gravity,	0.85
Ash (%) max.	0.10

2.1.2.C. Tetra methyl thiuram disulphide (TMTD) (Accelerator)

TMTD supplied by Rubochem. Industries, Kottayam had the following specifications.

Melting point	138°C
Specific gravity	1.405 ± 0.025
Ash (%) max	0.5
Moisture (%) max	1

2.1.2.D. Mercaptobenzthiazyl disulphide (MBTS) (Accelerator)

Bayer Chemicals Mumbai, supplied MBTS required in the present study. It had the following specifications

Specific gravity	1.51
Melting point	165°C

2.1.2.E. Cyclohexyl Benzothiazyl Sulphenamide (CBS) (Accelerator)

CBS used in the study was Santocure CBS supplied by Polyolefins Industries, Mumbai having the following specifications.

Ash (%) max.	0.5
Moisture (%) max.	0.5
Specific gravity	1.27

2.1.2.F. Thiourea (TU) (Accelerator)

Thiourea used for this study was of analytical grade supplied by Sisco Research Laboratory, Mumbai

Purity (%)	99.5
Sulphurated ash (max)	0.1

2.1.2.G. Ethylene Thiourea (NA22) (Accelerator)

Ethylene thiourea was obtained from National Physical and Oceanographic Laboratory, Cochin, India and was of commercial grade.

2.1.2.H. Sulphur (Crosslinking agent)

Standard Chemical Co. Pvt. Ltd Chennai supplied sulphur and had the following specifications.

Specific gravity	2.05
Acidity (%) max	0.01
Ash (%) max	0.1
Solubility in CS_2 (%) max	98

2.1.2.I. Magnesium Oxide (Cross linking agent)

Magnesium oxide used in the study was calcined light magnesia with specific gravity of 3.6, supplied by Central Drug house (P) Ltd., Mumbai.

2.1.2.J. Fillers

(a) High Abration Furnace Black (N 330) used in the study was supplied by M/s. Carbon and Chemicals India Ltd., Cochin. It had the following specifications:

Appearance	black granules
DBP absorption	102 ± 5 cc/100g
Pour density	376.0 Kg/m^3
Iodine number	82
Loss on heating (100°C, 1 hr) (%) max.	2.5

(b) Precipitated silica used was of commercial grade supplied by Rubo-Chem Industries Pvt. Ltd., Mumbai. The specifications of this are given below:

pH (5%aqueous solution)	6.3
Specific gravity	2.03
SiO_2 hydrate on dried sample, min	90%
Loss on heating (105°C, 2 hrs.)	5.5%

2.1.2.K. Process Oils

(a) Aromatic oil

Supplied by Hindustan Organic Chemicals Ltd., Kochi. It had the following specifications:

Specific gravity	0.98
Aniline point (°C)	43.00
Ash content % by mass	0.01
Viscosity gravity constant	0.96

(b) Naphthenic oil

Naphthenic oil was supplied by Indian Oil Corporation. It had the following specifications.

Colour	Light
Pour point (°C)	-20

Aniline point (°C)	78
Viscosity gravity constant (VGC)	0.85-0.9
Aromaticity	10-30

2.1.2.L. Dispersol F (Dispersing agent)

Dispersol F was used as the dispersing agent in the preparation of dispersions of solid ingredients. It was supplied by M/s. Indian Explosives Ltd., Kolkotta

2.1.2.M. Potassium Oleate (Stabilising agent)

It is an anionic soap soluble in water and is used as a stabilizing agent in latex. This was prepared from chemically pure oleic acid and potassium hydroxide. A 10% solution of potassium oleate is prepared by warming a mixture of 28.2g oleic acid and 5.6g potassium hydroxide with 270 ml water.

2.1.2.N. Other Chemicals Used

Other reagents such as toluene and benzene used for swelling studies, guanidine carbonate, phenyl isothiocyanate, sodium hydroxide, ethylene glycol etc. were all of analar grade.

2.2 EXPERIMENTAL METHODS

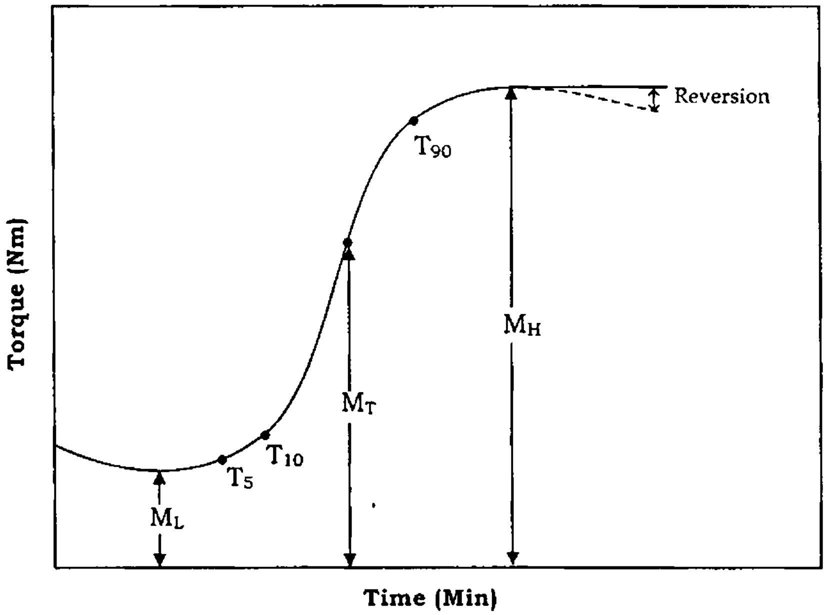
2.2.1 Compounding

Mixes were prepared on a laboratory size two roll-mixing mill (15 × 33 cm) as per ASTM designation D 3182-89. The mixing was carried out at a friction ratio of 1:1.22 for natural rubber 1:1.1 for styrene butadiene rubber and 1:1.25 for chloroprene rubber. The mill opening was set at 0.2 mm and the elastomer was passed through the rolls twice without banding. This was then banded on the slow roll with mill opening at 1.4 mm and was increased to 1.9 mm as the band become smooth. The temperature of the rolls was maintained at 70±5° C. The compounding ingredients were added as per procedure given in ASTM D 3184-89 and ASTM D 3182-89 in the following order: activator, filler, accelerator and curing agents. Before the addition of accelerator and sulphur the batch was thoroughly cooled.

After the completion of mixing, homogenisation of the compound was carried out by passing the rolled stock endwise six times at a mill opening of 0.8 mm. The mill is opened to give a minimum stock thickness of 6mm and the stock was passed through the rolls four times folding it back on itself each time.

2.2.2 Determination of Cure Characteristics

The cure characteristics of the mixes were determined using Goettfert elastograph model 67.85. It is a microprocessor controlled cure meter with a quick temperature control mechanism and well defined homogeneous temperature distribution in the die or test chamber. In this instrument, a specimen of definite size is kept in the lower half of the cavity, which is oscillated through a small deformation angle (±0.2). The frequency of oscillation is 50 per minute. The torque is measured on the lower oscillating die half. The following data can be obtained from a typical elastograph cure curve shown below:



i.	Minimum torque,	M_L	Torque obtained by the mix after homogenizing at the test temperature before the onset of cure.
ii.	Maximum torque,	M_H	This is the torque recorded after the curing of the mix is completed
iii.	Torque,	M_T	Torque at any time T
iv.	Optimum cure time,	T_{90}	It is the time taken for obtaining 90% of the maximum torque
v.	Scorch time,	T_{10}	This is the time for attaining 10% of the maximum torque.
vi.	Induction time,	T_5	It is the time taken for 5% vulcanisation
vii.	Cure rate index:	CRI	It is calculated as: $100/(T_{90}-T_{10})$ where T_{90} and T_{10} are the time corresponding to optimum cure time and scorch time respectively.

2.2.3 Moulding of Test Specimens

For determining the physical properties, the test specimens were moulded in standard moulds by compression moulding in an electrically heated hydraulic press having 30 x 30cm platens at a pressure of 11.764 MPa on the mould. The rubber compounds were vulcanised upto their optimum cure times and at specified temperatures. Mouldings were cooled quickly in water at the end of the curing cycle and stored in a cool and dark place for 24 hours and were used for subsequent physical tests. Additional curing time based on the sample thickness for samples having thickness higher than 6mm (compression set, abrasion resistance etc.) was given to obtain satisfactory mouldings.

2.2.4 Physical Tests on Vulcanisates

Physical tests carried out on vulcanisates such as tensile strength, tear strength, hardness, compression set, abrasion resistance etc. have been standardised in the rubber industry to design compounds to meet service conditions, to investigate product or process failures and to ascertain quality assurance for a quicker prediction of quality. The most commonly sought physical property of any rubber vulcanisate is its tensile strength and it is defined as the force per unit area of cross section which is required to break the test specimen, the condition being such that the stress is substantially uniform over whole of the cross section. The elongation at break (EB) is the maximum value of elongation expressed as a percentage of the original length. The value of tensile stress (force/unit area) required to stretch the test piece from the unstrained condition to a given elongation is called modulus or more accurately 'tensile stress at a given strain'.

Tensile strength in itself bears little relation to product service. But it is extremely useful for many comparative studies. High tensile strength coupled with a reasonable EB can be obtained with quality rubber mixes. They are also useful in the determination of cure properties of compounds. The cure conditions giving the highest tensile strength being widely adopted as optimum cure. Deterioration on ageing can be followed by the drop in the tensile strength. Effect of many compounding ingredients can be decided by tensile property studies. Finally, as a control test, it is valuable since any mistake in mixing or processing giving inferior product is indicated by a drop in tensile strength. For parameters described below, at least three specimens per sample were tested for each property and the mean values are reported.

(A) Tensile Properties: Modulus, tensile strength, and elongation at break

The tensile properties of the vulcanisates were determined on a 'Zwick' universal testing machine, model1445, using a crosshead speed of 500mm/min as per ASTM D 412-87 (method A). All the tests were carried out at 28 ± 2°C. Dumbbell specimens for the test were punched out of the moulded sheet along the mill grain direction using a dumbbell die (C-type). The thickness of the narrow portion was measured using a bench thickness gauge. The sample was held tight by the two grips, the upper grip being fixed. The tensile strength, elongation at break and modulus were evaluated and printed out after each measurement by the microprocessor.

(B) Tear Resistance

This test was carried out as per ASTM D 624 (1981) using unnicked, 90° angle test pieces. The samples were cut from the compression moulded sheets parallel to the mill grain direction. The test was carried out on the 'Zwick' universal testing machine. The speed of extension was 500mm/min and the test temperature 28 ± 2°C.

(C) Hardness

The hardness (Shore A) of the moulded samples was determined using Zwick 3114 hardness tester in accordance with ASTM D 2240 (1986). The tests were performed on unstressed samples of 30mm diameter and 6 mm thickness. A load of 12.5 N was applied and the readings were taken after 10 seconds of indentation after firm contact had been established with the specimen.

(D) Compression Set

The samples (6.25mm thick and 18mm diameter) in duplicate, compressed to constant deflection (25%) were kept for 22 hours in an air oven at 70°C. After the heating period, the samples were taken out, cooled at room temperature for half an hour and the final thickness was measured. The compression set was calculated as follows:

$$\text{Compression set (\%)} = 100 \times \frac{t_0 - t_1}{t_0 - t_s}$$

Where t_0 and t_1 are the initial and final thickness of the specimen respectively and t_s the thickness of the spacer bar used. The procedure used was ASTM D 395 (1982 method B)

(E) Abrasion Resistance

The abrasion resistance of the samples was determined using a DIN abrader (DIN 53516). Sample having a diameter of 6±0.2 mm and a thickness of 6mm was kept on a rotating sample holder and 10 N load was applied. Initially a pre-run was given for the sample and its weight taken. The weight after the final run was also noted. The difference in weight is the abrasion loss. It is expressed as the volume of the test piece abraded by its travel through 42 m on a standard abrasive surface. The abrasion loss was calculated as follows:

$$V = \frac{\Delta M}{\rho}$$

Where ΔM = mass loss, ρ = density of the sample and V = abrasion loss. The result is expressed in cm^3/hr.

(F) Rebound Resilience

Rebound resilience is measured using a vertical rebound resilience tester as per ASTM D 2632-88. A plunger weighing 28 ± 0.5 g is dropped from a height of 40 cm to the sample of thickness 12.5 mm and the rebound height is measured.

(G) Density

Density of the samples was determined as per ASTM D 297 (1981). In this method the weight of the specimen in air was first noted and then specimen was immersed in water and its loss of weight in water was determined. The density of the sample was calculated as:

$$\text{Density} = \frac{\text{Weight of specimen in air} \times \text{density of water}}{\text{Loss of weight of specimen in water}}$$

Density of water is taken as $1\ g / cm^3$

(H) Ageing Studies

Ageing studies were carried out according to ASTM D 573-88. Dumbbell samples were punched out from the vulcanised sheets and kept in air oven at predetermined temperatures for specified periods. Physical properties like tensile strength, elongation at break, modulus etc. were determined after ageing. Knowing the values of these tests before ageing, the retention of these properties was calculated for assessing the effect of ageing.

2.2.5 Chemical Test Methods

Determination of Chemical Crosslinks of the Vulcanisates

The crosslink density of the vulcanisates was determined from the equilibrium swelling data as follows:

Approximately 0.2 gm of sample was punched out from the central portion of the vulcanisate and the accurately weighed sample was allowed to swell in suitable solvent for 24 hrs. The outer portion of the swollen sample was then dried using a filter paper and then weighed. The solvent was removed in vacuum by placing in an oven at 50°C for 22hrs.The deswollen weight was determined. The volume fraction of rubber, in the deswollen network was then calculated by the method reported by Ellis and Welding[3,4] from the following equation.

$$Vr = \frac{(D - FT)\rho_r^{-1}}{(D - FT)\rho_r^{-1} + A_0\rho_s^{-1}}$$

Where T is the weight of the test specimen, D the deswollen weight, F the weight fraction of the insoluble components of the vulcanisates, A_0 the weight of the absorbed solvent corrected for the swelling increment; ρ_r and ρ_s are the density of rubber and solvent respectively. Knowing the value of Vr the total cross-link density, $1/2M_c$ was calculated using Flory-Rehner equation[5,6].

$$-[\ln(1-Vr) + Vr + \chi Vr^2] = \frac{\rho r\ Vs\ (Vr)^{1/3}}{Mc}$$

Where Vs = molar volume of solvent, χ = the parameter characteristic of the interaction between rubber and solvent, Mc=the number average molecular weight of the rubber chains between crosslinks.

The values of the parameter χ taken for calculation were the following[7]:

For	NR-toluene	=	0.42
	SBR-toluene	=	0.32
	CR-benzene	=	0.26

Although natural rubber gum vulcanisates have received much attention, fewer details are available on network structure of filled vulcanisates. This is because of the uncertainties introduced by the filler - rubber interactions. The volume fraction of rubber (Vr) here is calculated assuming that the filler does not swell. It is then converted to V_{r0} (the value V_r would have had in the absence of filler) according to Cunneen and Russel[8] as:

$$\frac{V_{r0}}{V_r} = ae^{-z} + b$$

Here a & b are constants characteristic of the system and ^{z} is the weight fraction of the filler in the vulcanisate. The values for a and b for HAF black filled systems are ; a = 0.56 and b = 0.44. The corresponding values for silica filled system are a = 1.41and b = -0.41[9]. The values of V_{r0} were then substituted in the Flory-Rehner equation in place of Vr to obtain the crosslink density

2.2.6 Compounding of Latex

Preparation of Dispersions

The solid ingredients were added into latex as solutions/dispersions. The materials are made to disperse in water by grinding action and the dispersing agents prevent the dispersed particles from reaggregating. The quantity of the dispersing agent to be used for preparing dispersions depends on the nature of the materials to be dispersed. For very fine particle size ingredients the quantity of dispersing agent required is about 1% by weight whereas for materials like sulphur 2 to 3 % is required. There are different types of grinding equipments like ball mill, ultrasonic mill and attrition mill. In the present study a ball mill was used for making the dispersions of the ingredients.

A ball mill consists of a cylindrical container in which the slurry is placed together with a charge of balls. When the mill is working the balls are carried round with the container a short way and then cascade. It is this process of cascading which causes the particles of slurry to be comminuted. The efficiency of the mill depends on the speed of rotation of the jar, size and material of the ball, viscosity of the slurry, period of ball milling, etc.

The formulations of the dispersions used in this study are given below:

(i) Sulphur dispersion (50%)

Sulphur	100
Dispersol F	3
Deionised water	97

Ball milled for 72 hours

(ii) ZnO dispersion (50%)

ZnO	100
Dispersol F	3
Deionised water	97

Ball milled for 24 hours

(iii) APT dispersion (10%)

APT	10.00
Dispersol F	0.15
Water (deionised)	89.85

Ball milled for 24 hrs.

(iv) TMTD dispersion (33%)

TMTD	100.00
Dispersol F	1.50
Water (deionised)	198.50

Ball milled for 24 hrs.

(v) CBS dispersion (33%)

CBS	100.00
Dispersol F	2.5
Water (deionised)	197.50

Ball milled for 24 hrs.

De-ammoniation of Latex

High ammonia (HA) type concentrated latex was de-ammoniated to 0.23% by stirring in a laboratory type de-ammoniation tank for 3 hours.

Otherwise the high ammonia content in latex will create problems during conversion to solid products or in the stability of the latex compound in presence of zinc oxide[10]. The concentration of ammonia in latex was estimated as per ASTM D 1076-88.

Compounding

The mixing of ingredients was done as per the order given in the respective chapter. The stabilisers were first added as solutions, followed by the other ingredients. Mixing was done in a glass vessel and stirring for homogenisation was done using a laboratory stirrer at 10-20 rpm. It was occasionally stirred during storage also in order to prevent settling of the ingredients.

Maturation

The latex compound was matured at ambient temperature for 24 hours. This ensures the compound to free itself of air entrained during the preparation and allows the stabilisers to distribute themselves uniformly throughout the aqueous and dispersed medium. During this maturation period important changes takes place[11]. Absorption of vulcanisation ingredients into the rubber particle surface commences and becomes a continuous process with time and temperature. Further it allows time for the reaction of ammoniated latex with zinc oxide for getting uniform physico- chemical properties.

Preparation of Latex Films

Latex films were cast on glass dishes using the latex compound as described by Flint and Naunton[12]. The size of the glass dishes was 6" × 6" and about 25 ml of the latex compound was poured and uniformly distributed so that a film of thickness 1-1.25mm was obtained upon drying. These glass dishes with the latex compound were placed on levelled tables and dried overnight.

Vulcanisation of Latex Films

The vulcanisation of latex films was carried out in a laboratory type air oven at 120 and at 100°C. The time for optimum cure was determined by vulcanising the film for different duration of time and determining the tensile strength of the vulcanisate in each case. The optimum cure time was taken as the time for attaining maximum tensile strength.

2.2.7 Rheological Study of Latex

A Haake viscometer VT550 was used to study the effect of temperature and shear rate on viscosity. This has been designed to meet the most sophisticated requirements of continuous shear rheometry with 60 different rotational speed steps covering a wide range from 0.5 rpm to 800 rpm. The functional units consist of viscotester, power supply unit, temperature control vessel, sensor system and Pt 100 temperature sensor. The equipment operates over a temperature range from –30 to 150°C. Thirty different sensor systems are available. Sensor system NV was used for this study.

Latex is located in the measuring gap of the sensor system. Rotational speed, measuring time, number of measuring points and measuring temperature are preset. The rotor is rotated at the preset speed range. The latex exert a resistance to the rotational movement due to its viscosity which become apparent as a torque value applied on the measuring shaft of the VT550. The computer attached to the system calculates the relevant values for the following factors from the measured variables of speed, torque and sensor geometry.

Viscosity η in mPa.s

Shear rate γ in s^{-1}

Shear stress τ in Pa

The temperature T is also measured in °C. In the present study measurements were taken at 25, 35 and 45° C at shear rates ranging from 1 to 150 s^{-1}. The rheological behaviour of the latex has been analysed using Power law equation.

τ = $K\gamma^n$, where τ =shear stress (Pa)
K = viscosity index
γ = Shear rate (s^{-1})
n = flow index

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Chapter 3

STUDIES ON NEW BINARY SYSTEMS CONTAINING AMIDINO PHENYL THIOUREA IN SULPHUR VULCANISATION OF NATURAL RUBBER

Natural rubber is the preferred polymer in many areas of rubber use. This is because of its superior building tack, green stock strength, better processing, high resilience and excellent dynamic properties. The most important commercial source of natural rubber is the latex from *Hevea brasiliensis*. This latex is a weak lyophilic colloidal system consisting of particles of rubber hydrocarbon and non-rubbers suspended in an aqueous serum phase. The solid part contains approximately 94% rubber hydrocarbon, 3.5% proteins and 2.5% of other materials including fatty acids and resins[1]. Purified natural rubber hydrocarbon is a long chain polymer made up of cis-1,4 polyisoprenoid units arranged in a highly stereo regular manner. The molecular weight of the polymer ranges from 10^5 to 10^6 and it varies widely[2]. Natural rubber has high structural regularity and tends to crystallise on stretching. This strain induced crystallisation gives it the unique high tensile strength in gum and non-reinforcing filled vulcanisates.

The raw polymer, while at room temperature having considerable strength, elasticity and resilience, is sensitive to hot and cold conditions and is liable to oxidise to a sticky product. Compounding and vulcanisation transforms this raw rubber into a range of materials suitable for varied applications. During vulcanisation, the long chain rubber molecules become crosslinked to form three dimensional structures which restrict the mobility of molecules and gives a product having reduced tendency to crystallise, improved elasticity, and substantially constant modulus and hardness characteristic over a wide range of temperature[3]. The extent of changes in properties is governed by the choice of compounding ingredients added to rubber to bring about the vulcanisation process and also the conditions of vulcanisation. The vulcanisation of NR may be effected with the aid of sulphur, organic peroxides, synthetic resins and other poly functional reagents and also by ionising radiations[4]. Among the many available vulcanisation agents for rubber, sulphur is the most widely used, for several reasons[5]. Sulphur vulcanisation of natural rubber forms the subject of numerous publications. Accelerated sulphur formulations are the most common vulcanisation systems used in industrial applications. Natural rubber is usually vulcanised at a temperature around 150°C with a combination of sulphur (1-3 phr.), one or more accelerators (0.5-1.5 phr.), zinc oxide (3-5 phr.), fatty acid (1-3 phr.) and other additional ingredients.

The nature of accelerators used influence to a large extent, the course of vulcanisation. Among thiuram accelerators tetramethyl thiuram disulphide (TMTD) is the fastest and safer one. They have to be activated with zinc oxide. Inclusion of fatty acids improves the degree of vulcanisation. Another class of accelerators widely used in NR are the thiazoles. These are the accelerator class of highest economic importance. Mercapto benzothiazole and its derivatives belong to this class. These thiazole accelerators can be subdivided into mercapto accelerators (eg: MBT, MBTS, ZMBT etc.) and benzothiazole sulphenamide accelerators (eg: CBS, TBBS, MBS etc.). Compared to thiuram accelerators mercapto accelerators give compounds with higher processing safety. Dibenzothiazyl disulphide (MBTS) has a delayed onset of vulcanisation based on the fact that MBTS has to decompose thermally to MBT fragments before vulcanisation begins and this in turn gives higher processing safety. Benzothiazole sulphenamide accelerators are considered as derivatives of mercaptobenzothiazole where an amine is oxidatively bound to the mercapto sulphur. These accelerators become active as the amines are split off during vulcanisation and the base activates mercaptobenzothiazole as it is formed. Consequently sulphenamides produce a retarded vulcanisation start and therefore improved processing safety. Addition of zinc oxide is necessary for the activation of all these accelerators.

Thiourea (TU) and its derivatives have also been developed as powerful secondary accelerators in the vulcanisation of natural and synthetic rubbers. They give good synergistic behaviour with thiazole and thiuram accelerators. In NR for example, the accelerator MBTS gives very slow cross linking by itself, even if it is heavily dosaged. If however, substituted or unsubstituted thiourea is used very rapid vulcanisation occurs at normal temperature. The vulcanisates have reasonably high tensile strength and good resistance to ageing[6]. The effects of combinations consisting of thiourea and conventional accelerators or vulcanising agents have been investigated thoroughly. Because of the high scorchiness practical use of these combinations became difficult. Thiourea derivatives act as effective secondary accelerators with TMTD or CBS, especially in latex vulcanisation[7]. Philpott suggested an ionic mechanism in these systems where the S-S bond or S-N bond of the primary accelerator is cleaved by the nucleophile produced from thiourea. But no conclusive proof has been given. Earlier work in our laboratory indicates that different derivatives of thiourea can act as effective secondary accelerators in the sulphur vulcanisation of natural and synthetic rubbers and it can be used in practical rubber product manufacture[8-10]. Also the results were correlated to the mechanism of the activity of secondary accelerators in these binary systems. The present work aims at compounding, vulcanisation and study of vulcanisate properties of different binary systems using the amidinothiourea derivative viz. N-amidino N'-phenyl thiourea (APT). The important considerations of the present study with natural rubber systems are the following:

One of the aims was to get further proof with regard to the theory of nucleophilic reaction in such binary systems. A new method is adopted here, as monitoring a vulcanisation reaction is otherwise difficult. We have evaluated the rate of the reaction based on the nucleophilic character of the secondary accelerator used. The effect of APT as a secondary accelerator was compared with that of TU in these binary combinations where thiourea is taken as control. By virtue of the presence of guanidinyl group in amidinothiourea derivative, (Ref: chapter I p.20) APT is more nucleophilic than TU and is expected to behave more effectively as a secondary accelerator. Polarisation of C=S bond to create a nucleophilic centre is more easy in APT due to the presence of the guanidinyl group in it.

Non-toxic nature of APT is another consideration in selecting it as an accelerator in these vulcanisation systems of natural rubber. Many of the rubber compounding ingredients especially antioxidants and accelerators are reported to be toxic. Recently research work on safe accelerators has gained interest. APT is reported to be non-toxic and is used in many pharmaceutical applications. In this context we thought it worthwhile to see whether APT can be used in practical cure systems useful in rubber product manufacture as a non-toxic accelerator. The effect of APT in binary systems containing MBTS, TMTD and CBS as primary accelerators in NR gum and filled systems is described in this chapter. Gum formulations were tried, as reaction mechanism will be more specific with unfilled compounds. Conventional binary combinations like TMTD-MBTS, TMTD-CBS, MBTS-CBS etc. are taken as reference combinations and their properties are also compared with those of APT systems.

Although reasonable in physical strength, gum natural rubber vulcanisates are suitable only for very few commercial applications. Fillers are incorporated while compounding for improved processability, reinforcement, and/or cost reduction. The effect of filler on rubber vulcanisate depends on its physical properties such as particle size, surface area, surface reactivity, electrical charge on the particle etc.[11-13]. By far carbon blacks are the most effective reinforcing fillers in the rubber industry[14,15]. The functional groups present at the carbon black surface contribute, along with the microstructure, to the surface activity that is known to be an important parameter for the rubber reinforcing properties[16]. Coming closer to carbon blacks in the reinforcing properties is precipitated silica which is the best non-black reinforcing filler. Silica has fine particle size as that of carbon black and has an extremely reactive surface. One distinct advantage imparted by silica to many rubbers is the increased resistance to air ageing at elevated temperatures[17]. In our studies on NR with APT we used carbon black (N 330) and precipitated silica (Vulcasil-S) as reinforcing fillers.

PART - A
3.1 INVESTIGATIONS ON NR GUM FORMULATIONS

3.1.1 Experimental

Synthesis of N-amidino N'-phenyl thiourea (APT)

APT was synthesised according to Furukawa et al.[18]. Guanidine carbonate (0.05 mol.) and powdered sodium hydroxide (0.01mol.) were suspended in acetonitrile (50ml). Phenyl isothiocyanate (0.1mol.) was added drop wise with stirring till the smell of thiocyanate vanished. The reaction mixture was then diluted with cold water and the precipitate was filtered out. It was crystallised from aqueous alcohol (MP 174°C).

In this study we tried the above amidinothiourea derivative as a secondary accelerator in the vulcanisation of NR gum compounds along with MBTS/TMTD/CBS. Thiourea binary systems containing 1:1 molar combinations of MBTS-TU, TMTD-TU, and CBS-TU were taken as references for comparing the cure properties and to see whether the reaction follows the nucleophilic pattern. To see whether practical cure systems useful in rubber industry can be prepared with APT, different compounds were prepared and properties of the vulcanisates were compared with other conventional systems containing different combinations of MBTS, TMTD and CBS. Mix with APT alone without any other accelerator was also formulated for comparing the cure properties.

Tables 3.1.1-3.1.3 show the composition of various mixes prepared. In all these mixes zinc oxide (5 phr.), stearic acid (2phr.) and sulphur (1.5 phr.) were incorporated as activator, co-activator and vulcanising agent respectively. Accelerators were added in molar equivalents. An attempt was made to find the optimum concentration of APT required in these various binary combinations under investigation. Mixes A_1-A_4 are MBTS-APT systems containing varying amounts of APT ranging from 0.25 to 1.5 molar equivalent with one molar equivalent of MBTS, B_1-B_4 used 0.25, 0.5, 1 and 1.5 molar equivalent of APT with one molar equivalent of TMTD; and C_1-C_4 contain varying amounts of APT as above with one molar equivalent of CBS. R_1, R_2 and R_3 contain 2 molar equivalents of MBTS, TMTD and CBS respectively. Mix R_6 is MBTS-TU, R_7 is TMTD-TU and R_8 is CBS-TU in 1:1 molar ratio. Mix A_5 contains 2 molar equivalents of APT alone as accelerator. Conventional binary combinations in 1:1 ratio such as MBTS-TMTD (R_4) and CBS-TMTD (R_5) were also investigated.

Table 3.1.1 Formulations of the mixes containing MBTS

Ingredients	**A_1**	**A_2**	**A_3**	**A_4**	**A_5**	**R_1**	**R_4**	**R_6**
Natural rubber	100	100	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2
MBTS	1.66	1.66	1.66	1.66		3.32	1.66	1.66
TMTD	–	–	–	–	–	–	1.2	–
TU	–	–	–	–	–	–	–	0.38
APT	0.243	0.485	0.970	1.455	1.94	–	–	–
Sulphur	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5

Table 3.1.2 Formulations of mixes containing TMTD

Ingredients	**B_1**	**B_2**	**B_3**	**B_4**	**R_2**	**R_5**	**R_7**
Natural rubber	100	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2
TMTD	1.2	1.2	1.2	1.2	2.4	1.2	1.2
CBS	–	–	–	–	–	1.32	–
TU	–	–	–	–	–	–	0.38
APT	0.243	0.485	0.970	1.455	–	–	–
Sulphur	1.5	1.5	1.5	1.5	1.5	1.5	1.5

Table 3.1.3 Formulations of mixes containing CBS.

Ingredients	**C_1**	**C_2**	**C_3**	**C_4**	**R_3**	**R_8**
Natural rubber	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2
CBS	1.32	1.32	1.32	1.32	2.64	1.32
TU	–	–	–	–	–	0.38
APT	0.243	0.485	0.970	1.455	–	–
Sulphur	1.5	1.5	1.5	1.5	1.5	1.5

All the mixes were prepared on a laboratory size two roll mixing mill according to ASTM D 3182-89 (details are as given in chapter 2). The cure characteristics of the mixes were determined using a Goettfert elastograph (model 67.85) at 150°C. The compounds were then vulcanised up to the optimum cure time in an electrically heated laboratory type hydraulic press at 150°C at a pressure of 11.76 MPa. The tensile properties of the vulcanisates were determined on a Zwick Universal Testing Machine model 1445. Dumbbell tensile test specimens were punched out of the test sheets along the mill grain direction. To measure the tear resistance angular test specimens were used (ASTM D 624-86). Heat ageing resistance of the vulcanisates was determined after ageing the samples for 48 hours at 70°C in a laboratory air oven (ASTM D 573 - 88). Compression set and hardness were tested as per ASTM D 395 – 89 (method B), and D 2240 – 86 respectively. Abrasion resistance was measured using DIN abrader (DIN 53516). The values for the tensile properties (both before and after ageing) are reported in tables 3.1.7 - 3.1.9. Other physical properties studied are reported in tables 3.1.10 - 3.1.12. The concentration of the chemical crosslinks (crosslink density) of the various vulcanisates was determined from the equilibrium swelling data as per details reported in chapter 2.

3.1.2 Results and Discussion

Cure characteristics

Geottfert elastograph is used for evaluating the cure characteristics of various mixes. The cure curves obtained are given in figs. 3.1.1-3.1.3 and the corresponding cure characteristics are reported in tables 3.1.4-3.1.6. The results obtained in these studies indicate that APT shows very good acceleration activity with MBTS/TMTD/CBS as primary accelerator. Considering the MBTS-APT binary systems (table 3.1.4 & fig. 3.1.1) their cure characteristics are found to be better than those of the reference mixes. The stocks, A_3, R_1, R_4 and R_6 contain equimolar quantities of accelerators. The optimum cure time of mix A_3 containing MBTS and APT in 1:1 molar equivalents is found to be 3.5 min. which is much lower than that of the control mix with TU (8.5min.). APT being more nucleophilic than TU, this result supports a nucleophilic reaction mechanism in these systems.

Compared to other conventional systems also the corresponding APT system shows much lower t_{90} value (fig. 3.1.4). The cure rate for the experimental mix A_3 is also correspondingly much higher than the other systems. But the scorch time and induction time values of the APT mix containing equimolar amount with MBTS is comparatively less which may cause processing problems. Considering the optimum cure time and scorch time, the binary system containing 0.5 molar equivalent of APT with one molar equivalent of MBTS can be considered to be the optimum level. Addition of APT initially reduces the optimum cure time and scorch time considerably, which remains practically unaffected with higher loading (Fig. 3.1.5). Cure rate index (CRI) is a measure of the speed with which the cure reaction takes place and is given by the equation CRI = $100/(t_{90}-t_{10})$ where t_{90} and t_{10} are the optimum cure time and scorch time respectively. The CRI values are found to increase with increasing dosage of APT. The curing of mix A_6 containing APT alone as accelerator was very slow as indicated by the cure curve (fig. 3.1.1). Thus APT alone is unable to function as an accelerator and hence the mix was not studied further.

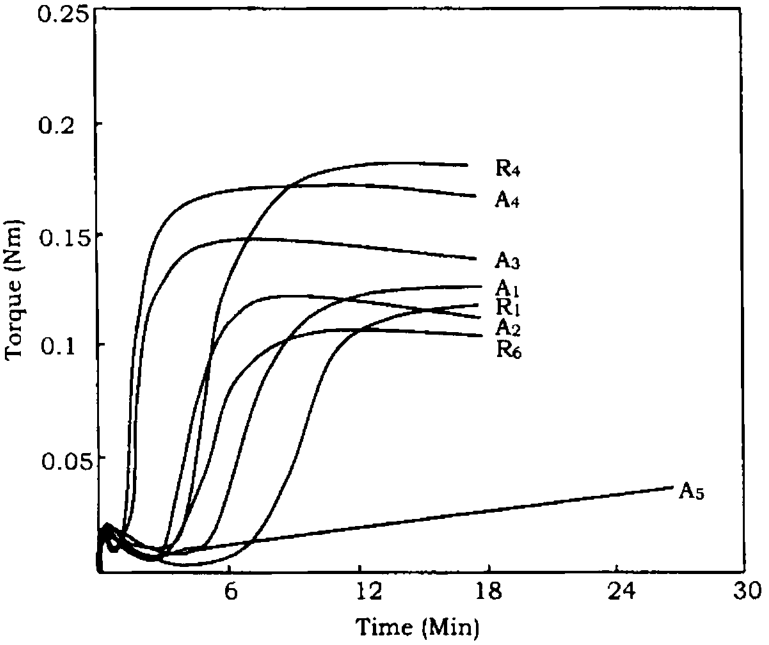


Fig. 3.1.1 Cure curves of mixes with MBTS

Table 3.1.4. Cure characteristics of mixes with MBTS

Mix No.	A_1	A_2	A_3	A_4	R_1	R_4	R_6	A_5
Optimum cure time, t_{90} (min.)	10.30	6.70	3.50	3.40	13.20	7.8	8.50	25.20
Elastographic scorch time, t_{10} (min.)	5.20	3.30	1.30	1.20	7.20	3.8	3.70	2.70
Induction time, t_5 (min.)	4.50	3.00	1.10	1.00	6.00	3.5	3.30	1.70
Cure rate index	19.6	29.4	45.45	45.45	16.67	25.0	20.83	4.44
Minimum torque (Nm)	0.005	0.011	0.007	0.005	0.004	0.032	0.007	0.004
Maximum torque (Nm)	0.128	0.122	0.146	0.171	0.125	0.183	0.108	0.042

In the case of TMTD-APT binary systems, it can be seen from table 3.1.5 that the optimum cure time for the system B_3 containing TMTD -APT is less than that of the control mix R_7 containing TU in similar proportion. Compared with other conventional binary systems also the APT systems show lesser t_{90} values. A corresponding increase in cure rate is also observed. These results clearly indicate the acceleration effect of phenyl amidinothiourea in vulcanisation of natural rubber using TMTD-sulphur systems. A comparative study of the equivalent mixtures of TMTD-APT (mix B_3) with TMTD–TU (mix R_7), TMTD-MBTS (mix R_4) and TMTD-CBS (mix R_5) reveals that the least optimum cure time is shown by TMTD- APT system. However, along with the reduction in optimum cure time the scorch time also decreases, which affects the scorch safety of the compound. Optimum dosage of APT required in these systems has also been estimated based on t_{90} and t_{10} values. Mix B_2, containing 0.5 molar APT with 1 molar equivalent TMTD can be considered to be optimum. The amidinothiourea derivative being more nucleophilic than thiourea, these cure values point to a nucleophilic reaction mechanism in the sulphur vulcanisation of these natural rubber systems also. The cure behaviour of CBS-APT combination is also found to be better compared to the other reference systems evaluated (table 3.1.6 and fig. 3.1.3). It is seen that as the concentration of APT increases the optimum cure time (t_{90}) decreases significantly. Maximum torque value is also found to be higher for the APT mixes. Here also one disadvantage noticed is the low scorch time and induction time at higher dosages of the secondary accelerator.

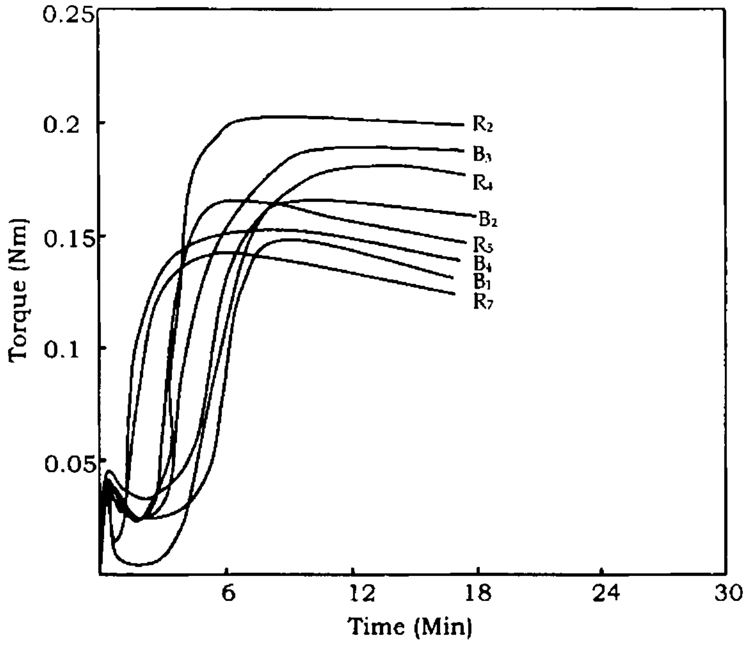


Fig. 3.1.2 Cure curves of mixes with TMTD

Table 3.1.5 Cure characteristics of mixes with TMTD

Mix No.	B_1	B_2	B_3	B_4	R_2	R_4	R_5	R_7
Optimum cure time, t_{90} (min.)	4.3	2.3	1.3	1.3	4.2	7.8	6	2.2
Elastographic scorch time, t_{10} (min.)	2.3	1.7	0.5	0.48	2.7	3.8	2.6	1.6
Induction time, t_5 (min.)	2.2	1.5	0.48	0.38	2.3	3.5	2.5	1.5
Cure rate index	49.5	166.7	125	142.86	66.69	25	29.41	166.67
Minimum torque (Nm)	0.013	0.005	0.026	0.027	0.026	0.032	0.004	0.018
Maximum torque (Nm)	0.168	0.170	0.211	0.165	0.200	0.183	0.186	0.141

Table 3.1.6 Cure characteristics of mixes with CBS

Mix No.	**C_1**	**C_2**	**C_3**	**C_4**	**R_3**	**R_5**	**R_8**
Optimum cure time, t_{90} (min.)	5.4	3.2	2.5	2.0	8.2	6.0	3.2
Elastographic scorch time, t_{10} (min.)	2.8	1.9	1.0	0.6	4.0	2.6	1.7
Induction time, t_5 (min.)	2.6	1.8	0.8	0.5	3.8	2.5	1.7
Cure rate index	38.46	76.92	66.67	71.43	23.8	29.4	66.7
Minimum torque (Nm)	0.040	0.029	0.008	0.016	0.004	0.012	0.023
Maximum torque (Nm)	0.173	0.112	0.193	0.183	0.206	0.186	0.126

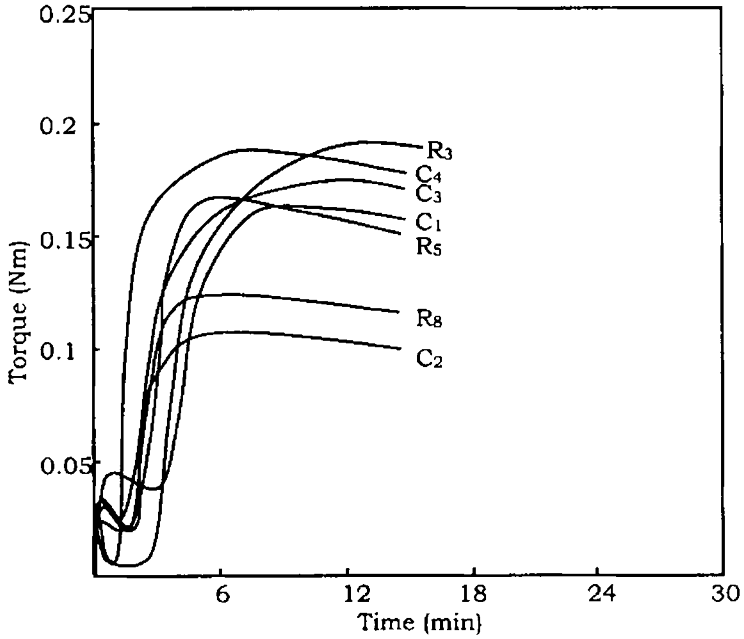


Fig. 3.1.3 Cure curves of mixes with CBS

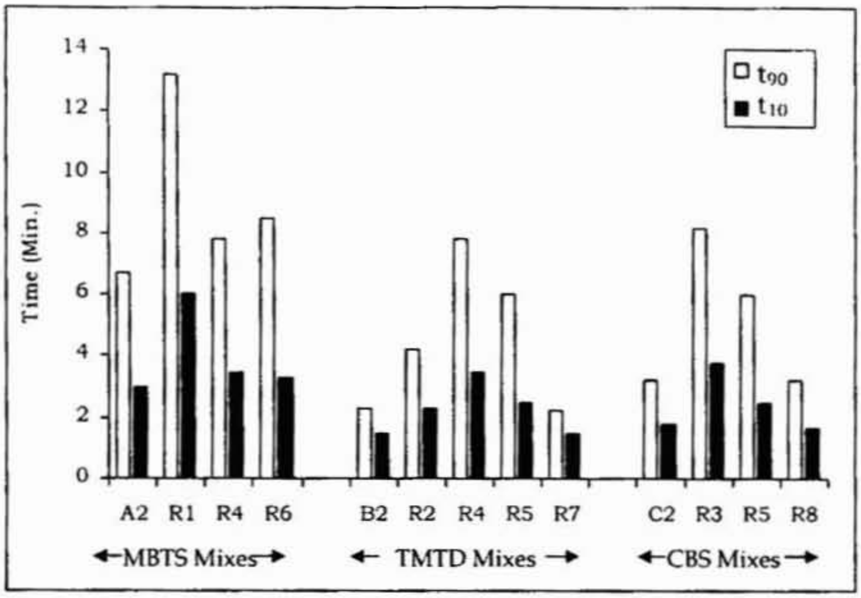


Fig. 3.1.4 A comparative study of optimum cure time and induction time of mixes containing optimum dosage of APT with references

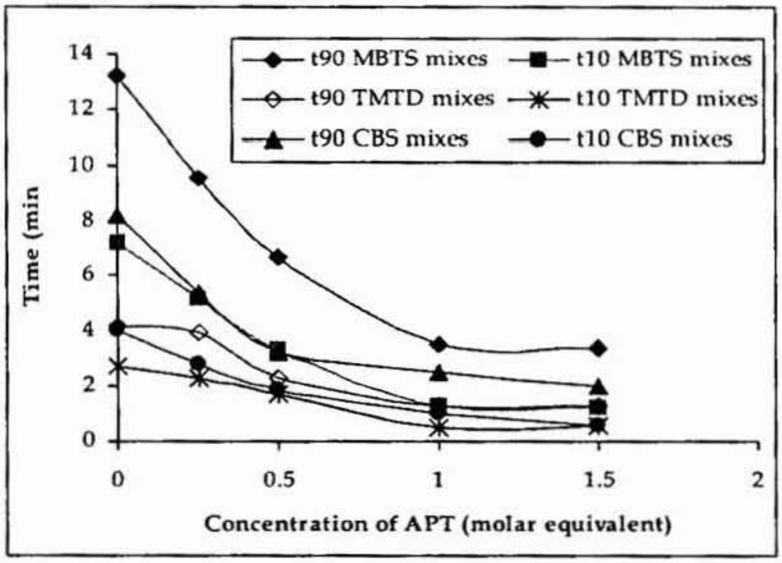
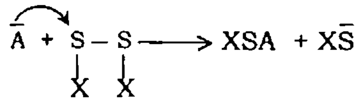
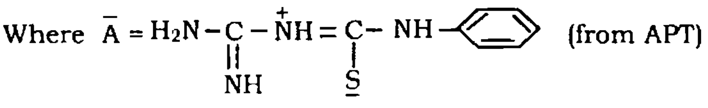


Fig. 3.1.5 Variation of optimum cure time and scorch time with concentration of APT

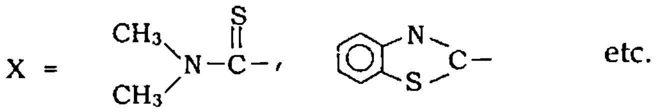
After investigating various formulations with TMTD, Manik and Banerjee[19] suggested that the TMTD-S-ZnO-stearic acid system in NR vulcanisation is predominantly polar. According to Moore et al.[20] presence of secondary accelerator like thiourea is found to increase the rate of formation of the thiuram polysulphides required in the ultimate crosslinking reaction. N-amidino N'-phenyl thiourea (APT) is also expected to behave in a similar way and the S-S bond cleavage can be represented as:



$$\bar{A} + \underset{X}{S} - \underset{X}{S} \longrightarrow XSA + X\bar{S}$$



and



Here $\bar{A}$ serves as a nucleophile. The nature of the attached group will help the polarization of C=S bond in it thereby producing negative charge on the sulphur atom.

The speed with which the above reaction takes place depends on the nucleophilicity of the attacking reagent. APT being more nucleophilic than TU, the APT systems show faster reaction and hence lower induction time and optimum cure time. (figs. 3.1.4 & 3.1.5).

Tensile properties

Tensile properties of rubber vulcanisates are of much importance. One obtains a characteristic sinusoidal stress-strain curve when rubber is extended up to sufficient deformations. Rupture can occur under various imposed mechanical conditions. Tensile strength is the simplest for measurement and for this a standard test specimen is subjected to a uniform uniaxial tensile stress. Natural rubber has very good gum strength due to the strain induced crystallisation. This behaviour is greatly beneficial as far as the mechanical properties are concerned. The correct choice of vulcanisation system is also important in getting good tensile strength in the rubber vulcanisates.

We have evaluated the tensile properties of the vulcanisates obtained from different systems mentioned earlier except those containing 0.25 molar equivalent of APT, which showed somewhat higher optimum cure time. These test results are given in tables 3.1.7 - 3.1.9. The effect of variation of the amount of APT on tensile strength, modulus and elongation at break, (before and after ageing) for MBTS-APT, TMTD-APT and CBS-APT are shown graphically in figs. 3.1.6 - 3.1.8. Regarding the tensile properties of MBTS-APT vulcanisates the maximum tensile strength is shown by the combination having one molar equivalent APT. These values are also seen to be much higher than those of the corresponding thiourea systems (table 3.1.7). 100% modulus and elongation at break values of the experimental systems are also found to be better compared to the thiourea binary combinations. For TMTD-APT and CBS-APT systems mixes containing optimum dosages of APT show maximum tensile strength values (tables 3.1.8-3.1.9). The experimental systems also give values comparable with other conventional systems like MBTS-TMTD and TMTD-CBS. After ageing properties are also found to be satisfactory for the mixes containing APT.

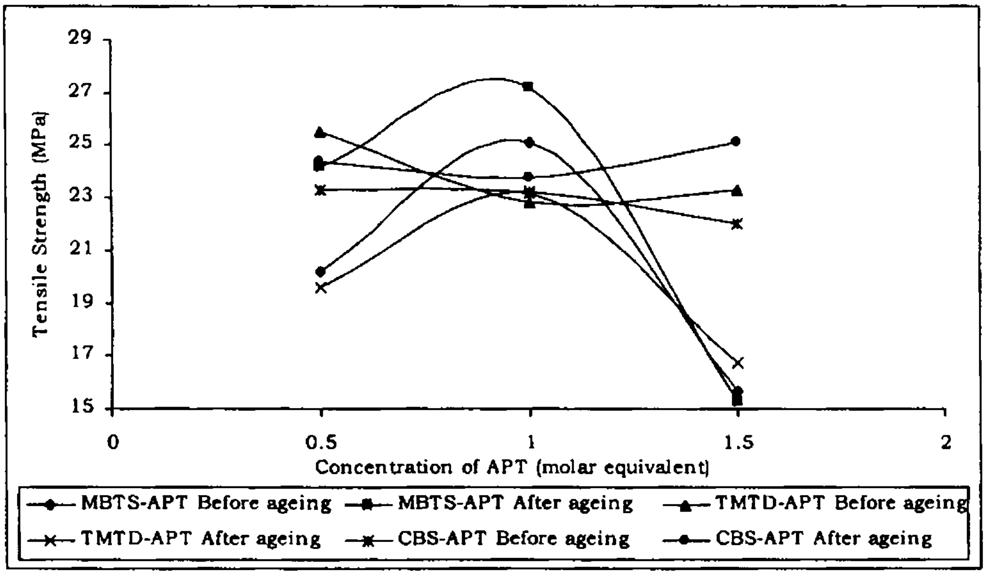


Fig.3.1.6 Variation of tensile strength of vulcanisates with the concentration of APT

Table 3.1.7 Tensile properties of vulcanisates containing MBTS.

Mix. No.	Tensile Strength (MPa)			100% modulus (MPa)			Elongation at break, (%)		
	Before ageing	After ageing	Retention %	Before ageing	After ageing	Retention %	Before ageing	After ageing	Retention %
A_2	20.17	24.13	119.63	0.83	0.95	114.46	866.01	731.87	84.51
A_3	25.09	27.17	108.29	1.16	1.12	96.55	739.87	760.02	102.72
A_4	15.67	15.26	97.38	1.09	0.97	88.99	766.31	640.08	83.53
R_1	22.86	25.04	109.54	1.21	0.98	80.99	752.65	733.22	97.42
R_4	2.03	1.72	84.73	1.63	1.52	93.25	129.55	114.3	88.02
R_6	19.67	19.89	101.12	0.93	0.72	77.42	743.10	836.75	112.30

Table 3.1.8 Tensile properties of vulcanisates containing TMTD.

Mix. No.	Tensile Strength (MPa)			100% modulus (MPa)			Elongation at break (%)		
	Before ageing	After ageing	Retention %	Before ageing	After ageing	Retention %	Before ageing	After ageing	Retention %
B_2	25.51	19.67	77.12	1.49	1.24	83.22	661.37	604.55	91.41
B_3	22.83	23.14	101.33	1.01	1.15	113.86	719.55	745.76	103.56
B_4	23.30	16.72	71.76	0.97	0.92	94.85	749.52	627.42	83.71
R_2	18.29	11.59	63.37	1.74	1.37	78.74	527.85	430.81	81.62
R_4	2.03	1.72	84.37	1.63	1.52	93.25	129.85	114.3	88.02
R_5	2.10	2.28	108.50	1.19	1.53	128.53	172.17	119.58	69.45
R_7	16.89	19.70	116.64	0.87	1.05	120.69	646.35	677.01	104.74

Table 3.1.9 Tensile properties of vulcanisates containing CBS.

Mix. No.	Tensile Strength(MPa)			100% modulus (MPa)			Elongation at break (%)		
	Before ageing	After ageing	Retention %	Before ageing	After ageing	Retention %	Before ageing	After ageing	Retention %
C_2	23.26	24.35	104.69	0.77	0.83	107.79	875.35	862.57	98.54
C_3	23.18	23.37	102.37	0.93	0.97	104.30	804.58	832.78	103.50
C_4	21.97	25.08	114.15	0.97	1.01	104.12	770.41	728.28	94.53
R_3	19.50	22.40	86.90	1.84	2.22	150.80	594.66	588.00	100.90
R_5	2.10	2.28	108.50	1.19	1.53	128.57	172.17	119.58	69.45
R_8	15.34	20.91	136.36	0.66	1.20	181.82	834.68	646.57	77.40

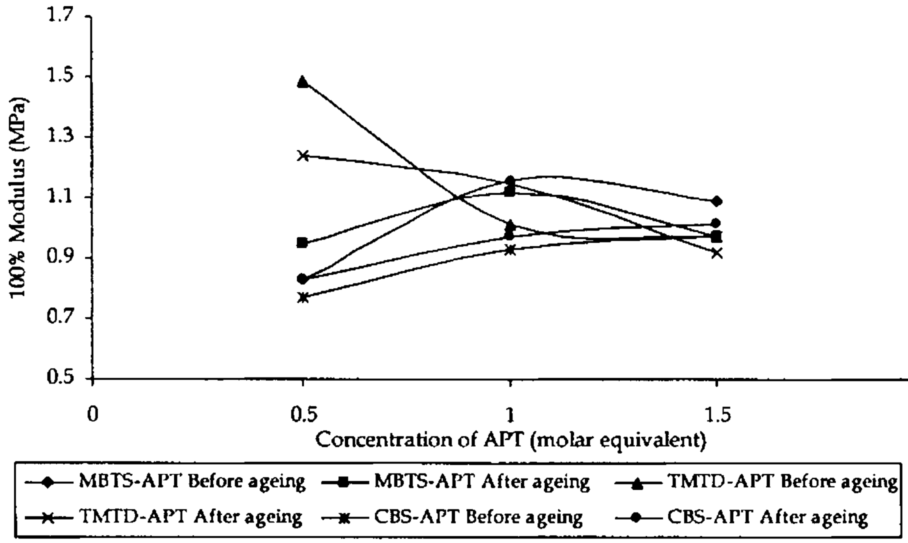


Fig. 3.1.7 Variation of 100% modulus of vulcanisates with the concentration of APT

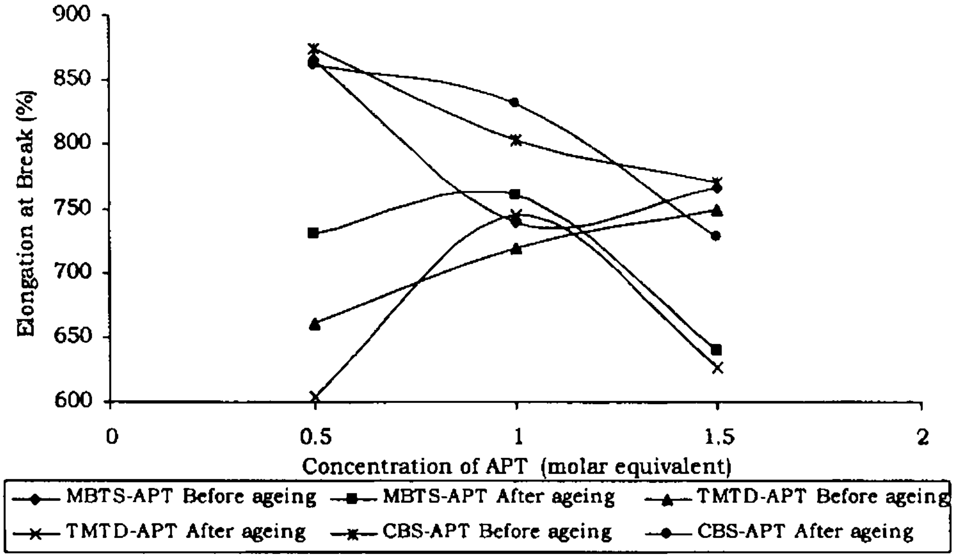


Fig. 3.1.8 Variation of elongation at break of vulcanisates with the concentration of APT

Other physical properties

Hardness, compression set, abrasion loss and tear strength are the other physical properties of the various vulcanisates studied. The results observed are given in tables 3.1.10-3.1.12. Considering the MBTS-APT systems, as the concentration of APT increases tear strength, abrasion resistance and hardness values are found to increase. These variations are also in accordance with the observed variations in crosslink density values. Mix with 1 molar equivalent of APT however, showed a higher compression set value compared to other mixes with MBTS. In other properties like hardness and tear strength MBTS-APT systems show better results compared to equivalent references.

Table 3.1.10 Other physical properties evaluated for vulcanisates with MBTS.

Mix No.	Tear strength (N/mm)	Hardness (Shore A)	Compression set (%)	Abrasion loss (cm^3 /hr)	Total crosslink density× 10^5 ($g.molcm^{-3}$)
A_2	32.11	25.5	28.19	5.84	4.1975
A_3	32.16	26.0	37.93	5.77	4.4225
A_4	36.32	27.0	29.38	5.57	4.4114
R_1	29.73	29.0	21.97	6.70	4.5205
R_4	17.72	32.0	12.45	6.49	7.4102
R_6	22.40	24.0	31.40	5.73	3.5210

Table 3.1.11 Other physical properties evaluated for vulcanisates with TMTD.

Mix No.	Tear strength (N/mm)	Hardness (Shore A)	Compression set (%)	Abrasion loss (cm^3 /hr)	Total crosslink density× 10^5 ($g.molcm^{-3}$)
B_2	48.88	39.0	20.39	3.88	5.8633
B_3	43.95	38.0	24.28	4.80	5.3478
B_4	46.74	37.0	25.71	5.70	5.5325
R_2	43.29	38.5	13.18	3.39	6.8655
R_4	17.72	32.0	12.45	6.49	7.4102
R_5	4249	34.0	16.12	6.29	7.2533
R_7	37.71	33.0	33.10	6.27	5.2505

Table 3.1.12 Other physical properties evaluated for vulcanisates with CBS.

Mix No.	Tear strength (N/mm)	Hardness (Shore A)	Compression set (%)	Abrasion loss (cm^3 /hr)	Total crosslink density×10^5 (g.mol.cm^{-3})
C_2	35.67	27.5	27.12	3.56	5.1967
C_3	33.65	30.0	31.45	1.73	5.0010
C_4	37.12	29.0	26.61	2.54	5.5325
R_3	37.00	31.0	13.80	5.40	6.1005
R_5	42.49	34.0	16.12	6.29	7.2533
R_8	40.96	31.0	31.32	5.84	4.0645

For TMTD-APT systems also hardness, abrasion loss and compression set showed similar trend as that of MBTS-APT. In comparison with the TMTD-TU reference system the binary system of APT with TMTD (mix B_2) showed better results for all the physical properties studied. In the case of CBS, the effect of change in concentration of APT is not seen to have much influence in the various properties studied. Tear strength, hardness and compression set values of mix containing optimum dosage of APT are comparable with those of the reference system containing CBS and TU. Abrasion resistance is found to be higher (less abrasion loss) for APT systems compared to the other formulations of MBTS-TMTD and TMTD-CBS. Considering the cure characteristics and other properties, the mixes with 0.5 molar APT with 1 molar equivalent MBTS, TMTD or CBS can be taken as the optimum binary combinations in these systems.

Crosslink density is an important parameter, which can be related to the physical properties of rubber vulcanisate[21]. The nature of the crosslinks and the presence of other rubber bound side products of vulcanisation may also influence physical properties. The vulcanisates with optimum dosage of APT showed higher crosslink density compared to the corresponding thiourea binary systems.

PART - B

3.2 NR FILLED SYSTEMS

As reported in part A of this chapter gum vulcanisation systems of NR with APT is found to be effective with respect to cure characteristics and physical properties in MBTS-APT, TMTD-APT and CBS-APT. In this context, we thought it worthwhile to investigate the filled systems of NR also. Here APT is used in different formulations containing carbon black / precipitated silica. A detailed study on these systems was carried out aiming at developing practical cure systems, which will be useful in rubber product manufacture. The study covers different aspects like mixing, curing and determination of the various physical properties of the vulcanisates. Reference mixes were also prepared and the properties of the experimental mixes were compared with those of the references. Optimum dosages of APT required in different formulations have also been derived. Total chemical crosslinks were also estimated using the equilibrium swelling method.

3.2.1 Experimental

Formulations of the different mixes used in the study are shown in tables 3.2.1 - 3.2.3. Mixes Ac_1- Ac_4 contain 0.25, 0.5, 1 and 1.5 molar equivalents of APT with 1 molar equivalent MBTS and with 50 phr. carbon black. As_1-As_4 contain 0.25 -1.5 molar equivalents of APT with 1 molar MBTS and also 30phr. precipitated silica. Similarly mixes of the B & C series contain TMTD/CBS with APT in similar proportions. Mixes Rc_1-Rc_3 are formulations containing the primary accelerator alone and Rc_4-Rc_9 are systems containing MBTS/TMTD/CBS/TU in different binary combinations containing 50 phr. carbon black. Similarly formulations Rs_1-Rs_3 and Rs_4-Rs_9 are prepared with 30 phr.precipitated silica as filler. Aromatic oil (5phr.) is used as the process oil for mixes containing carbon black and naphthenic oil (5phr.) is used in the case of silica. When silica is used as filler in rubber compounds the hydroxy groups in silanols on the surface of the filler can interact with basic accelerators. This usually results in unacceptable long cure times and slow cure rates. In order to normalise the cure rate, diethylene glycol (DEG) is included in the compound preparation. In our study also, for mixes containing silica, 2 phr. of DEG is used.

All the above mixes were prepared in a two roll mixing mill as per ASTM D 182-89. Goettfert elastograph was used for determining the cure characteristics. Cure curves obtained are shown in figs. 3.2.1-3.2.6.

Table 3.2.1 Formulations of filled mixes containing MBTS

Ingredients	Ac$_1$	Ac$_2$	Ac$_3$	Ac$_4$	As$_1$	As$_2$	As$_3$	As$_4$	Rc$_1$	Rc$_4$	Rc$_6$	Rc$_7$	Rs$_1$	Rs$_4$	Rs$_6$	Rs$_7$
NR	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
ZnO	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
MBTS	1.66	1.66	1.66	1.66	1.66	1.66	1.66	1.66	3.32	1.66	1.66	1.66	3.32	1.66	1.66	1.66
TMTD										1.2				1.2		
CBS											1.32				1.32	
Thiourea												0.38				0.38
APT	0.243	0.485	0.970	1.455	0.243	0.485	0.970	1.455								
Carbon black	50	50	50	50					50	50	50	50				
Silica					30	30	30	30					30	30	30	30
DEG					2	2	2	2					2	2	2	2
Sulphur	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Aromatic oil	5	5	5	5					5	5	5	5				
Naphthenic oil					5	5	5	5					5	5	5	5

Table 3.2.2 Formulations of filled mixes containing TMTD

Ingredients	B_{C1}	B_{C2}	B_{C3}	B_{C4}	B_{S1}	B_{S2}	B_{S3}	B_{S4}	R_{C2}	R_{C5}	R_{C8}	R_{S2}	R_{S5}	R_{S8}
NR	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Zno	5	5	5	5	5	5	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2	2	2	2	2	2	2
TMTD	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	2.4	1.2	1.2	1.2	1.2	1.2
CBS										1.32			1.32	
Thiourea											0.38			0.38
APT	0.243	0.485	0.970	1.455	0.243	0.485	0.970	1.455						
Carbon black	50	50	50	50					50	50	50			
Silica					30	30	30	30				30	30	30
DEG					2	2	2	2				2	2	2
Sulphur	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Aromatic oil	5	5	5	5					5	5	5			
Naphthenic oil					5	5	5	5				5	5	5

Table 3.2.3 Formulations of filled mixes containing CBS

Ingredients	Cc$_1$	Cc$_2$	Cc$_3$	Cc$_4$	Cs$_1$	Cs$_2$	Cs$_3$	Cs$_4$	Rc$_3$	Rc$_6$	Rc$_9$	Rs$_3$	Rs$_6$	Rs$_9$
NR	100	100	100	100	100	100	100	100	100	100	100	100	100	100
ZnO	5	5	5	5	5	5	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2	2	2	2	2	2	2
CBS	1.32	1.32	1.32	1.32	1.32	1.32	1.32	1.32	2.64	1.32	1.32	2.64	1.32	1.32
MBTS										1.66			1.66	
Thiourea											0.38			0.38
APT	0.243	0.485	0.970	1.455	0.243	0.485	0.970	1.455						
Carbon black	50	50	50	50					50	50	50			
Silica					30	30	30	30				30	30	30
DEG					2	2	2	2				2	2	2
Sulphur	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Aromatic oil	5	5	5	5					5	5	5			
Naphthenic oil					5	5	5	5				5	5	5

Tables 3.2.4 - 3.2.6 represent the cure characteristics of mixes with MBTS, TMTD and CBS respectively. Figs. 3.2.1-3.2.3 represent the cure curves of the mixes containing carbon black and figs. 3.2.4-3.2.6 that of mixes containing precipitated silica. The compounds were vulcanised up to the optimum cure time in a laboratory type hydraulic press at 150°C and at a pressure of 11.76 MPa. The tensile properties, tear strength, hardness, compression set and abrasion resistance were determined by methods described in chapter 2. The tensile properties of various vulcanisates evaluated are reported in table 3.2.7. Other physical properties evaluated and the total crosslink density values obtained are reported in table 3.2.8.

3.2.2 Results and Discussions

The acceleration activity of APT in carbon black and silica filled NR vulcanisation is clearly indicated by the results obtained in this study. From the cure properties estimated in all the three binary systems of MBTS, TMTD and CBS, APT functions effectively as a secondary accelerator in both filled compounds. It is also seen that the nucleophilic mechanism proposed earlier in gum vulcanisation reaction holds good for the filled systems also. There is an appreciable reduction in the cure time for mixes containing the amidino phenyl thiourea compared to the systems containing equivalent amounts of thiourea. Physical properties of the APT mixes are also comparable with other reference formulations.

Cure characteristics

The addition of APT reduces the optimum cure time considerably in the systems under review. By increasing the amount of APT from 0.25 to 1.5 molar levels the optimum cure time is reduced to almost half in the MBTS combinations. However, scorch time of the mixes is also reduced to a great extent. The cure rate is seen to be more than doubled in these binary systems containing silica as the concentration of APT is increased up to the optimum level. Considering the optimum cure time and scorch time values a practical cure system seems to be the one containing one molar equivalent of APT with similar concentration of MBTS. Mix As_3 containing 1 molar equivalent of APT and MBTS each shows an optimum cure time value of 3.8 min. where as the similar mix with TU (Rs_7) shows 6.2 min. Mix Rs_1 that contains MBTS alone did not cure properly and hence this was not proceeded further. In general, the t_{90} and t_{10} values of the experimental mixes in this MBTS series are considerably less than those of the corresponding reference mixes containing TMTD, CBS etc.

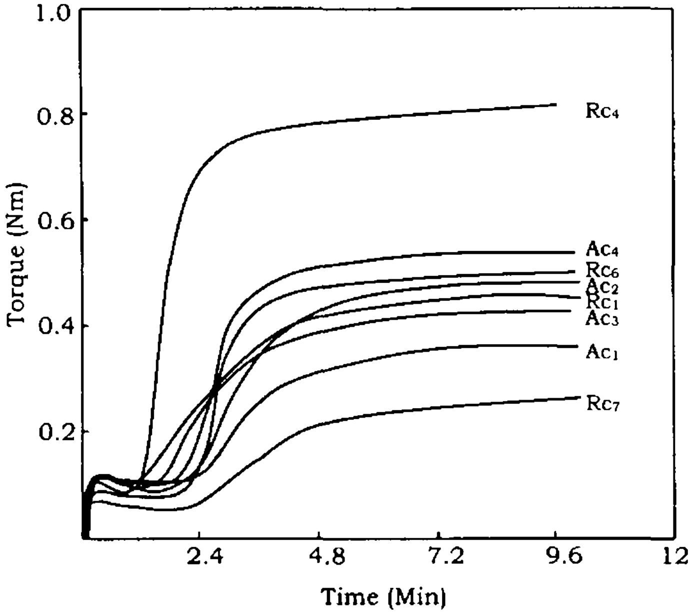


Fig. 3.2.1 Cure curves of carbon black filled systems (MBTS)

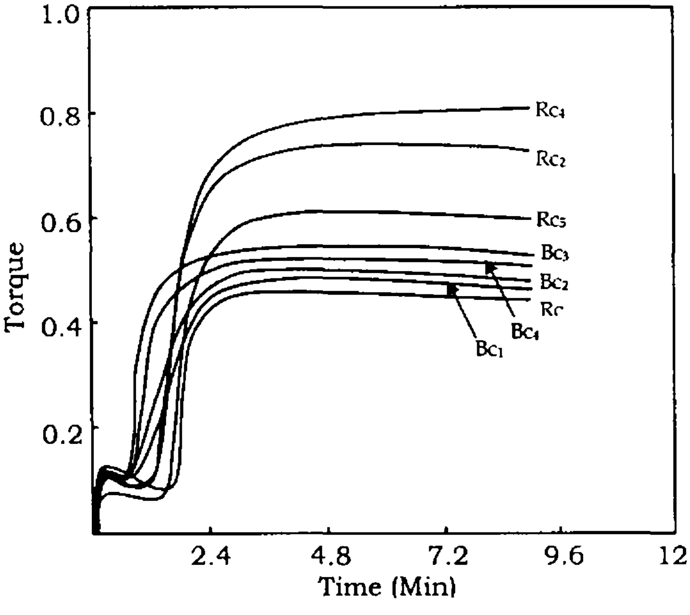


Fig. 3.2.2 Cure curves of carbon black filled systems (TMTD)

Table 3.2.4 Cure characteristics of mixes containing MBTS (filled systems)

Mix No.	Optimum cure time t_{90} (min)	Scorch time t_{10} (min)	Cure rate index	Minimum torque (Nm)	Maximum torque (Nm)
Ac$_1$	6.1	2.2	27.43	0.12	0.37
Ac$_2$	5.2	1.8	29.07	0.09	0.47
Ac$_3$	4.7	1.6	32.05	0.11	0.42
Ac$_4$	3.8	1.1	37.31	0.10	0.53
As$_1$	8.6	1.9	14.85	0.01	0.25
As$_2$	4.9	1.9	32.79	0.01	0.14
As$_3$	3.8	1.4	41.67	0.01	0.14
As$_4$	3.6	1.2	41.67	0.01	0.14
Rc$_1$	6.0	2.7	30.12	0.09	0.43
Rc$_4$	3.5	1.4	48.08	0.09	0.81
Rc$_6$	3.8	2.4	71.43	0.08	0.48
Rc$_7$	6.3	2.5	26.60	0.06	0.25
Rs$_4$	5.0	2.6	41.67	0.01	0.34
Rs$_6$	5.9	3.1	36.36	0.08	0.21
Rs$_7$	6.2	2.4	26.53	0.01	0.21

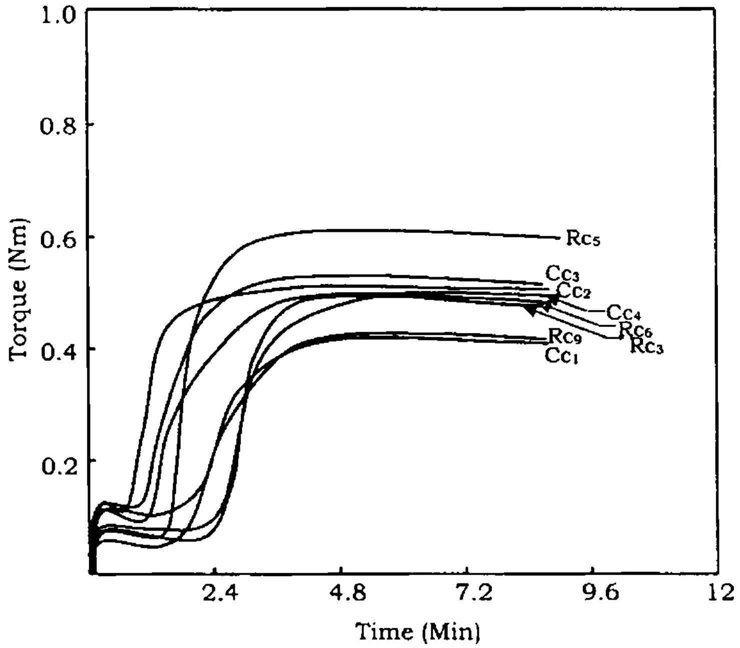


Fig. 3.2.3 Cure curves of carbon black filled systems (CBS)

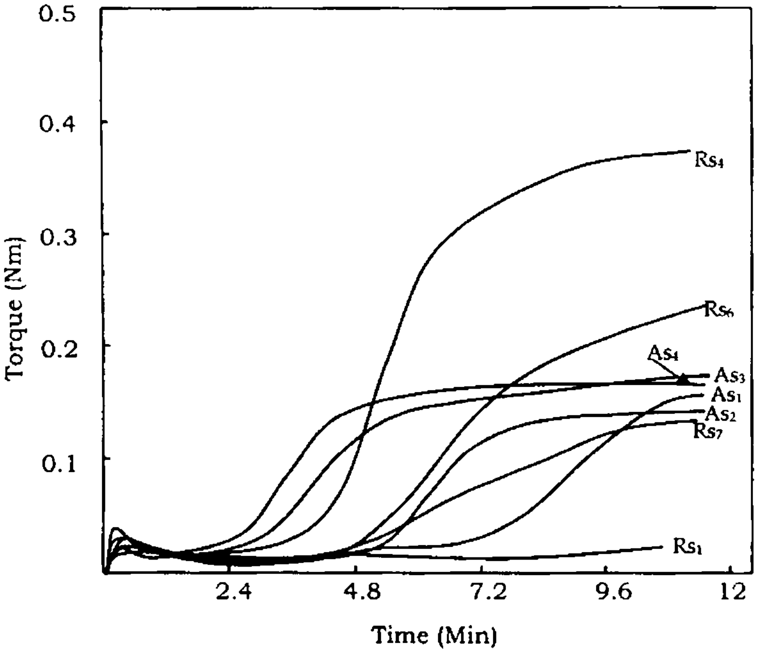


Fig. 3.2.4 Cure curves of silica filled systems (MBTS)

Table 3.2.5 Cure characteristics of mixes containing TMTD (filled systems)

Mix No.	Optimum cure time t$_{90}$ (min)	Scorch time t$_{10}$ (min)	Cure rate index	Minimum torque (Nm)	Maximum torque (Nm)
Bc$_1$	2.0	1.2	131.57	0.12	0.45
Bc$_2$	1.8	1.2	138.89	0.11	0.51
Bc$_3$	1.4	0.8	156.25	0.11	0.52
Bc$_4$	1.2	0.6	166.67	0.11	0.49
Bs$_1$	2.4	1.7	142.85	0.01	0.14
Bs$_2$	2.2	1.4	120.50	0.01	0.14
Bs$_3$	1.4	0.7	151.52	0.01	0.16
Bs$_4$	1.2	0.5	147.06	0.02	0.26
Rc$_2$	2.4	1.4	096.15	0.09	0.71
Rc$_4$	3.5	1.4	048.08	0.09	0.81
Rc$_5$	2.5	1.7	131.58	0.08	0.59
Rc$_8$	2.3	1.5	125.00	0.06	0.44
Rs$_2$	3.0	2.0	101.01	0.03	0.26
Rs$_4$	5.0	2.6	041.67	0.01	0.34
Rs$_5$	3.9	2.0	052.08	0.04	0.30
Rs$_8$	2.3	1.8	185.18	0.01	0.18.

In TMTD systems also mixes containing APT (Bc_1-Bc_4 & Bs_1-Bs_4) are found to be better than those of the corresponding reference mixes. In carbon black filled systems the optimum cure time is reduced from 2min.to 1.2min. as the concentration of APT is increased from 0.25 to 1.5 molar levels. Comparing mixes containing equivalent amounts of APT and TU (Bc_3&Rc_8) the t_{90} value for APT system is almost half of that of TU. In the case of systems containing the amidinothiourea derivative and TMTD, the 1:1 molar combination shows comparatively lesser optimum cure time values for both filled systems of carbon black and silica (1.4 min.). In other mixes (Rc_2, Rc_4, Rc_5, and Rc_8) the t_{90} values obtained are far more than the above value. There is appreciable reduction in optimum cure time as the concentration of APT increases from 0.25 to 1.5 for both the filled mixes in CBS-APT systems also (table 3.2.6). These CBS mixes also follow almost similar pattern as MBTS and TMTD. In the above CBS systems evaluated also the cure properties point to a nucleophilic reaction mechanism. Considering the cure characteristics studied 1:1 molar combination of APT with MBTS/TMTD/CBS can be taken as optimum cure systems in these filled formulations.

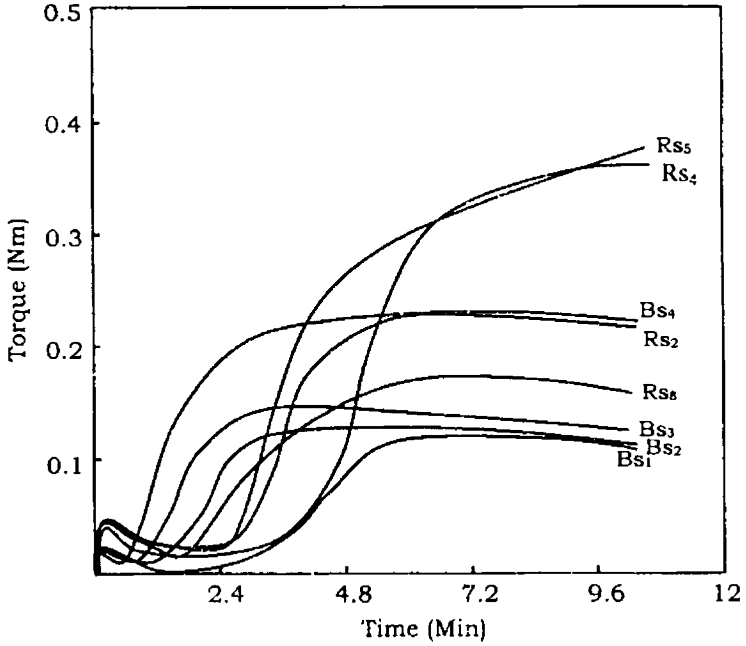


Fig. 3.2.5 Cure curves of silica filled systems (TMTD)

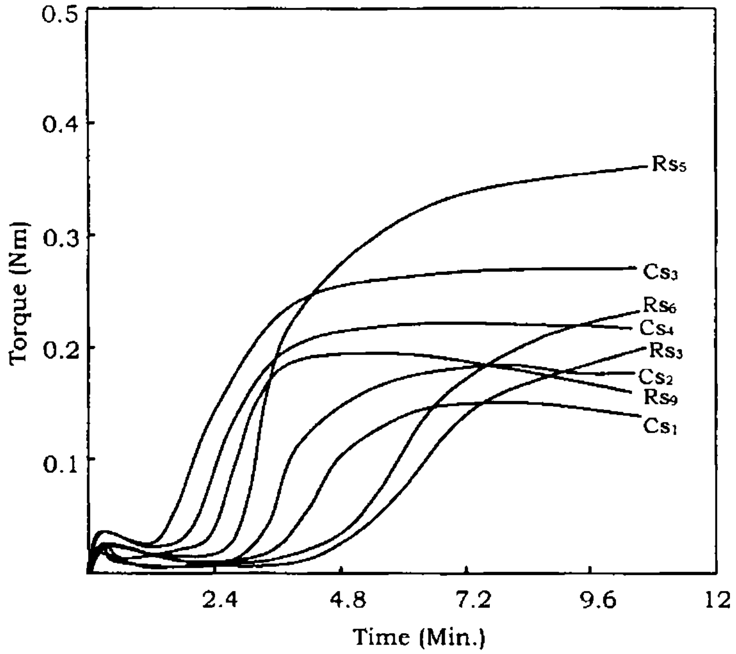


Fig. 3.2.6 Cure curves of silica filled systems (CBS)

Table 3.2.6 Cure characteristics of mixes containing CBS (filled systems)

Mix No.	Optimum cure time t_{90} (min)	Scorch time t_{10} (min)	Cure rate index	Minimum torque (Nm)	Maximum torque (Nm)
Cc$_1$	3.7	1.8	52.08	0.12	0.41
Cc$_2$	3.1	1.3	54.34	0.11	0.51
Cc$_3$	3.8	1.0	55.55	0.11	0.52
Cc$_4$	2.4	0.8	16.97	0.04	0.50
Cs$_1$	4.5	2.2	43.66	0.01	0.13
Cs$_2$	3.3	1.6	53.81	0.02	0.16
Cs$_3$	2.6	1.0	55.56	0.02	0.20
Cs$_4$	2.4	0.8	62.89	0.02	0.22
Rc$_3$	3.4	2.7	138.88	0.07	0.48
Rc$_5$	2.4	1.7	131.57	0.08	0.59
Rc$_6$	3.8	2.4	71.43	0.08	0.48
Rc$_9$	3.7	1.8	51.02	0.06	0.41
Rs$_3$	6.6	3.4	31.25	0.01	0.19
Rs$_5$	3.9	2.0	52.08	0.36	0.31
Rs$_6$	5.9	3.1	36.36	0.01	0.21
Rs$_9$	3.7	1.2	39.52	0.01	0.15

Evaluation of physical properties

In view of the fact that favourable cure characteristics can be obtained using APT as a secondary accelerator in these filled systems of NR, the vulcanisates were further investigated with respect to their various physical properties. In black filled vulcanisates the tensile strength of experimental systems are comparatively lesser than the control formulations whereas elongation at break values of the APT systems are found to be satisfactory.

Table 3.2.7 Tensile properties of various filled vulcanisates (References and those containing optimum dosage APT)

Mix No.	Tensile strength (MPa)			Elongation at break (%)		
	Before ageing	After ageing	Retention %	Before ageing	After ageing	Retention %
Ac3	13.30	10.40	78.195	293.0	301.4	102.867
Bc3	19.70	14.90	75.635	410.4	271.7	66.204
Cc3	23.80	19.40	81.513	348.2	202.0	58.013
As3	18.00	21.20	117.778	536.0	521.2	97.239
Bs3	24.63	25.80	104.750	442.5	407.5	92.090
Cs3	24.62	25.01	101.584	490.7	540.5	110.149
Rc1	15.86	13.96	88.020	367.5	323.5	88.027
Rc2	16.28	15.98	98.157	390.7	234.4	60.251
Rc3	26.62	19.79	74.343	367.5	118.2	32.163
Rc4	18.57	17.01	91.599	256.9	92.2	35.889
Rc5	20.35	18.44	90.614	259.7	136.3	52.484
Rc6	27.46	22.8	82.957	410.6	196.5	47.857
Rc7	20.37	15.88	77.958	462.7	283.1	61.184
Rc8	26.46	18.24	68.934	432.7	116.3	26.678
Rc9	25.96	23.18	89.291	451.1	251.5	55.753
Rs2	22.27	12.25	55.007	577.6	359.6	62.258
Rs3	25.78	23.00	89.216	592.8	500.6	84.447
Rs4	18.35	12.99	70.790	407.2	380.2	93.369
Rs5	17.10	15.95	90.643	505.0	388.2	76.871
Rs6	24.30	21.04	86.584	579.6	475.5	82.039
Rs7	15.15	19.70	130.033	543.3	545.6	100.423
Rs8	23.16	19.20	82.902	625.6	455.7	72.842
Rs9	18.50	25.60	138.378	612.4	581.9	95.020

In the silica filled systems, however, the tensile strength values of the experimental systems containing optimum dosage of APT are found to be better than the systems containing MBTS / TMTD / CBS with thiourea. Percentage retention of tensile strength after heat ageing is also found to be better for the APT systems containing silica (table 3.2.7). Elongation at break values also follow more or less similar pattern. Compared to MBTS and TMTD, CBS systems containing optimum concentration of APT shows better results with regard to these tensile properties.

Other physical properties such as hardness, compression set, abrasion resistance and tear strength were evaluated for mixes containing optimum dosages of APT with MBTS/TMTD/CBS and for the reference systems. The values are reported in table 3.2.8. Considering MBTS mixes, experimental systems with carbon black show better results in all the physical properties studied compared to the TU systems. The mix Ac_3 containing MBTS and optimum dosage of APT showed tear strength value of 111.9N/mm, which is more than double that of MBTS-TU (47.56N/mm). Compression set and abrasion resistance are also better in this case. In silica filled systems also the MBTS-APT mixes show better results compared to the control system for tear strength and abrasion resistance. Hardness and compression set results are also found to be satisfactory for the APT systems. In the case of TMTD and CBS systems the physical properties showed comparable results with the controls in both silica and black filled formulations.

Reinforcing fillers like carbon black are known to have significant effect on the network structure of filled vulcanisates while semi-reinforcing fillers such as silica do not have similar effect on rubber-network[22,33]. Moreover, silica is reported to cause a reduction in crosslinking efficiency in accelerated sulphur systems, which may be due to accelerator absorption by the filler[24]. The crosslink density values estimated by the swelling studies on these vulcanisates are given in table 3.2.8. As expected higher values of crosslink density are obtained in the case of carbon black filled vulcanisates for all the binary combinations studied.

Table 3.2.8 Other physical properties of filled vulcanisates (References and those containing optimum dosage APT)

Mix No.	Hardness (Shore A)	Compression set (%)	Abrasion loss (cm^3/hr)	Tear strength (N/mm)	Total crosslink density x 10^5 (g.mol/cm^3)
Ac$_3$	63.4	22.32	3.83	111.90	5.57
Bc$_3$	66.6	20.78	3.73	82.00	6.49
Cc$_3$	62.6	34.53	3.71	124.25	5.04
As$_3$	44.0	40.41	8.36	73.15	1.72
Bs$_3$	45.3	36.39	7.26	66.50	2.41
Cs$_3$	49.3	42.35	4.98	81.87	2.47
Rc$_1$	62.6	26.27	3.14	115.90	3.31
Rc$_2$	73.0	15.08	3.51	84.85	7.24
Rc$_3$	70.0	39.87	3.04	110.00	6.22
Rc$_4$	75.5	12.98	3.33	60.42	9.42
Rc$_5$	70.5	21.38	3.40	81.10	7.46
Rc$_6$	66.5	34.91	3.48	93.78	5.42
Rc$_7$	57.0	42.90	4.20	47.56	3.90
Rc$_8$	67.0	24.91	3.63	72.66	6.02
Rc$_9$	62.5	25.07	3.76	93.00	4.72
Rs$_1$	51.3	29.45	7.58	55.44	2.58
Rs$_2$	46.0	24.02	5.35	52.35	3.12
Rs$_3$	55.0	30.96	4.40	60.24	2.78
Rs$_4$	62.3	23.06	5.15	51.90	3.90
Rs$_5$	56.0	25.30	4.43	50.80	3.15
Rs$_6$	53.4	33.06	5.41	70.40	2.87
Rs$_7$	50.0	29.23	10.30	55.60	2.28
Rs$_8$	47.0	23.50	8.23	80.00	2.54
Rs$_9$	49.0	41.28	6.44	80.15	2.32

3.3 CONCLUSIONS

The effect of N-amidino N'-phenyl thiourea (APT) as a secondary accelerator in the binary systems of MBTS-APT, TMTD-APT and CBS-APT in NR gum and filled vulcanisation systems were investigated in this part of the study. Evaluation of the cure characteristics of NR gum mixes showed appreciable reduction in the optimum cure time for mixes containing APT compared to thiourea, which is used as the control. The cure behaviour of these NR formulations provided supporting evidence to the nucleophilic reaction mechanism of the accelerator activity in these systems as suggested by Philpott. The lower scorch time observed in the case of mixes containing APT, when used in higher dosages, is a disadvantage. Practical cure systems with optimum concentrations of APT are proposed. As the systems containing this amidinothiourea derivative showed characteristics of practical rubber product mixes, they were further investigated for their various physical properties. One of the aims was also to report the use of a non-toxic secondary accelerator. The tensile properties evaluated viz. tensile strength, elongation at break, hardness, compression set, abrasion resistance and tear résistance were found to give satisfactory results compared to reference formulations. APT showed promising results in the after ageing properties also in these gum formulations.

It is also found from further studies that APT can be effectively used as an accelerator in the binary systems containing MBTS, TMTD or CBS in NR filled vulcanisation systems also. The cure characteristics, especially optimum cure time obtained, point to a nucleophilic reaction mechanism in these vulcanisation reactions also. The physical properties evaluated for all the three filled systems gave values better than / comparable to those of the reference mixes. The optimum dosages of APT required for the above binary systems have also been derived.

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Chapter 4

INVESTIGATIONS ON THE EFFECT OF APT AS A SECONDARY ACCELERATOR IN NR LATEX SYSTEMS.

Natural rubber latex obtained from *Havea brasiliensis* is a colloidal dispersion of negatively charged rubber particles suspended in an aqueous medium. It has a rubber content of 25-40 percent by weight, which depends on the type of tree, the tapping intensity, soil condition, season etc. It is a white opaque liquid of density between 0.975 and 0.98 $gm.cm^{-3}$ and has a variable viscosity. Its pH ranges from 6.5 to 7. The rubber hydrocarbon in latex is 1,4 cis-poly isoprene and it occurs as molecular aggregates with an average diameter ranging from 0.025 to 0.3 microns[1]. A layer of protein and phospholipids surrounds these rubber particles. Latex contains a variety of other non-rubber constituents which also varies according to season, soil condition, clonal variations, tapping system etc. The composition (in percentage) of NR latex is as given below: Rubber 30-40, proteins 2-2.5, resins 1-2, sugar 1-1.5, water 55-66 and ash 0.7-0.9. In latex the rubber hydrocarbon is a polymer with a broad distribution of molecular weight ranging from 10^5 to 10^6 with the major part of hydrocarbon in high molecular weight ranges[2].

The latex, as it comes out of the tree gets contaminated with microorganisms like bacteria and yeast[3]. Due to its high water content and susceptibility to bacterial attack the latex gets coagulated within a few hours of leaving the tree unless it is added with preservatives. The microorganisms metabolise the non-rubber constituents of the latex and produce volatile fatty acids such as formic, acetic and propionic acid which leads to coagulation of the latex[4]. Johnson[5] solved this problem with the discovery of ammonia as a preservative for natural rubber latex. The most widely used preservative is ammonia and it inhibits bacterial growth, acts as an alkaline buffer and raises the pH and neutralises the free acid formed in latex. Latex preserved with higher percentage of ammonia is known as high-ammonia (HA) latex. But high percentage of ammonia is hazardous to the workers dealing with it and also causes processing problems. Now the common practice is to use NR latex containing lesser percentage of ammonia and a secondary preservative[6-8]. For higher wet gel strength, to avoid unnecessary transportation of water content and for better uniformity in composition, the normal latex is concentrated, whereby a large portion of serum and some small rubber particles are removed. For most product manufacture, latex of 60% minimum rubber content is essential. The important methods used for the concentration of preserved field latex are (a) evaporation (b) creaming (c) centrifugation and (d) electro decantation, among which centrifuging and creaming are commonly used[8]. NR latex concentrate is a highly specified raw material. The significant latex properties are dry rubber content (D.R.C.) non-rubber solid content (N.R.S), mechanical stability time (M.S.T) volatile fatty acid number (V.F.A), potassium hydroxide number (KOH No:) and alkalinity[9]. Latex concentrate is a non-Newtonian fluid and its viscosity decreases with increasing shear rate[10].

Compared to dry rubber latex processing requires relatively light and simple machinery. Capital outlay and power requirements are also relatively low. Absence of polymer degradation step such as mastication not only saves time and energy but also gives a vulcanisate, which will display inherently greater resistance to deterioration. Natural rubber latex is extensively employed in the manufacture of dipped goods and these include a wide range of products such as gloves, balloons, catheters, teats, contraceptives etc.[11]. NR latex is outstanding in this respect due to the exceptional tensile strength and elongation, coupled with relatively low modulus values. Foam rubber products are another area where this latex is employed in large quantities. Articles manufactured using latex give service performances superior to those made of rubber solutions[12].

RHEOLOGY OF LATEX

The flow properties of latex are of vital importance in the manufacture of latex products. Natural rubber latex is a non-Newtonian fluid that exhibits pseudoplastic flow pattern. At rest the rubber particles in latex are in random movement and when sheared the particles are progressively aligned and offers less resistance to flow[13]. Under processing conditions, latex is subjected to different forms of stress and undergoes flow and other deformations. Hence, study of rheology in significant and very much relevant for understanding and evaluating the scope and limitations of its use and applications. Diverse types of flow behaviour are encountered during processing at different temperatures by various techniques. A thorough evaluation and understanding of the rheological characteristics are necessary prerequisites for satisfactory operation and control of such processes. For example during the manufacture of dipped rubber products by straight dipping the thickness of the film deposited on the former depends on the viscosity of the latex compound[14].

Various techniques used in latex processing such as dipping, extrusion, casting etc. involve a critical relation between temperature, stress and inherent fluid property such as viscosity of latex. For satisfactory operation a thorough evaluation and understanding of the factors that can be used to alter the flow behaviour of the latex are of vital importance. Owing to the non-Newtonian behaviour, a single viscosity measurement of latex at a particular temperature is not enough to understand its flow behaviour. Viscosity of latex also depends considerably on its solid content and particle size distribution. Effect of dry rubber content and viscosity of NR latex was investigated by Smith[15]. Peethambaran et al. reported the effect of surface active agents on the rheological properties of centrifuged and creamed latices[16]. The important factors affecting rheological behaviour of latex are shear rate, particle size distribution and presence of electrolytes. The relation between stress and shear rate for lattices is given by Power law equation:

$\tau = k\gamma n$ where τ = shear stress (Pa), k= viscosity index, γ = shear rate (s^{-1}) and n= flow index.

Temperature has got a tremendous effect on the viscosity of latex. Latex becomes less viscous as the temperature is increased. Viscosity is the most important physico-chemical property, which influences the processing characteristics of the latex.

VULCANISATION OF LATEX

Compounding Ingredients

Vulcanisation of latex is the result of colloidal chemical reactions taking place in the heterogeneous system. The conversion of NR latex into a product can be accomplished in many ways. Until it is converted into a solid product the colloidal system should be maintained stable[11]. The different ingredients used in a latex compound are (i) surface active agents (ii) curing agents (iii) accelerators (iv) activators (v) antioxidants (vi) fillers and (vii) special additives. The water-soluble materials are added as solutions, insoluble solids as dispersions and immiscible liquids as emulsions[12]. The particle size of the ingredients should be reduced to that of the rubber particles in latex for getting uniform distribution in the latex compound[17,18]. The most common technique used to produce dispersions for latex compounding is ball milling. In the ball mill, the particle size of the materials is reduced to the colloidal range.

The surface-active agents are substances present only in very small amounts (of the order of 1% or less) which bring about marked modifications in the surface properties of aqueous media[19]. The surface-active agents can be classified as wetting agents, viscosity modifiers, protective colloids, dispersing agents, dispersion stabilizers, emulsifiers etc. according to their function. The universal vulcanising agent for natural rubber latex is sulphur. Sulphur should be of the required quality and should be finely ground. In sulphurless vulcanisation systems TMTD may be used, but the vulcanisation proceeds at a useful rate only at relatively higher temperatures (140°C). For getting products of a high order of translucency organic peroxides and hydro peroxides may be used to vulcanise natural rubber latex[19].

In latex vulcanisation also ZnO is the activator used. If zinc containing accelerators such as zinc dialkyl dithiocarbamates are used, ZnO is not essential but it is commonly used in latex compounds to provide further activation of vulcanisation and to contribute to gelation process[20]. Zinc oxide increases the tensile strength and modulus of the vulcanisates. Amine and phenolic derivatives are the common antioxidants used in latex[19]. Among these, amine derivatives are more powerful antioxidants but tend to cause discolouration of the product during ageing while the phenolic derivatives have the advantage of not causing discolouration but are not as effective as amines.

Fillers can be added to natural rubber latex to modify its properties and to reduce cost[21]. It is seen that no effect analogues to the reinforcement of dry rubber by fillers are observed when the same fillers are added to latex compounds[22]. Carbon black does not reinforce latex in the manner that it does dry rubber and is used only for colour as various other dyes and pigments[23]. The important non-black fillers used in latex compounding are precipitated silica, calcium carbonate and china clay[24]. Special additives like gelling agents, foaming agents, flame proofing agents, tackifiers, colour etc. are added depending on end use.

Accelerator Systems in NR Latex

The use of organic accelerators in latex compounding is basically different from their use in dry rubber compounding[25,26]. The accelerators introduced into the latex mixture should become evenly distributed without causing the mixture to coagulate or to thicken[27,28]. As there is no danger of scorching ultra accelerators are generally used in latex compounding[29]. The accelerators used should be readily dispersible in water in order to achieve uniform dispersion. Natural rubber latex contains a lot of non-rubber materials, which function as accelerators or activators. Vulcanisation temperature of a latex compound is substantially lower than that of a dry rubber compound. So in the choice of accelerators their properties are to be considered and compounding should be made carefully. Of the wide range of rubber vulcanisation accelerators commercially available, only those of highest activity are of importance for latices. The important class of these accelerators is metallic dialkyl dithiocarbamates. In the manufacture of high quality products two or more accelerators are usually used[30]. A combination of ZDC and ZMBT is used for getting improved modulus. TMTD may be used to cure natural rubber latex with or without the addition of sulphur to prepare heat resistant articles[31,32].

The vulcanisation of latex using TMTD proceeds only at relatively high temperature. At low temperature (100° C or below) the reaction is very slow and of no technical interest. Philpott[33] showed that certain sulphur containing nucleophiles like thiourea are able to activate vulcanisation of NR latex with TMTD, so that well cured natural rubber vulcanisates may be prepared rapidly around 100° C. He has also observed that sulphenamide accelerators which do not vulcanise natural rubber latex in the absence of added sulphur or at low dosages of sulphur are also activated by thiourea to such an extent that the combination will effect cure at technologically useful rates. He suggested a nucleophilic reactivity in these vulcanisation reactions, even though no conclusive evidence is given. It is suggested that accelerators like TMTD, CBS etc. in which sulphur is combined as S-C, C-S-C, or S-N, are inactive below 100° C because of the high thermal stability of the sulphur bonds. Sulphur containing nucleophiles enable such accelerators to operate at lower vulcanisation temperatures.

The results of our study reported in chapter 3 indicate that the thiourea derivative viz. N-amidino N'-phenyl thiourea functions effectively in binary accelerator combinations for dry natural rubber vulcanisation. Based on these encouraging results obtained, we thought it worthwhile to investigate the effect of this thiourea derivative as a secondary accelerator in NR latex systems also. Control formulations containing thiourea were also prepared to see the effectiveness of a nucleophilic reaction mechanism in these latex systems. This study was undertaken in view of the fact that natural rubber latex requires special combination of accelerators compared to dry rubber and because latex vulcanisation temperature is comparatively lower than that of dry rubber. As reported earlier, based on the fact that rheology of latex is of utmost importance in latex product manufacture, a detailed study on the effect of shear rate and temperature on the viscosity of these latex compounds were also carried out. The non-toxic nature of this amidino thiourea derivative was considered to be an added advantage.

In this part of study APT is used along with TMTD / CBS and latex compounds were prepared using standard formulations. Different mixes with varying concentration of APT were prepared and the optimum concentration of APT required is derived based on the cure characteristics and tensile properties obtained. Mixes containing thiourea were taken as control. Latex films prepared from the matured compounds were vulcanised under standard conditions. In order to study the effect of temperature on cure of these latex compounds, they were cured at two different temperatures viz. 120 and 100°C. Tensile properties of the vulcanisates like tensile strength, elongation at break, tear strength etc. were also evaluated and compared with those of reference mixes. Chemical characterisation of vulcanisates was also carried out using standard procedures reported in the following sections.

EXPERIMENTAL

In order to study the effect of APT as secondary accelerator for the vulcanisation we selected TMTD and CBS as the primary accelerators. High ammonia type 60% centrifuged latex was used. Compounding ingredients were added to latex as aqueous solutions or dispersions and compounding was done in a glass vessel, which is chemically resistant to ammoniated latex and the compounding ingredients. The ingredients were added to the continuously stirred latex in a slow and steady stream with minimum of splashing. Dispersions of sulphur, ZnO, TMTD, CBS and APT were prepared using a ball mill. The details of the preparation of dispersions are given in chapter 2. Potassium hydroxide, potassium oleate and thiourea were added as 10 % aqueous solutions. The latex was de-ammoniated to ammonia content of 0.2%. Ingredients were added according to the following order. Stabilizing agent, sulphur, accelerator and zinc oxide[11]. Mixing was done in a glass vessel and stirred well for homogenisation using a laboratory stirrer at 20 - 30 rpm. This was then occasionally stirred during storage in order to prevent settling of the ingredients. After compounding the mixes were kept for maturation at room temperature (35°C) for 24 hrs.

Latex films were prepared by casting the matured compound in shallow glass dishes. About 30-35 ml of the latex compound was poured and distributed evenly so that a film of thickness 1-1.25 mm was obtained upon drying. The films were then vulcanised at 120 and at100° C for specific time periods ranging from10 to 80 minutes in an air oven. The tensile properties of these latex films were determined and a tensile – time graph was generated. The optimum cure time was found out from the tensile strength – time graph. This is calculated as the time for attaining maximum tensile strength. The samples were then vulcanised to the optimum cure time and their physical properties evaluated. The ageing resistance was evaluated by keeping the specimens in an air oven at 70° C for seven days. The tear strength of the vulcanisates was determined as per ASTM D 624-86. The total crosslink density of samples containing optimum concentration of APT was also determined by swelling the samples in toluene.

Table 4.1 Formulations of the mixes

Ingredients	Wet weight in gm.											
	T_1	T_2	T_3	T_4	C_1	C_2	C_3	C_4	TR_1	TR_2	CR_1	CR_2
60% centrifuged NR Latex	167	167	167	167	167	167	167	167	167	167	167	167
10% KOH solution	1	1	1	1	1	1	1	1	1	1	1	1
10% Potassium oleate solution	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
50% ZnO dispersion	1	1	1	1	1	1	1	1	1	1	1	1
33% TMTD dispersion	3.6	3.6	3.6	3.6	-	-	-	-	7.2	3.6	-	-
33% CBS dispersion	-	-	-	-	4	4	4	4	-	-	8	4
10% TU solution	-	-	-	-	-	-	-	-	-	3.8	-	3.8
10% APT dispersion	2.24	4.85	9.70	14.55	2.24	4.85	9.70	14.55	-	-	-	-
50% sulphur dispersion	3	3	3	3	3	3	3	3	3	3	3	3

Formulations of the different mixes used in the present study are given in table 4.1. The weight of various ingredients given is wet weight in gm. calculated on dry rubber content. Mixes T_1 - T_4 contain varying amounts of APT viz. 0.25, 0.5, 1 and 1.5 molar equivalents with 1 molar equivalent of TMTD. Mix TR_1 contains TMTD alone and TR_2 is the control mix with TMTD and TU in 1:1molar ratio. Similarly C series are mixes with CBS as the primary accelerator.

Rheological study of the compounded latex was made by taking compounds matured for 24 hrs. The experimental systems containing optimum dosage of APT and the corresponding references were only used for the rheological studies. Haake viscometer VT 550 was used for these investigations. The functional units of this instrument consist of viscotester VT550, power supply unit, temperature control vessel, sensor system and Pt 100 temperature sensor. The equipment operates over a temperature range from - 30 to 150° C. Thirty different sensor systems are available. Sensor system NV was used for this study. Latex was located in the measuring gap of the sensor system. Rotational speed, measuring time, number of measuring points and measuring temperature were preset. The rotor was rotated at the preset speed range. The latex exert a resistance to the rotational movement due to its viscosity which becomes apparent as a torque value applied on the measuring shaft of the viscometer. The computer attached to the system calculates the relevant values like viscosity η in mPa.s, shear rate γ in s^{-1} and shear stress τ in Pa from the measured variables of speed, torque and sensor geometry. The temperature T was measured in °C. The present study was conducted at three different temperatures viz. 25, 35 and 45°C which are the normal range of temperature encountered during compounding/ processing of NR latex. Shear rate employed ranged from 1 to 150 s^{-1}.

RESULTS AND DISCUSSION

Cure Characteristics and Tensile Properties

The tensile strength – cure time graph for the samples from TMTD-APT systems at 120 and 100° C are given in figs. 4.1 and 4.2 respectively. Optimum cure time of different mixes is estimated as the time to reach maximum tensile strength. It can be seen that the optimum cure time values decrease as the concentration of APT increases. Considering systems containing equivalent accelerator combinations at 120° C, TMTD – APT mix in 1:1 molar ratio (T_3) shows an optimum cure time of 30 min. to attain optimum tensile strength, while system containing TMTD and TU (mix TR_2) takes 36min. and TMTD alone takes 44.8 min. (table 4.2). AT 100° C also the optimum cure time for TMTD - APT (42 min.) is much lower than for TMTD-TU (60 min.) and TMTD alone (70 min.). There is definite decrease in cure time with increase in concentration of APT at 100° C also.

Table 4.2 Optimum cure time and tensile strength values of TMTD mixes

Mix. No.	Cured at 120°C		Cured at 100°C	
	Optimum cure time (min.)	Maximum tensile strength (MPa.)	Optimum cure time (min.)	Maximum tensile strength (MPa.)
T_1	40	26.8	50	29.3
T_2	37	28.0	45	32.0
T_3	30	31.2	42	33.8
T_4	27.5	31.3	39	34.0
TR_1	44.8	26.2	70	29.5
TR_2	36	30.8	60	32.1

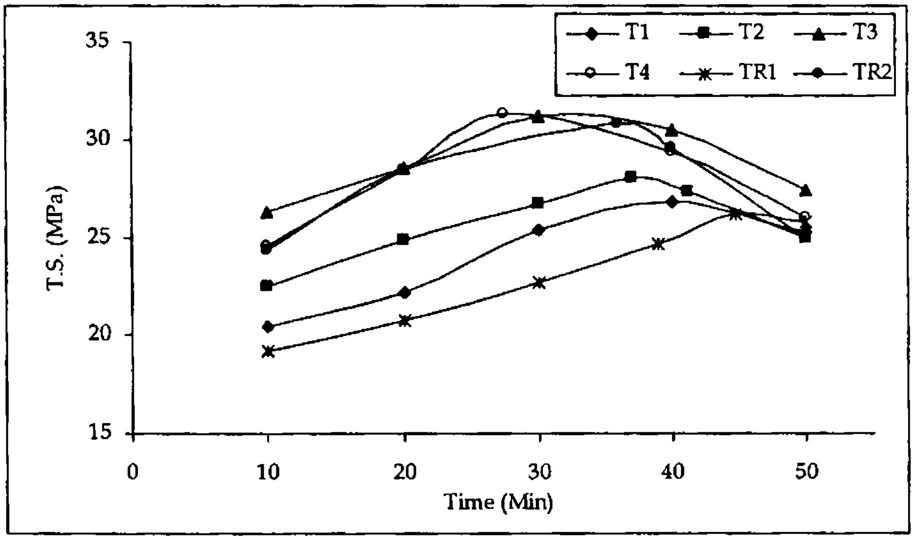

Fig. 4.1 Variation of tensile strength with cure time of TMTD mixes at 120°C

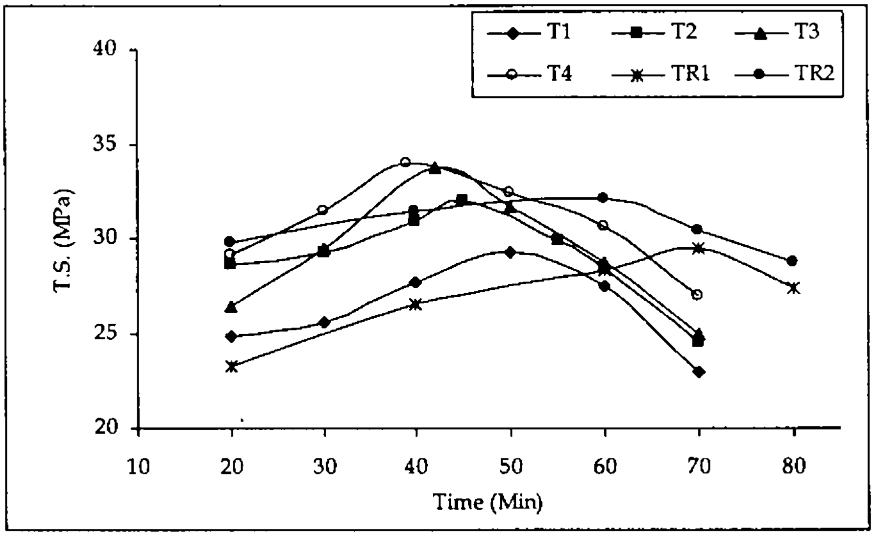

Fig. 4.2 : Variation of tensile strength with cure time of TMTD mixes at 100°C

The optimum cure time values evaluated for the CBS systems at 120 and 100°C are given in table 4.3. The corresponding cure curves are given in figs.4.3 and 4.4 respectively.

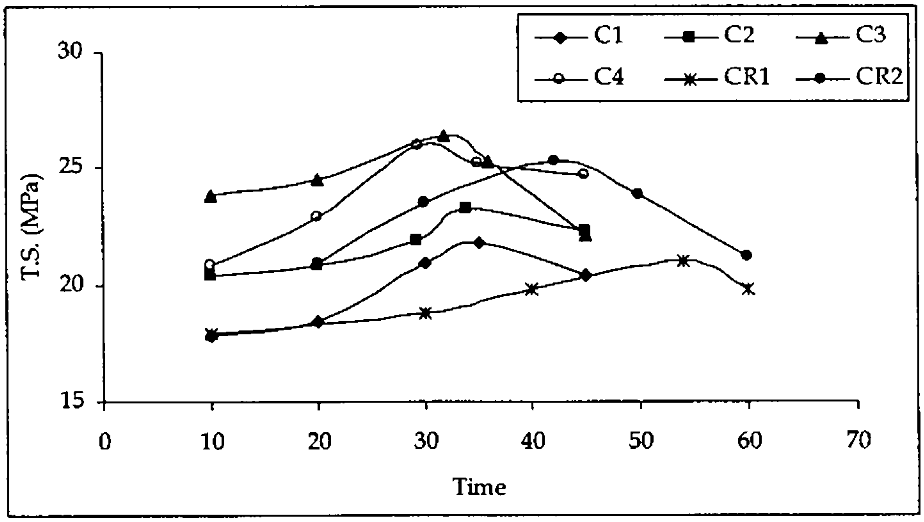

Fig. 4.3 : Variation of tensile strength with cure time of CBS mixes at 120°C

In CBS systems also as the dosage of APT increases the optimum cure time is found to decrease. The cure time for the mix containing 1:1 molar equivalents of CBS and APT (C_3) is considerably less than that for the reference mix CR_2 containing CBS and TU. This is true for vulcanisation at 120° and at 100°C. The CBS-APT mixes take 32 min. and 42.5 min. at 120°C and 100°C respectively. The control systems containing CBS with TU show values of 42.1 min. and 51 min. at similar temperatures. These results indicate that N- amidino N'-phenyl thiourea can be used as a secondary accelerator in the vulcanisation of natural rubber latex containing TMTD or CBS advantageously. There is substantial reduction in optimum cure time for the binary systems containing APT. Also considering the nucleophilic character of APT and comparing it with TU, the reduction in optimum cure time for APT systems gives supporting evidence for the nucleophilic reaction mechanism for such binary systems suggested by Philpott[33] and by Moore[34]. Considering the cure time and tensile strength values mixes T_3 and C_3 containing TMTD/CBS and APT in 1:1 molar ratio can be taken to be the optimum concentrations. The physical properties of these vulcanisates cured at 120° C were further investigated.

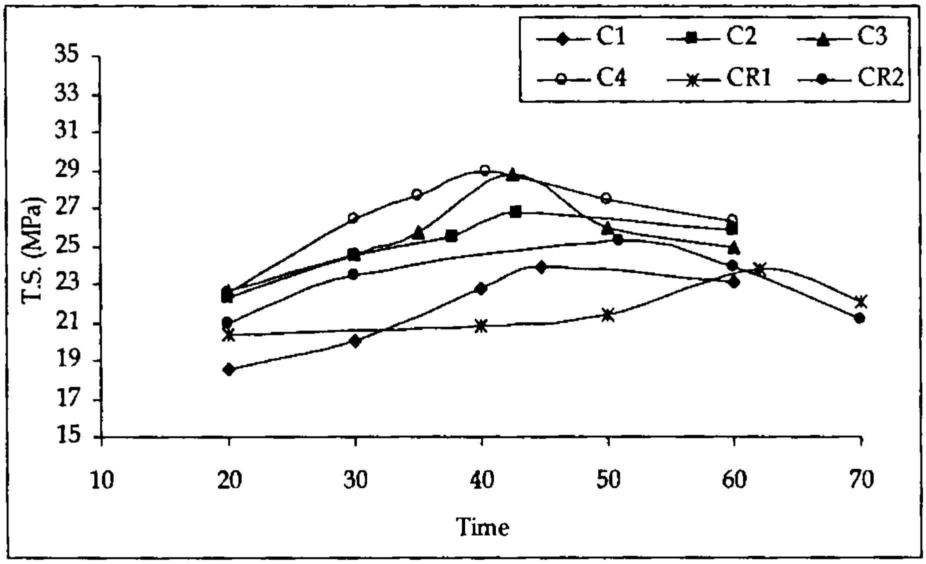

Fig. 4.4 : Variation of tensile strength with cure time of CBS mixes at 100°C

Table 4.3 Optimum cure time and tensile strength values of CBS mixes

Mix. No.	Cured at 120°C		Cured at 100°C	
	Optimum cure time (min.)	Maximum tensile strength (MPa.)	Optimum cure time (min.)	Maximum tensile strength (MPa.)
C_1	35.6	21.8	44.8	23.9
C_2	34.0	23.2	42.9	26.8
C_3	32.0	26.4	42.5	28.8
C_4	29.5	26.0	40.4	29.1
CR_1	54.0	21.0	62.0	23.8
CR_2	42.1	25.3	51.0	28.6

Tensile properties of the vulcanisates containing optimum concentration of APT and of references prepared using the optimum cure time calculated as above are given in tables 4.4 and 4.5. It can be seen that properties like tensile strength of APT systems show slightly better values compared to the reference mixes. Heat ageing studies show that the ageing resistance of APT systems are comparable with that of reference systems containing TU. The tear strength values of these experimental systems are also comparable to those of control mixes.

Table 4.4 Properties of vulcanisates containing TMTD (Cured at 120°C)

Mix. No	Tensile strength (MPa)			Elongation at break (%)	Tear strength (N/mm)	Total crosslink density × 10^5 (g.mol.cm^{-3})
	Before ageing	After ageing	Retention %			
T_3	31.4	30.96	97.36	825	55.4	5.03
TR_1	26.2	23.46	89.54	1004	53.2	4.95
TR_2	30.6	29.98	97.97	985	51	4.76

Table 4.5 Properties of vulcanisates containing CBS (Cured at 120°C)

Mix. No	Tensile strength (MPa)			Elongation at break (%)	Tear strength (N/mm)	Total crosslink density × 10^5 (g.mol.cm^{-3})
	Before ageing	After ageing	Retention %			
C_3	26.4	24.8	93.93	565.0	48.7	4.88
CR_1	21.0	20.1	95.71	451.5	46	4.37
CR_2	25.4	22.56	88.81	590.8	47.9	4.5

Chemical characterisation of the vulcanisate samples was carried out using the equilibrium swelling method. The results obtained for the various systems are reported in tables 4.4 and 4.5. Mixes T_3 and C_3 containing optimum dosage of APT with TMTD/CBS showed higher values for crosslink density. This can be correlated to the better tensile properties observed with these vulcanisates. It may be noted that at 100°C also these systems cure during a reasonable time period and this may be attributed to the nucleophilic reactivity of the secondary accelerator. The overall cure and vulcanisate properties of these formulations studied indicate that APT can advantageously be used as a non-toxic accelerator for the preparation of natural rubber latex products.

Flow Behaviour

The effect of shear rate on compounded latex for various TMTD formulations at 25°C, 35°C and 45°C are shown in figs. 4.5-4.7. On increasing the shear rate viscosity is found to be decreasing confirming the pseudoplastic behaviour of these latex compounds. As the temperature is raised to 45°C the APT and TU systems do not show much variation in viscosity with shear rate whereas mix containing TMTD alone shows higher viscosity values. APT and thiourea are seen to stabilise the systems at this temperature.

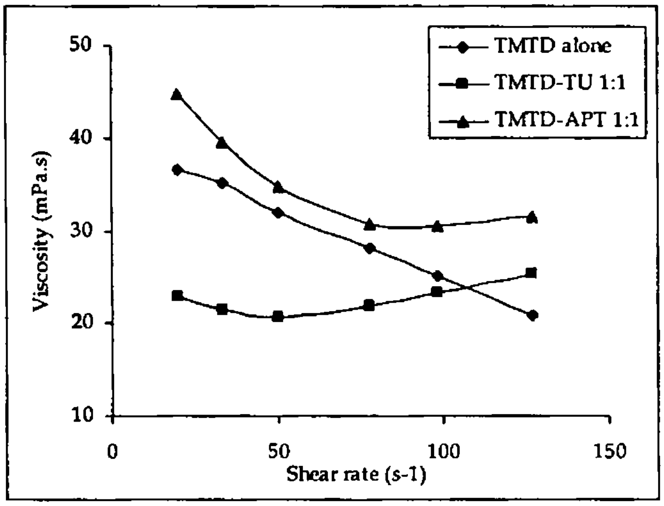

Fig. 4.5 Variation of viscosity with shear rate at 25°C (TMTD Mixes)

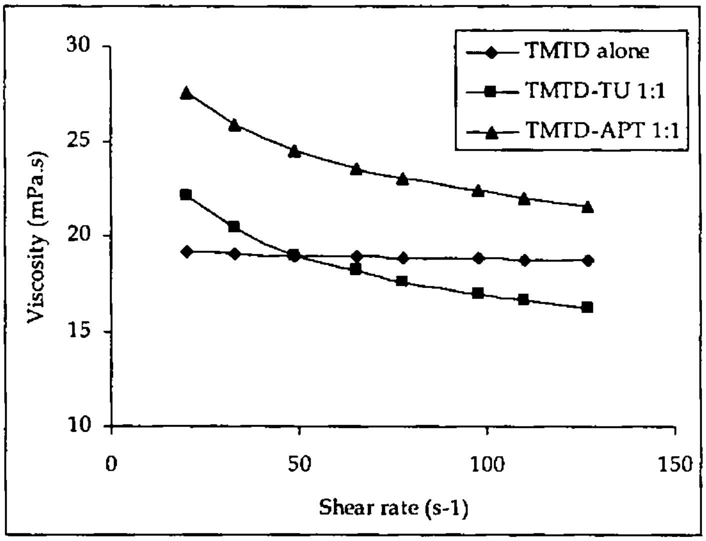

Fig. 4.6 Variation of viscosity with shear rate at 35°C (TMTD Mixes)

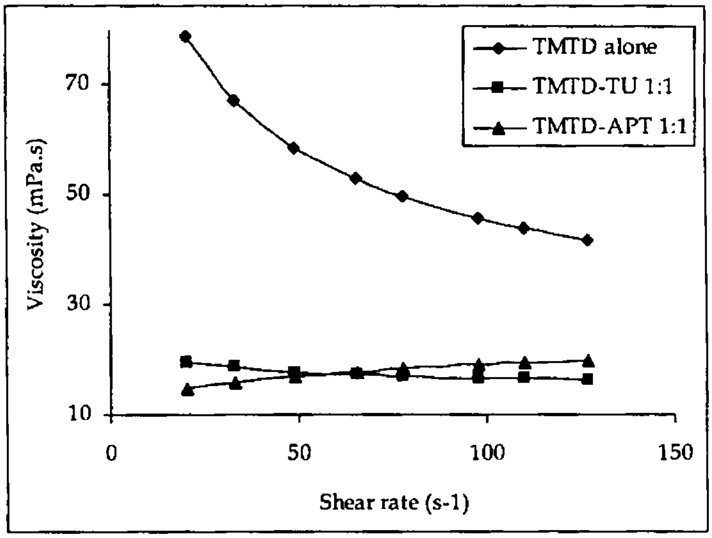

Fig. 4.7 Variation of viscosity with shear rate at 45°C (TMTD Mixes)

In the case of CBS the effect of shear rate on viscosity is different from that of TMTD mixes. Here APT systems show a tendency of increase in viscosity at high shear rate region. Similar trend is shown by thiourea systems also. At higher temperature (45° C) this tendency is more prominent.

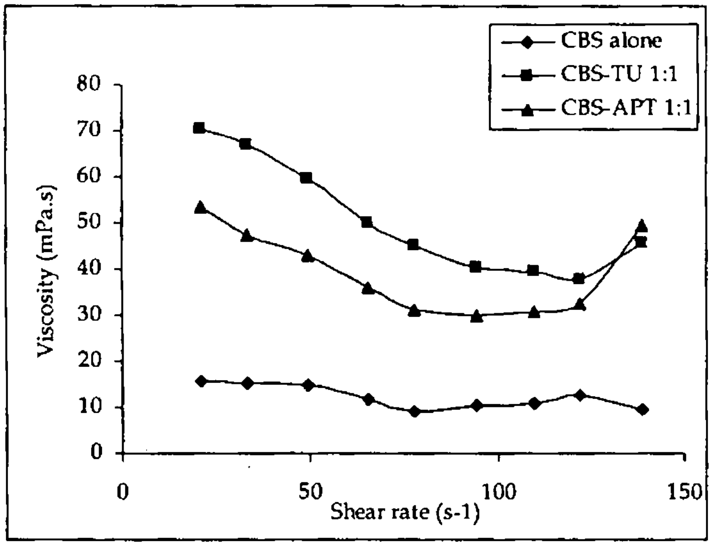

Fig. 4.8 Variation of viscosity with shear rate at 25°C (CBS Mixes)

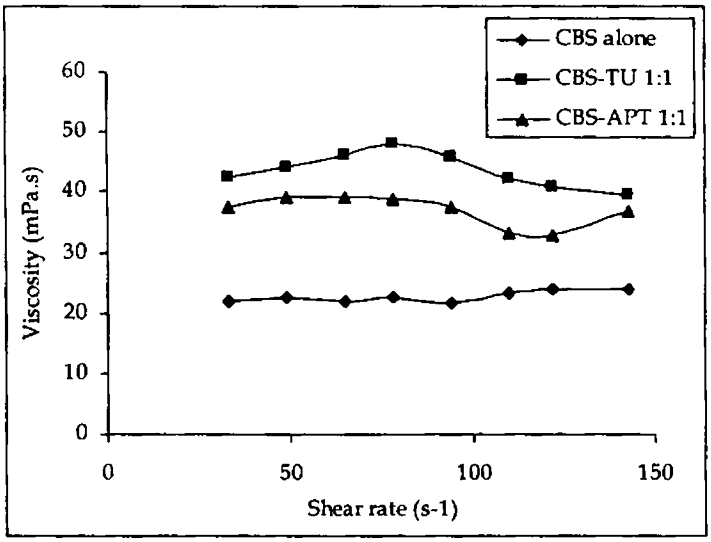

Fig. 4.9 Variation of viscosity with shear rate at 35°C (CBS Mixes)

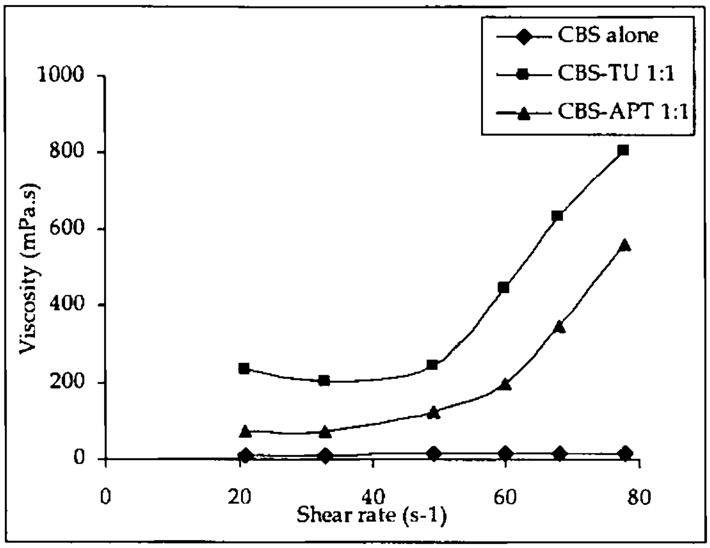

Fig. 4.10 Variation of viscosity with shear rate at 45°C (CBS Mixes)

The effect of temperature on viscosity of latex compounds (at constant shear rate) is shown in figs 4.11 and 4.12. Taking the case of TMTD mixes, as the temperature is increased from 25 to 35°C viscosity is found to be decreasing in all the three systems under review. But as the temperature is increased to 45°C mix TR_1 (containing TMTD alone) shows a sharp increase in viscosity indicating destabilisation of the compound. The presence of amidino thiourea and thiourea is found to stabilise the mix. The addition of APT to CBS mix also is found to change the flow characteristics of this binary system as temperature varies. At about 45°C CBS-APT mix show a sudden tendency to thicken as indicated by the sharp increase in the viscosity value. Similar is the behaviour of the control mix containing thiourea. This indicates that when CBS systems are employed APT and thiourea are not useful especially when processing temperature is above 35°C.

The zero shear viscosity values of the various systems at different temperatures are given in table 4.6. The system with higher zero shear viscosity exhibits more pseudoplastic behaviour. The experimental mix containing optimum dosage of APT with TMTD behaves as a typical pseudoplastic fluid, considering the change in viscosity with temperature. Compared to the control mix (TMTD-TU) the viscosity value is higher for the

APT mix at lower temperatures. In the case of the CBS systems variation of zero shear rate viscosity values with temperature of the CBS-APT and CBS-TU systems is more or less similar and is more than that of the CBS mix.

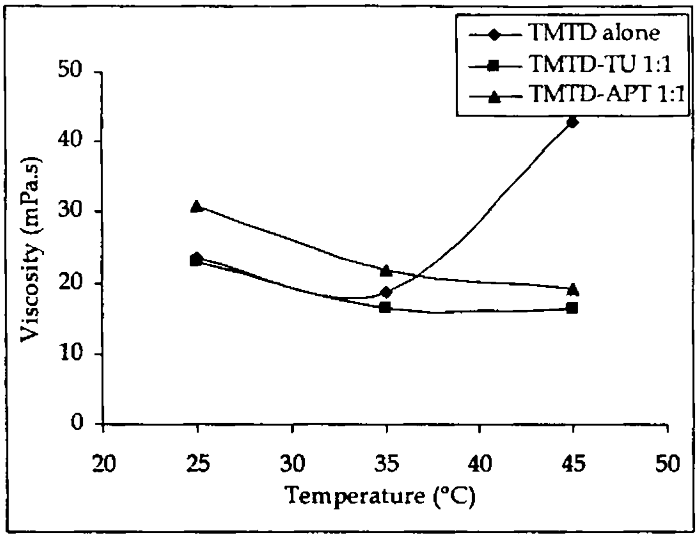

Fig. 4.11 Variation of viscosity with temperature at shear rate 110 s^{-1} (TMTD mixes)

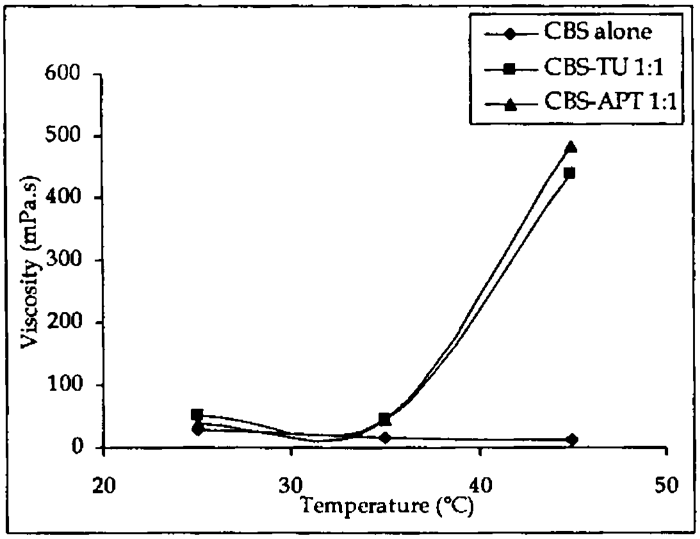

Fig. 4.12 Variation of viscosity with temperature at shear rate 110 s^{-1} (CBS mixes)

Table 4.6 Zero shear viscosity at various temperatures

Mix No.	Zero shear viscosity (mPa.s)		
	25°C	35°C	45°C
T_3	50.3	30.0	10
TR_1	38.0	18.2	92
TR_2	27.5	25.1	26
C_3	63.0	36.7	48
CR_1	17.5	22.0	5
CR_2	75.4	37.5	37.5

CONCLUSIONS

From the results obtained in this study, it is clear that N-amidino N'- phenyl thiourea can be used as an effective secondary accelerator in NR latex especially with TMTD which is a very popular accelerator for latex systems. The disadvantage of APT in dry rubber processing is its scorchiness at high concentrations. But in latex systems as there is no problem of scorching APT can be used safe. Based on cure time values at 120 and 100°C, it can be stated that APT being more nucleophilic than TU, the results support a nucleophilic reaction mechanism in these binary combinations. The systems containing optimum dosages of APT give satisfactory values for mechanical properties like tensile strength and tear strength. Non-toxic nature of APT is especially beneficial in these latex formulations. The rheological studies of the compounded latex show that the introduction of APT in the systems do not have adverse effect in processing especially in comparison to the control mixes. At higher temperature, APT stabilises the TMTD mix where as the CBS-APT shows a tendency to thicken, as is the case with control mixes containing thiourea.

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Chapter 5

STUDIES ON NEW BINARY ACCELERATOR SYSTEMS CONTAINING APT FOR THE SULPHUR VULCANISATION OF SBR

In vulcanisation of diene rubbers using sulphur and accelerators, the efficiency of sulphur intake during crosslink formation depends on the type of accelerator systems, structure of the base polymer, temperature of vulcanisation etc.[1] The study of amidino phenyl thiourea (APT) in natural rubber and NR latex systems gave encouraging results. Based on the fact that the mechanism of vulcanisation also depends on the nature of the elastomer used, we extended our study to a synthetic rubber. A lot of differences are encountered in the compounding and vulcanisation of natural rubber vis-à-vis synthetic rubbers[2]. Compared to natural rubber synthetic rubbers are more consistent in both processing and product properties. As they are prepared synthetically they are available at viscosity ranges, which facilitates better dispersion of ingredients and ease of flow in extrusion, calendaring, moulding etc. This in turn saves both time and energy consumption and hence cost of production.

We selected styrene butadiene rubber (SBR) for the present investigation. It is a general-purpose synthetic rubber which is widely used in rubber industry. It is a co-polymer of styrene and butadiene, manufactured by polymerising them under controlled conditions of reaction using mainly emulsion polymerisation technique. At present cold and hot polymerised SBR are marketed in numerous varieties under various trade names[3]. These brands differ from one another in the relative proportion of styrene and butadiene, content of different initiators, emulsifiers, oils etc. and temperature of polymerisation. The degree of unsaturation in SBR is less than that of natural rubber and the double bonds are less active chemically than the double bonds of the isoprenoid unit in NR. Hence styrene butadiene rubbers are slower curing than NR and require either more accelerators or a more active accelerator system. Also scorch problems are less with SBR than with natural rubber stocks. We have selected synaprene 1502, which is a non-staining non-discolouring cold rubber, for our investigation. Viscosity is an important parameter, which decides the processability of SBR. Lower viscosity grades band more easily on mills and incorporate fillers and oils more readily. These show less heat generation during milling, are more easily calendered and often give a higher extrusion rate than the high viscosity grades. The vulcanisates of high molecular weight rubber show higher resilience and an improvement in the mechanical properties particularly tensile strength and compression set. Compounding of styrene butadiene rubber can be done somewhat similar to that of natural rubber and other unsaturated hydrocarbon rubbers[4].

Sulphur is the most widely used vulcanising agent for SBR. Thiazoles and thiurams are the usual conventional accelerators used in conjunction with sulphur. Presumably because of the reduced overall unsaturation compared to natural rubber, less amount of sulphur is required and somewhat higher accelerator sulphur ratio. For a given vulcanising system SBR vulcanises more slowly than NR and it is therefore a practice to add small amounts of very active accelerators like TMTD. MBTS and sulphenamides provide good processing safety and these accelerators can be activated by the presence of thiurams or guanidines as secondary. TMTD can be used as primary accelerator, which imparts high modulus and good mechanical and ageing properties to the vulcanisates. Large proportion of TMTD with small quantity of sulphur improves heat resistance. The onset of vulcanisation of compounds containing TMTD can be improved by the addition of secondary accelerators such as DPG, dithiocarbamates, thiourea etc. For soft vulcanisates, thiazoles and sulphenamides are used as primary accelerators along with thiurams, guanidines etc. acting as secondary. For low modulus, guanidines are preferred, as thiurams and dithiocarbamates give high modulus and are fast curing[5]. Thiurams alone with normal amounts of sulphur are too scorchy, so also dithiocarbamates. SBR vulcanisates based on TMTD have a tendency to bloom and also impart odour.

Natural rubber gum vulcanisates have very high tensile strength, tear strength, hardness, abrasion and flex resistance. Gum vulcanisates of SBR have a much lower tensile strength and resistance to tear propagation than similar vulcanisates based on NR. The molecular irregularity and large pendent groups present in SBR prevent aligning of the molecules, which prevents crystallisation on stretching. This lack of crystallisation gives lower green strength and lower gum tensile strength for SBR. However, reinforcing carbon blacks and other reinforcing fillers give the same level of mechanical properties for SBR as for NR vulcanisates. The relative order of activity of fillers is the same in SBR as in NR, but the degree of reinforcement of the fillers is higher in the former[6]. Among the commonly used fillers and reinforcing agents, carbon black offers the most potential reinforcement[7]. Carbon black contributes much to increase the desirable properties of the vulcanised rubber and it is a universal compounding ingredient for quality stocks[8]. Several authors studied the mechanism of reinforcement by carbon black[9-12]. Carbon black reinforcement generates a unique three dimensional visco-elastic network and as a result the elastomer is modified from a soft to a strong elastic product[13]. Furnace black is the most preferred reinforcing black for SBR compounding. Next to furnace black, precipitated silica, calcium carbonate etc. are also used as fillers. By the incorporation of 50 phr. of reinforcing black the tensile strength of pure gum vulcanisate of SBR can be easily raised to about ten times. HAF black with average particle size in the range of 24-28nm are most widely used for general purpose SBR. The role of reinforcing black in the sulphuration process of vulcanisation is discussed by Porter[14] as well as by Bhowmic and De[15].

Precipitated silica is the best non-black reinforcing filler used in SBR to improve processing and reinforce the polymer in the production of light coloured products[16]. Good strength and abrasion resistance can be achieved with precipitated silica, although they are somewhat inferior in this respect to carbon black[17]. Precipitated silica is having high adsorptive nature and as a result retard cure at high loading. In order to balance this, cure time activators such as diethylene glycol have to be used during compounding. SBR gives good physical properties in either black or light coloured products. It has high loading capacity and is used in the manufacture of tyres and other moulded and extruded products, footwear, coated fabrics etc.

In the present investigation we used N-amidino N'-phenyl thiourea as a secondary accelerator in the sulphur vulcanisation of SBR with MBTS/TMTD as primary. Binary systems containing thiourea as the secondary accelerator are taken as control. The results obtained for the experimental systems containing APT were compared with those of the references. As one of the aims of the study is to see whether these vulcanisation reactions follow a nucleophilic pattern, we prepared and studied the gum formulations first. In order to investigate the effect of APT on filled systems, vulcanisates were prepared with carbon black and precipitated silica as fillers. Different mixes with varying concentrations of APT and TMTD/MBTS were tried in standard recipes for gum and filled compounds. The study covered different aspects like mixing, curing and determination of various physical properties of vulcanisates. The fact that the amidinothiourea derivative is a non-toxic material will be an added advantage. To understand the variation in physical properties of the vulcanisates, chemical crosslinks were also estimated using the equilibrium swelling method.

PART A

5.1 GUM FORMULATIONS OF SBR

5.1.1 Experimental

Different SBR gum compounds were prepared taking MBTS/TMTD as primary and APT as secondary accelerator. In the formulations reported (table.5.1.1) all the accelerators are taken in molar concentrations and other compounding ingredients are in parts per hundred rubber (phr.). Thiourea binary systems containing 1:1 molar combinations with TMTD and MBTS were taken as reference formulations for comparing the cure properties and to see whether the reaction follows a nucleophilic pattern. Properties of the APT mixes were compared with conventional accelerator systems like TMTD-MBTS also. Table 5.1.1 shows the formulations of different mixes prepared. Compounds A_1-A_4 contain different concentrations of APT, viz. 0.25, 0.5, 1 and 1.5 molar equivalents with 1 molar equivalent TMTD; mixes R_1 and R_2 contain 2 molar equivalents of TMTD and MBTS respectively. R_3 contains TMTD and MBTS in 1:1 molar ratio and R_4 is the control mix with TMTD and TU in 1 molar proportion. Mixes B_1-B_4 represent systems with different concentrations of APT ranging from 0.25 to1.5 molar equivalents with 1 molar equivalent MBTS. R_5 contains 1 molar equivalents of MBTS and TU each.

Table 5.1.1 Formulations of SBR gum mixes

Ingredients	**A_1**	**A_2**	**A_3**	**A_4**	**B_1**	**B_2**	**B_3**	**B_4**	**R_1**	**R_2**	**R_3**	**R_4**	**R_5**
SBR	100	100	100	100	100	100	100	100	100	100	100	100	100
Zno	5	5	5	5	5	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2	2	2	2	2	2
TMTD	1.2	1.2	1.2	1.2	-	-	-	-	2.4	-	1.2	1.2	-
MBTS	-	-	-	-	1.66	1.66	1.66	1.66	-	3.32	1.66	-	1.66
TU	-	-	-	-	-	-	-	-	-	-	-	0.38	0.38
APT	0.243	0.485	0.970	1.455	0.243	0.485	0.970	1.455	-	-	-	-	-
Sulphur	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5

The mixes were prepared on a laboratory size two roll mixing mill as per ASTM D 3182-89 as detailed earlier. Goettfert elastograph was used to determine the cure characteristics of the various compounds at 150°C. The values obtained for maximum and minimum torque, cure rate index, optimum cure time, elastographic scorch time etc. of the various formulations are reported in table 5.1.2 and 5.1.3. The compounds were vulcanised up to the optimum cure time in an electrically heated hydraulic press at 150°C at a pressure of 11.76MPa. The tensile properties of the vulcanisates reported in this chapter were determined on a Zwick Universal Testing Machine model 1445 using a crosshead speed of 500mm/min. Heat ageing of the samples was studied as per ASTM designation D 573-88. The tensile and other physical properties evaluated are reported in table 5.1.4. The concentration of the chemical crosslinks (total crosslink density) of the vulcanisates was determined from the equilibrium swelling data. Swelling was done in toluene for 24hrs.using samples of approximately 0.2cm thickness, 1cm. diameter and 0.2gm weight. Angular test specimens were used to measure tear resistance according to ASTM D 624-86. Compression set and hardness were measured as per ASTM D 395-89 and D 2240-86 respectively. Abrasion loss was measured using DIN abrader (DIN 53516).

5.1.2 Results and Discussion

Cure characteristics

The cure curves obtained for TMTD and MBTS systems are shown in figs 5.1.1 and 5.1.2 respectively. Corresponding cure characteristics such as optimum cure time (t_{90}) scorch time (t_{10}), cure rate index, minimum and maximum torque values obtained are given in tables 5.1.2 and 5.1.3. A definite accelerator activity of APT in the sulphur vulcanisation of these styrene butadiene rubber systems is indicated by the above values obtained.

Considering the binary systems with TMTD, as the concentration of APT increases from 0.25 to1.50 molar levels optimum cure time is reduced to one third and cure rate is seen to be doubled. Also a sharp decrease in scorch time is observed. The optimum cure time of the experimental system A_3 (2.6min.) is almost half of that with TU (4.4min.). The scorch time is also reduced much. Among the APT systems mix A_2 containing 0.5 molar equivalent of APT with one molar equivalent TMTD showed comparatively safer scorch time. But considering the other cure characteristics (t_{90} value, cure rate index and maximum torque value) mix A_3 with an APT level of one molar equivalent with one molar equivalent of TMTD can be taken to be an optimum cure system.

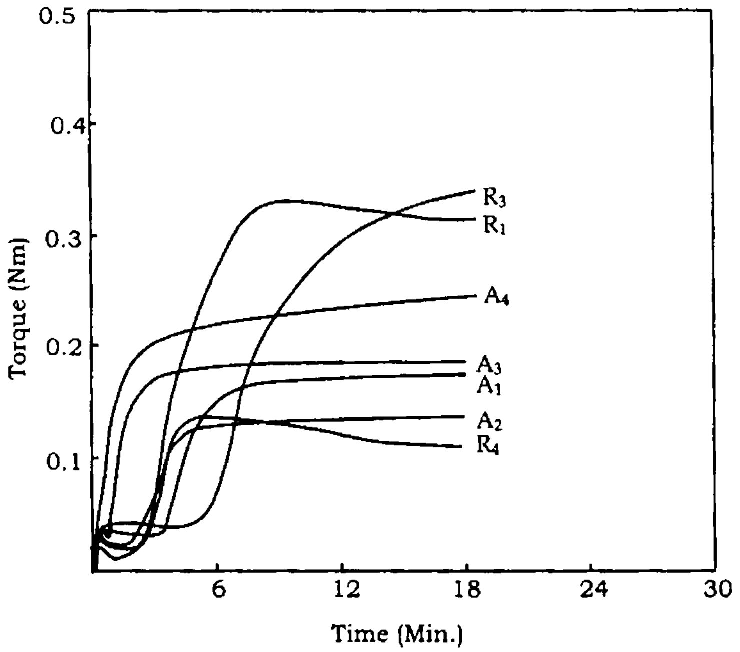

Fig. 5.1.1 Cure curves of SBR gum mixes containing TMTD

Table 5.1.2 Cure characteristics of TMTD systems

	A_1	A_2	A_3	A_4	R_1	R_3	R_4
Optimum cure time t_{90} (min)	6.6	5	2.6	2.2	10.6	13.7	4.4
Scorch time t_{10} (min)	3.2	2.2	0.8	0.6	2.7	5.6	2.4
Cure rate index	29.41	35.71	55.56	62.50	12.66	12.35	52.63
Minimum torque (Nm)	0.03	0.02	0.03	0.02	0.05	0.04	0.05
Maximum torque (Nm)	0.17	0.14	0.18	0.24	0.32	0.34	0.13

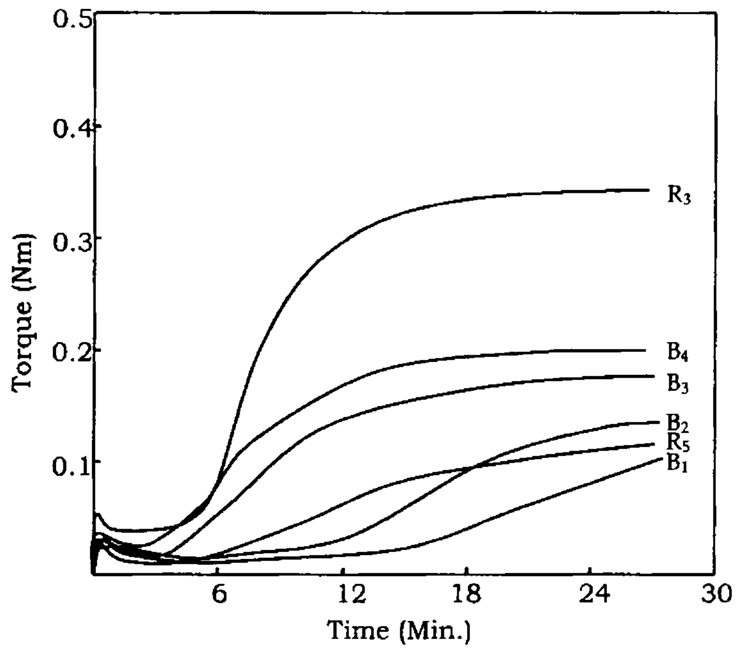

Fig. 5.1.2 Cure curves of SBR gum mixes containing MBTS

The effectiveness of APT in MBTS binary systems also is indicated by the results obtained for the cure characteristics reported in table 5.1.3. As the concentration of APT is increased from 0.25 to 1.5 molar level along with one molar equivalent MBTS, the t_{90} value reduces from 28min. to 10.1min. However, a corresponding decrease in scorch time is also noticed. MBTS alone (2 molar level) was not seen to cure properly. Comparing MBTS-APT mixes with control systems containing equivalent concentrations of MBTS and TU, the t_{90} value, cure rate index, maximum torque value etc. are much favourable for the experimental systems of MBTS-APT compared to MBTS-TU. A bar graphical comparison of optimum cure time and scorch time of the mixes containing optimum concentration of APT and of references is shown in fig. 5.1.3. As far as torque value is concerned TMTD-MBTS mix is superior to other combinations.

The effectiveness of APT as a secondary accelerator in both TMTD-APT and MBTS-APT systems is clearly indicated by the cure characteristics obtained. The disadvantage to be noted here is the lower scorch time at higher dosage of APT. Amidino phenyl thiourea being more nucleophilic than thiourea, by virtue of the guanidinyl group present in it, the nucleophilic reaction mechanism proposed in similar vulcanisation reactions reported by Moore et al.[18] can be applied for the sulphur vulcanisation of styrene butadiene rubber also.

Table 5.1.3 Cure characteristics of MBTS systems

	B_1	B_2	B_3	B_4	R_3	R_5
Optimum cure time t_{90} (min)	28	25.6	17.1	10.1	13.7	24
Scorch time t_{10} (min)	15.2	10.2	4.9	3.2	5.6	7
Cure rate index	7.81	6.49	8.19	14.49	12.35	5.88
Minimum torque (Nm)	0.02	0.02	0.02	0.03	0.04	0.02
Maximum torque (Nm)	0.12	0.15	0.18	0.19	0.34	0.13

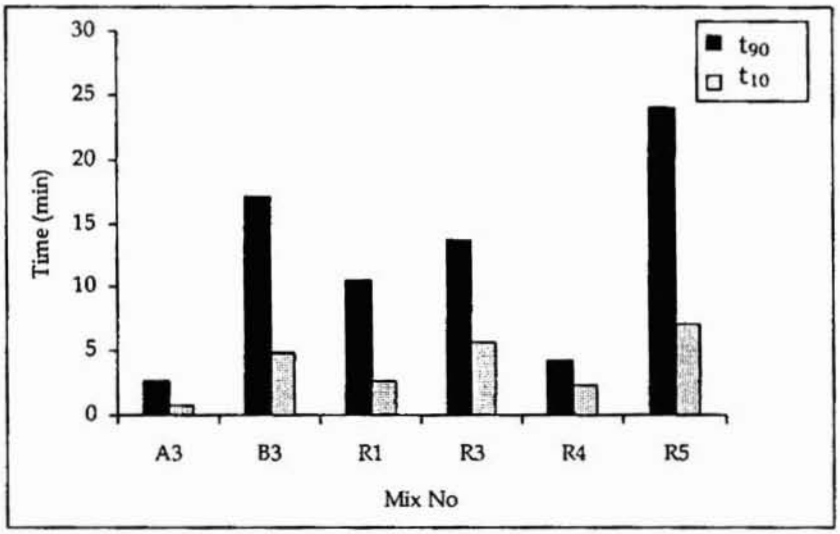

Fig. 5.1.3 Comparison of optimum cure time (t_{90}) and scorch time (t_{10}) of SBR (gum) mixes containing optimum dosage of APT with references.

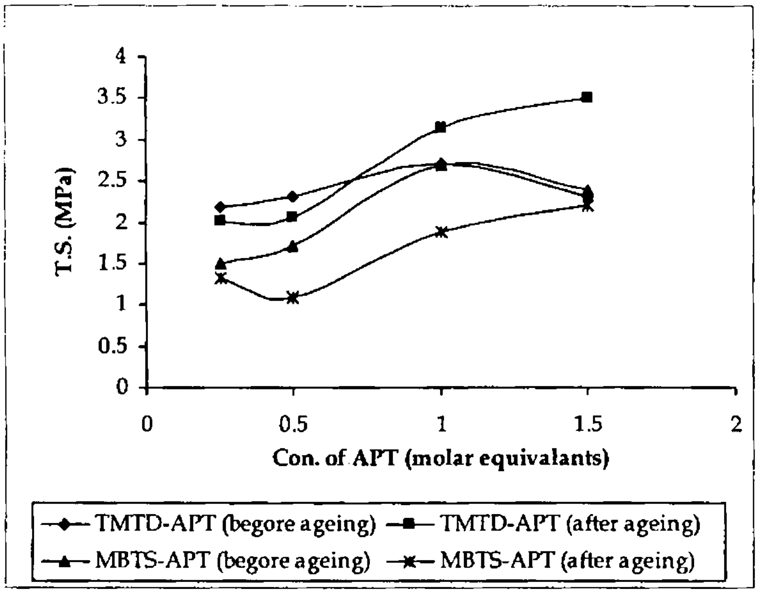

Fig. 5.1.4 Variation of Tensile Strength of SBR gum vulcanisates with concentration of APT.

Tensile and other physical properties

SBR being a non-strain crystallising rubber has poor gum strength. However, APT when used as a secondary accelerator is found to improve the tensile properties compared to the reference systems. These vulcanisates show higher tensile values both before and after ageing (table 5.1.4) The variation of tensile strength with concentration of APT is shown in fig. 5.1.4. In TMTD binary systems mix A_3 shows a tensile strength of 2.718 MPa, which is more than double the value for the equivalent TMTD-TU system. The heat-aged samples also show higher tensile strength values compared to the reference formulations. The elongation at break values remain more or less comparable with the reference systems. Mix R_2 containing MBTS alone is very slow curing and hence it was not studied further. Experimental systems of APT with MBTS showed almost a similar trend as that of TMTD. Here also much improvement in the tensile strength is shown by the APT binary combinations (fig. 5.1.5).

Table 5.1.4 : Physical properties of SBR gum vulcanizates

Mix No.	Tensile strength (MPa)			Elongation at break (%)			Tear strength (N/mm)	Hardness (Shore A)	Compression set (%)	Abrasion loss (cm^3/hr)	Total cross link density × 10^5 (g.mol cm^{-3})
	Before ageing	After ageing	Retention %	Before ageing	After ageing	Retention %					
A_1	2.191	2.008	91.66	296.68	217.65	73.36	13.06	47.6	15.12	13.71	3.55
A_2	2.326	2.066	88.82	364.20	278.50	76.47	11.71	48.0	13.89	13.80	3.75
A_3	2.718	3.145	115.72	422.06	397.00	94.06	16.96	48.0	23.80	8.05	3.81
A_4	2.317	3.509	151.45	249.20	228.30	91.68	19.75	54.0	20.69	12.70	5.01
B_1	1.36	1.32	97.06	511.40	331.60	64.84	6.81	19.66	13.52	14.08	1.27
B_2	1.71	1.09	63.62	359.02	344.75	96.03	13.72	27.0	11.25	13.87	2.31
B_3	2.69	1.88	69.91	498.25	359.60	72.18	16.30	31.0	11.88	13.09	1.82
B_4	2.39	2.21	92.16	424.75	348.88	82.14	17.82	34.0	10.95	11.81	2.91
R_1	1.869	3.35	179.24	483.59	230.75	47.72	11.82	38.30	8.12	12.47	5.12
R_3	1.693	3.20	189.01	258.28	200.30	71.55	10.35	49.00	14.22	17.09	6.3
R_4	1.218	1.40	114.94	494.38	412.38	83.41	12.86	28.30	19.46	11.09	5.21
R_5	1.58	1.62	102.80	441.00	441.00	100.00	8.93	23.66	13.70	13.36	1.89

Elongation at break values are found to increase up to optimum level of APT and then decreases in both the binary systems. The variations in tensile properties are more or less in accordance with the total cross link density values.

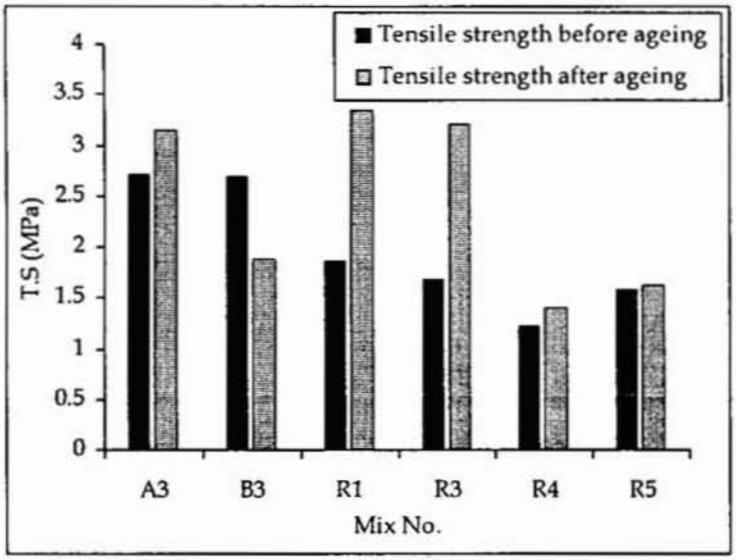

Fig. 5.1.5 Comparison of tensile strength of SBR gum vulcanisates

Hardness, tear strength, compression set and abrasion loss are the other physical properties studied and the values estimated are also reported in table 5.1.4. In the case of TMTD - APT vulcanisates, as the dosage of APT increases, hardness and tear strength are found to increase and the vulcanisate with optimum concentration of APT is found to show better values for these properties compared to those of references. Compression set and abrasion loss values are found to vary much and set property is not found to be so favourable compared to those of the references. In the MBTS-APT systems, hardness and tear strength values reach a maximum with increase in concentration of APT whereas compression set does not show much variation with increase in dosage of APT. Abrasion loss is found decreased (abrasion resistance increased) with increase in concentration of APT.

PART B

5.2 FILLED SYSTEMS OF STYRENE BUTADIENE RUBBER

5.2.1 Experimental

Formulations of the filled systems studied are given in tables 5.2.1 and 5.2.2. 50 phr. of carbon black was incorporated in different mixes. Since higher loading of silica was found to be difficult due to high temperature development, mixes with 30 phr. of silica were only investigated. Mixes Ac_1–Ac_4 and Bc_1–Bc_4 are black filled experimental mixes containing varying concentrations of APT ranging from 0.25 to 1.5 molar with 1 molar equivalent TMTD and MBTS respectively.

Table 5.2.1 Formulations of filled mixes containing TMTD

Ingredients	**Ac_1**	**Ac_2**	**Ac_3**	**Ac_4**	**As_1**	**As_2**	**As_3**	**As_4**	**Rc_1**	**Rc_3**	**Rc_4**	**Rs_1**	**Rs_3**	**Rs_4**
SBR	100	100	100	100	100	100	100	100	100	100	100	100	100	100
ZnO	5	5	5	5	5	5	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2	2	2	2	2	2	2
Carbon black	50	50	50	50	-	-	-	-	50	50	50	-	-	-
Aromatic oil	5	5	5	5	-	-	-	-	5	5	5	-	-	-
Precipitated silica	-	-	-	-	30	30	30	30	-	-	-	30	30	30
Naphthenic oil	-	-	-	-	5	5	5	5	-	-	-	5	5	5
DEG	-	-	-	-	2	2	2	2	-	-	-	2	2	2
TMTD	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	2.4	1.2	1.2	2.4	1.2	1.2
MBTS	-	-	-	-	-	-	-	-	-	1.66	-	-	1.66	-
TU	-	-	-	-	-	-	-	-	-	-	0.38	-	-	0.38
APT	0.243	0.485	0.970	1.455	0.243	0.485	0.970	1.455	-	-	-	-	-	-
Sulphur	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5

Similar is the formulations used for As_1- As_4 and Bs_1- Bs_4 where 30 phr. precipitated silica is used. Rc_1- Rc_5 represent reference mixes with carbon black and Rs_1-Rs_5 represent those of silica. For mixes containing carbon black aromatic oil (5phr.) is used as process aid while naphthenic oil (5phr.) is used for silica compounds. 2phr. diethylene glycol (DEG) is added in formulations containing silica. Procedure for mixing and vulcanisation, determination of cure characteristics of the compounds, evaluation of physical properties and chemical characterisation of the vulcanisates are all carried out as per relevant standards described in detail in chapter 2.

Table 5.2.2 Formulations of filled mixes containing MBTS

Ingredients	**Bc_1**	**Bc_2**	**Bc_3**	**Bc_4**	**Bs_1**	**Bs_2**	**Bs_3**	**Bs_4**	**Rc_2**	**Rc_5**	**Rs_2**	**Rs_5**
SBR	100	100	100	100	100	100	100	100	100	100	100	100
ZnO	5	5	5	5	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2	2	2	2	2
Carbon black	50	50	50	50	-	-	-	-	50	50	-	-
Aromatic oil	5	5	5	5	-	-	-	-	5	5	-	-
Precipitated silica	-	-	-	-	30	30	30	30	-	-	30	30
Naphthenic oil	-	-	-	-	5	5	5	5	-	-	5	5
DEG	-	-	-	-	2	2	2	2	-	-	2	2
MBTS	1.66	1.66	1.66	1.66	1.66	1.66	1.66	1.66	3.32	1.66	3.32	1.66
TU	-	-	-	-	-	-	-	-	-	0.38	-	0.38
APT	0.243	0.485	0.970	1.455	0.243	0.485	0.970	1.455	-	-	-	-
Sulphur	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5

5.2.2 Results and Discussion

Cure characteristics

Cure curves obtained for the various filled systems of SBR are shown in figs. 5.2.1- 5.2.4 and the respective cure characteristics are given in tables 5.2.3 and 5.2.4. The positive effect of APT as a secondary accelerator is very evident from the results obtained. Considering the MBTS systems definite decrease in optimum cure time and scorch time with increase in concentration of APT in both black and silica filled formulations are noticed. As the concentration of APT is increased from 0.25 to 1.5 level the t_{90} value decreased from 19.6 min. to 8.4 min. in black containing mixes.

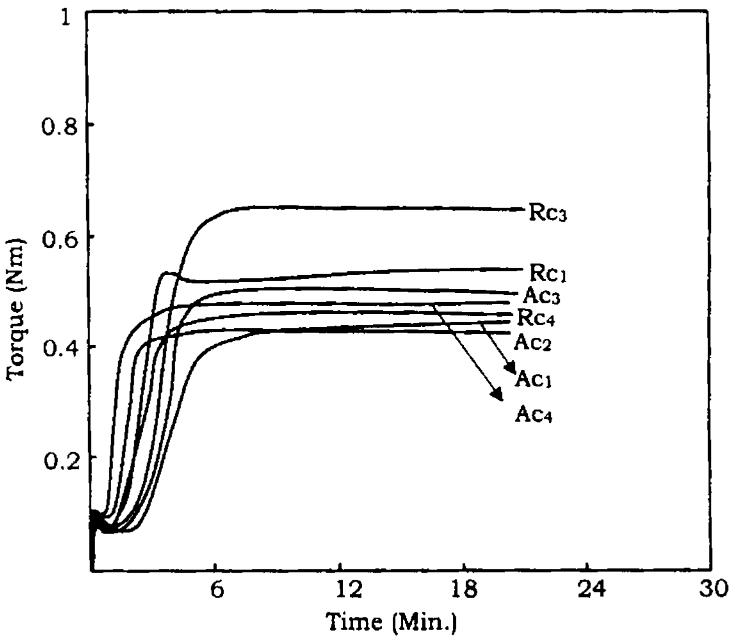

Fig 5.2.1 Cure curves of SBR black filled mixes containing TMTD.

In silica systems mix Bs_1 containing 0.25 molar equivalent of APT is seen to be not curing properly. But as the concentration increases from 0.5 to 1.5 molar level the t_{90} value is found to decrease from 27 min. to 19.7 min.

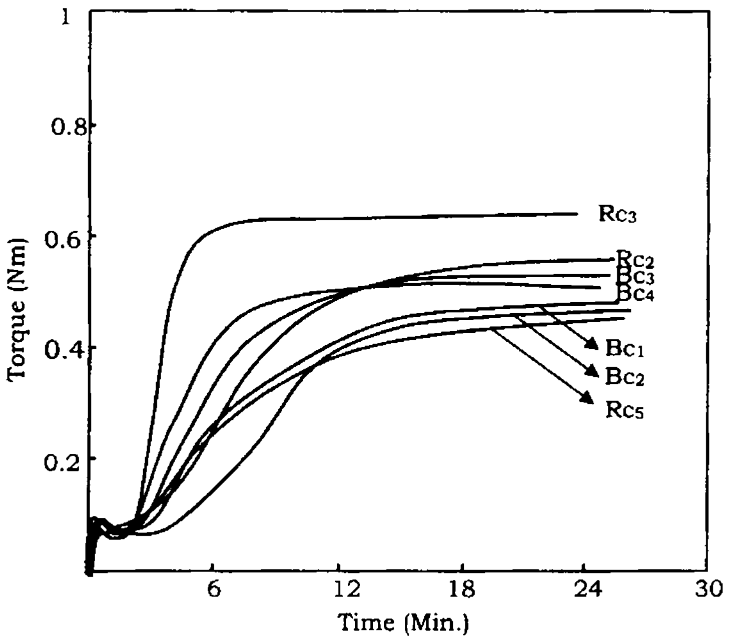

Fig. 5.2.2 Cure curves of SBR black filled mixes containing MBTS

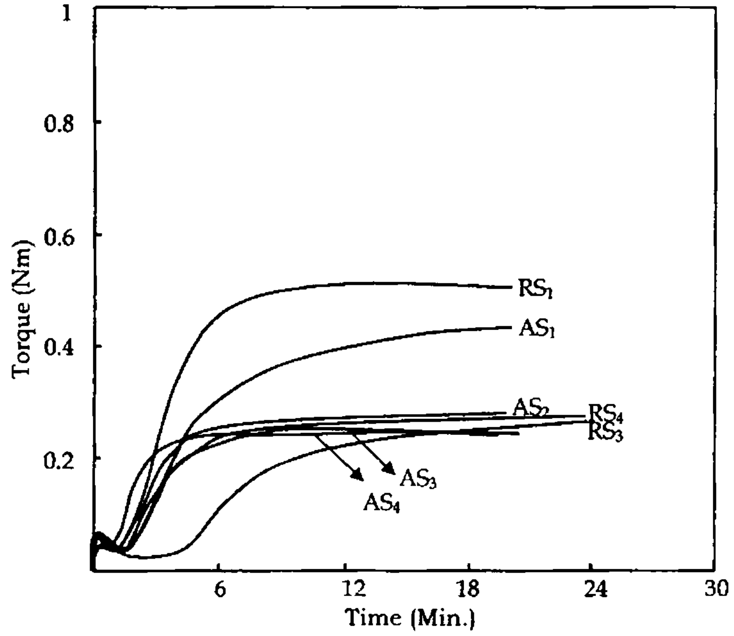

Fig. 5.2.3 Cure curves of SBR silica filled mixes containing TMTD

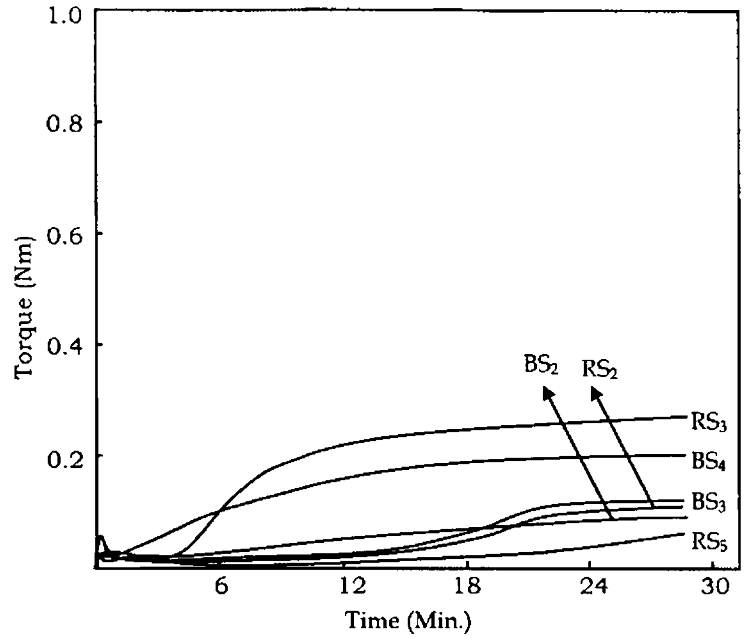

Fig. 5.2.4 Cure curves of SBR silica filled mixes containing MBTS

Table 5.2.3 Cure characteristics of filled compounds containing TMTD

	Ac_1	**Ac_2**	**Ac_3**	**Ac_4**	**As_1**	**As_2**	**As_3**	**As_4**	**Rc_1**	**Rc_3**	**Rc_4**	**Rs_1**	**Rs_3**	**Rs_4**
Optimum cure time t_{90} (min)	3.5	3.0	2.3	2.0	13.6	6.8	5.9	3.7	3.3	4.7	3.2	6.1	18.7	5.7
Scorch time t_{10} (min)	1.7	1.7	0.9	0.6	2.2	2.2	2.1	1.2	1.6	2.3	1.6	1.9	4.7	1.6
Cure rate index	59.56	76.92	71.43	77.43	81.77	21.74	26.30	40.0	5882	41.67	62.50	23.80	7.14	24.39
Minimum torque (Nm)	0.08	0.075	0.08	0.092	0.034	0.021	0.023	0.021	0.068	0.062	0.075	0.031	0.017	0.023
Maximum torque (Nm)	0.518	0.451	0.474	0.560	0.446	0.218	0.246	0.242	0.537	0.642	0.462	0.499	0.279	0.244

A corresponding decrease in scorch time also takes place (table 5.2.4). In the TMTD systems also a similar trend is seen for the optimum cure time and scorch time values in both the filled formulations (table 5.2.3) under review. However, in the TMTD system mix containing 0.25 APT also cures properly.

Table 5.2.4 Cure characteristics of filled compounds containing MBTS

	Bc_1	Bc_2	Bc_3	Bc_4	Bs_2	Bs_3	Bs_4	Rc_2	Rc_3	Rc_5	Rs_2	Rs_3	Rs_5
Optimum cure time t_{90} (min)	19.6	18.5	11.6	8.4	27.0	26.6	19.7	16.4	4.7	15.7	29.2	18.7	25.5
Scorch time t_{10} (min)	3.3	3.5	2.6	1.8	11.9	6.2	2.2	2.4	2.3	2.7	17.8	4.7	6.0
Cure rate index	6.13	6.67	4.11	15.15	6.62	4.9	5.7	7.67	41.67	7.69	8.7	7.14	5.12
Minimum torque (Nm)	0.077	0.071	0.068	0.073	0.015	0.014	0.017	0.075	0.062	0.063	0.016	0.017	0.017
Maximum torque (Nm)	0.51	0.48	0.54	0.53	0.101	0.113	0.213	0.591	0.642	0.46	0.079	0.279	0.096

Considering systems containing equivalent amounts of APT and thiourea t_{90} values are found to be lesser for the former in the black filled mixes. But in TMTD and MBTS systems where silica is used as filler, optimum cure time and scorch time values of the APT mixes are slightly higher than the corresponding TU systems (tables.5.2.4 & 5.2.5).

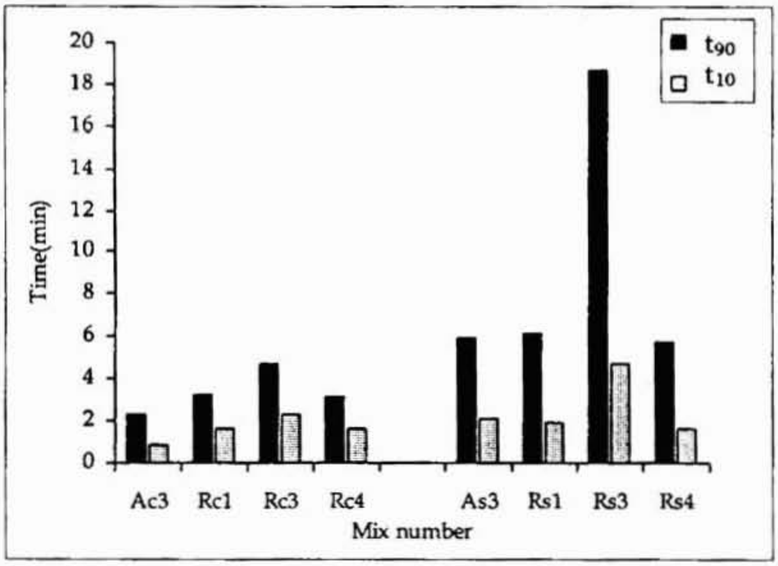

Fig. 5.2.5 Comparison of t_{90} and t_{10} values of SBR filled mixes containing optimum dosage of APT and of references (TMTD systems)

This observation is somewhat different from what we noticed in NR (gum and filled systems) and SBR gum formulations. Here it is most probable that instead of a nucleophilic reaction mechanism there may be mixed polar/radical type reactions involved in these silica filled binary combinations as suggested by Shelton and McDonel[19] and by Coran[20]. Compared to the conventional combination of MBTS and TMTD the APT-TMTD mixes with equivalent molar concentration show better values for the cure characteristics studied. Considering the maximum torque developed, cure rate and the scorch time values, a better cure system can be the one with one molar equivalent of APT with one molar TMTD/MBTS in both carbon black and silica formulations. In comparison to MBTS, TMTD systems are found to be faster curing and show better cure rate values. The main disadvantage of high scorchiness at higher dosages of APT is found in almost all the systems studied but is more pronounced in TMTD black filled formulations.

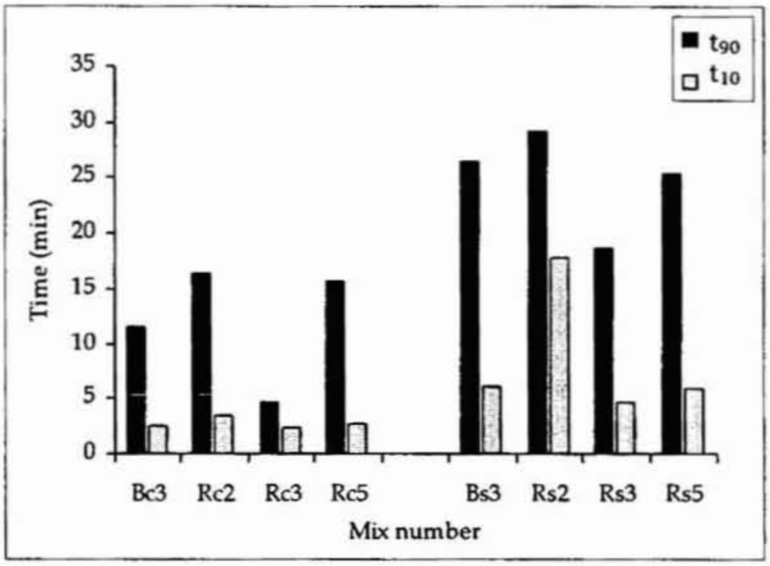

Fig. 5.2.6 Comparison of t_{90} and t_{10} values of SBR filled mixes containing optimum dosage of APT and of references (MBTS systems)

Tensile and other physical properties

Tensile properties of the various filled vulcanisates are shown in table 5.2.5. Tensile strength values of MBTS-APT systems are found to be higher than that of TMTD-APT systems in both the filler types.

Table 5.2.5 Physical properties of filled vulcanisates

Mix No.	Tensile strength (MPa)			Tear strength (N/mm)	Hardness (Shore A)	Compression set (%)	Abrasion loss (cm^3/hr)	Total cross link density × 10^5 (g.mol cm^{-3})
	Before ageing	After ageing	Retention %					
Ac$_1$	12.74	11.68	91.6	79.53	70.0	17.00	3.33	4.90
Ac$_2$	13.53	13.65	100.8	100.53	70.0	16.54	3.24	4.35
Ac$_3$	13.65	11.42	83.6	80.40	74.6	16.09	3.24	5.30
Ac$_4$	9.56	12.28	128.4	74.97	77.0	14.98	3.20	6.26
Bc$_1$	19.02	17.90	94.1	79.10	57.0	15.11	4.04	2.47
Bc$_2$	19.37	18.66	96.3	86.09	59.0	32.12	3.73	2.74
Bc$_3$	16.33	16.62	101.7	82.30	60.0	27.41	3.42	2.54
Bc$_4$	13.29	18.05	135.8	85.45	60.0	14.98	4.01	2.38
As$_1$	4.44	5.55	125.0	21.83	39.6	15.64	10.30	2.13
As$_2$	4.52	4.04	89.3	29.94	40.0	24.19	8.20	2.33
As$_3$	5.02	7.09	141.0	33.22	45.0	22.99	13.30	2.11
As$_4$	5.47	7.49	136.0	29.01	48.3	30.06	14.36	1.87
Bs$_2$	7.72	7.39	102.0	39.71	42.0	16.34	18.37	2.26
Bs$_3$	7.39	7.87	106.5	40.53	39.0	20.83	10.89	1.53
Bs$_4$	6.94	7.12	102.5	37.30	42.3	36.57	15.52	2.29
Rc$_1$	11.84	11.84	100.0	72.32	68.0	14.09	3.20	3.70
Rc$_2$	19.02	18.67	98.2	68.93	48.0	17.77	4.43	1.79
Rc$_3$	13.29	12.15	91.4	39.14	62.0	13.98	3.23	5.07
Rc$_4$	10.59	10.37	97.9	78.64	71.0	21.79	3.14	4.90
Rc$_5$	14.71	14.21	96.5	74.03	63.0	23.75	4.07	1.79
Rs$_1$	3.39	3.69	108.8	27.64	45.7	22.44	12.96	3.29
Rs$_2$	5.02	8.37	166.7	30.68	39.0	28.30	13.60	2.26
Rs$_3$	2.94	4.47	154.1	29.93	45.0	33.90	10.21	3.85
Rs$_4$	5.15	6.36	123.4	34.37	46.6	37.47	11.11	2.32
Rs$_5$	6.03	7.49	124.2	30.06	35.3	53.50	16.74	2.05

In TMTD black systems the vulcanisate containing optimum concentration of APT shows higher tensile strength. Percentage retention of tensile strength after heat ageing is comparable with that of reference formulations in both filled systems. Comparing the tensile values of APT systems with reference formulations, vulcanisates containing the amidinothiourea derivative show higher values.

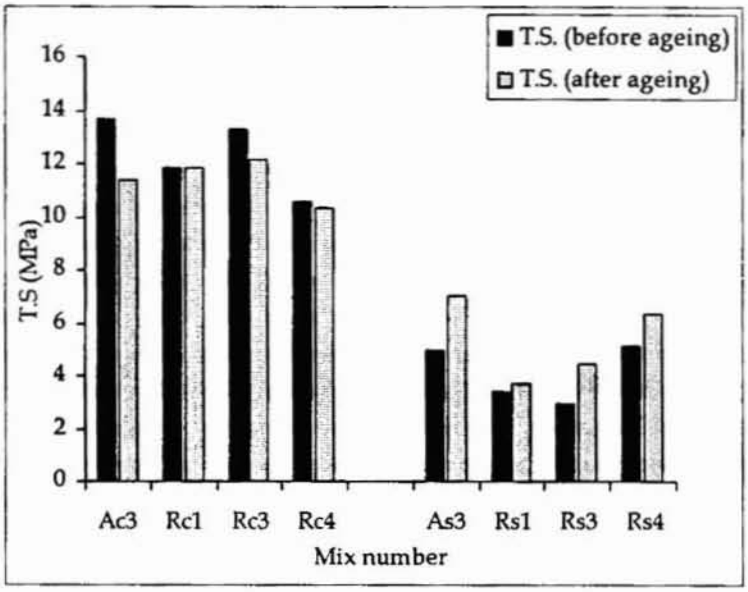

Fig. 5.2.7 Comparison of tensile strength of SBR filled vulcanisates containing optimum dosage of APT and of references (TMTD systems)

Properties such as hardness, tear strength, compression set and abrasion loss studied for the different filled vulcanisates are reported in table 5.2.5. In the case of TMTD systems it is seen that as dosage of APT increases hardness also increase for both filled systems. Compression set and abrasion loss values show a favourable decrease. It is also noted that as the dosage of APT increases the tear strength increases up to an optimum level. In MBTS-APT binary systems also there is a regular increase in hardness values as the concentration of APT increases. Compression set values tend to show an initial increase.

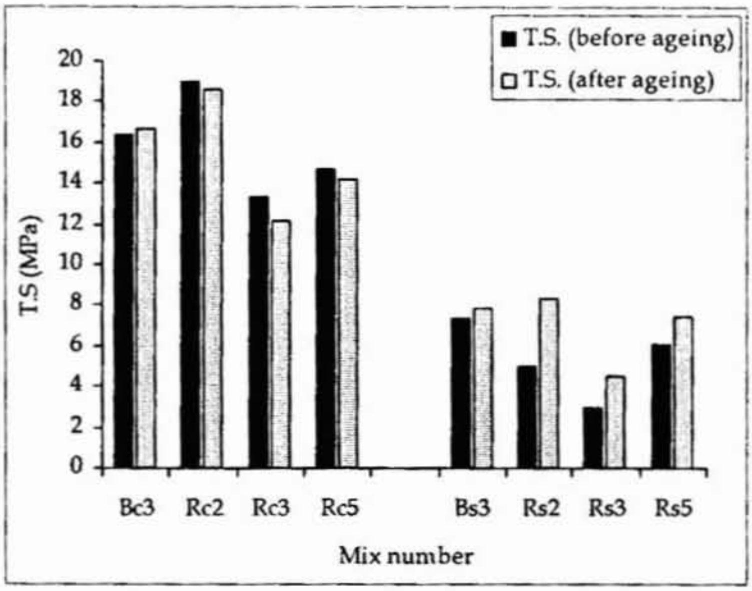

Fig. 5.2.8 Comparison of tensile strength of SBR filled vulcanisates containing optimum dosage of APT and of references (MBTS systems)

CONCLUSIONS

The results obtained from the above studies on the effect of N-amidino N'-phenyl thiourea on vulcanisation systems of styrene butadiene rubber indicate that APT can act as an effective secondary accelerator in the sulphur vulcanisation of this rubber with TMTD or MBTS as primary accelerator. The introduction of the amidino thiourea derivative reduces the optimum cure time considerably. Comparing the mixes TMTD-APT and TMTD-TU, the former showed lower cure time and higher cure rate values. The results with MBTS systems are also more or less similar. Analysis of the cure properties of the various gum formulations reveals that the nucleophilic reaction mechanism proposed for NR binary systems is applicable to these SBR systems also. TMTD-APT and MBTS-APT systems are found to be effective with SBR filled vulcanisates also. Even though the cure characteristics obtained in gum formulation of SBR point to a nucleophilic reaction mechanism, the silica filled systems of SBR do not seem to follow a similar pattern. Here a mixed polar-radical mechanism is most probable. The vulcanisates obtained with these filled systems with carbon black/silica showed satisfactory tensile properties and good retention of these properties after ageing. In the evaluation of other physical properties also these vulcanisates gave results comparable to other reference formulations. Considering the cure characteristics of the different mixes and tensile properties of the vulcanisates, practical cure systems with optimum concentration of APT required have also been proposed. The non-toxic nature of this amidino phenyl thiourea derivative will be an added advantage in this context.

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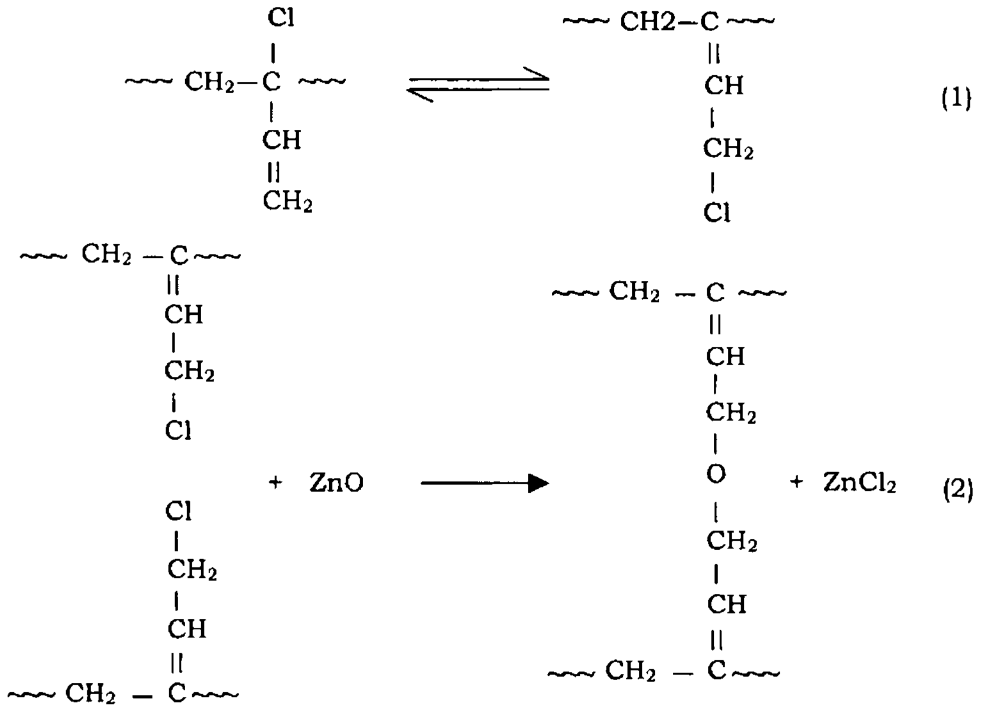
Chapter 6

STUDIES ON THE EFFECT OF AMIDINO PHENYL THIOUREA IN THE VULCANISATION OF POLYCHLOROPRENE RUBBER (CR)

Neoprene is the generic name for polymers of 2-chloro 1,3 butadiene (chloroprene) introduced commercially by DuPont in 1931. The molecular structures of neoprene polymers are primarily trans 1,4 chloroprene units (88-92%), but three other configurations viz. cis 1,4 (7-12%), 1,2 (1.5%) and 3,4 (1%) also occur. The 1,2 addition of chloroprene results in polymer having some chlorine available in allylic position. This is a labile form and is believed to be the main site of vulcanisation. The degree of crystallinity in neoprene is largely dependent upon the amount of trans configurations in the polymer. CR is a polar rubber and it contains one chlorine for every four carbon atom in the chain of this homopolymer. Therefore, by comparison with non-polar diene rubbers, CR has a better resistance to swelling in mineral, animal and vegetable oils and fats. The chlorine atom also imparts to CR better flame, weather and ozone resistance than normally encountered with diene rubbers.

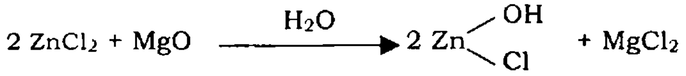
There are different types of neoprenes. Dry neoprene is either of the speciality type or the widely used general-purpose type. The special purpose types are designed primarily for a particular application, eg. adhesives, coatings, crepe soles etc. General-purpose neoprenes are classified into G, W and T types. The G types are copolymerised with sulphur and contain thiuram disulphide stabiliser. W and T types are much more stable than G types[1]. W types have more uniform distribution of molecular weight. The G types cure rapidly without accelerator where as the W types require accelerators for acceptable curing and vulcanisate properties. These have many processing advantages over the G types. Neoprene W type is used in our present study. Polychloroprene vulcanises in a considerably different manner from that of natural rubber and other synthetic rubbers. Contrary to other diene rubbers the vulcanisation of CR compounds is carried out using metal oxides. The metal oxides most often used are zinc oxide, as crosslinking agent and magnesium oxide, which is mainly used as an acid acceptor. As magnesium oxide serves as an acid acceptor preventing premature crosslinking and cyclisation of polychloroprene compounds, it is usually the first compounding ingredient to be incorporated. Zinc oxide, having a relatively strong influence on the onset of vulcanisation is added later. A typical combination of zinc oxide (5phr.) and specially calcined magnesium oxide (4phr.) is preferred for compounding. When used in conjunctions with ZnO, MgO improves processing safety by removing the $ZnCl_2$ formed. $ZnCl_2$ also catalyses the cross linking reaction, and that is why the vulcanisation reaction is scorchy in the absence of MgO.

The vulcanisation chemistry of chloroprene rubbers is also fundamentally different from that of other rubbers. The carbon-carbon double bonds in the polychloroprene chains are deactivated by the presence of the electronegative chlorine atoms. It is usually assumed that crosslinking of polychloroprene molecules occur by way of ether formation accompanied by loss of chlorine atoms. The chlorine atoms, which participate in the crosslinking reaction, are believed to be those, which are present in small proportion of 1,2 addition units. The chlorine atom in a 1,4 unit (vinylic) are considerably less reactive than in 1,2 and 3,4 units (allylic). It thus appears that the possibility of vulcanising a chloroprene rubber by heating it with a metal oxide depends upon the presence in the polymer molecules of a few allylic chlorine atoms arising from 1,2 and 3,4 additions during polymerisation. Equations (1) and (2) illustrate the vulcanisation mechanism of polychloroprene.



Scheme 6.1

It is believed that the principal curing site is at the location of the 1,2 addition configuration of the monomer unit in the polymer chain. The chlorine atom in the 1,2 addition configuration chain is allylic and accordingly labile[2,3]. The $ZnCl_2$ formed is an active catalyst of vulcanisation, and unless it is scavenged, its presence during processing operations can cause scorching problems. Equation (a) shows how MgO acts as a stabilizer during processing.

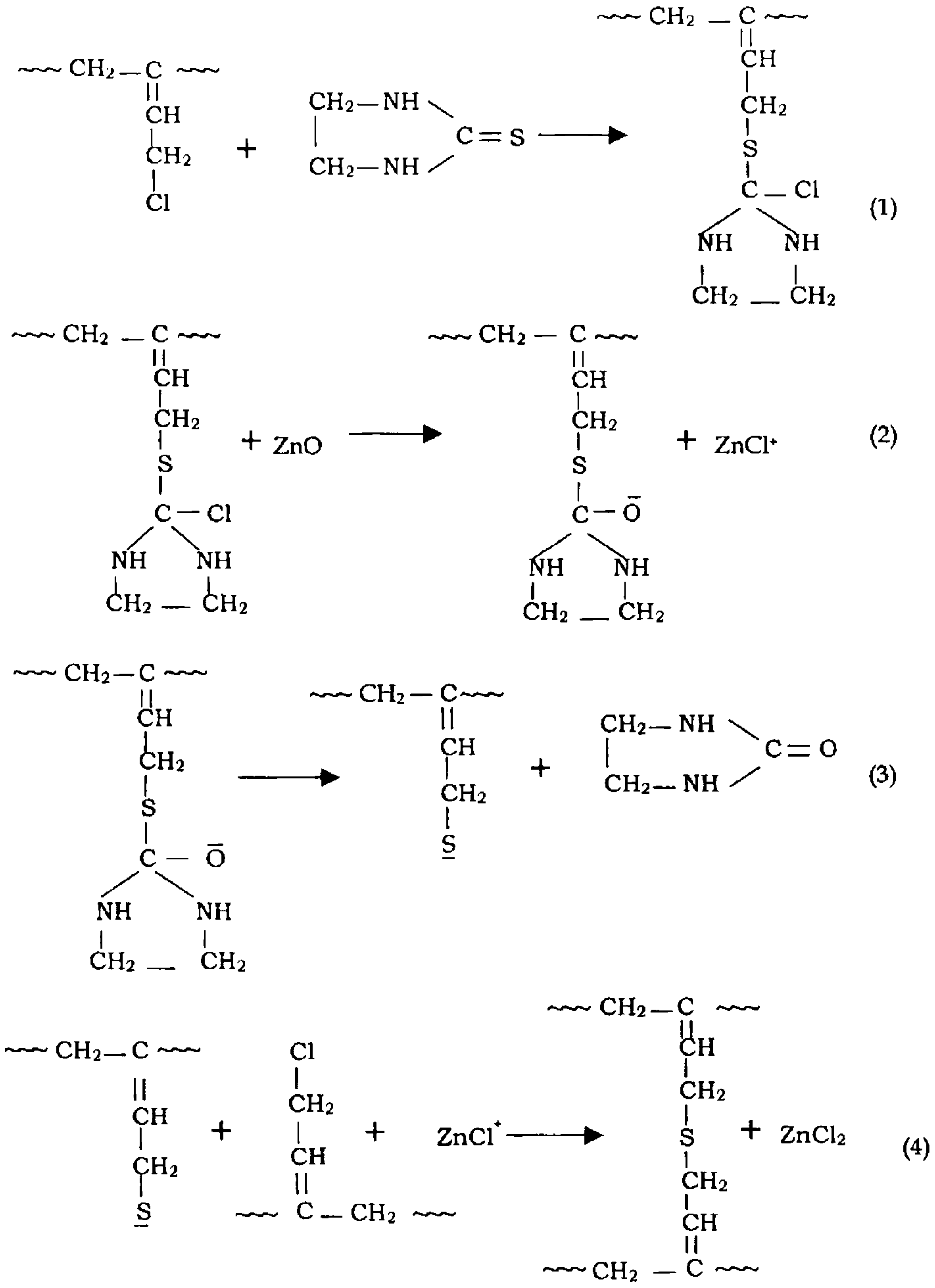


$$2\,ZnCl_2 + MgO \xrightarrow{H_2O} 2\,Zn\begin{matrix} OH \\ Cl \end{matrix} + MgCl_2 \qquad (a)$$

Those accelerators, which are suitable for natural rubber vulcanisation, are usually unimportant where polychloroprene is concerned. In CR, some of them vulcanise too fast, while some are not fast enough and some even retard the vulcanisation. For practical cure rate and vulcanisate properties, an organic accelerator is also required in addition to metal oxides for the W type neoprenes. The most widely used substance which has become essential in the vulcanisation of polychloroprene is a thiourea derivative viz. ethylene thiourea (NA22)[4]. This gives fast vulcanising compounds and the vulcanisates are characterised by high modulus, good tensile strength, low permanent set and high rebound resilience. The use of NA22, in combination with thiuram and guanidine accelerators, in addition to sulphur, gives vulcanisates with improved tear resistance and rebound resilience. However, the compounds are less safe to process[5].

Thiourea accelerators particularly ethylene thiourea, have for many years been the accelerator of choice for a wide range of applications. Today ethylene thiourea is the single popular accelerator. The choice of accelerators for CR is also governed by different rules compared to other diene rubbers. In general, cure systems that provide faster cure rates tend to be more scorchy. Also those that give a higher degree of vulcanisation (ie. higher tensile strength, lower elongation at break, higher rebound elasticity and less compression set) tend to have less scorch safety. For a good compromise between scorch safety and cure rate, combination of small amounts of NA22 with thiurams or guanidines are used.

According to Pariser[6] the nature of cross linking reaction in the presence of thiourea derivatives (eg. NA22) is such that the allyl bound chlorine atom takes part in the reaction during which it is substituted by an accelerator residue. He has proposed the following scheme of reactions to explain the ability of NA22 to accelerate the vulcanisation of CR by metal oxides.



Scheme 6.2

Oxide linkages are also formed as shown in scheme 6.1.

In view of the fact that nature and mechanism of vulcanisation in polychloroprene rubber is different from other rubbers, we thought of trying N-amidino N'-phenyl thiourea (APT) in different vulcanisation systems of this rubber. It is also reported that many accelerators employed in rubber compounding are toxic. For example NA22, the single popular accelerator used in CR vulcanisation is toxic and is reported to be carcinogenic[7,8]. Under this background the search for non-toxic accelerators gains importance. One of the aims of our study with CR is to investigate the possibility of replacing the conventionally used thiourea derivative NA22 with a non-toxic derivative of thiourea like APT[9]. A similar mechanism suggested in scheme 6.2 may be applied with APT also. When sulphur is used along with APT some sulphidic linkages are also expected to be formed during the cure reactions.

The effect of replacement of ethylene thiourea by amidino phenyl thiourea was investigated by comparing the cure characteristics of binary accelerator systems containing TMTD-APT with those of TMTD - NA22 which is taken as the control. In order to establish the optimum requirement of APT, mixes with varying concentration of APT were investigated. The cure and mechanical properties of these experimental binary systems were compared with those of the controls. To ascertain the effect of APT as an accelerator for the vulcanisation of CR in presence of fillers, mixes were also prepared with carbon black / precipitated silica and their various cure and physical properties were compared with control vulcanisates containing NA22.

EXPERIMENTAL

Chloroprene rubber (CR B 30) confirming to the specifications given in chapter 2 was used in the present investigation. Zinc oxide, stearic acid, sulphur, tetramethyl thiuram disulphide (TMTD), ethylene thiourea (NA22), carbon black (HAF 330), precipitated silica (Vulcasil-S), aromatic oil and naphthenic oil used were all of the rubber grade. Light magnesium oxide and diethyleneglycol were of analar grade. Amidino phenyl thiourea (APT) was prepared accordingly to the procedure given in chapter 3.

Table 6.1 Formulations of CR gum mixes

Ingredients	A_1	A_2	A_3	A_4	R_1	R_2
CR	100	100	100	100	100	100
MgO	4	4	4	4	4	4
Stearic acid	2	2	2	2	2	2
Sulphur	1	1	1	1	1	1
TMTD	0.6	0.6	0.6	0.6	0.6	1.2
NA22	-	-	-	-	0.255	-
APT	0.121	0.242	0.485	0.727	-	-
ZnO	5	5	5	5	5	5

The experimental and control mixes were prepared in a two roll mixing mill as per ASTM D 3182-89 at a friction ratio of 1:1.25 using the formulations given in tables 6.1and 6.2. In the formulations, all the accelerators are taken in molar concentrations and other compounding ingredients are in parts per hundred rubber (phr.). Preparations of the mixes are as detailed in chapter 2. Mixes A_1-A_4 represent CR gum formulations containing varying molar concentrations of APT ranging from 0.25-1.5 with 1 molar equivalent of TMTD. Mix R_1 contains TMTD and NA22 in 1:1 molar proportion and R_2 contains TMTD alone (2 molar equivalent) as accelerator.

Table 6.2 Formulation of CR filled mixes

Ingredients	Ac_1	Ac_2	Ac_3	Ac_4	As_1	As_2	As_3	As_4	Rc_1	Rc_2	Rs_1	Rs_2
CR	100	100	100	100	100	100	100	100	100	100	100	100
MgO	4	4	4	4	4	4	4	4	4	4	4	4
Stearic acid	2	2	2	2	2	2	2	2	2	2	2	2
Carbon black	50	50	50	50	-	-	-	-	50	50	-	-
Aromatic oil	5	5	5	5	-	-	-	-	5	5	-	-
Precipitated silica	-	-	-	-	50	50	50	50	-	-	50	50
Naphthenic oil	-	-	-	-	5	5	5	5	-	-	5	5
DEG	-	-	-	-	2	2	2	2	-	-	2	2
Sulphur	1	1	1	1	1	1	1	1	1	1	1	1
TMTD	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	1.2	0.6	1.2
NA22	-	-	-	-	-	-	-	-	0.255	-	0.255	-
APT	0.121	0.242	0.485	0.727	0.121	0.242	0.485	0.727	-	-	-	-
ZnO	5	5	5	5	5	5	5	5	5	5	5	5

Ac_1-Ac_4 are filled mixes with varying amounts of APT with TMTD and containing 50 phr. carbon black. As_1-As_4 are similar systems containing 50 phr. precipitated silica. Aromatic oil (5 phr.) is used as processing aid for black filled systems and naphthenic oil (5phr.) for silica mixes. When silica is used as filler in rubber compounds acidic silanols (hydroxyl groups on the surface of the filler) can interact with accelerators. This usually results in unacceptable long cure times and slow cure rates. In order to normalise the cure rate, diethylene glycol (DEG) is usually included in the compound preparation. In our study also 2phr. DEG was used for the preparation of silica systems.

The cure characteristics of CR mixes were determined at 150°C using Goettfert elastograph model 67.85 and the cure properties obtained are reported in tables 6.3 and 6.4. Optimum cure time, scorch time, cure rate index etc. were determined as per details reported in chapter 2. The compounds were vulcanised up to their optimum cure time in a laboratory type hydraulic press at 150°C at a pressure of 11.76 MPa. Tensile properties were determined as per ASTM D 412 87. For these tests dumbbell specimens were punched out of the moulded sheets along the mill grain direction. Tear resistance was determined as per ASTM method D 62224-86, hardness according to ASTM D 2240-86 and compression set as per ASTM D 395-86 (method B). Ageing studies were carried out as per ASTM D 573-88 at 100°C for 96 hrs. in an air oven. The crosslink density of CR vulcanisates was determined by swelling the samples in benzene at 27°C for 24 hrs. The total crosslink density is calculated using Flory – Rehner equation[10,11]:

$$\frac{1}{2}\,Mc = \frac{-\left(\ln(1-Vr_0) + Vr_0 + \chi Vr_0^2\right)}{2\rho_r\, Vs\, (Vr)^{1/3}}$$

The value of the interaction parameter χ taken for the calculation for CR-benzene = 0.26. The experimental details are as given in chapter 2

RESULTS AND DISCUSSION

The cure characteristics of various mixes evaluated are reported in tables 6.3 and 6.4. The corresponding cure graphs are given in figs. 6.1-6.6.

Table 6.3 Cure characteristics of CR gum mixes.

Mix No.	Optimum Cure time t_{90} (Min)	Scorch time t_{10} (Min)	Cure rate index	Minimum torque (Nm)	Maximum torque (Nm)
A_1	21.8	5.4	6.10	0.016	0.325
A_2	19.5	4.7	4.27	0.010	0.455
A_3	18.2	3.4	6.75	0.012	0.481
A_4	18.0	2.7	6.50	0.005	0.490
R_1	17.2	3.2	7.14	0.012	0.420
R_2	23.6	5.3	5.46	0.010	0.280

In the case of CR gum systems, for the control mix R_1 (TMTD-NA22), t_{90} value obtained is 17.2 min. where as the corresponding TMTD-APT mix shows slightly higher t_{90} value (18.2 min.). Comparing the nucleophilic character

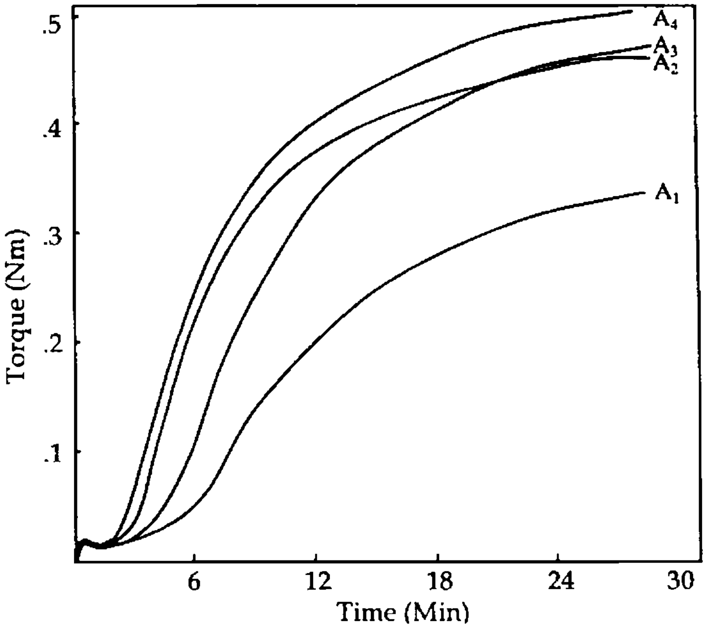


Fig. 6.1 Cure curves of CR gm mixes containing APT

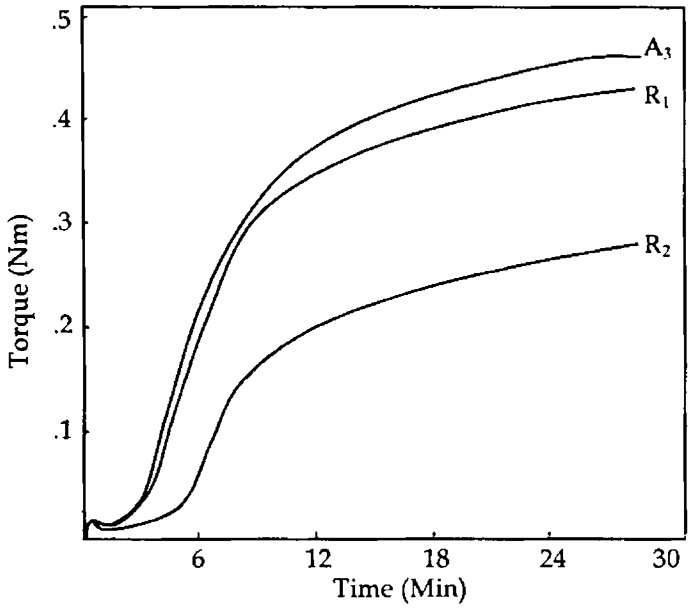


Fig. 6.2 Cure curves of CR gum mixes containing optimum dosage of APT and of references

of amidino phenyl thiourea with ethylene thiourea, by virtue of the higher hyperconjugative effect of–CH_2 groups present in the latter, NA22 is more nucleophilic than APT. Lower optimum cure time observed in the NA22 mixes points to a nucleophilic reaction mechanism in sulphur vulcanisation of these CR systems. As the concentration of APT increases from 0.25 to 1.5 molar level there is gradual decrease in optimum cure time values also. The scorch time also decreases accordingly (table. 6.3). Comparing with the control mix, the experimental system is found to have slightly higher scorch safety. The maximum torque recorded is higher for the APT system at the optimum level of the accelerator and the cure rate index is almost comparable with the control mix. Considering the different cure properties, the 1:1 molar combination of TMTD with APT can be considered as the optimum level for the unfilled CR vulcanisation systems.

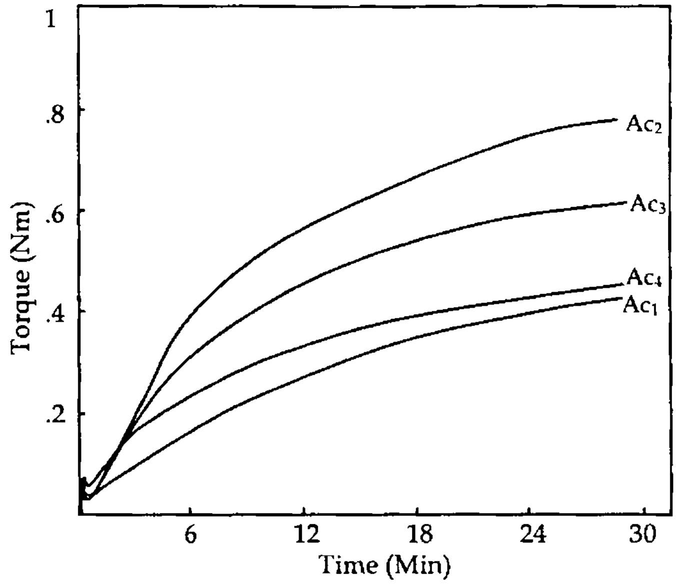


Fig. 6.3 Cure curves of carbon black filled CR mixes containing APT

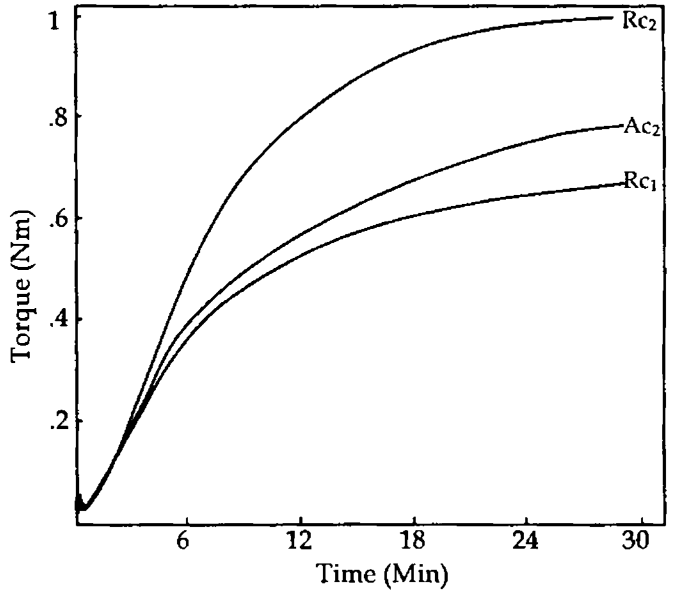


Fig. 6.4 Cure curves of black filled CR mixes containing optimum dosage of APT and of references.

Taking the cure characteristics of the CR filled mixes into account, TMTD-APT gives satisfactory results in both black and silica systems. In the case of black filled mixes as the concentration of APT increases from 0.25 to 0.5 molar level the optimum cure time is found to decrease from 24.4 min. to 21.5 min. Further increase in APT dosage does not make much change in the t_{90} value. Considering the optimum cure time, scorch time, cure rate index, maximum torque developed etc. mix containing TMTD and APT in 1:0.5 molar ratio can be considered to be a practical formulation. However, in the silica filled systems there is not much change in the t_{90} values with change in APT level. It is also noted that both experimental and control formulations show a tendency for marching cure.

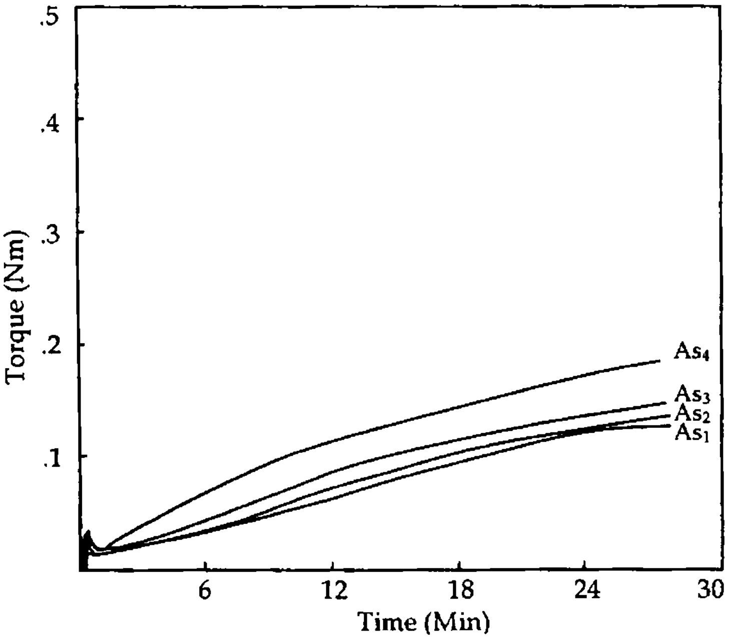


Fig. 6.5 Cure curves of silica filled CR-APT mixes

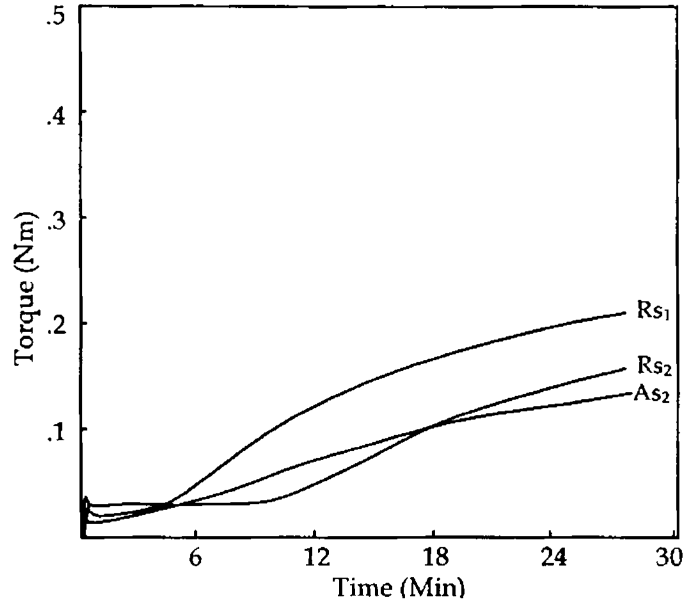


Fig. 6.6 Cure curves of silica filled CR mixes containing optimum dosage of APT and of references.

Here also comparing mixes containing equivalent concentrations of APT and NA22 the optimum cure time value for the former is found to be higher than the NA22 formulation indicating that the proposed nucleophilic reaction mechanism is applicable to these filled systems also.

Table 6.4 Cure characteristics of CR filled systems.

Mix No.	Optimum Cure time t_{90} (Min)	Scorch time t_{10} (Min)	Cure rate index	Minimum torque (Nm)	Maximum torque (Nm)
Ac$_1$	24.4	1.7	4.31	0.031	0.434
Ac$_2$	21.5	1.8	5.07	0.038	0.761
Ac$_3$	21.3	1.5	5.05	0.026	0.601
Ac$_4$	21.9	1.1	4.80	0.035	0.452
Rc$_1$	19.9	1.8	5.52	0.050	0.668
Rc$_2$	16.3	2.2	5.52	0.064	0.995
As$_1$	26.0	3.9	4.52	0.018	0.134
As$_2$	25.8	3.2	4.42	0.015	0.139
As$_3$	25.9	3.7	4.50	0.015	0.159
As$_4$	25.4	2.3	4.33	0.014	0.190
Rs$_1$	24.5	4.6	4.63	0.016	0.215
Rs$_2$	26.5	10.7	6.33	0.031	0.158

The physical properties such as tensile strength, elongation at break and modulus (100%) evaluated for CR gum vulcanisates are given in table 6.5. From the values obtained it is clear that increase in concentration of APT increases the tensile strength and 100% modulus values of these vulcanisates.

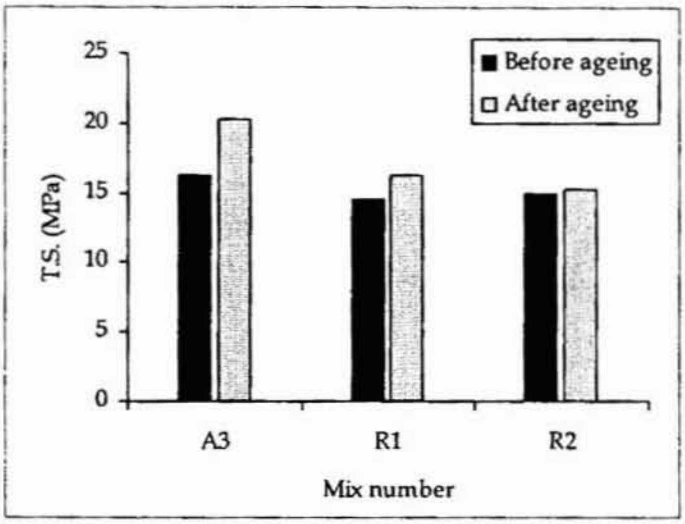


Fig. 6.7 Tensile strength of CR gum vulcanisates containing optimum dosage of APT and of references

Table 6.5 Tensile properties of CR gum vulcanisates

Mix No.	Tensile strength (MPa)			Elongation at break (%)			100 % modulus (MPa)		
	Before ageing	After Ageing	Retention %	Before ageing	After Ageing	Retention %	Before ageing	After Ageing	Retention %
A_1	14.66	18.76	127.96	661.67	723.40	109.30	0.87	0.98	112.64
A_2	15.64	20.14	128.77	596.50	640.80	107.40	1.04	1.14	109.69
A_3	16.18	20.2	124.84	712.30	661.90	92.83	1.02	1.00	98.04
A_4	17.77	20.41	114.85	741.20	677.53	91.40	1.08	1.05	97.22
R_1	14.49	16.20	111.80	732.18	623.00	85.10	1.11	0.93	83.78
R_2	14.99	15.20	101.40	538.90	691.62	158.53	1.05	1.03	98.09

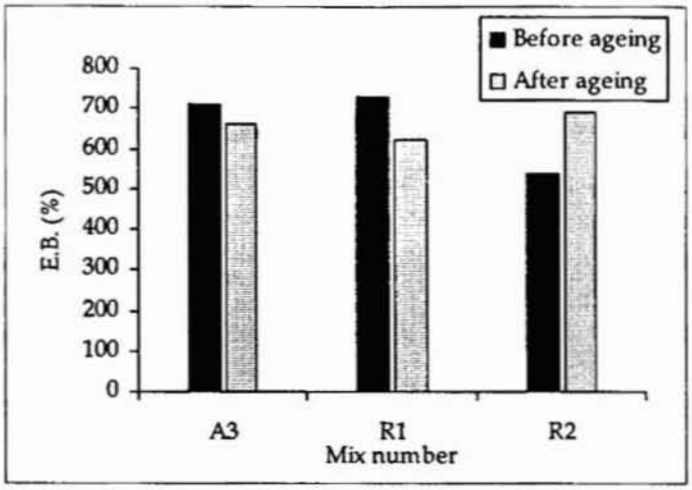


Fig. 6.8 Elongation at break of CR gum vulcanisates containing optimum dosage of APT and of references

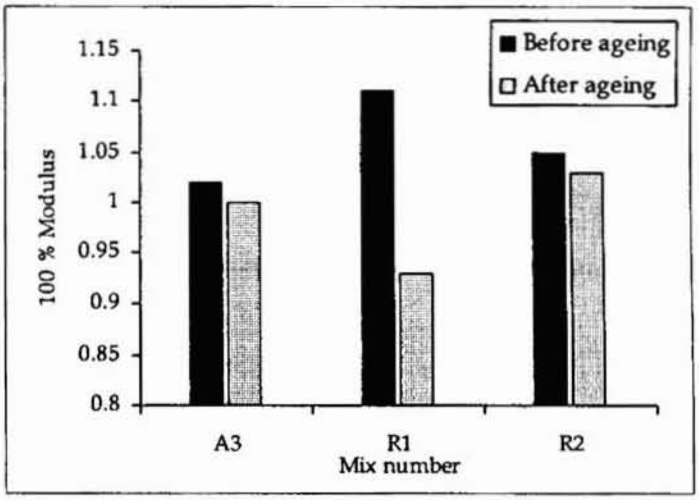


Fig. 6.9 100% modulus of CR gum vulcanisates containing optimum dosage of APT and of references

Comparing systems containing equivalent concentrations of APT and NA22, APT systems show higher tensile strength values. 100% modulus and elongation at break values are comparable with those of the reference formulations (figs 6.7-6.9). Considering the tensile strength values of filled vulcanisates, the change in concentration of APT does not seem to alter the tensile strength much. However, compared to control systems, the experimental formulations containing optimum concentration of APT show slightly higher tensile strength values in both carbon black and silica filled vulcanisates (figs.6.10 & 6.11).

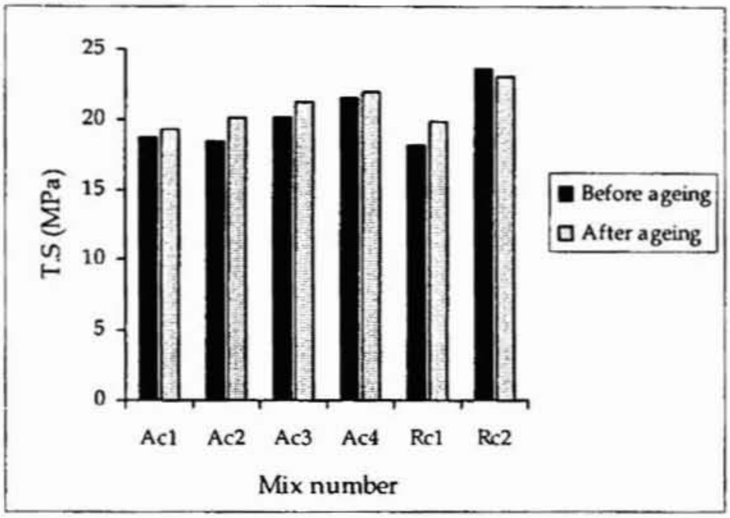


Fig. 6.10 Tensile strength of black filled CR vulcanisates.

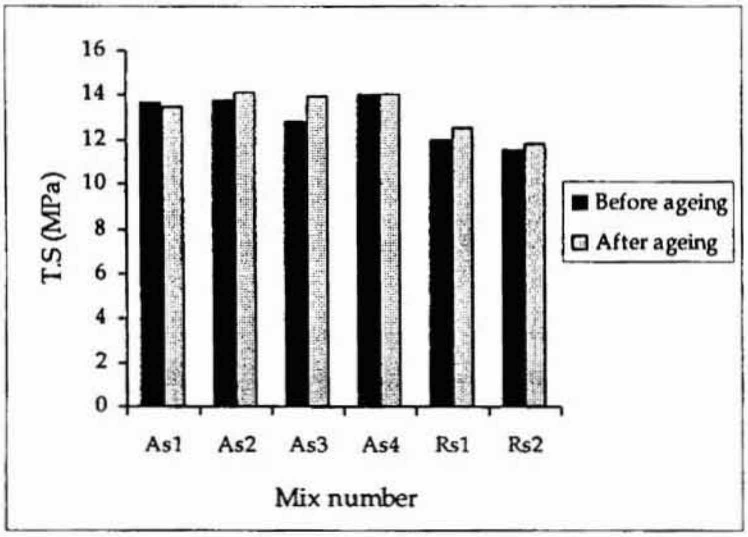


Fig. 6.11 Tensile strength of silica filled CR vulcanisates.

Comparing the tensile strength values of the gum and filled vulcanisates of CR, there is not much increase in these values when fillers are incorporated. This is to be attributed to the fact that neoprene is a highly stress crystallisable rubber. But other physical properties such as tear strength, compression set, abrasion resistance etc. are found to be much improved in the filled vulcanisates. The values obtained for other physical properties such as tear strength, hardness, compression set, abrasion loss and total crosslink density of gum and filled vulcanisates are reported in tables.6.6 & 6.7. respectively.

Table 6.6 Other properties of CR gum vulcanisates

Mix No.	Hardness (Shore A)	Tear strength (N/mm)	Compression set (%)	Abrasion loss (cm^3/hour)	Cross link density × 10^5 (g.mol. cm^{-3})
A_1	22	21.40	26.04	14.03	14.4
A_2	23	27.30	25.00	16.93	14.3
A_3	23	26.46	21.50	15.67	15.9
A_4	23	27.46	20.90	11.88	16.1
R_1	18	19.15	20.58	17.92	14.5
R_2	25	22.19	31.76	15.97	12.4

Considering properties of gum vulcanisates, the tear strength values are found to be increasing with increase in concentration of APT. Tear strength value is found to be better for the APT formulation and the compression set and abrasion loss values are comparable with the reference systems. The values of these physical properties studied can more or less be correlated with the total crosslink density calculated.

In black filled vulcanisates as the concentration of APT increases a regular increase in tear strength and favourable decrease in compression set values are seen. Abrasion loss is also found to be decreased (abrasion resistance increased) with increase in concentration of APT. Comparing mixes containing equivalent concentrations of APT with that of NA22, the tear strength value is much higher (62.5 N/mm) for the experimental mix compared to the NA22 system (44.56 N/mm).

Table.6.7 Properties of evaluated for CR filled valcunisates

Mix No.	Tensile strength (MPa)			Hardness (Shore A)	Tear strength (N/mm)	Compression set (%)	Abrasion loss (cm^3/hour)	Cross link density × 10^5 (gmol. cm^{-3})
	Before ageing	After ageing	Retention %					
Ac$_1$	18.75	19.24	102.61	35.0	58.34	12.86	4.07	25.90
Ac$_2$	18.40	20.18	109.67	36.5	60.24	15.92	3.93	14.10
Ac$_3$	20.10	21.20	105.47	38.0	62.50	10.92	3.78	35.90
Ac$_4$	21.50	21.96	102.14	38.5	66.29	8.01	3.27	26.70
Rc$_1$	18.17	19.78	108.86	33.0	44.56	13.40	3.21	24.70
Rc$_2$	23.60	23.10	97.88	32.0	56.35	12.78	3.23	22.20
As$_1$	13.64	13.48	98.83	31.3	49.50	23.36	10.88	7.98
As$_2$	13.77	14.10	102.40	32.0	52.50	20.81	10.68	8.07
As$_3$	12.87	13.93	108.24	31.0	49.50	18.35	10.38	8.21
As$_4$	14.01	14.00	99.93	32.0	52.41	13.42	10.35	6.67
Rs$_1$	12.05	12.53	103.98	29.0	42.22	16.85	9.66	8.03
Rs$_2$	11.57	11.86	102.51	28.0	39.78	12.06	12.86	6.91

Compression set, hardness and abrasion loss values for the APT mixes are also comparable with those of references. In the case of the silica filled systems, tear strength and hardness observed are better, and abrasion loss and compression set values are more or less comparable with the reference formulations (table 6.7).

CONCLUSIONS

From these investigations it is found that experimental mixes containing TMTD-APT are effective for the vulcanisation of polychloroprene rubber. A nucleophilic reaction mechanism for the above sulphur vulcanisation reactions can be established here also. It is to be emphasised that the conventional accelerator used in CR vulcanisation viz. ethylenethiourea (NA22) is a toxic chemical and is reported to be carcinogenic. From the results obtained in this study it is clear that NA22 can be replaced by a non-toxic and safe secondary accelerator like the amidinothiourea derivative (APT). The cure characteristics and tensile and other physical properties evaluated are found to be better /comparable to the control systems in both gum and filled formulations studied.

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Chapter 7

EFFECT OF APT IN NR-CR BLENDS

It is recognised that a single elastomer cannot meet all the requirements like oil and chemical resistance, dynamic properties, weathering resistance etc. of a rubber product. There are therefore technical reasons for blending, as it makes possible to obtain the right compromise in properties by blending different elastomers. The difficulties encountered in the processing and vulcanisation of some rubbers also emphasise the need for blending. Economic reasons can also be given for blending since appreciable price differences exist between different rubbers. For example the resistance of polychloroprene to ozone is outstandingly good but its price is high and accordingly blending of CR with cheaper rubbers is normally practiced for various applications[1]. Blends make up over 30% of the market of polymeric materials[2].

Blends of elastomers may be broadly classified into miscible and immiscible types. The most important polymeric properties pertaining to elastomer blends are phase morphology (homogeneity of mixing) and cure compatibility. The complete miscibility of polymers requires that the free energy of mixing be negative, which can only be achieved by exothermic mixing or large entropy of mixing[3]. Therefore, most blends of elastomers are immiscible because mixing is endothermic and the entropy contribution is small because of high molecular weights. Fortunately miscibility is not a requirement for most rubber applications. Homogeneity at a fairly fine level is necessary for optimum performance but some degree of microheterogenity is usually desirable to preserve the individual properties of the respective polymer components. Homogeneity is favoured by a similarity in polymer viscosities and solubility parameters, as well as by the presence of polar groups[4]. It should be emphasized that most of the commercially useful blends have practical compatibility, even though they do not have thermodynamic miscibility. Theoretically, blends of chemically dissimilar (immiscible) elastomers can attain a wider variation in properties than blends of miscible and thus chemically similar elastomers[5]. To obtain the optimum compromise in the properties of a rubber blend it is always better to use rubbers of closest solubility parameter values. However, for purposes like damping applications rubbers with dissimilar parameters give the desired low resilience compounds[6]. Such incompatible blends of dissimilar polymers like natural rubber (NR) and polychloroprene (CR) are found to have dynamic properties, which are characteristic of the component of higher Tg at ambient temperature, but the lower Tg component appears to dominate at higher temperature[6]. In cases where NR is used for vibration isolation i.e., under conditions where resonance may occur, a degree of damping is required. Blending of NR with a synthetic rubber of suitable Tg and cure characteristics is one of the techniques for increasing the damping characteristics of NR vulcanisates.

Polarity and unsaturation both play a role in curative migration, therefore, the greatest effect was observed for CR. Gardiner[7] emphasized that curative migration is related to diffusion during curing and not transfer during mixing. Sulphur type cures alone are not satisfactory for curing low unsaturation rubbers in blends with high unsaturations or more polar polymers. The properties of elastomer blends are more significantly affected by filler distribution than they are by morphology. One advantage of heterogeneous polymer blends is the ability to alter the phase morphology for specific performance criteria[8]. This type of alteration is more difficult with homogeneous blends.

The engineering properties of elastomers (tensile strength, hysteresis, shifts in loss tan peaks etc.) in vulcanised compounds depend not only on the elastomer itself, but also on the amount and identity of the fillers and plasticisers, as well as the extent of cure. In an immiscible blend, the amount of these additives in any phase can be modulated by changes in the viscosity and chemical identity of the elastomer, the surface chemistry of filler, the sequence of addition of the components and the details of the mixing procedure. The mixing methods for preparing elastomer blends may be divided into two general categories of 'preblending' and 'phase mixing' [4]. In the first case, the compounding ingredients (fillers, curatives, accelerators etc.) are added to the premixed polymers in a manner similar to the mixing of a single elastomer. In a phase mix, an attempt is made to control the specific location of filler and/or extender oil and curing agents. This is usually accomplished by the preparation of separate master batches, which are then blended mechanically. In our present work preblending technique is used for preparing the NR-CR blends.

Usual elastomer blend is a dispersion of one component in a matrix of the other. The elastomer of lower viscosity tends to be the continuous phase as with other polymer blends[9,10]. The detailed morphology of elastomer blends depends on the mixing procedure, the rheology of the components of the blend and the interfacial energy. Co-continuous blend morphology is observed only for elastomers with similar viscosities. During mixing curatives are initially located within the continuous phase[11]. Since curatives dissolve in the elastomer, curative migration across phase boundaries can occur[12]. On vulcanisation large differences in cross link density of the different phases may occur owing to the higher solubility of sulphur in elastomers containing diene group and the greater affinity of many accelerators for polar rubbers. At processing temperatures, elastomers are viscous fluids with persistent transport phenomena. These transport phenomena lead to changes in the size and shape of the elastomer phases and migration of fillers, curatives etc. from one phase to another in immiscible blends. These changes are accelerated by processing and plasticisation, but are retarded by the ultimate vulcanisation.

NR is a very versatile raw material, on account of its unique chemical and physical properties including high green strength, tackiness and excellent gum tensile strength due to the very high stereo specificity in structure. But its heat and swelling resistance is comparatively less than synthetic rubbers. Chloroprene rubbers are known for their better flame resistance and resistance to oils and fats, weathering and ozone. But comparing with NR, CR costs more. An elastomer blend with NR and CR will make an ideal compromise with the individual properties like reduced compound cost, reducing the disadvantage of individual rubber and enhancing the final product performance. NR will improve the elasticity and low temperature flexibility of CR. In view of the fact that APT functions effectively as a secondary accelerator in NR and CR formulations, we thought it worthwhile to investigate the effect of this non-toxic amidino thiourea derivative in the different vulcanisation systems of NR-CR blends. The variations in cure characteristics of compounds and tensile properties of the vulcanisates brought about by using APT as an accelerator in gum and filled NR-CR blends has been investigated. The blends are prepared in 50:50 ratio of NR and CR. Binary accelerator systems containing TMTD-TU and TMTD-NA22 were evaluated as control mixes. The cure and tensile properties of the experimental mixes were compared with those of these control formulations. Heat ageing characteristics and swelling studies were also carried out for these various formulations of blends.

EXPERIMENTAL

Natural rubber and polychloroprene, having the specifications reported in Chapter 2 are used in this study. Other compounding ingredients viz. ZnO, stearic acid, TMTD, ethylene thiourea (NA22), sulphur, carbon black (HAF 330) and aromatic oil are all of rubber grade and MgO used is calcined light magnesia. Benzene used for swelling studies is of analar grade. Specifications of all the compounding ingredients used in the study are also detailed in Chapter 2.

The procedure adopted for blending these two elastomers is preblending in which the compounding ingredients are added to the premixed NR and CR in a manner similar to mixing in a single elastomer. For premixing NR was first masticated for 2 min. so as to reduce its viscosity to that of polychloroprene. CR is then added and again masticated for another 2 minutes so as to obtain a smooth band. This was followed by the addition of MgO, stearic acid, ZnO, carbon black, aromatic oil and finally accelerator and sulphur. The total mixing time was kept at 10min. for gum and 15 min. for black filled systems, with the following break up. The rubbers were premixed for 4min. followed by adding activators, accelerators and finally sulphur within 6 min. in gum formulations. For filled mixes after adding activators (MgO, stearic acid and ZnO) within 3 min., carbon black mixed with oil was incorporated within 7 min. and finally sulphur within 1min. The formulations used for gum and black filled mixes are given in table 7.1.

Table 7.1 Formulations of mixes

Ingredients	A_1	A_2	A_3	A_4	Ac_1	Ac_2	Ac_3	Ac_4	R_1	R_2	R_3	Rc_1	Rc_2	Rc_3
NR	50	50	50	50	50	50	50	50	50	50	50	50	50	50
CR	50	50	50	50	50	50	50	50	50	50	50	50	50	50
MgO	2	2	2	2	2	2	2	2	2	2	2	2	2	2
Stearic acid	2	2	2	2	2	2	2	2	2	2	2	2	2	2
ZnO	5	5	5	5	5	5	5	5	5	5	5	5	5	5
Carbon Black	-	-	-	-	50	50	50	50	-	-	-	50	50	50
Aromatic oil	-	-	-	-	5	5	5	5	-	-	-	5	5	5
TMTD	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	2.4	1.2	1.2	2.4	1.2
TU	-	-	-	-	-	-	-	-	.38	-	-	.38	-	-
NA22	-	-	-	-	-	-	-	-	-	-	0.51	-	-	0.51
APT	0.243	0.485	0.970	1.455	0.243	0.485	0.970	1.455	-	-	-	-	-	-
Sulphur	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5

All these mixes were prepared on a two roll mixing mill as per ASTM D 3182-89 at friction ratio of 1:1.25. In the formulations A series indicate gum mixes and Ac series the filled systems. Mixes A_1-A_4 are blends containing varying concentrations of APT ranging from 0.25 to 1.5 molar equivalent with 1 molar equivalent TMTD. An attempt is made here to find out the optimum concentration of APT required in these vulcanisation reactions. Mixes R_1 and R_3 contain TMTD-TU and TMTD-NA22 in 1:1 ratio. Mix R_2 contains TMTD alone (2 molar equivalents) as accelerator. Mixes A_{c1}–A_{c4} are filled mixes containing varying concentrations of APT viz. 0.25, 0.5, 1 and

1.5 molar level with 1 molar equivalent TMTD and with 50 phr. carbon black. R_{C1}, R_{C2} and R_{C3} are reference formulations of the filled series.

The cure characteristics of various mixes were evaluated at 150° C using Goettfert elastograph. The cure curves obtained are given in figs. 7.1- 7.4. The cure properties evaluated are given in tables 7.2 and 7.3. Optimum cure time, scorch time, cure rate index, maximum torque and minimum torque are reported therein. Vulcanisation of the various mixes was carried out in an electrically heated hydraulic press of 18" x 18" platens maintained at 150°C and at a pressure of 11.76MPa. Tensile properties were determined using Zwick Universal Testing machine at a pulling rate of 500mm/min. at 27°C. Tear strength, hardness, compression set and abrasion loss of gum and filled vulcanisates were determined as per ASTM standards (details are as given in earlier chapters). Ageing studies on the vulcanisates were carried out at 100°C for 24 hrs in an air oven (ASTM D 573-88). Rebound resilience was measured using a vertical rebound resilience tester as per ASTM D 2632-88. The swelling index, an indirect way of measuring total cross link density, was determined by immersing 0.2 g. of the sample in benzene for 24 hrs. at room temperature. The swollen samples were weighed, solvent removed in vacuum and weighed again. Swelling index was calculated using the equation given below:

$$\text{Swelling index} = \frac{\text{Swollen weight} - \text{deswollen weight}}{\text{Original weight of sample}}$$

RESULTS AND DISCUSSIONS

Figs. 7.1 - 7.4 show the cure curves and tables 7.2 and 7.3 give the different cure characteristics of NR-CR gum and filled mixes containing TMTD-APT and the reference systems. In the case of the gum formulations of NR-CR blends, corresponding to the decrease in optimum cure time scorch time is also found to decrease with the addition of APT. Based on the cure characteristics such as cure rate index, optimum cure time, scorch time and maximum torque developed a 1:1 molar combination of TMTD and APT can be considered to be the optimum level of the accelerator combination but the scorch time is low. Comparing this mix with the control formulations the t_{90} value of the experimental mix containing APT is lesser than that of TMTD-TU and TMTD-NA22 systems of similar concentration of accelerator. Taking the black filled formulations the reduction in cure time with increase in concentration of APT is not so pronounced as in gum systems. Considering the cure characteristics such as t_{90}, t_5 values, cure rate index and maximum torque developed, mix Ac_2 containing 0.5 molar equivalent APT with 1 molar TMTD can be considered as the optimum cure system. Here also the scorch time is found to be less. Comparing mixes with equivalent concentration of accelerators, the experimental mix containing APT shows lesser t_{90} value compared to the TMTD-TU and TMTD-NA22 control mixes in filled formulations also. APT being less nucleophilic than NA22 the proposed nucleophilic mechanism for sulphur vulcanisation applied to single elastomer systems of NR and CR is seen to be not applicable to these NR-CR blends. A combination of polar and radical mechanism may be operating in these blend systems as suggested by Nieuwenhuizen et al.[13] This is true for both filled and unfilled formulations.

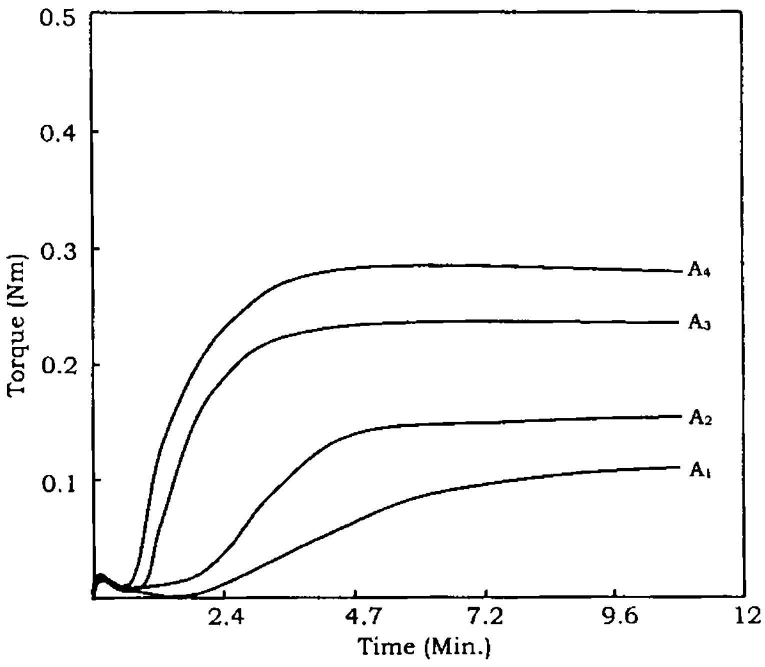

Fig. 7.1 Cure curves of mixes containing APT

Table 7.2 Cure characteristics of NR-CR blend (gum formulations)

	A_1	A_2	A_3	A_4	R_1	R_2	R_3
Maximum torque (Nm)	0.112	0.153	0.236	0.277	0.205	0.185	0.227
Minimum torque (Nm)	0.004	0.004	0.005	0.008	0.010	0.004	0.006
Optimum cure time t_{90} (min)	7.76	4.96	3.08	2.88	5.44	7.88	3.96
Scorch time t_{10} (min)	2.44	1.88	1.12	0.84	2.20	2.84	1.76
Induction time t_5(min)	2.04	1.64	1.04	0.80	1.96	2.48	1.60
Cure rate index	18.8	32.47	51.02	49.02	30.86	19.84	45.45

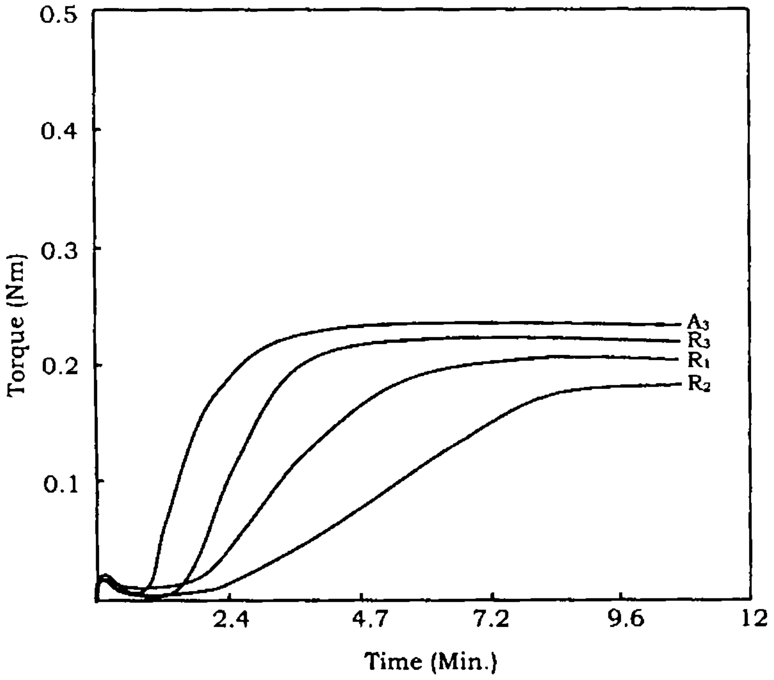

Fig. 7.2 Cure curves of mixes containing optimum dosage of APT and references

Table 7.3 Cure characteristics of filled NR-CR blends

	Ac_1	Ac_2	Ac_3	Ac_4	Rc_1	Rc_2	Rc_3
Maximum torque (Nm)	0.517	0.518	0.612	0.587	0.626	0.513	0.619
Minimum torque (Nm)	0.061	0.062	0.062	0.061	0.093	0.048	0.181
Optimum cure time t_{90} (min)	3.92	3.16	3.0	2.68	4.10	4.76	3.24
Scorch time t_{10} (min)	1.0	0.96	0.72	0.60	0.96	1.28	1.08
Induction time t_5 (min)	0.60	0.68	0.48	0.48	0.60	0.64	0.80
Cure rate index	32.25	45.55	43.86	48.07	31.85	28.74	46.30

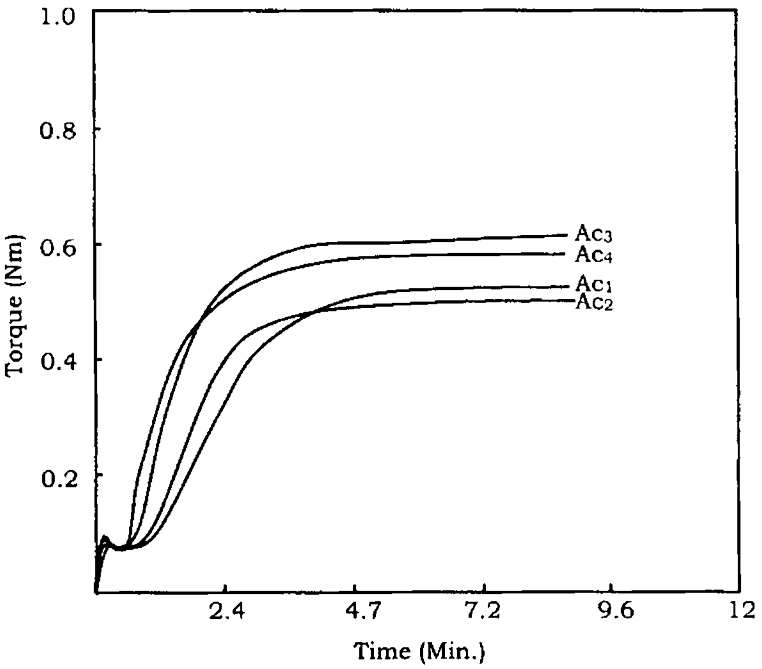

Fig. 7.3 Cure curves of filled mixes containing APT

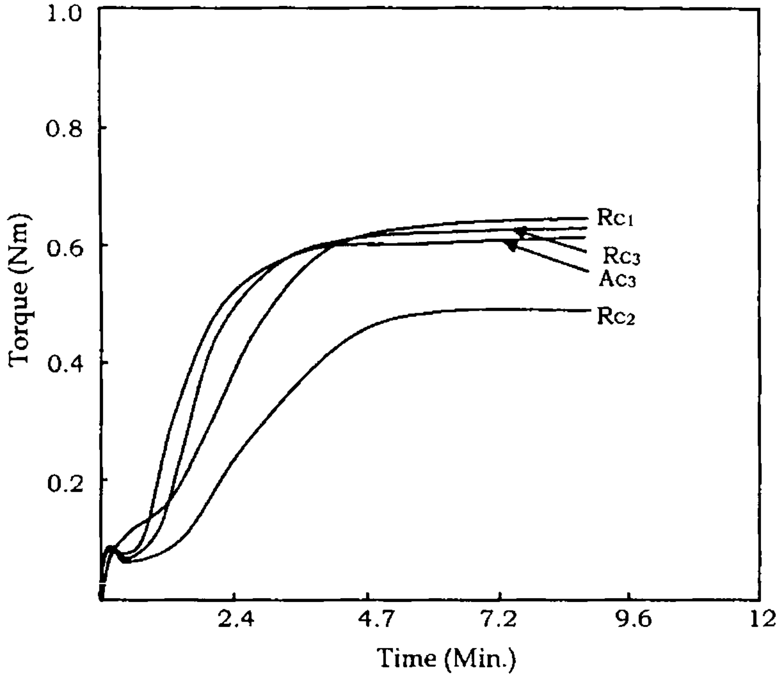

Fig. 7.4 Cure curves of filled mixes containing optimum dosage of APT and references

Table 7.4 Comparison of cure characteristics of TMTD-APT systems

Parameter	Gum formulations			Black filled systems		
	NR	CR	NR-CR blend	NR	CR	NR-CR blend
Optimum cure time	1.3	18.2	3.08	1.4	21.3	3
Scorch time	0.5	3.4	1.12	0.8	1.5	0.72
Cure rate index	125	6.75	51.02	156.25	5.05	43.86

Table 7.4 shows a comparative evaluation of the cure characteristics of NR (ref. tables 3.1.5 and 3.2.5), CR (ref. table 6.3 and 6.4) and NR-CR blends containing TMTD and APT in 1:1 molar ratio. Some of the favourable cure properties of these blends in comparison to the individual polymers may also be stated here. Considering the unfilled formulations of NR, CR and blend, the optimum cure time is much less for the blend system than that of

CR. The scorch time value of NR mix is 0.5 min. where as that of corresponding blend is 1.12 min. Thus the scorch safety of NR-APT system is found to be improved in the blend formulation. Taking the case of black filled systems, the optimum cure time of CR mix containing this amidino thiourea derivative is 21.3 min., while it is 3 min. in the blend formulation. However, the black filled APT mixes are little more scorchy in the blend compared to the individual elastomer systems. One of the other advantages of the blend systems to be noted is the fact that when all the systems of CR show a marching cure, the blend systems show plateau cure.

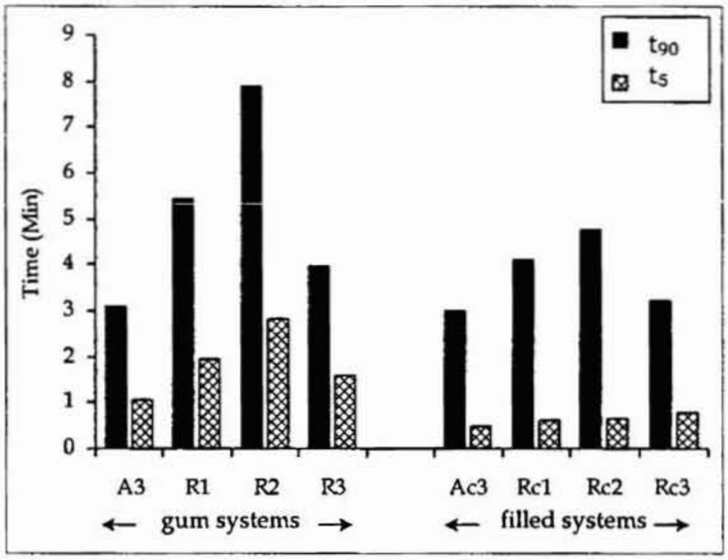

Fig. 7.5: Comparative study of optimum cure time and induction time of mixes containing optimum dosage of APT and references

The tensile properties such as tensile strength, elongation at break and 100% modulus of gum and filled systems are shown in table 7.5. As the concentration of APT increases the tensile strength of gum vulcanisates are found increasing up to an optimum level. Mix A_3 containing optimum concentration of APT shows tensile strength of 27.58 MPa, which is much higher than those of control mixes containing equivalent amounts of TU and NA22. 100% modulus and elongation at break values are comparable with those of the reference formulations.

Table 7.5 Tensile properties of NR-CR blend vulcanisates

Mix No.	Tensile strength (MPa)			100% modulus (MPa)			Elongation at break (%)		
	Before ageing	After ageing	Retention %	Before ageing	After ageing	Retention %	Before ageing	After ageing	Retention %
A_1	16.39	13.17	80.34	0.81	0.73	90.12	411.01	480.82	116.70
A_2	25.57	16.47	65.47	1.03	0.90	87.37	587.19	494.70	84.15
A_3	27.58	19.63	71.15	1.00	0.99	99.00	629.72	607.99	96.50
A_4	25.09	15.90	63.36	1.06	0.96	90.56	568.66	484.88	84.20
R_1	19.81	12.73	64.24	0.78	0.67	85.89	480.97	529.72	110.20
R_2	21.11	14.09	66.76	1.37	1.17	85.40	502.70	515.99	102.50
R_3	22.20	21.48	96.76	0.73	0.79	108.20	611.19	516.17	94.27
Ac_1	16.65	21.12	126.88	4.76	5.61	117.80	375.71	359.15	95.73
Ac_2	23.52	21.15	89.92	5.19	4.99	96.15	386.80	316.89	81.86
Ac_3	24.14	20.30	84.11	7.94	7.14	89.92	251.21	233.14	92.82
Ac_4	23.60	23.89	101.05	5.68	5.63	99.12	286.90	332.42	116.10
Rc_1	21.10	18.07	85.64	6.71	7.23	107.75	239.75	208.23	87.02
Rc_2	16.30	15.52	95.20	5.44	5.49	100.90	238.85	233.34	97.90
Rc_3	18.21	17.94	96.20	4.97	4.70	94.56	213.48	262.95	123.40

The retention of the tensile properties after heat ageing is also better/comparable to the reference systems. Considering the tensile properties of black filled vulcanisates, it is to be noted that there is not much improvement in the tensile strength values compared to that of the gum formulations (fig. 7.6). Similar is the case of gum and black filled vulcanisates of individual elastomers viz. NR and CR (ref. tables 3.1.8,3.2.7(Ch.3), 6.5&6.7(Ch.6)). This may be attributed to the high stress-crystallising nature of NR and CR. When the tensile strength values of the blend vulcanisates also are compared with that of individual elastomers containing equal amounts of APT, the blend systems show higher values than that of NR and CR. As expected 100% modulus values of filled systems are found to increase manifold from that of gum formulations (fig. 7.7). Retention in these properties is also somewhat higher for the filled systems than the gum vulcanisates. Here also system containing APT shows better results in comparison with the references.

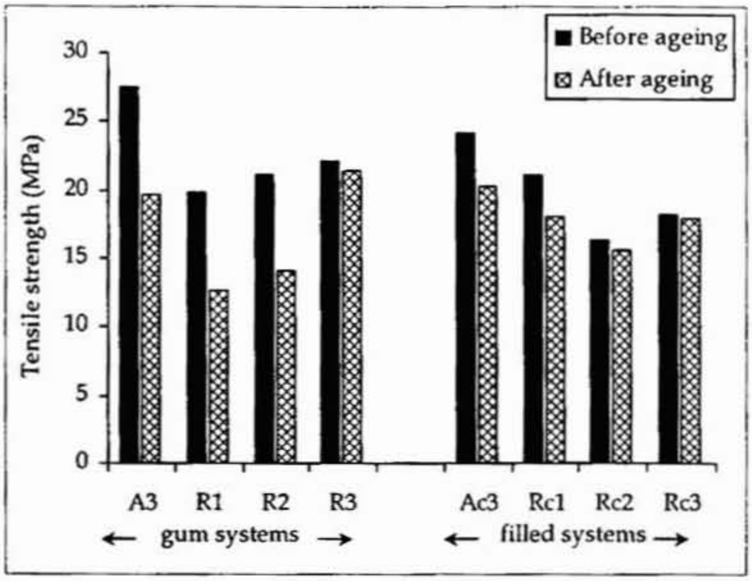

Fig. 7.6 : Comparative study of tensile strength of vulcanisates containing optimum dosage of APT and references

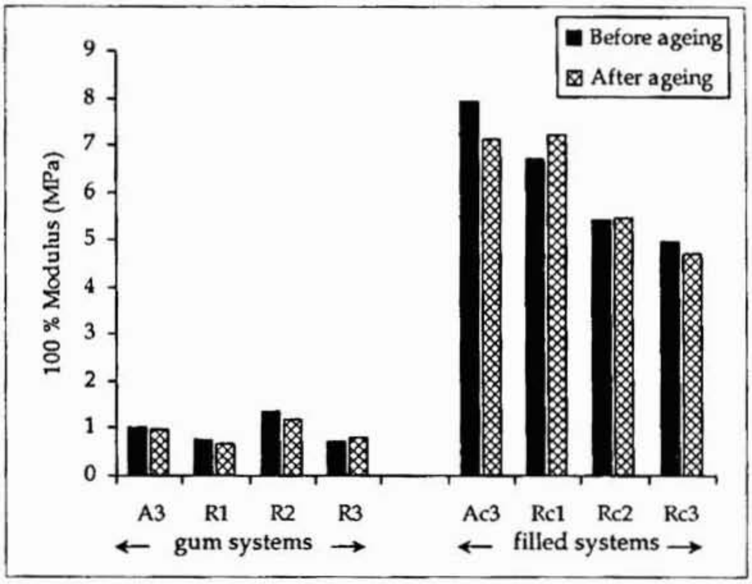

Fig. 7.7: Comparative study of 100% modulus of vulcanisates containing optimum dosage of APT and references

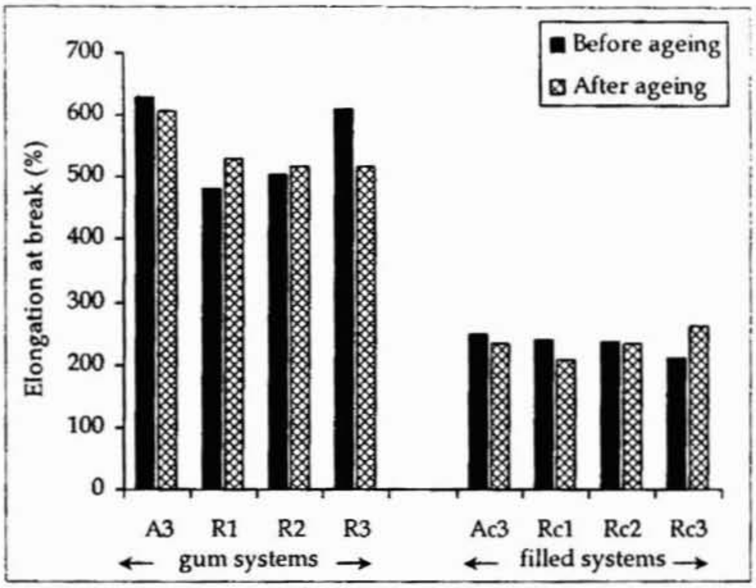

Fig. 7.8 : Comparative study of elongation at break (%) of vulcanisates containing optimum dosage of APT and references

Other physical properties evaluated like tear strength, compression set, resilience, hardness and abrasion loss are reported in table 7.6. In the gum formulations, tear strength values are found increasing with increase in concentration of APT. Other properties like hardness and resilience values are better/comparable with the reference formulations. Compression set and abrasion resistance values are also found to be satisfactory. Considering the case of black filled vulcanisates, properties such as tear strength and hardness of APT system is comparable with the control mixes whereas compression set and abrasion resistance is better. The tensile properties reported for the gum and filled vulcanisates can in general be correlated to the observed swelling index values. Hence it can be reported that systems containing TMTD and APT is an effective accelerator combination for vulcanisation of NR-CR blends in both gum and filled systems. Compared with properties of vulcanisates obtained from individual elastomers there is general improvement in properties for the blend vulcanisates.

Table 7.6 Other physical properties of NR-CR blends.

Mix No.	Tear strength (N/mm)	Hardness (Shore A)	Resilience (%)	Compression set (%)	Abrasion loss (cm^3/hr)	Swelling index
A_1	51.45	46.00	60.00	40.98	4.88	3.43
A_2	55.40	49.00	66.30	48.41	5.30	3.57
A_3	63.36	53.00	72.00	47.17	4.49	3.86
A_4	72.32	50.00	70.60	53.35	5.25	3.48
R_1	65.40	44.00	74.30	58.30	4.98	4.09
R_2	58.90	49.00	73.00	52.48	4.73	3.74
R_3	59.78	58.00	70.60	49.24	5.21	3.96
Ac_1	59.00	31.33	47.53	30.43	3.94	1.26
Ac_2	66.00	35.67	91.00	56.16	4.45	1.64
Ac_3	72.3	32.00	98.90	21.50	4.33	2.44
Ac_4	73.00	34.30	49.01	26.22	4.21	1.40
Rc_1	74.00	30.00	65.98	36.42	4.17	1.44
Rc_2	73.00	38.30	134.41	50.22	4.76	1.46
Rc_3	69.00	36.49	103.50	48.94	5.3	1.49

CONCLUSIONS

Studies on the effect of amidino phenyl thiourea in the vulcanisation of NR-CR blends showed that APT can be advantageously used as a secondary accelerator along with TMTD. The optimum cure time and scorch time of the TMTD-APT system is seen to be less than the corresponding TMTD-TU and TMTD-NA22 control mixes. Noting these cure properties the proposed nucleophilic reaction mechanism for the NR and CR vulcanisation does not hold good for these blend systems. A mixed radical/polar mechanism is most probable here. Considering the cure characteristics and tensile properties, the optimum dosage of APT required for a practical cure system for the gum and black filled blend systems seems to be a 1:1 molar combination of TMTD and APT. The effect of APT as an accelerator is more noticeable in NR-CR blends than in the mixes of the individual elastomers. It is also noted that the different vulcanisates prepared with this non-toxic accelerator also show better/comparable tensile and other physical properties compared with the reference formulations.

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Chapter 8

SUMMARY AND CONCLUSIONS

The reason for the increasing use of binary accelerator systems for rubber vulcanisation is a result of several factors including a desire to optimise the end use properties, better acceleration of vulcanisation, better control of processing safety etc. Further, the physical and chemical properties of vulcanised rubber depend on the fine structure of the rubber vulcanisate which in turn is greatly affected by the type of accelerator used, the nature of the curing agent, conditions of vulcanisation etc. In spite of the widespread use of binary accelerator systems the mechanism of the combined action of accelerators in rubber vulcanisation is not fully understood even now. It is known that the accelerators in which sulphur is combined as S-S, C-S-C, S-N etc. are generally inactive at lower vulcanisation temperatures because of the high thermal stability of the sulphur bonds. Thiourea and its derivatives have advantageous properties in this context. It has been known that sulphur containing nucleophiles such as thiourea enhances the activity of accelerators like TMTD, CBS etc. to operate at lower vulcanisation temperatures. Many authors have suggested that mechanism of vulcanisation whether polar or radical depends on the nature of accelerator, vulcanising condition, nature of elastomer used etc., even though no conclusive evidence has been given. In our laboratories binary systems containing derivatives of thiourea were tried as secondary accelerators in the sulphur vulcanisation systems of different elastomers and they gave supporting evidence, in general, to a nucleophilic reaction mechanism suggested by Philpott and by Moore. In the present study we synthesised an amidinothiourea derivative viz. N-amidino N'-phenyl thiourea (APT) and tried it as a secondary accelerator in the binary systems containing TMTD/MBTS/CBS for the vulcanisation of different elastomers and their blends. This study was undertaken with a view to giving further proof with regard to the theory of nucleophilic reaction mechanism or otherwise in such binary systems. Thiourea binary combinations were taken as controls. It may be noted that by virtue of the guanidinil group present in it APT is more nucleophilic than thiourea.

Now a days a lot of importance is given world wide for the use of non-toxic chemicals for rubber compounding. APT is known to be a non-toxic substance and is used in the pharmaceutical industry. Search for a safe and non-toxic accelerator is another point in selecting this amidinothiourea derivative for our study.

The thesis is divided into eight chapters. In the first chapter, a general introduction to various compounding ingredients, rubber vulcanisation reactions and different accelerator systems are described. Literature survey on the mechanism of vulcanisation reactions and the importance of binary accelerator systems is included in this section. It also includes the scope and objectives of the present work.

The specifications of different elastomers and compounding ingredients used in the study are given in chapter 2. A detailed description of the experimental procedures adopted is also included in this section. It covers methods used for compounding, vulcanisation and determination of the different physical properties of the vulcanisates. Estimation of total cross link density of the vulcanisates and the rheological study of NR latex is also explained in this chapter.

In chapter 3 investigations on the accelerator activity of APT in binary systems containing MBTS, TMTD and CBS for the sulphur vulcanisation of natural rubber using standard procedures is described.

The procedure for the synthesis of N- amidino N'- phenyl thiourea is also given in this section. Part A of this chapter deals with the study of NR gum formulations. Compounding, evaluation of different cure characteristics, vulcanisation and determination of the physical properties of the different formulations containing APT and the control are described in detail. Evaluation of the cure characteristics of NR gum mixes showed appreciable reduction in the optimum cure time for mixes containing APT compared to thiourea, which is used as the control. The cure behaviour of these NR formulations provided supporting evidence to the nucleophilic reaction mechanism for the accelerator activity in these systems as suggested by Philpott. The lower scorch time observed in the case of mixes containing APT, when used in higher dosages, is to be considered as a disadvantage. Practical cure systems with optimum concentrations of APT are proposed. As the systems containing this amidino thiourea derivative showed characteristics of practical rubber product mixes, they were further investigated for the various physical properties. The tensile properties evaluated were found to give satisfactory results compared to reference formulations. APT showed promising results in the after ageing properties also in these gum formulations.

Studies on the effect of APT in filled natural rubber systems are included in part B of this chapter. Carbon black and silica were used as fillers in this study. It is found that APT can be effectively used as an accelerator in the binary systems containing MBTS, TMTD or CBS in NR filled systems. The cure characteristics, especially optimum cure time obtained, point to a nucleophilic reaction mechanism here also. The physical properties evaluated viz. tensile strength, elongation at break, hardness, compression set, abrasion resistance and tear strength values of all the three experimental systems gave values better than / comparable to those of the reference mixes. Based on the cure characteristics and tensile properties obtained, the optimum dosages of APT required for the above binary systems have been derived as a 1:1 molar combinations of APT with TMTD/MBTS/CBS. The percentage retention of tensile properties on heat ageing of the vulcanisates containing APT is also found to be satisfactory.

Chapter four focusses on studies on the effect of TMTD-APT and CBS-APT systems in natural rubber latex. The use of accelerators in rubber latex is basically different from their use in dry rubber. Scorch problems are less in latex compounds and vulcanisation temperature is also lower. All accelerators useful in dry rubber cannot be employed in latex, as the colloidal stability of the latex has also to be taken in to account. In latex studies also thiourea binary systems were taken as control. Latex films were prepared using standard procedures and their vulcanisation was carried out at two different temperatures viz. 120 and 100°C. Optimum cure time of different mixes is estimated as the time to reach maximum tensile strength by generating a tensile strength - time graph. It is seen that the optimum cure time values decrease substantially as the concentration of APT increases. Considering systems containing equivalent accelerator combinations, TMTD - APT mix in 1:1 molar ratio shows an optimum cure time value that is much lower than that of the reference formulations (TMTD-TU and TMTD alone). In CBS systems also as the dosage of APT increases the optimum cure time is found to decrease considerably. Here also the mixes containing APT give better cure values compared with the reference formulations. These observations are true for both the cure temperatures viz. 100 and 120°C. Based on these cure values, it can be stated that APT being more nucleophilic than TU, the results point to a nucleophilic reaction mechanism in these binary combinations in NR latex also. The systems containing optimum dosages of APT give satisfactory values for mechanical properties like tensile strength and tear strength also. Non-toxic nature of APT is especially beneficial in these latex formulations.

A thorough understanding of the rheological properties of any latex compound is essential to evaluate its processing properties. Flow behaviour of latex especially shear rate - temperature relationship on viscosity is important here. In this context rheological behaviour of these latex compounds was also investigated in detail. These rheological studies of the compounded latex show that the introduction of APT in these systems do not have adverse effect in processing especially in comparison to the control mixes. At higher temperatures, APT seems to stabilise the TMTD mixes where as the CBS-APT shows a tendency to thicken, as is the case with control mixes containing thiourea.

It may be noted that compounding and vulcanisation of natural rubber differs from many other synthetic rubbers. In the fifth chapter the effectiveness of APT in the accelerated sulphur vulcanisation of styrene butadiene rubber is investigated. Binary systems containing MBTS / TMTD as primary accelerator were studied. We evaluated the cure characteristics, tensile properties and network structure of the various systems under review in detail. Even though gum formulations of SBR are not industrially important, they will be of much advantage for study of reaction mechanism. The effect of APT in SBR gum formulations is described in part A of this chapter. As the concentration of APT is increased from 0.25 to 1.5 molar level the t_{90} value is seen to be much reduced in both TMTD and MBTS systems. Scorch time is also found to be decreased accordingly. The effectiveness of APT as a secondary accelerator in both TMTD-APT and MBTS-APT systems is clearly indicated by the cure characteristics obtained. Here also it is reasonable to assume that the vulcanisation proceeds through a nucleophilic attack by the amidinothiourea derivative.

APT showed promising results with filled systems of SBR also. The cure characteristics, tensile properties and chemical cross link studies carried out on filled mixes containing carbon black/silica are described in part B of this chapter. Considering the optimum cure time values of the experimental mixes containing filler with that of the control mix, the silica formulations showed slight difference from that of NR (gum and filled systems) and SBR gum formulations. Here in these silica systems it may be inferred that instead of a pure nucleophilic reaction mechanism there may be mixed polar/radical type reactions involved. The vulcanisates obtained with these filled systems showed satisfactory tensile properties and good retention of these properties after heat ageing. Evaluation of other physical properties of the vulcanisates also gave comparable values. Optimum concentrations of APT required for practical cure systems are also derived based on the cure characteristics and tensile properties of the vulcanisates obtained.

Compounding, curing etc. of polar rubbers are different from other hydrocarbon rubbers. Study on the effect of amidino phenyl thiourea in the vulcanisation of a typical polar rubber viz. polychloroprene is given in the sixth chapter. The presence of the electronegative chlorine atoms will deactivate the carbon-carbon double bonds present in polychloroprene chains. Usual accelerators suitable for natural rubber vulcanisation are found unimportant where polychloroprene is concerned. The most widely used accelerator in the vulcanisation of chloroprene rubber is ethylene thiourea (NA22). In this study we tried sulphur vulcanisation along with MgO and ZnO. TMTD-NA22 combination is used as control. From our investigations it is found that the experimental mixes containing TMTD-APT are effective for the vulcanisation of polychloroprene rubber also. The optimum cure time values shown by NA22 mixes are found to be lower than that of the corresponding APT formulations. NA22 being more nucleophilic than APT by virtue of the higher hyperconjugative effect of $-CH_2$ groups present in it, this fact points to a nucleophilic reaction mechanism in sulphur vulcanisation of these CR vulcanisation systems. From the results obtained it is clear that conventional accelerator used in CR vulcanisation viz. ethylene thiourea which is reported to be toxic, can be replaced by the non-toxic amidinothiourea derivative APT. The tensile and other physical properties evaluated were also found to be better /comparable to the control systems in both gum and filled formulations.

There are technical reasons for blending of elastomers as it makes possible to obtain the right compromise in properties of individual elastomers, reduces the difficulties encountered in processing and vulcanisation of some rubbers and also for economic reasons. The use of APT as a secondary accelerator for the vulcanisation of NR-CR blends was attempted and details of this study is described in chapter 7. Preblending is the procedure adopted by us for blending these two rubbers in which the compounding ingredients are added to the premixed elastomers. Cure characteristics and tensile properties of TMTD-APT systems in both gum and filled blends were studied and these properties compared with TMTD-TU and TMTD-NA22 reference mixes. Noting the optimum cure time values of mixes containing equivalent concentration of accelerators, it is found that APT mixes showed the least t_{90} values compared to those of TU and NA22 mixes in both gum and filled formulations. Considering the nucleophilic character of APT, NA22 and TU, mix containing NA22 is expected to show the lowest t_{90} value. So the proposed nucleophilic reaction mechanism applied to the individual elastomers (NR and CR) does not hold good for the blend systems. There may be a combination of polar and radical type mechanisms applicable in these blend vulcanisation reactions. The effect of change in concentration of APT on cure and tensile properties were investigated and the optimum dosage of APT required for a more or less ideal cure system is derived. Comparing the cure and tensile properties of NR-CR blend systems with those of the individual elastomers, some favourable cure properties and improvement in tensile properties are noticed for the former. The favourable effects of this non-toxic amidino phenyl thiourea as a secondary accelerator is more noticeable in NR-CR blends than in the mixes containing the individual elastomers viz. natural rubber and polychloroprene.

The list of publications from this work is included at the end of the thesis.

List of Publications

1. "Studies on Novel Binary Accelerator System in Sulfur Vulcanization of Natural Rubber". *J. Appl. Polym. Sci.* (U.S.A), **79,** 1- 8 (2001)
2. "Effect of Fillers on a New Binary Accelerator System for Sulphur Vulcanisation of NR". Paper presented in the thirteenth Kerala Science Congress held at Thrisur 29-30 January 2001
3. "A New Binary Accelerator System for the Sulfur Vulcanization of Filled Systems of Natural Rubber." Accepted for publication in *Iranian Polymer Journal* (Iran)
4. "New binary accelerator systems containing N-amidino N'-phenyl thiourea as a secondary accelerator for the sulphur vulcanization of Styrene-butadiene rubber". (Communicated)
5. "Studies on new binary accelerator systems in sulphur vulcanization of NR latex" (Communicated)
6. "New binary accelerator systems for the vulcanization of NR-CR blends". (To be communicated)