STUDIES ON A NEW VULCANIZATION SYSTEM

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APRIL 1997

Dedicated in memory of
my Father

CERTIFICATE

This is to certify that the thesis entitled "Studies on a New Vulcanization System", is an authentic record of the research work carried out by Mr. Cyriac Mathew under my supervision and guidance in the Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, and no part of the work reported in this thesis has been presented for any other degree or diploma earlier.

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Kochi
23 rd April 1997.

DECLARATION

I hereby declare that the thesis entitled "Studies on a New Vulcanization system", is an authentic record of the research work carried out by me under the supervision of Prof. (Dr.) A.P.Kuriakose, Head of the Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, and no part of the work reported in this thesis has been presented for any other degree or diploma earlier.

Kochi
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CHAPTER I

INTRODUCTION

Rubber, in its raw state, is not the material in everyday use. To be practically useful, all rubbers will have to undergo the process of vulcanization. Vulcanization is the process of conversion of rubber, by any treatment, from a plastic substance of very low strength and breaking elongation into a resilient highly elastic material of considerable strength. From the chemical point of view vulcanization is the process whereby the flexible, discrete rubber chains are joined together by crosslinking reactions giving a three dimensional network.

Studies on the chemistry of vulcanization[1,2] play a central role in the efforts to achieve better product performance from natural and synthetic rubbers. They provide rubber technologists with an increasingly realistic picture of molecular framework of vulcanizates, from which relation between physical properties and chemical constitution may be deduced. Moreover, these studies are also aimed at the understanding of the vulcanization process, in sufficiently advanced chemical mechanistic terms, so that the effect of changes on vulcanizate structure can rationally be predicted.[3,4]

The oldest method of vulcanization consisted of heating rubber with sulphur. This was the first vulcanization system, introduced by Charles Goodyear in 1844 in United States and Thomas Hancock at about the same time in England.[5] But this form of "sulphur only" vulcanization does not provide an optimum product even if it lessens the disadvantages of uncrosslinked elastomers. Vulcanization of rubber with sulphur alone is a very slow process and takes several hours or even days to reach optimum curing depending on the temperature of vulcanization and the nature of the rubber used. This yields vulcanizates of very low physical and mechanical properties. Also they have a strong tendency to revert and their resistance to ageing is poor. Sulphur bloom is also very common. Vulcanization with sulphur alone is therefore of no technological importance at all. As compared to sulphur alone, the presence of small amounts of accelerator along with it may reduce the cure time from hours to minutes or even seconds at higher temperatures. Oenslanger[5] found that the addition of small amounts of aniline, the first organic accelerator used, to a rubber/sulphur formulation greatly increased the rate of vulcanization and also improved the final vulcanizate properties. Later it was discovered that a wide variety of amines function similarly.[6] The ultimate goal of vulcanization is to obtain the desired vulcanizate end properties. These properties to a great extent depend on the network structure of the cured elastomer, which in turn, depend on the chemistry of vulcanization. Therefore an understanding of the vulcanization chemistry and its relationship with the resulting network is important to tailor and achieve desired end properties. However, it may be noted that the vulcanization chemistry of rubber is not fully understood even now.

An essential step before vulcanization is the mixing of rubber with various ingredients, generally known as compounding. The main objectives of compounding are to facilitate processing and fabrication, to achieve the required balance in vulcanizate properties and provide durability, all at the lowest possible cost. The various ingredients, generally added to rubber during compounding include processing aids, accelerators and activators, fillers, antidegradants and a variety of other materials. Each ingredient added to maximize one property may reduce another. Thus compounding also involves a compromise. The compounded stock is then vulcanized using heat and pressure under specified conditions. The practical aspect of compounding and vulcanization also varies from rubber to rubber depending on whether it is saturated or unsaturated, natural or synthetic etc. The compounding procedure adopted for latices are different from those of dry rubber. A number of differences are encountered in the compounding and vulcanization of natural rubber vis-a-vis synthetic rubbers. Synthetic rubbers are slower curing[7] than natural rubber and so more accelerators are needed for the former. This is due to comparatively lower unsaturation levels and lesser active chemical bonds of synthetic rubbers. Also it is seen that problems due to scorch are lesser in synthetic rubbers compared to natural rubber stocks. Since natural rubber is more stress crystallizable than synthetic rubbers, gum vulcanizates of the former have good strength whereas reinforcing fillers are essential to impart strength to synthetic rubber vulcanizates. Both types of rubbers require mastication before compounding but for synthetic rubbers, generally mastication requires longer time. Usually synthetic rubbers need higher temperature for vulcanization while an increase in temperature will give rise to degradation in the case of natural rubber. For both natural and synthetic·rubbers compounding ingredients are mostly the same but the quantities may vary, especially those of sulphur and accelerator.

1.1 ACCELERATORS

Vulcanization accelerators are substances which are added in small amounts during compounding to improve the physical, mechanical and service properties of the finished articles. The decrease in cure time in presence of accelerator is of tremendous economic importance because of increased turn over and consequent reduction in the cost of production. Moreover, in the presence of an accelerator a very small amount of sulphur, generally 0.1 to 3.0 parts per hundred rubber (phr) is enough to give a vulcanizate of desired properties. The first accelerators used in rubber vulcanization were, in fact, inorganic compounds[6]. Among them, litharge, lime, magnesium oxide and zinc oxide were the most widely used ones. Organic compounds were not used as accelerators until 1906 when the effect of aniline and its derivatives (thiocarbanilides) on sulphur vulcanization was discovered by Oenslanger[5]. Later several other organic compounds were shown to have accelerating activity and majority of them were nitrogen containing organic bases[8-10]. Earlier it was believed that the basicity of these substances, rather than chemical constitution, primarily governs its effectiveness. But it was subsequently established that the accelerating activity of organic bases is not proportional to their basicity.[11,12] The discovery of nitrogen free accelerators such as zinc alkyl xanthates[13] and zinc thiophenol[14], rejected the theory that the element nitrogen was responsible for the accelerating activity.

A large variety of accelerators were developed during the first two decades of the present century. By this time thiurams, dithiocarbamates and alkyl xanthates came into use as accelerators.[15] Molony[16] introduced a reaction product of amines from beet molasses with CS_2 which was later identified as tetramethylthiuram disulphide (TMTD). Investigations on the effects of zinc oxide led to the discovery of two most important accelerators, diphenyl guanidine (DPG) and mercaptobenzthiazole (MBT).[18] Around 1920 organic accelerators came into common use and it was discovered that thiuram disulphides enable vulcanization to proceed without sulphur.[13] Further investigations in the field of accelerators were aimed at the development of a new class of accelerators which reacted slowly and safely at processing temperatures but rapidly at vulcanization temperatures. Sebrell and Bedford[14] introduced the first delayed action accelerator mercaptobenzthiazyl disulphide (MBTS) which gave greater scorch safety at higher processing temperatures. Later, even more delayed action and yet faster curing vulcanization systems were made possible from thiazole derivatives of sulphenamide. Thiocarbamyl sulphenamides have been reported to be more productive than the corresponding benzothiazole derivatives, due to the combined scorch delay of sulphenamides and ultra accelerative activity of thiocarbamates, both being present in their structure.[19] Further step in the development of accelerators was the discovery of ultra accelerators, used for vulcanization at room temperature, particularly in the processing of latex.

1.2 ACTIVATORS

Activators are compounding ingredients which enable an accelerator to exercise its maximum effect. Inorganic activators are metallic oxides such as zinc, lead and magnesium oxides. The generally used activator system is a combination of zinc oxide and a long chain fatty acid such as stearic acid which act as a co-activator. The commonly accepted combination is 5 phr zinc oxide and 1-3 phr stearic acid.[20] Zinc oxide has been an important ingredient since the early days of rubber compounding. Originally used as an extender to reduce cost, it was subsequently found to have a reinforcing effect and was later found to reduce vulcanization time.[21] Organic accelerators depend on zinc oxide to activate them.

1.3 THE MECHANISM OF RUBBER VULCANIZATION

Vulcanization processes, in general, are not simple chemical reactions but complex mechanisms are involved. Although, for several decades, there has been much discussions in scientific literature on the mechanism of sulphur vulcanization, it is now clear that the sulphuration of rubber under vulcanizing conditions involves a whole series of consecutive and competing reactions and hence no single mechanism can be appropriate.

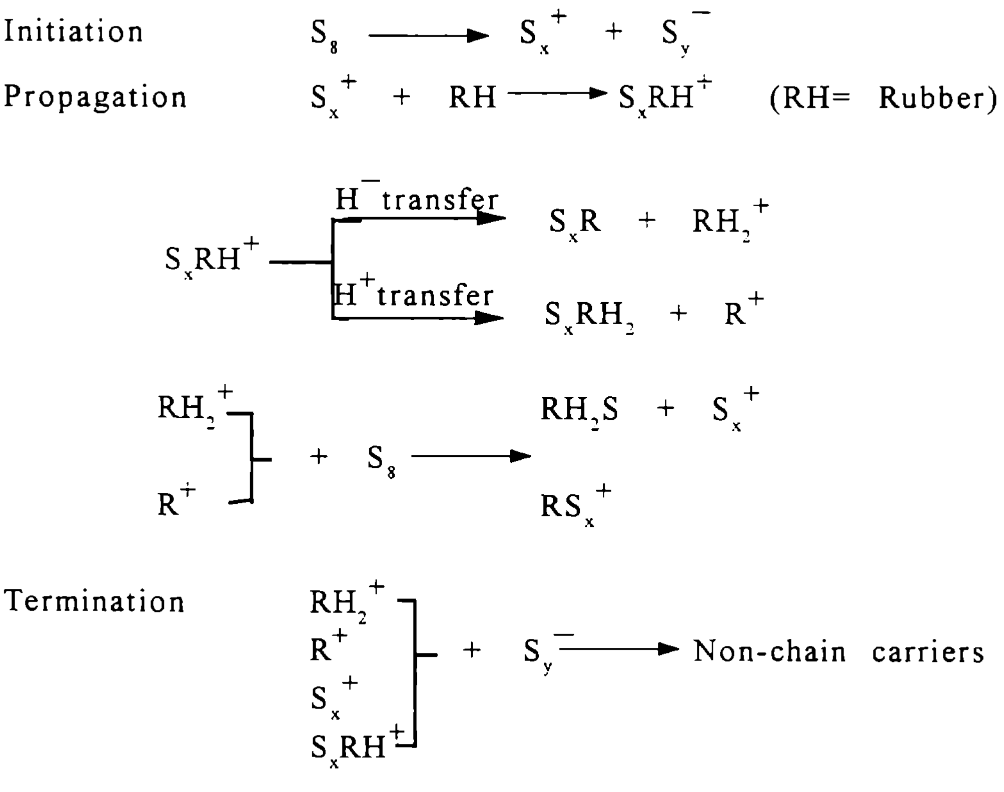
Sulphur vulcanization reactions can broadly be classified into two categories viz., the unaccelerated and the accelerated sulphur vulcanization. Unaccelerated sulphur formulation consists of rubber and sulphur while the accelerated sulphur system contain rubber, accelerator and sulphur. In addition to this, both the types include zinc oxide stearic acid activator system also. A third category is also there, in which elemental sulphur is not present, instead, the accelerator provides the sulphur for vulcanization. These sulphurless systems are generally referred to as sulphur donor formulations.

Both sulphur and non-sulphur vulcanization systems have advantages and disadvantages of their own, but the former still remain versatile. This is mainly due to the high vulcanization rate, low cost, flexibility of the system with respect to rate of crosslinking and choice of additives, substantial insensitivity to other compounding ingredients and excellent balance of vulcanizate properties in these systems.[22] Non-sulphur systems were developed mainly due to the poor compression set and heat resistance properties of the vulcanizates in the sulphur systems.

1.3.1 UNACCELERATED (SULPHUR-ONLY) VULCANIZATION

Unaccelerated or the sulphur-only vulcanization, which is not widely used today, is the oldest form of vulcanization and has been extensively studied with respect to the reaction mechanism. The mechanism of sulphur-only vulcanization is not so simple. It involves reactions such as double bond migration, isomerization, chain cleavage, cyclization, formation of vicinal crosslinks etc.[1,22-29]

The mechanism of unaccelerated sulphur vulcanization was studied using radical scavengers[30] and electron paramagnetic resonance (EPR) techniques.[31] These studies revealed a polar (ionic) mechanism in these systems. However, the possibility of the S_8 ring undergoing homolytic ring opening, producing a radical reaction also is possible.[26] Although certain experimental results would be explained by a radical process, the general consensus is that sulphur-only vulcanization occurs via polar mechanism. A general mechanism of the proposed sulphur-only vulcanization can be represented as shown in scheme 1.1.



Scheme 1.1

In sulphur-only vulcanization systems, the interaction of sulphur with zinc oxide and stearic acid was analysed using differential scanning calorimetry (DSC)[32]. These results indicated the formation of zinc stearate and its subsequent reaction with sulphur. The sulphur-zinc stearate interaction helps to explain the activating role of zinc oxide in unaccelerated sulphur vulcanization but does not give the details of the actual interactions.

1.3.2 ACCELERATED SULPHUR VULCANIZATION

The most common vulcanization systems used in industrial applications are the accelerated sulphur formulations. This method is an improvement from the sulphur-only vulcanization because it has much shorter cure time and a better scorch period. The accelerated sulphur systems can further be classified into single accelerator systems and binary accelerator systems. A schematic representation of a typical cure curve for the accelerated sulphur system is shown in Fig.1.1[33]. The curve illustrates three main regions of cure (labelled I-III). The first region is the scorch delay period or the induction period in which majority of the accelerator chemistry takes place. The extent of this region varies with different accelerators. For instance, there is very little scorch delay in thiuram types and very long scorch delay in sulphenamide and sulphenimide types. The second region is the crosslinking period, where the initial network structures are formed and the accelerator intermediates are consumed. The final stage is the overcure or reversion period, during which

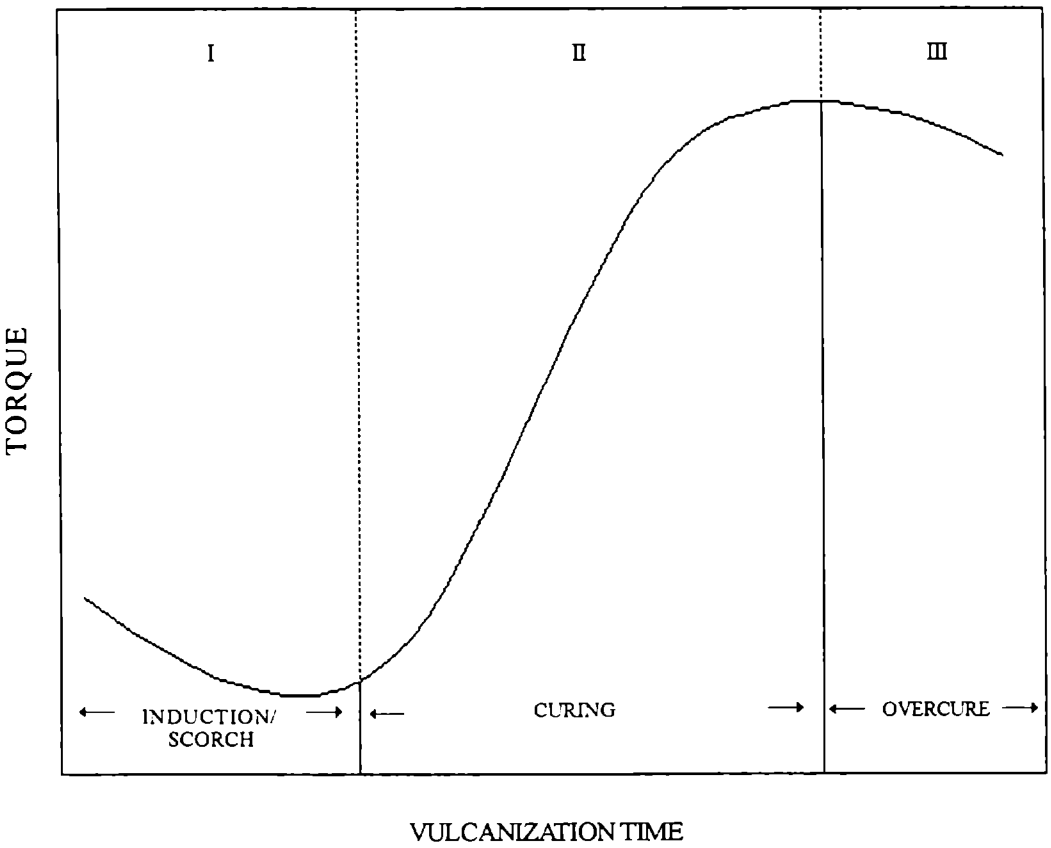


Fig. 1.1 Typical cure curve for the accelerated sulphur system.

maturation and resulting property deterioration occurs.

In the vulcanization network sulphur is combined in a number of ways. In the form of crosslinks it remains as monosulphide, disulphide or polysulphide. It may also be present as pendent sulphides or cyclic monosulphides and disulphides (Fig. 1.2). An estimate of the number of sulphur atoms for each crosslink formed is a measure of the efficiency of the vulcanization system. An unaccelerated rubber sulphur vulcanizate may give a figure of 40-45, while in conventional accelerated sulphur vulcanizate it may drop to 10-15 and finally for an efficient vulcanizate system it may reduce still further upto mono, di, etc.[34]

The ratio of accelerator to sulphur determines the efficiency with which sulphur is converted into crosslinks and upon it will depend the nature of crosslinks and the extent of main chain modification. Based on the sulphur accelerator ratio the suphur vulcanizing systems can be classified as:[35]

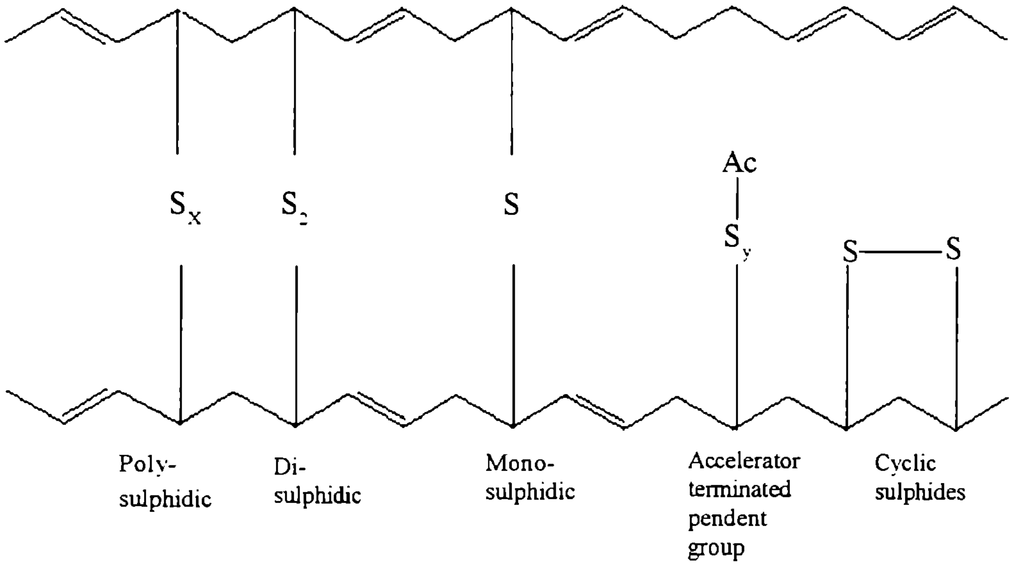


Fig: 1.2 A diagramatic representation of the network structure of a sulphur vulcanizate.

(a) the conventional or high sulphur vulcanization system in which the level of sulphur is in the range of 2.0-3.5 phr and the corresponding level of accelerator is in the range of 1.0-0.4 phr;

(b) the efficient vulcanizing (EV) system consisting of 0.3-0.8 phr sulphur and 6.0-2.5 phr accelerator, and

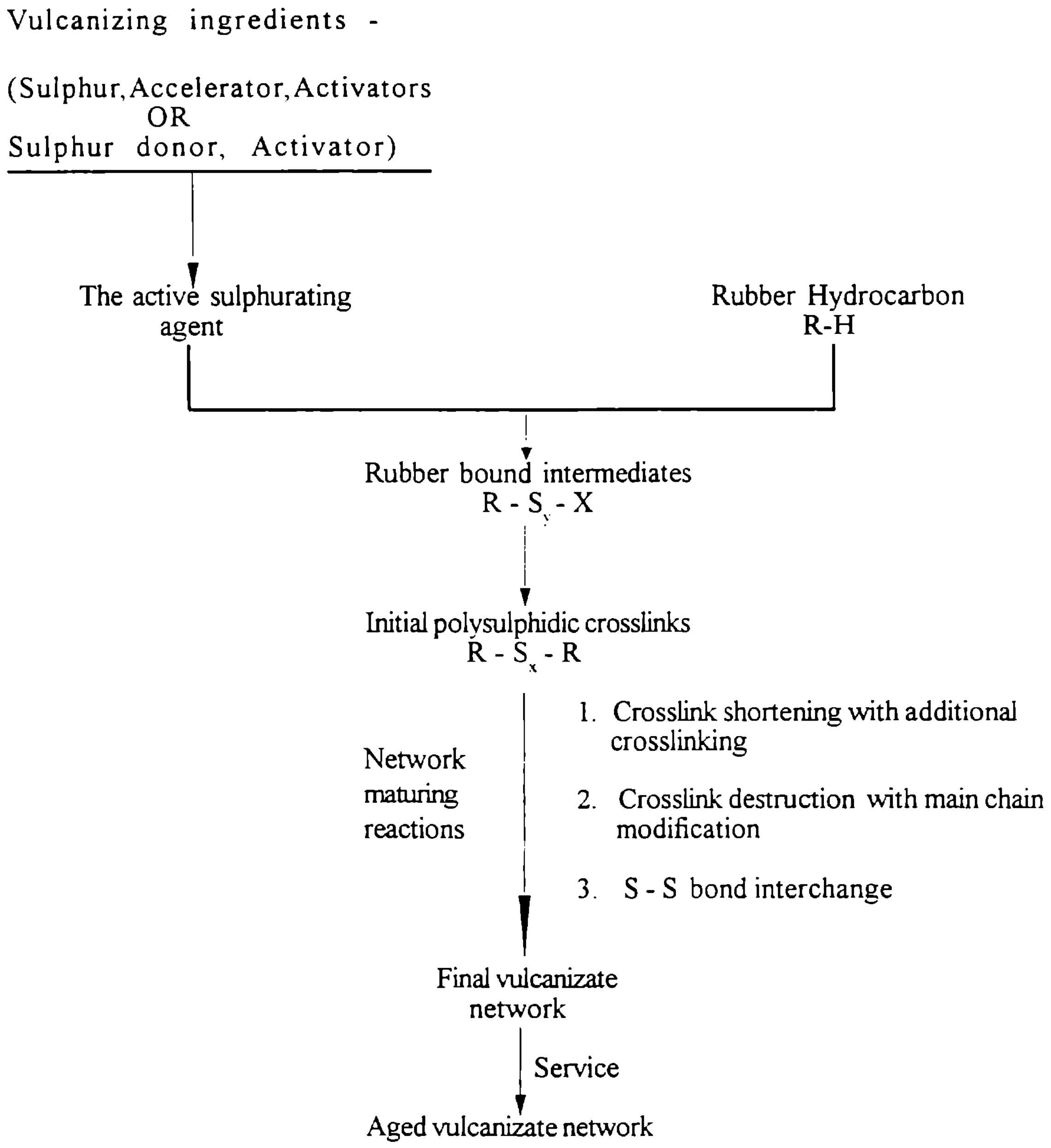
(c) the semi EV system with level of sulphur lying between 1.0-1.8 phr and that of accelerator between 2.5-1.0 phr.

In EV systems, at optimum cure the network will contain an abundance of monosulphidic crosslinks usually accounting for at least eighty per cent of the total. As a measure of the improved crosslinking efficiency the number of sulphur atoms combined for every chemical crosslink is unlikely to exceed five and can be as low as two.[36] Owing to the increased number of polysulphidic crosslinks the conventional sulphur vulcanization system find use in products that do not require substantial heat resistance during manufacture and service. These systems are comparatively inexpensive. EV systems are usually suitable for products that need improved reversion resistance during vulcanization and those which are exposed to higher temperatures. But these systems are expensive compared to the semi EV and conventional systems. Semi EV system is actually a compromise over conventional and EV systems.

From the mechanistic point of view of accelerated sulphur vulcanization, the single accelerator systems are the most widely studied. This is mainly due to their widespread use and simplicity of the mechanism. However, the amount of research in the fundamental chemistry of binary accelerator systems is also rapidly growing.

1.3.2.1 Single Accelerator Systems

Direct studies on rubber networks and analysis of model olefinic systems have made it possible to gain considerable insight in to the course of accelerated vulcanization. It is now generally accepted that, in the case of natural rubber at least, vulcanization by sulphur and accelerator or by a sulphur donor system follow the simplified reaction sequence shown in scheme 1.2.[37] In the scheme, R-H denotes the rubber hydrocarbon, 'H' being an allylic hydrogen in a methyl or methylene group. The active sulphurating agent is the species which reacts with rubber hydrocarbon to form C-S bonds. It is produced by a sequence of reactions from sulphur, accelerator and activator or from a sulphur donor such as TMTD and activator. The active sulphurating agent reacts directly with the rubber molecule to give a rubber bound pendent group, in which a fragment derived from the accelerator or sulphur donor, is linked through two or more sulphur atoms to the rubber chain. These pendent groups forms crosslinks either by direct reaction with another rubber molecule or by disproportionation with a second pendent group of a neighbouring rubber chain. The polysulphidic crosslinks are formed first. These are thermally unstable and chemically reactive and undergo a number of competing reactions, which are termed network maturing reactions, leading to the final network structure.



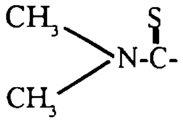
Scheme 1.2 - Generalised mechanism of vulcanization; R = Rubber chain, H = Allylic proton and X = accelerator residue.

(a) Formation of active sulphurating agents

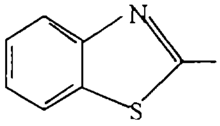
Majority of the accelerator chemistry occurs during the scorch delay or induction period. During this period various accelerator complexes are formed which are the active sulphurating agents. There is yet no general agreement as to the nature of the active sulphurating agents and the mechanism of its reaction with the rubber molecules. The most common accelerators are the thiazoles, thiuram disulphides and sulphenamides. These three types may be represented by one or other of the schematic formulae;

XSH, XSSX, XSNR

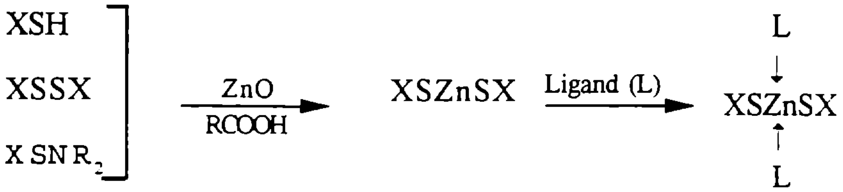
where X is,



or



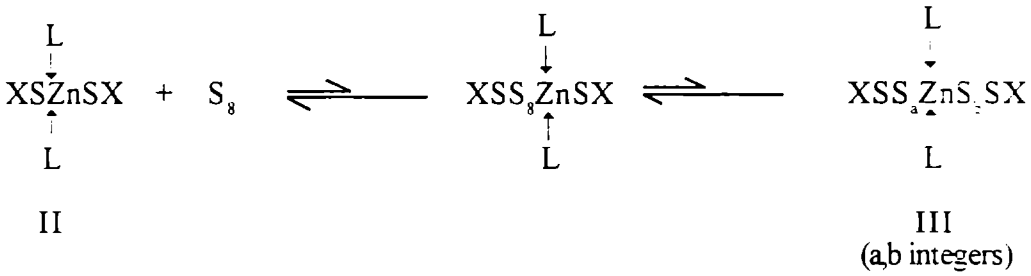
The first step may therefore be schematically represented by,



I II

Scheme 1.3

The initial zinc thiolate (I) is sparingly soluble in rubber. It is rendered soluble through coordination with nitrogen bases (Ligands- either naturally occuring in rubber or added as accelerators) or as zinc carboxylates.[38] In the next step the zinc thiolate complex (II) is believed to react with sulphur to form zinc perthiolates (III) through a series of equilibria[39], which strongly favour dissociation into zinc thiolate complex and sulphur.



Scheme 1.4

Recently several techniques have been used to study the chemistry during the induction period. One of the widely used techniques is DSC.[40-46] McGill et al.[40,42,44,46], Kok[41], and Luyt[43], studied the chemical interactions between all possible combinations of curatives in a particular formulation using DSC. They used MBT, MBTS and TMTD as accelerators. Zinc ion was found to form zinc complexes with MBT but not with MBTS.[44,45] The DSC analysis detected no reaction of zinc ions with TMTD or tetramethyl thiuram monosulphide (TMTM) which is a product of TMTD decomposition.[42] In these systems the role of zinc oxide is mostly to catalyse conversion of rubber bound intermediate to crosslinks.

Another approach to study the accelerator chemistry is to determine the distribution of accelerator complex and other curatives as a function of cure time.[47,48] This was done mainly on benzothiazole based accelerators both in the presence and absence of zinc oxide and stearic acid. These studies showed the presence of zinc complex of the type BtS_xZnS_xBt (Bt = 2 benzothiazolyl) as a key accelerator intermediate. Aarts and Baker[49] using isotopic labelling (N-15) of the amine fragment of the sulphenamide accelerator showed that the amine present in the accelerator complex is probably as a ligand. This gives an indirect evidence as to the nature of the accelerator complex.

(b) Reaction of active sulphurating agent with rubber

The mechanism of the formation of rubber bound intermediates by the reaction of active sulphurating agent is yet not very clear. Many authors have worked on this subject and arguments for both radical and polar mechanisms have been put forward without definite conclusive evidences for either of them. The various techniques used to study this subject are: radical scavenger studies[30,52,53], Raman spectroscopy[51,54,66] ESR analysis[31,54-57], combined use of dicumyl peroxide and accelerators in the formulation[58-64] and analysis of a wide variety of accelerators. As a result of these studies a number of conclusions have been arrived at, with the general idea that the polar or radical nature of the reaction mechanism depends on the nature of the sulphurating species and accelerator complex formed. Studies using flash photolysis[65] revealed that the favoured mechanism depends on the nature of the elastomers also.

Colemann et al.[54,66] proposed a predominantly free radical mechanism for accelerated sulphur vulcanization in the absence of zinc compounds. Here the active sulphurating agent is an accelerator polysulphide IV. Using the ESR spectra of quenched TMTD mixtures, they have established the formation of the persulphenyl radicals ($X\dot{S}_b$, $X\dot{S}_c$) at vulcanization temperatures.[54] The persulphenyl radicals react with rubber forming the rubber bound intermediates.

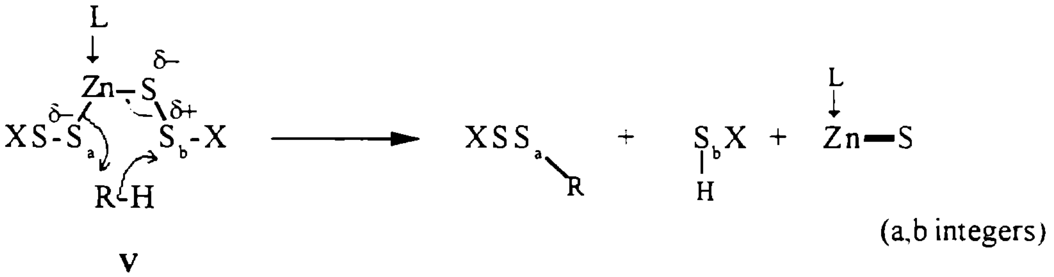
$$\underset{\textbf{IV}}{XSS_aX} \xrightarrow{\text{thermolysis}} X\dot{S}_b + X\dot{S}_c$$

$$X\dot{S}_b + R\text{-}H \rightleftharpoons \dot{R} + XS_bH$$
$$\dot{R} + XSS_aX \longrightarrow RS_xX + X\dot{S}_d$$
$$\dot{R} + X\dot{S}_c \longrightarrow RS_cX$$

Scheme 1.5

In their investigation of the vulcanization of natural rubber by dicumyl peroxide together with TMTD, N-cyclohexylbenzthiazole-2-sulphenamide (CBS)-sulphur, TMTD-sulphur or MBTS-sulphur, Manik and Banerjee[60,63,64] found that the course of the reaction was substantially altered by the addition of zinc oxide or zinc oxide and stearic acid. They concluded from their results that the mechanism of sulphur vulcanization is predominantly polar when zinc oxide is present.

Bateman, Moore, Porter and Saville[1] proposed a polar, largely concerted mechanism for sulphuration process in presence of zinc compounds. The active sulphurating agent is assumed to be the zinc accelerator perthiolate complex V (Ligands-'L', 'H' in R-H is an allylic hydrogen in methyl or methylene group).



Scheme 1.6

This mechanism not only provides a reasonable explanation for the superiority of zinc over other metals in promoting sulphur vulcanization but also rationalize the influence of added ligands. The coordination of electron donating ligands to the zinc atoms 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 S_N2 character of the process. Consequently, on both steric and electronic grounds, substitution at methyl carbon will be promoted relative to substitution at the methylene carbons.

Various studies with TMTD and MBT systems reveal the generalized conclusion that TMTD systems favour radical or mixed polar/radical reactions while MBT derivatives coupled with zinc oxide and stearic acid favour polar or mixed polar/radical reactions. Zinc oxide in general tends to favour polar or mixed polar/radical reactions.

(c) Conversion of rubber bound intermediates into crosslinks

As mentioned earlier in the second stage of accelerated vulcanization the zinc accelerator perthiolate complex III (model compound, ligands not shown) react with rubber hydrocarbon to produce the rubber-bound pendent group RS_aSX (or RS_xX)

$$RH + \underset{\textbf{III}}{XSS_aZnS_bSX} \longrightarrow RS_aSX + ZnS + XS_bH$$

One of the earlier techniques for analysing accelerated sulphur vulcanization is model compound studies. Skinner[67] analysed the allylic sulphuration of CBS accelerated vulcanization of natural rubber and polybutadiene using model compounds. The sulphuration would occur as shown in Fig. 1.3.

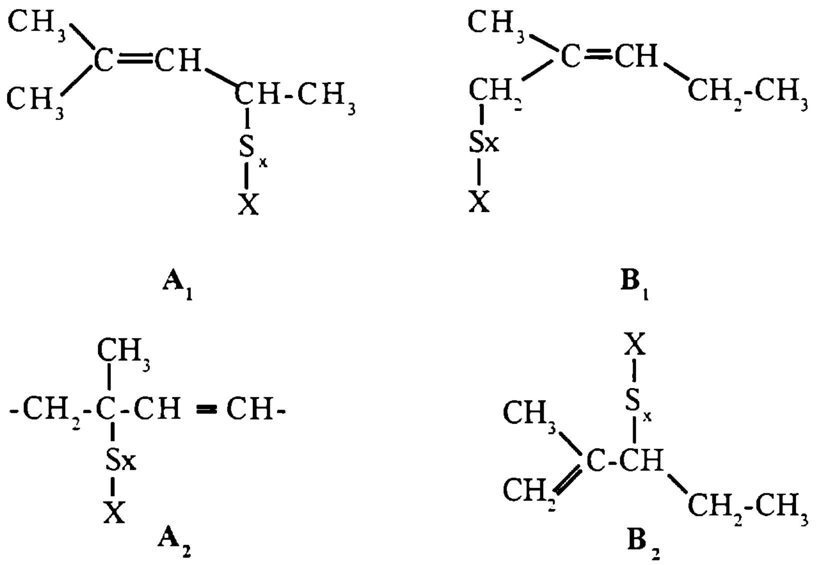


Figure 1.3

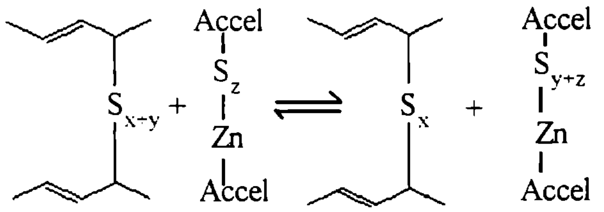
Model compound studies have established that conversion of intermediates to crosslinks proceeds by two distinct processes[68],

(a) $2RS_xX \longrightarrow RS_yR + XS_zX$

(b) $RS_xX + R'\text{-}H \longrightarrow RS_yR' + XS_wH$

It has been found that the initial crosslinks formed are largely polysulphidic but as reaction proceeds shortening of the crosslink occur, polysulphidic links being replaced by disulphidic and monosulphidic linkages. Duchacek[69] proposed three kinetic steps for crosslinking and reversion based on the effect of temperature on kinetic constants: fast crosslinking, slow crosslinking and degradation. It was concluded that fast crosslinking reaction was mainly ionic, while the slow crosslinking and degradation reactions were principally radical in nature.

After the formal vulcanization is over changes may continue to occur in the network structure, especially if the vulcanizate is in service under elevated temperatures. Layer[70] proposed that the key step in curing and reversion process was the sulphur exchange reaction shown in scheme 1.7. Blackman and McCall[71] analyzed the change in network structure of natural rubber vulcanizates during the ageing process and concluded that the key component in the ageing process is the residual accelerator.



Scheme 1.7 Accel = accelerator

1.3.2.2 Binary Accelerator Systems

The use of vulcanization system composed of two or more accelerators finds wide technological applications in recent years. Such systems generally possess an increased activity over that obtained with individual compounds. The benefits of binary systems are mainly factors like optimized vulcanization properties, faster cure and better control of processing safety. In spite of the wide practice of using combinations, the mechanism of the joint action of accelerators has been inadequately studied and only recently have scientists begun to fully probe the complicated mechanism of binary systems. Typically, accelerator present at a reasonably high level is called primary accelerator and that present in smaller amounts is called the secondary accelerator. The binary system usually give a faster cure-rate than either of the accelerators used alone due to synergistic effect. A large number of binary systems have been developed for practical applications. These include thiuram disulphides, sulphenamides, benzothiazyl disulphides, some derivatives of morpholine, piperidine, pyrrole, pyrrolidine, piperazine, phthalimides etc. Many amines like diphenylguanidine are used in combination with other accelerators such as MBT or sulphenamides to activate the vulcanization reaction. However, present day binary accelerator systems usually consist of benzothiazole and thiocarbamate derivatives. To increase the scorch delay of thiuram systems usually MBT and sulphenamides are often added additionally.[72] Thiourea and its derivatives are also known to be good secondary accelerators in rubber vulcanization.[53,73,74]

Though great deal of work has been done on elucidating the mechanism of vulcanization with single accelerator, work on binary system is less. Minatoya and Aoe[75,76] explained the higher activity of binary system by the formation of either eutectic mixture or salt forming compounds having better solubility in rubber and greater chemical reactivity. Layer[77] studied the binary system containing N-oxydiethylene-2-benzothiazole sulphenamide (OBTS) and N-oxydiethylenethiocarbamyl-N'-oxydiethylene sulphenamide (OTOS) in NR in detail. Dogadkin and collaborators[78,79,80] investigated a number of accelerator combinations and found mutual activation with many of them. They classified the binary systems into three groups:

1. Systems with synergistically active accelerators.
2. Systems with a pair of accelerators in which the activity of the pair does not exceed the activity of the most active accelerator.
3. Systems with additive action of vulcanization accelerators.

Systems with considerable mutual activation of accelerators include mixtures of disulphides (eg: MBTS, TMTD, etc.) or mercaptans (eg: MBT) with nitrogen containing organic bases, and disulphides with sulphenamides. Combinations of sulphenamides with nitrogen containing organic bases belong to the second system. The third category involves systems containing sulphenamides together with TMTM and those containing combinations of accelerators belonging to the same chemical class. It was established that[78] in the case of systems with mutual activity such as MBTS with DPG or N-cyclohexylbenzthiazole-2-sulphenamide (CBS) , the reaction between the accelerators were observed higher under vulcanization conditions than when they are reacted alone. Based on these observations it was suggested that in the initial stage of vulcanization an active accelerator complex is formed by the interaction of accelerators.[79] The complex then disintegrates with the formation of free radicals in the following manner.

$$\mathrm{RSSR} + \mathrm{R'R''NH} \longrightarrow \begin{bmatrix}\mathrm{RSSR}\\ \mathrm{R'R''NH}\end{bmatrix} \rightleftharpoons \mathrm{RSH} + \mathrm{R\dot{S}} + \mathrm{R'R''\dot{N}}$$

The reaction is believed to propagate as follows:

$$\mathrm{R\dot{S}} + \mathrm{R'R''NH} \longrightarrow \mathrm{RSH} + \mathrm{R'R''\dot{N}}$$

$$\mathrm{R'R''\dot{N}} + \mathrm{RSSR} \longrightarrow \mathrm{RSNR''R'} + \mathrm{R\dot{S}}$$

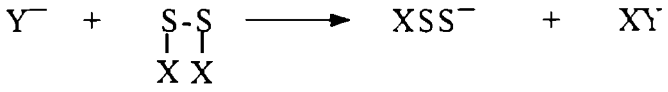
These stages explain the formation of the new highly active accelerators. viz., RSH and RSNR"R'. Eventhough the above classification of binary accelerator systems is useful, the mechanism do not explain all the facts exhibited by the combined accelerator systems.

Philpot[81] studied the accelerator activity of certain sulphur-bearing accelerators in presence of S-reactive nucleophiles. He suggested a polar mechanism for the activity of binary systems. It was proposed that the accelerator activity of sulphur-bearing accelerators (XSSX, XSX etc.) depends partly on the nature of X group and partly on the mode of attachment of the functional sulphur atom to other atomic grouping in the accelerator molecule. Accelerator in which sulphur is covalently linked to another sulphur. carbon or nitrogen are invariably of the delayed action type. They have very little activity at 100°C. The comparative inactivity at low temperatures of these compounds may be accounted for by assuming that such compounds can act as accelerators only if the sulphur has been made free. This can be done by breaking the S-S, S-C or S-N bond so that a reactive entity, capable of initiating a sequence of fast reactions leading to vulcanization, is liberated. The cleavage reaction of sulphur-sulphur bond have been extensively studied and Philpot suggested an ionic mechanism of the following type:

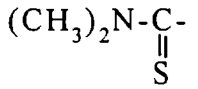
$$RS\text{-}SR' + Y^- \longrightarrow RSY + R'S^-$$

Here the S-S bond undergoes nucleophilic attack by a base Y^- producing a displacement reaction provided the attacking base has a greater sulphur nucleophilicity than the displaced thioanion $R'S^-$ Philpot[81] tried several accelerator combination in latex systems providing supporting evidence for the above mechanism.

Moore and co-workers studied in detail the mechanism of thiuram disulphide vulcanization of NR.[74] It is proposed that in presence of ZnO, vulcanization involving TMTD follows an ionic chain mechaniam as shown below.



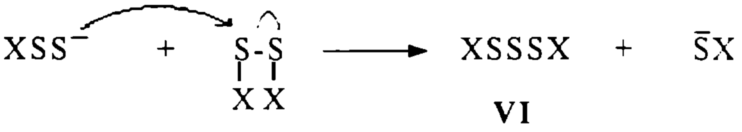
$$Y^- + \underset{X\ \ X}{\underset{|\ \ |}{S\text{-}S}} \longrightarrow XSS^- + XY \qquad (1)$$

where X = 

$$(CH_3)_2N\text{-}\underset{S}{\underset{\|}{C}}\text{-}$$

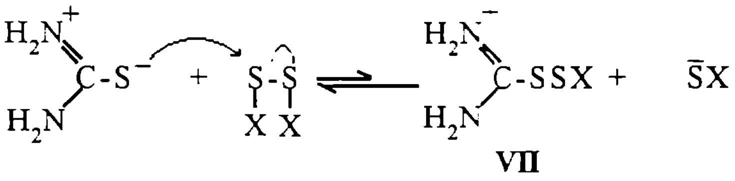
Y^- = nucleophile of a basic oxy-anion type
(from $Zn^{2-}....O^{2-}....$)

The perthioanion (XSS^-) forms a trisulphide (VI) with another thiuram-disulphide molecule (step 2). Further attacks by the nucleophile results



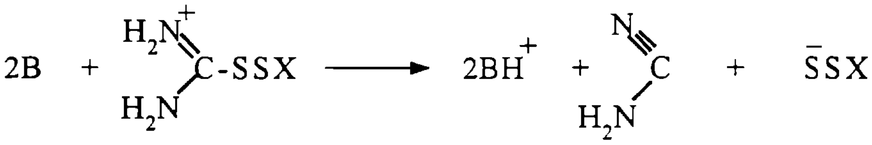
$$XSS^- + \underset{X\ \ X}{S{-}S} \longrightarrow \underset{\textbf{VI}}{XSSSX} + \bar{S}X \qquad \textbf{(2)}$$

in the formation of higher polysulphides from trisulphides which act as precursors for the formation of active sulphurating agents which initiates the crosslinking reactions. It is believed that the slow steps in the formation of thiuram polysulphides are reactions, exemplified by (1) above, in which the perthioanions are released during relatively difficult X-S bond fissions. If thiourea is added to the systems it will engage in a thioanion disulphide interchange reaction of the type:



(3)

The species (VII) formed in the above reaction would lose a proton to a suitable base and then decompose into a perthioanion:



(4)

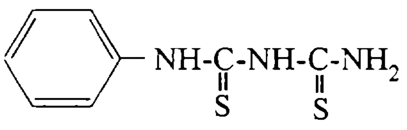
where B = base

Thus the relatively easy processes (3) and (4) lead to a rapid production of perthioanion precursor of the thiuram polysulphides required in the ultimate crosslinking reactions. Manik and Banerjee[60] based on the result of their investigations proposed that vulcanization in presence of TMTD, sulphur and ZnO also proceed mainly by ionic chain mechanism.

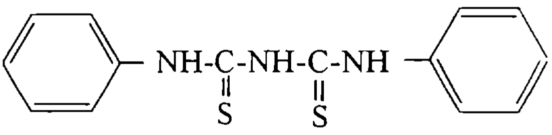
Recently many authors have turned their work on binary systems[82-86] and their conclusions also points to the formation of complexes. As in the case of single accelerator systems here also evidences are available for a polar or radical mechanism, eventhough no conclusive evidences have been found so far.

1.4 SCOPE AND OBJECTIVES OF THE PRESENT INVESTIGATION

Thiourea (TU) and its derivatives are reported[22,73,74,81] to be effective secondary accelerators with TMTD or CBS especially in latex vulcanization systems. Some of the important members of this class include ethylene thiourea, N,N'-dimethyl thiourea, diphenyl thiourea, Sym-di-o-tolylthiourea etc. In the vulcanization of NR latex using TMTD-TU binary system, thiourea is found to enable TMTD to operate at lower vulcanization temperatures.[81] Philpot proposed a nucleophilic reaction mechanism where TMTD was cleaved by the nucleophile produced from thiourea. This was supported by the fact that accelerators like MBTS or CBS when used alone does not give much crosslinking in diene rubbers but when used with thiourea rapid crosslinking follows.[22,87] Based on these facts, investigations were made in our laboratory[88-92] on binary systems containing thiourea derivative as secondary accelerators in the vulcanization of different elastomers. The studies were made using dithiobiuret derivatives of thiourea viz., 1-phenyl-2,4-dithiobiuret (VIII) and 1.5-diphenyl-2,4-dithiobiuret (IX) along with TMTD/CBS as primary accelerators in sulphur vulcanization of natural rubber. Mixes containing thiourea were used as reference mixes. It was assumed that (VIII), being more nucleophilic than (IX), will be more reactive in the rubber vulcanization reaction with accelerators of the thiuram or sulphenamide type. The results obtained were in agreement with the above assumption, indicating a nucleophilic reaction mechanism in these systems under review as suggested by Philpot[81] and Kemperman.[22,87] Compound (VIII) showed the lowest optimum cure time while thiourea which is least nucleophilic of the three showed a maximum value. Compound (IX) showed intermediate values.[88,89] This was true for both TMTD and CBS systems. The above vulcanization systems were further investigated using different cure temperatures and with different fillers. The study was extended to NR latex and synthetic rubbers also. The results obtained in synthetic rubbers show a different trend and the cure characteristic do not follow the same pattern as in natural rubber. It is evident that in a synthetic rubber like SBR either a free radical mechanism



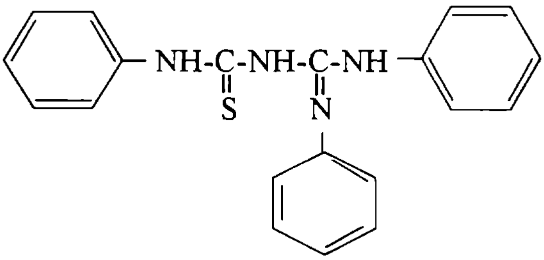
VIII



IX

or a mixed polar/free radical mechanism of vulcanization operates in different mixes considered.[88]

In view of the fact that dithiobiuret drivatives of thiourea can act as very effective secondary accelerators in sulphur vulcanization of natural and synthetic rubbers, we selected an amidinothiourea derivative, viz., I-phenyl-3-(N,N'-diphenylamidino)thiourea (X) as a secondary accelerator. One of the aims was to get further information with regard the theory of nucleophilic reaction mechanism in such binary systems.



X

The accelerator activity of (X) was compared with thiourea and diphenyl guanidine. The fact that (X) can condense with isothiocyanate even in the absence of alkali, unlike thiourea, shows its greater nucleophilic reactivity.[93] Also, the guanidinyl group of the amidinothiourea will facilitate the polarization of C=S bond favouring a nucleophilic reaction.

1-Phenyl-3-(N,N'-diphenylamidino)thiourea (ATU) used in the present study was prepared according to Kurzer and Sanderson.[94] First we tried ATU in binary systems containing TMTD or MBTS in sulphur vulcanization of NR using standard compounding recipes and compared it with mixes containing TU/DPG as secondary accelerators. We made detailed investigations of these mixes with special reference to cure characteristics, physical properties and network structure. The cure characteristics studied were, optimum cure time, cure rate index, scorch time etc. Various tensile properties of the vulcanizates were also investigated. Network structure of the vulcanizates were estimated by calculating the crosslink density using swelling studies. The effect of fillers on these systems were also studied. For this, mixes were prepared with different fillers such as carbon black, precipitated silica and china clay. The cure characteristics and mechanical properties of these binary systems were also estimated. In both gum and filled vulcanizates the ageing behaviour also was investigated.

Based on the facts and findings of the above investigations, we thought it would be worthwhile to study the effect of binary systems containing ATU in NR latex also. The vulcanization of latex is different from that of dry rubber. It occurs in colloidal phase in a heterogeneous state. The ingredients are added as emulsion or dispersion. The use of accelerators in latex also is basically different from their use in dry rubber.[95] Ultra accelerators are frequently employed in latex mixtures since there is no danger of scorching. Philpot[81] studied several accelerator combinations such as TMTD-TU, MBTS-TU, CBS-TU etc. in latex vulcanization. In the present study we compared TMTD-ATU binary systems with TMTD-TU binary systems.

Tensile properties of the vulcanizates were determined after curing the vulcanizates in air oven at a fixed temperature, with different cure times. Ageing studies were also made. In order to correlate the tensile properties with network structure, crosslink densities of the vulcanizates were estimated using swelling studies. Filled vulcanizates were also prepared and their properties investigated.

Based on the fact that ATU gave encouraging results in these NR vulcanization systems and that the mechanism of vulcanization depend also on the nature of the elastomer used, we extended our study to a synthetic rubber of the diene type. We carried out the study with styrene butadiene rubber (SBR 1502) with 1-Phenyl-3-(N,N'-diphenylamidino)thiourea as secondary accelerator. Mixes containing DPG/TU as secondary accelerator were used as control mixes. Here also we investigated the cure characteristics, physical properties and network structures of the various binary systems containing amidinothiourea as secondary accelerator and compared them with those of the reference mixes. Ageing properties were also investigated. Different fillers such as carbon black, precipitated silica and china clay were used in the second part of the study.

Chapterwise division of the above study is as given below

Chapter I	Gives a general introduction on rubber vulcanization and use of different accelerators
Chapter II	Explains the various experimental procedures adopted

		in the present study.
Chapter III		
	Part I	Investigates the effect of amidinothiourea as secondary accelerator in sulphur vulcanization of NR gum compounds.
	Part II	Studies the effect of amidinothiourea in NR filled systems.
Chapter IV		Studies the effect of amidinothiourea in NR latex systems.
Chapter V		
	Part I	Studies on the effect of amidinothiourea in sulphur vulcanization of a typical synthetic rubber viz., SBR (1502) in gum vulcanizates.
	Part II	Studies the effect of amidinothiourea in SBR filled vulcanizates.
Chapter VI		Overall summary and conclusions of the present study.

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CHAPTER II

EXPERIMENTAL TECHNIQUES

This chapter provides a detailed description of the experimental procedures adopted and the materials used in the present study.

2.1 ELASTOMERS

2.1.1 Natural Rubber (NR)

Natural rubber used in the present study was solid block rubber conforming to ISNR - 5 grade of Mooney viscosity (M_L 1+4, 100°C) equal to 85, obtained from Rubber Research Institute of India, Kottayam. In a particular experiment rubber from the same lot has been used. This is because, the molecular weight, molecular distribution and non rubber constituent of natural rubber are known to be affected by clonal variation, season, use of yield stimulants and method of preparation.[1,2] Specifications of the ISNR-5 grade rubber used are 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_0, min.	30.00

Plasticity retention index (PRI) Min.	60.00

2.1.2 Natural Rubber Latex

High ammonia type 60 per cent centrifuged natural rubber latex conforming to the specifications of the Bureau of Indian Standards, BIS 5430-1981 was used in this study. It was obtained from M/s. Harrisons Malayalam Ltd., Cochin. The properties of the latex used are given below:

Dry rubber content, % by mass	60.04
Total solid content, % by mass	61.05
Coagulam content, % by mass	0.0053
Sludge content, % by mass	0.0042
Alkalinity as ammonia, % by mass	0.7300
KOH number	0.4960
Copper	Traces
Manganese	Traces

2.1.3 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 52.0. The specifications are given below:

Volatile matter, % by mass	0.23
Ash, % by mass	0.24
Organic acid, %	5.53
Soap	Traces
Bound styrene	24.30

2.2 OTHER INGREDIENTS

2.2.1 Zinc Oxide (activator)

Zinc oxide supplied by M/S. Meta Zinc Ltd., Bombay, had the following specifications:

Specific gravity (g/cm^3)	5.5
Zinc oxide content, % by mass	98.0
Acidity (%)	0.4
Loss on heating (2 hrs at 100°C, %)	0.5

2.2.2 Stearic acid (co-activator)

Stearic acid was supplied by Godrej Soaps (Pvt.) Ltd., Bombay and the specifications are given below:

Melting point	65°C
Acid number	200
Iodine number	9.05
Specific gravity (g/cm^3)	0.85
Ash (%)	0.10

2.2.3 Tetramethylthiuram disulphide (accelerator)

Tetramethylthiuram disulphide (TMTD) supplied by Polyolefins Industries Ltd., Bombay, had the following specifications:

Melting point	138°C
Specific gravity (g/cm^3)	1.3
Ash, % by mass, max.	0.5
Moisture, % by mass, max.	1.0

2.2.4 Mercaptobenzthiazil disulphide (accelerator)

Bayer Chemicals, Bombay, supplied mercaptobenzthiazil disulphide (MBTS) used in the present study. It had the following specifications:

Specific gravity (g/cm^3)	1.51
Melting point	165°C

2.2.5 Zinc diethyl dithiocarbamate (accelerator)

Zinc diethyl dithiocarbamate (ZDC) used in the present study was obtained from ICI India Ltd., Calcutta, the specifications of which are given below:

Specific gravity (g/cm^3)	1.47
Melting point	178°C

2.2.6 Diphenyl guanidine (accelerator)

Diphenyl guanidine (DPG) was supplied by ICI India Ltd., Calcutta, and had the following specifications:

Specific gravity (g/cm^3)	1.15
Melting point	144°C

2.2.7 Thiourea (accelerator)

Thiourea (TU) used in the present study was supplied by M/s. Sisco Research Laboratories, Bombay. Its specifications are:

Purity, % by mass	99.5
Sulphated ash, % by mass, max.	0.1 %

2.2.8 Sulphur (crosslinking agent)

M/s. Standard Chemicals Co. Pvt. Ltd., Madras, supplied sulphur used in the present study. The specifications are:

Specific gravity (g/cm^3)	2.05
Ash %	0.10
Solubility in CS_2	98%

2.2.9 Process Oils

(a) Aromatic oil

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

Specific gravity (g/cm^3)	0.98
Aniline point (°C)	43.00
Ash content, % by mass	0.01
Viscosity gravity constant	0.96

(b) Naphthenic oil

Naphthenic oil supplied by M/s. Hindustan Petroleum Corporation Ltd., Bombay had the following specifications:

Colour	light
Pour point	20
Aniline point	78
Viscosity gravity constant	0.87
Aromaticity as %	20

2.2.10 Fillers

(a) High Abrasion Furnace Black (N 330) used in the present 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 (per hour at 25°C),	max.2.5%

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

pH (5% aqueous solution)	6.30
Specific gravity (g/cm^3)	2.03
SiO_2 hydrate on dried sample, min.	90%
Loss on heating (105°C, 2 hrs)	5.5%

(c) China clay used was hard clay (rubber grade) supplied by English Indian Clays Ltd., Thiruvananthapuram. It had the following specifications:

Particle size	0.5 microns
Specific gravity (g/cm^3)	2.6
pH	7.0

2.2.11 Dispersol F

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., Calcutta.

2.2.12 Potassium oleate

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.

2.2.13 Other reagents used

Other reagents such as toluene used for swelling studies, phenylisothiocyanate, N,N'-diphenyl guanidine, sodium hydroxide, acetic acid, benzene etc. were of analar grade.

2.3 EXPERIMENTAL METHODS

2.3.1 Synthesis of 1-phenyl-3-(N,N'-diphenyl amidino)thiourea

1-Phenyl 3-(N,N'-diphenyl amidino)thiourea was synthesized according to Kurzer and Sanderson[3]. A solution of N,N'-diphenyl guanidine (0.01 mol) and phenyl isothiocyanate (0.01 mol) in benzene was refluxed for two hours. The reaction mixture was then concentrated under reduced pressure to 10-15 ml. Petroleum ether (60-80°C) was added until the solution became cloudy. After 12-14 hrs the product that crystallized out was collected and recrystallized from acetone-ethanol mixture (melting point 163°C).

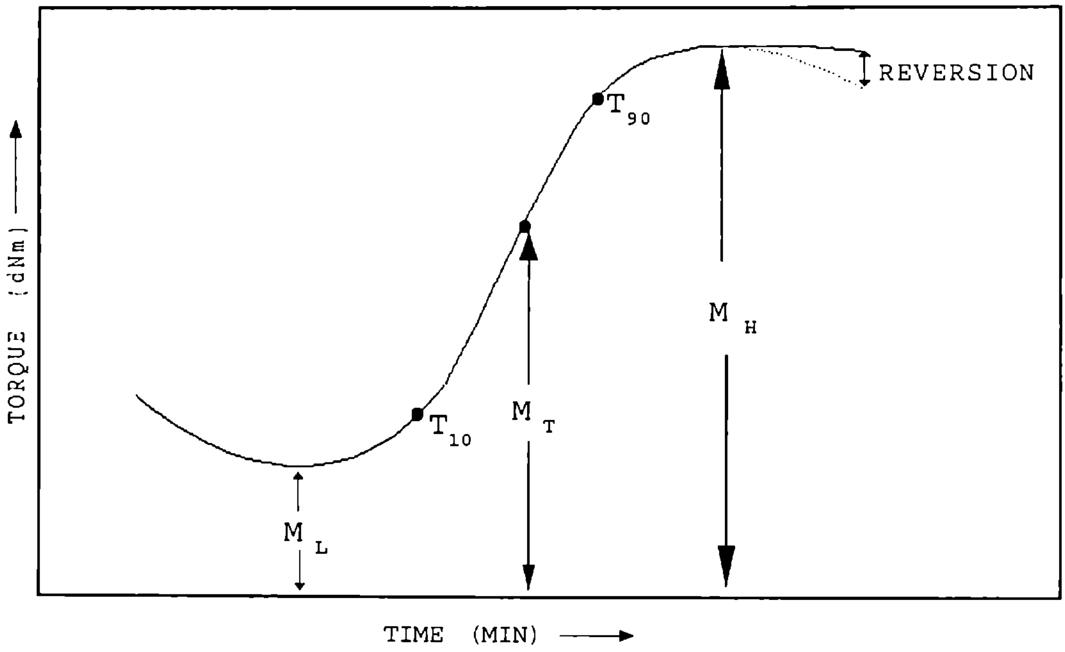
2.3.2 Compounding

Mixes were prepared on a laboratory size two roll mixing mill (15x33 cm) as per ASTM designation D 3182-89. The mixing was carried out at a friction ratio of 1:1.25 for natural rubber and 1:1.1 for styrene butadiene 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 became 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, homogenization 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 6 mm and the stock was passed through the rolls four times folding it back on itself each time.

2.3.3 Determination of cure characteristics of rubber compounds

Goettfert elastograph, model 67.85, was used for the determination of the cure characteristics of the mixes. It uses two directly heated, opposed biconical dies that are designed to achieve a constant shear gradient over the entire sample chamber. The specimen is kept in the lower die which is oscillated through a small deformation angle (±0.2°) at a frequency of 50 oscillations per minute. The torque transducer on the upper die senses the force being transmitted through rubber. A typical cure curve is shown in the following figure.



i) Minimum torque, M_L

Torque obtained by mix after homogenizing at the test temperature, the onset of cure.

ii) Maximum torque, M_H

Maximum 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 taken for two unit rise (0.02 Nm) above minimum torque (i.e. about 10% vulcanization)

vi) Induction time, T_5

It is the time taken for one unit rise above minimum torque (about 5% vulcanization).

vii) Cure rate index

It is calculated as: $100/(T_{90}-T_{10})$ where T_{90} and T_{10} respectively are the time corresponding to optimum cure and scorch respectively.

The elastograph microprocessor evaluates the vulcanization curve and prints out the data after each measurement.

2.3.4 Moulding of test specimen

The test specimens for determining the physical properties were prepared in standard moulds by compression moulding on an electrically heated press having 30x30 cm platens at a pressure of 140 $Kg\,cm^{-2}$ on the mould. The rubber compounds were vulcanized upto their respective optimum cure times at 150°C. Mouldings were cooled quickly in water at the end of the curing cycle and stored in a cool and dark place for 24 hrs and were used for subsequent physical tests. For samples having thickness more than 6 mm (compression set, abrasion resistance etc.) additional curing times based on the sample thickness was given to obtain satisfactory mouldings.

2.4 PHYSICAL TEST METHODS

For each property studied, at least three specimens per sample were tested and the mean values are reported.

2.4.1 Tensile properties: Modulus, tensile strength and elongation at break

The tensile properties of the vulcanizates were determined on a 'Zwick' Universal testing machine, model 1445, using a crosshead speed of 500 mm min^{-1} 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 guage. The sample was held tight by two grips, the uppergrip being fixed. The tensile strength, elongation at break and modulus were evaluated and printed out after each measurement by the microprocessor.

2.4.2 Tear Resistance

Angular test specimens were used to measure the tear resistance on a Zwick universal testing machine model 1445, according to ASTM D 624-86. The samples were cut from the moulded sheets parallel to the mill grain direction. The speed of extension was 500 mm min^{-1} and the test temperature was 28±2°C.

2.4.3 Hardness

The hardness (shore A) of the moulded sample was tested using Zwick 3114 hardness tester in accordance with ASTM D 2240-86. The tests were carried out on mechanically unstressed sample of 12 mm diameter and minimum 6 mm thickness. A load of 12.5 N was applied and the readings were taken after 10 seconds of identation after firm contact had been established with the specimen.

2.4.4 Compression Set

Samples (6.25 mm thick and 18 mm diameter) in duplicate, compressed to constant deflection (25 %) were kept for 22 hrs in 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 using the following expression:

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

where, t_0 = initial thickness of the specimen, t_1 = final thickness of the specimen, t_s = the thickness of the spacer bar. The procedure adopted was in accordance with ASTM D 395-86 (method B).

2.4.5 Abrasion resistance

The abrasion resistance of the samples were tested using a DIN abrader based on DIN 53516. Cylindrical samples having diameter 15 mm and length 20 mm was kept on a rotating sample holder and 10N load was applied. Initially a pre-run was given for the sample and its weight was taken. The sample is then given a complete run and the final weight noted. The difference in weight is the abrasion loss. It is expressed as the volume of the test piece getting abraded by its travel through 42 m on a standard abradant surface. The abrasion loss was calculated as follows:

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

where V = abrasion loss, Δm = mass loss, ρ = density of the sample.

2.4.6 Heat build-up

The heat build-up was measured using the Goodrich flexometer conforming to ASTM D 623-78 (Method A). Cylindrical samples of height 25 mm and 19 mm diameter were used to carry out the test. The oven temperature was kept constant at 50°C. The stroke was adjusted to 4.45 mm and the load to 10.9 Kg. The sample was preconditioned to the oven temperature for 20 minutes. The heat development at the base of the sample was sensed by a thermocouple and relayed to a digital temperature indicator. The temperature rise ($\Delta T^{\circ}C$) at the end of 20 minutes was taken as the heat build-up.

2.4.7 Rebound resilience

Dunlop Tripsometer (BS 903, part I A8) was used to measure rebound resilience. The sample was held in position by suction. It was conditioned by striking with the identor six times. The temperature of the specimen holder and sample was kept constant at 35°C. Rebound resilience was calculated as follows:

$$\text{Rebound resilience (\%)} = \frac{1-\cos\theta_2}{1-\cos\theta_1} \times 100$$

where θ_1 and θ_2 are the initial and rebound angles respectively. θ_1 was 45° in all tests.

2.4.8 Density

The density of the samples were measured according to ISO 2781 (method A). Samples weighing about 2.5 g with smooth surface were used. The test piece is weighed in air and then in water. For specimens which were less dense than water a sinker was used. The weight of the sinker in water was also measured. Density of the sample were calculated as:

$$\text{Density} = \frac{\text{weight of sample in air}}{\text{loss of weight in water}} \times \text{density of water}$$

Density of water is taken as 1g $cm^{-3.}$

2.4.9 Ageing Studies

Ageing studies were carried out in air oven as per ASTM D 573-88. Dumbbell samples were punched out from the vulcanized sheets and kept in the air oven at predetermined temperatures for specified periods. Physical properties like tensile strength, elongation at break, modulus etc. were measured before and after ageing. The percentage retention of these properties was evaluated for assessing the effect of ageing.

2.5 CHEMICAL TEST METHODS

2.5.1 Determination of the concentration of crosslinks of the vulcanizates

The chemical crosslink density of the vulcanizates was evaluated as follows. Samples of approximately 10 mm diameter and 2 mm thickness and 0.2 g weight were punched out from the central portion of the vulcanizates and allowed to swell in toluene for 24 hrs. The swollen samples were taken out and weighed. The solvent was removed in vacuum and the samples weighed again. The volume fraction of rubber, V_r, in the swollen network was then calculated by the following equation.[4,5]

$$V_r = \frac{(D-FT)\,\rho_r^{-1}}{(D-FT)\,\rho_r^{-1} + A_o\rho_S^{-1}}$$

where,

T = the weight of the test specimen

D = the weight of the deswollen test specimen

F = the weight fraction of insoluble components

A_o = the weight of the absorbed solvent corrected for the swelling increment

ρ_r = density of the test specimen

ρ_s = density of the solvent.

Knowing the value of V_r, the total chemical crosslink density $1/2M_c$ was calculated using Flory-Rehner equation[6,7].

$$-[\ln(1-V_r)+V_r+\chi V_r^2] = \frac{\rho_r V_s (Vr)^{1/3}}{M_c}$$

where,

V_s = molar volume of solvent

χ = the parameter characteristic of the interaction between rubber and solvent.

M_c = the number average molecular weight of the rubber chains between crosslinks.

The values of the parameter χ taken for calculation were the following[8].

For NR-toluene, χ = 0.42

SBR-toluene, χ = 0.32

Although natural rubber gum vulcanizates have received much attention, less details are available on network structure of filled vulcanizates. This is because of the uncertainities introduced by the filler-rubber interactions. The volume fraction of rubber (V_r) is calculated assuming that the filler does not swell. It is then converted to V_{ro} (the value V_r would have had in the absence of filler) according to Cunneen and Russel[9]:

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

Here a and b are constants characteristic of the system and z is the weight fraction of the filler in the vulcanizate. The values for a and b for HAF black filled systems are; a = 0.56 and b = 0.44. The corresponding values for silica and clay filled systems are[10]:

Silica system a = 1.41, b = -0.41

Clay system a = 0.21, b = 0.79

The values of V_{ro} were then substituted in the Flory-Rehner[6,7] equation in place of V_r to obtain the crosslink density $1/2M_c$.

2.6 COMPOUNDING OF LATEX

2.6.1 Preparation of dispersions

The compounding ingredients are added to latice as aqueous solution, dispersion or emulsion according as they are water soluble solid, water insoluble solids or water-immiscible liquids. Aqueous dispersions are made by grinding action and the materials are made to disperse in water. Dispersing agents are used to prevent the dispersed particles from reaggregating. The quantity of the dispersing agent to be used for preparing dispersions depend on the nature of materials to be dispersed. For very fine particle size ingredients like ZnO the quantity of dispersing agent required is about 1% by weight whereas for materials like sulphur 2-2.5% is required. Different types of grinding equipments such as, ball mill, ultrasonic mill and attrition mill, are available for making dispersions.

A ball mill consists of a cylindrical container in which the slurry is placed together with a charge of porcelain 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 the slurry to be pulverized. The efficiency of the ball mill depends on the speed of rotation of jar, size and material of ball, viscosity of slurry, period of ball milling etc.

In the present study the following dispersions were made using a ball mill. Dispersol F was used as the dispersing agent. Thiourea is added to latex as 10% aqueous solution.

a. Zinc oxide dispersion (50%)

Zinc oxide	100.00
Dispersol F	2.00
Water (de-ionised)	98.00
Ball milled for	48 hrs

b. TMTD dispersion (33%)

TMTD	100.00
Dispersol F	2.50
Water (de-ionised)	197.50
Ball milled for	48 hrs

c. Sulphur dispersion (50%)

Sulphur	100.00
Dispersol F	3.00
Water (de-ionised)	97.00
Ball milled for	48 hrs

d. ZDC dispersion (50%)

ZDC	100.00
Dispersol F	2.50
Water (de-ionised)	97.50
Ball milled for	48 hrs

e. ATU dispersion (33%)

ATU	100.00
Dispersol F	2.50
Water (de-ionised)	197.50
Ball milled for	48 hrs

f. China clay dispersion (50%)

China clay	100.00
Dispersol F	2.00
Water (de-ionised)	98.00
Ball milled for	48 hrs

g. Precipitated silica dispersion (25%)

Precipitated silica	100.00
Dispersol F	2.00
Water (de-ionised)	298.00
Ball milled for	48 hrs

h. Precipitated calcium carbonate dispersion (50%)

Precipitated calcium carbonate	100.00
Dispersol F	2.00
Water (de-ionised)	298.00
Ball milled for	48 hrs

2.6.2 De-ammoniation of latex

As HA type concentrated latex was obtained, it was de-ammoniated to 0.3% by stirring in a laboratory type deammoniation tank for 3 hours. The high ammonia content in latex will create problems in its conversion to solid products or in the stability of latex compound in presence of zinc oxide. The total alkalinity of latex as percentage of ammonia was estimated according to ASTM D 1076-88.

2.6.3 Compounding

Mixing of ingredients to natural rubber latex was done in the following order: stabilising agents, sulphur, accelerators, fillers and zinc oxide[11]. Stabilizers were added as solutions followed by the other dispersions or solutions. Mixing was carried out in a glass vessel and stirred for homogenization using a laboratory stirrer at 10-20 rpm. It was occasionally stirred during storage in order to prevent settling of the ingredients.

2.6.4 Preparation of latex film

After completion of mixing the latex compound was matured at ambient temperature for 24 hours. Latex films were then cast in glass cells as described in ASTM D 1076-88. The size of the glass cell was 15x15 cm and about 30-35 ml of the latex compound was poured and distributed so that a film of thickness 1-1.25 mm was obtained upon drying. The glass cells with the latex compound were placed in a levelled table and dried overnight at ambient temperature.

2.6.5 Vulcanization and testing of latex film

The vulcanization of latex film was carried out in a laboratory air oven at 120°C. The time for developing maximum tensile strength was determined by vulcanizing the film at different durations (10 minutes, 20 minutes, 30 minutes, 40 minutes etc.) and determining the tensile strength of the sample in each case. The time taken for getting optimum value of tensile strength was then determined by plotting tensile strength against vulcanization time. The time taken for optimum tensile strength is taken as the optimum cure time.

The tensile properties of the vulcanized latex film were determined both before and after ageing as per ASTM D 412-87 (method A) using a Zwick Universal testing machine. The specimens for ageing were kept in an air oven at 70°C for 7 days. The chemical crosslink density was determined by equilibrium swelling method.

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CHAPTER III

STUDIES ON BINARY SYSTEMS CONTAINING ATU IN SULPHUR VULCANIZATION OF NR

The only important commercial source of natural rubber is the latex from the trees of *Hevea brasiliensis*. Natural rubber latex consists of particles of rubber hydrocarbon and non-rubbers suspended in an aqueous serum phase. The raw rubber contains approximately 94% rubber hydrocarbon, 3% proteins and 3% of other materials including fatty acids and resins[1]. Purified natural rubber hydrocarbon is a long chain polymer made up of cis 1,4-poly isoprenoid units arranged in a highly stereoregular manner. The molecular weight of the polymers ranges from 10^5 to 10^6 and it varies widely[2]. Due to the high structural regularity, natural rubber tends to crystallize on stretching. This strain induced crystallization gives it the unique high tensile strength in gum and non-reinforcing filler vulcanizates. Natural rubber is a preferred polymer in many areas because of its superior building tack, green stock strength, better processing, high resilience and excellent dynamic properties.

The conversion of raw rubber to useful products needs the process of compounding and vulcanization. During vulcanization the long chain rubber molecules become crosslinked by reaction with the vulcanizing agents to form three dimensional structures. The reaction transforms the weak plastic like material to a strong elastic product. The properties of the latter, in particular, the modulus, hardness, elastic properties, resistance to swelling etc. are considerably influenced by the course of vulcanization[3]. The extent of changes in properties is governed by the choice of vulcanization agents added to the rubber to bring about the vulcanization process and also by the vulcanization conditions. Therefore to obtain rubber products with best possible properties it is always necessary to use the most suitable combination of vulcanization agents and vulcanization conditions. The vulcanization of natural rubber may be effected with the aid of sulphur, peroxides, resins, ionizing radiation, metal oxides etc[4]. Sulphur vulcanization of natural rubber forms the subject of numerous publications[3-8]. Natural rubber is usually vulcanized at 140 - 180°C with a combination of sulphur (2-3 phr), one or more accelerators (0.5-1.0 phr), zinc oxide (3-5 phr) and a fatty acid (1-3 phr). The vulcanizates so obtained have the best overall combination of physical properties for many applications but at the same time the ageing properties deteriorate even when antidegradants are present. This deficiency is largely due to the low thermal stability of the network and is characterized by a rapid reversion in properties when the vulcanizate is subjected to overcure.

Vulcanizates with high heat resistance are obtained by using a high ratio of accelerator to sulphur. These systems consist of 0.3-0.8 phr sulphur and 2.5-6.0 phr accelerator[9], which are usually recommended for products in need of improved reversion resistance during vulcanization and for products exposed to higher service temperatures. Conventional sulphur vulcanizing systems continue to find widespread general purpose use for products that do not require sustained heat resistance during manufacture or service. The course of vulcanization, to a large extent, depends on the nature of the accelerators used. Among thiuram accelerators tetramethyl thiuram disulphide (TMTD) is one of the safer and fastest accelerators. Thiurams act as ultra accelerators and impart relatively high modulus, good mechanical and ageing properties of the vulcanizates[10]. Mixes containing TMTD are suitable for vulcanization by all methods, viz., press, steam and hot air curing. Generally thiurams are used as secondary accelerators to raise the rate of vulcanization of mercapto and sulphenamide accelerators. Another class of accelerators most widely used are the thiazole and sulphenamide type. Compared to thiuram accelerators mercapto accelerators give compounds with higher processing safety. Because of their somewhat lower rate of vulcanization the mercapto accelerators are included among semi-ultra accelerators. Of the main accelerators of this class, mercaptobenzthiazole (MBT) and zinc mercaptobenzthiazole (ZMBT) have relatively fast onset of vulcanization and hence lowest processing safety. But mercaptobenz thiazyl disulphide (MBTS) has a delayed onset of vulcanization and hence affords higher processing safety. Compounds containing mercapto accelerators are suitable for all type of vulcanization namely, press, steam and hot air. When mercapto accelerators are combined with thiurams, the onset of vulcanization takes place faster than when they are used alone. In such combinations of a primary and a secondary accelerator a synergistic effect has been obtained. Compounds with mercapto accelerators which are activated by secondary accelerators have little tendency to overcure and give vulcanizates with excellent ageing properties. Thiurams and guanidines are the most frequently used secondary accelerators with mercapto accelerators. Sulphenamide accelerators act slowly in the beginning of the vulcanization process and subsequently become very active. Such vulcanization behaviour is especially desirable in the case of multilayered and complex articles such as automobile tyres.

Thiourea (TU) and its derivatives are known to have advantageous properties especially when they are used in binary systems along with a primary accelerator. They give good synergistic behaviour with thiazole and thiuram accelerators[11]. Thiourea act as effective secondary accelerator with TMTD or CBS, especially in latex vulcanization[12]. In these systems Philpot suggested an ionic mechanism where the S-S bond or S-N bond of the accelerator is cleaved by the nucleophile formed from thiourea. But no conclusive proof has been given. Similar results were also obtained in studies made using dithiobiuret derivatives of thiourea[13]. Considering the above facts, we made an attempt to find the accelerating effect of an amidinothiourea. We selected 1-phenyl-3-(N,N'-diphenyl amidino)thiourea (ATU) for our investigation. In this chapter the behaviour of ATU in both NR gum and filled vulcanizates is described.

PART I

3.1 NR GUM VULCANIZATES

3.1.1 EXPERIMENTAL

We tried ATU as a secondary accelerator along with MBTS and TMTD as primary accelerators in NR gum compounds. The following systems – MBTS-TU, TMTD-TU, MBTS-DPG, TMTD-DPG, MBTS-TMTD, MBTS alone, TMTD alone – were taken as reference formulations. Mix with ATU alone was also investigated.

Tables 3.1 and 3.2 shows the composition of various mixes used. In all these mixes 5 phr of zinc oxide, 2 phr stearic acid and 1.5 phr sulphur were incorporated as activator, co-activator and vulcanizing agent respectively for hundred parts of rubber (phr). An attempt was made to find out the optimum concentration of the amidinothiourea in vulcanization reaction under standard condition. Mixes A_1 , A_2 and A_3 contained ATU ranging from 0.5 to 1.5 phr with 1 phr of MBTS. Mix B_1 contained only MBTS as accelerator. Mixes B_2, B_3 and B_4 contained 1 phr each of TMTD, DPG and TU with 1 phr of MBTS. Mix B_5 is a trial mix prepared with 2 phr of ATU alone as accelerator.

Formulations C_1 , C_2 and C_3 (Table 3.2) contained ATU ranging from 0.5 to 1.5 phr with 1 phr of TMTD. Mixes D_1 , B_2 , D_3 and D_4 are reference mixes. Mix D_1 contained

Table 3.1 Formulation of the mixes containing MBTS

Ingredients	A_1	A_2	A_3	B_1	B_2	B_3	B_4	B_5
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	1	1	2	1	1	1	--
TMTD	--	--	--	--	1	--	--	--
DPG	--	--	--	--	--	1	--	--
Thiourea	--	--	--	--	--	--	1	--
ATU	0.5	1.0	1.5	--	--	--	--	2
Sulphur	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5

Table 3.2 Formulation of the mixes containing TMTD

Ingredients	C_1	C_2	C_3	D_1	B_2	D_3	D_4
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
MBTS	--	--	--		1	--	--
TMTD	1	1	1	2	1	1	1
DPG	--	--	--	--	--	1	--
Thiourea	--	--	--	--	--	--	1
ATU	0.5	1.0	1.5	--	--	--	--
Sulphur	1.5	1.5	1.5	1.5	1.5	1.5	1.5

2 phr of TMTD alone as accelerator. Mixes D_3 and D_4 contained 1 phr each of DPG and TU with 1 phr of TMTD.

The mixes were prepared on a laboratory size two roll mixing mill (15x33 cm) as per ASTM designation D 3182-89 (details are given in chapter II). The cure characteristics of the mixes were determined on a Geottfert elastograph, model 67.85, at 150°C. The compounds were then vulcanized up to the optimum cure time in an electrically heated laboratory type hydraulic press at 150°C at a pressure of 140 Kg cm^{-2}, Dumbbell tensile test specimens were punched out of the test sheets along the mill grain direction. The tensile properties of the vulcanizates were determined on a Zwick Universal Testing Machine model 1445. Heat ageing resistance of the vulcanizates was obtained by ageing the samples for 48 hrs. at 70°C in a laboratory air oven (ASTM D573-88). Angular test specimens were used to measure the tear resistance according to ASTM D 624-86. Compression set, hardness and heat-build up were tested as per ASTM D395-89 (method B), D2240-86 and D623-88 (method A) respectively. Rebound resilience was measured using Dunlop Tripsometer (BS 903, part A8) and abrasion resistance was measured using DIN abrader (DIN 53516). The chemical crosslink density was estimated by swelling the sample in toluene as described in detail in chapter II.

3.1.2 RESULTS AND DISCUSSION

3.1.2.1 Cure Characteristics

The cure characteristics of various mixes cured at 150°C were evaluated using Geottfert elastograph and are given in Tables 3.3 and 3.4. The cure curves are shown in Fig. 3.1 and 3.2. The various experimental observartions of the present investigation indicate clearly the acceleration effect of the amidinothiourea in this vulcanization system of natural rubber. With respect to the cure characteristic, (Table 3.3 and Fig. 3.1) vulcanization system containing MBTS and ATU are found to be better than the reference systems. Compared to Mix B_1 , containing MBTS alone as accelerator, the addition of 1.5 phr of ATU (mix A_3) reduces the optimum cure time to almost one third. This points to a very effective accelerator activity of the amidinothiourea. However, the very low scorch time of this mix is likely to cause processing problems. The rate of cure for mix A_3 is much higher than that of B_1 , which is also evident from the low induction time for mix A_3. A comparative study of the equivalent mixture of MBTS - ATU (mix A_2) with MBTS-TMTD (mix B_2), MBTS-DPG (mix B_3), and MBTS-TU (mix B_4) reveals that the least optimum cure time is shown by the MBTS-ATU system (Fig. 3.3). This indicate that ATU behaves as a better secondary accelerator compared to TMTD, DPG and TU as far as the optimum cure time is considered. One disadvantage of the MBTS-ATU systems is their low scorch times at high loadings. The scorch time decreases considerably with the increase

Table 3.3 Cure characteristics of the mixes with MBTS (cured at 150°C)

Mix No.	A_1	A_2	A_3	B_1	B_2	B_3	B_4
Min. torque (dNm)	0.70	0.50	0.50	0.50	0.60	0.40	1.00
Max. torque (dNm)	13.2	16.4	17.7	12.9	24.0	17.1	18.9
Optimum cure time, t_{90} (min.)	6.00	4.00	3.60	11.4	7.40	4.60	5.00
Scorch time^a, t_{10} (min.)	2.60	1.40	1.20	6.00	3.00	2.20	1.60
Induction time, t_5 (min.)	2.10	1.00	0.90	5.70	2.10	1.80	1.40
Cure-rate index	24.91	38.46	41.67	18.52	22.73	41.67	29.41

a. Elastograph scorch time (t_{10})

Table 3.4 Cure characteristics of the mixes with TMTD (cured at 150°C)

Mix No.	C_1	C_2	C_3	D_1	B_2	D_3	D_4
Min. torque (dNm)	0.500	0.80	0.70	0.70	0.60	0.40	0.70
Max. torque (dNm)	20.40	22.2	23.2	22.6	24.0	17.8	25.0
Optimum cure time, t_{90} (min.)	2.600	1.80	1.60	4.40	7.40	2.60	1.80
Scorch time^a, t_{10} (min.)	2.000	1.20	1.00	2.40	3.00	1.80	1.20
Induction time, t_5 (min.)	1.300	0.70	0.50	1.80	2.10	1.50	0.90
Cure-rate index	166.66	166.66	166.66	50.0	22.72	55.55	166.66

a. Elastograph scorch time (t_{10})

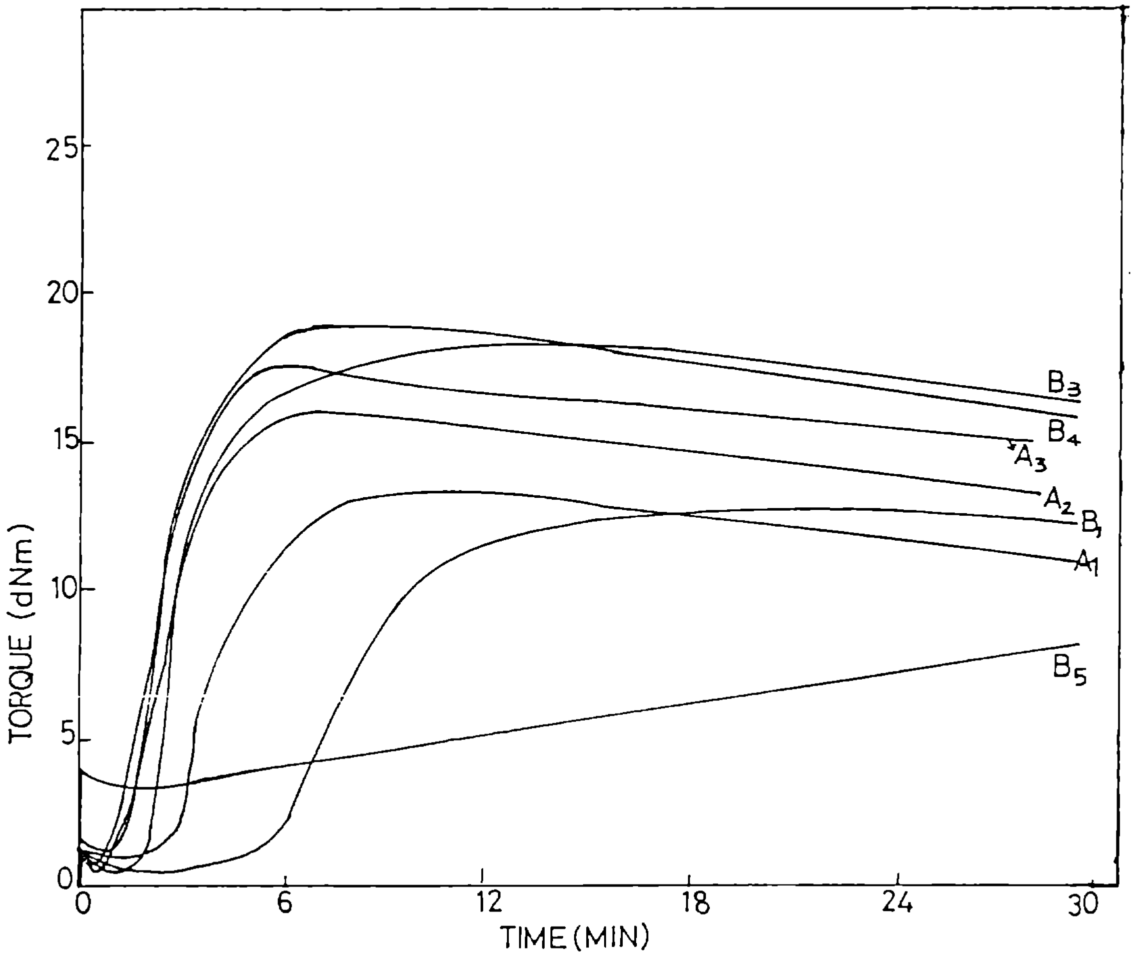


Fig. 3.1 Cure curves of mixes with MBTS

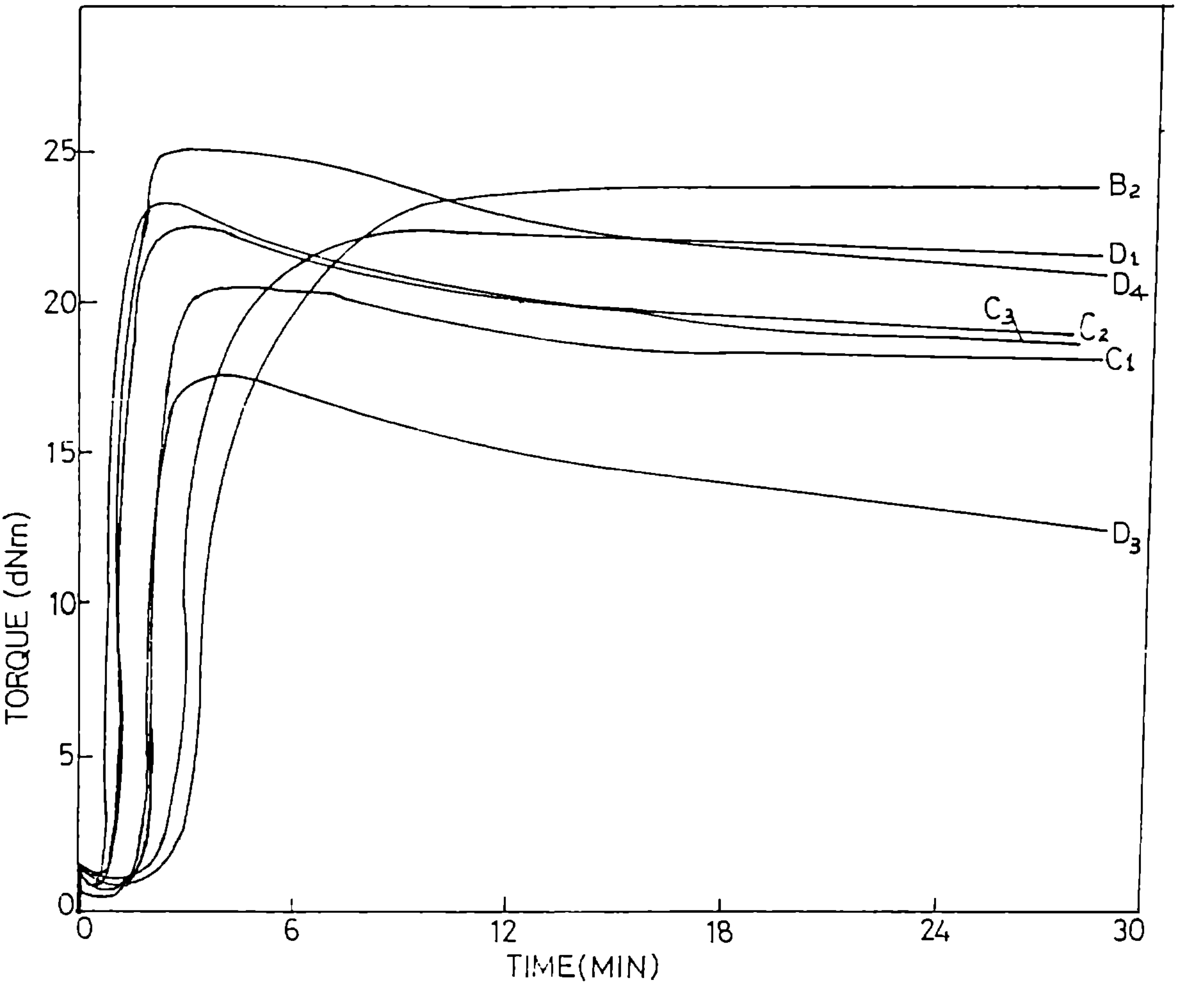


Fig. 3.2 Cure curves of mixes with TMTD

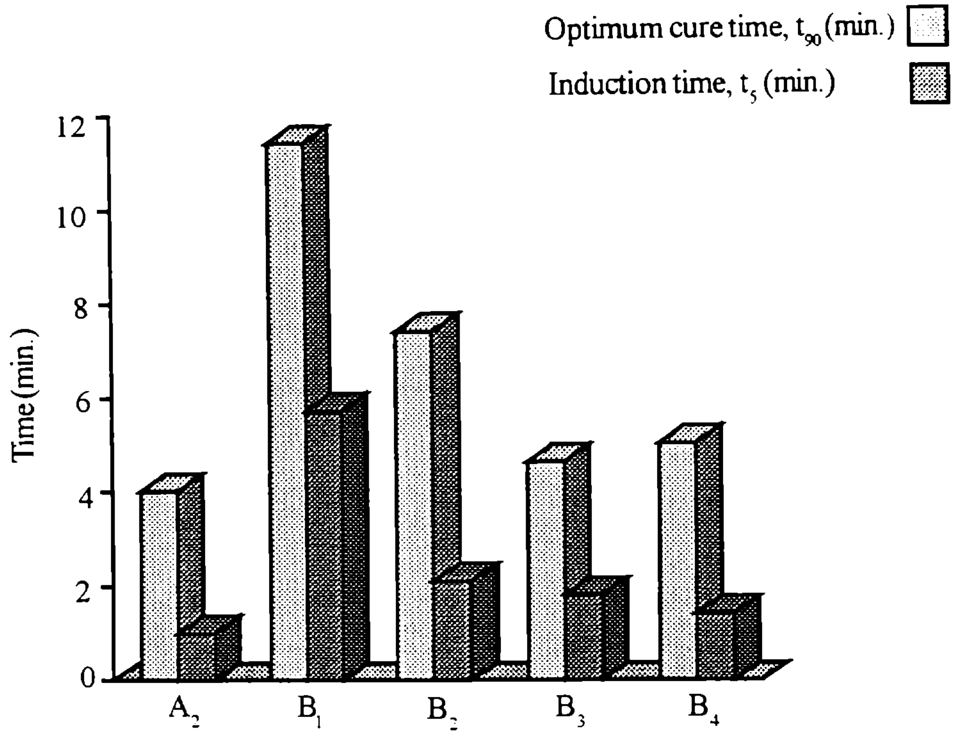


Fig. 3.3 A comparative study of optimum cure time and induction time of mixes with MBTS

in the amount of ATU. Mix A_3, containing 1.5 phr of ATU, is too scorchy. On the otherhand mix A_1, containing 0.5 phr ATU gives a practical system with reasonable optimum cure time and sufficient scorch safety. Mix B_5 contained 2 phr of ATU alone as accelerator. The curing of this mix was very slow as indicated by the cure curve (Fig. 3.1). Thus ATU alone is unable to function as an accelerator and hence the mix was not studied further.

The cure behaviour of TMTD-ATU systems was also found to be better compared to the corresponding reference mixes (Table 3.4 and Fig. 3.2). The mix D_1 contained TMTD alone as accelerator and compared to mix C_3 , containing 1.5 phr ATU, the latter shows an optimum cure time of almost one third of that of the former. This reveals that ATU has a very effective accelerator activity in TMTD-ATU systems also. But at the same time mix C_3 shows very low scorch time which may cause processing problems. When the amount of ATU is reduced to 1 phr (mix C_2) cure time is found to increase slightly, but the mix remain still scorchy. However when the amount of ATU is reduced to 0.5 phr (mix C_1) there is substantial reduction in cure time (almost half compared to mix D.) with sufficient scorch safety and this can be considered as a practical system with the optimum level of secondary accelerator. Comparing mixtures of TMTD and ATU containing 1 phr each (mix C_2), with MBTS-TMTD (mix B_2), TMTD-DPG (mix D_3) and TMTD-TU (mix D_4) the cure rate is maximum for TMTD-ATU and TMTD-TU mixes (Table 3.4 and Fig.3.4). The maximum torque values are also comparable. Both MBTS - ATU and TMTD-ATU systems show slight reversion tendency compared to the reference mixes as evident from the cure curves (Figs. 3.1 and 3.2). The reversion tendency is less for MBTS- ATU systems than for TMTD-ATU systems. Also, increase in the amount of ATU increases reversion in both systems.

Analysis of the cure characteristics of both MBTS-ATU and TMTD-ATU systems indicate that ATU can function as an effective secondary accelerator. One disadvantage of these mixes is their low

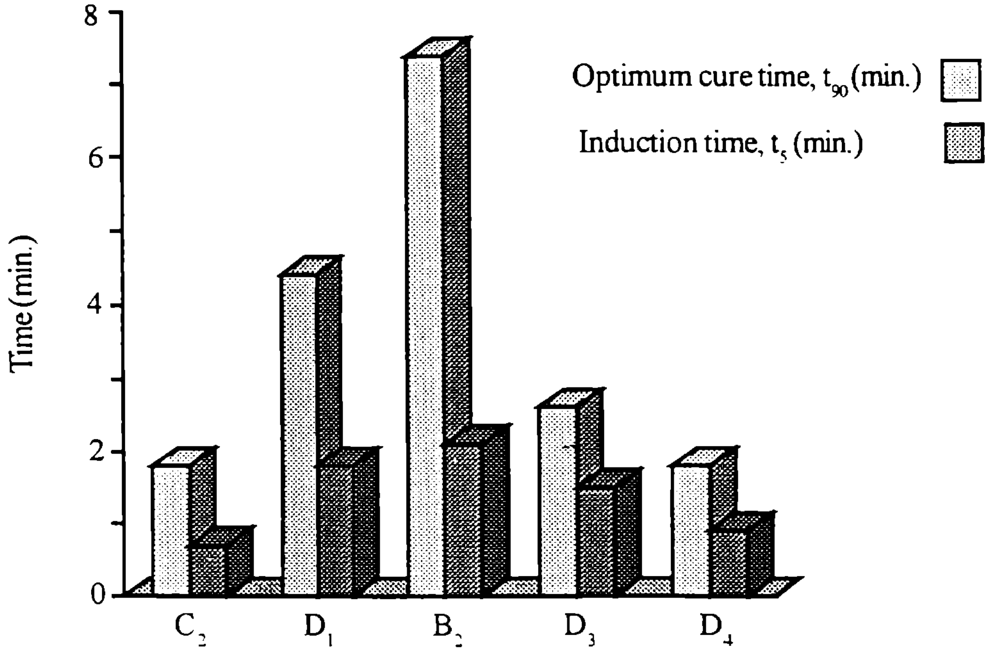
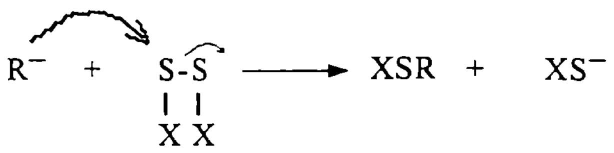


Fig. 3.4 A comparative study of optimum cure time and induction time of mixes containing TMTD

scorch times at high dosages of the secondary accelerator. Manik and Banerjee[14], after investigating various formulations with TMTD, suggested that the TMTD/S/ZnO/stearic acid system in NR vulcanization is predominantly polar. The presence of secondary accelerator like thiourea is found to increase the rate of formation of the thiuram polysulphides required in the ultimate corsslinking reactions[15]. ATU can also be expected to behave in a similar way. The cleavage reaction of the S-S bond can be represented as[14],



$$R^- + \underset{X}{S}-\underset{X}{S} \longrightarrow XSR + XS^-$$

Here the S-S bond undergoes nucleophilic attack by R^-(the nucleophile).

The ease with which the above reaction takes place depend on the S-nucleophilicity of the attacking reagent (R^-)[12]. Thus ATU being more nucleopilic compared to DPG and TU shows a lower induction time (Table 3.4 and Fig. 3.4, mixes C_2, D_3 and D_4) indicating a rapid onset of vulcanization. When TMTD alone is used as the accelerator (mix D_1) the induction time is much higher. Also when the amount of ATU is increased from 0.5 phr to 1.5 phr induction time decreases rapidly. These observations clearly point to a nucleophilic mechanism, as suggested by Philpot[12], in binary systems of NR vulcanization under review. Similar arguments are applicable in MBTS systems also. Shelton and McDonel[16] suggested that in MBTS-S systems the crosslinking is effected through a combination of polar and radical mechanisms. When MBTS alone (mix B_1) is used as the accelerator the cure and induction times are much higher compared to other formulations (Table 3.3 and Fig 3.3). But with ATU (mix A_2) and DPG (mix B_3) a substantial reduction in cure time as well as induction time is observed. Presence of thiourea also reduces cure time, but to a lesser extent. These observations clearly indicate an initial nucleophilic attack by the secondary accelerator in these systems of vulcanization.

3.1.2.2 Tensile Properties

Natural rubber is strain crystallizable and hence it has very good gum strength. The strength of natural rubber can be improved by incorporation of reinforcing fillers. The correct choice of vulcanization system is also important in getting good tensile properties in the rubber vulcanization. ATU is found to improve many of these properties of the vulcanizates in the systems under review. The tensile properties of the various systems investigated are given in Tables 3.5 and 3.6. The effect of the variation of the amount of ATU on tensile strength, 100% modulus and elongation at break, before and after ageing for MBTS-ATU and TMTD-ATU systems are shown graphically in Figs. 3.5-3.7. In order to compare the tensile properties of the vulcanizate containing ATU with that of the reference mixes, both before and after ageing, bar graphs are used. Figs. 3.8-3.10 and Figs. 3.11-3.13 represent the bargraphical representation of the tensile properties for MBTS and TMTD systems respectively.

For the MBTS-ATU system a steady increase in tensile strength and 100% modulus is observed with increasing concentration of ATU from 0.5 phr to 1.5 phr (Figs. 3.5 and 3.6). The percentage retention of these properties is found to be maximum for mix A_1 which has the optimum cure characteristics also. Elongation at break (Fig. 3.7) shows a steady decrease with the increase in concentration of ATU as expected. The bar graphs shown in Fig. 3.8-3.10 give a comparison of the tensile properties of the reference mixes (B_2 , B_3 and B_4) with those of MBTS-ATU systems of equivalent concentration both before and after ageing. The tensile strength of MBTS-ATU system (mix A_2) is found to be slightly less than that of the MBTS-DPG (mix B_3). Also the percentage retention

Table 3.5 Tensile properties of various vulcanizates 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_1	17.78	22.68	127.6	0.66	1.10	166.7	838.27	818.16	97.6
A_2	20.90	21.07	100.8	1.29	1.75	135.7	790.76	724.82	91.7
A_3	24.05	17.84	74.2	1.48	1.79	120.9	793.45	689.28	86.9
B_1	20.96	20.82	99.3	0.74	0.81	109.5	886.95	837.33	94.4
B_2	20.29	15.38	75.8	1.25	1.33	106.4	660.03	531.98	80.6
B_3	24.78	28.53	115.1	0.95	1.17	123.2	775.85	763.03	98.3
B_4	15.95	20.48	128.4	0.66	0.93	140.9	834.00	799.06	95.8

Table 3.6 Tensile properties of various vulcanizates 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 %
C_1	22.88	12.00	52.4	1.92	2.00	104.2	702.10	560.45	79.8
C_2	21.91	13.36	61.0	1.85	1.94	104.9	704.70	602.75	85.5
C_3	22.82	10.91	47.8	1.92	2.00	104.2	704.52	530.68	75.3
D_1	20.23	2.47	12.2	0.78	1.24	159.0	607.01	168.31	27.7
B_2	20.29	15.38	75.8	1.25	1.33	106.4	660.03	531.98	80.6
D_3	23.29	21.16	90.9	1.02	1.16	113.7	749.20	695.70	92.9
D_4	23.39	20.37	87.1	1.00	1.20	120.0	779.36	673.73	86.4

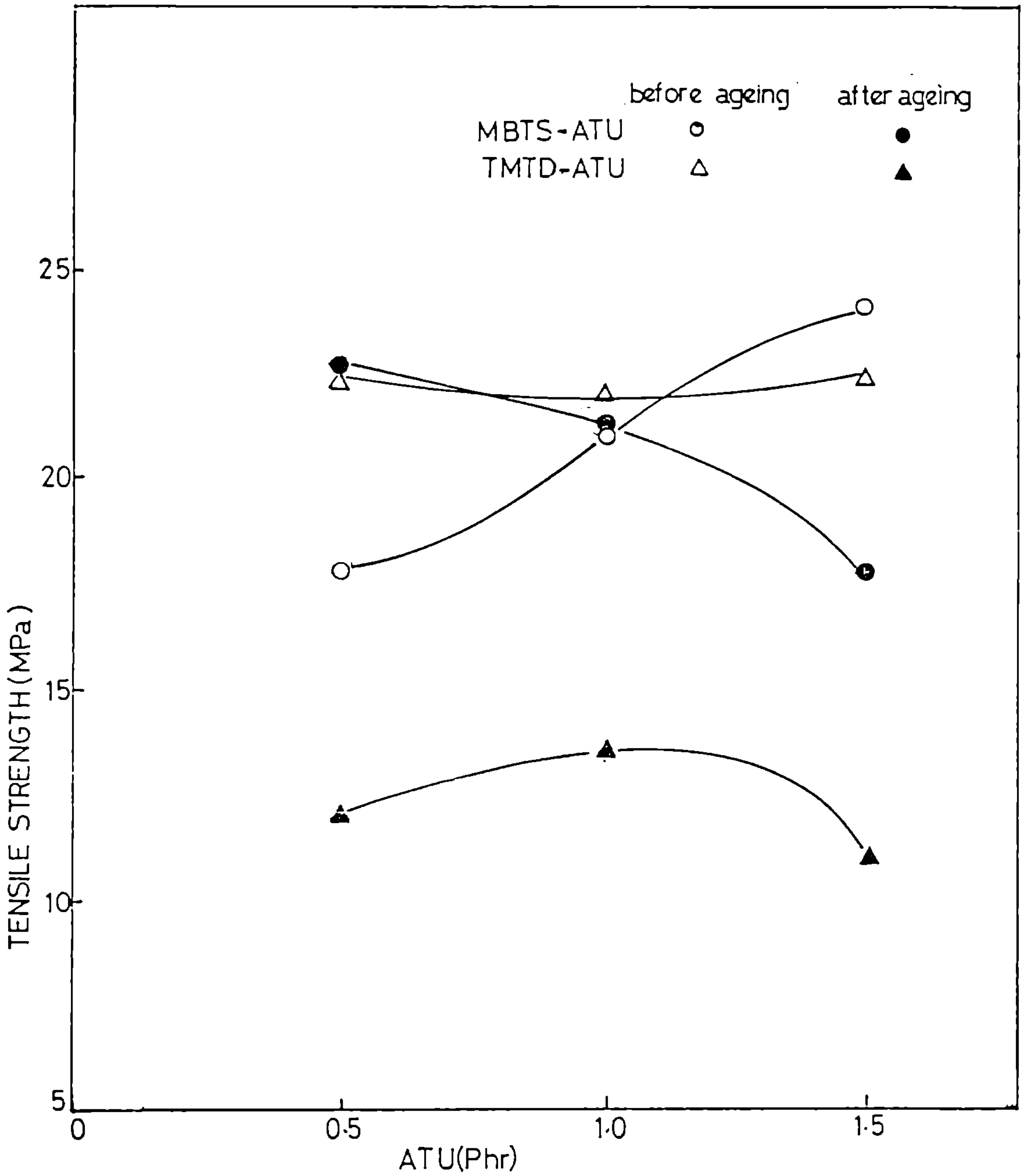


Fig. 3.5 Effect of concentration of ATU on tensile strength of vulcanizates

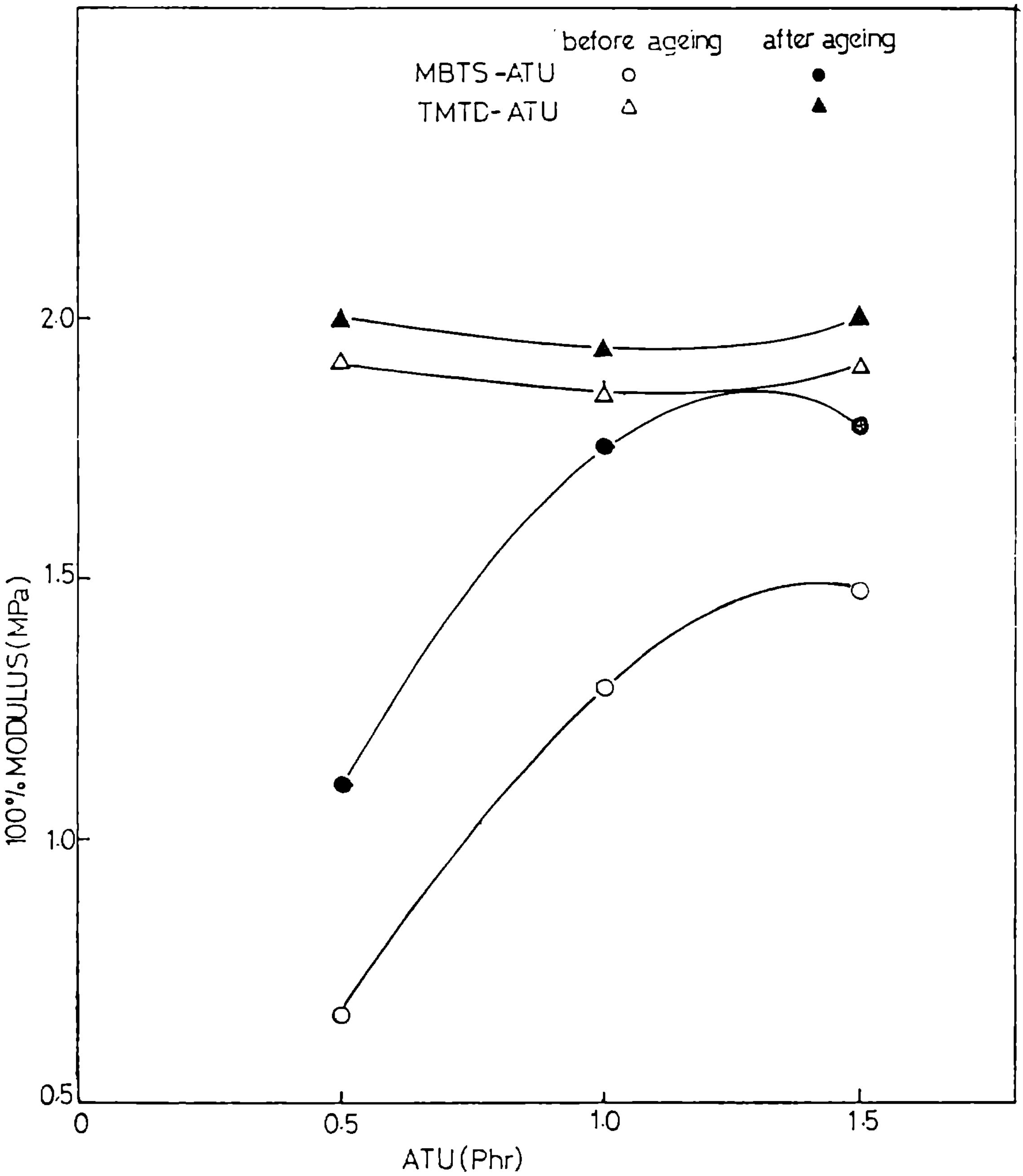


Fig. 3.6 Effect concentration of ATU on modulus (100%) of vulcanizates

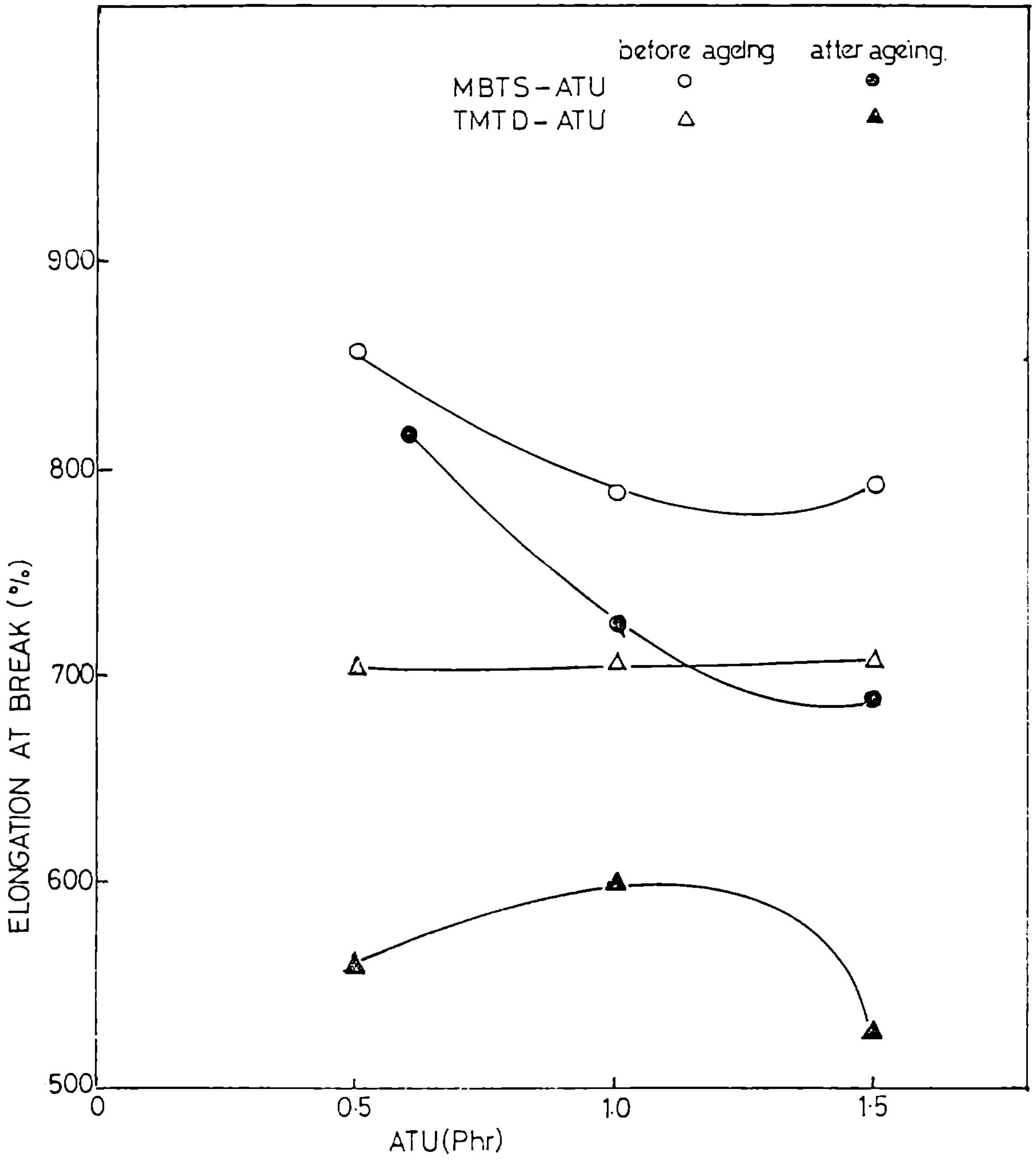


Fig. 3.7 Effect of concentration of ATU on elongation at break of vulcanizates

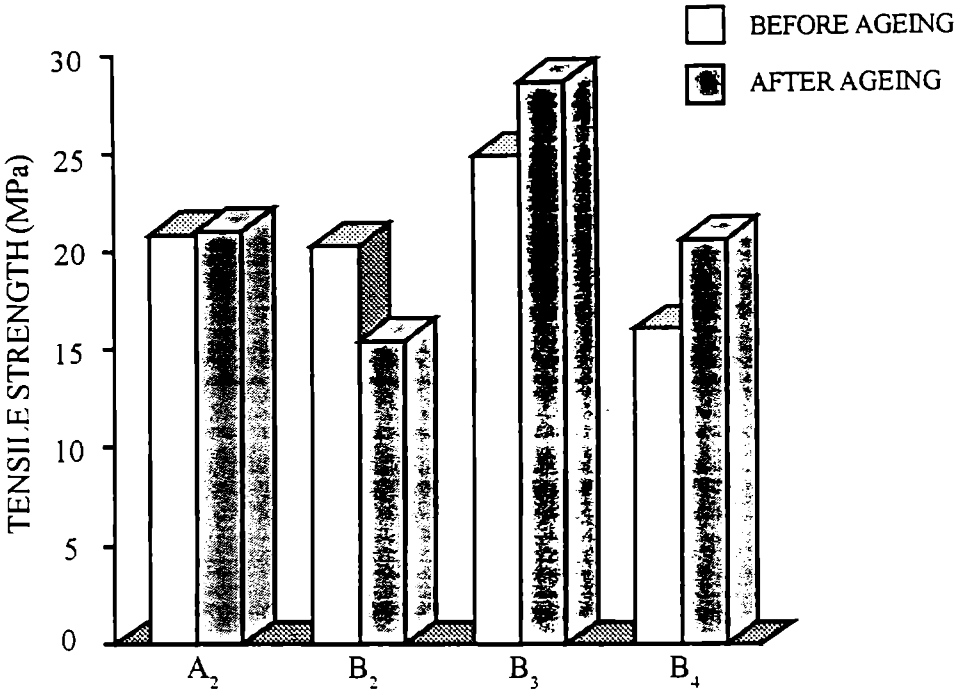


Fig. 3.8 Tensile strength of vulcanizates containing equivalent concentrations of MBTS with ATU, TMTD, DPG and TU

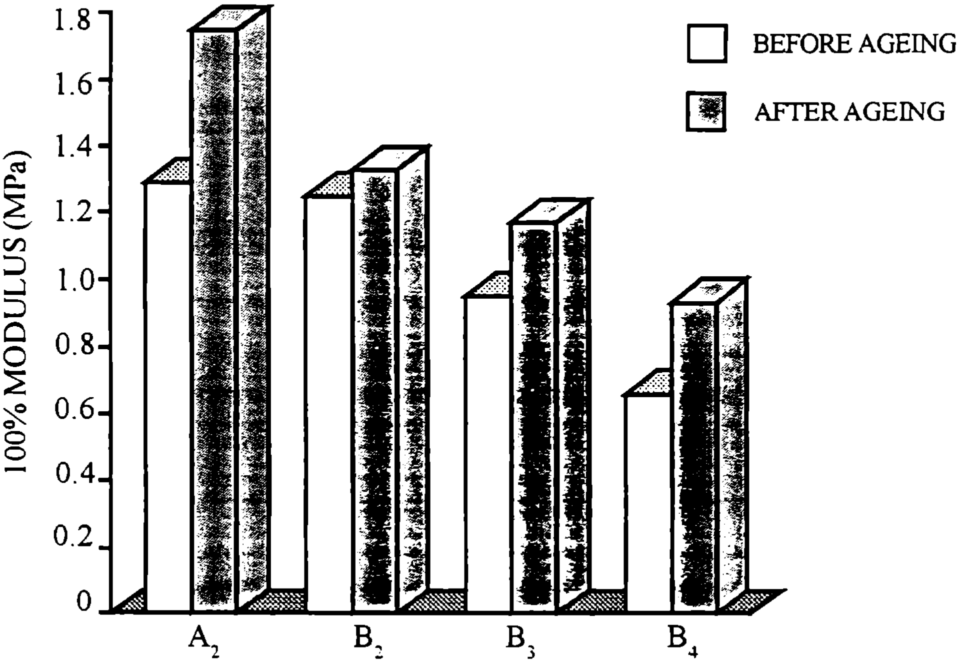


Fig. 3.9 Modulus (100%) of vulcanizates containing equivalent concentrations of MBTS with ATU, TMTD, DPG and TU

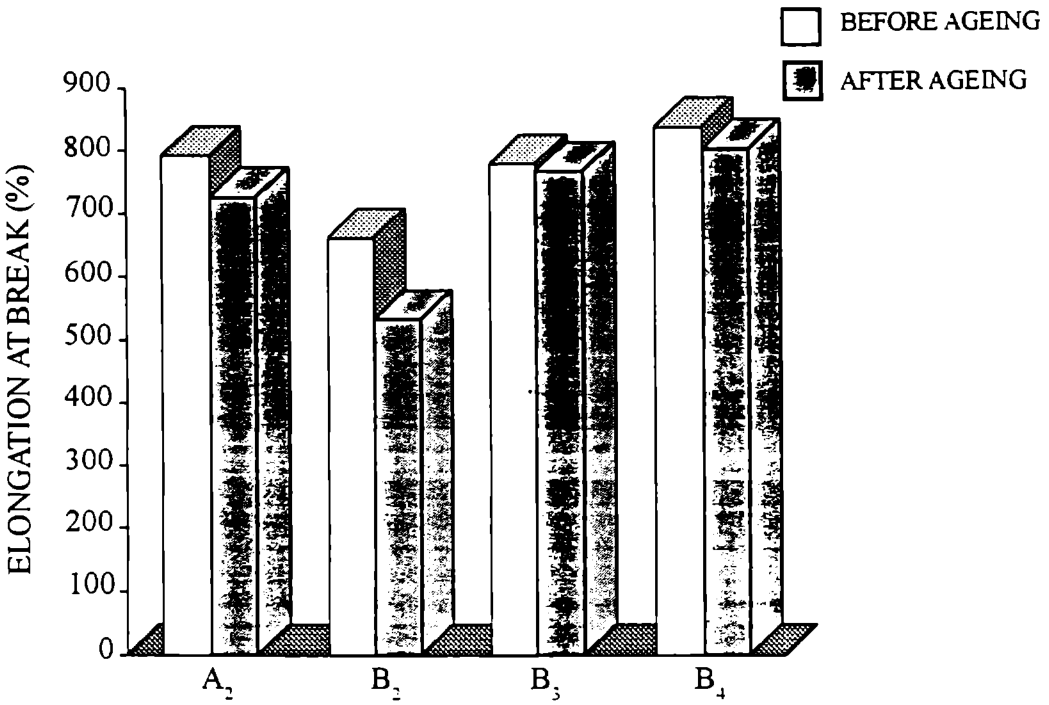


Fig. 3.10 **Elongation at break of vulcanizates containing equivalent** concentrations of MBTS with ATU, TMTD, DPG and TU

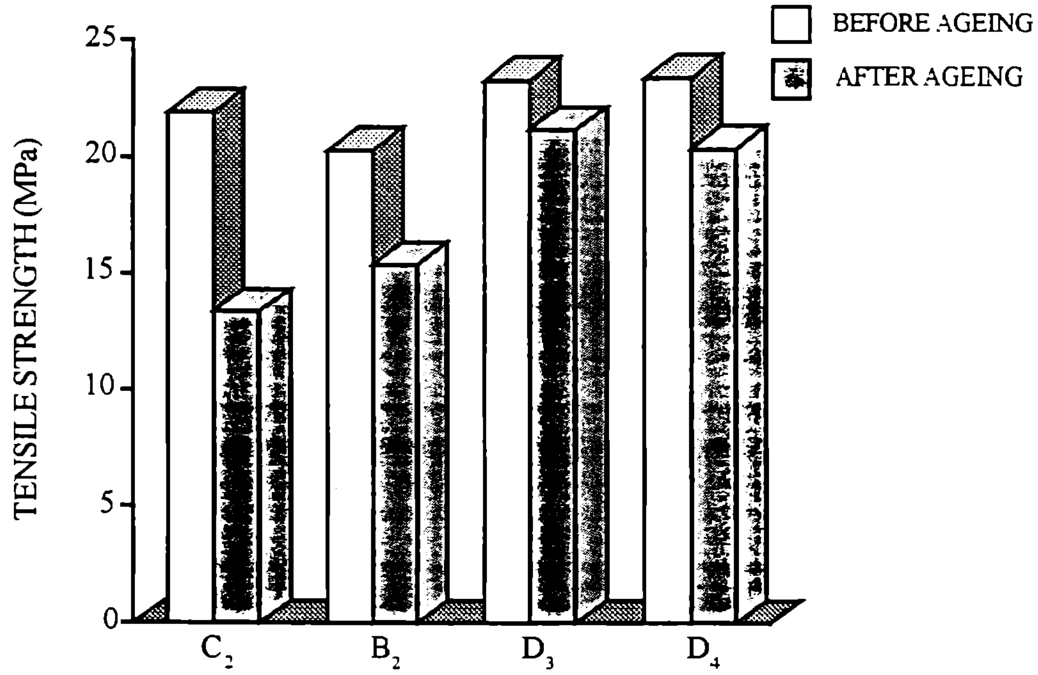


Fig. 3.11 **Tensile strength of vulcanizates containing equivalent concentrations of TMTD with ATU, MBTS, DPG and TU**

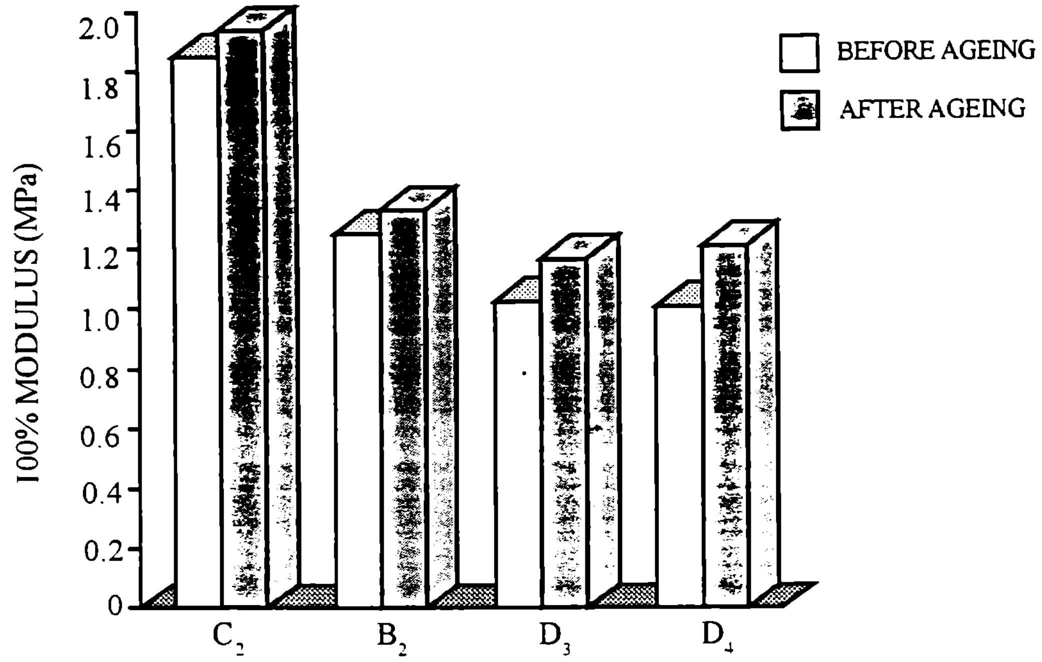


Fig. 3.12 Modulus (100%) of vulcanizates containing equivalent concentrations of TMTD with ATU, MBTS, DPG and TU

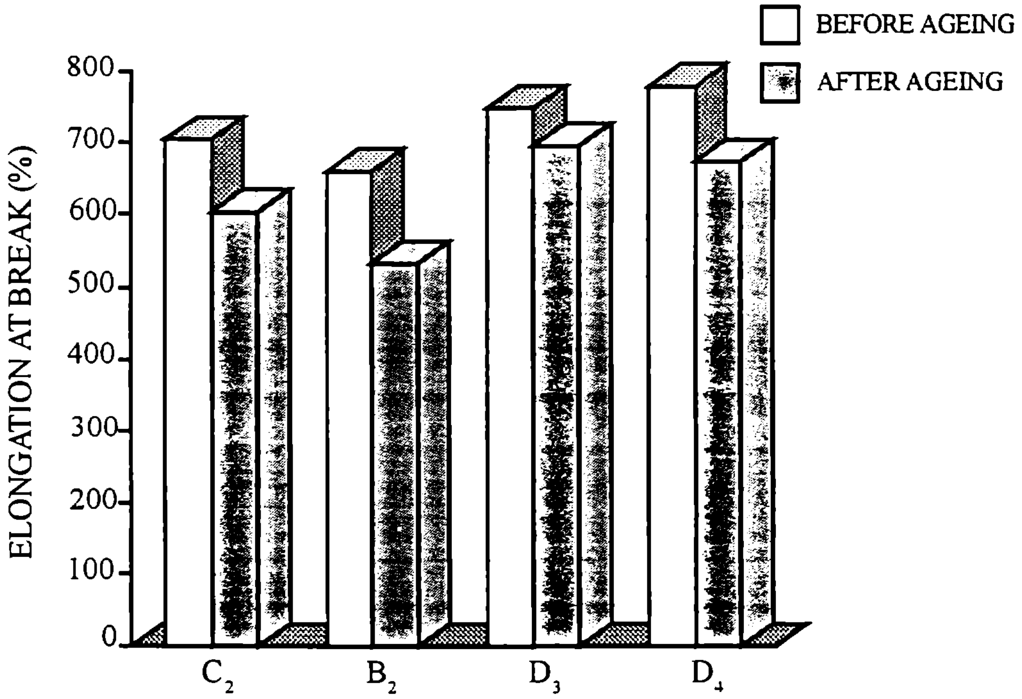


Fig. 3.13 Elongation at break of vulcanizates containing equivalent concentrations of TMTD with ATU, MBTS, DPG and TU

is higher for the latter. But compared to MBTS-TU (mix B_4), mix A_2 shows better values. The MBTS-TMTD system (mix B_2) shows lower values compared to other mixes with equal amounts of both accelerators. In the case of 100% modulus also the MBTS-ATU system gives better values compared to other reference mixes. But elongation at break remain more or less the same for all these mixes.

Tensile properties of the TMTD-ATU vulcanizates also shows variations more or less similar to that of MBTS-ATU systems. Table 3.6 shows the various tensile properties both before and after ageing. These are shown graphically in Fig. 3.5-3.7. The tensile strength, 100% modulus and elongation at break do show some variation with increasing concentration of amidinothiourea up to 1.5 phr. This is also in agreement with estimation of the total chemical crosslinks (Table 3.7) which also show slight variations with concentration of ATU. Mix C_1 containing 0.5 phr of ATU which can be taken as the optimum dosage of the ATU with respect to cure characteristics, shows comparable values of tensile strength with that of mixes C_2 and C_3 containing 1 and 1.5 phr of ATU respectively. Unlike MBTS-ATU, TMTD-ATU systems do not show increase in tensile strength after ageing. A bar graphical comparison of tensile strength, 100% modulus and elongation at break both before and after ageing among mixes containing 1 phr each of TMTD and ATU (mix C_2) and reference mixes (D_2, D_3 and D_4) are given in Figs. 3.11-3.13.

Table 3.7 Other physical properties evaluated for mixes with MBTS

Mix No.	Hardness (shore A)	Compression set (%)	Heat build-up ($\Delta T^{\circ}C$)	Resilience (%)	Abrasion loss (cm^3/hr)	Tear strength (N/mm)	Total crosslink density x 10^5 g mol/cm^3
A_1	20	26.85	13.3	70.94	9.33	23.24	4.16
A_2	17	27.54	13.7	76.85	6.25	24.04	4.23
A_3	23	29.43	11.2	78.76	4.82	26.88	4.63
B_1	27	18.88	12.7	72.38	9.88	25.47	4.03
B_2	36	13.55	5.0	85.32	15.20	31.66	6.87
B_3	29	38.46	9.4	78.73	6.20	37.29	5.70
B_4	30	57.93	20.0	72.37	14.17	23.21	4.53

3.1.2.3 Other Physical Properties

Other physical properties studied for the systems under review are hardness (shore A), compression set, heat build-up, resilience, abrasion loss and tear strength. These are given in Tables 3.7 and 3.8 respectively for MBTS-ATU and TMTD-ATU systems.

For the MBTS-ATU system, the values of tear strength, compression set and resilience of the vulcanizates are seen to increase with increase in concentration of ATU whereas abrasion loss shows a decrease. These variations are more or less in accordance with the observed variations in crosslink density values (Table 3.7). Mix A_3 shows higher values regarding hardness and heat build-up compared to mixes A_2 and A_1. With respect to equivalent reference mixes also MBTS-ATU system shows favourable results.

Table 3.8 shows the other physical properties in respect of TMTD-ATU systems. Here, the compression set values are seen to increase with the concentration of ATU (mixes C_1-C_3). The heat build-up and resilience first increase and then decrease. The total crosslink density values do not show any appreciable changes with increase in amount of ATU. Compared to reference mixes, mix C_2 shows lower values for hardness. Also this mix shows higher values of compression set and heat build-up. But these properties for mix C_2 is almost same as that of equivalent TMTD-TU system (mix D_4). The resilience shows lower values than reference mixes.

Table 3.8 Other physical properties evaluated for mixes with TMTD

Mix No.	Hardness (shore A)	Compression set (%)	Heat build-up ($\Delta T^{\circ}C$)	Resilience (%)	Abrasion loss (cm^3/hr)	Tear strength (N/mm)	Total crosslink density x 10^5 g mol/cm^3
C_1	30	28.30	12.1	72.74	5.09	31.92	4.90
C_2	30	33.43	12.5	74.59	4.80	28.48	5.44
C_3	31	34.42	11.9	73.13	5.38	31.97	5.18
D_1	39	19.21	7.8	78.35	7.60	34.52	6.31
B_2	36	13.55	5.0	85.32	15.20	31.66	6.87
D_3	32	20.04	9.1	77.23	2.54	33.24	5.82
D_4	37	33.10	12.4	76.48	4.80	34.16	5.66

Abrasion properties of C_2 is better than that of B_2 and D_1. Tear strength values are also comparable. In general it may be stated that the MBTS-ATU and TMTD-ATU systems show comparatively better values than those of the reference mixes.

3.1.2.4 Degree of Crosslinking

The most important single factor upon which the physical properties of the vulcanizate depend is the degree of crosslinking[18]. All network properties depend to some extent on this variable, although not always in a state forward way. For this reason, there is usually no single degree of crosslinking at which each property is at its optimum for a given application. Based on the accelerator-sulphur ratios, the vulcanization systems studied in the present work comes under the semi-efficient vulcanizing (semi-EV) systems[18]. For the MBTS-ATU mixes (Table 3.7) the crosslink density values show a regular increase, though small, with increase in the concentration of ATU. Corresponding changes are also seen in tensile strength, tear strength and resilience. Abrasion values show a corresponding decrease. But hardness, compression set and heat build-up do not show much variation. Depending on the cure characteristics, mix A_1 is taken as to contain optimum dosage of the secondary accelerator, and this mix shows comparable values of physical properties with reference mixes. In the case of TMTD-ATU systems, the degree of crosslinking remain more or less same with concenteration of ATU. However, vulcanizates containing higher amounts of ATU show slightly higher values. Also, the tensile and other physical propeties do not show any marked variation with concentration of ATU. In both MBTS-ATU and TMTD-ATU systems, the vulcanizates with optimum dosage of ATU show slightly lower crosslink density values compared to the references.

PART II

3.2 NR- FILLED VULCANIZATES

Gum natural rubber vulcanizates, although high in physical strength, are suitable only for very few commercial applications. Fillers are generally incorporated for improved processability, reinforcement or for cost reduction. The effect of a filler on rubber vulcanizates 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. Fillers may be classified as reinforcing and non-reinforcing. A reinforcing filler is one that improves modulus and failure properties such as tensile strength, tear resistance, abrasion resistance etc. of the final vulcanizate. On the other hand a non-reinforcing filler is used to cheapen and/or stiffen the final product. In general the best reinforcing fillers are those that have the smallest particle size. The basic aspect of polymer filler interaction has been studied in detail in a number of polymers[19-22]. Studies on filled systems have also been reviewed by Kraus[23] and Voet[24] The role of reinforcing blacks in the sulphuration process in vulcanization has been discussed by Porter[25] as well as Bhowmic and De[26]. Bhowmic et. al.[26] has also studied the polymer filler interactions that control the properties of rubber vulcanizates.

Carbon blacks are the most effective reinforcing fillers. They are essentially elemental carbon and are composed of aggregated particles. Carbon blacks are produced by converting either liquid or gaseous hydrocarbons to elemental carbon and hydrogen by partial combustion or thermal decomposition. Depending on the process adopted for the preparation, carbon blacks are named as furnace black, thermal black, channel black, lamp black etc. For application where resistance to abrasion and high strength are required, fine carbon blacks are almost universally used. With general purpose elastomers like NR, high abrasion furnace (HAF) blacks with average particle size in the range of 24-28 nm are most widely used. It is known that carbon black contain active functional groups such as phenolic, ketonic and carboxylic, together with lactones[27]. During vulcanization carbon black enters into chemical reaction with sulphur, accelerator etc., participating in the formation of vulcanized network. Two of the most important effects of reinforcing fillers on the properties of vulcanized rubber are a substantial increase in modulus and a reduction in the extent to which the vulcanizate will swell in a rubber solvent. Thus the filler may influence the degree of cross linking. Carbon black interacts strongly with unsaturated hydrocarbon rubbers during milling and the rubber is adsorbed on the filler. This alters the stress-strain properties and reduces the extent of swelling in a solvent[28]. Porter[29] studied the mechanism by which the carbon black increases the efficiency of crosslinking of sulphur system, and the general conclusion is that presence of the filler makes desulphuration faster.

Precipitated silica is the best non-black reinforcing filler so far developed, and come closest to carbon black in its reinforcing properties. They have particle size as fine as that of carbon black and they have an extremely reactive surface. In the mill mixing of the silica loaded natural rubber compounds, some precautions are necessary to ensure good dispersion. Excessive milling may cause reduction in properties and hence a complete batch should be mixed and cut from the mill as quickly as possible. 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 active. Reinforcement and cure characteristics of silicas and silicates has been reviewed by Wagner[30]. Special consideration needs to be given for the proper choice of accelerator and activator to obtain appropriate scorch and cure times with silica and silicate filled rubbers. Thiazole accelerators show cure retardation with silica and they need a secondary accelerator and an activator such as diethylene glycol (DEG). In NR, SBR and BR, guanidine type accelerators with glycol activators are commonly recommended with thiazole or sulphenamide primary accelerators[30]. Silica and silicates are known for the relatively low modulus imparted to rubber compared to that expected from carbon black of comparable size. One distinct advantage imparted by silica to many rubbers is the increased resistance to air ageing at elevated temperatures[30]. In the case of reinforcing silica, it was found that in the presence of additives it did not have any effect on the sulphuration process of NR vulcanizates[31]. Clays represent the largest volume of non-black fillers used in rubber. They owe this popularity to a combination of low cost, low to moderate reinforcement and benefits in processing, especially extrusion and calendering. They have a pronounced stiffening effect and impart hardness and fairly good abrasion resistance. Clays are also highly adsorptive and are known to reduce the cure rate[32]. So an activator such as diethylene glycol should be used in formulations containing clay.

As reported in part I of this chapter, in gum vulcanizates of NR, ATU is proved to be very effective with respect to cure characteristics and physical properties both in MBTS-ATU and TMTD-ATU systems. In this context, we thought it would be worthwhile to investigate also the filled vulcanizates of NR containing ATU as a secondary accelerator along with MBTS and TMTD. A thorough study on the filled systems was carried out aiming at developing practical cure systems which can be used in rubber product manufacture. The present study covers different aspects like variations in mixing and curing and the evaluation of various physical properties of the vulcanizates of the filled systems of NR with MBTS-ATU and TMTD-ATU as accelerators. Reference mixes were also prepared and the properties of the experimental mixes were compared with those of the reference mixes. To understand the variations in physical properties of the different vulcanizates, total chemical crosslinks were also estimated using the equilibrium swelling method[36].

3.2.1 EXPERIMENTAL

Formulations of the different mixes used in the study are shown in Table 3.9 and 3.10. The various fillers used are carbon black,precipitated silica and china clay. All mixes contain 50 phr of the respective filler. Mixes A_1-A_3, C_1-C_3 and E_1-E_3 contain 0.5, 1.0 and 1.5 phr of ATU with 1 phr of MBTS and mixes A_1'-A_3', C_1'-C_3' and E_1'-E_3' contain 0.5, 1.0 and 1.5 phr of ATU with 1 phr of TMTD respectively. The reference formulations B, D and F are equivalent mixes of MBTS and TMTD with 50 phr each of carbon black, precipitated silica and china clay respectively. The rest of the mixes are also reference mixes. Aromatic oil (5 phr) is used as the process oil for mixes containing carbon black while naphthenic oil (5 phr) is used in the case of silica and clay filled compounds. In mixes containing clay and silica 2 phr of DEG is used as activator.

All the above mixes were prepared as per ASTM designation D3182-89 in a two roll mixing mill. Goettfert elastograph model 67.85 was used for determining the cure characteristics of different mixes. The compounds were vulcanized up to optimum cure time in an electrically heated laboratory type hydraulic press at 150°C at a pressure of 140 Kg cm^{-2}. The tensile properties of the vulcanizates were determined on a Zwick Universal testing machine model 1445 using a cross head speed of 500mm/min. as per ASTM designation D412-87 (method A). Heat ageing was studied according to ASTM

TABLE 3.9 FORMULATION OF MIXES CONTAINING MBTS

Ingredients	A_1	A_2	A_3	B	B_1	B_2	B_3	C_1	C_2	C_3	D	D_1	D_2	D_3	E_1	E_2	E_3	F	F_1	F_2	F_3
Natural rubber	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	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	2	2	2	2	2
MBTS	1	1	1	1	2	1	1	1	1	1	1	2	1	1	1	1	1	1	2	1	1
TMTD	—	—	—	1	—	—	—	—	—	—	1	—	—	—	—			1			
DPG						1			—	—	—	—	1			—	—		–	1	
Thiourea	—	—					1		—	—	—	—	—	1		—	—				1
ATU	0.5	1.0	1.5	—	—	—	—	0.5	1.0	1.5					0.5	1.0	1.5		—		—
Carbon black	50	50	50	50	50	50	50	—	—	—	—	—	—	—	—			—			
Silica		—	—		—	—	—	50	50	50	50	50	50	50	—	—	—		—		
China clay	—	—	—				—	—	—	—	—	—	—		50	50	50	50	50	50	50
DEG		–				—		2	2	2	2	2	2	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	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	5	5	5	5	5	5	5

Table 3.10 FORMULATION OF MIXES CONTAINING TMTD

Ingredients	A_1'	A_2'	A_3'	B	B_1'	B_2'	B_3'	C_1'	C_2'	C_3'	D	D_1'	D_2'	D_3'	E_1'	E_2'	E_3'	F	F_1'	F_2'	F_3'
Natural rubber	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	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	2	2	2	2	2
TMTD	1	1	1	1	2	1	1	1	1	1	1	2	1	1	1	1	1	1	2	1	1
MBTS	—	—	—	1	—	—	—	—	—	—	1	—	—	—	—	—	—	1	—	—	—
DPG	—	—	—	—	—	1	—	—	—	—	—	—	1	—	—	—	—	—	—	1	—
Thiourea	—	—	—	—	—	—	1	—	—	—	—	—	—	1	—	—	—	—	—	—	1
ATU	0.5	1.0	1.5	—	—	—	—	0.5	1.0	1.5	—	—	—	—	0.5	1.0	1.5	—	—	—	—
Carbon black	50	50	50	50	50	50	50	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Silica	—	—	—	—	—	—	—	50	50	50	50	50	50	50	—	—	—	—	—	—	—
China clay	—	—	—	—	—	—	—	—	—	—	—	—	—	—	50	50	50	50	50	50	50
DEG	—	—	—	—	—	—	—	2	2	2	2	2	2	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	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	5	5	5	5	5	5	5

designation D573 at 70°C for 48 hrs. Tear resistance was tested as per ASTM designation D624-86 using angular test pieces. Compression set, hardness and heat build-up were tested as per ASTM D395-89 (method B), D2240-86 and D623-88 (method A) respectively. Rebound resilience was evaluated using Dunlop tripsometer (BS 903 Part A8) and abrasion resistance using DIN abrader (DIN 53516). The cross link density of the vulcanizates was determined from the equilibrium swelling data. All these experiments are described in detail in chapter II.

3.2.2 RESULTS AND DISCUSSION

The results obtained clearly indicate the acceleration activity of ATU in the carbon black, precipitated silica and clay filled NR vulcanization systems containing either TMTD or MBTS as the primary accelerator. It is seen that the nucleophilic mechanism proposed earlier in gum vulcanization reactions hold good for the filled systems also. This is obvious from the reduction in cure time for mixes containing amidinothiourea compared to those containing equivalent amounts of thiourea, DPG etc. Eventhough a nucleophilic reaction mechanism is proposed in these vulcanization systems the possibility of a mixed mechanism involving ionic and radical types cannot be ruled out as evident from the following discussions.

3.2.2.1 Cure Characteristics

The vulcanization systems containing MBTS and ATU (mixes A_1-A_3, C_1-C_3 and E_1-E_3) are found to be better than the corresponding reference systems containing MBTS alone (mixes B_1, D_1 and F_1) as far as cure characteristics are concerned, irrespective of the filler used (Table 3.11 and Figs. 3.14-3.16). A substantial reduction in the optimum cure time with increase in the concentration of ATU is observed when carbon black or silica is the filler used. However, a corresponding reduction in scorch time is observed in these mixes. In the case of clay-filled system also a more or less similar trend is observed. In all the filled systems under investigation, a practical cure system seems to be the one containing 1.0 phr of ATU and that may be taken as the optimum dosage of ATU to be used with MBTS. The other cure characteristics of the experimental mixes containing MBTS and ATU are comparable to those of the corresponding reference mixes and are most favourable when carbon black is the filler (mixes A_1-A_3) and least in clay-filled systems (mixes E_1-E_3).

Cure characteristics of the systems containing TMTD and ATU (mixes A_1'-A_3', C_1'-C_3' and E_1'-E_3') are found to be better than those of the corresponding reference mixes containing (Table 3.12 and Figs. 3.17-3.19). Here also, the addition of ATU has reduced the optimum cure time considerably. Correspondingly, scorch time of the mixes has also been reduced. From the data the

Table 3.11 CURE CHARACTERISTICS OF MIXES WITH MBTS (CURED AT 150°C)

Mix No.	Optimum cure time, (t_{90}) min.	Scorch time[a] (t_{10}) min.	Induction time, (t_5) min.	Cure-rate index	Minimum torque, dNm	Maximum torque, dNm
A_1	6.8	1.7	1.0	19.61	6.1	41.2
A_2	5.8	1.5	0.9	23.26	4.7	44.9
A_3	5.6	1.3	0.9	23.26	4.3	37.5
B	3.8	1.6	1.1	45.46	4.0	67.9
B_1	7.1	2.3	1.4	20.83	3.0	38.4
B_2	4.2	1.3	1.0	34.48	3.2	52.8
B_3	8.1	1.6	1.3	15.39	3.8	29.8
C_1	5.8	1.9	1.7	25.64	1.7	16.9
C_2	4.4	1.2	1.1	31.25	3.7	40.3
C_3	3.9	1.0	0.8	34.48	3.2	43.9
D	4.7	2.2	1.9	40.00	1.8	35.2
D_1	8.4	3.7	3.2	21.28	2.1	27.0
D_2	4.2	1.6	1.4	38.46	2.2	42.7
D_3	5.4	1.6	1.2	26.32	3.0	26.8
E_1	4.3	1.4	1.3	34.48	0.5	16.7
E_2	3.7	1.2	1.1	40.00	0.5	17.6
E_3	3.3	1.0	0.9	43.48	0.6	20.0
F	3.5	1.3	1.3	45.45	0.5	30.7
F_1	3.8	1.8	1.7	50.00	0.8	18.6
F_2	3.4	1.3	1.3	47.62	0.4	23.9
F_3	4.5	1.3	1.2	31.25	0.8	18.5

a : Elastographic scorch time (t_{10})

TABLE 3.12 CURE CHARACTERISTICS OF THE MIXES WITH TMTD (CURED AT 150°C)

Mix No.	Optimum cure time, (t_{90}) min.	Scorch time[a] (t_{10}) min.	Induction time, (t_5) min.	Cure-rate index	Minimum torque, dNm	Maximum torque, dNm
A_1'	2.2	1.3	1.1	111.11	2.1	44.8
A_2'	2.1	1.2	0.8	111.11	3.4	41.5
A_3'	1.8	1.0	0.8	125.00	4.5	46.7
B	3.8	1.6	1.1	45.46	4.0	67.9
B_1'	2.8	1.5	1.1	76.92	3.7	64.8
B_2'	2.1	1.3	1.0	125.00	5.2	59.3
B_3'	2.6	1.4	1.2	83.33	6.4	60.4
C_1'	2.6	1.4	1.2	83.33	2.3	33.8
C_2'	1.9	0.9	0.8	100.00	3.0	41.1
C_3'	1.7	0.8	0.6	111.11	3.4	42.3
D	4.7	2.2	1.9	40.00	1.8	35.2
D_1'	2.9	1.8	1.6	90.91	1.8	34.4
D_2'	2.1	1.2	1.1	111.11	2.7	40.8
D_3'	2.3	1.3	1.2	100.00	2.7	33.9
E_1'	1.8	1.1	1.1	142.86	0.2	12.5
E_2'	1.5	0.9	0.9	166.67	0.4	20.0
E_3'	1.3	0.7	0.7	166.67	0.6	21.3
F	3.5	1.3	1.3	45.45	0.5	30.7
F_1'	3.5	1.5	1.4	50.00	0.4	28.8
F_2'	2.2	1.2	1.2	100.00	0.5	21.9
F_3'	1.4	0.7	0.7	142.86	0.8	23.6

a : Elastographic scorch time (t_{10}).

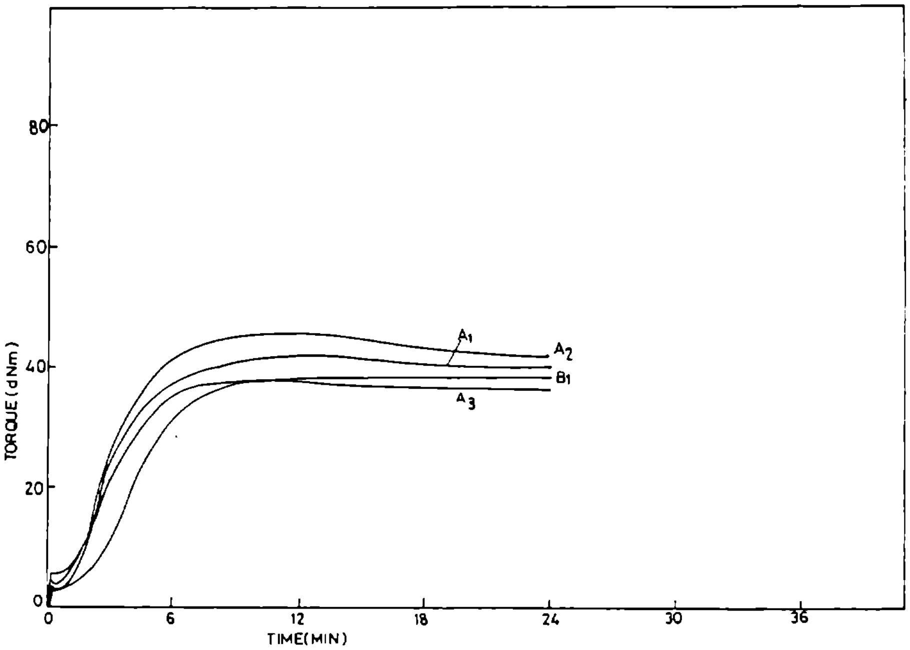


Fig. 3.14 Cure curves of carbon black-filled systems (MBTS)

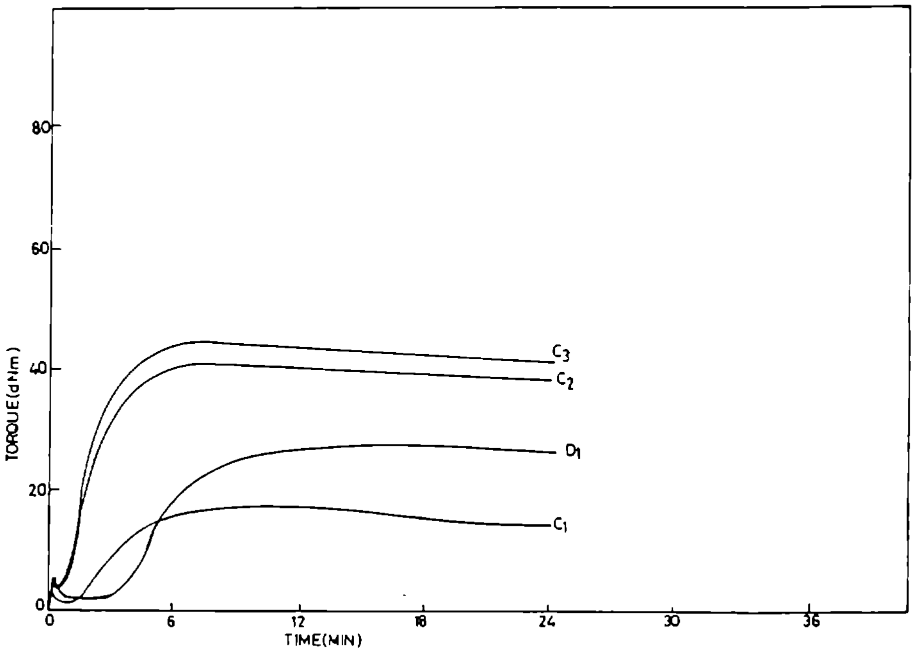


Fig. 3.15 Cure curves of silica- filled systems (MBTS)

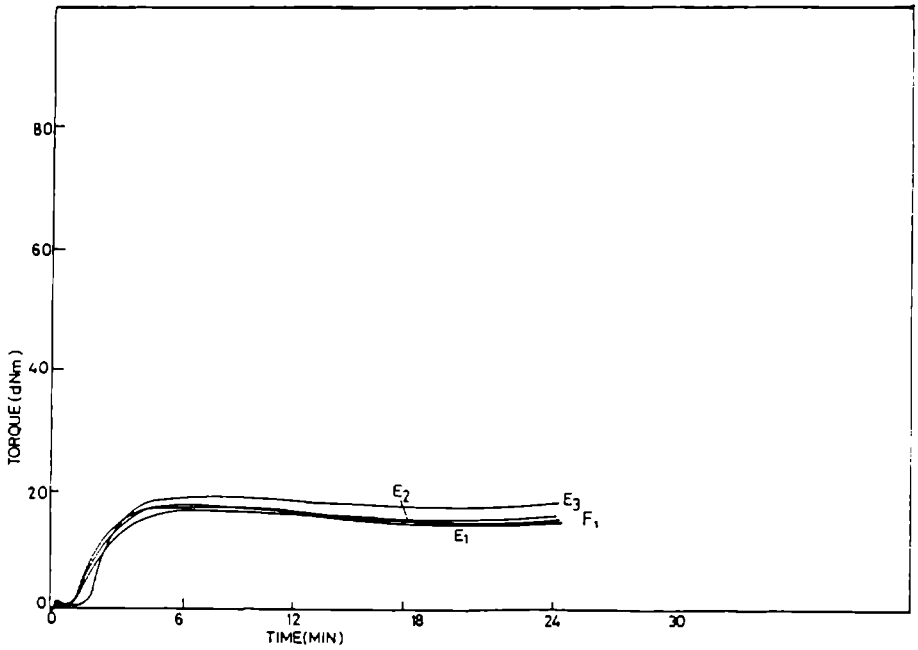


Fig. 3.16 Cure curves of clay- filled systems (MBTS)

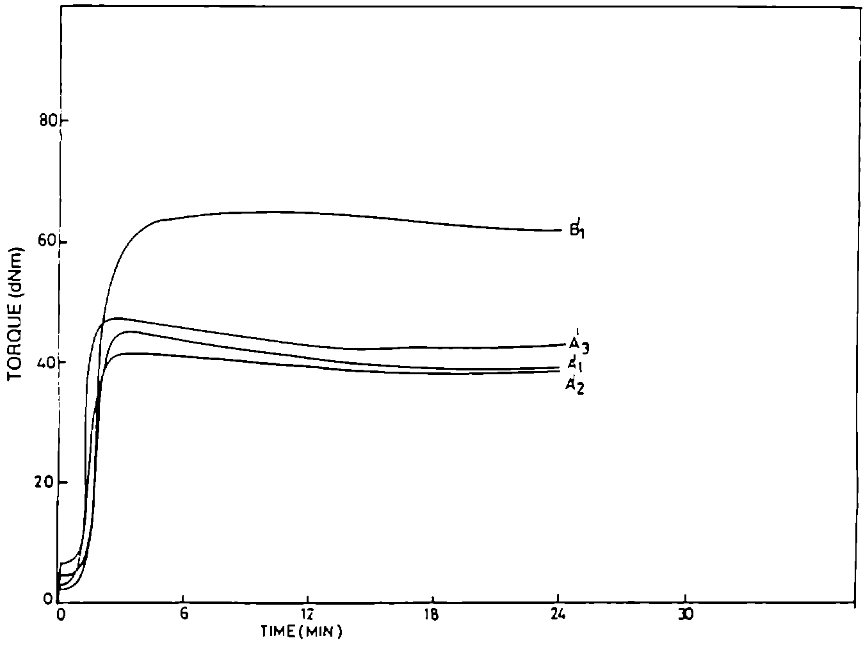


Fig. 3.17 Cure curves of carbon black-filled systems (TMTD)

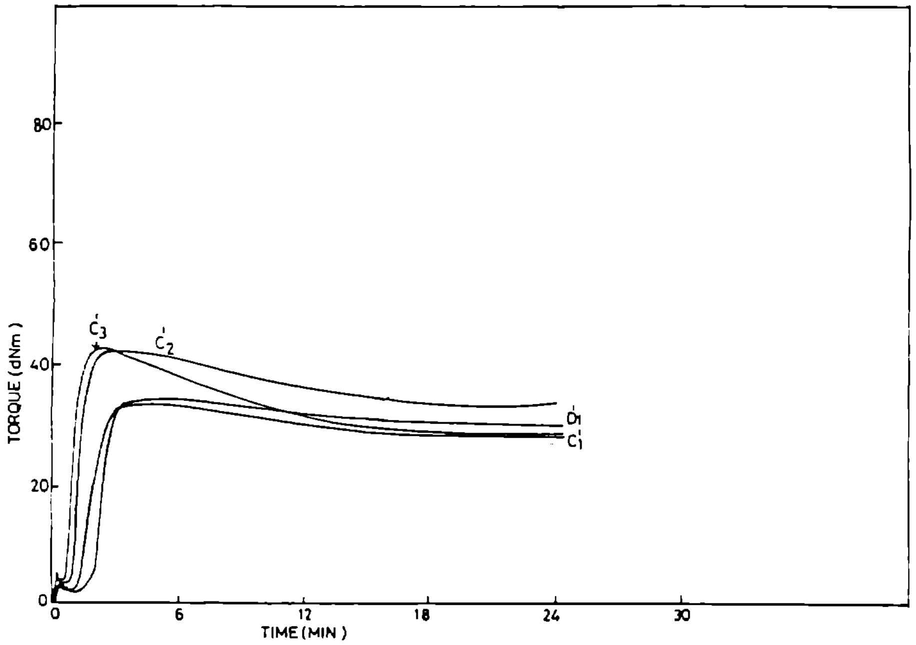


Fig. 3.18 Cure curves of silica- filled systems (TMTD)

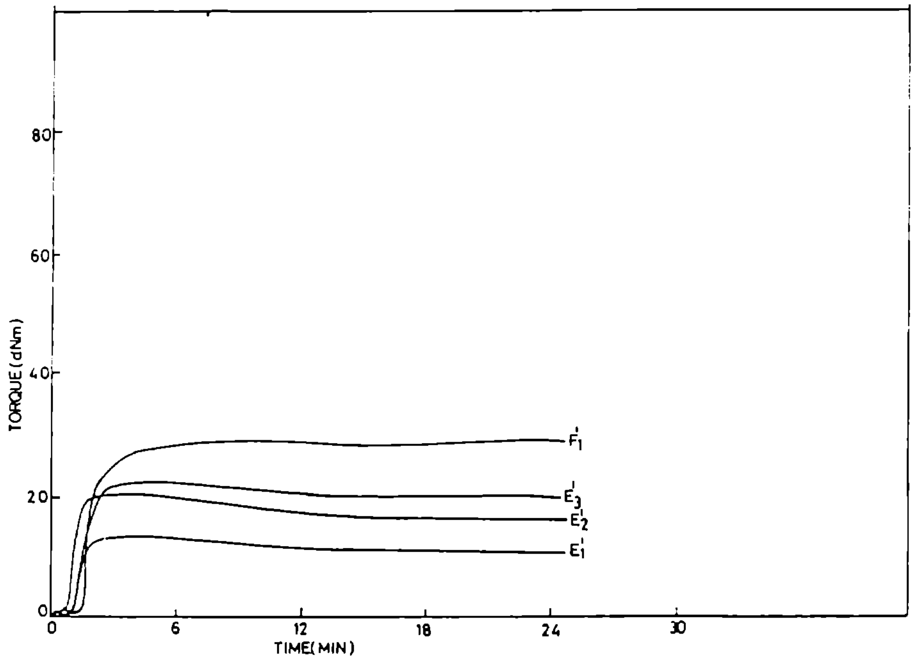


Fig. 3.19 Cure curves of clay-filled systems (TMTD)

optimum dosage of ATU to be used with TMTD may be taken as 0.5 phr since this gives the most practical combination of optimum cure time and scorch safety. Other cure characteristics of TMTD-ATU systems are comparable to those of the reference mixes and the trend of variation of these properties with respect to filler is more or less same as that for MBTS-ATU mixes.

3.2.2.2 Tensile Properties

Tensile properties of the vulcanizates containing ATU are found to be satisfactory in both the binary systems under review (Tables 3.13, 3.14). The effect of ATU concentration on tensile properties of the carbon black, silica and clay filled vulcanizates (MBTS-ATU), both before and after ageing, are shown in Figs. 3.20-3.22. These properties of the vulcanizates from TMTD-ATU systems are similarly shown in Figs. 3.23-3.25. For both silica and clay-filled vulcanizates of the MBTS-ATU systems the tensile strength slightlty increases with increase in the concentration of ATU. But the tensile strength of the carbon black-filled vulcanizates first decreases to a minimum and then increases. The same trend is observed in the estimation of total chemical crosslink also, in carbon black systems. The 100% modulus of the silica and clay-filled vulcanizates show variations similar to that of tensile strength. However, modulus (100%) of carbon black-filled vulcanizates increases to a maximum and then decreases with increase in the concentration of ATU. As expected

TABLE 3.13 TENSILE PROPERTIES OF THE VARIOUS MBTS VULCANIZATES

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	23.29	24.80	106.48	3.11	1.24	39.87	516.83	559.88	108.33
A_2	20.53	22.72	110.67	3.88	3.70	95.36	422.61	454.65	107.58
A_3	22.10	23.58	106.70	2.53	1.20	47.43	503.55	543.73	107.98
B	22.56	19.20	85.11	5.15	5.80	112.67	317.08	257.71	81.28
B_1	27.24	27.17	99.74	3.34	2.98	89.22	489.90	531.48	108.49
B_2	29.78	29.50	99.06	3.08	3.60	116.88	533.02	491.15	92.14
B_3	16.58	19.21	115.86	2.45	2.74	111.84	441.85	448.02	101.40
C_1	17.43	17.39	99.77	1.76	2.08	118.18	626.95	577.96	92.19
C_2	18.60	19.03	102.31	1.96	2.38	121.43	613.78	560.87	91.38
C_3	19.10	19.25	100.79	2.10	2.47	117.62	595.90	558.47	93.72
D	20.05	17.44	86.98	2.72	2.91	106.99	527.26	469.87	89.12
D_1	19.34	19.23	99.43	2.07	2.35	113.53	602.76	571.28	94.78
D_2	20.44	20.76	101.57	2.48	2.83	114.11	560.70	537.45	95.85
D_3	14.49	15.45	106.63	1.78	2.07	116.29	570.37	552.43	96.85
E_1	19.95	20.75	104.01	1.02	1.33	130.39	820.10	757.87	92.41
E_2	20.42	22.19	108.67	1.18	1.30	110.17	804.17	759.91	94.5
E_3	20.99	22.24	105.96	1.12	1.47	131.25	813.51	717.35	88.18
F	17.72	3.28	18.51	1.59	1.80	113.21	619.76	178.76	28.84
F_1	23.32	23.36	100.17	1.17	1.51	129.06	803.28	730.10	90.89
F_2	23.80	24.84	104.37	1.55	1.55	100.00	733.16	713.88	97.37
F_3	19.45	19.52	100.36	1.13	1.28	113.27	799.30	762.81	95.43

Table 3.14 TENSILE PROPERTIES OF VARIOUS TMTD VULCANIZATES

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'	26.70	21.63	81.01	3.82	4.16	108.90	437.32	354.60	81.08
A_2'	25.63	23.16	90.36	3.09	3.67	118.77	474.22	410.42	86.55
A_3'	26.95	23.04	85.49	3.64	4.35	119.51	454.98	373.46	82.08
B	22.56	19.20	85.11	5.15	5.80	112.67	317.08	257.71	81.28
B_1'	21.62	18.89	87.37	5.35	5.79	108.22	296.96	256.40	86.34
B_2'	26.22	10.67	40.69	4.14	5.79	139.86	432.66	170.27	39.35
B_3'	26.57	22.71	85.47	4.02	4.80	119.40	429.06	347.78	81.06
C_1'	18.58	16.61	89.40	2.03	2.15	105.91	614.40	557.20	90.69
C_2'	18.11	16.82	92.88	2.23	2.40	107.62	559.82	528.76	94.45
C_3'	18.73	16.15	86.23	2.31	2.34	101.31	559.63	527.17	94.20
D	20.05	17.44	86.98	2.72	2.91	106.99	527.26	469.87	89.12
D_1'	18.86	17.96	95.23	2.94	3.00	102.04	486.98	476.52	97.85
D_2'	20.95	18.08	86.30	2.62	2.81	107.25	559.48	505.91	90.43
D_3'	17.10	15.61	91.29	2.12	2.20	103.77	559.05	525.97	94.08
E_1'	22.06	16.72	75.79	1.23	1.37	111.38	801.32	688.78	85.96
E_2'	22.51	17.70	78.63	1.21	1.35	111.57	812.83	702.91	86.48
E_3'	21.21	19.29	90.95	1.19	1.36	114.29	797.93	711.48	89.17
F	17.72	3.280	18.51	1.59	1.80	113.21	619.76	178.76	28.84
F_1'	12.72	3.040	23.90	1.51	1.83	121.19	574.07	182.70	31.83
F_2'	22.06	18.37	83.27	1.45	1.65	113.79	713.26	626.45	87.83
F_3'	17.85	17.43	97.65	1.31	1.47	112.21	679.70	666.70	98.09

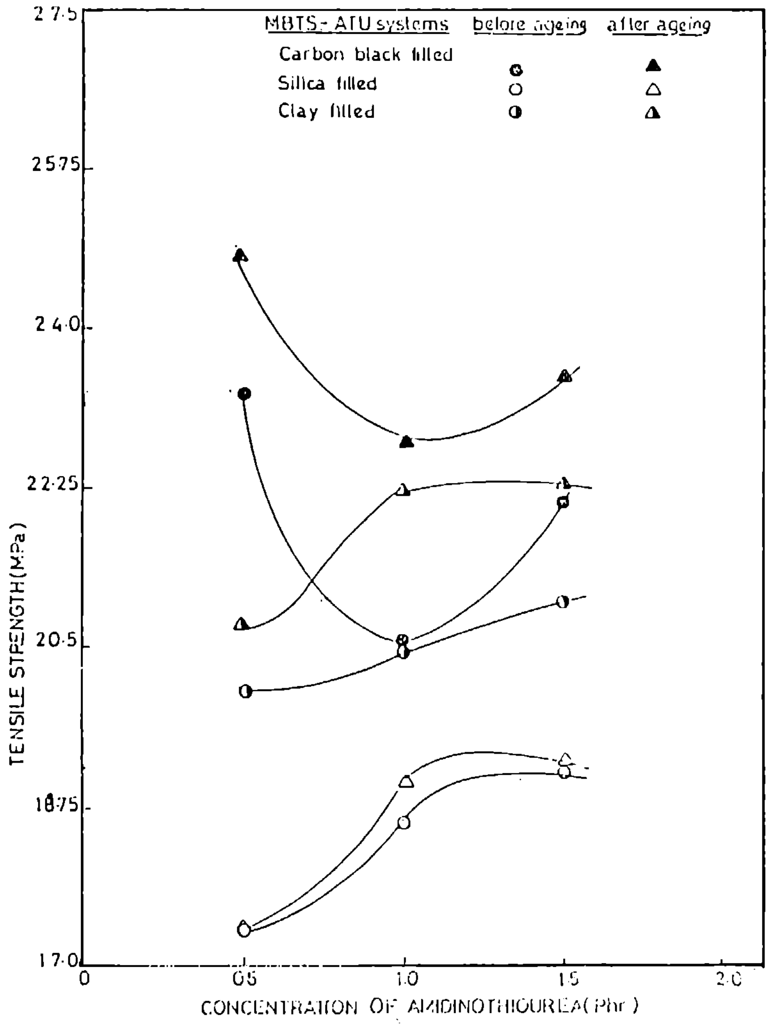


Fig. 3.20 Effect of concentration of ATU on tensile strength of MBTS-ATU vulcanizates

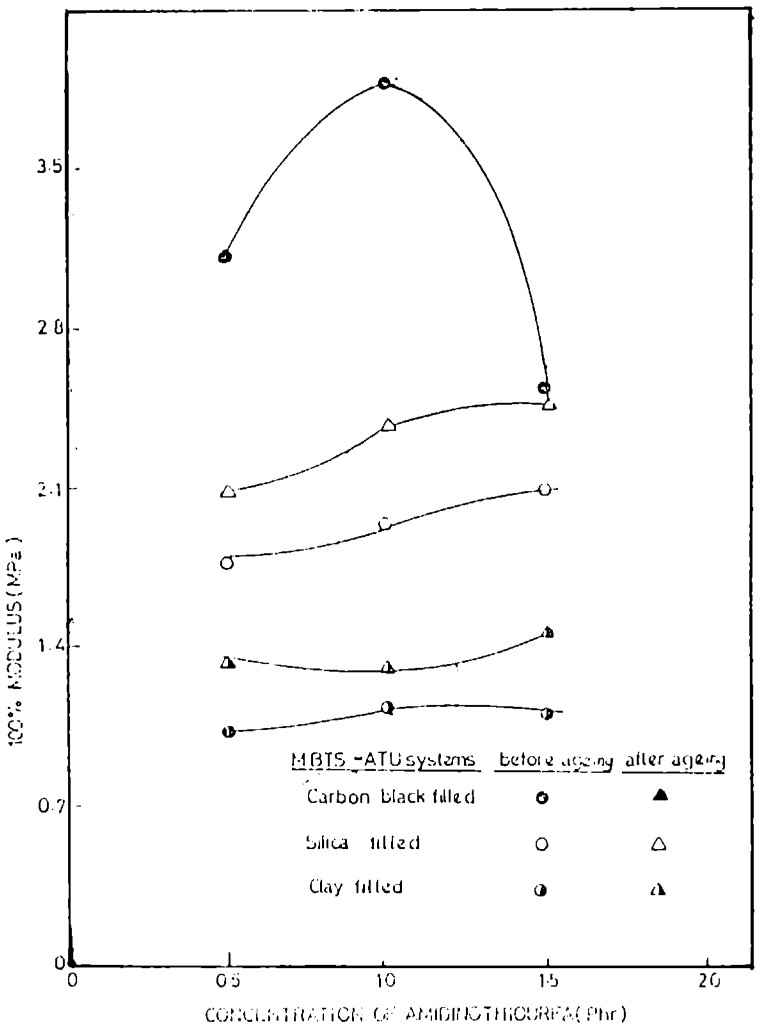


Fig. 3.21 Effect of concentration of ATU on 100% modulus of MBTS-ATU vulcanizates

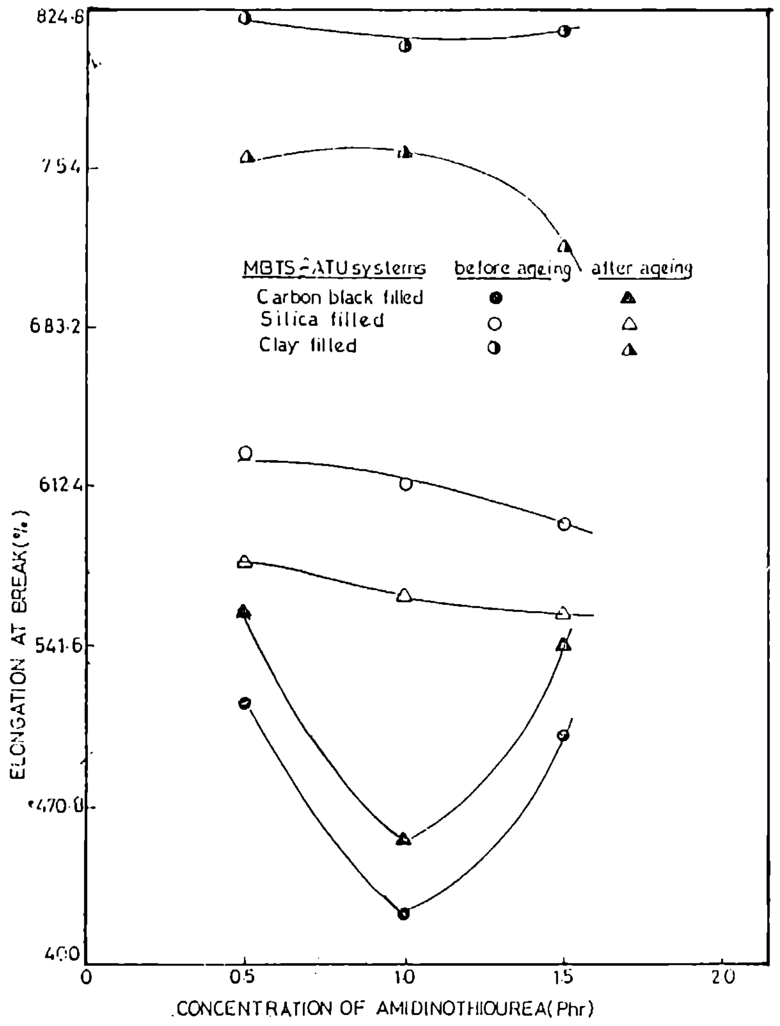


Fig. 3.22 Effect of concentration of ATU on elongation at break of MBTS-ATU vulcanizates

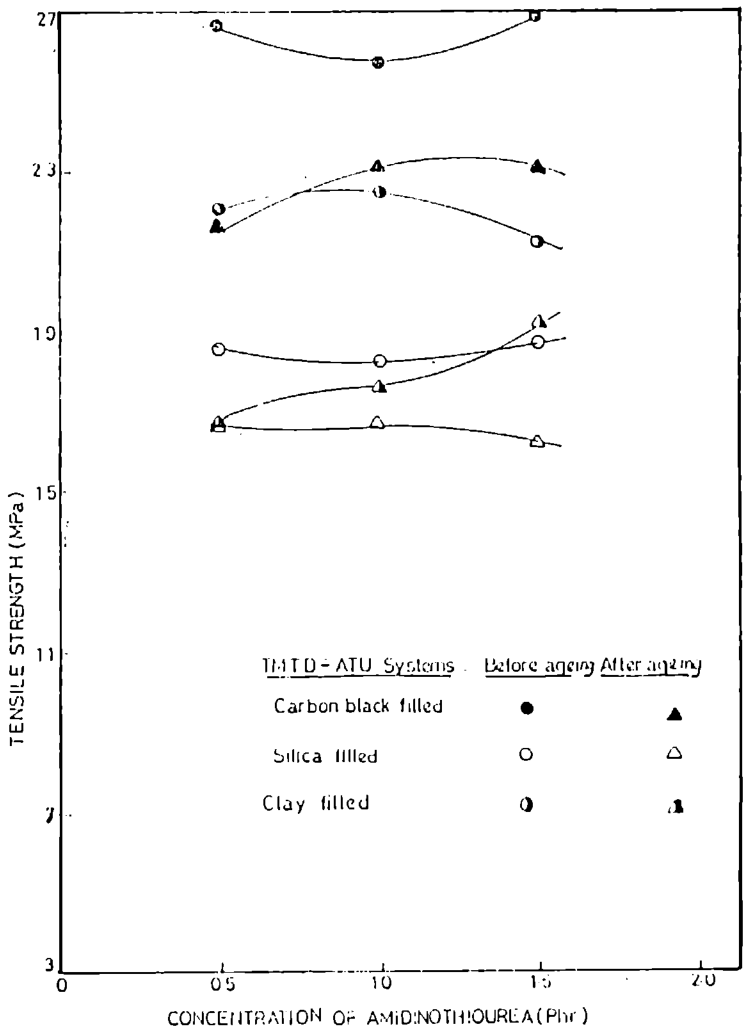


Fig. 3.23 Effect of concentration of ATU on tensile strength of TMTD-ATU vulcanizates

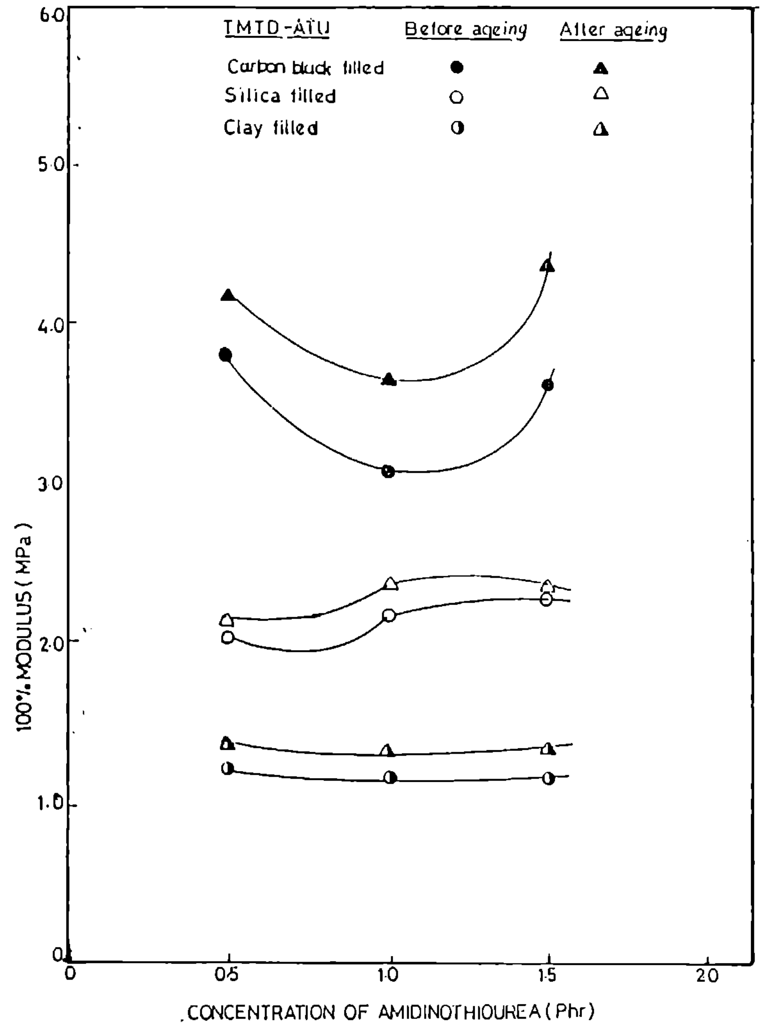


Fig. 3.24 Effect of concentration of ATU on 100% modulus of TMTD-ATU vulcanizates

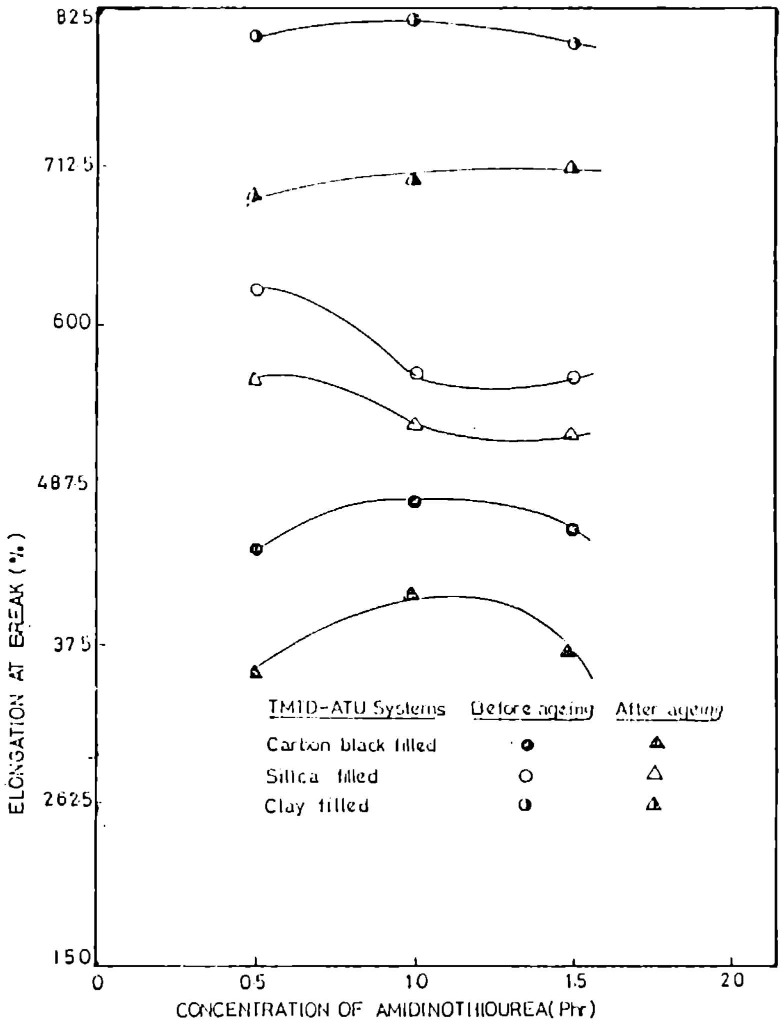


Fig. 3.25 Effect of concentration of ATU on elongation at break of TMTD-ATU vulcanizates

the highest values of tensile strength and modulus in the MBTS-ATU systems are given by the carbon black filled vulcanizates. Ageing resistance of the vulcanizates with amidinothiourea is seen to be comparable to other mixes used in the present study.

The variation in tensile properties of the vulcanizates (TMTD-ATU systems) with concentration of ATU, both before and after ageing is shown graphically in Figs. 3.23-3.25. Here the variations are not marked as in the case of MBTS-ATU combinations. Tensile strength, 100% modulus and elongation at break of the clay-filled TMTD-ATU systems show very little variation with increase in the concentration of ATU. For silica-filled systems also there is no significant variation in the tensile strength and 100% modulus. But elongation at break decreases initially with increase in the concentration of ATU and then stabilizes. Carbon black-filled TMTD-ATU systems are the only ones that show any marked variation in their tensile properties with change in concentration of ATU (Fig 3.23 and Table 3.14). Both tensile strength and modulus first decrease and then increase while elongation at break shows the reverse trend, 100% modulus is higher and elongation at break lower for the vulcanizates containing TMTD alone compared to TMTD-ATU combinations in all the three filler types. The values of tensile strength of the carbon black and clay-filled vulcanizates containing only TMTD are lower than those of TMTD-ATU combinations. However, the silica filled TMTD vulcanizates has a tensile stength approximately the same as that of the TMTD-ATU systems. All the three filler types in the TMTD-ATU systems show very good retention of tensile strength, elongation at break, and modulus, after heat ageing.

3.2.2.3 Other Physical Properties.

Other Physical properties such as hardness, compression set, heat build-up, resilience, abrasion loss and tear strength were also evaluated and are reported in Tables 3.15 and 3.16. All the above properties of the MBTS-ATU vulcanizates give values that are comparable to the corresponding reference mixes irrespective of the type of filler used. These properties do not show much variation with change in concentration of ATU in both MBTS-ATU and TMTD-ATU systems. For both the above systems, better values for hardness, abrasion resistance and tear strength are shown by carbon black-filled vulcanizates and least by clay-filled systems as expected. As far as heat build-up and resilience are concerned, clay-filled vulcanizates are better than silica filled ones, which in turn are better than carbon black-filled systems. Compression set values are almost the same for all the filler types.

3.2.2.4 Crosslink density

Reinforcing fillers such as carbon black are known to have significant effect on the network structure of filled vulcanizates while, semi-reinforcing or non-reinforcing fillers such as silica and clay do not have much effect on rubber-net work[31,33,34]. Moreover, silica

Table 3.15 OTHER PHYSICAL PROPERTIES EVALUATED (MBTS SYSTEMS)

Mix No.	Hardness (Shore A)	Compression set (%)	Heat build-up (Δ T°C)	Resilience (%)	Abrasion loss (cm^3/hr)	Tear strength (N/mm)	Total cross-link density, x 10^5 g mol/cm^3
A_1	49	42.28	39	48.77	3.79	64.74	3.1101
A_2	53	38.50	40	49.38	4.25	103.84	2.3929
A_3	43.5	37.34	35	47.54	5.00	60.69	2.7149
B	60	18.74	21	63.12	2.60	83.88	7.4864
B_1	45	42.17	30	51.89	3.92	106.27	3.9179
B_2	51	32.93	27	56.39	3.66	118.12	4.0852
B_3	45	55.58	57	44.56	5.07	32.93	3.2025
C_1	31	43.22	31	63.12	7.44	53.63	1.6929
C_2	42	43.83	25	65.20	6.37	58.33	1.6753
C_3	47	39.12	23	64.51	6.24	70.40	1.9882
D	52	30.07	16	74.59	5.48	53.10	1.8790
D_1	45	40.40	25	65.91	5.95	63.43	1.3996
D_2	48	44.00	21	68.03	5.42	70.84	1.6865
D_3	43	50.00	44	59.04	7.87	45.65	1.6331
E_1	26	37.69	18	77.59	9.82	25.25	2.9236
E_2	27	39.44	19	75.34	9.48	25.29	2.8083
E_3	30	38.00	19	73.85	7.32	26.16	2.6956
F	40	24.32	17	82.97	8.94	32.02	6.4511
F_1	31	43.51	14	80.64	7.54	28.59	3.0291
F_2	31	35.97	11	81.41	7.14	26.20	3.3051
F_3	28	34.78	17	77.59	9.36	24.00	2.9361

Table 3.16 OTHER PHYSICAL PROPERTIES EVALUATED (TMTD SYSTEMS)

Mix No.	Hardness (Shore A)	Compression set (%)	Heat build-up (Δ T°C)	Resilience (%)	Abrasion loss (cm^3/hr)	Tear strength (N/mm)	Total cross-link density, x 10^5 g mol/cm^3
A_1'	52	25.85	24	61.06	3.33	78.92	5.2443
A_2'	50	24.73	34	55.08	3.58	68.19	4.8168
A_3'	52.5	22.96	30	58.37	3.87	96.87	5.0721
B	60	18.74	21	63.12	2.60	83.88	7.4864
B_1'	62	24.16	22	61.74	3.67	73.04	7.6011
B_2'	57.5	27.20	30	43.97	3.53	107.42	6.8367
B_3'	55	25.52	31	59.04	2.96	98.09	6.5830
C_1'	42	35.09	31	59.04	6.61	65.20	1.7999
C_2'	46	37.31	26	63.81	6.48	57.63	1.7937
C_3'	47	33.70	24	68.03	6.21	55.86	1.9963
D	52	30.07	16	74.59	5.48	53.10	1.8790
D_1'	50	31.51	19	71.64	6.18	50.09	1.7643
D_2'	52	19.87	24	63.12	6.59	62.55	1.3805
D_3'	44	44.44	29	59.71	7.18	51.89	1.6721
E_1'	32	30.87	14	76.09	7.74	28.35	4.1302
E_2'	33	25.00	14	76.08	6.89	29.65	4.0240
E_3'	34	24.68	13	74.59	6.66	30.32	3.4275
F	40	24.32	17	82.97	8.94	32.02	6.4511
F_1'	39	30.83	11	79.88	7.85	26.65	3.8827
F_2'	33	28.29	12	76.84	9.23	26.64	3.6586
F_3'	32	35.81	16	76.08	7.43	28.78	3.7601

is reported to cause a reduction in crosslinking efficiency in accelerated sulphur systems[35].

The total crosslink density values of various systems studied are given in Tables 3.15 and 3.16. As expected higher values of crosslinks and subsequently higher modulus are obtained in the case of carbon black-filled vulcanizates for both the binary systems. The other two fillers show comparitively lower values for these properties. It is seen that the variation in crosslink density can be correlated to the variation in the different tensile and other physical properties for both MBTS-ATU and TMTD-ATU systems (Tables 3.13 and 3.14). For the carbon black-filled MBTS-ATU system the crosslink density values first decrease and then increase with increase in concentration of ATU. But for the silica and clay filled vulcanizates of same system crosslink density remains more or less the same with concentration of ATU. Almost the same trend is observed in the case of TMTD-ATU systems also.

3.3 CONCLUSIONS

Analysis of the vulcanizate properties of NR gum and filled compounds clearly indicate that 1-phenyl-3-(N,N'-diphenylamidino)thiourea can be very effectively used as a secondary accelerator in the sulphur vulcanization of natural rubber along with MBTS or TMTD as the Primary accelerator.

Examination of the cure behaviour of the gum formulations provides a supporting evidence to the nucleophilic reaction mechanism of accelerator activity, where the S-S bond of the primary accelerator is cleaved by the nucleophile from the secondary accelerator as given in section 3.1.2.1. Amidinothiourea reduces the optimum cure time of the mixes considerably and practical cure systems with optimum concentration of amidinothiourea have been developed. This will be of definite advantage to the rubber product manufacturing industry. When used alone, ATU is unable to function as an effective accelerator, which limits its activity as a secondary accelerator only. In most of the tensile properties studied, vulcanizates containing amidinothiourea showed better performance. Comparable values with those of reference mixes were obtained in the case of other physical properties such as hardness, compression set, heat build-up, resilience and tear strength. Cross link density values evaluated also support the above conclusions. Regarding after ageing properties, ATU shows promising results. The main disadvantage observed in the case of mixes containing ATU is the lower scorch times, which may cause processing problems when used in higher dosages. Even here the optimum dosages of ATU arrived at in the case of these systems show sufficient scorch safety.

Both binary systems containing MBTS and TMTD are found to be very effective in filled NR vulcanizates also. The results obtained in these systems are also in favour of a nucleophilic reaction mechanism. The cure characteristics of the mixes and tensile properties of the vulcanizates containing ATU are comparable to/better than those of the reference mixes. The optimum dosages of ATU required for the above systems have also been derived. The variation of cure characteristics and tensile properties with the filler types does not indicate a set pattern. The percentage retention of tensile properties on heat ageing of the vulcanizates containing ATU is found to be quite satisfactory. Other physical properties such as hardness, resilience, compression set, heat build-up, abrasion resistance and tear strength of these vulcanizates from both the binary systems give values comparable to/better than those of the reference mixes. The results of the above investigation indicate that the systems reviewed, both in the gum and filled stocks of natural rubber, can be used in a practical rubber product manufacture.

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CHAPTER IV

STUDIES ON THE EFFECT OF AMIDINOTHIOUREA IN NR LATEX SYSTEMS

Natural rubber latex obtained from the bark of *Hevea-brasiliensis* has a rubber content between 25 and 40 percent by weight. The variation is due to factors such as the type of the tree, the tapping method, the soil condition, the season etc. NR latex is a white opaque liquid with a specific gravity between 0.974 and 0.986. It is a weak lyophilic colloidal system of spherical or pear shaped rubber globules suspended in an aqueous serum. The rubber hydrocarbon in latex is predominantly cis-polyisoprene and it occurs as molecular aggregates in the form of discrete particles with an average diameter ranging from 0.25 and 0.8μm[1] NR latex contains also a wide variety of non-rubber materials both organic and inorganic. The major constituents are known to be proteins and their decomposition products, fatty acids and a range of organic and inorganic salts. The proportion of these constituents may vary with clones, soil condition, climate etc. In general, the composition (in percentage) of NR latex is as given below:

Rubber 30-40, Proteins 2.0-2.5, Resins 1.0-2.0, Sugar 1.0-1.5, Water 55-66, Ash 0.7-0.9.

The rubber hydrocarbon in latex, as it leaves the tree is already a high polymer with a broad distribution of molecular weight ranging from 10^5 to 10^6 with the major part of hydrocarbons in higher molecular weight ranges[2].

Due to its high water content and susceptibility to bacterial attack, it is necessary to preserve and concentrate latex so that it is stable and contain 60 percent or more of rubber. The latex, as it comes out of the tree gets contaminated with micro organisms like bacteria and yeast[3]. The micro organisms metabolise the non-rubber constituents of the latex and produce volatile fatty acids such as formic, acetic and propionic acids which leads to coagulation of the latex[4]. Therefore preservatives are added to latex immediately after collection[5,6,7]. The most widely used preservative is ammonia and it inhibits bacterial growth, act as an alkaline buffer and raises the pH and nutralise free acid formed in latex. NR latex preserved only by ammonia is known as high-ammonia (HA) latex. As the high percentages of ammonia is hazardous for the workers involved, and also causes processing problems the common practice is to use NR latex containing a reduced level of ammonia and a secondary latex preservative[8]. The preserved field latex is unsuitable for most latex applications as its rubber content is low. For most product manufacture, a latex of 60 percent minimum rubber content is essential[3]. The important methods for the concentrations of preserved field latex are, (1) evaporation (2) creaming (3) centrifugation and (4) electrodecantation. Only centrifuging and creaming are commonly used for the production of latex concentrate[3].

The processing of latex requires only relatively light and simple machinery. Capital outlay and power requirements are relatively low compared to the requirements for the heavy expensive equipments which are used for processing of dry rubber. The absence of any polymer degradation step such as mastication, in the processing of latex not only saves time and energy but also gives a vulcanizate which will display inherently greater resistance to deteriorative influences.

Natural rubber latex is extensively employed in the manufacture of dipped goods[9]. Dipped goods include a wide range of products such as, gloves, balloons, catheters, teats, contraceptives etc. In this type of processes, the latex used must produce continuous film on the former and maintain film integrity during drying/vulcanizing stage. NR latex is outstanding in this respect. Also NR latex products are exceptional in terms of tensile strength and elongation, coupled with relatively low modulus values, which are ideal characteristics for gloves, balloons and teats. Other articles manufactured from NR latex include, foam and cellular rubbers, threads, impregnated coir, fabrics etc. Articles manufactured using latex give service performances superior to that of articles made of rubber solutions[10].

4.1 Compounding ingredients in latex systems

The conversion of NR latex into a product is accomplished in many ways and stable colloidal system is maintained until it is converted into a solid product[9]. The different ingredients used in a latex compound are, (1) surface active reagents (2) vulcanizing agents (3) accelerators (4) activators (5) antioxidants (6) fillers and (7) special additives. The water soluble materials are added as solutions, insoluble solids as dispersions and immiscible liquids as emulsions[9]. The particle size of the ingredients should be reduced to that of rubber particles in latex, for getting uniform distribution in latex compound[11].

The surface active agents are substances which bring about marked modification in the surface properties of aqueous media, eventhough they are present only in very small (about 1% or less)[11]. The surface active agents include wetting agents, viscosity modifiers, protective colloids, dispersing agents, dispersion stabilizers, emulsifiers etc. The most universal vulcanizing agent for NR latex is sulphur. Sulphur should be of good quality and should be finely ground. TMTD may be used as a curing agent in sulphurless systems. But vulcanization of these systems proceeds at a useful rate only at relatively high temperatures (140°C).

Zinc oxide is used as activator in latex vulcanization also. Zinc oxide is not essential if zinc containing accelerators such as zinc dialkyl dithiocarbamate type are used, but it is commonly used in latex compounds to provide further activation of vulcanization and to contribute to gelation processes[9]. Also zinc oxide increases the tensile strength and modulus of the vulcanizates[12]. The common antioxidants used in latex are amine and phenolic derivatives[11].

Amine derivatives are powerful antioxidants but, tend to cause discolouration of the rubber during ageing. On the otherhand phenolic derivatives are less effective but have the advantage of not causing discolouration. Depending on the nature of process or on end use, special additives like gelling agents, foaming agents, flame proofing agents, tackifiers, colour etc. are also added.

4.1.1 Accelerator systems

The use of organic accelerators in latex compounding is basically different from their use in dry rubber compounds[13]. NR latex contains a lot of non-rubber materials which function as accelerators and activators. As there is no danger of scorching ultra accelerators are used in latex compounding and the accelerators should be dispersed uniformly in latex mixture without causing coagulation or thickening. The accelerators used should be readily dispersible in water in order to achieve uniform dispersion. Also, the vulcanization temperature for a latex compound is substantially lower in comparison with that for dry rubber compound. Consequently the choice of accelerator and their properties is to be made carefully. Of the wide range of rubber vulcanization accelerators which are commercially available it is only those of the highest activity are of importance for the technology of rubber lattices. The most important classes are the metallic dialkyl dithiocarbamates[11]. Among these the most widely used are is the zinc dialkyl dithiocarbamates.

a lesser extent. TMTD may be used to cure natural rubber latex without the addition of sulphur or with small amounts of sulphur to prepare heat resistant articles[14]. It may also be used to prepare vulcanizates which can prevent copper catalysed oxidative degradation[14]. To obtain high quality products, usually a combination of accelerators is used in latex. A combination of zinc diethyl dithiocarbonate (ZDC) and zinc mercapto benzthiazole (ZMBT) are used for getting products with improved modulus[15]. The vulcanization of latex using TMTD proceeds only at relatively high temperatures. At low temperature (100 °C or below) the reaction is too slow to be of any technological interest. It has been shown by Philpot[14], that certain sulphur containing nucleophiles like thiourea are able to activate vulcanization by TMTD so that well cured natural rubber vulcanizates may be produced rapidly at or around 100 °C.

4.1.2 Fillers

Inorganic fillers and pigments are commonly added to latex in order to cheapen and stiffen the product or to colour it[14]. The fillers may also affect the flow behaviour. It may be mentioned that no effect analogous to the reinforcement of dry rubber by certain inorganic fillers are observed when the same fillers are incorporated in latex compounds. Carbon black does not reinforce latex in the manner that it does dry rubber and is used only in small amounts in latex for colour, as various other dyes and pigments[17]. The important non-black fillers used in latex compounding are precipitated silica, precipitated calcium carbonate and china clay. The poor rubber filler interaction in latex vulcanization is attributed to many factors such as insufficient distribution of fillers, non-simultaneous deposition of filler and rubber particles, and the presence of protective layer of stabilizers around the rubber and filler particles in latex which prevent direct contact between them[18].

As mentioned in chapter I, it has been suggested[14] that accelerators in which sulphur is combined as S-S, C-S-C or S-N are virtually inactive at temperatures below 100°C because of the compritively higher thermal stability of their S-bonds. But reagents containing S-reactive nucleophiles facilitates S-bond cleavage, enabling such accelerators to operate at lower vulcanization temperatures. Also investigations made in our laboratories[16] using dithiobiuret derivatives showed results which are also in favour of the nucleophilic reaction mechanism for the activity of such secondary accelerators. It has also been suggested that higher the S-nucleophilicity of the secondary accelerator lower will be the cure time[16]. Based on these findings, we decided to investigate the effect of 1-phenyl-3-(N,N'-diphenyl amidino)thiourea as a secondary accelerator in latex systems also.

4.2 EXPERIMENTAL

We selected TMTD as the primary accelerator and compared the properties of the TMTD-ATU systems with those of TMTD-TU systems. We also compared the properties of the TMTD-ATU systems with systems containing TMTD alone and ZDC alone as accelerators. In order to study the effect of fillers on these systems under review, we used precipitated silica, precipitated calcium carbonate and china clay. Latex films were cast using these fillers and their vulcanization properties were investigated.

The compounding ingredients were added to latex as aqueous solutions/dispersions. The dispersions were prepared using a ball mill. The materials were made to disperse in water by grinding action and the dispersing agent was used to prevent the dispersed particles from reaggregating. The details of the preparation of dispersions are given in chapter II. For the present study high ammonia (HA) type latex was used, the specifications of which are also given in chapter II. It was de-ammoniated to about 0.3% by stirring in a laboratory type de-ammoniation tank for 3 hrs. The total alkalinity of latex as percentage of ammonia was estimated according to ASTM D 1076-88.

Mixing of ingredients with NR latex was done in the following order: stabilizing agent, sulphur, accelerator, filler and zinc oxide[9]. Mixing was done in a glass vessel and stirred for homogenization using a laboratory stirrer at 20-30 rpm. It was occasionally stirred during storage in order to prevent settling of ingredients. The latex compound was then matured for 24 hours. The latex films were then cast in glass cells as described in ASTM D 1076-88. These glass cells with the latex were placed on a levelled table and dried overnight at ambient temperature.

The vulcanization of the latex film was carried out in a laboratory air oven at 120°C. The time for optimum cure was determined by vulcanizing the film for different durations of time and determining the tensile strength of the vulcanizate in each case. The optimum cure time was taken as the time for attaining maximum tensile strength. The tensile properties of the vulcanized latex films were determined using a Zwick Universal Testing Machine as per ASTM D 412-87 (method A). The ageing resistance was evaluated by keeping the specimen in an air oven at 70°C for seven days. The total chemical crosslink density of the sample was determined by swelling the sample in toluene[10,11]. Latex films containing china clay, precipitated silica and precipitated calcium carbonate were also cast, inorder to investigate the effect of fillers.

Formulations of the different mixes used in the present study are given in Tables 4.1 and 4.2. The weight of various ingredients shown are wet weights in grams. Table 4.1 shows the gum formulations. Mixes A and B contained TMTD and ZDC alone as accelerator, respectively. Mix C contain TMTD and thiourea equivalent to 1 phr each. Mixes D, E and F contain varying amounts of ATU viz., 0.5, 1.0 and 1.5 phr with 1 phr of TMTD. Mix G contain 2 phr of ATU alone as accelerator but it did not cure properly. So this mix was not studied further. Formulations

Table 4.1 Formulations of mixes without filler

Ingredients	wet weight in g.						
	A	B	C	D	E	F	G
60% NR latex	167	167	167	167	167	167	167
10% KOH	1	1	1	1	1	1	1
10% Potassium oleate	0.5	0.5	0.5	0.5	0.5	0.5	0.5
50% Sulphur	3	3	3	3	3	3	3
33% TMTD	6	-	3	3	3	3	-
50% ZDC	-	4	-	-	-	-	-
10% TU	-	-	10	-	-	-	-
10% ATU	-	-	-	5	10	15	20
50% ZnO	1	1	1	1	1	1	1

Table 4.2 Formulations of mixes with filler

Ingredients	wet weight in g.																	
	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	V	W	X	Y
60% NR latex	167	167	167	167	167	167	167	167	167	167	167	167	167	167	167	167	167	167
10% KOH	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
10% Potassium oleate	0.5	0.5	0.5	0.5	0.5	0.5	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% Sulphur	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
33% TMTD	6	-	3	3	3	3	6	-	3	3	3	3	6	-	3	3	3	3
50% ZDC	-	4	-	-	-	-	-	4	-	-	-	-	-	4	-	-	-	-
10% TU	-	-	10	-	-	-	-	-	10	-	-	-	-	-	10	-	-	-
10% ATU	-	-	-	5	10	15	-	-	-	5	10	15	-	-	-	5	10	15
50% ZnO	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
50 % Clay	30	30	30	30	30	30	-	-	-	-	-	-	-	-	-	-	-	-
50% Silica	-	-	-	-	-	-	30	30	30	30	30	30	-	-	-	-	-	-
50% calcium carbonate	-	-	-	-	-	-	-	-	-	-	-	-	30	30	30	30	30	30

of mixes containing fillers are given in Table 4.2. Mixes H-M, N-S and T-Y contain china clay, precipitated silica and precipitated calcium carbonate respectively.

4.3 RESULTS AND DISCUSSION

4.3.1 Cure characteristics

Optimum cure time of different mixes were estimated by plotting tensile strength against time. The time to reach maximum tensile strength is taken as the optimum cure time. The results of the various experimental observations indicate clearly that ATU can function as an effective secondary accelerator with TMTD in NR latex system. It does not cause coagulation or destabilization of the latex. As observed in the case of dry NR systems, ATU alone is not able to function as an accelerator in latex systems also. Fig. 4.1 show the variation of tensile strength with time, of mixes A-F. Table 4.3 shows the optimum cure time estimated and maximum tensile strength obtained. A bar graphical comparison of the cure time of the mixes are shown in Fig. 4.2. Mix A contained 2 phr of TMTD alone as accelerator and this mix showed the highest value for cure time compared to other mixes. Thiurams when used alone are known to be slow curing in latex systems[11]. But the accelerating activity of thiurams can be increased markedly by the incorporation of thiourea, as suggested by Philpot[14]. This is evident from the present investigation also. Mix C which contain 1 phr TMTD and 1 phr TU showed much lower cure time compared

Table 4.3 Optimum cure time and maxumum tensile strength of mixes without filler (cured at 120°C)

Mix No.	Optimum cure time (min.)	Maximum Tensile Strentgh (MPa)
A	40.0	25.03
B	33.3	27.00
C	32.0	23.07
D	34.6	28.75
E	31.0	26.00
F	28.3	26.67

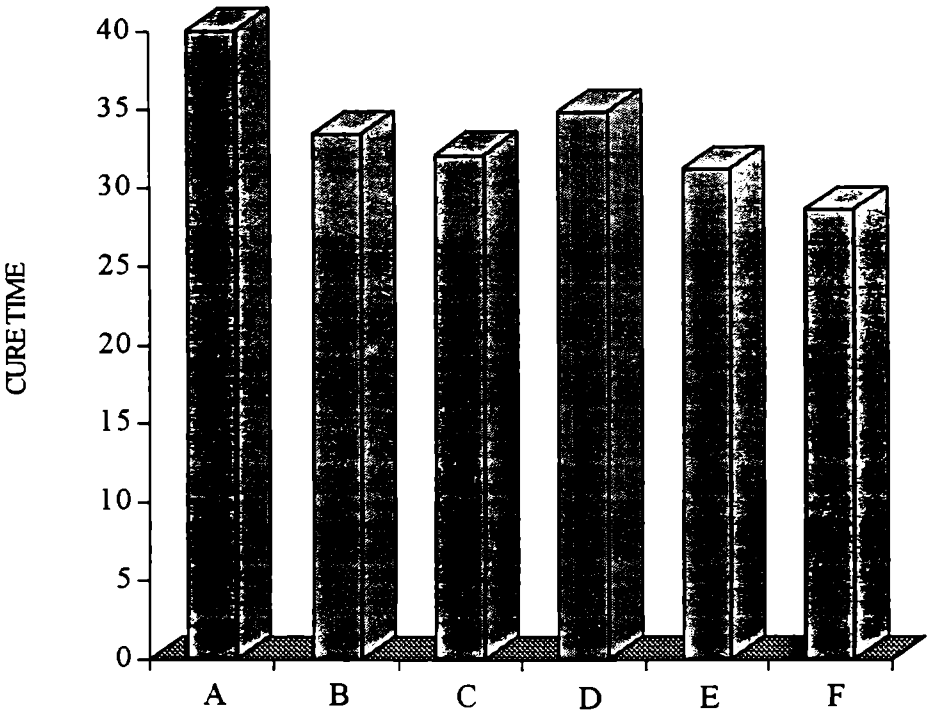

Fig. 4.2 Comparison of optimum cure time of various mixes

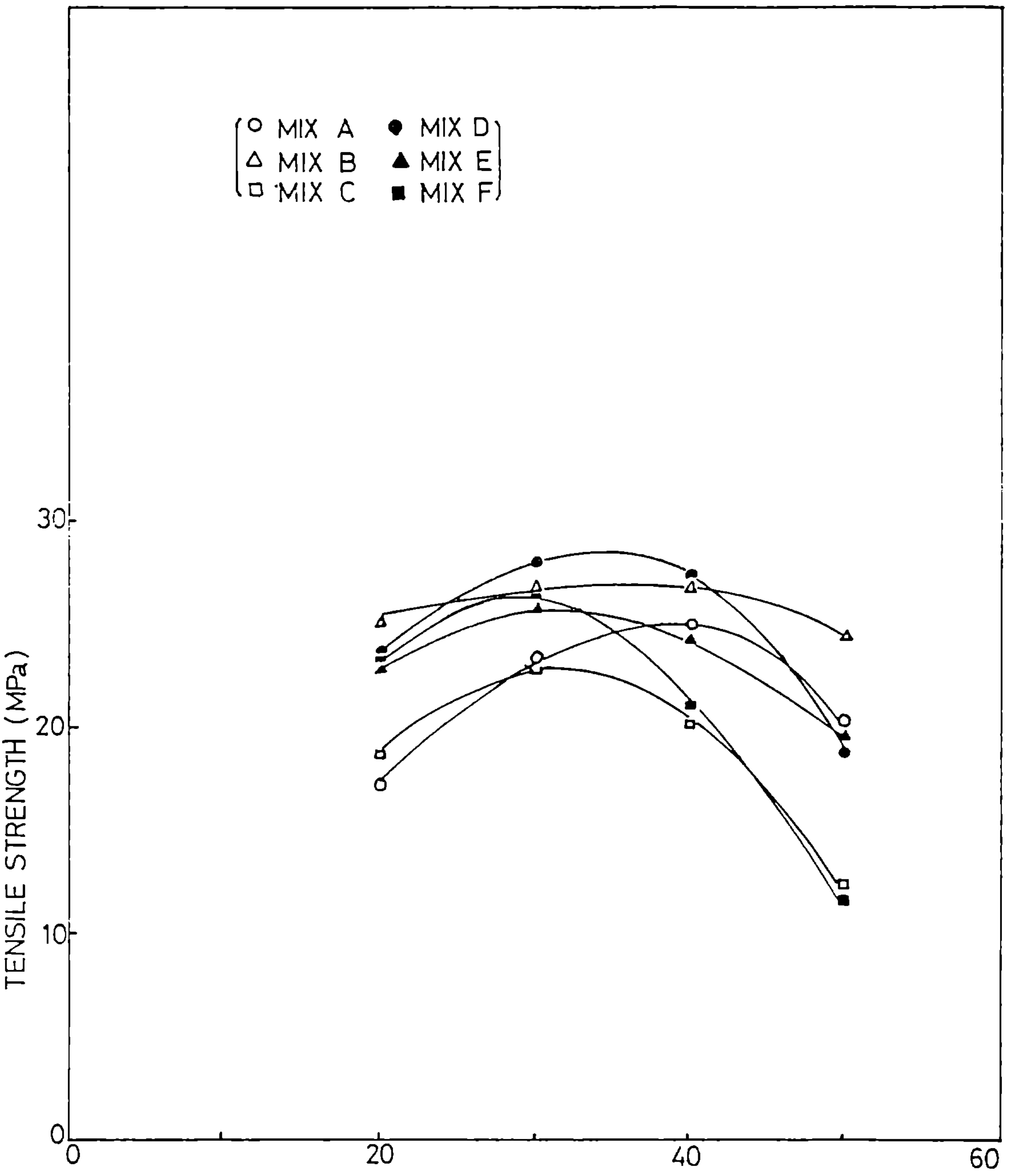

Fig. 4.1 Variation of tensile strength with time of cure of vulcanizates without filler

to mix A. This can be explained on the basis of the nucleophilic attack by the thiourea molecule which enhances the S-S bond cleavage of the thiuram disulphide leading to a faster cure as explained in chapter I. It has also been suggested that higher the nucleophilic character of the attacking agent faster will be the cure[14]. Comparison of the optimum cure time of TMTD-ATU (mix E) and TMTD-TU (mix C) systems, showed a lower value for the former. ATU being more nucleophilic compared to TU showed a faster cure. This gives further evidence to the proposed nucleophilic mechanism of the activity of the secondary accelerator. Mix B which contain 2 phr ZDC as accelerator, showed optimum cure time very near to that of TMTD ATU (mix E) system. ZDC is one of the most widely used accelerators in NR latex systems[11]. It seems that in ZDC systems the nucleophilic reaction mechanism is not applicable. It is also observed that among TMTD-ATU systems the optimum cure time decreases with increase in the amount of ATU. Thus going from mix D to F, containing 0.5, 1.0 and 1.5 phr ATU, the optimum cure time showed a steady decrease.

4.3.2 Tensile properties

The tensile properties of the gum vulcanizates are given in Table 4.4. A bar graphical comparison of the tensile strength of samples from various systems before and after ageing are given in Fig. 4.3. Regarding tensile strength before ageing, the TMTD-

Table 4.4 Tensile properties and crosslink density of mixes without filler

Mix No.	Tensile strength (MPa)			300% Modulus (MPa)			Elongation at break (%)			Tear Strength (N/mm)	Total crosslink density x 10^5 g mol/cm^3
	Before ageing	After ageing	Retention %	Before ageing	After ageing	Retention %	Before ageing	After ageing	Retention %		
A	25.03	4.36	17.4	2.08	2.46	118.2	732.2	431.15	58.18	33.31	4.9716
B	27.00	22.20	84.5	2.61	2.92	111.8	820.71	798.50	97.20	42.40	5.3704
C	23.07	17.54	76.0	1.16	1.98	170.6	995.47	877.15	88.10	36.93	5.1904
D	28.75	19.95	69.4	1.75	2.27	129.7	829.5	807.26	97.30	38.48	5.8794
E	26.00	22.91	88.1	1.53	2.29	149.6	987.0	778.72	78.90	42.90	4.9827
F	26.67	22.48	84.3	1.92	2.16	112.5	924.6	795.00	86.00	37.91	4.9419

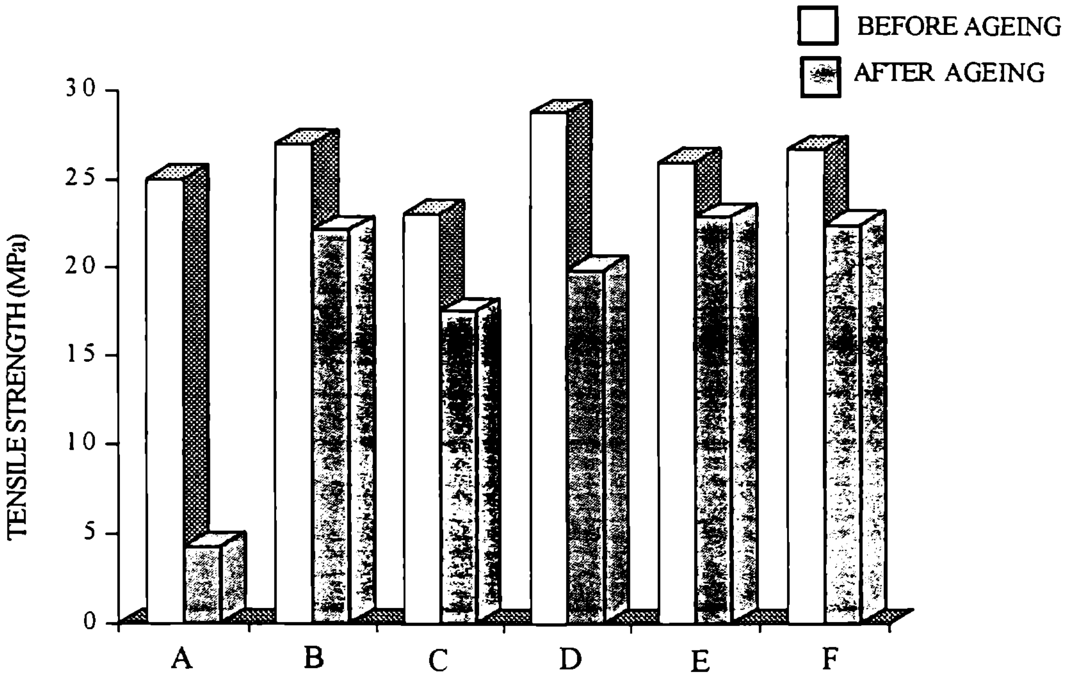

Fig. 4.3 Comparison of tensile strength before and after ageing (vulcanizates without filler)

ATU systems show better values compared to the reference mixes. Mix D containing 0.5 phr of ATU with 1 phr of TMTD showed the highest value for tensile strength. Moreover all the TMTD-ATU systems showed better values of tensile strength compared to TMTD-TU (mix C). The ageing resistance of the vulcanizates were determined by heating the samples in an air oven at 70°C for seven days. It is clear from the results that the heat ageing resistance of the TMTD-ATU systems are comparable with that of reference systems. Vulcanizate with TMTD alone (mix A) showed very poor ageing resistance. With increase in the concentration of ATU, it is found that, the tensile strength decreases first and then remains more or less the same. This behaviour may also be correlated to the variation in total crosslink density of the vulcanizates. Regarding modulus (300%) the systems with ATU showed lower values compared to mix C. After ageing the modulus increases for all systems showing corresponding decrease in elongation values. Figs. 4.4 and 4.5 show the variation in tensile strength, 300% modulus and elongation at break, with concentration of ATU before and after ageing. Table 4.4 also gives the tear strength of various vulcanizates. The tear strength values of TMTD-ATU vulcanizates are found to be better than those of A and C.

The total chemical crosslink density of the samples was estimated by swelling the samples in toluene and the values are given in Table 4.4. Mix D containing 1 phr of TMTD and 0.5 phr of ATU showed the highest value for crosslink density. This

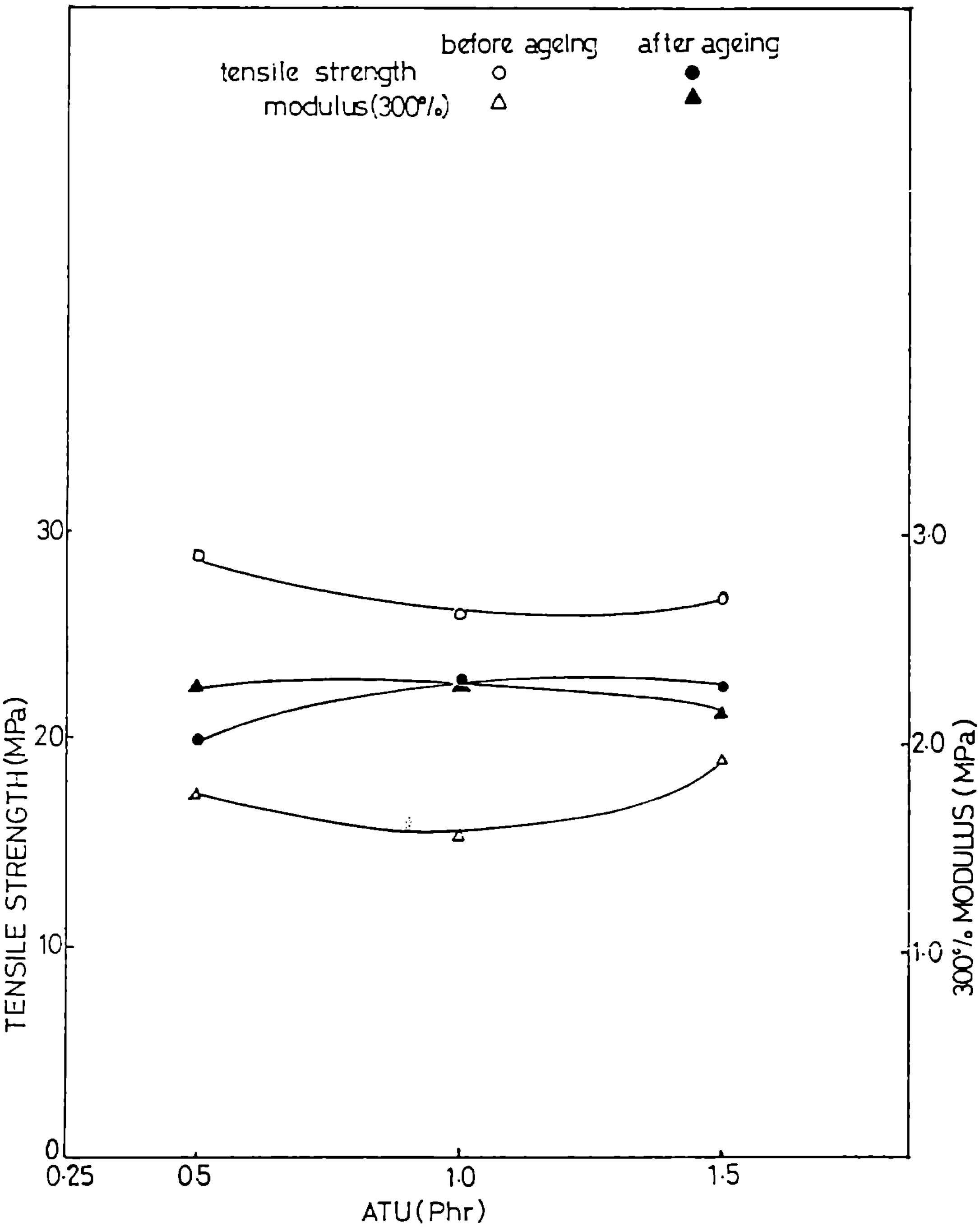

Fig. 4.4 Variation of tensile strength and modulus (300%) with concentration of ATU, before and after ageing

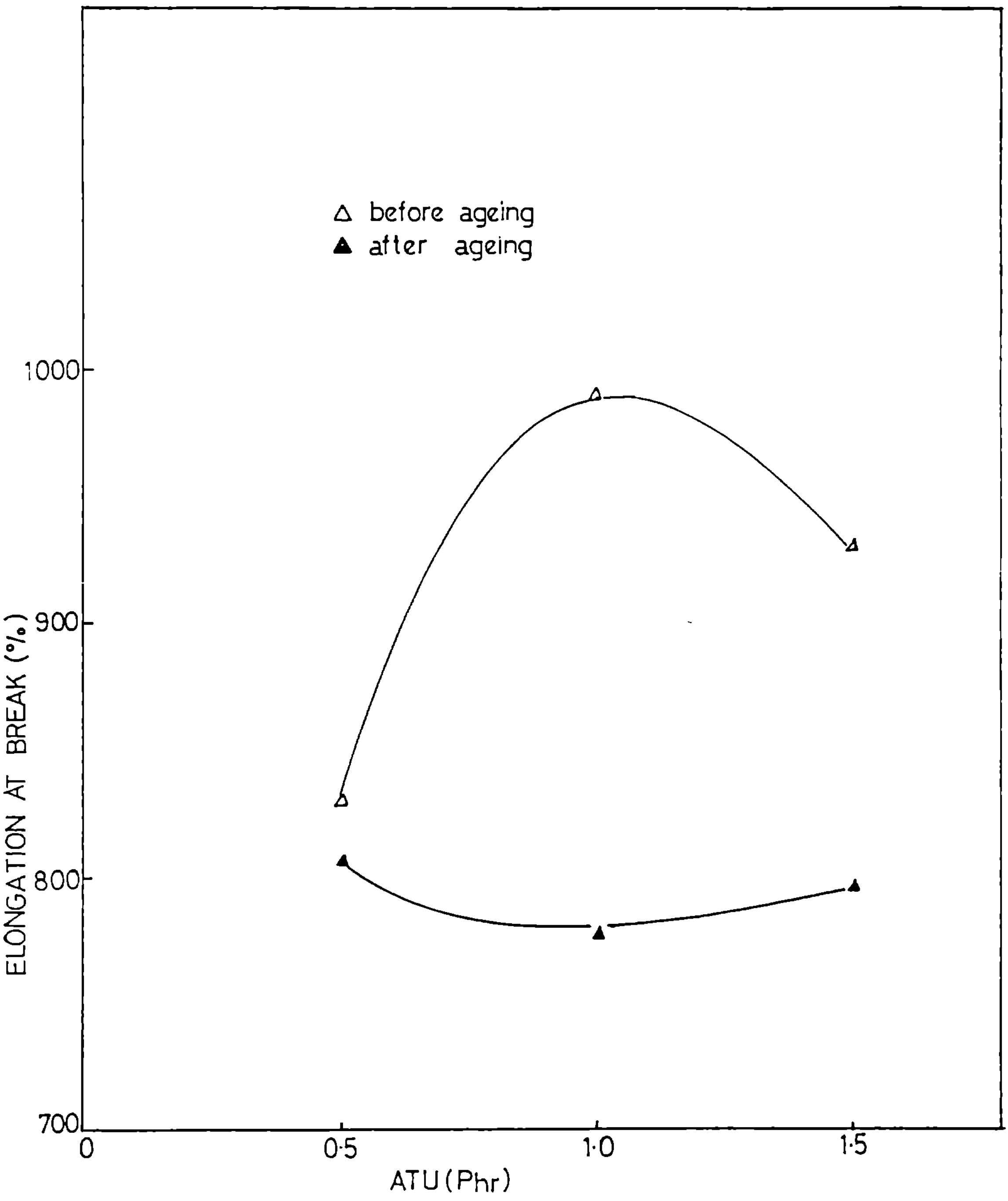

Fig. 4.5 Variation of elongation at break with concentration of ATU, before and after ageing

mix also showed better tensile properties. With increase in concentration of ATU upto 1.5 phr, the crosslink density decreases and then remains more or less the same.

4.4 Effect of Fillers

Having found that ATU can function as an effective secondary accelerator in latex systems without fillers, we investigated the effect of fillers also in these systems. The various fillers used are china clay, precipitated silica and precipitated calcium carbonate. The formulations of different mixes used are given in table 4.2. All mixes contain 15 phr of the respective filler. Here also the optimum cure time for various mixes is determined by plotting tensile strength against time, and the time taken for maximum tensile strength is taken as the optimum cure time. Mixes were also prepared varying the amount of ATU for all the three types of fillers. The optimum cure time and maximum tensile properties obtained for various mixes are given in Table 4.5. The tensile strength before and after ageing and tear strength values are given in Table 4.6. It is seen from the results that addition of fillers weaken the latex films. The same trend is observed in the case of all the three fillers used. As suggested earlier this results from the poor rubber-filler interactions in latex vulcanization. Also it is observed that incorporation of filler, in general, increases the cure time. This is also explained to be due to adsorption of accelerator molecules on filler particles.

Table 4.5 Optimum cure time and maximum tensile strength of mixes with filler

Mix No.	Optimum cure time (min.)	Maximum tensile strength (MPa)
H	41.6	22.04
I	36.6	24.86
J	37.6	20.86
K	40.0	23.82
L	39.0	24.52
M	35.0	22.63
N	43.5	23.26
O	40.0	24.86
P	38.2	21.74
Q	41.6	25.62
R	40.0	25.69
S	38.0	22.52
T	42.3	21.69
U	38.0	23.65
V	36.6	21.80
W	42.3	24.62
X	40.0	22.29
Y	38.3	19.73

Table 4.6 Tensile properties of filled vulcanizates

Mix No.	Tensile strength (MPa)			300% Modulus (MPa)			Elongation at break (%)			Tear Strength (N/mm)
	Before ageing	After ageing	Retention %	Before ageing	After ageing	Retention %	Before ageing	After ageing	Retention %	
H	22.04	7.31	33.2	1.28	2.50	195.0	976.00	544.28	55.80	42.40
I	24.86	21.79	87.7	1.83	3.98	217.0	881.60	727.41	82.50	50.90
J	20.86	19.79	94.8	2.55	4.01	157.0	895.71	619.95	69.20	48.08
K	23.82	18.44	77.4	2.79	3.08	110.4	753.60	707.26	93.80	42.90
L	24.52	18.16	74.1	2.33	3.18	136.0	861.24	727.41	84.50	37.91
M	22.63	15.46	68.3	1.63	3.94	239.0	914.78	575.36	62.90	55.48
N	23.26	16.37	69.8	2.12	2.17	102.4	879.00	786.66	89.40	64.88
O	24.86	22.04	88.7	1.83	4.86	238.5	881.68	600.00	68.00	67.44
P	21.74	16.69	76.8	2.24	4.42	197.3	791.95	604.11	76.28	58.32
Q	25.62	20.31	79.3	2.01	4.45	221.3	868.71	633.72	73.00	65.40
R	25.69	22.19	86.4	1.92	2.97	154.7	871.18	733.63	84.20	61.69
S	22.52	17.43	77.4	2.03	2.26	111.3	803.75	743.85	92.50	45.72
T	21.69	12.04	55.5	2.26	2.36	104.0	903.00	673.50	74.60	56.18
U	23.65	21.23	89.8	2.28	2.87	125.8	812.93	780.15	96.00	46.32
V	21.8	20.20	92.7	1.72	4.06	236.0	869.00	620.30	71.40	52.03
W	24.62	20.87	84.8	3.00	4.45	148.3	739.62	653.72	88.40	61.48
X	22.29	17.91	80.3	2.61	3.03	116.1	740.12	654.00	88.46	57.92
Y	19.73	17.00	86.2	2.90	2.97	102.4	683.35	644.00	94.24	48.63

Irrespective of the nature of the filler used, the mixes containing TMTD alone as accelerator (mixes H. N and T) showed the highest values of the cure time compared to other mixes. But when a binary system of TMTD-TU or TMTD-ATU is used a considerable decrease in cure time is observed. Figs. 4.6-4.8 show the variation in tensile strength with time. It is observed that in presence of fillers the TMTD-TU systems showed comparatively lower cure time to the corresponding TMTD-ATU systems. ATU being more nucleophilic compared to TU, this is contradictory to what is observed in gum systems. This is probably due to the increased adsorption of ATU molecules on the filler particles compared to thiourea. It is also observed that the optimum cure time decreases with increase in the amount of ATU. The same trend is observed for all the three fillers. The tensile properties estimated are given in Table 4.6. Compared to gum formulations filled systems showed lower tensile strength but at the same time modulus is seen to increase and elongation at break showed lower values. Figs. 4.9-4.11 show the variation of tensile strength, 300% modulus and elongation at break, before and after ageing, with the amount of ATU. With increase in concentration of ATU the tensile strength do not show much variation both before and after ageing. For the clay filled vulcanizates the 300% modulus decreases with concentration of ATU before ageing and after ageing the reverse trend is observed. For the other two fillers modulus remains more or less the same with concentration of ATU before ageing. But after ageing it is seen to decrease.

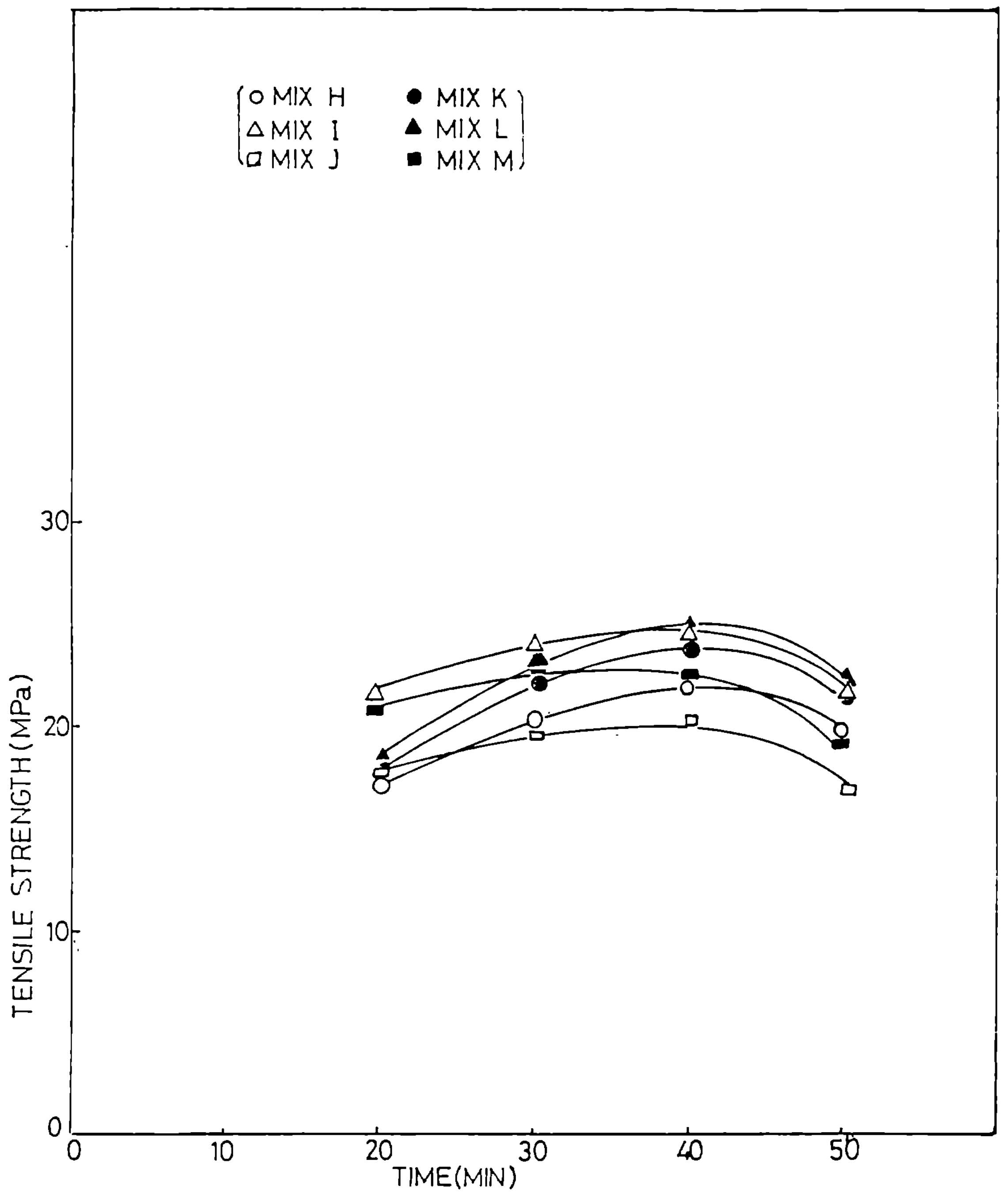

Fig. 4.6 Variation of tensile strength with time of cure of clay filled vulcanizates

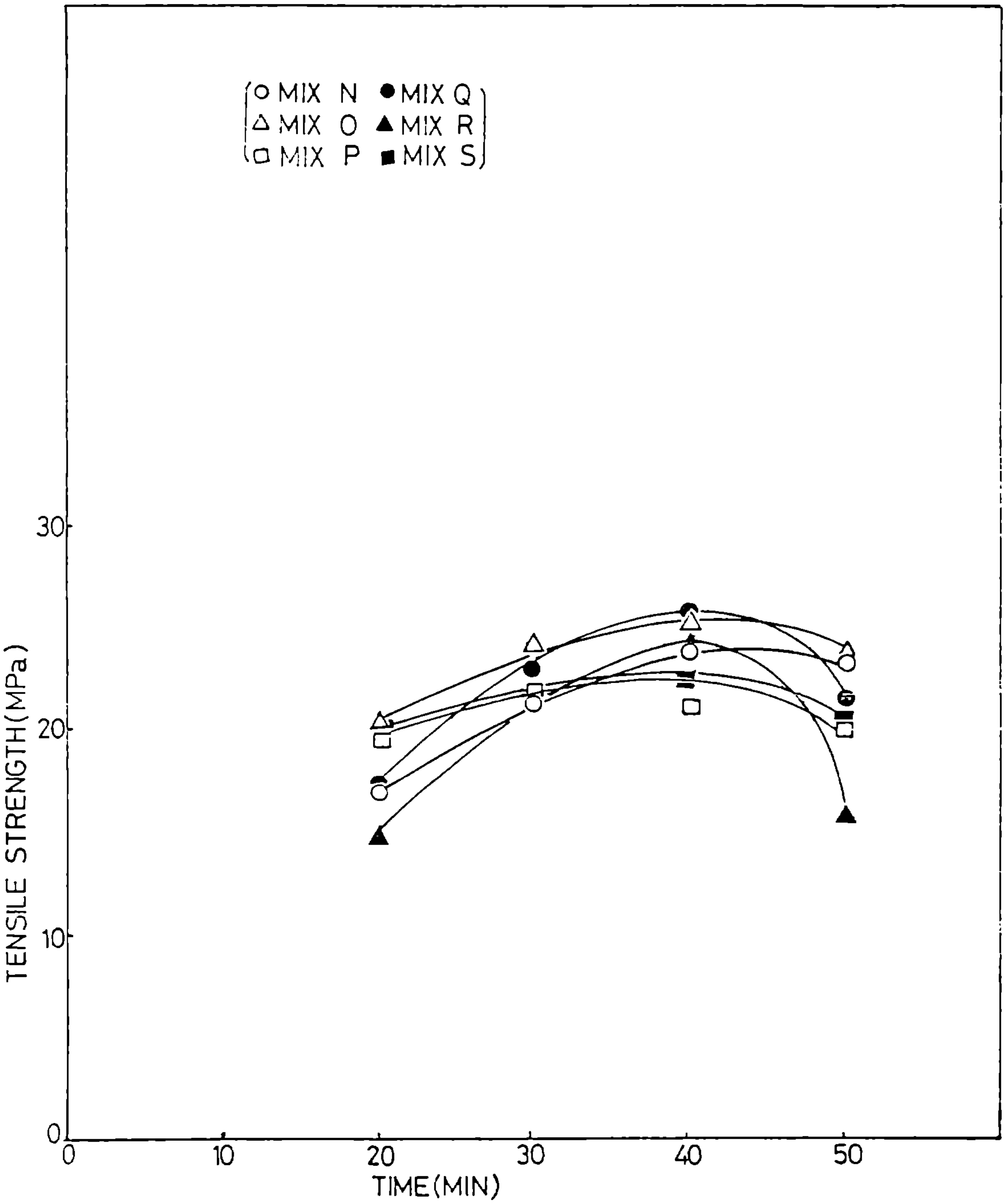

Fig. 4.7 Variation of tensile strength with time of cure of silica filled vulcanizates

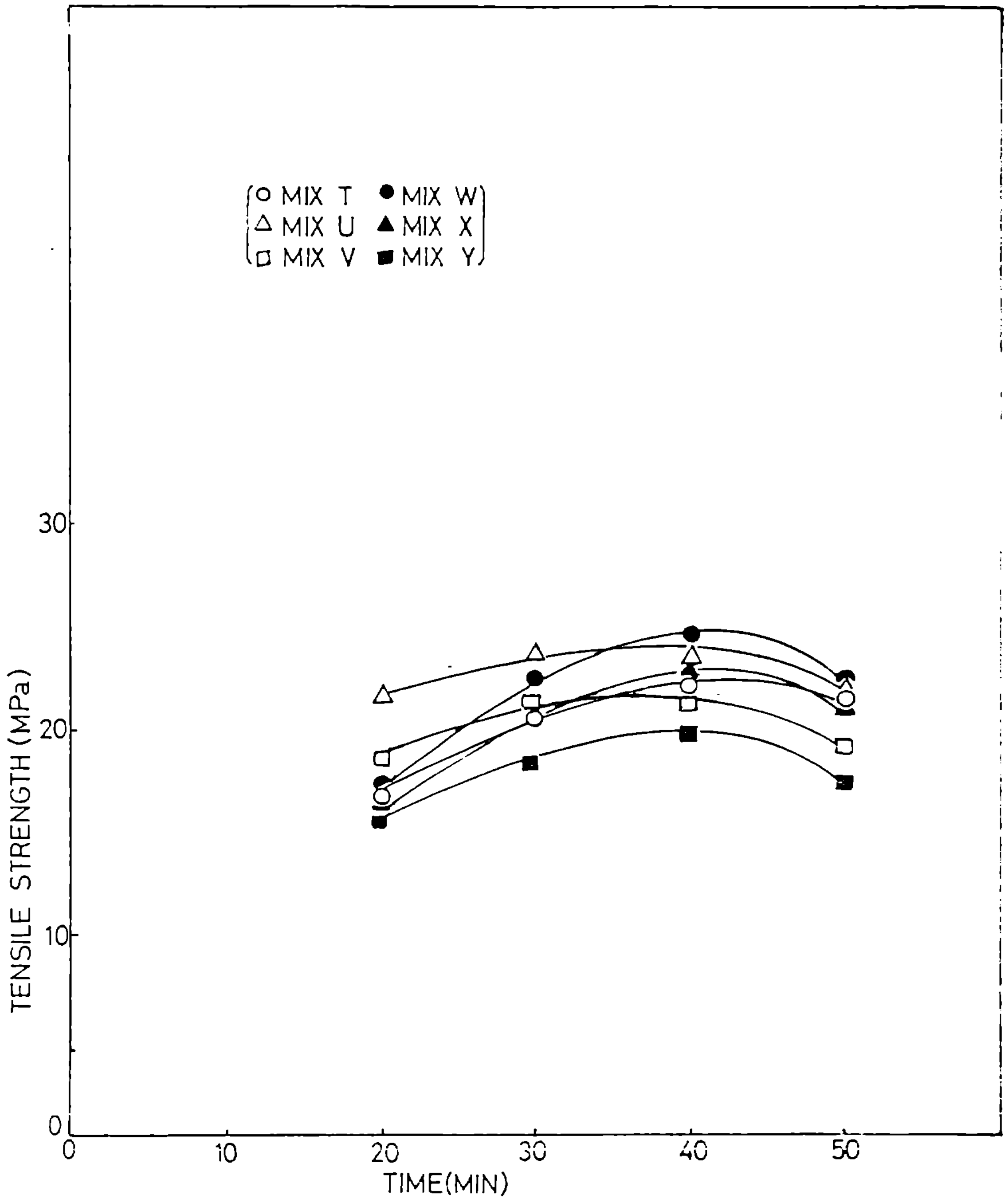

Fig. 4.8 Variation of tensile strength with time of cure of calcium carbonate filled vulcanizates

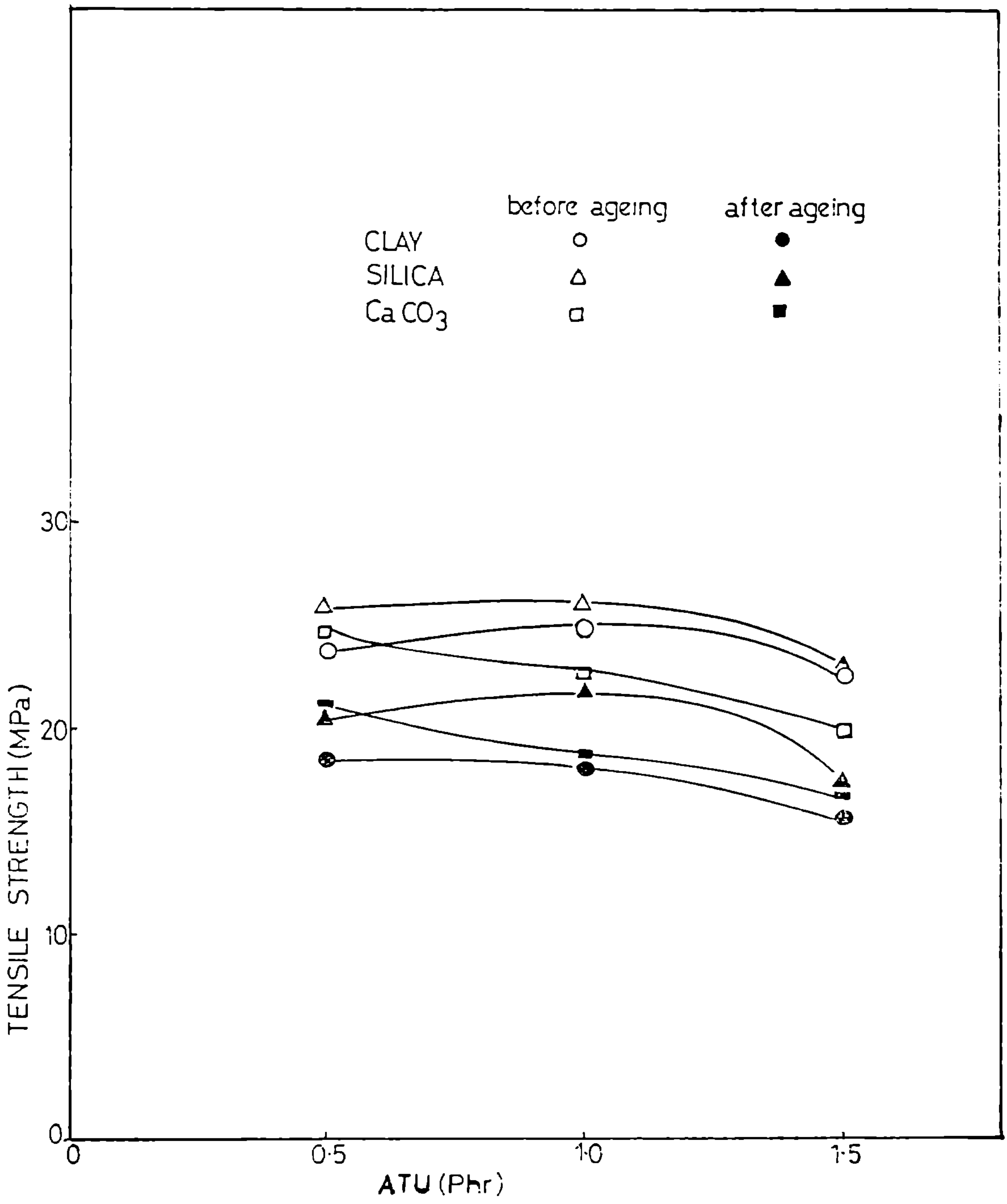

Fig. 4.9 Variation of tensile strength of filled vulcanizates with concentration of ATU, before and after ageing

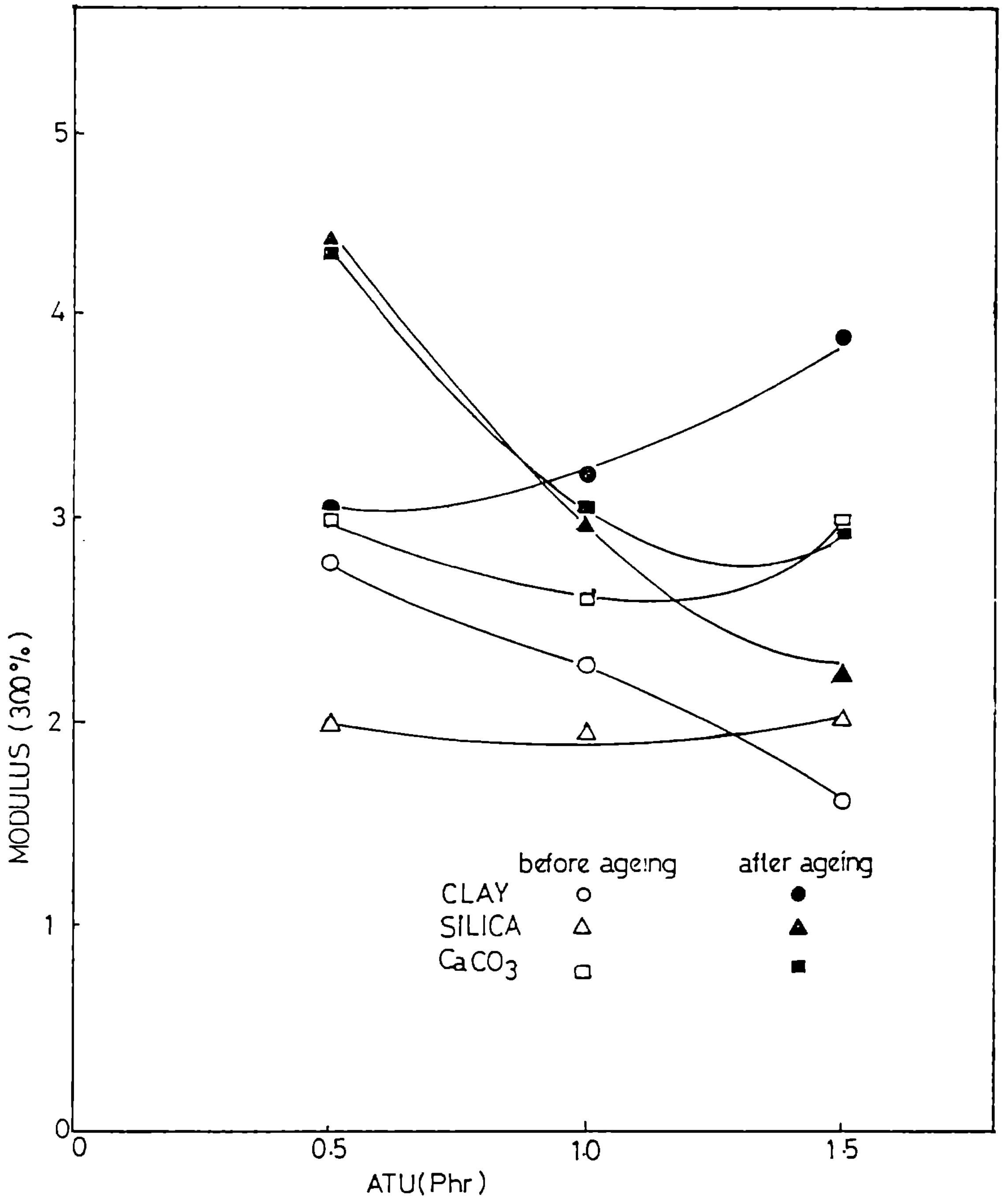

Fig. 4.10 Variation of modulus (300%) of filled vulcanizates with concentration of ATU, before and after ageing

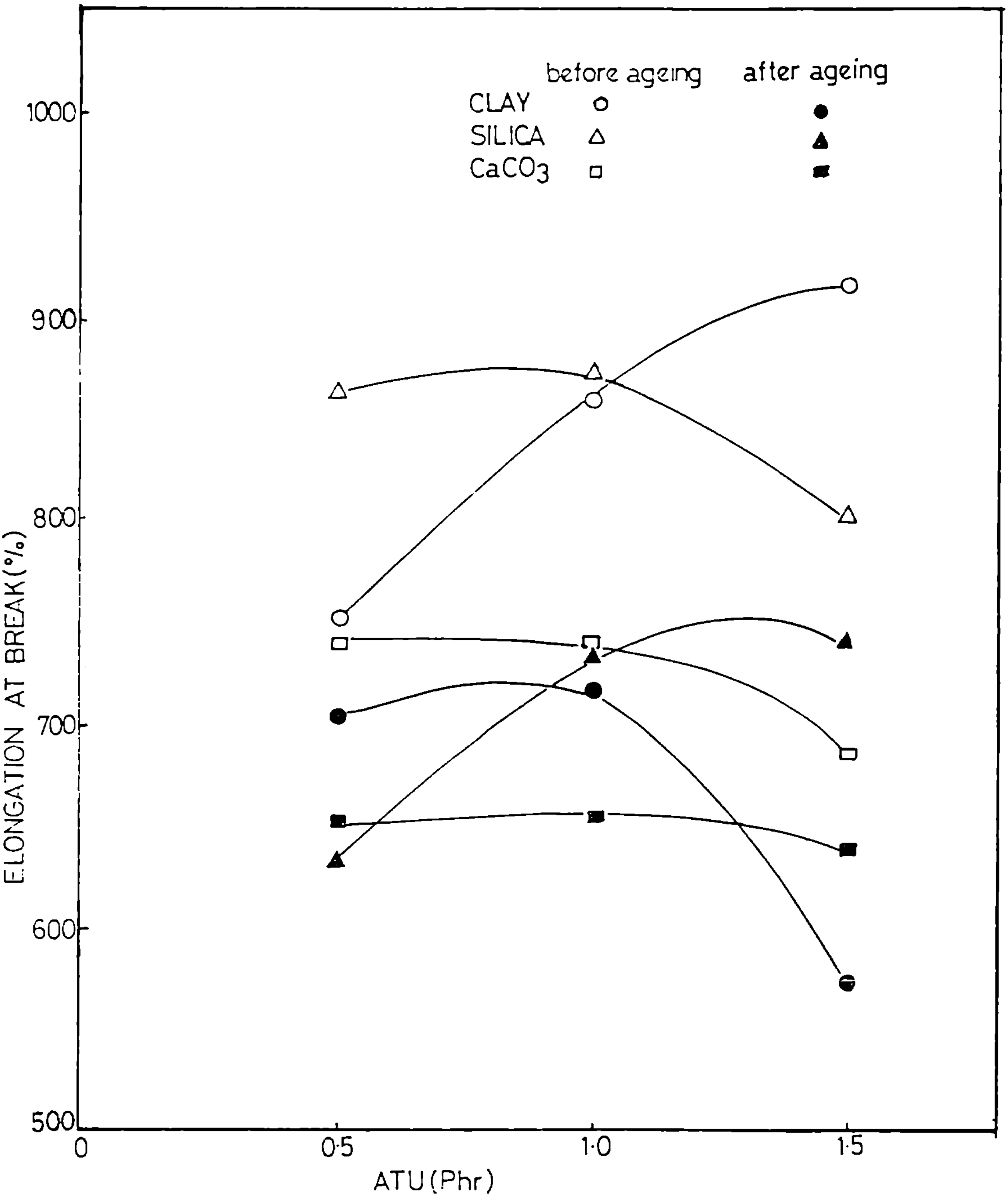

Fig. 4.11 Variation of elongation at break of filled vulcanizates with concentration of ATU, before and after ageing

4.5 Conclusion

From this study it is clear that 1-phenyl-3-(N,N'-diphenyl amidino)thiourea can be used as a safe and effective secondary accelerator along with TMTD in NR latex systems. The main disadvantage of ATU when used in dry rubber is its scorchiness at higher concentrations. But in latex systems the use of ATU is much safer Also the behaviour of the TMTD-ATU binary system is better than/comparable to that of the ZDC systems which are known to be very effective in latex vulcanization. The tensile properties of vulcanizates containing TMTD-ATU showed better values compared to the reference mixes in gum formulations. Moreover the TMTD-ATU system showed lower optimum cure times compared to TMTD-TU systems. These results point to a nucleophilic reaction mechanism of the secondary accelerator. However, when fillers are incorporated much favourable properties are not observed. This may be attributed to the adsorption of accelerator molecules on the filler particles. The behaviour of these filled systems are similar to that generally observed in the filled systems of natural rubber latex.

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CHAPTER V

STUDIES ON BINARY SYSTEMS CONTAINING ATU IN SULPHUR VULCANIZATION OF SBR

In view of the fact that 1-phenyl-3-(N,N'-diphenyl amidino)thiourea (ATU) exhibited definite accelerating activity in dry natural rubber and natural rubber latex, we thought it worthwhile to investigate the accelerating effect of ATU in a synthetic rubber also This study was undertaken mainly because, a lot of differences exist in the compounding and vulcanization behaviour of natural rubber vis-a-vis synthetic rubbers[1] Compared to natural rubber synthetic rubbers are more uniform in quality and compounds are more consistent in both processing and product properties. They are also supplied at viscosity ranges which facilitate good dispersion of ingredients and ease of flow in extrusion, calendering and moulding. This saves both energy consumption and time and hence cost. It is also to be noted that mill mixing of synthetic rubbers is more difficult compared to natural rubber.

For the present investigation we selected styrene butadiene rubber. It is a general purpose synthetic rubber of large tonnage use. It is a copolymer of styrene and butadiene manufactured by polymerizing them under controlled conditions of reaction using different techniques of polymerization such as by emulsion or solution method[2] Both cold and hot polymerized styrene butadiene rubbers are marketed in numerous varieties under various trade names.

These brands differ from one another in the relative proportion of butadiene and styrene, amount of different initiating agents, emulsifiers, oils, fillers etc., and also on the temperature of polymerization The degree of unsaturation in SBR is less than that of natural rubber and the double bonds are less active chemically than the double bond of the isoprenoid unit in NR. Hence styrene butadiene rubbers are slower curing than NR and need either more accelerator or a more active accelerator system. Scorch problems are less likely with SBR than with natural rubber stocks

SBR possess lower green strength and gum tensile strength. This is due to its molecular irregularity and the presence of large pendent groups which prevent crystallization on stretching. To overcome this type of behaviour of SBR, incorporation of fine reinforcing filler is required. Addition of fillers increases tensile strength several times to that of gum vulcanizates[3] The processability of SBR depends mainly on the viscosity Lower viscosity grades band more easily on mills, incorporate fillers and oils more readily They show less heat generation during mixing and are more easily calendered, often give a higher extrusion rate than the higher viscosity grades On the other hand higher viscosity grades have better green strength, they tend to give porosity in the vulcanizate and at the same time accept higher filler and oil loading which is attractive pricewise. The vulcanizates of high molecular weight SBR show higher resilience and an improvement in the mechanical properties particularly tensile strength and compression set. The method of compounding of styrene butadiene rubber is more or less similar to that of natural rubber and other unsaturated hydrocarbon rubbers[2] Mastication prior to compounding is required for both NR and many types of SBR. The increase of temperature during mastication leads to degradation of NR to some extent while SBR is not much degraded. The combination of zinc oxide and stearic acid is the most common activator used for SBR and the amount of activator used is same for both NR and SBR. But at the same time, the concentration of accelerator and sulphur used are different for both rubbers. Compounding recipes with low sulphur or with only organically bound sulphur leads to vulcanizates with better ageing properties but are slower curing. Suitable accelerator combinations can be used, that speed-up slow curing stocks and at the same time reduces scorch problems As in the case of natural rubber, sulphur vulcanization of SBR involves heating it with accelerator, activator, co-activator, anti-oxidant, fillers, processing oils etc. to obtain products of required properties

SBR used in the present study is synaprene 1502 It is a non-staining cold rubber and gives good physical properties in either black or light coloured products. It has high loading capacity and is used in the manufacture of tyres, moulded and extruded products, footwears, coated fabrics etc. TMTD can be used as a primary accelerator in the normal sulphur vulcanization of this SBR. It imparts the vulcanizates relatively good mechanical and ageing properties. High proportions of TMTD with small quantity of sulphur improves heat resistance. For soft vulcanizates thiazole and sulphenamides are used as primary accelerators while guanidines, thiurams and dithiocarbamates are used as secondary accelerators. For low modulus, guanidines are preferred, as thiurams and dithiocarbamates always give high modulus stocks and are fast curing[4] Only guanidines have synergistic effect on thiazole and sulphenamides. While other secondary accelerators have only additive effect[4] For SBR stocks sulphenamides are the best for balanced rate of cure, safety and physical properties. Thiurams alone with normal amount of sulphur are too scorchy So also dithiocarbamates. TMTD based SBR vulcanizates usually have a tendency to bloom and also impart odour Sulphur is a versatile curing agent for SBR also, but in comparison with NR the dosages required are lower

In the present investigation we used 1-phenyl-3-(N,N'-diphenyl amidino)thiourea as a secondary accelerator in the sulphur vulcanization of SBR with MBTS/TMTD as primary accelerator. Secondary accelerators such as thiourea (TU) or DPG were used for comparison and the results obtained were compared with that of ATU In order to investigate the effect of ATU on filled systems, vulcanizates were also prepared with carbon black, precipitated silica and china clay.

PART I

5.1 SBR GUM VULCANIZATES

5.1.1 EXPERIMENTAL

SBR gum compounds were prepared using ATU as secondary accelerator along with MBTS/TMTD as primary accelerator. The following systems were taken as reference formulations: MBTS-TU, TMTD-TU, MBTS-DPG, TMTD-DPG, MBTS-TMTD, MBTS alone and TMTD alone. Table 5 1 show the composition of mixes with MBTS Mixes L_1-L_3 contain ATU ranging from 0 5 to 1 5 phr with 1 phr MBTS Mix M_1 contain 2 phr MBTS only as accelerator Table 5.2 gives formulation of mixes with TMTD Mixes N_1-N_3 contain ATU ranging from 0 5 to 1.5 phr with 1 phr TMTD Mix O_1 contain 2 phr of TMTD alone as accelerator

As detailed in chapter II, the mixes were prepared on a laboratory size two toll mixing mill as per ASTM D 3182-89 Goettfert elastograph, model 67 85 was used to determine the cure characteristics (at 150 °C) of the various mixes. The compounds were then vulcanized upto the optimum cure time in an electrically heated laboratory type hydraulic press at 150 °C at a pressure of 140 Kg cm^{-2} The tensile properties of the vulcanizates were determined using a Zwick Universal Testing Machine, model 1445 Heat ageing resistance of the vulcanizates was studied by ageing the samples for 48 hrs at 100 °C in a laboratory air oven (ASTM D 573-88)

Table 5.1 Formulations of SBR gum (MBTS) mixes

Ingredients	L_1	L_2	L_3	M_1	M_2	M_3	M_4
SBR	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
MBTS	1	1	1	2	1	1	1
TMTD	—	—	—	—	1	—	—
ATU	0.5	1.0	1.5	—	—	—	—
TU	—	—	—	—	—	1	—
DPG	—	—	—	—	—	—	1
Sulphur	1.5	1.5	1.5	1.5	1.5	1.5	1.5

Table 5.2 Formulations of SBR gum (TMTD) mixes

Ingredients	N_1	N_2	N_3	O_1	M_2	O_3	O_4
SBR	100	100	100	100	100	100	100
Zinc oxide		5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2
TMTD	1	1	1	2	1	1	1
MBTS	—	—	—	—	1	—	—
ATU	0.5	1.0	1.5	—	—	—	—
TU	—	—	—	—	—	1	—
DPG	—	—	—	—	—	—	1
Sulphur	1.5	1.5	1.5	1.5	1.5	1.5	1.5

Angular test specimens were used to measure the tear resistance according to ASTM D 624-86 Compression set and hardness were measured as per ASTM D 395-89 (method B) and D 2240-86 respectively Abrasion resistance was measured using DIN abrader (DIN 53516). The total chemical crosslink density was estimated by swelling the samples in toluene.

5.1.2 RESULTS AND DISCUSSION

5.1.2.1 Cure characteristics

Tables 5 3 and 5 4 show the cure characteristics of various mixes. The cure curves are given in Figs. 5 1 and 5.2 The results obtained in the present study provide a clear indication of the accelerating effect of ATU in sulphur vulcanization of styrene butadiene rubber. In this case also it was found that ATU alone cannot function as an accelerator Unlike in NR, when 2 phr of MBTS alone (mix M_1) is used as accelerator, it gave very long cure time and very poor cure rate (Fig 5 1). This is in accordance with the differences in the vulcanization behaviour that exist between NR and SBR with respect to the use of accelerator But when equivalent amounts of MBTS and ATU (Mix L_2) is used appreciable reduction in cure time and induction time is observed. Correspondingly the cure rate also showed an increase which is indicative of the accelerating activity of ATU in SBR gum systems. Comparing the the mixes containing 1 phr of MBTS and 1 phr each of ATU (mix L_2) and TU (mix M_3), the one containing ATU showed lower

Table 5.3 Cure charateristics of MBTS systems

	L_1	L_2	L_3	M_1	M_2	M_3	M_4
Optimum cure time, t_{90}(min)	25.40	17.20	10.10	25.00	16.20	20.10	13.60
Scorch time, t_{10}(min)	8.50	3.90	2.20	11.00	3.90	3.00	6.30
Induction time t_5(min)	7.60	2.70	1.80	11.40	3.30	2.70	5.70
Cure rate index	5.92	7.52	12.66	7.14	8.13	5.85	13.70
Min. torque (dNm)	0.21	0.28	0.31	0.20	0.21	0.22	0.25
Max. torque (dNm)	18.7	25.3	26.6	13.0	35.2	19.7	26.9

Table 5.4 Cure characteristics of TMTD systems

	N_1	N_2	N_3	O_1	M_2	O_3	O_4
Optimum cure time, t_{90}(min)	9.40	6.20	4.70	9.00	16.20	6.10	4.20
Scorch time, t_{10}(min)	2.10	1.80	1.20	2.40	3.90	1.50	2.40
Induction time t_5(min)	1.80	1.00	0.90	1.90	3.30	1.20	1.80
Cure rate index	13.70	22.73	28.57	15.15	8.13	21.74	55.56
Min. torque (dNm)	0.26	0.32	0.32	0.23	0.21	0.30	0.30
Max. torque (dNm)	34.00	32.00	30.20	40.80	35.20	29.00	34.60

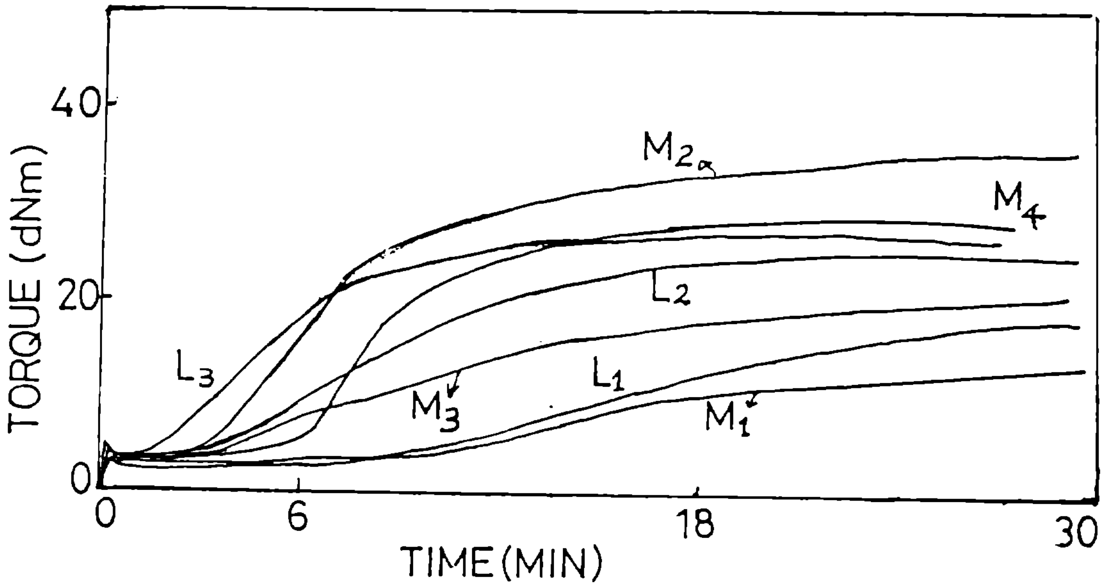

Fig. 5.1 Cure curves of mixes containing MBTS

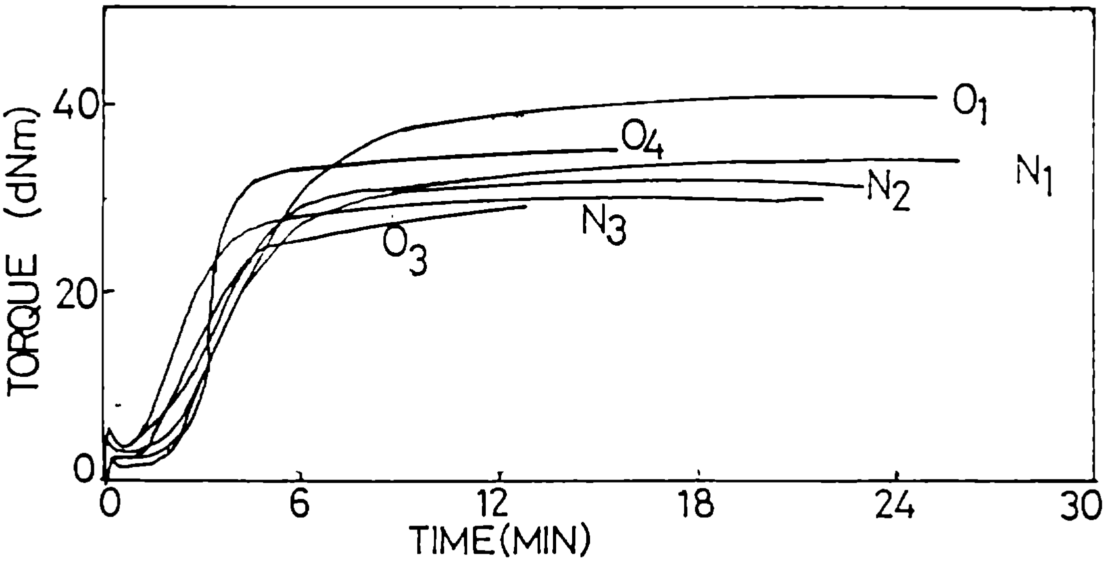

Fig. 5.2 Cure curves of mixes containing TMTD

cure time and higher cure rate. A bar graphical comparison of optimum cure time and induction time of various mixes are given in Figs. 5 3 and 5 4 ATU being more nucleophilic compared to thiourea, the nucleophilic reaction mechanism proposed in similar vulcanization reaction of NR can be envisaged in SBR systems also. As the amount of ATU is increased from 0 5 to 1 5 phr an appreciable reduction in cure time is observed with a corresponding increase in cure rate. But at the same time, scorch time also reduces considerably Mix L_3 containing 1 5 phr of ATU showed very low scorch time which may cause processing problems Eventhough mix L_2 showed higher cure time compared to mix L_3, the former showed higher scorch safety Hence, as far as the cure characteristics are concerned, mix L_2 can be taken to contain the optimum dosage of ATU. Also mix L_2 showed satisfactory torque value in comparison with mix L_3.

The cure characteristics of different mixes with TMTD are shown in table 5 4 Examination of the various mixes containing TMTD and ATU reveals an appreciable reduction in cure time with increase in the amount of ATU Mix N_1 contain only 0.5 phr of ATU with 1 phr of TMTD When the amount of ATU is increased to 1 5 phr (mix N_3) the cure time reduces to half Also, a sharp decrease in scorch time is observed. Mix N_2, when compared with mix O_1 (containing 2 phr TMTD alone) and mix M_2 (containing equivalent amounts of MBTS and TMTD) showed lower cure and induction times. Mixes O_3 and N_2 showed almost

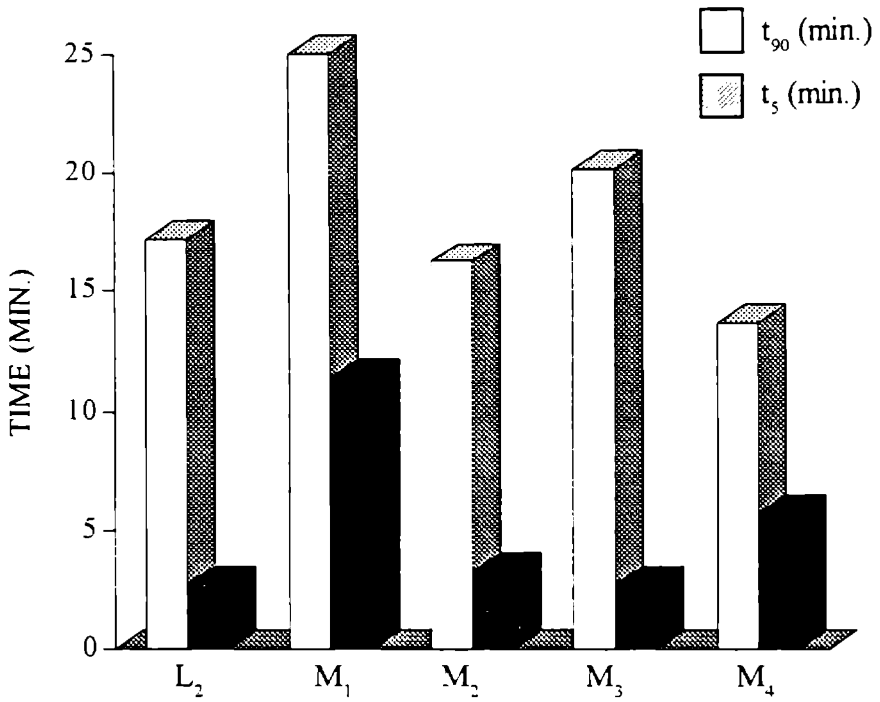

Fig. 5.3 A Comparitive study of optimum cure time (t_{90}) and induction time (t_5) of mixes containing MBTS

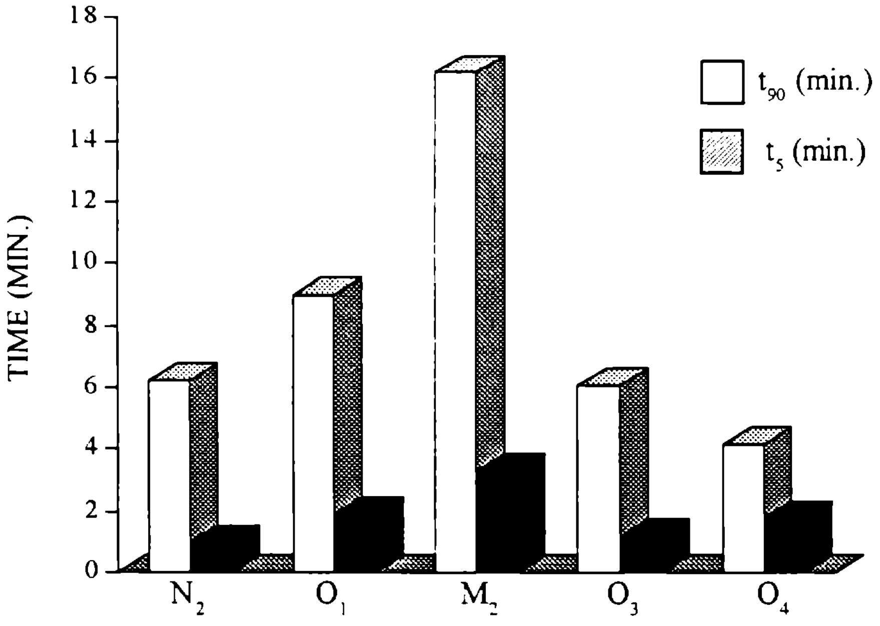

Fig. 5.4 A Comparitive study of optimum cure time (t_{90}) and induction time (t_5) of mixes containing TMTD

the same cure time. But when compared with mix O_4, N_2 showed higher cure time value. Even then the induction time for N_2 is lower than that of both O_3 and O_4 indicating a faster onset of vulcanization for N_2. This is indicative of a nucleophilic reaction mechanism in TMTD-ATU systems at least in the initial stages The cure rate of mix N_2 is also comparable with that of the reference mixes. Again, with the increase in the amount of ATU the cure time and scorch time showed sharp decrease. Among mixes N_1, N_2 and N_3. N_1 showed higher scorch time and hence safer compared to N_2 and N_3 as far as processing is considered Also N_1 showed maximum torque value compared to the other two. Hence based on the cure characteristics mix N_1 can be considered as to contain the optimum dosage of ATU, for the TMTD systems

Analysis of the cure characteristics of both MBTS-ATU and TMTD-ATU systems indicates that ATU can function as an effective secondary accelerator in the sulphur vulcanization of styrene butadiene rubber under review As in the case of NR the main disadvantage of ATU systems is their lower scorch times at high dosages. The nucleophilic mechanism for the secondary accelerator suggested earlier in NR systems is applicable in SBR systems also. However, in both MBTS and TMTD stocks, those containing DPG showed lower cure times compared to mixes containing equivalent amount of ATU But here also the ATU stocks showed a lower induction time suggesting an initial polar mechanism of vulcanization. In the subsequent stages of vulcanization a radical mechanism cannot be ruled out. Also in both the above systems the mixes show no tendency of reversion as revealed by the cure curves (Fig 5 1 and 5.2).

5.1.2.2 Tensile properties

Since SBR is not a strain crystallizable rubber it has got very low gum strength. So SBR gum stocks are not of much technological importance. The tensile properties of various mixes containing MBTS studied in the present investigation are given in Table 5 5 As mix M_1 showed very slow curing behaviour it was not further proceeded with. The tensile properties of MBTS-ATU (mix L_2) showed comparable values with those of the reference mixes (M_2, M_3 and M_4). Also the ageing behaviour of Mix L_2 is found to be satisfactory Figs. 5.5 and 5.6 show the variation of tensile properties with concentration of ATU, where the amount of the primary accelerator is fixed constant at 1 phr. The tensile strength (before and after ageing) showed an increase with concentration of ATU A similar trend is observed in the case of modulus values also. Correspondingly elongation at break values showed a decrease with increase in concentration of ATU

Table 5.6 shows the tensile properties of vulcanizates containing TMTD as the primary accelerator. Here the TMTD-ATU vulcanizate (mix N_2) showed a lower tensile strength compared to the corresponding reference vulcanizates. On the other hand, the above mix showed

Table 5.5 Tensile properties of mixes containing MBTS (cured at 150°C)

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 %
L_1	1.49	1.37	92.0	1.20	–		148.47	95.10	64.00
L_2	1.63	1.54	94.5	1.33	1.51	113.5	140.17	104.38	74.50
L_3	1.75	1.93	110.3	1.50	1.52	101.3	121.40	126.40	104.00
M_2	1.83	1.73	94.5	1.67			108.76	89.73	82.50
M_3	1.76	1.78	101.1	1.38	1.65	119.6	140.70	110.75	78.70
M_4	1.45	1.48	101.3	1.38	--	--	106.66	98.58	92.42

Table 5.6 Tensile properties of mixes containing TMTD (cured at 150oC)

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 %
N_1	1.56	1.62	103.9	1.37			120.65	97.37	80.7
N_2	1.76	1.74	98.9	1.64			107.26	86.01	80.2
N_3	1.70	1.76	103.5	1.68			99.45	91.72	92.2
O_1	1.72	1.73	100.6	1.69			101.30	84.50	83.4
M_1	1.83	1.73	94.5	1.67			108.78	89.73	82.5
O_3	2.08	1.82	87.5	1.82			121.45	87.55	72.1
O_4	2.40	1.93	80.4	1.65			159.86	94.65	59.2

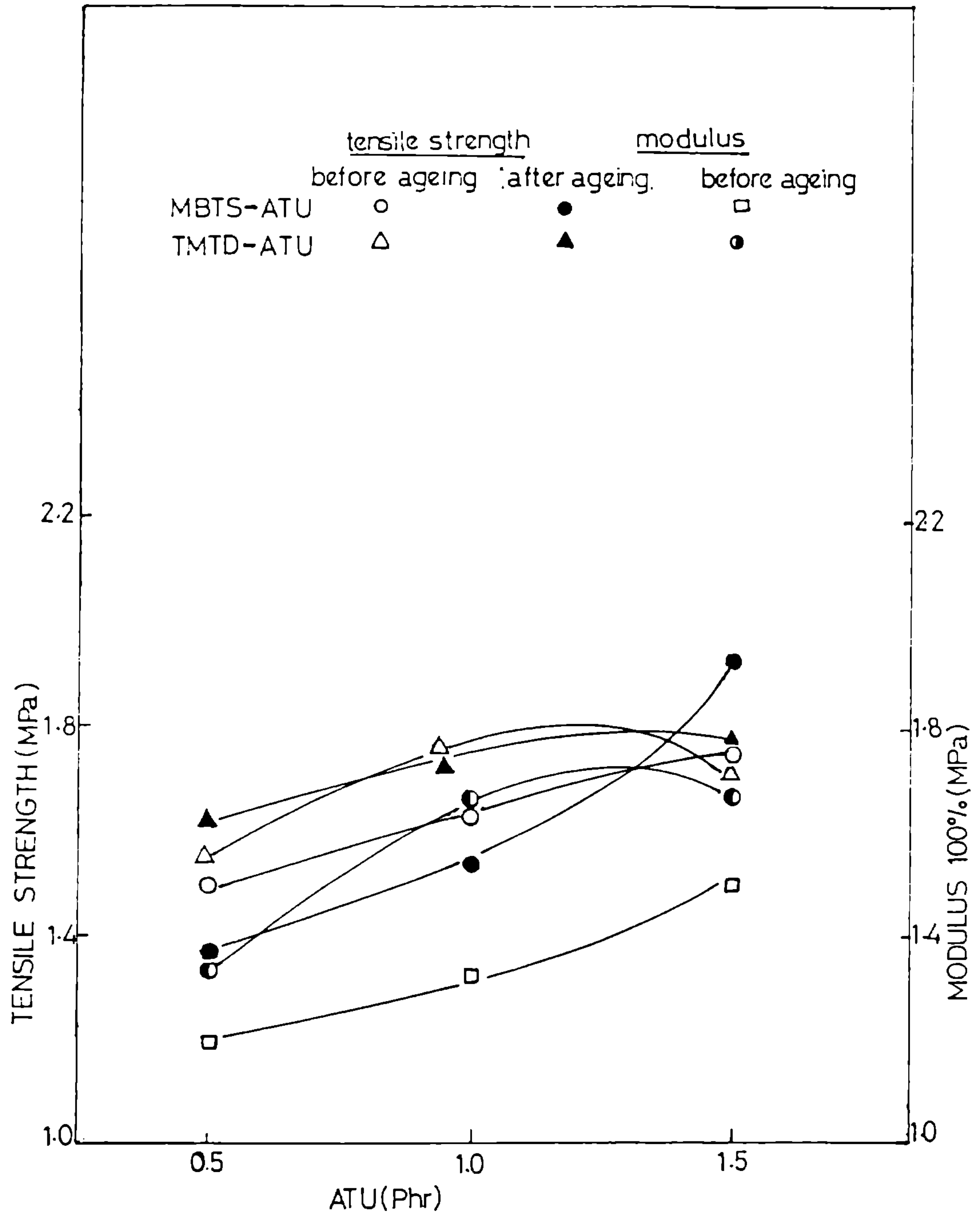

Fig. 5.5 Variation of tensile strength and modulus with concentration of ATU

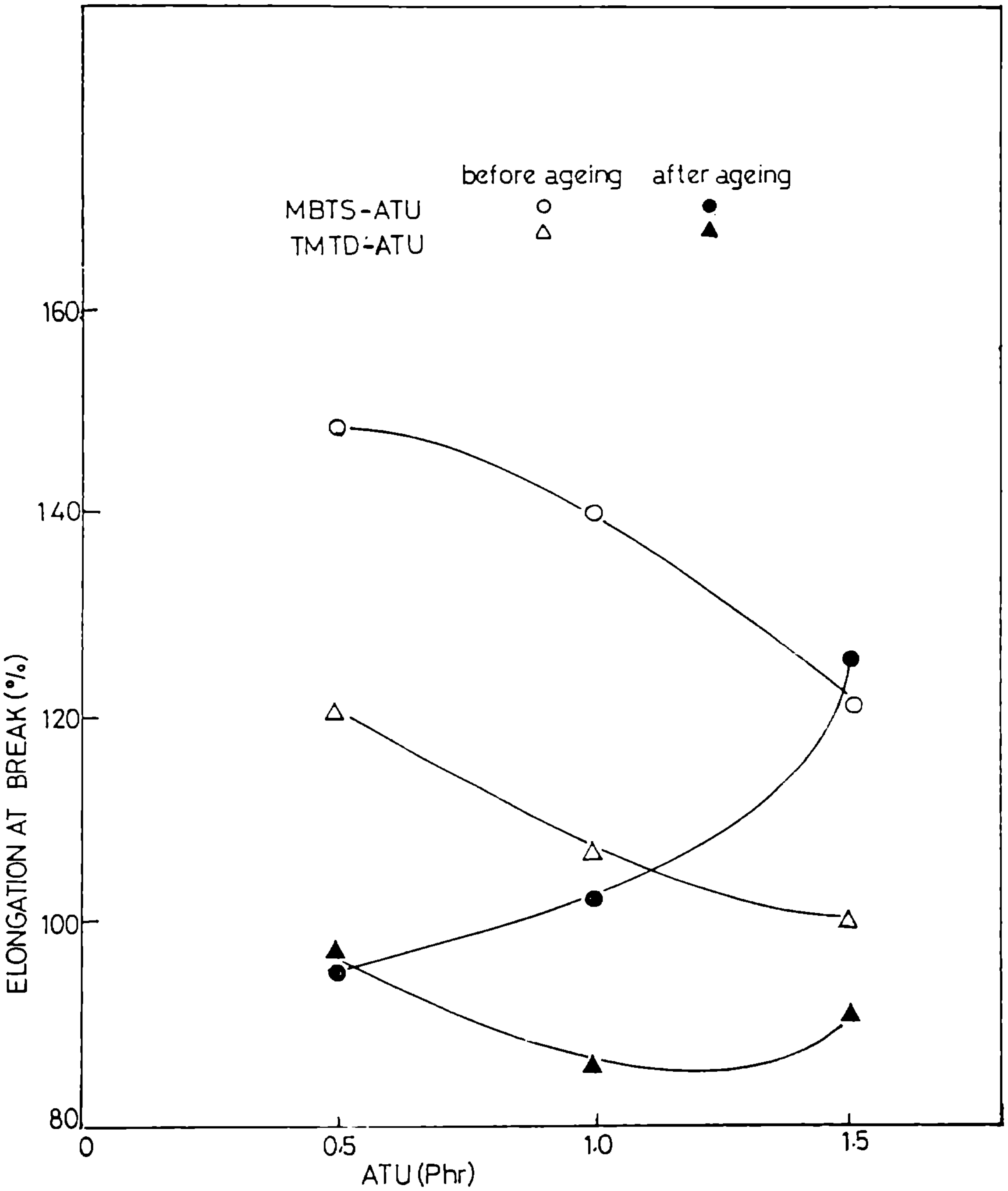

Fig. 5.6 Variation of elongation at break with concentration of ATU

better ageing characteristics. Mix N_1 which can be taken as the one containing optimum amount of ATU based on cure behaviour and physical properties showed slightly lower values of tensile strength compared to N_2 and N_3. Also variations are more or less in accordance with the crosslink density values observed (Table 5 8) Elongation at break values show a decrease with increase in the amount of ATU

5.1.2.3 Other physical properties studied

Other physical properties evaluated are tear strength, compression set, abrasion loss and hardness. The values obtained for these properties are given in Tables 5 7 and 5 8 For MBTS-ATU the abrasion loss shows a decrease with increase in the concentration of ATU Tear strength also shows a similar trend. Compared to mixes L_1 and L_3, mix L_3 showed the lowest compression set value This mix also shows the highest crosslink density. Hardness also is maximum for this mix. Compared to the reference systems, MBTS-DPG and MBTS-TU, mix L_2 showed lower compression set values Other physical properties evaluated for mix L_2 show more or less similar values with those of the reference mixes.

For the TMTD-ATU mixes abrasion loss decreases first and then increases with increase in concentration of ATU Also mix N_2 shows the maximum value of crosslink density compared to N_1 and N_3. Among the reference mixes the mix containing TMTD

Table 5.7 Other physical properties of mixes containing MBTS

Mix No.	Abrasion loss (cm^3/hr)	Tear strength (N/mm)	Compression set (%)	Hardness (Shore A)	Total crosslink density x 10^5 gmol/cm^3
L_1	6.4378	10.05	14.62	27	6.8590
L_2	4.7668	11.07	11.45	36	7.4683
L_3	3.5806	11.55	12.28	29	7 1949
M_2	11.7070	12.39	6.85	40	10.5100
M_3	4.9359	11.98	18.30	40	8.5960
M_4	7 1775	10.17	13.90	34	8.4037

Table 5.8 Other physical properties of mixes containing TMTD

Mix No.	Abrasion loss (cm^3/hr)	Tear strength (N/mm)	Compression set (%)	Hardness (Shore A)	Total crosslink density x 10^5 gmol/cm^3
N_1	4.6780	9 85	14.10	35	8.987
N_2	4.2187	10.70	15.25	39	9.336
N_3	5.0422	11.24	18.80	35	8.255
O_1	12.2088	9.33	10.15	45	10.410
M_2	11.7077	12.29	6.85	40	10.510
O_3	5.0040	9.62	17.01	37	8.565
O_4	8.7703	14.77	8.53	41	10.070

alone (mix O_1) and MBTS-TMTD (mix M_2) showed higher values for abrasion loss. Regarding hardness, mix N_2 showed highest value among TMTD-ATU mixes. Tear strength also is seen to increase with increase in concentration of ATU For MBTS-ATU systems the degree of crosslinking is found to be lower compared to the reference mixes. The variations in physical properties of the different vulcanizates are found to be more or less consistent with the variations in crosslink density values for both MBTS-ATU and TMTD-ATU systems.

PART II

5.2 FILLED VULCANIZATES OF SBR

Gum vulcanizates of natural rubber have very high tensile strength, elongation and resilience, but low modulus. hardness, tear strength, abrasion and flex resistance. At the same time, gum vulcanizates of SBR exhibits low physical properties When NR and SBR are compounded at optimum level of reinforcing fillers they are almost alike in most of the physical properties. The molecular irregularity and large pendent groups of SBR prevent aligning of the molecules to give crystals on stretching unlike in the case of NR. The lack of crystallization gives lower green strength and also lower gum tensile strength for SBR. To overcome this type of behaviour incorporation of fine reinforcing fillers is necessary for SBR. It also requires some optimum filler loadings for properties such as wear and tear resistance Reinforcing carbon blacks like, furnace black is preferred in compounding of SBR. Next to furnace black, precipitated silica, calcium carbonate and aluminium silicate, clays etc. are also used. Although precipitated and activated calcium carbonates are moderate in reinforcement, the processing characteristics imparted are very good[4]

Among the commonly used fillers and reinforcing agents, carbon black offers the most potential reinforcement[5] Carbon black contribute much to increase the desirable properties of vulcanized rubber and it is almost a universal compounding ingredient for quality stocks[6] The mechanism of reinforcement by carbon black has been studied by several authors[6-10] The modification of an elastomer by carbon black reinforcement generates a unique three dimensional visco-elastic network that transfer the soft elastomer into a strong elastic product[11] Carbon black improves the tensile properties and resistance to failure of the SBR vulcanizates. A pure gum vulcanizate of SBR has a very low tensile strength, but by the incorporation of 50 phr of reinforcing black the tensile strength can easily be raised to about ten times that of the gum stock. This results from the interaction between the carbon black and the elastomer Porter[12] as well as Bhowmick and De[13] have discussed the role of reinforcing black in the sulphuration process in vulcanization. With the general purpose elastomer like SBR, HAF black with average particle size in the range of 24-28 mμ are most widely used The optimum black level vary from 30 to 60 phr, although if more oil is added considerably larger loadings can be employed

Non-black fillers like precipitated silica are used in SBR to improve processing and to reinforce the polymer in the production of white or coloured compounds[14] Good strength and abrasion resistance can be achieved with precipitated silica, although they are somewhat inferior in this respect to carbon black[15] Reinforcement and subsequent cure characteristics of silicas and silicates has been reviewed by Wagner[16] Due to the high adsorptive nature, precipitated silica retard cure at a high loading and to balance the cure time activators such as polyethylene glycols have to be used. Clays are widely used as non-black filler in SBR. This is due to the low cost, low to moderate reinforcement and benefits in processing, especially extrusion and calendering. Clays also are highly adsorptive and are known to reduce cure rate[17] This reduction in cure rate necessitates the addition of activators such as triethanolamine, diethylene glycol, polyethylene glycol etc.

As reported in part I of this chapter, 1-phenyl-3-(N,N'-diphenyl amidino)thiourea (ATU) is found to be an effective secondary accelerator with MBTS/TMTD in SBR gum vulcanizates. In this context we further investigated the filled vulcanizates of SBR containing ATU as secondary accelerator along with MBTS/TMTD A thorough study on the filled systems was carried out using carbon black precipitated silica and china clay as fillers aiming at developing practical cure systems which can be used in rubber product manufacture. The study covers the different aspects like mixing, curing and evaluation of various physical properties of the vulcanizates. We studied MBTS-ATU and TMTD-ATU systems. Reference mixes were also prepared and the properties of the experimental mixes were compared with those of the reference. To understand the variations in physical properties of the vulcanizates, total chemical crosslinks were estimated using equilibrium swelling method[20]

5.2.1 Experimental

Tables 5 9 and 5.10 show the formulations of different

Table 5.9 Formulation of Mixes Containing MBTS

Ingredients	L_1	L_2	L_3	M	M_1	M_2	M_3	N_1	N_2	N_3	P	P_1	P_2	P_3	R_1	R_2	R_3	S	S_1	S_2	S_3
SBR	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	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	2	2	2	2	2
MBTS	1	1	1	1	2	1	1	1	1	1	1	2	1	1	1	1	1	1	2	1	1
TMTD	—	—	—	1	—	—	—	—	—	—	1	—	—	—	—	—	—	1	—	—	—
DPG	—	—	—	—	—	1	—	—	—	—	—	—	1	—	—	—	—	—	—	1	—
Thiourea	—	—	—	—	—	—	1	—	—	—	—	—	—	1	—	—	—	—	—	—	1
ATU	0.5	1.0	1.5	—	—	—	—	0.5	1.0	1.5	—	—	—	—	0.5	1.0	1.5	—	—	—	—
Carbon black	50	50	50	50	50	50	50	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Silica	—	—	—	—	—	—	—	50	50	50	50	50	50	50	—	—	—	—	—	—	—
China clay	—	—	—	—	—	—	—	—	—	—	—	—	—	—	50	50	50	50	50	50	50
DEG	—	—	—	—	—	—	—	2	2	2	2	2	2	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	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	5	5	5	5	5	5	5

Table 5.10 Formulation of Mixes containing TMTD

Ingredients	L'_1	L'_2	L'_3	M	M'_1	M'_2	M'_3	N'_1	N'_2	N'_3	P	P'_1	P'_2	P'_3	R'_1	R'_2	R'_3	S	S'_1	S'_2	S'_3
SBR	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	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	2	2	2	2	2
TMTD	1	1	1	1	2	1	1	1	1	1	1	2	1	1	1	1	1	1	2	1	1
MBTS	—	—	—	1	—	—	—	—	—	—	1	—	—	—	—	—	—	1	—	—	—
DPG	—	—	—	—	—	1	—	—	—	—	—	—	1	—	—	—	—	—	—	1	—
Thiourea	—	—	—	—	—	—	1	—	—	—	—	—	—	1	—	—	—	—	—	—	1
ATU	0.5	1.0	1.5	—	—	—	—	0.5	1.0	1.5	—	—		—	0.5	1.0	1.5	—	—	—	—
Carbon black	50	50	50	50	50	50	50	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Silica	—	—	—	—	—	—	—	50	50	50	50	50	50	50	—	—	—	—	—	—	—
China clay	—	—	—	—	—	—	—	—	—	—	—	—	—	—	50	50	50	50	50	50	50
DEG	—	—	—	—	—	—	—	2	2	2	2	2	2	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	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	5	5	5	5	5	5	5

mixes used in this study All mixes contain 50 phr each of the respective filler. Mixes L_1-L_3 contain 0 5, 1 0 and 1 5 phr of ATU with 1 phr MBTS and 50 phr carbon black. Similar is the formulations N_1-N_3 and R_1-R_3 except that the former contain 50 phr of precipitated silica and the latter 50 phr of china clay. The rest of the formulations are for reference. Table 5 10 gives the formulations of mixes containing TMTD Here mixes L_1'-L_3', N_1'-N_3' and R_1'-R_3', contain 0 5, 1 0 and 1.5 phr of ATU in each set respectively. Aromatic oil (5 phr) is used as process oil for mixes containing carbon black while naphthenic oil (5 phr) is used in the case of silica and clay filled compounds Two phr diethylene glycol (DEG) is added as an activator for formulations containing white fillers. Cure characteristics of the mixes and physical properties of the vulcanizates are evaluated as per relevent standards mentioned in chapter II.

5.2.2 RESULTS AND DISCUSSION

5.2.2.1 Cure characteristics

The cure properties of the systems with MBTS and TMTD are given in Tables 5 11 and 5 12 respectively. Figs. 5 7-5 12 show the cure curves of various mixes. It has been observed that in the case of MBTS systems variation in optimum cure time do not show any set pattern as observed in gum systems. Also these mixes showed very low cure rates. This is probably due to the fact that thiazole derivatives are slow curing with SBR[4] and also that the fillers adsorb accelerators to different extents. At the same

Table 5.11 Cure characteristics of filled systems containing MBTS (cured at 150°C)

Mix No.	Optimum cure time, (t_{90}) min.	Scorch time• (t_{10}) min.	Induction time, (t_5) min.	Cure-rate index	Minimum torque, dNm	Maximum torque, dNm
L_1	13.3	2.6	1.5	9.35	0.066	0.453
L_2	8.80	2.0	0.9	14.71	0.085	0.524
L_3	6.70	1.6	0.6	19.61	0.076	0.470
M	4.80	1.9	1.2	34.48	0.073	0.650
M_1	15.4	3.4	2.4	8.33	0.075	0.546
M_2	6.4	2.4	1.2	25.64	0.077	0.553
M_3	8.0	1.3	1.2	14.93	0.054	0.315
N_1	25.3	6.5	6.3	5.32	0.095	0.288
N_2	24.3	3.9	3.0	4.90	0.090	0.275
N_3	22.9	3.6	2.7	5.18	0.099	0.283
P	17.1	1.4	1.2	6.37	0.102	0.385
P_1	24.3	9.0	7.8	6.54	0.113	0.377
P_2	21.1	7.4	6.0	7.30	0.067	0.305
P_3	23.8	2.9	2.7	4.78	0.103	0.246
R_2	14.8	4.6	4.4	9.80	0.069	0.256
R_2	8.3	2.3	2.1	16.67	0.066	0.329
R_2	4.7	1.4	1.3	30.30	0.055	0.314
S	6.3	2.4	2.1	25.64	0.037	0.423
S_1	18.9	6.1	5.7	7.81	0.050	0.302
S_2	10.0	2.9	2.7	14.08	0.063	0.269
S_3	10.0	2.1	1.8	12.66	0.070	0.305

Table 5.12 Cure characteristics of filled systems containing TMTD (cured at 150°C)

Mix No.	Optimum Cure time t_{90} (min)	Scorch time t_{10} (min)	Induction time t_5 (min)	Cure-rate Index	Minimum Torque (Nm)	Maximum Torque (Nm)
L_1	4.4	1.3	1.2	32.26	0.075	0.655
L_2'	3.3	1.2	0.9	47.62	0.076	0.604
L_3'	2.6	1.0	0.6	62.50	0.076	0.559
M	4.8	1.9	1.2	34.48	0.073	0.650
M_1'	3.9	1.6	0.9	43.48	0.078	0.718
M_2'	10.1	1.5	0.9	11.63	0.054	0.497
M_3'	3.1	1.0	0.9	42.62	0.077	0.520
N_1'	5.0	1.0	0.9	25.00	0.089	0.287
N_2'	3.8	1.0	0.9	35.71	0.108	0.286
N_3'	3.5	0.8	0.6	37.04	0.110	0.303
P	17.1	1.4	1.2	6.37	0.102	0.385
P_1'	3.8	0.8	0.6	33.33	0.117	0.417
P_2'	4.1	1.2	0.9	34.48	0.088	0.274
P_3'	15.9	0.9	0.8	4.39	0.119	0.193
R_1'	3.3	1.7	1.5	62.5	0.039	0.347
R_2'	2.3	1.2	1.0	90.9	0.042	0.317
R_3'	2.5	0.8	0.6	58.8	0.115	0.500
S	6.3	2.4	2.1	25.64	0.037	0.423
S_1'	3.6	1.6	1.2	50.00	0.034	0.450
S_2'	3.0	1.9	1.8	90.91	0.043	0.315
S_3'	2.4	0.8	0.6	62.50	0.049	0.329

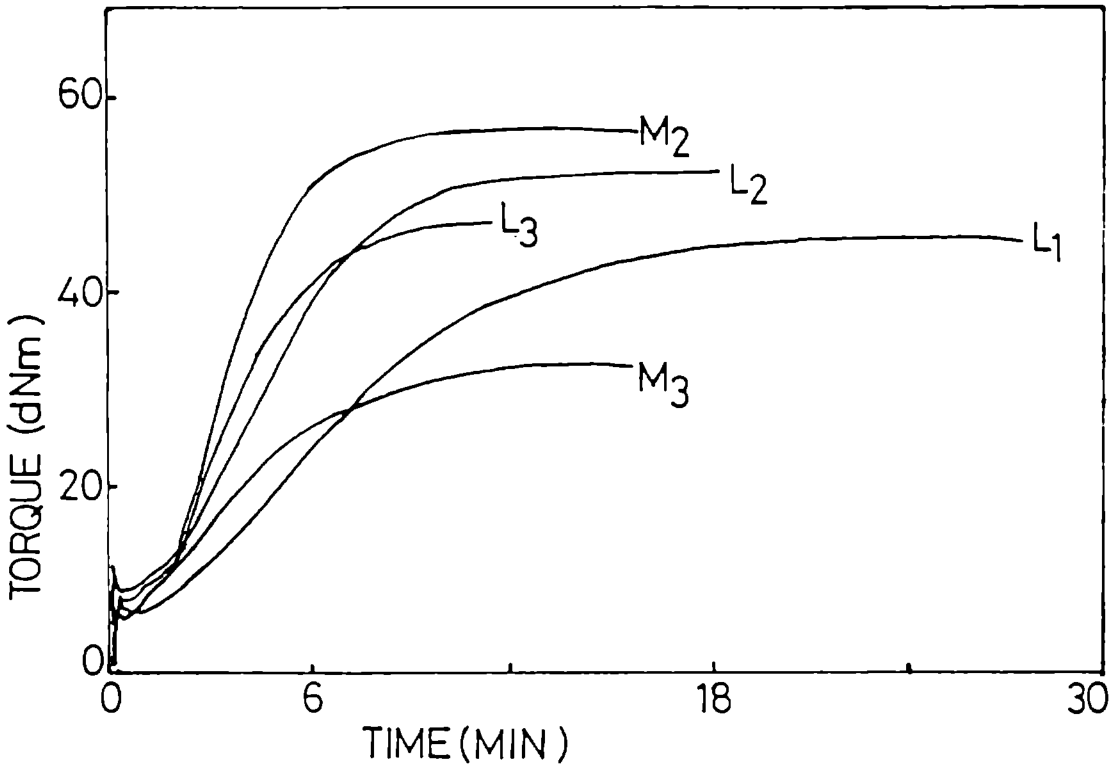

Fig. 5.7 Cure curves of carbon black filled systems (MBTS)

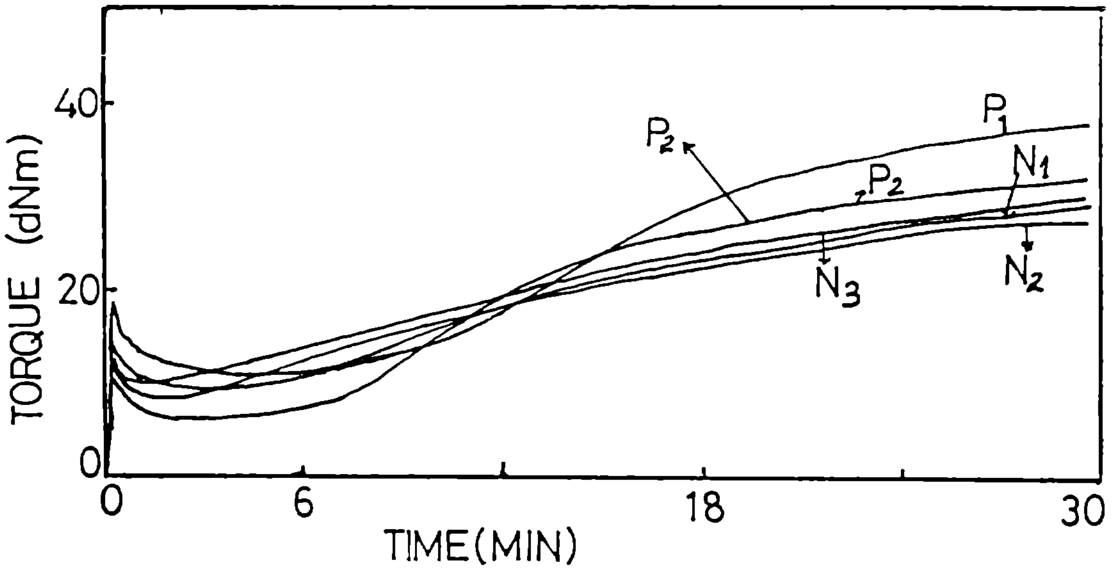

Fig. 5.8 Cure curves of silica-filled systems (MBTS)

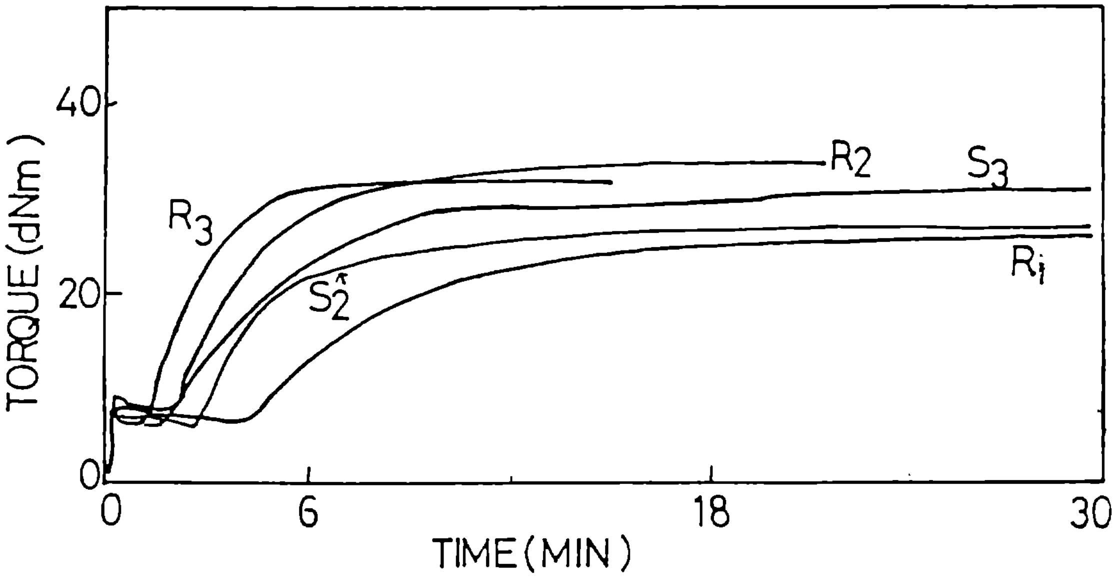

Fig. 5.9 Cure curves of clay-filled systems (MBTS)

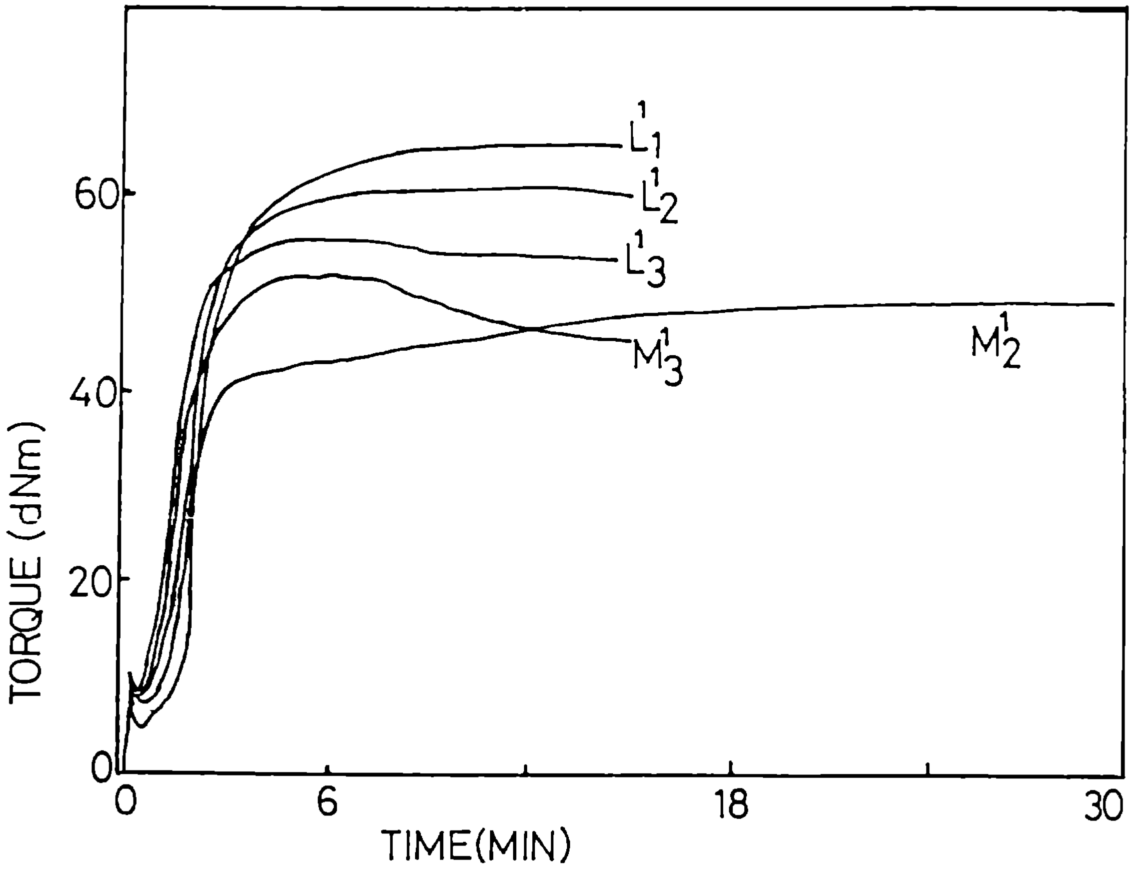

Fig. 5.10 Cure curves of carbon-black filled systems (TMTD)

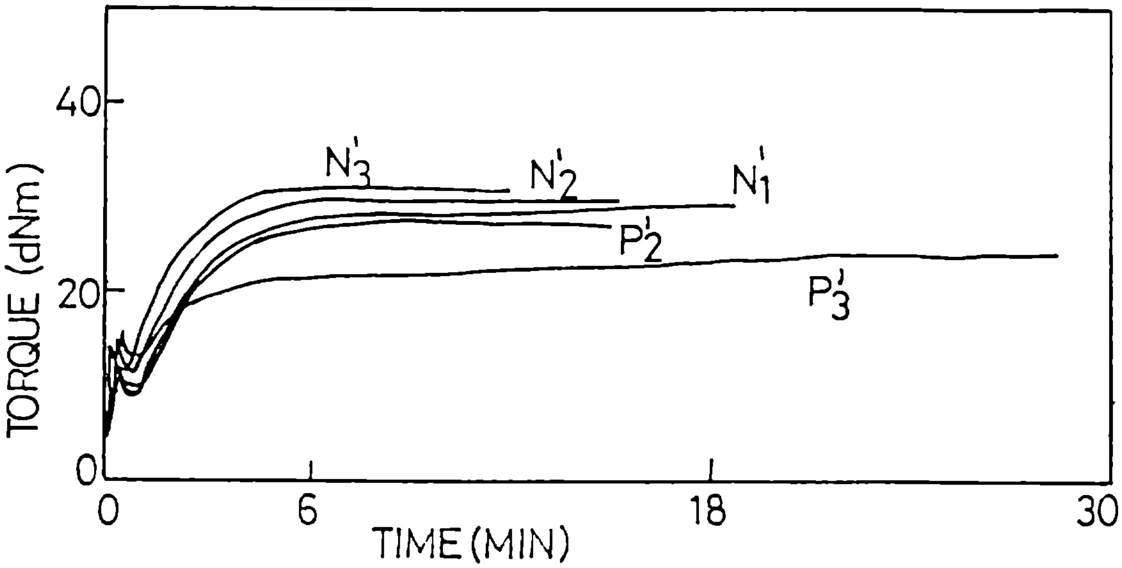

Fig. 5.11 Cure curves of silica-filled systems (TMTD)

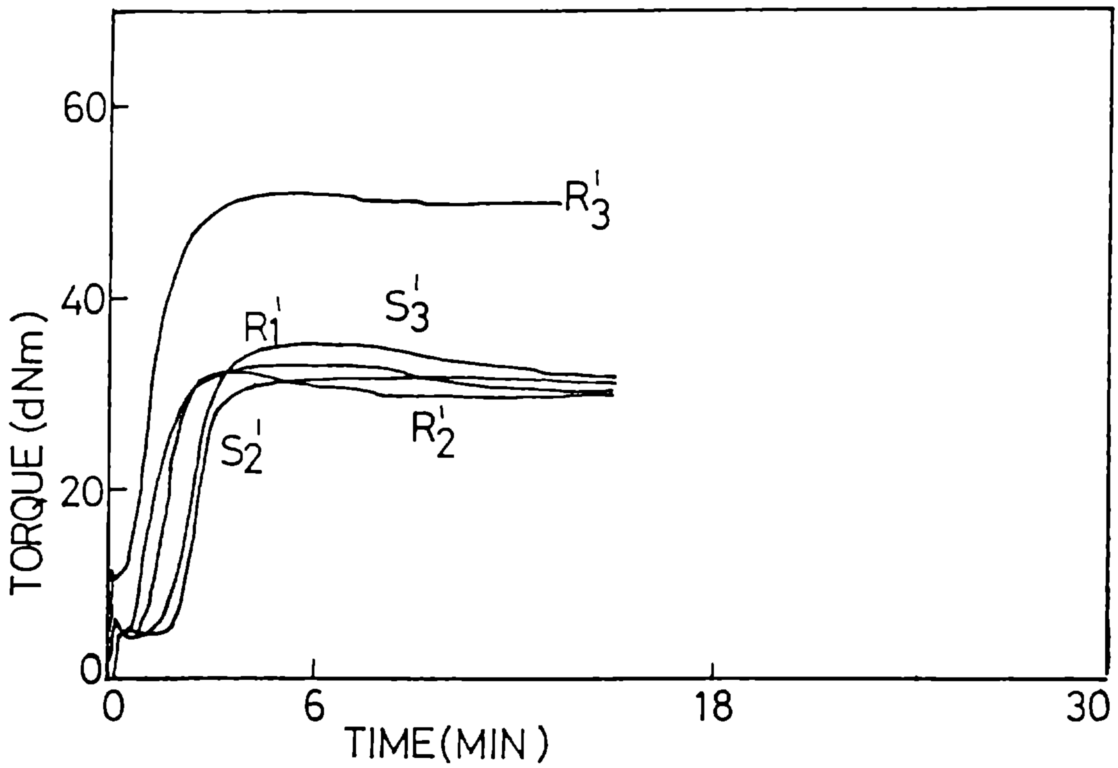

Fig. 5.12 Cure curves of clay-filled systems (TMTD)

time induction time showed definite variations. Among the carbon black filled systems L_2 showed the lowest induction time. Induction time being a measure of the onset of vulcanization, and ATU being more nucleophilic showed lower induction time compared to DPG and TU This is indicative of an initial nucleophilic attack by the secondary accelerator in filled systems of SBR also However, in this case a radical mechanism can also be involved at a later stage Among the three different fillers used, silica filled MBTS systems showed relatively higher optimum cure times and correspondingly poor cure rates. It is also observed that irrespective of the nature of the filler used, the optimum cure time is found to decrease with increase in concentration of ATU Unlike MBTS, TMTD is found to be faster curing and showed better cure rate values. In carbon black, silica and clay systems the TMTD-ATU mixes showed lower optimum cure time compared to reference. Also with increase in the concentration of ATU, optimum cure time showed a definite decrease (Table 5 12). The main disadvantage of these systems is their scorchiness at higher concentration of the secondary accelerator (ATU).

5.2.2.2 Tensile properties

Tensile properties of the different vulcanizates studied are given in Tables 5.13 and 5.14, Mixes containing MBTS showed very low cure rates as seen from the corresponding cure curves (Fig. 5.8). So these mixes were not investigated further. Among

Table 5.13 Tensile properties of filled vulcanizates 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 %
L1	16.55	10.94	66.10	1.71	5.58	326.32	355.30	167.45	47 13
L2	17.25	14.51	84.12	4.30	3.85	89.53	290.81	179.5	61.72
L3	15.71	13.45	85.61	4.12	6.12	148.54	292.47	184.55	63.10
M	13.61	13.00	95.52	5.85	10.60	181.20	193.81	119.78	61.80
M1	25.00	24.24	96.96	4.13	3.25	76.69	403.23	279.21	69.24
M2	23.06	18.14	76.68	2.32	6.9	297.41	314.62	238.02	75.65
M3	18.11	10.94	60.41	3.71	6.42	173.05	366.88	153.02	41.71
P	10.72	6.71	62.59	2.58	1.71	66.28	506.55	303.35	59.89
P2	9.71	10.63	109.47	2.29	3.13	136.68	618.48	454.87	73.55
P3	11.57	8.74	75.54	2.66	1.86	69.92	476.75	344.76	72.31
R1	2.92	2.87	98.29	1.55	1.89	121.94	260.91	208.43	79.89
R2	3.11	3.25	104.50	1.48	1.89	127.7	311.56	235.6	75.62
R3	3.75	4.30	114.67	1.85	2.09	112.97	268.10	254.7	95.00
S	2.87	2.56	89.20	1.96	0.00	0.00	189.62	87.45	46.12
S1	3.23	3.09	95.67	1.69	2.43	143.79	282.61	156.32	55.31
S2	5.65	5.11	90.44	1.53	2.33	152.29	457.73	277.12	60.54
S3	3.44	3.87	112.5	1.71	2.45	143.27	290.67	208.98	71.90

Table 5.14 Tensile properties of filled vulcanizates 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 %
L_1'	12.98	10.03	77.27	5.62	8.48	150.89	202.40	115.42	57.03
L_2'	12.60	9.21	73.10	5.40	8.47	156.85	199.91	103.08	51.56
L_3'	12.67	10.01	79.01	5.36	9.16	170.90	201.46	103.53	51.39
M	13.61	13.00	95.52	5.85	10.60	181.20	193.81	119.78	61.80
M_1'	15.02	10.10	67.24	6.98	0.00	0.00	181.16	76.15	42.03
M_2'	14.43	13.59	94.18	5.37	8.74	162.76	214.55	137.61	64.14
M_3'	15.16	9.32	61.48	5.58	0.00	0.00	226.51	95.76	42.26
N_1'	7.77	8.28	106.56	2.89	2.75	95.16	328.83	387.63	117.58
N_2'	7.09	8.77	123.70	3.69	3.20	86.72	219.11	289.02	132.32
N_3'	8.41	8.66	102.97	4.12	3.45	83.74	227.26	289.02	127.18
P	10.72	6.71	62.59	2.58	1.71	66.28	506.55	303.35	59.89
P_1'	8.63	7.22	83.60	3.60	4.09	113.6	258.50	201.82	78.10
P_2'	8.15	8.59	105.40	3.81	2.59	67.98	253.06	435.51	172.10
P_3'	7.89	6.56	83.14	3.32	4.21	126.80	428.40	353.64	82.50
R_1'	3.24	3.00	92.59	1.73	2.62	151.45	247.86	127.10	51.28
R_2'	3.58	3.56	99.44	2.07	2.96	142.90	217.72	111.53	51.22
R_3'	3.75	3.44	91.73	2.55	3.39	132.94	172.73	102.70	59.46
S	2.87	2.56	89.20	1.96	0.00	0.00	189.62	84.45	46.12
S_1'	2.81	2.89	102.85	1.84	0.00	0.00	197.35	96.58	48.93
S_2'	5.06	3.56	70.36	1.94	2.73	140.72	335.98	154.47	45.98
S_3'	3.82	3.90	102.09	2.61	3.63	139.08	167.90	111.00	66.11

the filled systems. only the carbon black systems showed appreciable reinforcement. Also, mixes containing ATU showed better/comparable after ageing properties, in comparison with the reference mixes. Variations in tensile strength, modulus (100%) and elongation at break with concentration of ATU for MBTS-ATU systems are shown in Figs 5 13-5 15 The tensile strength values for carbon black filled vulcanizates. increases first and then decreases with increase in concentration of ATU For clay filled systems tensile strength slightly increases with concentration of ATU The aged samples also show similar trend in variation of tensile strength for both carbon black and clay filled systems. For carbon black systems the modulus also increases and attains a maximum and then decreases with concentration of ATU. For the clay filled systems modulus remains almost same with concentration of ATU both before and after ageing.

In the case of TMTD-ATU systems, tensile strength both before and after ageing remain more or less the same for all three filler types (Figs. 5 16-5 18). The same trend is observed in the case of modulus also These variations are almost consistent with the variation in total chemical crosslink density values for these vulcanizates. These values also do not show any appreciable changes with the concentration of ATU For silica and clay filled vulcanizates the elongation at break decreases with concentration of ATU while for carbon black system it remains more or less the same

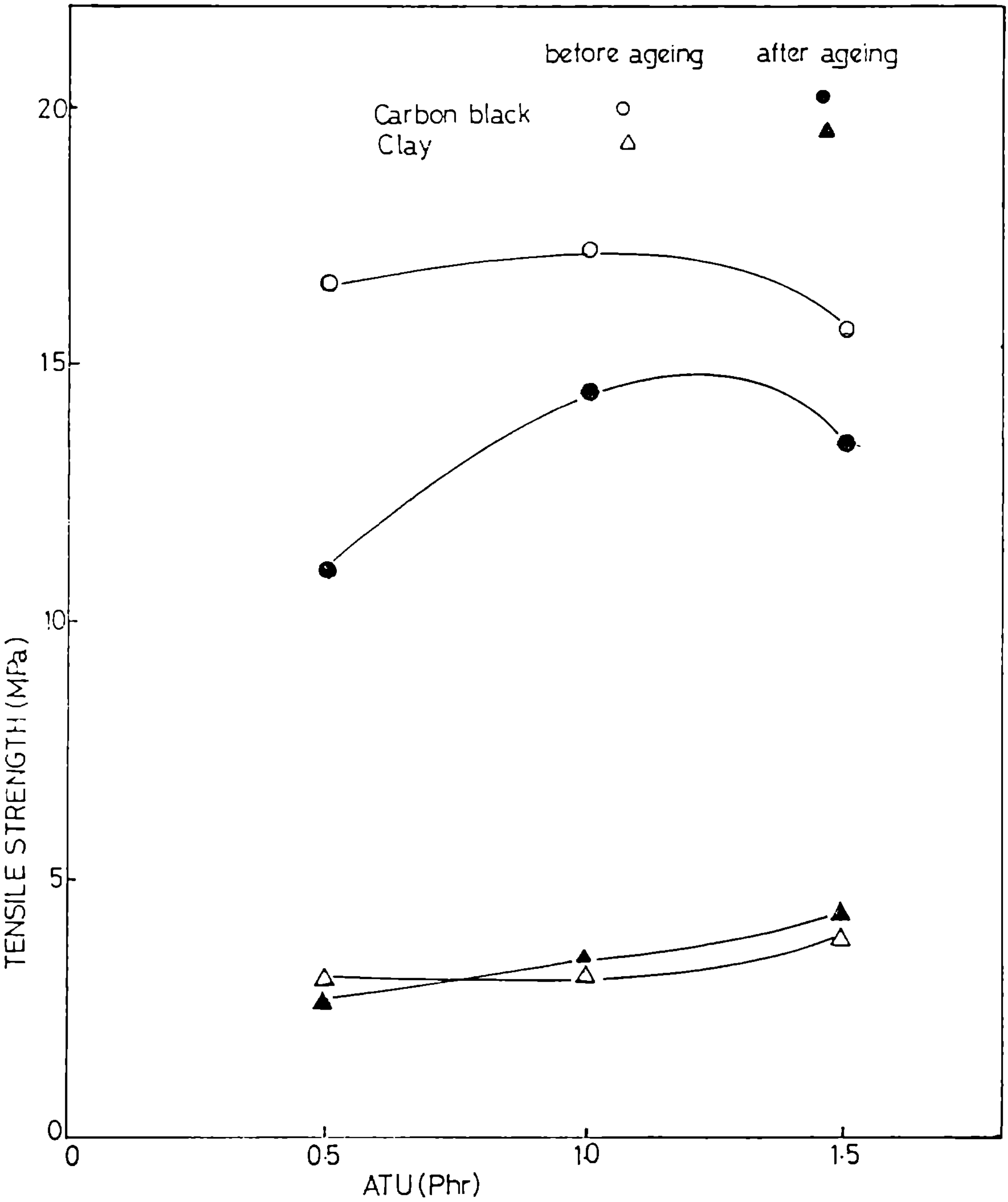

Fig. 5.13 Effect of the concentration of ATU on tensile strength of MBTS-ATU (filled) vulcanizates

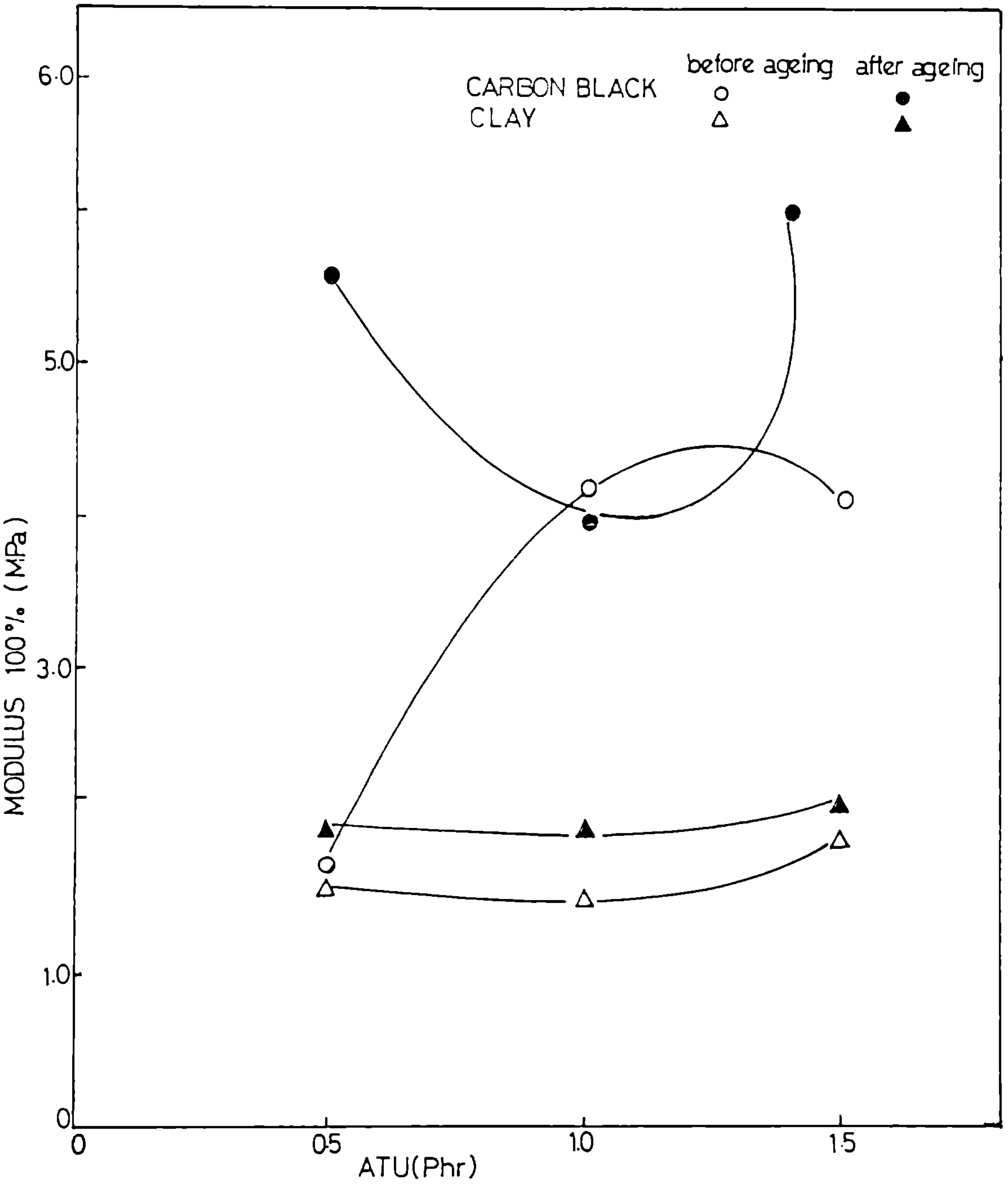

Fig. 5.14 Effect of the concentration of ATU on modulus of MBTS-ATU (filled) vulcanizates

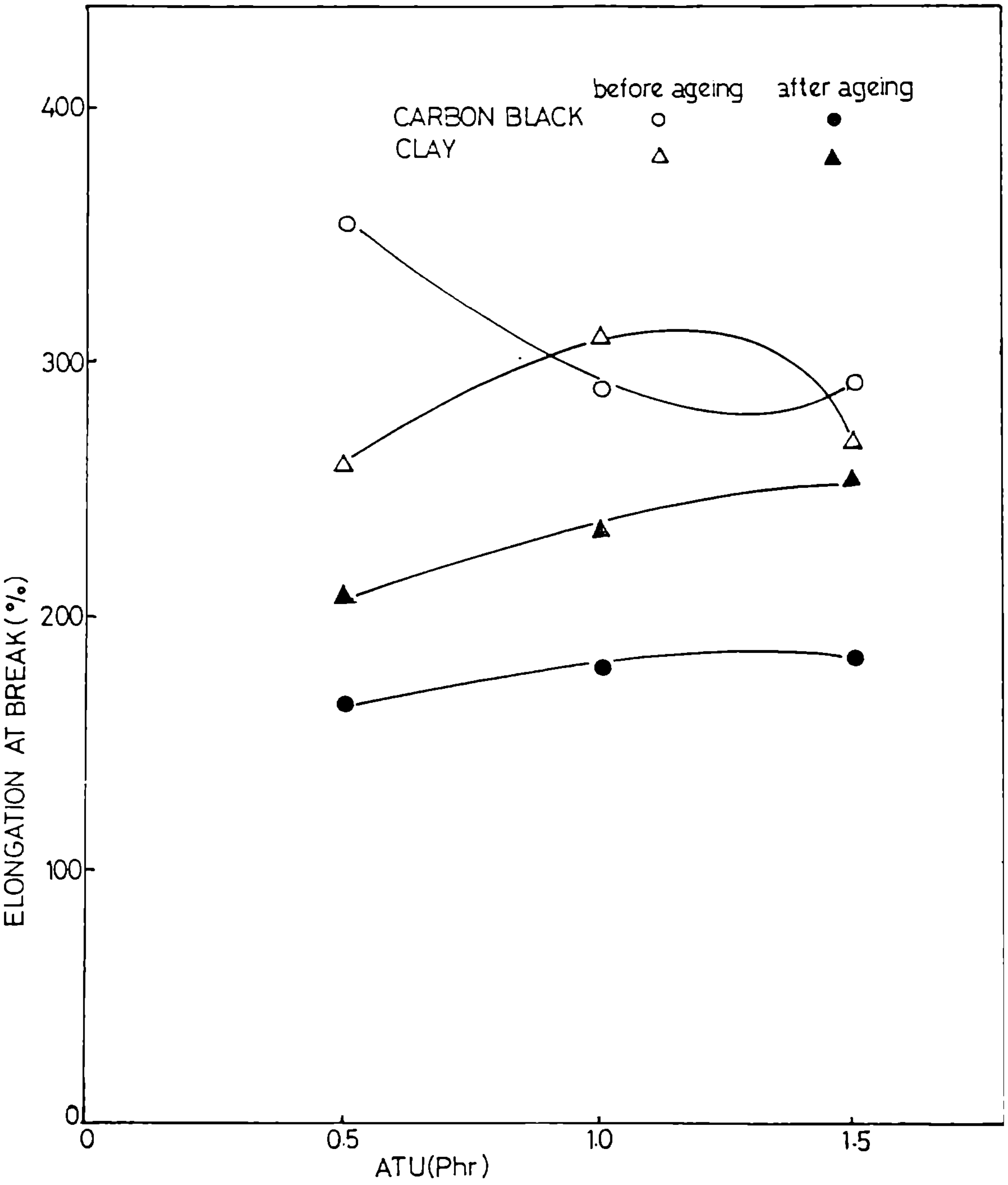

Fig. 5.15 Effect of the concentration of ATU on elongation at break of MBTS-ATU (filled) vulcanizates

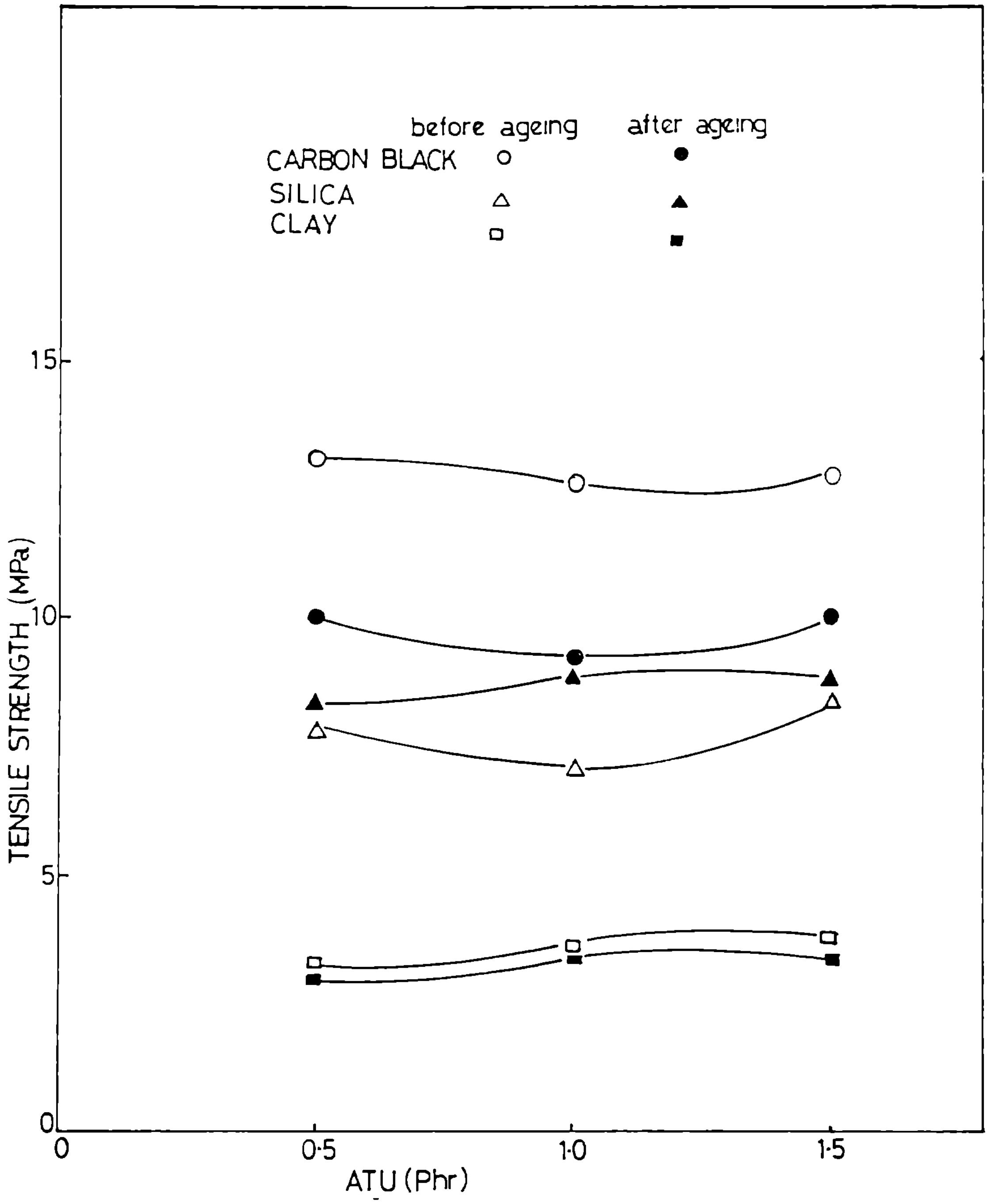

Fig. 5.16 Effect of the concentration of ATU on tensile strength of TMTD-ATU (filled) vulcanizates

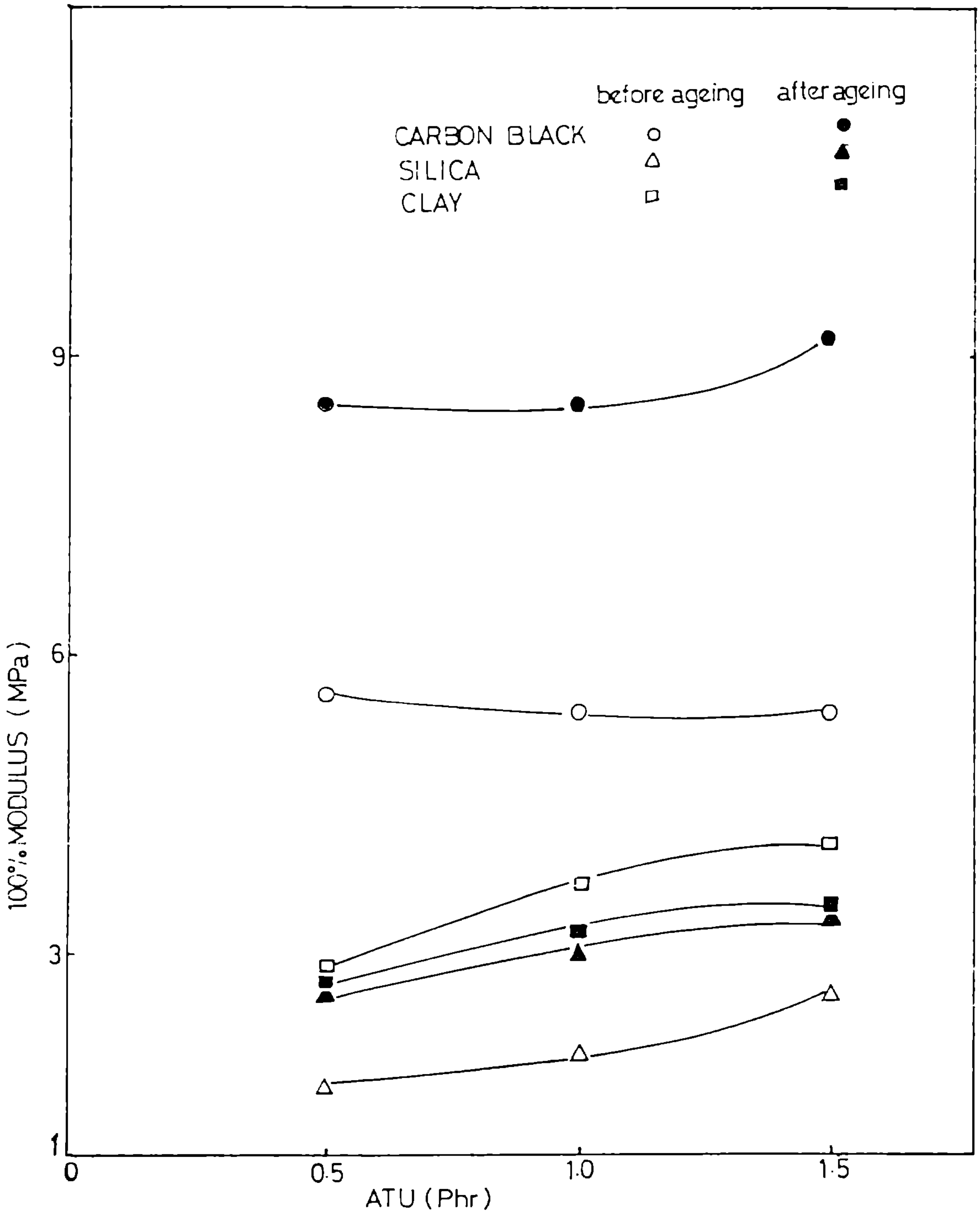

Fig. 5.17 Effect of the concentration of ATU on modulus of TMTD-ATU (filled) vulcanizates

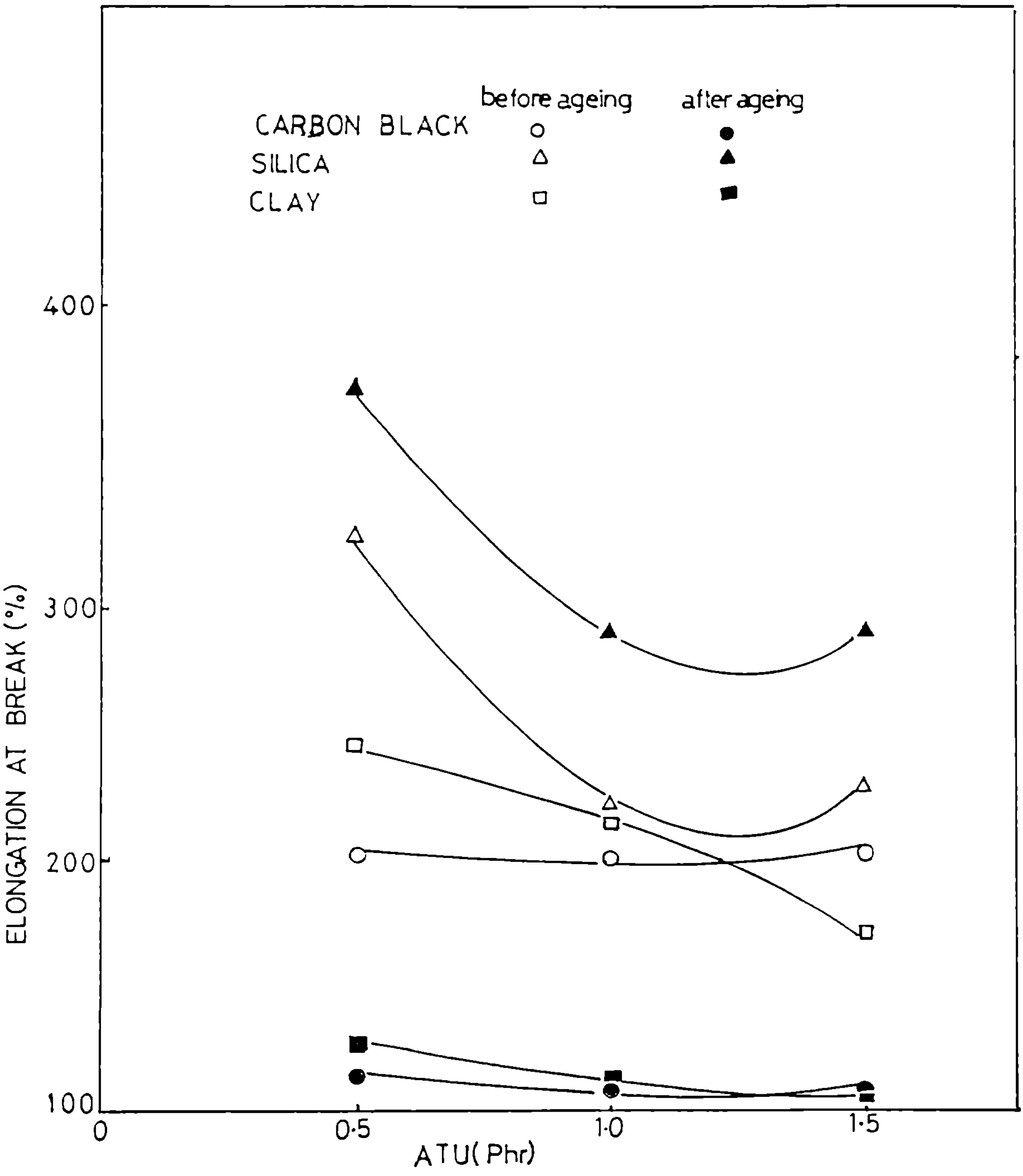

Fig. 5.18 Effect of the concentration of ATU on elongation at break of TMTD-ATU (filled) vulcanizates

5.2.2.3 Other physical properties evaluated

Hardness (shore A), compression set, abrasion loss and tear strength are the other physical properties evaluated for these systems. The results are given in Tables 5 15 and 5 16. For the MBTS-ATU system (Table 5 15), when carbon black is used the hardness is found to increase and abrasion is found to decrease with increase in concentration of ATU (mixes L_1-L_3) On the other hand compression set and tear strength showed an initial decrease When china clay is used the hardness is found to decrease with concentration of ATU (mix R_1-R_3) while the other properties do not show any regular variations. It is also observed that ATU systems show comparable values of hardness, compression set, abrasion loss and tear strength with those of reference mixes. This is true for the TMTD-ATU systems also In carbon black filled vulcanizates hardness is found to increase with concentration of ATU (mixes L_1'-L_3') and abrasion loss showed a decrease. Compression set and tear strength do not show appreciable variations.

The total crosslink density values of the vulcanizates are given in Tables 5 15 and 5 16. For both MBTS-ATU and TMTD-ATU systems carbon black filled vulcanizates showed higher crosslink density values. The silica filled vulcanizates showed the least while the clay filled showed intermediate values. It has been observed earlier that, while while carbon blacks have a significant effect on the network structure of filled vulcanizates, semi-reinforcing fillers

Table 5.15 Other physical properties evaluated (MBTS systems)

Mix No.	Abrasion loss (cm^3/hr)	Tear strength (N/mm)	Compression set (%)	Hardness (Shore A)	Total crosslink density x 10^5 $gmol/cm^3$
L_1	50	18.51	2.5951	68.63	6.8653
L_2	51	14.68	2.4436	67.50	8.9890
L_3	52	15.23	2.4170	83.13	8.1413
M	65	9.33	2.7660	70.15	11.5683
M_1	56	13.77	2.4897	61.03	12.7432
M_2	63	13.73	2.3336	72.25	10.1689
M_3	61	21.38	2.5631	66.00	8.2350
P	60	28.15	4.8513	45.08	3.1459
P_2	55	27.36	3.6246	50.41	2.1238
P_3	57	24.42	4.2018	48.48	2.4681
R_1	54	20.00	5.4049	26.21	5.9520
R_2	53	15.82	5.4895	22.89	6.1968
R_3	50	16.13	4.8731	28.31	6.7266
S	56	14.38	5.7022	19.24	7.4588
S_1	52	16.92	5.8167	21.63	6.8730
S_2	57	15.42	5.1104	22.37	6.5219
S_3	52	16.78	5.8641	29.67	5.8595

Table 5.16 Other physical properties evaluated (TMTD systems)

Mix No.	Abrasion loss (cm^3/hr)	Tear strength (N/mm)	Compression set (%)	Hardness (Shore A)	Total crosslink density x 10^5 gmol/cm^3
L_1'	55	13.13	3.0100	46.60	10.8040
L_2'	57	12.45	2.8942	60.78	10.8540
L_3'	68	13.53	2.6046	55.01	10.0232
M	65	9.33	2.7660	70.15	11.5683
M_1'	62	10.32	4.2307	82.49	13.3787
M_2'	66	10.74	3.8421	60.11	10.3552
M_3'	67	20.23	4.5517	51.78	11.0693
N_1'	58	24.68	4.6332	43.84	3.9092
N_2'	65	25.00	3.8696	55.47	4.5436
N_3'	61	22.29	4.4505	47.39	5.2312
P	60	28.15	4.8513	45.08	3.1459
P_1'	60	16.47	4.0578	52.78	4.5537
P_2'	54	28.19	2.3861	48.59	3.2239
P_3'	53	25.68	3.2602	46.64	3.8648
R_1'	53	19.23	4.4762	24.13	6.7496
R_2	56	18.53	4.9310	24.35	8.0726
R_3'	55	15.33	4.6238	25.11	8.2269
S	56	14.38	5.7022	19.24	7.4588
S_1'	54	17.69	6.2176	21.53	8.0219
S_2'	56	16.48	4.9631	21.26	7.1937
S_3'	52	15.96	5.7314	24.84	7.5561

such as silica and clay do not have much effect on rubber network[17,18] Also silica is reported to cause retardation in crosslinking efficiency in accelerated sulphur systems[19]

5.3 CONCLUSIONS

It is clear from the above investigation that 1-phenyl-3-(N,N'-diphenyl amidino)thiourea can act as an effective secondary accelerator with MBTS or TMTD as primary activator in the sulphur vulcanization of styrene butadiene rubber. Analysis of the optimum cure time as well as induction time values of various gum formulations reveal that the nucleophilic reaction mechanism proposed in NR systems for the activity of the secondary accelerator is applicable in SBR systems also, atleast in the initial stages of vulcanization. The nucleophile produced from ATU cleave the bond of the primary accelerator enhancing the crosslinking precursor reactions. The tensile properties of the vulcanizates containing ATU are also found to be satisfactory

Both MBTS-ATU and TMTD-ATU binary systems are found to be effective with SBR filled vulcanizates also. But it has been observed that when precipitated silica is used as the filler the MBTS-ATU combination showed very poor curing characteristics. Tensile properties of the filled vulcanizates of ATU are comparable to/ better than the reference combinations. The after-ageing properties of vulcanizates with ATU are also found to be satisfactory. Other physical properties such as hardness, abrasion loss, tear strength, compression set etc of these vulcanizates also showed comparable values with those of the reference mixes.

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CHAPTER VI

SUMMARY

In rubber technology, the use of mixed accelerator systems for vulcanization has received considerable attention since such systems usually exhibit synergism. Binary accelerator systems are increasingly used now-a-days as they provide efficient vulcanization and exhibit improved physical and chemical properties of the finished product Inspite of the widespread use of such systems the mechanism of the joint action of the accelerator is not fully understood even now It has been suggested that sulphur containing nucleophiles such as thiourea enhances the activity of accelerators such as TMTD, CBS etc., in which sulphur is combined as S-S, C-S-C or S-N The increased activity of the combined system is believed to be due to the capability of the nucleophile from the secondary accelerator to facilitate the cleavage of the above mentioned S-bonds of the primary accelerator, thus enhancing the crosslinking reactions. It has also been suggested that higher the S-nucleophilicity of the secondary accelerator, lower will be the induction time and optimum cure time. Earlier studies made in these laboratories using dithiobiurets as secondary accelerators in sulphur vulcanization of natural and synthetic rubbers also support this. Even though a number of thiourea derivatives have been tried in rubber vulcanization as secondary accelerators, there is no mention in the literature on the accelerator activity of an amidinothiourea. We synthesized 1-phenyl-3-(N,N'-diphenylamidino)thiourea (ATU) and tried it as a secondary accelerator in the binary systems containing TMTD/MBTS in sulphur vulcanization of natural rubber, natural rubber latex and a synthetic rubber In these systems amidinothiourea performed as an efficient secondary accelerator and also improved many of the physical properties of the vulcanizates. Moreover, amidinothourea being more nucleophilic compared to thiourea. showed lower optimum cure time, induction time and higher cure rate than the latter This obviously indicates a polar reaction mechanism involving a nucleophile. Also the lower cure times observed with these systems is of much practical significance to the rubber product manufacturing industry

The first chapter of the thesis gives an introduction to the rubber vulcanization the role of accelerator in these processes. mechanism of vulcanization reactions and the significance of binary systems. It also includes the scope and objectives of the present work. A detailed description of the experimental procedure adopted in the present study is given in chapter II. It covers the procedure for the synthesis of the amidino thiourea derivative, methods adopted for compounding, vulcanization and determination of the different physical properties. The method used for the estimation of total crosslink density is also given in this chapter.

The study of accelerator activity of the binary system containing ATU with TMTD, and with MBTS in sulphur vulcanization of dry natural rubber using standard procedures for compounding and vulcanization is described in the third chapter. The study of the gum vulcanizates form part I of this chapter The behaviour of the experimental mixes were compared with those of the controls containing thiourea/ diphenyl guanidine. We made detailed investigation of these mixes with special reference to cure characteristics, physical properties and network structure. Analysis of the cure behaviour of the gum systems provided a clear evidence for the proposed nucleophilic reaction mechanism. When MBTS or TMTD alone was used as the accelerator, curing was low as indicated by higher optimum cure time On the other hand, when binary systems containing amidinothiourea were used considerable reduction in optimum cure time was observed. Also it was found that, when used alone, ATU cannot function as an accelerator, which limits its activity as a secondary accelerator only Moreover, mixes containing ATU, when compared with other mixes containing equivalent amount of DPG or thiourea as secondary accelerator, showed lower cure time and induction time and a higher cure rate value. This shows that ATU brings about faster onset of vulcanization. ATU being more nucleophilic than DPG and thiourea, a nucleophilic reaction mechanism can be well envisaged in the activity of this secondary accelerator Tensile strength, modulus and elongation at break of vulcanizates were also evaluated. In most of these properties studied, vulcanizates containing ATU showed better performance. These vulcanizates also showed better retention in tensile properties after ageing. Comparable values with those of the reference mixes were obtained in the case of other physical properties such as hardness, compression set, heat build-up, resilience and tear strength. Total chemical crosslink density values estimated also supported the above conclusions. The optimum concentration of ATU required for both MBTS and TMTD systems were also determined.

The effect of fillers in the vulcanization of NR with TMTD-ATU, and with MBTS-ATU systems was also investigated. This study forms part II of this chapter The fillers used are carbon black, silica and china clay. Both the binary systems are found to be very effective in filled NR vulcanizates also. The results obtained in those systems are also in favour of a nucleophilic reaction mechanism. The cure characteristics of the mixes and the tensile properties of the vulcanizates, containing ATU are found to be better than/ comparable to those of reference mixes. The optimum dosage of ATU required for different experimental cure systems has also been derived. The percentage retention of tensile properties on heat-ageing of the vulcanizates containing ATU is found to be satisfactory. The variations of cure characteristics and tensile properties with filler types does not indicate any set patterns in these filled systems. This may be due to the variation in the adsorption of accelerators by the filler particles. Other physical properties such as hardness, resilience, compression set, heat build-up, abrasion resistance and tear strength of these vulcanizates from both the systems give values comparable to those of the reference mixes. One disadvantage of ATU mixes observed is their low scorch time when used in higher dosage especially with TMTD systems. Even then the optimum dosage of ATU arrived at show sufficient scorch safety The results of the above investigations indicate that the systems reviewed both in the gum and filled stocks of natural rubber can be used in a practical rubber product manufacture.

We have examined the accelerating effect of ATU in NR latex systems also. Chapter IV gives a comprehensive description of this investigation. In latex systems, the ingredients are added as dispersions or solutions. Here we also used TMTD alone, ZDC alone and TMTD-TU systems as reference mixes. The mixes were cured in a laboratory air oven at 120°C. The optimum cure time of different mixes were estimated by plotting tensile strength against time, and the time to reach maximum tensile strength is taken as the optimum cure time. From the results obtained in this study it is evident that ATU can function as an effective secondary accelerator in latex systems also. It is observed that ATU did not cause coagulation or destabilization of the latex. From the results obtained in the evaluation of the cure characteristics of mixes and physical properties of the vulcanizates it is evident that these values are comparable with/better than those of the reference systems. The optimum cure time was found to be less for the TMTD-ATU systems compared to TMTD-TU systems. This again points to the involvement of a polar mechanism in the vulcanization process. Vulcanizates containing ATU showed higher tensile strength and better retention compared to those containing TMTD alone and TMTD-TU As observed in dry NR systems, in latex systems also, ATU when used alone is unable to function as an effective accelerator Regarding tensile strength TMTD-ATU systems showed better values compared to the reference mixes. It is found that with increase in concentration of ATU the tensile strength decreases first and the remains more or less at the same level. This behaviour can also be correlated to the variation in total chemical crosslink density of the vulcanizates The heat ageing resistance of vulcanizates with ATU is found to be comparable with those of reference formulations.

Filled latex systems with ATU were also studied. The various fillers used are china clay, precipitated silica and calcium carbonate. It is observed that the reduction in tensile strength in presence of filler; which is usual with latex systems, is comparatively less for the ATU systems. It is also observed that incorporation of filler, in general, increases the cure time. But at the same time it is found that the optimum cure time decreases with increase in the amount of ATU The filled formulation showed lower tensile strength and elongation at break values compared to gum formulations but showed higher modulus. The filled vulcanizates containing ATU showed better ageing resistance also compared to the reference. Also, with increase in the concentration of ATU the tensile strength remains more or less the same both before and after ageing.

Chapter V deals with the study on the effect of amidinothiourea in the accelerated sulphur vulcanization of a synthetic rubber viz., styrene butadiene rubber. We carried out the study using SBR-1502, with MBTS/TMTD as primary accelerators. Mixes containing DPG or thiourea as secondary accelerator were also studied as reference mixes. Here also we evaluated the cure characteristics, tensile properties and the network structure of the various systems under review in detail. Part I of this chapter describes the effect of ATU in SBR gum formulations. When MBTS alone is used as the accelerator, the mix showed very high cure time and poor cure rate. But when equivalent amount of MBTS and ATU are used appreciable reduction in cure time and induction time is observed. This indicates that ATU can function as an effective secondary accelerator in SBR systems also. Comparing the mixes with MBTS-ATU and MBTS-TU, the former showed lower cure time and higher cure rate. So here also it is reasonable to assume that the vulcanization proceeds through a nucleophilic attack by the secondary accelerator. The same is true with TMTD-ATU systems also. In both systems, with increase in concentration of ATU the optimum cure time and scorch time showed a sharp decrease. As in the case of NR, the main disadvantage of the ATU systems is their lower scorch time at higher dosages. However, practical cure systems can be developed with sufficient scorch safety. Also it is observed that in both MBTS and TMTD stocks, mixes containing DPG showed lower cure time compared to mixes containing equivalent amount of ATU. But here also the ATU containing formulation showed a lower induction time indicating that at least initially a polar mechanism of vulcanization is operative. Thus a reasonable conclusion is that in SBR systems containing MBTS or TMTD a mixed polar/radical mechanism may be involved. SBR being a non-strain crystallizable rubber shows very low gum strength. Even then mixes with MBTS-ATU showed reasonable values of tensile strength. Also tensile strength values showed an increase with the concentration of ATU But TMTD-ATU mixes showed slightly lower tensile strength values compared to the reference. These variations are found to be more or less in accordance with the crosslink density values obtained. The other physical properties evaluated are tear strength, compression set, abrasion loss and hardness. In these properties also systems containing ATU showed comparable values with those of the reference mixes.

ATU showed promising results with filled systems of SBR also. The characteristics of these systems evaluated are described in part II of chapter V The fillers used are carbon black, precipitated silica and china clay The curing behaviour of the MBTS systems is found to be very poor. Also the variations in optimum cure time do not show any set patterns as observed with gum stocks. This may be due to the adsorptive nature of these fillers. However, induction time showed definite variations. Mixes containing ATU showed lower induction time compared to the corresponding reference systems. This suggests that the nucleophilic reaction mechanism suggested earlier is applicable in filled systems of SBR also at least in the initial stages of vulcanization. On the otherhand TMTD systems showed definite variations in optimum cure time. TMTD-ATU showed lower cure time compared to reference and this behaviour is in accordance with the proposed nucleophilic mechanism. Irrespective of the nature of the filler used, it is observed that the optimum cure time decreases with the increase in concentration of ATU for both MBTS and TMTD systems. As mentioned in section 3 2, precipitated silica, due to its high adsorptive nature, is known to have a retarding effect on curing. Here also the silica filled MBTS systems showed very low cure rate compared to other systems, and hence these systems were not investigated further. When compared with references, mixes containing ATU showed better values for the tensile properties. With increase in the concentration of ATU the tensile strength of the carbon black filled vulcanizates increases first reaches a maximum and then decreases. For clay filled systems tensile strength is seen to increase slightly with the concentration of ATU For the TMTD-ATU systems, the tensile strength does not show much variations with concentrations of ATU, for all filler types. The other physical properties studied are hardness (shore A), compression set, abrasion loss and tear strength. It is observed that systems containing ATU show comparable values for these properties with those of the reference vulcanizates. Even though the MBTS-ATU systems are not so efficient as that of TMTD-ATU, in general, it can be stated that both the binary systems are more or less effective with SBR filled vulcanizates also. From the different formulations studied, practical cure systems can be derived with sufficient scorch safety and satisfactory physical properties. The list of publications from this work is included at the end of the thesis.

LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
ATU	1-phenyl-3-(N,N'-diphenyl amidino)thiourea
BIS	Bureau of Indian Standards
BS	British Standards
DEG	Diethylene glycol
DPG	Diphenyl guanidine
dNm	deci Newton metre
HA	High Ammonia
HAF	High Abrasion Furnace
hrs	hours
ISNR	Indian Standard Natural Rubber
MBTS	Mercaptobenzthiazil disulphide
μm	micrometre
Min.	minutes
ML(1+4)100°C	Mooney Viscosity determined using large rotor after a dwell time of one minute and rotor run of 4 minutes at 100°C
MPa	Mega Pascal
nm	nanometre
Nm	Newton metre
phr	parts per hundred rubber
rpm	revolutions per minute
S	Sulphur

SBR	Styrene Butadiene Rubber
TMTD	Tetramethylthiuram disulphide
TU	Thiourea
ZDC	Zinc diethyl dithiocarbamate
ZMBT	Zinc mercapto benzthiazole
M_c	Number average molecular weight of rubber chains between crosslinks
V_r	Volume fraction of rubber
V_s	Molar volume of the solvent
χ	Polymer-solvent interaction parameter
ρ_s	Density of solvent
ρ_r	Density of rubber
z	Weight fraction of filler
t_{90}	Optimum cure time
t_{10}	Scorch time
t_5	Induction time

LIST OF PUBLICATIONS

1 Studies on a new binary accelerator system containing TMTD and amidinothiourea in sulphur vulcanization of NR

J Appl. Polym. Sci., **54**, 1033 (1994)

2. Amidinothiourea as a secondary accelerator in a binary system for sulphur vulcanization of NR.

J Materials Sci **30**, 2049 (1995)

3 Effect of fillers in the binary system containing TMTD/ATU and MBTS/ATU in NR vulcanization.

J Appl. Polym. Sci., **59**, 365 (1996)

4 A new binary system containing TMTD and amidinothiourea in sulphur vulcanization of SBR. Communicated

5 Studies on a new binary accelerator system containing MBTS and amidinothiourea in sulphur vulcanization of Styrene butadiene rubber. Communicated

6. Studies on a new binary accelerator system containing TMTD and amidinothiourea in sulphur vulcanization of NR latex systems. Communicated