AMIDINO THIOUREA AS A SECONDARY ACCELERATOR IN RUBBER VULCANIZATION

Thesis submitted to the

**COCHIN UNIVERSITY OF
SCIENCE AND TECHNOLOGY**

by

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

DOCTOR OF PHILOSOPHY

DEPARTMENT OF POLYMER SCIENCE AND RUBBER TECHNOLOGY
COCHIN UNIVERSITY OF SCIENCE AND TECHNOLOGY
KOCHI- 682 022

SEPTEMBER, 2002

CERTIFICATE

*This is to certify that this thesis entitled "**Amidino Thiourea as a Secondary Accelerator in Rubber Vulcanization**" is a report of the original work carried out by Smt. Mary Kurien under my supervision and guidance in the Department of Polymer Science and Rubber Technology. No part of the work reported in this thesis has been presented for any other degree from any other institution.*

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DECLARATION

*I hereby declare that the thesis entitled "**Amidino Thiourea as a Secondary Accelerator in Rubber Vulcanization**" is the original work carried out by me under the supervision of Prof. (Dr.) A.P.Kuriakose, Professor Emeritus, Department of Polymer Science and Rubber Technology, Kochi 682 022, and no part of this thesis has been presented for any other degree from any other institution.*

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Kochi-22,
7th September, 2002.

ACKNOWLEDGEMENT

I express the first and foremost word of my heart-felt gratitude to my supervising teacher Prof. A. P. Kuriakose, Professor Emeritus (former Head of the Department of Polymer Science and Rubber Technology and former Dean, Faculty of Technology, Cochin University of Science and Technology), for his critical and scholarly guidance and inspiring encouragement throughout this work.

I am extremely grateful to Prof. K.E.George, Head of the Department of Polymer Science and Rubber Technology, for his constant encouragement and support and for providing all facilities during my research.

I am greatly indebted to all faculty members and administrative staff of the Department of Polymer Science and Rubber Technology, for their whole-hearted cooperation and encouragement. I express my sincere gratitude to Prof. Rani Joseph for the help rendered to me at the various stages of my work. Thanks are also due to my fellow research scholars and friends in the Dept. of PS & RT, and my colleagues at Union Christian College, Alwaye.

I am sincerely thankful to Dr K.T.Thomas, Deputy Director, Dr. N.M. Claramma and Dr. N. R. Peethambaran, Rubber Research Institute of India, Kottayam, for providing the laboratory facilities at RRII, Kottayam and for their helpful suggestions and comments. I acknowledge with thanks the useful suggestions of Dr. K. Sreekumar, Department of Applied Chemistry, Cochin University of Science and Technology.

I remain thankful to Dr. Raju K John, Principal, Union Christian College, Alwaye and Dr. Rajan Varghese, former Principal, Union Christian College, Alwaye for their kind advice and encouragement.

I record my sincere gratitude to Mr. Sony K.T. for the help rendered in preparing this thesis.

I must thank the University Grants Commission for granting the Teacher fellowship, the Higher Education Department of Kerala for permitting me to proceed on leave.

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Chapter 1

INTRODUCTION

Elastomers form a class of oldest and widely used materials known to man with diverse applications. Raw rubber is an entanglement of high molecular weight hydrocarbon chains. For rubber to become truly useful, its chains must be permanently linked together to increase the strength. Vulcanization is the technique of transforming rubber, by some suitable treatment, from a plastic substance of very low strength and breaking elongation to a resilient highly elastic material of considerable strength and not so sensitive to temperature changes. The discovery that rubber can be vulcanized or cured by heating it with sulphur was a technological accomplishment of major importance. As our present study involves processing, curing and vulcanizate properties of different elastomers and their blends a detailed description of rubber compounding ingredients, different vulcanization systems, their mechanisms, etc. are described.

Vulcanization with sulphur is still the most important method for crosslinking of unsaturated rubbers. Sulphur vulcanization of a rubber is a chemical process by which individual polymer chains are united into a three dimensional network by connecting sulphur atoms. It was in 1894 that Weber, a British chemist, showed that the sulphur actually combined chemically with the rubber during vulcanization. The chemistry of the crosslinking reaction and the structure of the sulphur crosslinks have been studied extensively for natural rubber[1,2]. Studies on the chemistry of vulcanizaiton[3,4] play a central role in the efforts to achieve better product performance from natural and synthetic rubbers. They provide rubber technologists an increasingly realistic picture of molecular network of vulcanizates, from which relation between physical properties and chemical constitution may be deduced. Thus, the ultimate goal of understanding vulcanization chemistry is to be able to tailor formulations to produce desired mechanical and chemical properties.

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

Important characteristics related to the vulcanization process are the time taken before crosslinking starts, the rate of crosslink formation and the extent of crosslinking at the end of the process. There must be sufficient delay or scorch resistance to permit mixing, shaping and flowing in the mould. Then the formation of crosslinks should be rapid and the extent of crosslinking must be controlled. Natural rubber and most of the unsaturated synthetic rubbers can also be vulcanized by a wide variety of non sulphurated agents including organic peroxides, quinones and their oximes and imines, poly nitro benzenes, biz-azodicarboxylic esters, and by means of high energy radiations. Polychloroprene rubbers are usually vulcanized by metallic oxides like MgO along with other ingredients. Non-olefinic polymers generally require non-sulphurated agents or high energy radiations for effective vulcanization. The most common vulcanizing agent for diene rubbers is sulphur. A vast amount of technical literature is available for sulphur vulcanization of rubber. Depending on the application, either soluble or insoluble sulphur is used. Insoluble sulphur is polymeric, gives 60-95% CS_2 soluble fraction and does not bloom to the surface like soluble sulphur. For the preparation of vulcanizates of normal hardness 0.25 to 3 phr sulphur may be used.

Vulcanization is usually effected by heating the mechanically plasticized rubber with sulphur and other ingredients. Before vulcanization the mixing of rubber with other ingredients (compounding) is done. The main objectives of compounding are to facilitate processing, to achieve the required balance in vulcanizate properties and produce durability. The various ingredients generally added to rubber during compounding include processing aids, accelerators and activators, fillers, antidegradants, etc. Vulcanization of rubber with sulphur alone is a slow process and requires several hours or even days to acquire optimum curing depending on the nature of rubber and the temperature of vulcanization. This gives rise to vulcanizates of only very low physical properties. Moreover, they have a strong tendency to revert and their resistance to aging is very poor and sulphur blooming occurs. Hence vulcanization with sulphur alone is of no technological importance. The low crosslink density, which is obtained when sulphur is used alone is mainly due to the fact that multivalent polysulphidic bridges, cyclic sulphides and vicinal bridge links are formed. Sulphur, which exists as S_8 ring, requires a large amount of activating energy to split. This process of activation occurs at high temperature and can be promoted by accelerators. According to Le Brass[5].40-55 sulphur atoms have to be combined to form a single chemical bridge when the vulcanization is carried out with sulphur alone, whereas in the presence of accelerators and activators only about 1.6 sulphur atoms are required even at low temperature.

The rate of reaction between rubber and sulphur is slow even at elevated temperatures. So inorganic accelerators were used until 1906, when Oenslager discovered that small amounts of aniline accelerated the curing of rubber significantly and also improved the final vulcanizate properties[6]. Since then new accelerators have been sought which would not only improve processing and vulcanizate properties but which also would be more efficient and economical. Because of the toxicity of aniline, its derivatives were then investigated. The reaction product of aniline and carbon disulphide, thiocarbanilide (N, N'-diphenyl thiourea) was found to be less toxic and to give more uniform cured product from the various grades of rubber. Dithiocarbamates and xanthates have been extensively used as accelerators, but because of their instability, extreme activity and poor processing safety they are used today only where low-temperature processing and curing is possible. Dithiocarbamate salts are easily oxidized to thiuram disulphides, which give greater processing safety than the dithiocarbamates. Substituted guanidines were the most widely used organic accelerators in the early 1920s[7]. With the introduction of synthetic elastomers and the use of fine furnace blacks, accelerators with greater processing safety became necessary. The benzothiazole sulphenamides give long processing safety and satisfactory cure rates[8]. There are also accelerator systems in which elemental sulphur is not present, but the accelerator provides the sulphur for vulcanization. These sulphurless systems are generally referred to as sulphur donor systems.

The rate of vulcanization can be increased by the addition of metallic oxides, which function as activators. Activators enable an accelerator to exercise its maximum effect. Organic accelerators usually require the presence of organic acid or inorganic activators. ZnO is probably the most important inorganic activator but magnesium and lead oxides also find use. Fatty acids (eg. stearic acid) are used as coactivators. Polyalcohols (eg. ethylene glycol) and amino alcohols are used to counteract the retarding effect of white fillers. A combination of ZnO and a long chain fatty acid like stearic acid, which is used as a co-activator form an ideal activator system[9]. ZnO can also function as a filler to reduce cost and it was found to have reinforcing effect and was later found to reduce the curing time[10].

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

Carbon black is of the following grades depending on the manufacturing process. Channel blacks are manufactured by burning natural gas in small flames and particles get deposited on cooled channels. Furnace blacks are obtained by burning natural gas or oil in a controlled supply of air in furnaces. Lamp black and thermal black are obtained by burning oil or natural gas. Acetylene black is produced from acetylene gas by exothermic reactions. Furnace blacks are more reinforcing in NR as compared to all other grades. This is mainly due to its fine particle size and high structure. The finer the particle size the more will be the reinforcing properties. But fine particle size and high structure blacks are more difficult in incorporating in rubber compounds. Silicas are reinforcing white fillers that can be produced by two processes, precipitation and combustion methods. The precipitation process yields a filler with a particle size of 10-40nm. Silica can give tensile and tear strength equivalent to those obtainable from the use of carbon black, but the resilience, set and abrasion resistance are generally inferior. Hot tear strength is superior to that obtainable with carbon black. Diethylene glycol, triethanolamine or silane coupling agents are required to eliminate the cure retarding effect of silica fillers. White clay based fillers are useful compounding ingredients in rubber. They can be divided into hard and soft. The hard clays can be classed as semi-reinforcing fillers due to their smaller size. Elastomers undergo aging and deterioration that are characteristic of their structure and the environment in which they are used. Major degradation of rubber is due to oxygen and ozone attack. It is therefore, necessary to incorporate antioxidants and antiozonants in rubber compounds. Antioxidants can be divided into staining and non-staining. Amines are usually staining in nature. Phenyl β naphthyl amine (PBN) is one of the commonly used antioxidants, but causes staining. So PBN can only be used in black or dark colored compounds. Phenols are non-staining antioxidants. Styrenated phenols, though non-staining in character possess less antioxidant property than amines. Antiozonants are more relevant to diene rubbers and related polymers having unsaturation. Wax and some p-phenylene diamine derivatives are also useful in this regard.

In the case of accelerated sulphur vulcanization, the characteristics of the vulcanization process and the structure of the vulcanizate network are determined by the composition of the curing system[11]. The efficiency of the vulcanization system is measured by the nature and number of sulphur atoms in the crosslinks, and the extent of the chain modification will depend on the ratio of accelerator to sulphur. Based on the vulcanizate structures, the vulcanizing systems can be classified[12] as

a. The conventional vulcanization systems (CV) with very low accelerator: sulphur ratios including unaccelerated sulphur systems

b. The efficient vulcanizing (EV) system in which accelerator: sulphur ratio is very high

c. The semi EV system is in between these two. In EV systems, the network will contain about 80% mono sulphidic linkages and such vulcanizates will have improved reversion resistance. CV systems contain more polysulphidic linkages and their heat resistance is low. Semi EV system is a compromise over CV and EV systems.

The induction period of the vulcanization process (scorch safety) and rate of vulcanization after the induction period at a given temperature largely depend on the accelerator selection. The induction period can be additionally and independently controlled by the addition of a premature vulcanization inhibitor. The extent of vulcanization increases with increase in accelerator and in sulphur concentration. Accelerator selection and its concentration, relative to that of sulphur can have large effects on the thermal stability of the vulcanizates network[13]. This is especially true with polyisoprene rubbers (NR and IR). Most of the components of the curing system are mutually interactive and thus independent control of the various aspects of the vulcanization process and vulcanizate network structure is difficult. When one makes a change in the characteristics of the vulcanization process, the extent of cure, the stability of the vulcanizate network, or even the fatigue resistance of the vulcanizate may be inadvertently changed. Accelerated sulphur vulcanization is an improvement from the sulphur-only vulcanization because it has much shorter cure time and a better scorch period. The vulcanization process can be described by a rheometer curve for the accelerated sulphur system[14] (Fig.1).

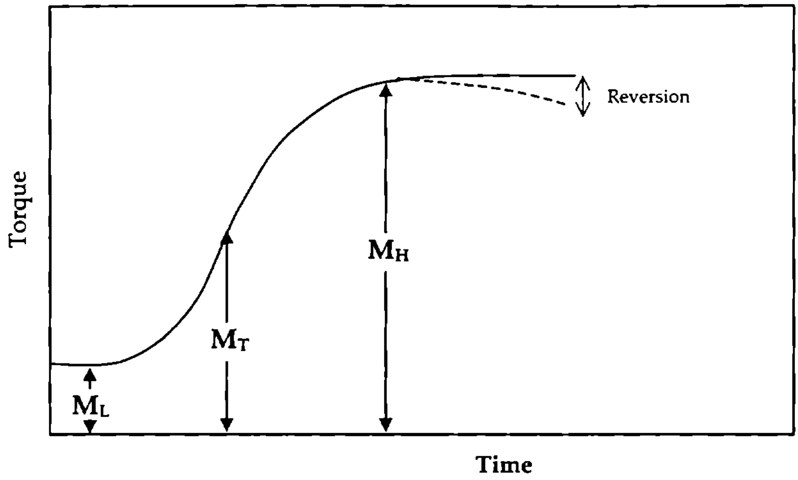


Fig.1. Typical curve for the accelerated sulphur system

There are three main regions for the cure curve. The first region is the scorch delay period or the induction period and the extent of this period depends on the accelerator system. For example there is very small scorch time for ultra accelerators like TMTD and very long scorch time for delayed action type accelerator. The second region is the crosslinking period, where the initial network structures are formed and the accelerator intermediates are consumed. The final state is the over cure period, where maturation or reversion occurs. The cure curve gives a complete picture of the kinetics of vulcanization. Scorch time is measured by the time at a given temperature at which the crosslinking reactions start and there is an abrupt increase in the torque value thereafter. All shaping and processing operations of rubber are done before the scorch time. In the curing region, permanent crosslinks are formed, which depend on the amount of vulcanizing agent, its activity, the reaction time and temperature and the nature of the rubber and other ingredients. The slope of the line in the curing region gives the rate of the reaction. Sulphur is combined in the vulcanization network in a number of ways. As crosslinks it may be present as monosulphide, disulphide or polysulphide, but it may also be present as pendent sulphides or cyclic monsulphides and disulphides (Fig.2).

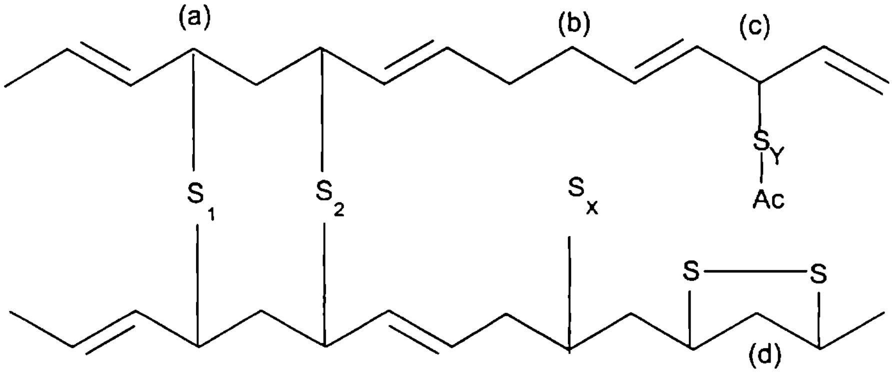
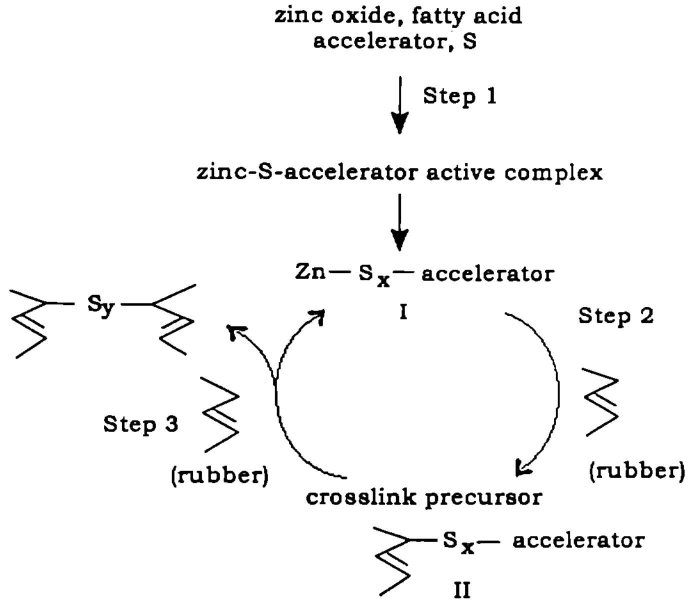


Fig.2 Net work structure of a typical rubber vulcanizate.

1.1 SINGLE ACCELERATOR SYSTEMS

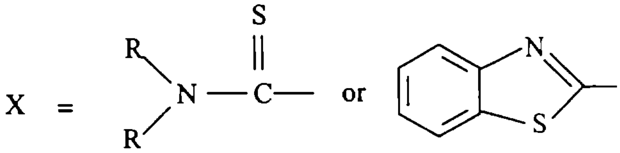
The nature of the vulcanizing system has a considerable influence since this will determine the structure of the crosslinks and the extent to which the polymer chains are modified chemically during vulcanization[15]. The majority of the research work concentrates on single accelerator systems due to the fact that the chemistry of single accelerator systems is inherently simpler. The accelerated sulphur vulcanization of NR has been studied extensively. Although it is mostly uncertain how the accelerator catalyses the reaction of sulphur with rubber[16,17], it is considered to proceed by the following sequence. First, the curatives combine to form a zinc-sulphur-accelerator complex, which attaches sulphur to the rubber to give rubber-S_x-accelerator intermediate. This intermediate either reacts with rubber, or more likely combines with another intermediate to form the sulphidic crosslink. As vulcanization continues, the initial polysulphidic crosslinks mature and become shorter or are involved in a variety of other reactions, depending on the rubber. Considering the generally accepted scheme of vulcanization, it can be seen that the zinc accelerator complex is continuously being reformed. Assuming a low steady state concentration of the rubber-S_x-accelerator intermediate at steady state, the concentration of the zinc complex remains constant, throughout the course of the entire vulcanization, which is in agreement with the observed constant rate of crosslink formation. This cyclic nature of the vulcanization[18] is depicted in scheme 1.



Scheme 1 Cyclic nature of the vulcanization reaction

The initially formed polysulphidic crosslinks may be de-sulphurated or degraded, leading to the final network structure.

During the scorch time or the induction period various accelerator complexes are formed which are the active sulphurating agents. The vast majority of accelerators used to assist the sulphur vulcanization of NR are thiazoles, thiuram disulphides and sulphenamides. They are represented as XSH, XSSX, XSZnSX, XSNRR', where



The initially formed zinc accelerator thiolates are insoluble in rubber but are rendered soluble through co-ordination with N_2 bases[19,20]. These ligands normally arise from the activators, accelerators, secondary accelerators or the nitrogenous non-rubbers in NR[21]. The basic nitrogen complexes are able to initiate vulcanization by opening the S_8 ring[22]. It is possible that electron donation from the amine ligand increases the nucleophilicity of the thiolate sulphur so as to enable it to open the S_8 ring. So zinc thiolate complex reacts with sulphur to form zinc perthiolates through a series of equilibria involving sulphur insertion and interchange. Zinc perthiolate complexes are believed to be the actual sulphurating agents in the vulcanization reactions. In some cases the primary and secondary amines cleave the S_8 rings to form polysulphidic ions[23,24]. Reactions of thiuram sulphides with amines have been known for a long time[25]. TMTD reacts exothermally with ZnO at 140°C to form zinc accelerator perthiolate and higher polysulphides. Thus the reaction sequence could lead to both types of active sulphurating agents, i.e. the accelerator polysulphide and zinc accelerator perthiolate. It is significant that sulphuration using a TMTD-sulphur-ZnO system also gave almost identical results[26]. Coleman et.al[27] reported that heating TMTD in the presence of sulphur and small amounts of amines leads to the formation of tetramethyl thiuram polysulphide (TMTP). The formation of TMTP from TMTD and sulphur in solution at 140°C was proven by means of HPLC by Versloot[28]. Carbon black appeared to catalyze the formation of TMTP[29], which explains part of the beneficial effect of carbon black in rubber vulcanization.

Formation of rubber-bound intermediate may be considered as the next step. Farmer and co-workers using model compounds proposed a new theory on the vulcanization of rubber by sulphur[30]. According to them α - methylinic hydrogen adjacent to olefinic double bonds is attacked by sulphur, and a hydrocarbon radical is formed. Then this radical couples with the diradical S_x and this leads to polysulphides. Farmer's theory laid the groundwork for the chemical investigation of vulcanization. Different techniques like radical scavenger studies[31], Raman spectroscopy[32], combined use of dicumyl peroxide and accelerators in the formulation[33-35] are used to study this subject. From these studies, they concluded 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[36] revealed that the mechanism depends on the nature of the elastomers also. The first evidence for a radical mechanism came from Scheele's studies[37] of thiuram vulcanization of NR. Wolfe suggested[38] a radical mechanism for accelerated vulcanization on the basis of model compound studies.

Dogadkin et.al[39] proposed that anions would mediate the crosslink formation by disproportionation. Manik and Banerjee[35,40] during their investigation of NR by DCP together with TMTD, CBS-S or MBTS-S found that the course of the reaction was altered by the addition of ZnO. They concluded from their results that the mechanism of sulphur vulcanization is predominantly polar when ZnO is present. Moore et.al[41] suggested an ionic mechanism and this was later adopted by Bateman[42]. Moore observed that the basic oxygen atom of ZnO performs a nulceophilic attack on accelerator forming the polysulphides. Then crosslink formation is by interchange between the rubber bound intermediate and zinc perthiolate followed by sulphuration at another rubber chain. In the next step of vulcanization sequence, the initial polysulphide crosslinks formed undergo further transformation by two reactions, desulphuration and decomposition. Desulphuration[43] leads to progressive shortening of the polysulphidic crosslinks producing mono and disulphide crosslinks. After the formal vulcanization, changes may continue to occur in the network structure, especially if the vulcanizate is in service at elevated temperatures. Blackman and McCall[44] analyzed the change in network structure of NR vulcanizates during the aging process and concluded that the aging process is due to the residual accelerator also.

1.2 BINARY ACCELERATOR SYSTEMS

Rubber vulcanization reaction can be effectively accelerated by the combined action of two or more accelerators. Mixed in the proper proportions, these accelerator combinations can lead to significant improvement in curing behaviour and mechanical properties and pre-vulcanization can be prevented[45]. The binary systems are increasingly used because of several factors including a desire to optimize the end-use properties and better control of processing safety. Such systems generally possess an increased activity over that obtained with the individual components. A binary accelerator system refers to the use of two accelerators in a given formulation. The accelerator present at a reasonably high level is called primary accelerator and that present in smaller amounts is called the secondary accelerator. The binary system usually gives a faster cure rate than either of the accelerators used alone due to synergistic effect. Some of the more widely used accelerators for binary systems are given in the work of Layer[46]. The synergistic behaviour of different binary systems has been studied by several authors[47-49]. Many amines such as diphenyl guanidine (DPG) are used in combination with other accelerators like MBT or sulphenamides to activate the vulcanization reaction. Some other binary accelerator systems used in rubber consist of benzothiazole and thiocarbamate or benzothiazole and thiuram systems[50,51].

In spite of the wide practice of using binary systems, the mechanism of the joint action of the accelerators has not been well studied. There are many approaches to analyze the vulcanization behaviour of binary accelerators. The method used by Layer to illustrate this effect is to measure mechanical or physical properties as a function of accelerator ratio. The results obtained in this method suggest the formation of specific complexes. Minatoya[52] and Aoe[53] explained the increase in activity arising from the use of two accelerators by the formation of a salt-like complex which is more active than either alone. Dogadkin and collaborators[54] investigated different combinations of most generally used accelerators and classified them into three groups:

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

The active complex formed depends on the molar raito of accelerators[55]. But this does not explain all the facts exhibited by the combined accelerator systems.

The use of certain coactivators in delayed action sulphur vulcanization had been reported[56]. Thiourea (TU) and its derivatives are popular in the mixed accelerator systems in rubber vulcanization. Some compounds in this class are diphenyl thiourea, sym-di-o-tolyl thioruea, N, N'-dimethyl thiourea, N-butyl-thiourea, diethylene thiourea, etc. Chloroprene rubber (CR) has been crosslinked on an industrial scale with TU systems. The reaction of thiourea in diene rubber is peculiar. For example, in NR the accelerator MBTS gives no crosslinking by itself, even if it is heavily dosed. If, however, substituted or un-substituted thiourea is used simultaneously very rapid vulcanization is obtained at normal temperature[57]. The vulcanizates have reasonably high tensile strength and good resistance to aging. Thiourea accelerates TMTD/ZnO vulcanization[42,58]. In this case the trithiocarbamate formed is a source of thiuram polysulphides. In the initial steps of vulcanization, characterized by an induction period and fast crosslinking, mainly ionic reactions take place[59]. This is in accordance with theories of Bateman and Moore[42]. In the next steps, characterized by degradation and slow crosslinking, mainly radical reactions occur. Support for this view derives from the influence of thiourea which is known not only as secondary accelerator of thiuram vulcanization but also as radical scavanger[31]. But if thiourea is used alone, no trace of crosslinking is seen indicating that this is a perfect example of synergistic behavior. The effects of combinations of thiourea or related compounds like thioamides and conventional accelerators have been investigated extensively[60]. A number of studies have been reported in the literature on the acceleration activity of thiourea and its derivatives[61-63]. According to Pariser[64] the ethylene thiorurea (NA_{22})-ZnO combination as a vulcanizing agent for CR crosslinks the rubber by forming monosulphide bridges and releasing ethylene urea.

The chemical reactions involved when a binary accelerator system is used in rubber vulcanization vary with the systems used and the elastomers involved[36]. But the exact mechanism of the crosslinking processes is not still understood clearly. It has been proved that accelerators in which sulphur is covalently linked to another sulphur, carbon or nitrogen are of the delayed action type, displaying little activity around 100°C. This is due to the inherent stability of their sulphur bonds. Some accelerators among them are the disulphide (XSSX) and sulphenamide ($XSNR_2$) accelerators of the benzthiazyl series like MBTS and CBS, and the monosulphide (XSX) and disulphide (XSSX) accelerators of the dithiocarbamyl series. The acceleration characteristics of these sulphur-bearing accelerators depend partly on the nature of the group X and partly on the mode of attachment of the functional sulphur atom to other atomic groupings in the molecule. The cleavage of the S-S, S-C or S-N bond is the preliminary step leading to a series of fast reactions in vulcanization. Activators are therefore required to favour the cleavage of the sulphur bonds. Philpott[65] studied the vulcanization of NR latex with TMTD-TU mixtures and showed that sulphur nucleophiles such as thiourea which are capable of releasing protons, enabled accelerators like TMTD and CBS to operate at low temperatures. An ionic mechanism was suggested, in which the S-S bond in TMTD is cleaved by the nucleophile Y^- produced from thiourea,

$$(CH_3)_2\,NC(S)S{-}S(S)C\,N\,(CH_3)_2 + Y^- \rightarrow (CH_3)_2\,NC\,(S)\,SY + (CH_3)_2\,NC\,(S)S^-$$

Similar arguments should apply to the activation of the monosulphide accelerators in which the characteristic sulphur linkage is S-C. In the case of the sulphenamides, $XS{-}NR_2$ scission at the S-N center would require the stabilization of the displaced nitrogen anion, R_2N^- by acquisition of a proton, preferably from the attacking reagent. Thus nucleophiles capable of releasing protons, like $(NH_2)_2C{=}S$ would attack the sulphenamides more readily. Of the different activators, the thioureas are particularly convenient to use with latex compounds because of their neutral reaction, absence of destabilizing action and general compatibility with latex.

This mechanism was further supported by Moore et.al[66]. This theory supports the formation of a polysulphidic intermediate I, in the presence of ZnO, which reacts with rubber hydrocarbon to form a further intermediate II leading to the production of sulphur crosslinks as follows,

$$(m-1)XSSX \xrightarrow{ZnO} \underset{\text{I}}{X - S_m - X} + \frac{m-2}{2}\{(XO)_2Zn + (XS)_2Zn\} \qquad \text{where } m > 2 \quad \ldots\ldots\ldots\ldots (1)$$

$$RH + X{-}S_m{-}X \xrightarrow{ZnO} \underset{\text{II}}{R{-}S_{m-1}{-}X} + \tfrac{1}{2}\{(XS)_2\,Zn + H_2O\} \quad \ldots\ldots\ldots\ldots (2a)$$

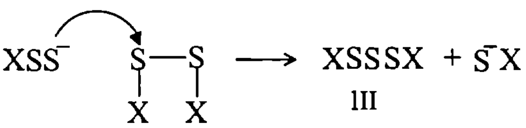
$$RH + R{-}S_{m-1}{-}X \xrightarrow{ZnO} R{-}S_{m-2}{-}R + \tfrac{1}{2}\{(XS)_2\,Zn + H_2O\} \quad \ldots\ldots\ldots\ldots (2b)$$

where $X = Me_2NC(S)$— and RH = rubber hydrocarbon.

Product II of reaction (2a), obtained from thiuram polysulphide reacts with rubber in vulcanization reaction (2b). Thus increase in the rate of formation of I leads to an increase in the vulcanization rate. TU and its derivatives activate TMTD to produce polysulphide I. The mechanism of polysulphide formation is as follows. The oxygen atoms of ZnO attack the thiocarbamyl carbon atoms of TMTD causing the polar substitution.

$$Zn^{2+} \ldots\ldots O^{2-} \ldots\ldots X \overset{\curvearrowright}{-} SSX \longrightarrow Zn^{2+} \ldots\ldots OX^{-} + \bar{S}SX \qquad \ldots\ldots\ldots\ldots (3)$$

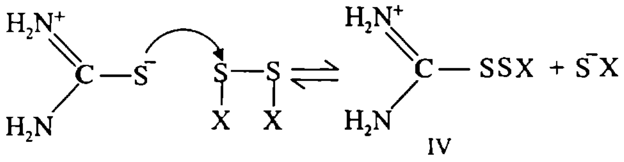
The perthioanion ^{-}SSX formed in reaction (3) causes the heterolysis of S-S bond in another TMTD molecule.



$$XSS^{-} + \underset{X}{S}-\underset{X}{S} \longrightarrow \underset{III}{XSSSX} + S^{-}X$$

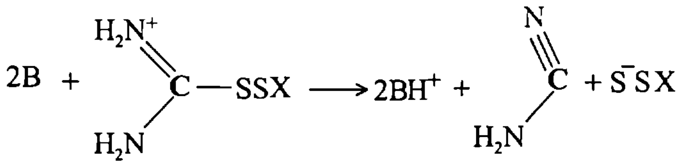
.... (4)

Compound III produces polysulphides by repeating reactions (3) and (4). It is observed that reaction (3), by which perthioanions are formed by cleavage of the X-S bond, is a slow process. When TU is added to the system, it accelerates the X-S bond fission by a thioanion-disulphide interchange reaction as follows.



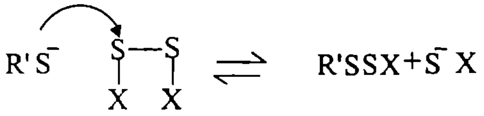
.... (5)

Compound IV easily loses a proton to a base in the medium forming the perthioanion. The easy steps (5) and (6) enable the formation of a perthioanion which leads to the formation of polysulphides in the presence of a base. This therefore results in accelerated vulcanization on the



.... (6)

addition of any thioanion R'S⁻ where the group R' is more easily attacked by bases than X group of TMTD. In general, the above mechanism can be written as follows.



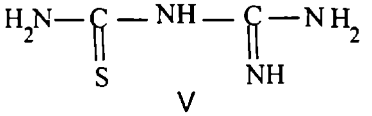
$$R'\bar{S}\ \ \underset{X}{S}{-}\underset{X}{S} \rightleftharpoons R'SSX + \bar{S}X$$ .... (7)

$$B + R'{-}SSX \longrightarrow BR'^{+} + \bar{S}SX$$ .... (8)

Reaction (7) is promoted by the removal of R'SSX in reaction (8) by a base. This condition is fulfilled in the case of TU, where R′ can liberate a proton easily. In a TMTD-ZnO-S system, TMTD and sulphur are reported to react in the presence of ZnO to form tetra methyl thiuram monosulphide (TMTM) and tetra methyl thiuram polysulphide (TMTP)[27]. According to Philpott, in the presence of ZnO and at low temperatures, the most probable mechanism for the formation of polysulphides is nucleophilic in nature. The above reaction can also occur in the presence of sulphur. The initial step is probably the reaction between TMTD and ZnO, but the dithiocarbamates produced can then react with the sulphur. Therefore, TU and its derivatives are reported to be effective secondary accelerators with TMTD or CBS particularly in latex vulcanization systems[66]. Even though these are convincing suggestions about the mechanism of rubber vulcanization, conclusive proof on these suggestions are still lacking.

1.3 SCOPE AND OBJECTIVES OF THE PRESENT STUDY

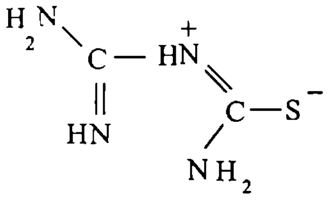
Earlier studies[67-73] in our laboratory showed that when a nucleophile is used along with disulphide or sulphenamide accelerators the vulcanization is accelerated greatly and the reaction mechanism is generally nucleophilic in nature. However it was observed that it also changes with the systems under review. The present study, deals with the use of unsubstituted amidino thiourea i.e. aminoimino methyl thiourea(AMT) V in the vulcanization studies of different elastomers and their blends. One of the aims of this study was to get further proof with regard to the theory of nucleophilic reaction mechanism in such binary systems.



$$H_2N{-}\underset{\underset{S}{\|}}{C}{-}NH{-}\underset{\underset{NH}{\|}}{C}{-}NH_2$$

V

Mixes containing thiourea are used as controls. AMT is more nucleophilic than TU and this is clear from the fact that the former can condense with isothiocynate even in the absence of alkali while TU cannot[74]. Also the guanidinyl group in AMT can facilitate the polarization of the C=S bond favouring a nucleophilic reaction as shown below.



It is reported[75,76] that many of the conventional accelerators used in rubber vulcanization are toxic in nature and some of them are banned in western countries. A lot of research work is undertaken world wide in search of non-toxic materials for rubber compounding. AMT is a non-toxic chemical and is used in the pharmaceutical industry[77,78]. The use of a non-toxic chemical in the vulcanization of different elastomers and their blends is also one of the aims of this study. The work includes a systematic study of compounding, curing and vulcanizate properties of different rubber systems.

In the first part of this study we tried amonoiminomethyl thiourea in different binary systems with MBTS/TMTD/CBS as primary accelerators in NR gum compounds and compared their properties with mixes containing control formulations. A detailed investigation of these mixes was made with special reference to cure characteristics, physical properties and network structure. There is found to be appreciable reduction in optimum cure time of the different experimental mixes. Their physical properties are also found to be encouraging. The effect of this secondary accelerator on filled systems was also studied. For this, mixes were prepared using different fillers like carbon black, precipitated silica and china clay. The cure characteristics, mechanical properties and the network structure of the filled systems were also investigated. These mixes were evaluated at two different temperatures, viz. 120 and 150°C, to study the effect of temperature on curing properties of these binary systems, especially with regard to the reaction mechanism.

The vulcanization of NR latex at low vulcanization temperatures using disulphide and sulphenamide type accelerators is not possible. Philpott[65] showed that sulphur nucleophiles like thiourea enabled accelerators like TMTD or CBS to operate at low temperatures and suggested an ionic mechanism in these binary systems. The compounding of NR latex is in principle similar to that of dry rubber. There are two major differences. First, as latex compounds are mixed at room temperature, highly active vulcanization systems can be used, which enable vulcanization to be performed at temperatures below 100°C. In dry rubber such systems are difficult or impossible because the heat developed in mixing causes premature vulcanization or scorch. Secondly, the reinforcing action of fillers, which is of major importance in dry rubber, is not obtainable in normally processed latex compounds. In our study also aminoiminomethyl thiourea was tried as secondary accelerator in natural rubber latex with primary accelerators like TMTD, ZDC or CBS at two different temperatures, viz. 100 and 120°C. The curing characteristics of the different mixes were investigated at these two temperatures. Mechanical properties like tensile strength and tear strength of the latex vulcanizate films were also evaluated. Chemical characterization of the vulcanizate samples was carried out using the equilibrium swelling method. The flow properties of latices are of great practical relevance for the industrial applications of polymers in latex form. The rubber industry operates with devices imparting shear stresses and shear rates over a wide range. Therefore the study of viscosity of a polymer as a function of shear rate and temperature is very important. Natural rubber latex is a pseudoplastic fluid and is non-Newtonian. When sheared the rubber particles are progressively aligned and offers less resistance to flow. So the apparent viscosity of the latex decreases on increasing the shear rate and continues until the flow curve becomes linear. Temperature has got tremendous effect on the viscosity of latex. Latex becomes less viscous as the temperature is increased. This is due to the reduction of viscosity of the dispersion medium. In our study also the rheological behaviour of the compounded latex was studied at different shear rates and temperatures.

Based on the encouraging results obtained in the study of the synergistic activity of aminoiminomethyl thiourea along with TMTD, MBTS or CBS in the sulphur vulcanization of natural rubber, we thought it worthwhile to try this secondary accelerator in the vulcanization studies of a synthetic rubber also. It is to be noted that the mechanism of rubber vulcanization depends on the type of elastomer also[79]. Many differences are encountered in the compounding and vulcanization of NR and synthetic rubbers. In this context we selected styrene butadiene rubber for this investigation. SBR, a general-purpose diene rubber has lower green strength and lower gum tensile strength by virtue of lesser stress crystallization. In order to improve these properties different fillers are incorporated in SBR compounds. Different compositions of AMT were tried in different SBR mixes using standard recipes and reference formulations were also studied. The effect of changes in concentration of AMT on the different cure characteristics is investigated. Mechanical properties like tensile strength, elongation at break, tear strength, etc. were evaluated and compared with control mixes. In order to correlate the variations in the physical properties of the various vulcanizates the total crosslink density values were also estimated using the equilibrium swelling method.

All the known elastomers do not exhibit all the properties desired and may have shortcomings in one or more properties. Therefore to obtain the right compromise in properties elastomers are often blended with others during processing[80]. Theoretically, blends of chemically dissimilar i.e. immiscible elastomers can attain a wider variation in properties than blends of miscible and thus chemically similar elastomers. Most blends of elastomers are immiscible, because mixing is endothermic and the entropic contribution is small because of high molecular weight[81]. Based on the results obtained with natural rubber and styrene butadiene rubber, we thought of investigating different blend systems of these elastomers using the amidino thiourea as a secondary accelerator. NR and SBR being general-purpose rubbers can be usefully blended if the fundamental differences and similarities between them are recognized. In this study the effect of binary systems containing different concentrations of AMT as secondary accelerator in the vulcanization of a 50-50 NR-SBR blend is investigated. Both gum and filled mixes are evaluated with regard to the various processing, curing and vulcanizate properties. Necessary control formulations were also prepared for comparison of these properties.

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

Chapter 1	General introduction on rubber vulcanization reaction mechanism and use of different accelerator systems.
Chapter 2	Explains materials used and the different experimental techniques adopted in the present study.
Chapter 3	
Part I	Investigations on the effect of aminoiminomethyl thiourea as secondary accelerator in sulphur vulcanization of NR gum mixes.
Part II	Studies on the effect of AMT in NR filled systems.
Chapter 4	Evaluations on the effect of aminoiminomethyl thoiurea in NR latex systems.
Chapter 5	
Part I	Studies on the effect of aminoiminomethyl thiourea in sulphur vulcanization of styrene butadiene rubber-gum compounds.
Part II	Effect of AMT in black and silica filled systems of SBR.
Chapter 6	Investigations on the effect of the new secondary accelerator in NR-SBR blends.
Chapter 7	Summary and conclusions

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Chapter 2

EXPERIMENTAL TECHNIQUES AND MATERIALS USED

The experimental procedures and the materials used in the present study are included in this chapter.

2.1 MATERIALS

2.1.1 Elastomers

Natural Rubber (NR)

Natural rubber used in this study was ISNR-5 of Mooney viscosity (M_L 1+4, 100°C) 85, obtained from Rubber Research Institute of India, Kottayam. The same lot of rubber has been used in a particular experiment, because molecular weight, molecular weight distribution and non-rubber constituents of natural rubber are affected by clonal variations, season and method of preparation[1]. Specifications of ISNR-5 rubber used in the study 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

Natural rubber latex

High ammonia type 60% centrifuged natural rubber latex conforming to the specifications of the Bureau of Indian Standards (BIS 5430-1981) was used in this study. The properties of the latex used are given below.

Dry rubber content, % by mass	60.040
Total solid content, % by mass	61.050
Coagulum content, % by mass	0.030
Sludge content, % by mass	0.007
Alkalinity as ammonia, % by mass	0.730
KOH number	0.496
Copper	Traces
Manganese	Traces

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. The specifications are given below:

Volatile matter, % by mass	0.23
Ash, % by mass	0.24
Organic acid, %	5.53
Soap	Traces
Bound styrene, % by mass	24.00

2.1.2 Other Ingredients

Zinc Oxide (Activator)

Zinc oxide supplied by Meta Zinc Ltd., Mumbai, had the following specifications:

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

Stearic acid (Co-activator)

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

Melting point (°C)	65.00
Acid number	200.00
Iodine number	9.05
Specific gravity	0.85
Ash (%)	0.10

Tetramethylthiuram disulphide (Accelerator)

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

Melting point (°C)	138.0
Specific gravity	1.3
Ash, % by mass, max	0.5
Moisture, % by mass, max.	1.0

Mercaptobenzthiazyl disulphide (Accelerator)

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

Specific gravity	1.51
Melting point (°C)	165.00

Cyclohexyl benzthiazyl sulphenamide (Accelerator)

Cyclohexyl benzthiazyl sulphenamide used in the study was Santocure CBS supplied by Polyolefines Industries, Mumbai, having the following specifications:

Ash, % by mass, max	0.50
Moisture, % by mass, max	0.50
Specific gravity	1.27

Thiourea (Accelerator)

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

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

Sulphur (Crosslinking agent)

Standard Chemicals Co. Pvt. Ltd., Chennai, supplied sulphur used in the present study. The specifications are:

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

Aromatic oil (Process oil)

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

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

Naphthenic oil (Process oil)

Naphthenic oil supplied by Hindustan Petroleum Corporation Ltd., Mumbai had the following specifications:

Pour point (°C)	20.00
Aniline point (°C)	78.00
Viscosity gravity constant (V.G.C.)	0.87
Aromaticity (%)	20.00

Fillers

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

Appearance	Black granules
DBP absorption (cc/100g)	102 ± 5
Pour density (Kg/m^3)	376.0
Iodine number	82.0
Loss on heating (per hour at 100°C, %), max.	2.5

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

pH (5% aqueous solution)	6.30
Density (g/cm^3)	2.03
SiO_2 hydrate on dried sample (% min.)	90.00
Loss on heating (105°C, 2 hrs, %)	5.50

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

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

Dispersol F

The dispersing agent used in the preparation of dispersions of solid ingredients is dispersol F. It was supplied by Indian Explosives Ltd., Kolkotta.

Potassium oleate

It is the soap used as a stabilizing agent in latex. This was prepared by reacting chemically pure oleic acid and potassium hydroxide. A 10%

solution of potassium oleate was prepared by warming a mixture of 28.2g oleic acid and 5.6g potassium hydroxide in 270 ml water.

Other reagents used.

Other reagents like toluene used for swelling studies, dicyanodiamide, thioacetamide, ammonia, etc. were of analytical grade.

2.2 EXPERIMENTAL METHODS

2.2.1 Synthesis of aminoiminomethyl thiourea (AMT)

AMT used in this study was prepared by mixing dicyanodiamide (8.4g) and thioacetamide (7.5g) and then adding con. Hydrochloric acid (10 ml) at 35°C. The mixture was then heated on a water bath for ten minutes. This was cooled and then diluted with water (100ml), boiled for two minutes, cooled and filtered. The filtrate was concentrated on a water bath to 50 ml and cooled to 0°C. Amidino thiourea hydrochloride separated was filtered and washed with ice-cold dilute HCl. An aqueous solution of the hydrochloride on treatment with 25% ammonia solution gave AMT which was recrystallised from ethanol, (m.p 171 °C).

2.2.2 Mixing and homogenization of the rubber compound

The compounding is done on a laboratory size two-roll mixing mill (33cmX15cm) at a friction ratio of 1:1.25 for natural rubber and 1:1.1 for styrene-butadiene rubber as per ASTM D 3182-89. For mastication of rubber, the elastomer was passed through the rolls. The temperature of the rolls was maintained at 70 ± 5°C during the mastication. After the nerve had disappeared, the compounding ingredients were added as per ASTM D 3184 (1980) in the order: activators, fillers, accelerators and sulphur. Before the addition of accelerators and curing agents, the batch was thoroughly cooled. After the addition of accelerators and curing agents, the band was properly cut from both sides to improve the homogeneity of the compound.

In the case of blends, natural rubber was masticated to a Mooney viscosity of 40 (approx.), comparable to that of SBR. These rubbers were pre-blended and then the additives were added. After complete mixing, the stock was sheeted out and passed six times end-wise through tight nip and finally sheeted out at a nip gap of 3mm. Mixing time and temperature were controlled during the process.

2.2.3 Determination of cure characteristics of rubber compound

The cure characteristics of the mixes were determined by using Goettfert elastograph, model 67.85. 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 that 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 Figure 1, Chapter I, p. 7.

The important data that could be taken from the torque-time curve are:

1. Minimum torque (M_L): This is the torque attained by the mix after homogenizing at the test temperature before the onset of cure.
2. Maximum torque (M_H): This is the torque attained by mix after the curing is completed.
3. Induction time (t_5): This is the time taken to attain a 5% torque increase.
4. Scorch time (t_{10}): This is calculated as the time taken to attain a 10% torque increase.
5. Optimum cure time (t_{90}): This is calculated as the time taken to attain 90% of maximum torque increase.
6. Cure rate index: The cure rate index is reported as $100/(t_{90} - t_{10})$, where t_{90} and t_{10} are time corresponding to the optimum cure and 10% rise in minimum torque respectively.

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

2.2.4 Vulcanization

The mixes were vulcanized up to the optimum cure time in an electrically heated hydraulic press at a pressure of 12 MPa on the mould at 150 and 120°C. Mouldings were cooled quickly in water at the end of the curing cycle and stored in cold and dark place for 24 hours, and were used for subsequent physical tests and chemical analysis. For samples having thickness more than 6mm additional time is given depending on the sample, to obtain satisfactory mouldings.

2.3 PHYSICAL TEST METHODS

At least three specimens per sample were tested and mean values are reported.

2.3.1 Tensile properties: Modulus, Tensile strength and Elongation at break.

All the above tensile properties were determined on a 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. Samples were punched from vulcanized sheets parallel to the mill grain direction using a dumb-bell die (C-type). The thickness of the narrow portion was measured by bench thickness gauge. The sample was held tight by the two grips in a Zwick tensile testing machine, the upper grip of which being fixed. The tensile strength, elongation at break and modulus were evaluated. The tensile strength and modulus are reported in MPa.

2.3.2 Tear resistance

The test was carried out as per ASTM method D624-86; unnicked, 90°angle test pieces were used. The samples were cut from the vulcanized sheets parallel to the grain direction. The test was carried out on a Zwick tensile testing machine. The speed of extension was 500 mm min^{-1} and the test temperature was 28 ± 2°C.

2.3.3 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 6 mm thickness. A load of 12.5 N was applied and the readings were taken after 10 seconds of indentation after firm contact had been established with the specimen.

2.3.4 Compression set

Samples (6.25 mm thickness 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 determined 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 = thickness of the space bar. This procedure is in accordance with ASTM D 395 - 86 (method B).

2.3.5 Abrasion resistance

The abrasion resistance of the samples was determined using a DIN abrader based on DIN 53516. Cylindrical sample having diameter 15 mm and length 20 mm was weighed and kept on a rotating sample holder. The sample was 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.

2.3.6 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, the density of which are less than that of water, a sinker was used. The weight of the sinker in water was also measured. Density of the sample was calculated.

2.3.7 Aging studies

Aging 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 air oven at predetermined temperatures for specified periods. Physical properties like tensile strength, elongation at break, modulus, etc. were measured before and after aging. The percentage retention of these properties was evaluated for assessing the effect of aging.

2.4 CHEMICAL TEST METHODS

2.4.1 Determination of the concentration of crosslinks of the vulcanizates

The crosslink density is calculated using equilibrium swelling data and the Flory-Rehner equation [3,4], $-[\ln(1-V_r) + V_r + \chi V_r^2] = \dfrac{\rho_r V_s (V_r)^{1/3}}{M_c}$

where ρ_r is the density of NR (0.921 g/cm^3), V_s = molar volume of solvent [V_s (toluene) = 106.2 cm^3/mol], χ = the parameter characteristic of the interaction between rubber and solvent[5,6], M_c = number average molecular weight of the rubber chains between crosslinks and V_r = volume fraction of rubber in the swollen network.

Vulcanizate samples weighing 0.2 to 0.3 g and 0.2 cm thickness are kept in toluene for 24 hrs. Swollen samples are weighed, the solvent is removed in vacuum and the samples are weighed again. The volume fraction of rubber (V_r) in the swollen network is calculated, according to Ellis and Welding,.[8,9]

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

where T = weight of the test specimen

D = weight of deswollen test specimen

F = weight fraction of insoluble non- rubber components

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

ρ_r = 0.921 g/cm^3 (density of test specimen)

ρ_s = 0.886 g/cm^3 (density of the solvent).

In the case of filled vulcanizates, the values of V_r are converted into V_{r0} (the value V_r would have had in the absence of filler), by using the following equation [9],

$$V_{r0} / V_r = a\, e^{-z} + b$$

where z is the weight fraction of the filler in the vulcanizate and a and b are constants characteristic of the system. For HAF filled system a = 0.56 and b = 0.44, for silica filled system a = 1.41 and b = –0.41 and for clay systems a = 0.21 and b = 0.79. V_{r0} values are then substituted in the Flory – Rehner equation to calculate the crosslink density $1/2M_c$.

2.5 COMPOUNDING OF LATEX

2.5.1 Preparation of dispersions

The soluble compounding ingredients are added to the latex as aqueous solutions, and water insoluble solids or water immiscible liquids as dispersion or emulsion. The materials were made to disperse in water by grinding action and the dispersing agent prevents the dispersed particles from re-aggregating. The quantity of dispersing agent to be used for preparing dispersions depends on the nature of materials to be dispersed. For very fine particles like ZnO the quantity of dispersing agent required is about 1% by weight whereas for materials like sulphur, 2 - 2.5% is required. A ball mill is used for making the dispersions of the ingredients. A ball mill consists of a cylindrical container in which the slurry is placed together with 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.

For the present study the following dispersions were made using a ball mill. Dispersol F (sodium salt of a sulphonic acid) is used as the dispersing agent. Aminoiminomethyl thiourea and thiourea are added to latex as 10% aqueous solutions.

1. 50 % zinc oxide dispersion:

Zinc oxide	100.00
Dipersol F	2.00
Water (de- ionised)	98.00

Ball milled for 48 hrs

2. 33% TMTD dispersion:

TMTD	100.00
Dipersol F	2.50
Water (de- ionised)	197.50

Ball milled for 48 hrs

3. 33% CBS dispersion

CBS	100.00
Dipersol F	2.50
Water (de- ionised)	197.50

Ball milled for 48 hrs

4. 50 % ZDC dispersion

ZDC	100.00
Dipersol F	2.50
Water (de- ionised)	97.50

Ball milled for 48 hrs

5. 50% sulphur dispersion

Sulphur	100.00
Dipersol F	3.00
Water (de- ionised)	97.00

Ball milled for 48 hrs

2.5.2 Compounding of latex

High ammonia type concentrated latex was used for the present study. So it was de-ammoniated to 0.3 % by stirring in a laboratory type de-ammoniation tank for 3 hrs. The high ammonia content in latex will affect the stability of latex compound in presence of zinc oxide. The total alkalinity of latex was estimated according to ASTM D 1076–88 as percentage of ammonia. Mixing of ingredients to natural rubber latex was in the following order[10]: stabilising agents, sulphur, accelerators and zinc oxide. All the ingredients were added with slow and thorough stirring. After the addition of ingredients, the compounds were kept for maturation at room temperature for 24 hours.

2.5.3 Rheology

The experimental mixes containing optimum dosage of AMT and the corresponding references were used for the rheological study. A Haake viscotester (VT 550) was used to study the effect of temperature and shear rate on viscosity. This viscometer has been designed to meet the most sophisticated requirements of continuous shear rheometry with 60 different rotational speed steps covering a wide range from 0.5 to 800 rpm. The functional units consist of viscotester and power supply unit, temperature control vessel with sensor system, Pt 100 temperature sensor and stand. The equipment operates over a temperature range from - 30 to 150°C. Thirty different sensor systems are available. Sensor system NV was used for the present study. (For details please see chapter IV)

2.5.4 Vulcanization and testing

Latex films were prepared by casting the matured compound in shallow glass dishes according to ASTM D 1076-88. The film thickness was controlled in the range of 1 to 1.25 mm. The films were then vulcanized at 120 and 100°C for specific time intervals in an air oven. The tensile strength of the vulcanized latex film was then determined both before and after aging as per ASTM D 412- 87 (method A) using a Zwick universal testing machine. The specimens for aging were kept in an air oven at 70°C for 7 days. The total chemical crosslink density and polysulphidic linkages were determined by equilibrium swelling method. For latex compounds, the optimum cure time was found out from the tensile strength – time graph. Tensile strength values were plotted against time of vulcanization. From the graph, the time taken for attaining the optimum property is taken as the optimum cure time.

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Chapter 3

STUDIES ON THE EFFECT OF AMINOIMINOMETHYL THIOUREA IN THE SULPHUR VULCANIZATION OF NATURAL RUBBER

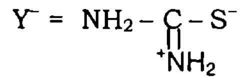
Natural rubber is cis- 1,4 polyisoprene with very small amounts of proteins, lipids, quebrachitol, inorganic salts and numerous other components including fatty acids and resins[1]. Polyisoprene has been reported in over 1000 species of plants, but Hevea brasiliensis is such a superior exploitable tree that it has now become virtually the sole source of supply. Purified NR hydrocarbon is a long chain polymer made up of isoprenoid units arranged in a highly stereo regular manner. The molecular weight of the polymer ranges from 200,000 to 600,000 with a relatively broad molecular weight distribution[2]. Due to its high stereo regularity NR crystallizes spontaneously on stretching. Because of this strain-induced crystallization, NR has high tensile strength in gum or non-reinforcing filler vulcanizates. Natural rubber is the preferred polymer in many industrial applications because of its superior building tack, green stock strength, high resilience, excellent dynamic properties, etc.

The raw rubber, which is not so elastic, is transformed into elastic useful products by the process of vulcanization. The long chain rubber molecules are crosslinked by curing agents to form three-dimensional structures. The vulcanization of NR may be effected with the aid of sulphur, organic peroxides, synthetic resins and other polyfunctional reagents and also by ionising radiations[3]. The intermolecular crosslinks thus formed have a profound effect on properties of the vulcanizates. The extent of changes in properties is governed by the choice of compounding ingredients added to the rubber and also by the vulcanization conditions. Sulphur is the principal vulcanizing agent used with NR. Sulphur vulcanization of NR is described in a number of publications[4-6]. The vulcanization temperature for NR ranges from 140 to 160°C and is carried out with a mixture of sulphur (2 - 3 phr), one or more accelerators (0.5 - 2.5 phr), ZnO (3 - 5 phr), a fatty acid (1 -3 phr) and other special additives. When sulphur is the vulcanizing agent accelerators are used to increase the rate of cure and to improve the physical properties and the age resistance of the products. The different types of accelerators used in NR are thiazoles, thiocarbamates, thiuram sulphides, guanidines, etc. With these accelerators or combinations of them it is possible to vulcanize rubber at the desired time and temperature. Many of the important physical properties of the vulcanizate can be controlled to a considerable extent by the choice of the accelerators, the sulphur level and the sulphur-accelerator ratio. The vulcanizates obtained by conventional vulcanization systems (high sulphur, low accelerator) deteriorate when subjected to heat aging. Vulcanizates with high heat resistance are obtained by using a high ratio of accelerator to sulphur or vulcanization with thiurams with small proportion of sulphur[7]. When thiurams are used as accelerators the vulcanizates have a relatively high modulus, good mechanical properties and good resistance to aging[8]. Thiazoles are the accelerator class of highest economic importance. Mercapto benzothiazole and its derivatives belong to this class. Mercapto accelerators give the compounds higher processing safety than the ultra accelerators and they require higher vulcanization temperatures. Sulphenamides are typical of accelerators with a delayed onset of vulcanization after which the vulcanization proceeds extremely fast[9]. This is because sulphenamide accelerators are derivatives of mercapto benzothiazole where an amine is oxidatively bound to the mercapto sulphur and these accelerators become active as the amines are split off during vulcanization.

Binary accelerator combinations can give faster cure rate in rubber vulcanization systems. Thiourea and its derivatives are known to be good secondary accelerators in NR vulcanization[10]. The exact mechanism of these vulcanization reactions varies with the systems used. In the work of Batemann et. al[11] they proposed a polar mechanism for the sulphuration process in the presence of zinc compounds. Thiourea derivatives act as effective secondary accelerators with TMTD or CBS especially in latex vulcanization. The sulphide and sulphenamide accelerators in which sulphur is covalently linked to another sulphur, carbon or nitrogen are of the delayed action type, displaying little activity around 100°C. This is due to the inherent stability of their sulphur bonds. The cleavage of the S-S, S-C or S-N bond is the preliminary step leading to a series of fast reactions in vulcanization. Therefore there should be some activators to favour the cleavage of these sulphur bonds. Philpott[12] in his studies on the vulcanization of NR latex with TMTD-thiourea mixtures showed that sulphur nucleophiles like thiourea [$(NH_2)_2$ C=S], which are capable of releasing protons, enabled the accelerators like TMTD, CBS, etc. to operate at low temperatures. He suggested an ionic mechanism, where the S-S bond in TMTD is cleaved by a nucleophile Y^- produced from thiourea.

$$(CH_3)_2\,NC(S)S - S(S)C\,N\,(CH_3)_2 + Y^- \rightarrow (CH_3)_2\,NC\,(S)\,SY + (CH_3)_2\,NC\,(S)S^-$$

where



$$Y^- = NH_2 - \underset{\underset{{}^{+}NH_2}{\|}}{C} - S^-$$

This was further supported by Moore et. al[13]. In our laboratory also the nucleophilic activity of different thiourea derivatives was investigated[14,15] and the results of these studies more or less agree with the suggestions made by Philpott and by Moore but the mechanism was found to vary with the systems used. Following the above observations the present study has been undertaken using an unsubstituted amidino thiourea, AMT, (ref. structure in chapter I, p.16) in different natural rubber formulations. One of the aims of this study is to get further proof with regard to the reaction mechanism in such binary systems of NR vulcanization. By virtue of the presence of guanidinyl group in AMT, it is more nucleophilic than thiourea and is expected to behave more effectively as a secondary accelerator. In this context the vulcanization was carried out at two different temperatures, viz. 120 and 150°C. It may be noted that many of the ingredients used in rubber compounding are reported to be toxic. AMT is a non-toxic chemical and is used in pharmaceutical applications[16]. The effect of AMT in binary systems containing MBTS/ TMTD/CBS as primary accelerator in NR gum and filled systems is described in this chapter. Gum formulations were tried as reaction mechanism will be more specific with unfilled compounds. Other conventional binary combinations like TMTD–MBTS, TMTD–CBS and MBTS–CBS were also prepared and their properties compared with those of the experimental systems. The first part of this chapter deals with the study in NR gum formulations and the second part reports the investigations on the effect of AMT in filled systems.

PART- I

3.1 STUDIES ON NR GUM COMPOUNDS

In this study an attempt is made to evaluate the synergistic effect of the above amidino thiourea in binary accelerator systems with TMTD/ MBTS/CBS in sulphur vulcanization of natural rubber. Different experimental mixes were prepared by varying the concentration of AMT along with primary accelerator. Mixes containing thiourea (TU) were studied as control. In order to study the effect of AMT on the temperature of vulcanization, cure characteristics of these mixes were evaluated at two different temperatures, viz., 120 and 150°C. The vulcanizates were further evaluated for various tensile properties and these properties were compared with other conventional systems prepared. Other physical properties studied include tear strength, compression set, hardness, abrasion resistance, etc. Chemical characterisation of the vulcanizates was also carried out using the swelling method.

3.1.1 Experimental

Synthesis of amidino thiourea (aminoiminomethyl thiourea, AMT)[17]

AMT used in this study was prepared by mixing dicyanodiamide (8.4g) and thioacetamide (7.5g) and then adding con. hydrochloric acid (10 ml) at 35°C. The mixture was heated on a water bath for ten minutes. This was cooled and then diluted with water (100ml), boiled for two minutes, cooled and filtered. The filtrate was concentrated on a water bath to 50 ml and cooled to 0°C. Amidino thiourea hydrochloride separated was filtered and washed with ice-cold dilute HCl. An aqueous solution of the hydrochloride on treatment with ammonia solution (25%) afforded AMT, which was recrystallised from ethanol, (m.p 171°C, yield 6.2g.). The substance was characterized by taking the IR spectrum (Fig 3.1).

Natural rubber (ISNR-5) of Mooney viscosity 85 was used in this study. The rubber additives, viz. zinc oxide, stearic acid, MBTS, TMTD, CBS, TU and sulphur used were all of rubber grade. The chemical reagents used for the synthesis of AMT were of analar grade. The formulations of the different mixes prepared are given in Table 3.1.

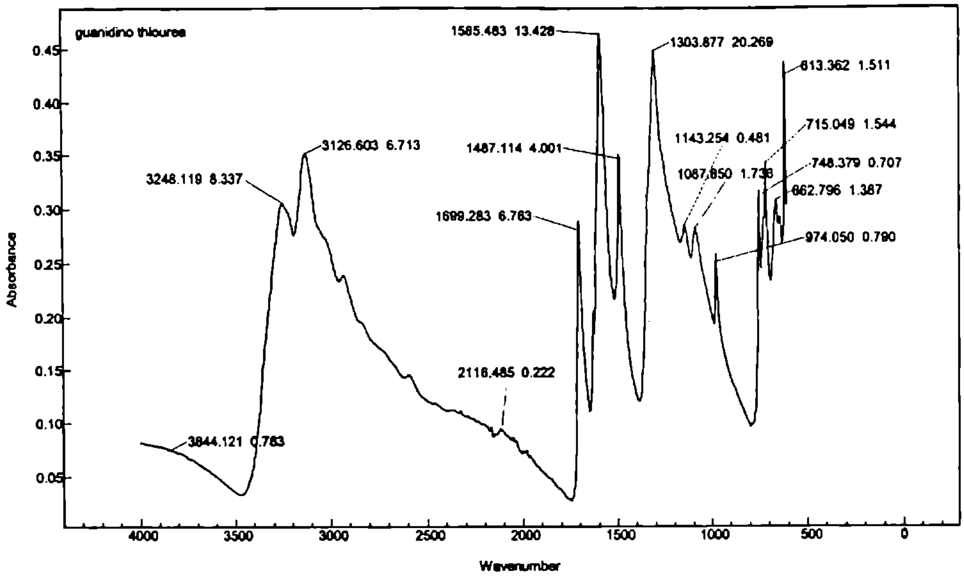


Fig. 3.1 IR spectrum of aminoiminomethyl thiourea

Accelerators were taken in molar concentrations and other compounding ingredients in parts per hundred rubber. Mixes A_1 – A_4 contain different concentrations of AMT ranging from 0.25 to 1.5 molar equivalents with 1 molar equivalent of TMTD. B_1 - B_4 are systems containing AMT ranging from 0.25 to 1.5 molar equivalents with MBTS. Mixes C_1 - C_4 contain similar concentrations of AMT with one molar equivalent of CBS. Mixes D_1 - D_3 contain two molar equivalents of TMTD, MBTS and CBS respectively. Mix D_4 is TMTD:TU, D_5 is MBTS:TU and D_6 is CBS:TU in 1:1 molar proportions. The properties of the AMT mixes were compared with other conventional accelerator combinations like TMTD:MBTS (mix D_7) and TMTD:CBS (mix D_8) also.

Natural rubber was compounded on a laboratory size two-roll mixing mill as per ASTM D 3182 – 89. The cure characteristics of the mixes were determined on a Goettfert elastograph (model 67.85). Optimum cure time (t_{90}) is calculated as the time taken for attaining 90% of the maximum torque rise. Scorch time (t_{10}) is the time taken for attaining a 10% torque rise. Induction time (t_5) is calculated as the time taken for attaining 5% rise in torque. The cure rate index is reported as $\frac{100}{t_{90} - t_{10}}$.

Table 3.1 Formulation of the mixes

Ingredients	A_1	A_2	A_3	A_4	B_1	B_2	B_3	B_4	C_1	C_2	C_3	C_4	D_1	D_2	D_3	D_4	D_5	D_6	D_7	D_8
Natural Rubber	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
Stearic acid	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
TMTD	1.2	1.2	1.2	1.2									2.4			1.2			1.2	1.2
MBTS					1.66	1.66	1.66	1.66						3.32			1.66		1.66	
CBS									1.32	1.32	1.32	1.32			2.64			1.32		1.32
Thiourea																0.38	0.38	0.38		
AMT	0.147	0.295	0.59	0.885	0.147	0.295	0.59	0.885	0.147	0.295	0.59	0.885								
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

The mixes were vulcanized up to the optimum cure time in an electrically heated hydraulic press at a pressure of 12 MPa. Tensile properties of the vulcanizates were determined according to ASTM D412 - 87 method A on a Zwick universal testing machine (model 1445). Aging was carried out at 70°C for 48 hours in a laboratory air oven (ASTM D 865-88). Tear resistance was determined by ASTM D 624-86. Test samples of 1.25 cm thickness and 2.8 cm diameter were used to determine the compression set as per ASTM D 395-89 - method B. Shore A durometer was used to find the hardness of the samples (ASTM D 2240 - 86). Abrasion resistance was measured using a DIN abrader (DIN 53516) and is expressed as loss in cc/hr. The total crosslink density was calculated using equilibrium swelling data. Details of the above experiments are as described in chapter II.

3.1.2 RESULTS AND DISCUSSION

Cure characteristics

The cure characteristics of the different mixes evaluated are given in Tables 3.2 and 3.3. The corresponding cure curves are given in Figs. 3.2 - 3.6. Considering the mixes cured at 150°C, the optimum cure time for mix A_3 containing TMTD-AMT is lower than that of other mixes containing similar proportions of accelerators (Table 3.2 and Fig. 3.2). A corresponding increase in the cure rate is also observed in the AMT mixes. These results clearly indicate the activating effect of AMT in the vulcanization of NR systems under review. Comparing the optimum cure time obtained for the system with TMTD-AMT with that for TMTD-TU, it is clear that AMT is a better accelerator than TU. However the very low scorch time observed in mixes containing high concentrations of AMT can cause processing problems. Reduction of the amount of AMT below 0.5 molar level gives higher scorch time values, but then the cure time is not appreciably reduced. By keeping the amount of AMT to one molar level, reasonable cure values can be obtained. It is also found that inclusion of AMT or TU in the TMTD mixes leads to slight reversion in the cure curves.

Table 3.2 Cure characteristics of the mixes (cured at 150°C)

Cure characteristics	A_1	A_2	A_3	A_4	B_1	B_2	B_3	B_4	C_1	C_2	C_3	C_4	D_1	D_2	D_3	D_4	D_5	D_6	D_7	D_8
Min. torque (dNm)	0.39	0.49	0.32	0.58	0.51	0.51	0.36	0.27	0.68	0.46	0.43	0.41	0.27	0.31	0.53	0.48	0.44	0.95	0.46	0.56
Max. torque (dNm)	13.1	14.3	9.88	16.2	12.1	11.6	10.7	8.2	18.2	15.2	13.4	17.8	15.6	11.0	20.8	15.2	11.3	18.3	21.1	20.2
Optimum cure time t_{90} (min)	3.24	2.56	1.92	1.52	13.1	10.8	7.96	6.48	7.9	3.9	3.3	2.9	4.56	15.5	10.2	2.8	11.6	5.1	7.0	5.08
Scorch time t_{10} (min)	2.2	1.7	1.3	0.8	6.1	4.8	3.4	2.5	3.6	2.1	1.7	1.3	2.52	7.7	7.0	2.0	5.2	3.1	3.6	2.96
Induction time t_5 (min)	2.0	1.6	1.2	0.8	4.7	4.4	3.3	2.8	3.2	2.1	1.4	1.3	2.36	5.7	6.8	1.8	3.9	2.8	3.1	2.7
Cure rate index	100	125	166	147	14.3	16.6	22.1	25.5	23.2	55.5	64.1	64.1	49	12.8	31.2	125	15.6	50	29.4	47.17

Table 3.3 Cure characteristics of the mixes cured at 120°C

Cure characteristics	A_1	A_2	A_3	A_4	B_1	B_2	B_3	B_4	C_1	C_2	C_3	C_4	D_4	D_5	D_6
Minimum torque (dNm)	0.7	1.0	1.0	1.4	1.4	1.0	1.0	0.7	1.0	1.0	1.0	1.0	0.007	0.01	0.01
Maximum torque (dNm)	16	21	18.6	19	12	13	14	13	18	20	19	24	0.15	0.14	0.21
Optimum cure time (t_{90}) min.	23.1	21.1	13.5	10.6	82.2	75.6	55.2	49.8	40.8	36.9	25.5	24.9	18.2	58.8	28.5
Scorch time (t_{10}) min.	9.4	6.3	3.7	2.1	27.6	9	11.4	7.2	13.8	8.4	5.7	2.7	6.3	15	6.6
Induction time (t_5) min.	8.7	5.7	3.3	1.8	7.8	3.6	6	3	12.6	7.8	5.1	1.8	5.7	7.8	6
Cure rate index	7.2	6.7	10.2	11.8	1.8	1.5	2.3	2.3	3.7	3.5	5.1	4.5	8.4	2.3	4.5

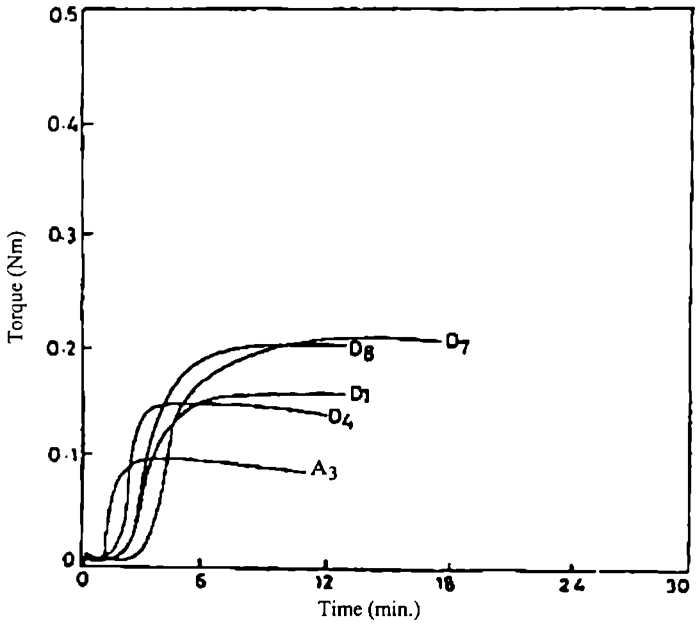


Fig. 3.2 Cure curves of mixes containing TMTD (cured at 150°C)

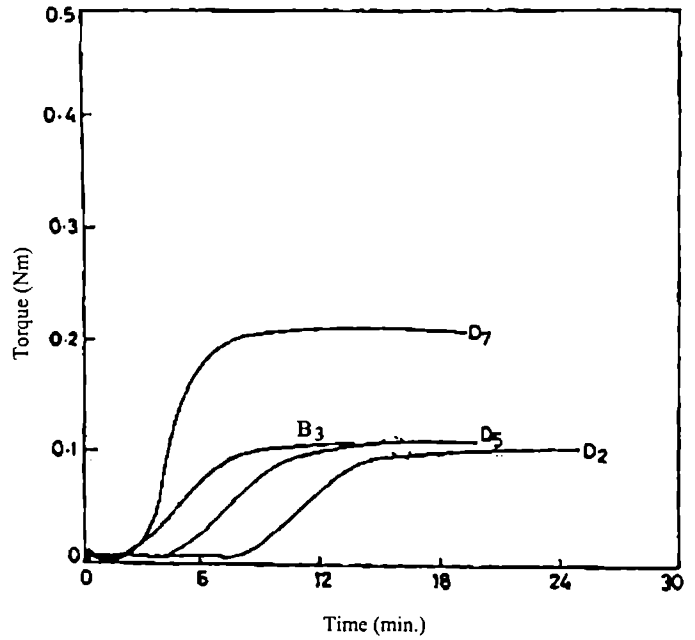


Fig. 3.3 Cure curves of mixes containing MBTS (cured at 150°C)

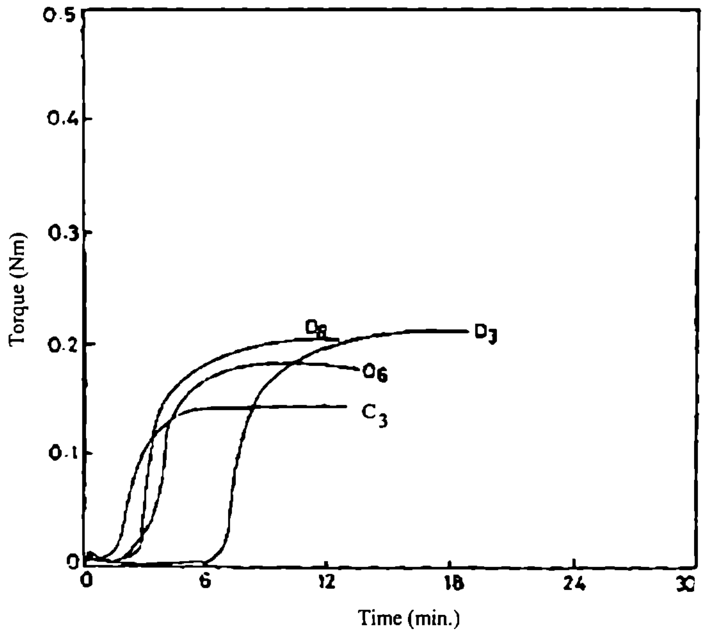


Fig. 3.4 Cure curves of mixes containing CBS (cured at 150°C)

In the case of CBS–AMT binary systems it is seen that the mix C_3 containing CBS-AMT gives an optimum cure time of 3.3 min., while the control mix D_6 containing TU gives 5.1min. Compared to the mix containing two molar equivalents of CBS, AMT mix reduces the cure time from 10.2 to 3.3 min. However scorch time is also considerably reduced. Considering the scorch safety and the torque value, one molar equivalent of AMT can be taken as the optimum concentration of the secondary accelerator here also. In the MBTS systems AMT shows a higher acceleration of vulcanization. The optimum cure time of mix B_3 containing MBTS and AMT in 1:1 molar proportion is found to be 7.9 min. which is lower than that of the control mix with TU (11.6min.). There is not much reversion in these MBTS mixes.

At 120°C the activation effect of AMT is found to be more significant. As the concentration of AMT is increased in the mixes, the optimum cure time is found to decrease substantially (Table 3.3). In TMTD systems the optimum cure time for TMTD–AMT (1:1) is 13.5 min, while for the corresponding TU mix it is 18.2 min. Similarly in MBTS and CBS systems

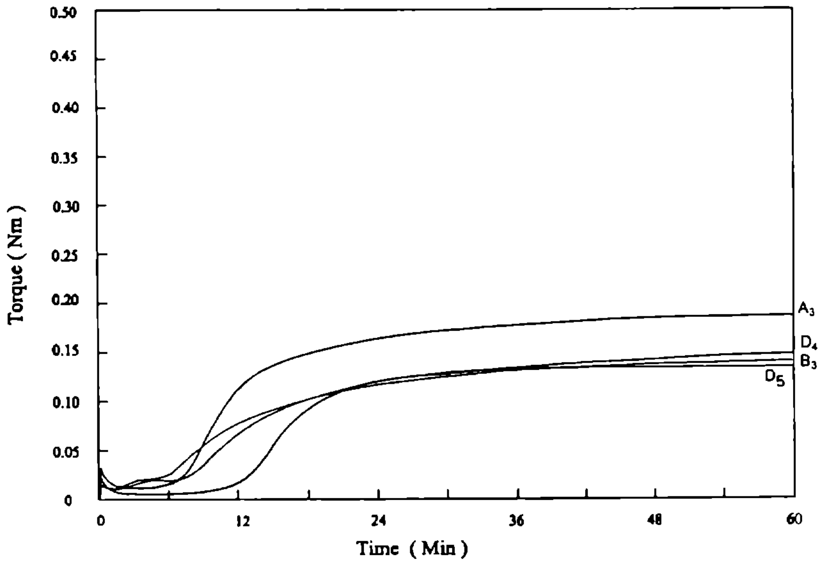


Fig. 3.5 Cure curves of mixes containing TMTD and MBTS (cured at 120°C)

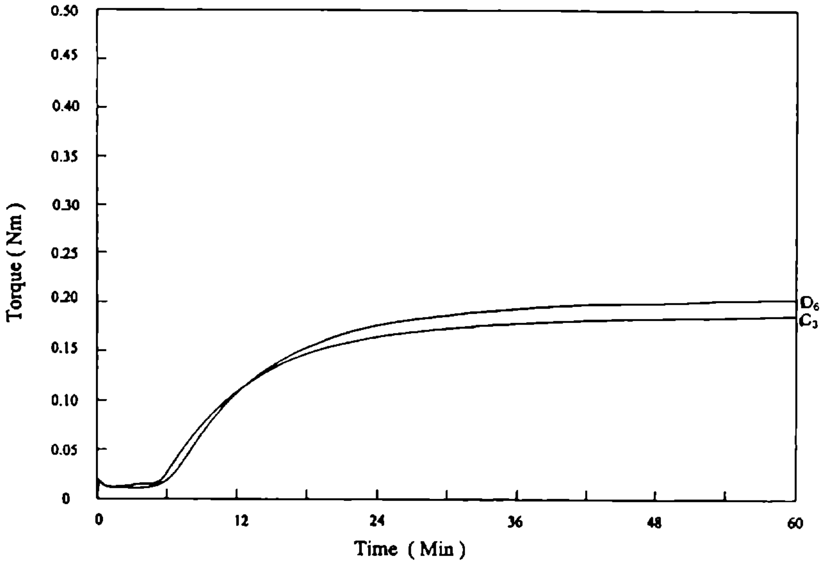
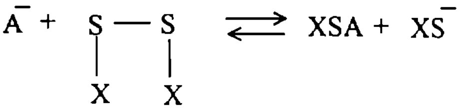


Fig. 3.6 Cure curves of mixes containing CBS (cured at 120°C)

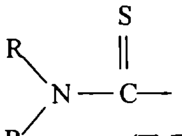
also there is considerable reduction in cure time for AMT mixes compared to TU. Even though the addition of AMT reduces the optimum cure time in MBTS systems compared to the controls, these systems still exhibit higher cure time values compared to other combinations. It is reported that MBTS require higher vulcanization temperature and larger proportions of sulphur for satisfactory cure[18]. Considering the nucleophilic character of AMT and TU, AMT is more nucleophilic than TU. The results reported above on the cure characteristics in these different binary systems point to a nucleophilic reaction mechanism. A polar mechanism was also suggested (Manik and Banerjee) in the vulcanization of natural rubber using similar systems[19]. Moore[13] et. al. also suggested a polar mechanism in which sulphur-containing nucleophiles like thiourea increases the formation of thiuram polysulphides required for the crosslinking reaction. Aminoiminomethyl thiourea (AMT) being a thiourea derivative behaves in a similar manner and helps the cleavage of S-S bond in disulphide and sulphenamide type accelerators. The reaction can be represented as:



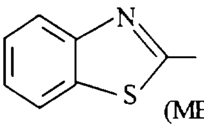
$$A^- + \underset{X}{\underset{|}{S}}-\underset{X}{\underset{|}{S}} \rightleftharpoons XSA + XS^-$$

where

X =

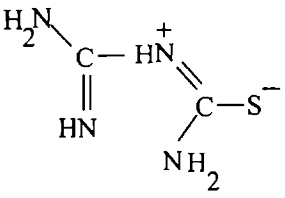


or (TMTD)



(MBTS)

A^- =



(AMT)

The guanidinyl group in AMT will favour the polarization of C = S bond in it thereby producing a negative charge on the sulphur atom. This nucleophile from AMT makes a nucleophilic attack on the S-S bond in primary accelerators. The speed of the above reaction depends on the nucleophilicity of the attacking agent. AMT being more nucleophilic than TU the AMT systems show faster reaction and hence lower induction and optimum cure time.

Tensile Properties

Based on the favorable results obtained in the cure properties of the different systems studied we thought of further probing into the physical properties of these vulcanizates. The total chemical crosslinks were also estimated. Tables 3.4 and 3.5 report the various tensile properties of the vulcanizates obtained. In the case of mixes cured at 120°C only those vulcanizates containing optimum concentrations of AMT were taken for testing the tensile properties. These vulcanizates show reasonable tensile strength and good resistance to aging as indicated by the percentage retention values. The variations of tensile properties of vulcanizates containing optimum concentrations of AMT before and after aging are represented in Figs. 3.7 - 3.9. Considering the tensile strength values of TMTD systems (cured at 150°C) inclusion of moderate levels of AMT or TU in these mixes considerably improves the poor tensile strength found in the mixes containing TMTD alone. Compared to the other conventional mixes D_7 and D_8, experimental mixes containing optimum dosage of AMT shows considerable increase in the tensile strength values. For MBTS-AMT and CBS-AMT systems also mixes containing optimum dosage of AMT show higher tensile values compared to other control systems. 100% modulus and elongation at break values of the experimental systems are also found to be better than the control mixes. With regard to after-aging properties MBTS mixes show comparatively lower percentage retention. The tensile properties of TMTD vulcanizates containing optimum concentration of AMT and cured at 120°C are higher than that cured at 150°C.

Table 3.4. Tensile properties of vulcanizates cured at 150°C

Mixes	Tensile Strength(MPa)			100% Modulus (MPa)			Elongation at Break (%)		
	Before aging	After aging	Retention (%)	Before aging	After aging	Retention (%)	Before aging	After aging	Retention (%)
A_1	3.1	2.9	93.5	1.4	1.7	121.4	267.8	224.4	83.8
A_2	2.8	2.5	89.2	1.5	1.7	113.3	228.6	178.8	78.2
A_3	13.4	12.9	96.2	1.2	1.6	133.3	600.7	529.4	80.1
A_4	18.1	15.7	86.7	1.4	1.8	128.5	617.3	570.3	92.3
B_1	19.1	18.6	97.3	1.0	1.8	180.0	828.3	709.3	85.6
B_2	16.3	16.6	101.8	1.1	0.9	81.8	768.7	724.8	94.2
B_3	17.3	18.9	109.2	1.0	1.2	120.0	794.1	780.8	98.3
B_4	20.3	17.6	86.7	1.3	1.2	92.3	826.7	718.6	86.9
C_1	24.7	25.6	103.6	1.6	1.2	75.0	750.8	713.3	95.0
C_2	25.4	25.9	102.0	1.5	1.3	86.6	780.1	724.5	92.8
C_3	23.7	25.6	108.0	1.4	1.5	107.1	736.7	728.2	98.8
C_4	24.7	27.9	112.9	1.4	2.0	142.8	749.6	701.2	93.5
D_1	2.4	2.5	104.2	1.7	2.0	117.6	154.3	131.0	84.9
D_2	18.5	20.5	110.9	1.2	2.0	166.6	725.1	665.5	91.7
D_3	19.5	22.4	114.9	1.8	1.2	66.6	593.3	588.0	99.1
D_4	14.2	12.5	88.0	1.2	1.4	116.6	627.7	577.3	91.9
D_5	13.6	10.3	75.7	1.0	1.2	120.0	748.2	613.0	81.9
D_6	20.7	19.4	93.7	1.9	1.6	84.2	655.4	644.5	98.2
D_7	2.7	2.1	77.8	1.4	1.8	128.5	184.3	120.8	65.5
D_8	2.2	2.9	131.8	1.6	1.9	118.7	143.8	163.4	113.6

Table 3.5 Tensile properties of the vulcanizates cured at 120°C (mixes of optimum secondary accelerator concentration)

Mixes	Tensile strength (MPa)			100% Modulus (MPa)			Elongation at break (%)		
	Before aging	After aging	Retention %	Before aging	After aging	Retention %	Before aging	After aging	Retention %
A_3	25.30	23.3	92	1.14	1.20	105	1074	1020	95
B_3	12.59	14.7	116	0.88	1.12	127	1129	1240	109
C_3	15.60	18.6	119	1.00	0.45	45	1021	1012	99
D_4	25.10	23.8	95	0.93	0.88	94	1133	1062	94
D_5	20.40	17.3	85	1.40	1.40	100	1218	1227	101
D_6	21.40	13.5	63	0.86	1.30	151	1259	974	77

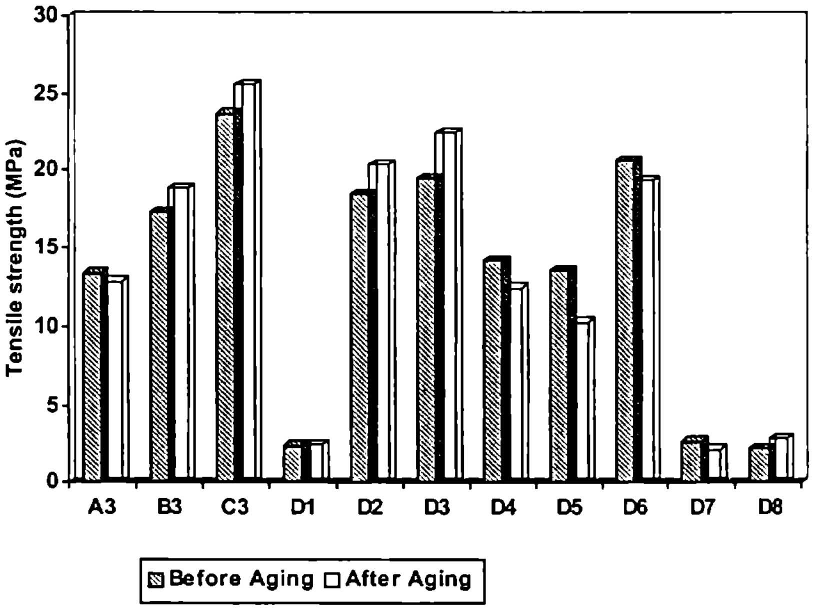


Fig. 3.7 Tensile strength of vulcanizates before and after aging

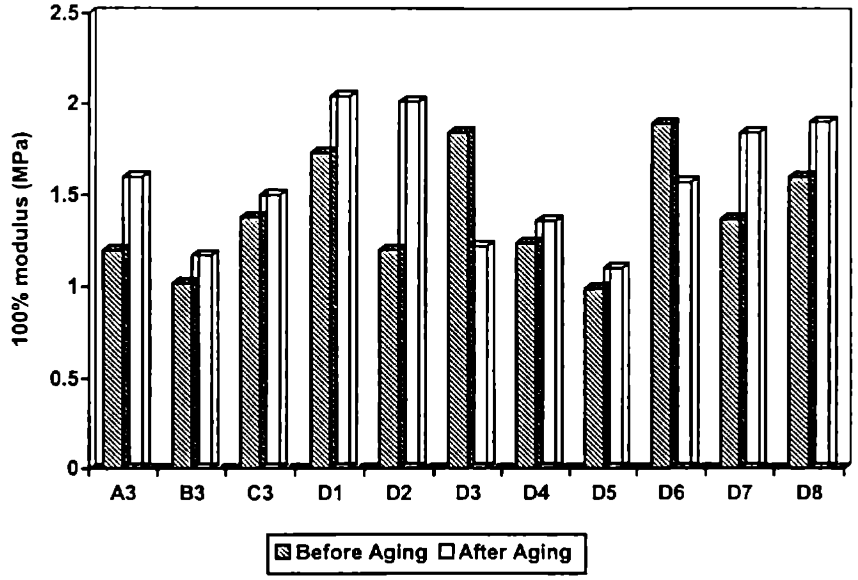


Fig. 3.8 100% modulus of vulcanizates before and after aging

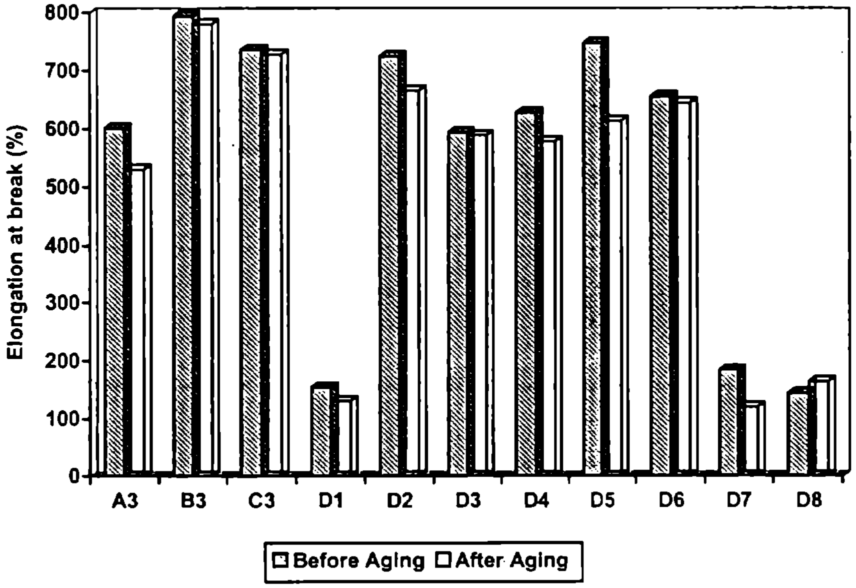


Fig. 3.9 Elongation at break of vulcanizates before and after aging

Other Physical Properties

Other physical properties studied for the various systems are hardness, compression set, abrasion resistance and tear strength. These results are given in Tables 3.6 and 3.7. Considering the vulcanizates cured at 150°C, for TMTD–AMT vulcanizates hardness is found to increase

Table3.6. Other physical properties of the vulcanizates cured at150°C

Mixes	Hardness (shore A)	Compression set (%)	Abrasion loss (cm^3/hr)	Total cross-link density x10^5 ($gm.mol/cm^3$)	Tear strength (N/mm)
A_1	38.0	17.2	5.2	5.1	31.3
A_2	39.6	18.8	4.9	5.3	31.5
A_3	38.0	25.2	5.5	4.9	32.4
A_4	42.7	28.8	5.9	5.4	35.2
B_1	31.0	23.6	11.3	3.3	30.6
B_2	31.0	30.7	13.4	3.6	36.2
B_3	31.0	24.6	11.5	3.5	35.8
B_4	31.0	24.8	13.1	3.5	37.9
C_1	38.0	19.4	5.4	5.4	45.1
C_2	37.6	17.7	5.0	5.7	42.0
C_3	42.3	22.7	4.3	5.7	35.3
C_4	40.3	30.1	4.0	5.4	43.6
D_1	45.0	15.6	6.0	6.7	22.1
D_2	35.3	11.1	8.5	4.6	35.3
D_3	44.6	13.8	5.4	6.7	37.6
D_4	37.0	24.0	7.0	5.0	39.1
D_5	30.0	28.4	15.8	3.3	38.5
D_6	39.0	27.5	4.6	5.4	43.4
D_7	46.0	14.9	7.5	7.8	28.4
D_8	46.3	16.5	4.7	7.7	24.8

with increase in the concentration of AMT. Abrasion resistance is found to decrease with the concentration of AMT and compression set values increase. The binary system of AMT with TMTD (mix A_3) showed comparable results for physical properties with that of TMTD-TU. In MBTS–AMT, tear strength increases with the concentration of AMT. Compression set, abrasion loss and hardness values of mixes containing optimum dosages of AMT are more or less similar to the reference mixes containing TU. In the case of CBS-AMT hardness and compression set increase with the amount of AMT and tear strength remains more or less similar. Abrasion resistance is found to increase (abrasion loss decreases) with AMT. In comparison with the other conventional systems experimental systems with AMT show higher tear strength and abrasion resistance, but compression set and hardness are slightly inferior. At 120°C the AMT systems show comparatively better results for compression set and abrasion resistance compared to the control mixes containing TU. The physical properties obtained for the various vulcanizates under review can, in general, be correlated to the calculated crosslink density values.

Table 3.7 Other physical properties of the vulcanizates cured at 120°C (mixes of optimum secondary accelerator concentration)

Mixes	Compression set (%)	Abrasion loss (cm^3/hr)	Hardness (Shore A)	Total cross-link density ×10^5 (g.mol/cm^3)	Tear strength (N/mm)
A_3	21.9	5.2	30.4	17.8	32.6
B_3	22.4	6.7	20.3	13.4	26.8
C_3	26.7	4.0	30.5	18.5	33.6
D_4	24.4	5.4	30.6	18.2	32.8
D_5	23.3	7.6	20.6	14.1	27.3
D_6	27.0	4.6	30.3	18.2	31.9

PART II

3.2 NR-FILLED SYSTEMS

The use of fillers in rubber is almost as old as the use of rubber itself[20]. Rubber vulcanizates are commonly reinforced with fillers in order to increase the strength and stiffness and for improved processability and/or cost reduction. There are reinforcing and non- reinforcing fillers. Reinforcing fillers are used for the enhancement of properties like tensile strength, abrasion resistance, tear strength, etc., while non-reinforcing fillers are incorporated to cheapen or stiffen the final product. The most important reinforcing fillers known are carbon black and silica. Silicates, clay, whiting and other mineral fillers are used where a high degree of reinforcement is not essential. The degree of reinforcement provided by a filler depends on a number of variables, the most important of which is the development of a polymer-filler interface. In general, the best reinforcing fillers are those having the smallest particle size. One can produce soft, filler-free NR vulcanizates of high tensile strength because of its high stress crystallization. However, for most applications the use of fillers is desirable or necessary. Effect of fillers on the mechanical properties of elastomers is primarily of great interest because fillers can be used very effectively to enhance the ultimate properties. Porter[21] and De et. al.[22] studied the effect of reinforcing black and silica on the sulphuration process during vulcanization. Carbon black appeared to catalyze the formation of the active sulphurating agent[23], which explains the beneficial effect of carbon black in rubber vulcanization.

With general-purpose elastomers like NR, high abrasion furnace (HAF) blacks with average particle size in the range 24 - 28 mμ are most widely used. It is known that carbon black contain active functional groups like OH, -COOH, C=C[24,25], etc. Silica is highly adsorptive and hence, in formulating NR compounds containing silica it is necessary to use more than the normal quantity of accelerator or a combination of accelerators, which is more active. In general, a silica-reinforced rubber has a poorer modulus than a carbon black reinforced one. However, silica provides a unique combination of tear strength, abrasion resistance, age resistance and adhesion properties[26]. Thiazole accelerators show cure retardation with silica and they need a secondary accelerator and an activator like diethylene glycol (DEG) to obtain appropriate scorch and cure times with silica. Clays are also widely used as filler in rubber due to their low cost and semi-reinforcing character. It has a pronounced stiffening effect and imparts hardness and fairly good abrasion resistance. Clays reduce the cure rate of NR vulcanizates because they are highly adsorptive[27].

As reported in the first part of this chapter it is found that AMT is an effective accelerator in NR along with TMTD/MBTS/CBS. In this context we thought it worthwhile to extend this study to the filled systems of NR vulcanization also. This part of the study includes different aspects like mixing, curing and the evaluation of various physical properties of different filled systems, viz. TMTD-AMT, MBTS-AMT and CBS-AMT. Reference mixes containing thiourea were also prepared and the properties especially cure properties of the experimental mixes compared with those of the references. Some conventional mixes containing TMTD-CBS, TMTD-MBTS and MBTS-CBS were also prepared for comparison of properties. To understand the variations in physical properties of the various vulcanizates, total chemical crosslinks were also estimated using the equilibrium swelling method. We have examined the effect of AMT in these binary systems with carbon black, precipitated silica and china clay as fillers. It is known that nucleophiles produced from thiourea derivatives are capable of breaking the sulphur bonds in the primary accelerator at comparatively low temperatures. So in order to evaluate the effect of this secondary accelerator on the vulcanization temperature these mixes were cured and physical properties evaluated at two different temperatures, viz. 120 and 150°C.

3.2.1 Experimental

The formulations of the mixes used are given in Tables 3.8 - 3.10. To determine the optimum concentration of AMT required in these binary systems, mixes with varying concentrations of AMT are prepared. These mixes contain different fillers, viz. carbon black, precipitated silica or china clay. The loading of silica in these mixes was limited to 30 phr as higher loading was found to give scorchy mixes and higher temperature development. Mixes containing carbon black, silica and clay are denoted by C, D and E respectively. Compounds C_1 - C_4 contain 0.25, 0.5, 1 and

Table 3.8 Formulation of mixes containing MBTS as primary accelerator

Ingredients	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	D_1	D_2	D_3	D_4	D_5	D_6	D_7	D_8	E_1	E_2	E_3	E_4	E_5	E_6	E_7	E_8
NR	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
ZnO	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	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	2	2	2
MBTS	1.66	1.66	1.66	1.66	3.32	1.66	1.66	1.66	1.66	1.66	1.66	1.66	3.32	1.66	1.66	1.66	1.66	1.66	1.66	1.66	3.32	1.66	1.66	1.66
TMTD						1.2								1.2								1.2		
CBS							1.4								1.4								1.4	
Thiourea								0.38								0.38								0.38
AMT	0.15	0.29	0.59	0.88					0.15	0.29	0.59	0.88					0.15	0.29	0.59	0.88				
Carbon black	50	50	50	50	50	50	50	50																
Aromatic oil	5	5	5	5	5	5	5	5																
Silica									30	30	30	30	30	30	30	30								
Clay																	50	50	50	50	50	50	50	50
Diethylene glycol									1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	2	2	2	2	2	2	2	2
Naphthenic - oil									3	3	3	3	3	3	3	3	5	5	5	5	5	5	5	5
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	1.5	1.5	1.5

Table 3.9 Formulation of mixes containing TMTD as primary accelerator

Ingredients	C'_1	C'_2	C'_3	C'_4	C'_5	C'_6	C'_7	C'_8	D'_1	D'_2	D'_3	D'_4	D'_5	D'_6	D'_7	D'_8	E'_1	E'_2	E'_3	E'_4	E'_5	E'_6	E'_7	E'_8
NR	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
ZnO	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	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	2	2	2
TMTD	1.2	1.2	1.2	1.2	2.4	1.2	1.2	1.2	1.2	1.2	1.2	1.2	2.4	1.2	1.2	1.2	1.2	1.2	1.2	1.2	2.4	1.2	1.2	1.2
MBTS						1.66								1.66								1.66		
CBS							1.4								1.4								1.4	
Thiourea								0.38								0.38								0.38
AMT	0.15	0.29	0.59	0.88					0.15	0.29	0.59	0.88					0.15	0.29	0.59	0.88				
Carbon black	50	50	50	50	50	50	50	50																
Aromatic oil	5	5	5	5	5	5	5	5																
Silica									30	30	30	30	30	30	30	30								
Clay																	50	50	50	50	50	50	50	50
Diethylene glycol									1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	2	2	2	2	2	2	2	2
Naphthenic oil									3	3	3	3	3	3	3	3	5	5	5	5	5	5	5	5
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	1.5	1.5	1.5

Table 3.10 Formulation of mixes containing CBS as primary accelerator

Ingredients	C''$_1$	C''$_2$	C''$_3$	C''$_4$	C''$_5$	C''$_6$	C''$_7$	C''$_8$	D''$_1$	D''$_2$	D''$_3$	D''$_4$	D''$_5$	D''$_6$	D''$_7$	D''$_8$	E''$_1$	E''$_2$	E''$_3$	E''$_4$	E''$_5$	E''$_6$	E''$_7$	E''$_8$
NR	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
ZnO	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	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	2	2	2
CBS	1.4	1.4	1.4	1.4	2.8	1.4	1.4	1.4	1.4	1.4	1.4	1.4	2.8	1.4	1.4	1.4	1.4	1.4	1.4	1.4	2.8	1.4	1.4	1.4
TMTD						1.2								1.2								1.2		
MBTS							1.66								1.66								1.66	
Thiourea								0.38								0.38								0.38
AMT	0.15	0.29	0.59	0.88					0.15	0.29	0.59	0.88					0.15	0.29	0.59	0.88				
Carbon black	50	50	50	50	50	50	50	50																
Aromatic oil	5	5	5	5	5	5	5	5																
Silica									30	30	30	30	30	30	30	30								
Clay																	50	50	50	50	50	50	50	50
Diethylene glycol									1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	2	2	2	2	2	2	2	2
Naphthenic oil									3	3	3	3	3	3	3	3	5	5	5	5	5	5	5	5
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	1.5	1.5	1.5

1.5 molar equivalents of AMT with MBTS and compounds C'_1 to C'_4 contain similar molar equivalents of AMT with TMTD. C''_1 to C''_4 contain corresponding molar equivalents of AMT with CBS. In silica mixes D_1 to D_4 represent MBTS–AMT, D'_1 to D'_4 represent TMTD–AMT and D''_1 to D''_4 represent CBS-AMT. Similarly mixes with china clay are denoted by E, E'and E''. The compounding was done on a laboratory size two-roll mixing mill and vulcanization was carried out at 120 and at 150°C in an electrically heated press at a pressure of 12 MPa. The cure characteristics of the various mixes were evaluated using Goettfert elastograph (model 67.85). Different cure properties reported are optimum cure time (t_{90}), scorch time (t_{10}), induction time (t_5), maximum torque, minimum torque, cure rate, etc. Details of the cure characteristics evaluated are given in Tables 3.11 - 3.16 and the corresponding cure curves in Fig. 3.10 - 3.22. Heat aging was carried out as per ASTM D 865–88. The tensile properties of the vulcanizates were determined on a Zwick universal testing machine (model 1445) using a cross head speed of 500 mm/min. Tear resistance was determined as per ASTM D 624–86. The tensile properties of the vulcanizates from these filled systems containing optimum concentration of AMT are given in Tables 3.17 - 3.19. Compression set and hardness were tested as per ASTM D 395–89 (method B) and D 2240–86 respectively. Abrasion resistance was determined using DIN abrader (DIN 53516). Values of these physical properties and crosslink density evaluated are reported in Tables 3.20 - 3.22.

3.2.2 RESULTS AND DISCUSSIONS

Cure characteristics

The cure curves for the filled compounds determined at 150 and 120°C are shown in Figures 3.10 - 3.22 and the cure characteristics calculated are given in Tables 3.11 - 3.16. All these binary systems containing AMT show noticeable reduction in cure time compared to the reference mixes irrespective of the filler used. At 150°C in TMTD–AMT mixes a significant reduction in cure time is observed with increase in the amount of AMT. Along with the reduction in optimum cure time the induction time and scorch time are also found to be reduced. In TMTD

Table 3.11 Cure characteristics of filled MBTS mixes (cured at 150°C)

Mixes	Optimum cure time (t_{90}) min	Scorch time (t_{10}) min	Induction time (t_5) min	Cure rate index	Minimum torque (d Nm)	Maximum torque (d Nm)
C_1	6.3	1.20	0.72	19.60	4.0	43.8
C_2	5.9	1.26	0.84	21.55	2.2	28.3
C_3	5.8	1.32	0.96	22.32	2.5	37.2
C_4	5.4	1.14	0.72	23.47	3.0	32.0
C_5	6.7	1.60	0.90	19.60	3.2	52.8
C_6	3.8	1.44	1.29	42.37	4.6	81.0
C_7	4.4	1.98	1.86	41.32	4.6	64.3
C_8	6.0	1.80	0.84	25.64	4.2	33.5
D_1	8.5	4.30	4.00	23.80	2.1	17.8
D_2	8.3	3.30	2.50	20.00	2.8	18.6
D_3	5.5	1.86	1.38	27.40	2.8	17.8
D_4	5.0	1.38	0.84	27.60	2.1	15.7
D_5	10.1	5.70	4.60	22.70	2.1	22.8
D_6	4.5	2.70	2.50	55.50	1.4	26.4
D_7	7.5	5.10	4.80	41.60	2.1	27.8
D_8	6.9	3.20	2.70	27.00	2.1	16.4
E_1	8.2	3.00	2.60	19.20	0.7	12.5
E_2	7.7	2.70	2.40	20.00	0.7	12.8
E_3	7.2	2.10	1.80	19.60	0.7	9.3
E_4	6.4	1.80	1.60	21.90	0.7	7.8
E_5	9.8	4.60	4.30	19.30	2.5	14.3
E_6	7.9	2.20	2.10	17.30	3.2	21.1
E_7	7.8	3.30	3.10	21.90	0.7	18.6
E_8	8.5	2.40	2.20	16.40	0.7	11.4

systems one molar equivalent of AMT, which is found to give reasonable cure characteristics with somewhat satisfactory scorch safety can be considered to be the optimum level of the secondary accelerator for all the three types of fillers used. Compared with other conventional binary systems also the AMT systems show lesser t_{90} values. Other cure characteristics, viz. minimum torque, maximum torque and induction time of the TMTD-AMT systems are comparable to those of the references. The effect of AMT in MBTS-AMT systems is more or less similar to that in TMTD-AMT. In these mixes also there is noticeable reduction in cure time with the incorporation of AMT. By increasing the amount of AMT from 0.25 to 1.5 molar level the optimum cure time is reduced from 6.3 to 5.4 min. in the MBTS combination. Mix C_3 containing one molar equivalent of AMT and MBTS show an optimum cure time value of 5.4 min. whereas the similar mix with TU (C_8) shows 6min. in carbon black filled systems. In the silica and clay filled systems also a similar trend is observed. In MBTS systems also the optimum dosage of AMT required can be taken to be one molar equivalent and at this level there is considerable reduction in cure time while the scorch time and induction time are more or less at the desirable range. Maximum torque developed in the mixes containing AMT are however lower than most of the reference mixes. In the case of mixes containing CBS-AMT also more or less similar behaviour in cure is observed. A comparative study of the equivalent mixtures of CBS-AMT (mix C_3'') with CBS–TU (mix C_8'') and CBS–MBTS (mix C_7'') reveals that the least optimum cure time is shown by CBS-AMT system.

Table 3.12 Cure characteristics of MBTS mixes (cured at 120°C)

Mixes	Optimum cure time (t_{90}) min.	Scorch time (t_{10}) min.	Induction time (t_5) min.	Cure rate index	Minimum torque (d Nm)	Maximum torque (d Nm)
C_1	47.7	7.2	3.0	2.40	3.5	30.0
C_2	46.8	7.5	3.0	2.50	4.3	39.0
C_3	42.1	6.6	2.4	2.80	2.8	41.0
C_4	41.1	6.3	3.9	2.87	4.2	32.0
C_8	45.3	7.8	3.3	2.66	4.3	35.7
E_1	45.2	18.0	8.5	3.60	5.1	18.0
E_2	43.8	17.4	8.1	3.70	5.7	17.5
E_3	35.4	9.3	5.1	3.80	1.4	12.8
E_4	28.8	6.3	5.4	4.40	1.1	12.1
E_8	36.9	13.8	12.9	4.30	3.9	15.7

Table 3.13 Cure characteristics of the TMTD mixes (cured at 150°C)

Mixes	Optimum cure time (t_{90}) min.	Scorch time(t_{10}) min	Induction time (t_5) min	Cure rate index	Minimum torque (d Nm)	Maximum torque (d Nm)
C'$_1$	3.1	1.26	0.90	54.3	4.2	53.0
C'$_2$	2.1	1.20	0.96	111.1	3.0	50.0
C'$_3$	1.9	1.08	0.84	121.9	2.5	50.3
C'$_4$	1.8	1.08	0.78	138.8	3.6	49.9
C'$_5$	3.6	1.26	1.02	42.7	3.2	76.0
C'$_6$	3.8	1.44	1.29	42.3	4.6	81.0
C'$_7$	3.2	1.53	1.41	59.8	4.2	70.0
C'$_8$	2.4	1.20	1.02	83.3	3.5	53.0
D'$_1$	2.7	1.70	1.30	104.1	2.1	24.0
D'$_2$	2.5	1.60	1.30	111.1	2.1	23.0
D'$_3$	2.3	1.26	1.02	96.1	1.4	21.0
D'$_4$	2.1	1.14	1.02	104.1	1.4	17.0
D'$_5$	3.0	1.90	1.60	90.9	1.4	31.0
D'$_6$	4.5	2.70	2.20	55.5	1.4	26.0
D'$_7$	3.9	2.50	2.40	71.4	1.7	31.0
D'$_8$	2.7	1.60	1.30	90.9	2.1	23.0
E'$_1$	3.3	1.50	1.40	53.7	0.7	14.0
E'$_2$	3.3	1.40	1.30	51.0	0.5	14.0
E'$_3$	2.8	1.30	1.20	66.6	0.7	16.0
E'$_4$	2.0	1.00	0.84	100.0	0.7	18.0
E'$_5$	4.7	1.68	1.50	33.3	0.3	22.0
E'$_6$	7.9	2.20	2.10	17.3	3.2	21.0
E'$_7$	6.0	1.80	1.60	23.8	0.7	26.0
E'$_8$	3.1	1.20	1.10	52.6	0.7	16.0

Table 3.14 Cure characteristics of the TMTD mixes (cured at 120°C)

Mixes	Optimum cure time (t_{90}) min.	Scorch time (t_{10}) min.	Induction time (t_5) min.	Cure rate index	Minimum torque (d Nm)	Maximum torque (d Nm)
C'$_1$	14.25	5.40	4.6	11.3	2.8	46.4
C'$_2$	11.5	5.50	4.3	16.6	2.8	48.0
C'$_3$	10.8	4.60	2.5	16.1	1.7	50.0
C'$_4$	7.5	3.15	3.0	23.2	2.8	43.5
C'$_8$	14.7	5.10	3.7	10.4	3.5	57.0
D'$_1$	28.3	11.90	10.7	6.1	1.1	8.5
D'$_2$	27.4	11.50	10.2	6.2	1.1	8.9
D'$_3$	26.0	10.00	9.3	6.3	1.1	8.2
D'$_4$	22.2	4.50	1.9	5.6	1.1	6.8
D'$_8$	26.1	11.50	6.7	6.8	1.1	7.8
E'$_1$	11.7	6.10	5.4	17.8	1.1	16.7
E'$_2$	10.6	5.50	5.1	19.6	1.1	16.4
E'$_3$	10.2	4.30	4.0	16.9	1.1	19.6
E'$_4$	9.0	3.45	3.0	17.8	0.7	18.5
E'$_8$	10.5	3.60	3.3	14.5	1.1	23.2

Table 3.15 Cure characteristics of the CBS mixes (cured at 150°C)

Mixes	Optimum cure time (t_{90}) min.	Scorch time (t_{10}) min.	Induction time (t_5) min.	Cure rate index	Minimum torque (d Nm)	Maximum torque (d Nm)
C''$_1$	4.2	1.80	0.96	41.6	3.6	53.0
C''$_2$	3.9	1.40	0.96	40.0	3.2	48.0
C''$_3$	3.6	1.20	0.96	41.6	3.1	44.0
C''$_4$	3.5	1.08	0.78	41.3	3.0	47.0
C''$_5$	4.6	2.20	1.80	41.6	3.6	69.0
C''$_6$	3.2	1.50	1.40	59.8	4.2	70.0
C''$_7$	4.4	1.90	1.80	41.3	4.6	64.3
C''$_8$	4.5	1.80	1.40	37.0	5.3	54.0
D''$_1$	6.1	2.60	2.40	28.5	2.1	26.0
D''$_2$	4.6	2.04	1.80	39.0	2.1	19.0
D''$_3$	3.6	1.30	1.02	43.4	1.4	18.0
D''$_4$	3.4	1.10	0.96	44.2	2.1	20.0
D''$_5$	6.9	4.60	4.30	43.4	1.4	25.7
D''$_6$	3.9	2.50	2.40	71.4	1.4	30.7
D''$_7$	7.5	5.10	4.80	41.6	2.1	27.8
D''$_8$	5.2	1.70	1.50	28.4	1.4	18.0
E''$_1$	6.2	2.20	2.10	25.0	0.7	16.0
E''$_2$	5.6	1.80	1.80	26.7	0.7	17.0
E''$_3$	4.8	1.50	1.40	30.3	0.7	15.0
E''$_4$	4.5	1.30	1.20	30.6	0.7	16.0
E''$_5$	7.4	2.50	2.40	20.4	0.7	20.0
E''$_6$	6	1.80	1.60	23.8	0.7	26.0
E''$_7$	7.8	3.30	3.10	21.9	0.7	18.0
E''$_8$	5.7	1.70	1.40	25.0	1.0	18.0

Table 3.16 Cure characteristics of the CBS mixes (cured at 120°C)

Mixes	Optimum cure time (t_{90}) min.	Scorch time (t_{10}) min.	Induction time (t_5) min.	Cure rate index	Minimum torque (d Nm)	Maximum torque (d Nm)
C"$_1$	27.8	7.8	6.6	5.0	4.2	52.8
C"$_2$	27.0	7.5	6.6	5.1	5.0	52.8
C"$_3$	23.1	4.8	3.9	5.4	4.3	55.0
C"$_4$	22.4	4.2	3.6	5.5	4.3	62.0
C"$_8$	28.8	7.2	6.3	4.6	5.0	61.4
D"$_1$	48.1	21.0	19.8	3.9	1.1	15.0
D"$_2$	45.6	20.7	19.5	4.0	1.1	16.8
D"$_3$	41.1	13.6	8.8	3.6	1.1	11.4
D"$_4$	32.0	4.2	2.7	3.6	1.1	10.0
D"$_8$	41.7	16.2	6.9	3.9	1.1	13.0
E"$_1$	26.0	2.3	2.0	3.3	0.7	21.0
E"$_2$	24.3	1.9	1.6	4.4	0.7	23.0
E"$_3$	20.7	2.4	1.9	5.4	0.7	19.0
E"$_4$	20.4	3.0	2.7	5.7	0.7	22.0
E"$_8$	21.3	3.1	3.0	12.0	3.5	21.0

At the relatively lower temperature of 120°C, the acceleration effect of AMT is more significant. The optimum cure time is reduced nearly by 40 percent in the case of mixes with AMT compared to the reference mixes containing TU. The trend in the variation of cure characteristics with respect to the filler is more or less similar to curing at 150°C for all the binary systems studied. In the case of TMTD-AMT systems, it can be seen from Table 3.14 that on increasing the amount of AMT from 0.25 to 1.5 molar level the optimum cure time decreases from 14.2 min. to 7.5 min. in black filled mixes. In silica filled and clay filled systems also a similar trend is observed. Compared to the TU system also the corresponding AMT system shows lesser t_{90} values. CBS-AMT mixes also show similar trends. In the case of MBTS-AMT, though the cure rate values at 120°C are low, there is appreciable reduction in cure time with addition of AMT (Table 3.12).

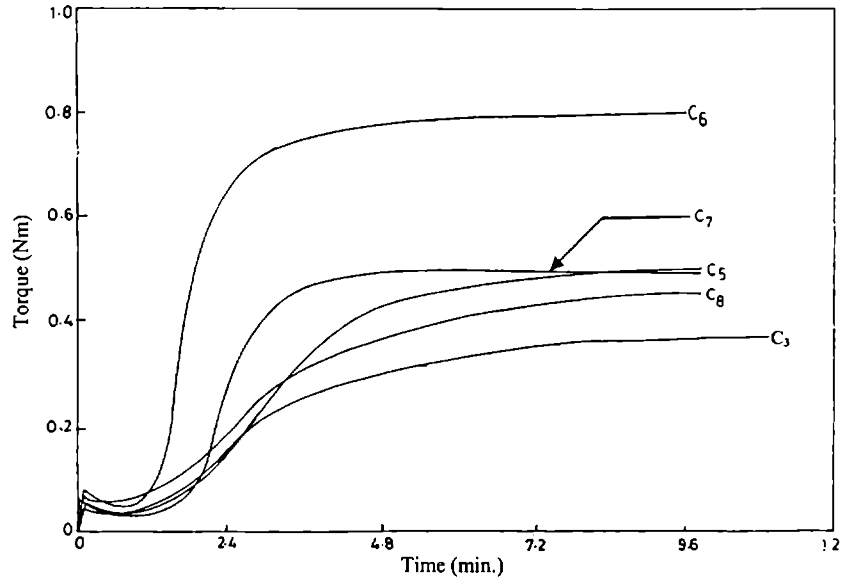


Fig. 3.10 Cure curves of MBTS mixes (carbon black filled, cured at 150°C)

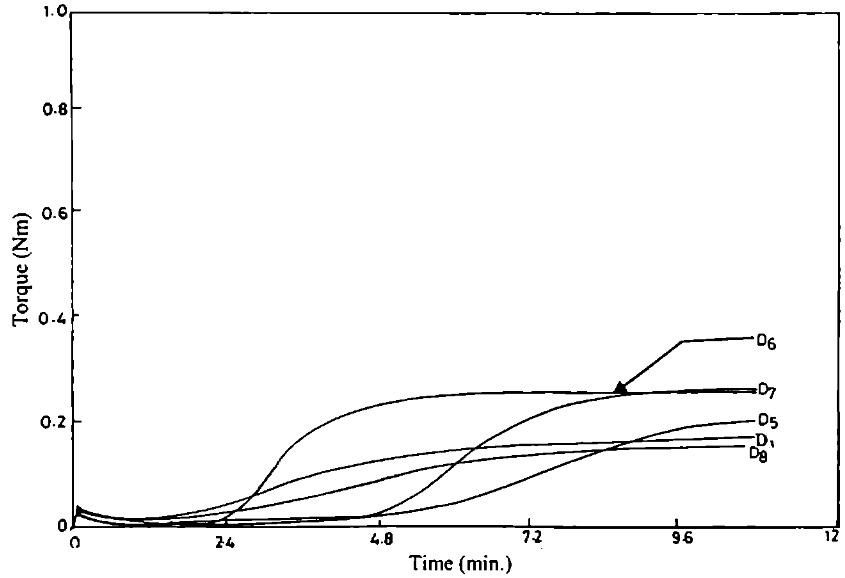


Fig. 3.11 Cure curves of MBTS mixes (silica filled, cured at 150°C)

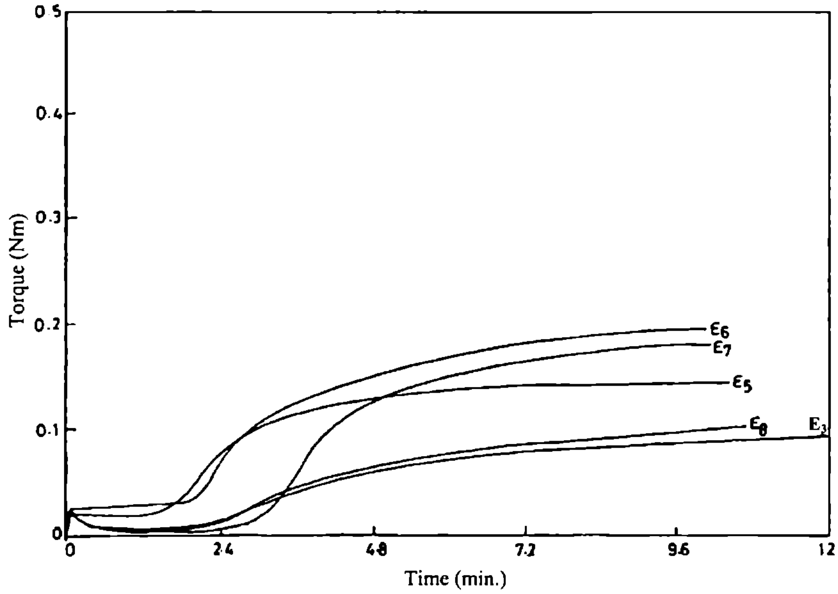


Fig. 3.12 Cure curves of MBTS mixes (clay filled, cured at 150°C)

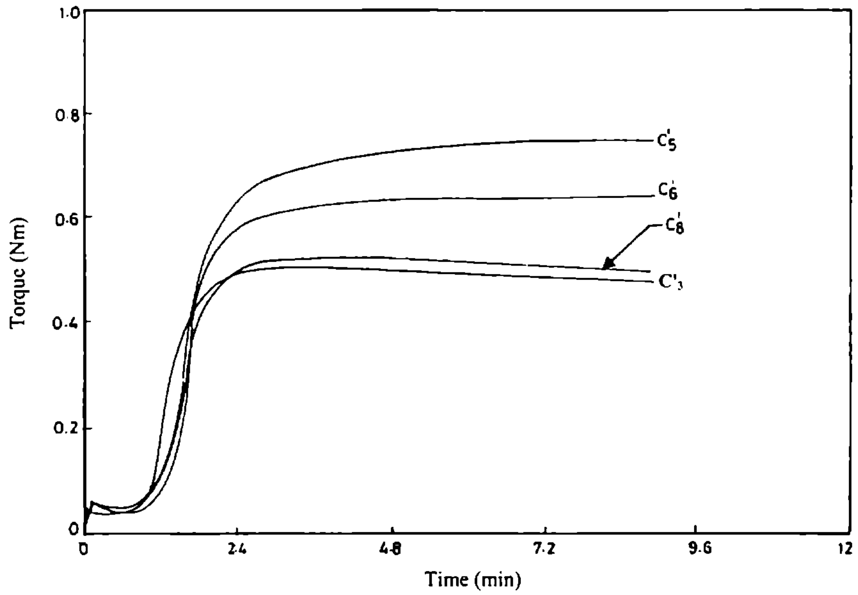


Fig. 3.13 Cure curves of TMTD mixes (carbon black filled, cured at 150°C)

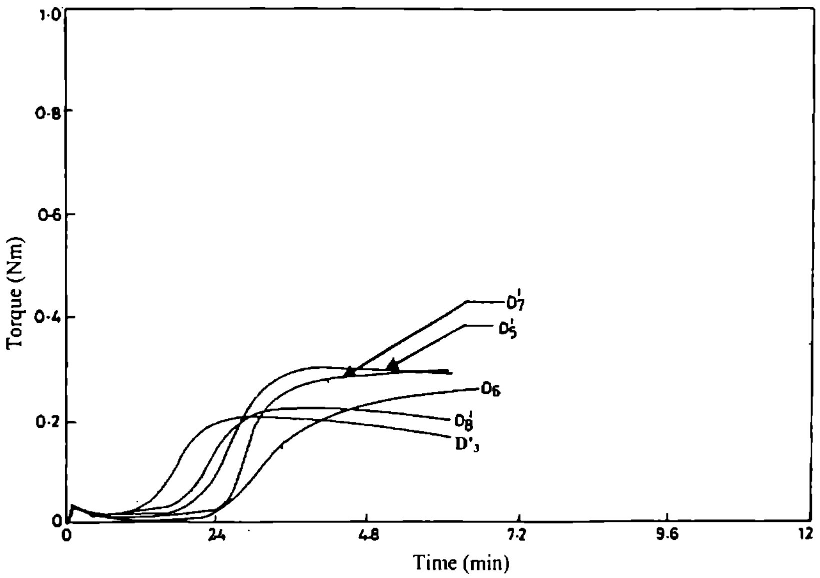


Fig. 3.14 Cure curves of TMTD mixes (silica filled, cured at 150°C)

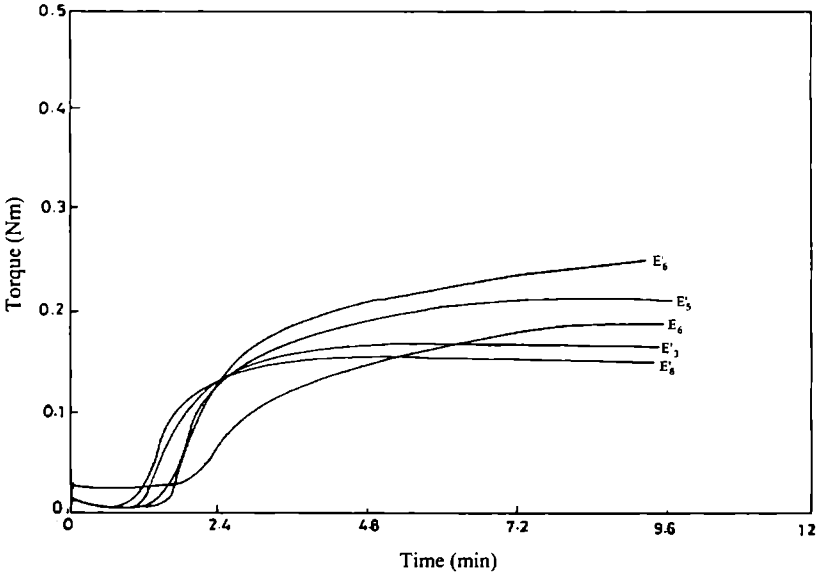


Fig. 3.15 Cure curves of TMTD mixes (clay filled, cured at 150°C)

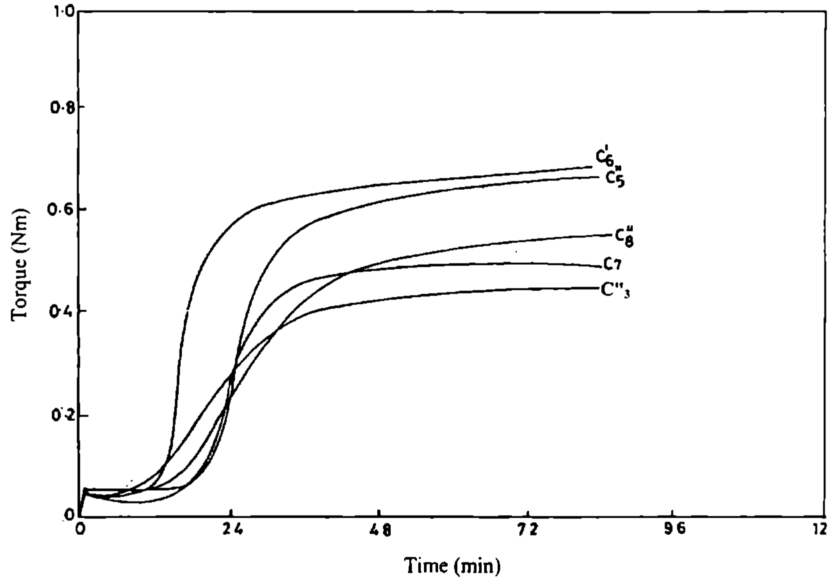


Fig. 3.16 Cure curves of CBS mixes (carbon black filled, cured at 150°C)

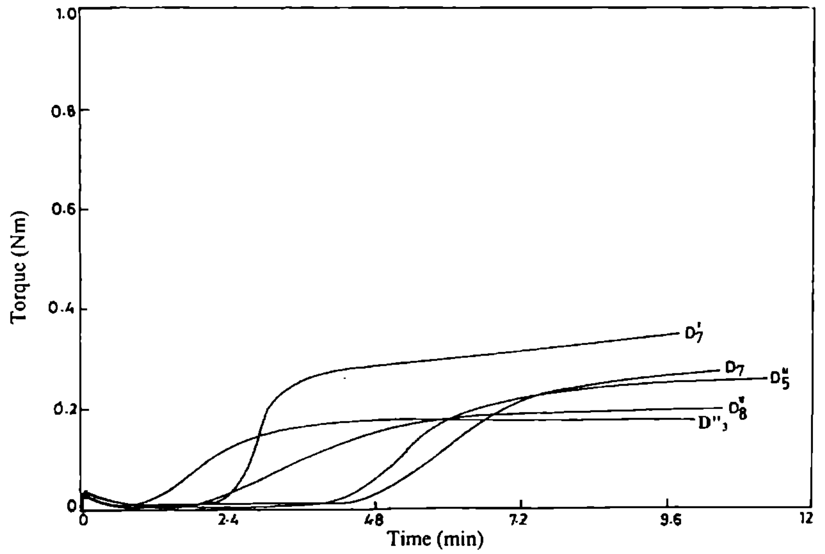


Fig. 3.17 Cure curves of CBS mixes (silica filled, cured at 150°C)

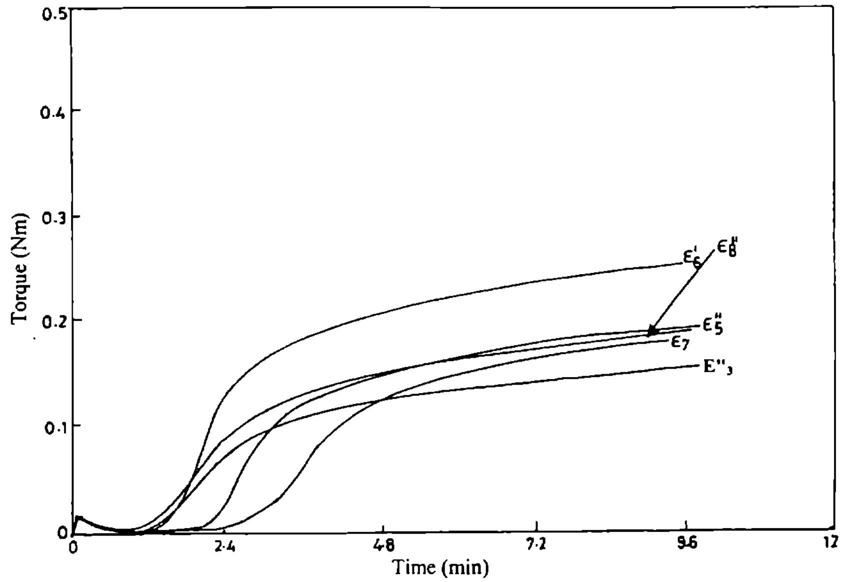


Fig. 3.18 Cure curves of CBS mixes (clay filled, cured at 150°C)

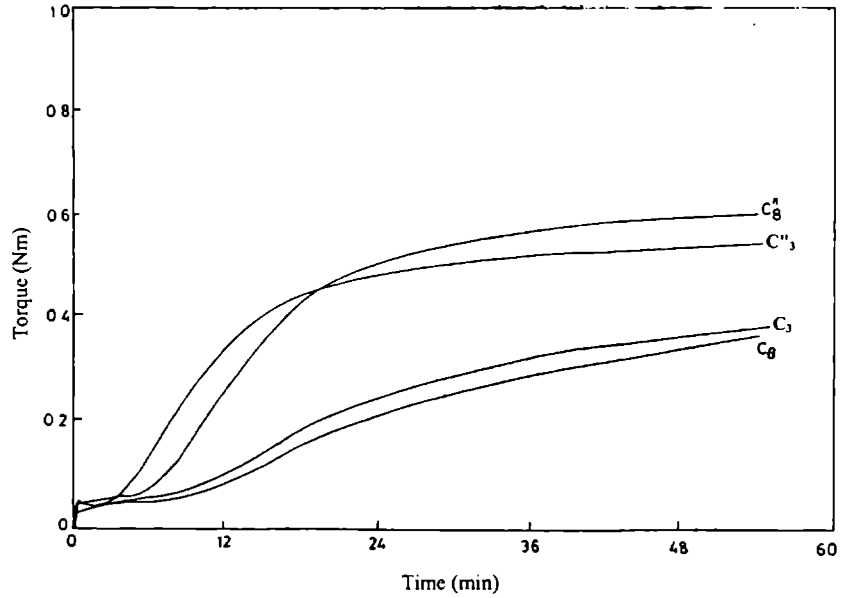


Fig. 3.19 Cure curves of MBTS and CBS mixes (carbon black filled, cured at 120°C)

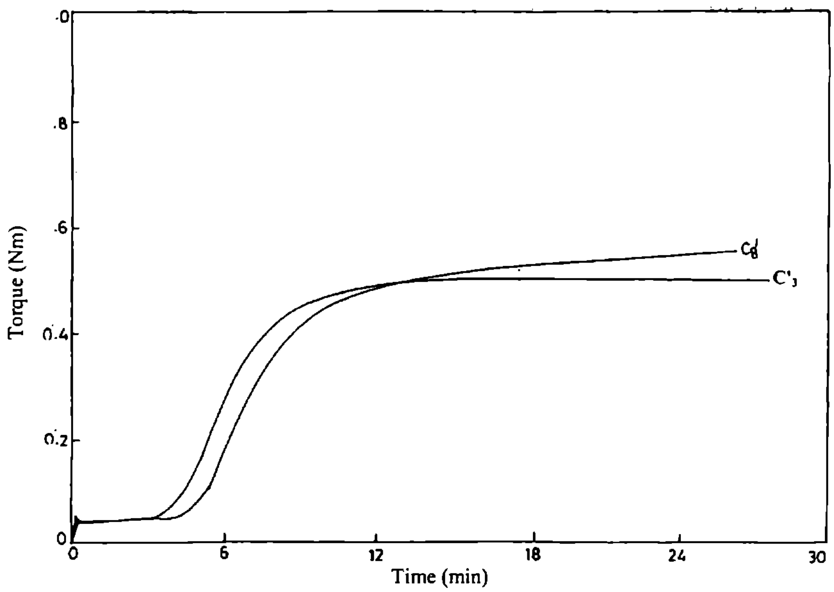


Fig. 3.20 Cure curves of TMTD mixes (carbon black filled, cured at 120°C)

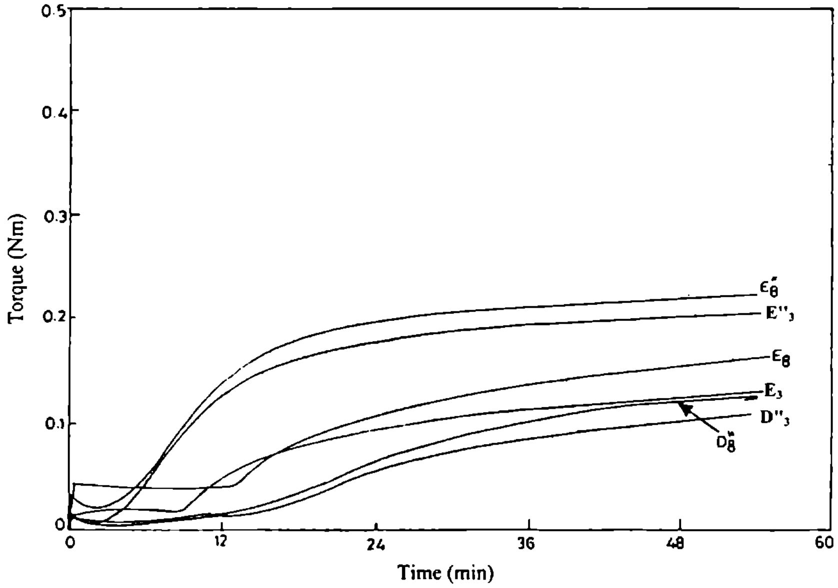


Fig. 3.21 Cure curves of MBTS and CBS mixes (silica and clay filled, cured at 120°C)

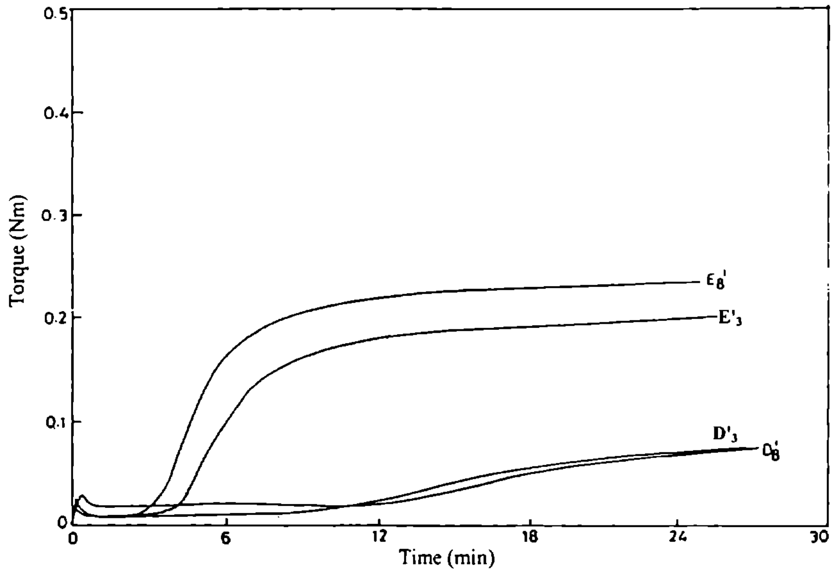


Fig. 3.22 Cure curves of TMTD mixes (silica and clay filled, cured at 120°C)

MBTS-AMT containing silica is found not to cure properly at 120°C. This may be due to the fact that MBTS is not at all active at lower vulcanization temperatures as reported by previous workers[18]. However mixes containing CBS-AMT and TMTD-AMT with silica are effective at this lower temperature also. In these mixes, with increase in the concentration of AMT cure time is reduced considerably at 120°C also. When the cure time values for AMT mixes are compared with that of TU it may be noted that AMT is more effective as a secondary accelerator. This is indicative of a nucleophile from AMT more effectively assisting the cleavage of sulphur links in the primary accelerator. A nucleophilic reaction mechanism is therefore most probable in these binary systems of natural rubber irrespective of the fillers used.

Tensile and other physical properties

Since favourable cure characteristics were obtained using AMT as secondary accelerator in these filled systems of NR, the vulcanizates were further investigated for their physical properties. The tensile properties of the different vulcanizates containing optimum concentrations of the secondary accelerator are given in Tables 3.17 - 3.19. At 150°C, in the case of the carbon black filled systems, tensile strength value for the mix with optimum concentration of AMT is found to be comparable with that of TU.

Table 3.17 Tensile properties of filled MBTS vulcanizates

Mixes	Mixes cured at 150°C								
	Tensile strength (MPa)			100% modulus (MPa)			Elongation at break (%)		
	Before aging	After aging	Retention (%)	Before aging	After aging	Retention (%)	Before aging	After aging	Retention (%)
C_3	14.8	14.9	101	1.9	2.3	121	435	457	105
C_5	21.4	18.7	87	1.9	3.3	173	411	399	97
C_6	16.2	14.8	92	5.8	5.9	101	229	218	95
C_7	20.5	20.6	100	3.1	3.1	100	367	393	107
C_8	13.7	13.7	100	2.1	2.3	109	383	393	102
D_3	12.2	12.7	104	0.9	1.2	127	646	626	96
D_5	19.9	15.9	79	1.2	1.5	130	698	625	89
D_6	17.1	14.8	89	1.6	2.5	151	530	465	87
D_7	24.8	22.1	89	1.8	2.1	116	664	589	88
D_8	12.7	15.9	71	1.1	1.7	115	658	635	96
E_3	10.5	8.8	91	1.4	0.9	63	545	496	91
E_5	13.2	11.8	89	1.5	1.5	100	517	495	95
E_6	11.9	9.8	82	2.3	2.4	101	427	351	82
E_7	19.2	18.3	95	1.6	2.2	136	570	488	85
E_8	10.4	8.5	82	0.8	1.5	173	558	482	86
	Mixes cured at 120°C								
C_3	17.9	15.7	87	2.5	3.3	132	407	425	104
C_8	19.1	21.3	108	2.9	3.1	106	400	388	97
E_3	18.9	18.3	97	1.1	1.2	109	880	822	93
E_8	17.2	16.9	98	0.9	1.1	115	869	842	97

Table 3.18 Tensile properties of the TMTD vulcanizates

Mixes	Mixes cured at 150°C								
	Tensile strength (MPa)			100% modulus (MPa)			Elongation at break (%)		
	Before aging	After aging	Retention (%)	Before aging	After aging	Retention (%)	Before aging	After aging	Retention (%)
C'$_3$	24.8	18.1	73	5.2	4.4	84	330	296	89
C'$_5$	19.2	13.4	70	7	5.7	81	224	216	96
C'$_6$	16.1	14.8	92	5.8	5.9	101	229	218	95
C'$_7$	17.2	14.5	84	4.6	5.1	111	255	256	101
C'$_8$	20.2	16.1	79	3.3	3.7	112	342	292	85
D'$_3$	17.4	14.3	82	0.9	2.1	214	679	616	90
D'$_5$	22.9	19.4	84	2.4	2.5	102	595	544	91
D'$_6$	17.1	14.8	86	1.6	2.5	151	530	465	87
D'$_7$	22.7	20.2	88	2.1	1.4	68	543	528	97
D'$_8$	17.5	16.8	98	1.2	1.7	141	684	669	97
E'$_3$	18.9	11.3	60	2	1.7	87	603	440	73
E'$_5$	13.4	11.3	84	2.2	1.9	90	528	418	79
E'$_6$	11.9	9.8	83	2.3	2.4	101	427	350	82
E'$_7$	14.4	12.5	86	1.9	3	154	485	372	76
E'$_8$	19.6	10.6	54	1.9	2	105	626	414	66
	Mixes cured at 120°C								
C'$_3$	24.8	15.8	63	4.8	5.1	106	336	232	69
C'$_8$	19.2	18.5	96	4.5	5	111	299	253	84
D'$_3$	21.6	18.5	86	1.2	0.8	66	1038	997	96
D'$_8$	20.1	16.8	83	1.3	0.9	73	1022	936	91
E'$_3$	21.6	20.3	94	1.4	1.6	114	903	869	96
E'$_8$	17.2	17.2	100	1.1	1.2	109	729	724	91

Table 3.19 Tensile properties of the CBS vulcanizates

Mixes	Mixes cured at 150°C								
	Tensile strength (MPa)			100% modulus (MPa)			Elongation at break (%)		
	Before aging	After aging	Retention (%)	Before aging	After aging	Retention (%)	Before aging	After aging	Retention (%)
C''_3	19.7	17.8	90	2.4	2.8	116	437	402	92
C''_5	21.7	17.2	79	3.7	4.0	108	365	296	81
C''_6	17.2	14.5	84	4.6	5.1	110	254	256	101
C''_7	20.5	20.6	100	3.1	3.1	100	367	393	107
C''_8	19.1	18.3	95	2.3	3.0	110	441	439	99
D''_3	18.2	18.8	103	1.4	1.2	90	695	689	99
D''_5	22.2	22.3	100	1.6	1.2	77	687	701	102
D''_6	22.7	20.2	89	2.1	1.4	68	543	528	97
D''_7	24.8	22.0	89	1.8	2.1	116	664	589	88
D''_8	9.2	13.0	140	0.9	1.2	134	629	608	96
E''_3	15.4	14.2	92	1.5	1.7	115	605	536	88
E''_5	18.3	17.8	97	1.8	2.5	133	594	489	82
E''_6	14.4	12.5	86	1.9	3.0	154	485	376	76
E''_7	19.2	18.3	95	1.6	2.2	136	570	488	85
E''_8	17.7	16.0	90	1.7	1.8	104	614	548	89
	Mixes cured at 120°C								
C''_3	26.9	26.2	97	3.6	2.1	59	442	603	136
C''_8	26.4	25.4	96	2.4	2.5	104	398	590	148
D''_3	27.7	23.8	86	1.7	1.1	64	1028	988	96
D''_8	25.9	23.3	89	1.7	0.9	55	1006	1007	100
E''_3	25.1	22.7	90	1.6	1.7	106	983	935	95
E''_8	23.8	19.1	80	1.3	1.4	107	935	831	89

The tensile strength value for TMTD-AMT mix (C_3) is higher than that of other conventional systems. However for CBS-AMT and MBTS-AMT tensile strength values are slightly lower. In silica and clay filled vulcanizates, the tensile strength values remain more or less similar to that of control mixes. There is not much variation in modulus (100 %) values among these three binary systems. Elongation at break values of the AMT mixes are higher in all the binary systems evaluated. Aging resistance of the vulcanizates with AMT is also seen to be comparable to the reference mixes. For the vulcanizates cured at 120°C, the tensile strength values are higher than those cured at 150°C. These values of the various experimental mixes with AMT at 120°C are better/comparable to the mixes containing TU.

Other physical properties like hardness, compression set, abrasion loss and tear strength are also evaluated and are reported in Tables 3.20 - 3.22. Considering MBTS systems, experimental mixes with carbon black show lower values for compression set and abrasion loss (higher abrasion resistance). Tear strength value is lower for AMT mixes compared to TU.

Table 3.20 Other Physical Properties of MBTS Vulcanizates

Mixes	Mixes cured at150°C				
	Hardness (Shore A)	Compression set (%)	Abrasion loss (cm^3/ h)	Tear strength (N/ mm)	Total crosslink density×10^5 (g.mol/cm^3)
C_3	53.0	32.3	4.9	39.0	3.1
C_8	52.0	34.5	5.7	40.0	3.1
D_3	40.5	41.1	7.9	30.0	2.5
D_8	40.7	41.0	9.8	57.0	2.5
E_3	30.6	36.7	11.0	27.3	2.7
E_8	30.4	33.8	10.0	27.0	4.5
	Mixes cured at 120°C				
C_3	58.3	47.3	4.2	58.0	3.9
C_8	50.6	45.7	4.1	62.0	3.6
E_3	40.0	27.0	5.1	43.7	3.9
E_8	39.6	36.0	5.6	38.0	3.9

Table 3.21 Other Physical Properties of TMTD Vulcanizates

Mixes	Hardness (Shore A)	Compression set (%)	Abrasion loss (cm^3/ h)	Tear strength (N/ mm)	Total crosslink density×10^5 (g.mol/cm^3)
	Mixes cured at 150°C				
C'$_3$	65	24	3.8	77	6.2
C'$_8$	66	31	3.9	80	4.9
D'$_3$	41	39	10.0	56	3.2
D'$_8$	40	40	8.1	55	2.9
E'$_3$	40	29	5.3	34	3.8
E'$_8$	41	36	5.2	42	3.3
	Mixes cured at 120°C				
C'$_3$	61	35.5	2.6	76	6.6
C'$_8$	60	21.5	2.8	76	6.7
D'$_3$	35	34.8	5.2	54	2.0
D'$_8$	39	27.0	5.0	58	2.2
E'$_3$	46	41.0	4.0	41	5.4
E'$_8$	47	41.0	4.8	41	5.4

Hardness values are more or less similar for AMT and TU mixes. These properties are slightly better for vulcanizates cured at 120°C. Vulcanizates from TMTD and CBS mixes also exhibit more or less similar behaviour. It is already reported that reinforcing fillers have significant effect on the network structure of filled vulcanizates while semi-reinforcing fillers like silica and clay do not have much effect[28]. The total crosslink density values evaluated for the different vulcanizates are given in Tables 3.20 - 3.22. As expected higher crosslink density values are obtained in the case of carbon black filled vulcanizates for all the binary combinations studied. Also higher crosslink density values are obtained for mixes cured at 120°C than those cured at 150°C.

Table 3.22 Other Physical properties of CBS vulcanizates

Mixes	Mixes cured at 150°C				
	Hardness (Shore A)	Compression set (%)	Abrasion loss (cm^3/h)	Tear strength (N/ mm)	Total crosslink density×10^5 $(g.mol/cm^3)$
C''_3	58	34	3.8	62	3.8
C''_8	55	19	4.3	60	3.5
D''_3	39	33	6.1	63	2.7
D''_8	31	41	10.0	54	2.3
E''_3	40	38	5.1	36	4.1
E''_8	40	39	5.0	39	4.1
	Mixes cured at 120°C				
C''_3	60	31.4	2.7	83	5.6
C''_8	50	35.0	2.6	93	5.5
D''_3	43	34.0	2.8	66	2.4
D''_8	44	33.0	3.5	67	2.3
E''_3	47	34.0	4.0	53	5.2
E''_8	48	39.0	4.2	44	5.0

CONCLUSIONS

Aminoiminomethyl thiourea (AMT) is found to be an effective secondary accelerator both in filled and unfilled binary systems of natural rubber vulcanization when MBTS-AMT, TMTD-AMT and CBS-AMT are used as binary combinations. The introduction of AMT is found to reduce the optimum cure time considerably compared to thiourea, which is used as the control. At the lower temperature of 120°C the effect of AMT as a secondary accelerator is found to be predominant in both gum and filled mixes. Considering the nucleophilic character of AMT and TU the results obtained in this study point to a nucleophilic reaction mechanism in these different systems of NR vulcanization as suggested by Philpott. Optimum concentrations of AMT required in these mixes have also been derived based on the cure characteristics obtained.

It may be stated that, in general, the tensile strength values of vulcanizates containing AMT are better/comparable to those of reference mixes. The percentage retention of these properties is also found to be satisfactory. Other physical properties studied, viz. compression set, abrasion resistance and elongation at break in all these AMT systems give values which are better than those of other reference formulations. It may be noted that AMT is a non-toxic chemical used in pharmaceutical industry, while many of the conventional accelerators used in rubber industry are reported to be toxic. This is an added advantage in favour of this amidino thiourea.

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Chapter 4

STUDIES ON THE EFFECT OF AMINOIMINO METHYL THIOUREA IN NR LATEX SYSTEMS

Latex is defined as a stable dispersion of a polymeric substance in an aqueous medium[1]. Natural rubber latex is a negatively charged colloidal dispersion of rubber particles suspended in an aqueous serum. Freshly tapped latex, before preservation and concentration is known as field latex. NR latex is a weak lyophilic colloidal system of spherical or pear shaped rubber globules. The rubber globule is surrounded by a protective layer of proteins and phospholipids which imparts the prophyllic colloidal nature to latex and the stability of the latex is due to the negative charge present on the protective layer[2]. The non-rubber constituents occurring in field latex are proteins, lipids, quebrachitol and inorganic salts. The last two components occur entirely in the aqueous phase or serum, the lipids are nearly all on the surface or in the interior of the rubber particles and the proteins are distributed between the serum and the rubber-serum interface[3,4]. The rubber particles themselves, excluding surface-active materials adsorbed on their surface, consist almost entirely of natural rubber hydrocarbon with which small amounts of oxygen may be combined. The size of the rubber particles ranges in diameter from less than 0.05μ to about 3μ. NR latex has specific gravity in the range of 0.975 to 0.98 and having variable viscosity. Its pH ranges from 6.5 to 7 and surface free energy from 40 to 45 ergs cm^{-2}.

Although the amount of rubber in the field latex may vary considerably, the constitution of the rubber hydrocarbon is very uniform in its micro-structure. The rubber hydrocarbon in NR is cis 1, 4-polyisoprene.

Characterization of rubber hydrocarbon by intrinsic viscosity, osmotic pressure, light scattering, sedimentation velocity analysis, etc. has yielded considerable information on the size and shape of rubber molecules and has established that the rubber hydrocarbon of Heava brasiliensis comprises a series of polymer homologues with average molecular weight in the region of 500,000 to 600,000 and with a broad distribution of molecular weight. Fresh latex, as it comes out from the tree, is slightly alkaline or neutral. It becomes acidic rapidly due to bacterial action. The formation of organic acids neutralises the negative charge on rubber particles and the latex gradually gets coagulated on keeping[5]. Therefore, fresh latex cannot be kept for long without adding preservative[6]. Ammonia is the most popular latex preservative. Latex preserved with higher percentage of ammonia is known as high ammonia (HA) latex. Usually concentrated latex is preserved with lesser percentage of ammonia and a secondary preservative. After the addition of ammonia as preservative, the latex phospholipids are gradually hydrolysed to free bases, glycerol, glycerophosphate and fatty acid soaps. The free bases, glycerophosphate and glycerol pass into the serum but much of the fatty acid soap remains adsorbed. Similarly hydrolysis of some of the adsorbed protein slowly occurs in the presence of ammonia forming aminoacids and polypeptides which also pass into the serum. Since the adsorbed materials are responsible for the stability of the latex, their hydrolysis leads to changes in stability. The mechanical stability actually increases since the formation of fatty acid soap more than compensates for the loss of phospholipids and proteins. Fatty acid soaps however, do not stabilize the latex against inorganic acids. Field latex with 30 - 40% rubber is concentrated to about 51- 60% dry rubber content (drc) for product manufacture. Concentration is advantageous since less water is transported and higher solid content is required for most manufacturing operations[7].

A rubber by itself has such poor properties that it has limited commercial value. A variety of materials must be added to rubber to improve its properties and to make it commercially useful. Natural rubber latex is used extensively in the manufacture of various articles like gloves, weather balloons, foam and cellular rubbers. These latex articles give service performance superior to that of articles made from rubber solutions[8]. In all latex processes a stable colloidal system is maintained until, at the desired time, it is made unstable and converted to a solid product[9]. The compounding of NR latex is in principle similar to that of dry rubber. There are two major differences. First, as latex compounds are mixed at room temperature, highly active vulcanization systems can be used, which enable vulcanization to be performed at temperatures below 100°C. In dry rubber such systems are difficult or impossible because the heat developed in mixing causes premature vulcanization or scorch. Secondly, the reinforcing action of fillers, which is of major importance in dry rubber, is not obtainable in normally processed latex compounds. In the manufacture of vulcanized latex products the common procedure is to compound the latex with aqueous dispersions of the vulcanizing components and other water insoluble ingredients that may be required. Water-soluble ingredients of the latex compound will normally be added as aqueous solutions. The different ingredients used in a latex compound are: (i) surface active agents, (ii) vulcanizing agents, (iii) accelerators, (iv) activators, (v) antioxidants, (vi) fillers and (vii) other special additives. The particle size of the ingredients should be reduced to that of rubber particles in latex for getting uniform distribution in latex compound[10]. The surface-active agents are substances which bring about marked modification in the surface properties of aqueous media even when they are present in very small amounts. Sulphur is the most important vulcanizing agent for NR latex. Thiuram polysulphides can be used as curing agents for heat resistant products. ZnO is used as an activator to the vulcanization process and its effect include increase in the tensile strength and modulus of the vulcanizate. If zinc containing accelerators like zinc dithiocarbamates are used ZnO is not essential, but it is commonly used in latex compounds to provide further activation of vulcanization and to contribute to gelation process[11]. Amine and phenolic derivatives are the common antioxidants used in latex[12]. Styrenated phenols are widely used antioxodants in latex industry and they have the advantage of not causing discolouration but are not as effective as amines.

The feasibility of using latices in most of their applications depends upon the compounded latex being fluid and having appropriate rheological properties. The flow properties of latices are therefore of great practical relevance for the industrial applications of polymers in latex form. The rubber industry operates with devices imparting shear stresses and shear rates over a wide range. Therefore,the viscosity of a polymer as a function of shear rate and temperature is very important. Natural rubber latex is a pseudoplastic fluid and is non-Newtonian. When sheared the rubber particles are progressively aligned and offers less resistance to flow[13]. So the apparent viscosity of the latex decreases on increasing the shear rate and continues until the flow curve becomes linear. The viscosity of latex also depends on its total solid content and temperature[14]. The rheology of rubber solutions, suspensions, latex and latex compounds had been studied by Leaman[15]. Temperature has got tremendous effect on the viscosity of latex. Latex becomes less viscous as the temperature is increased. This is due to the reduction of viscosity of the dispersion medium. Diverse types of flow behaviour are encountered during processing at different temperatures by various techniques such as dipping, extrusion, casting, spraying, etc. Each process or technique involves, at different stages of operation, a critical relation between temperature, applied stress and inherent fluid property such as viscosity. Among the various physico-chemical properties viscositv is the most important one, which influences the processing characteristics. Control of viscosity is more important than that of concentration.

The vulcanization of latex is the result of chemical reactions taking place in the heterogeneous systems. The use of organic accelerators in latex compounding accelerates the vulcanization process and also improves many of the physical properties of the product. A wide range of organic accelerators for the sulphur vulcanization of natural rubber is available. In general, only those of the highest activity are important for the vulcanization of rubber latices, because latex vulcanization temperatures are low[16] and there is no danger of scorching[17]. So the use of accelerators in latex is basically different from their use in dry rubber[18-20]. The accelerators should become evenly distributed without causing the mixture to coagulate or to thicken[21]. The most important type of accelerators are metal dialkyl dithiocarbamates. It has been found that tetra methyl thiuram disulphide (TMTD) can be used to cure natural rubber latex with or without sulphur to prepare heat resistant articles[22]. It may also be used to prepare vulcanizates which can prevent copper catalyzed oxidative degradation. The vulcanization of latex using TMTD proceeds only at relatively high temperature. At low temperatures (100°C or below) the reaction is very slow and is of no technical interest.

Philpott[23] has proposed that accelerators in which sulphur is combined as S – S, C – S – C or S – N are inactive at temperatures below 100°C, due to the high thermal stability of the sulphur bonds. He has also shown that sulphur-containing nucleophiles like thiourea enables such accelerators to become active even at lower temperatures. Moore[24] also showed that accelerative effect of TU is attributed to its interaction with TMTD under basic conditions to form thiuram polysulphides. Philpott[23] has also observed that sulphenamide accelerators, which do not vulcanize NR latex in the absence of sulphur or at very low dosages of sulphur are also activated by TU to such an extent that the combination will effect cure at technologically useful rates. He found that these combinations of latex compounds are resistant to copper staining. Earlier studies[25,26] in our laboratory have shown that different derivatives of TU can act as very effective secondary accelerators. These compounds have different nucleophilic character and it was observed, in general, that as the nucleophilic character increases, their activity as secondary accelerator also increases. However, it was noticed that the type of the system and the elastomer used has also an effect on the reaction mechanism.

In the present study we tried unsubstituted aminoiminomethyl thiourea (AMT) as a secondary accelerator along with primary accelerators like TMTD/CBS/ZDC in the vulcanization of NR latex. This study was undertaken in view of the fact that natural rubber latex requires combinations of more active accelerators compared to dry rubber. This is because latex vulcanization temperature is comparatively lower than that of dry rubber. It is also to be emphasized that this amidino thiourea is a non-toxic chemical[27] whereas some of the conventional accelerators used in rubber compounding are reported to be toxic[28]. In the present investigations the effect of various binary accelerator systems mentioned above on the viscosity of the latex mixes under different shear rates and temperatures has also been studied. Different mixes with varying concentrations of AMT were prepared and the optimum dosage of AMT required is derived based on the cure characteristics and tensile properties obtained. The mixes were cured at two different temperatures, viz.100 and 120°C. The different tensile properties of the vulcanizates were evaluated and chemical characterization of vulcanizates was also carried out. These properties are compared with those of different control mixes containing thiourea.

4.1 EXPERIMENTAL

NR latex compounds containing AMT as secondary accelerator along with TMTD/CBS/ZDC were prepared using formulations given in Table 4.1. The weight of various ingredients given is wet weight in gram calculated on dry rubber content. Mixes A_2 - A_5 contain varying amounts of AMT, viz. 0.25, 0.5, 1 and 1.5 molar equivalents with one molar equivalent of ZDC. Mix A_0 contains ZDC alone and A_1 contains ZDC and TU in 1:1 molar levels. Mixes C_2 - C_5 contain different amounts of AMT ranging from 0.25 to 1.5 molar equivalents along with TMTD. C_0 and C_1 are corresponding reference mixes. Similarly E series are mixes with CBS as the primary accelerator. Centrifuged NR latex of 60% drc and conforming to BS 5430 - 1981 was used in this study. Other compounding ingredients were of commercial grade. One part by weight of 10% KOH and 0.5 part by weight of potassium oleate (10%) were added to stabilize the latex throughout the compounding and processing stages. These soluble ingredients were added as aqueous solutions. The insoluble compounding ingredients were prepared into dispersions. The materials were made to disperse in water by grinding action and the dispersing agent prevents the dispersed particles from re-aggregating. A ball mill was used for making the dispersions of the ingredients. TU and AMT were added as 10% aqueous solutions. All the ingredients were added continuously with slow and thorough stirring to the latex taken in a glass vessel. This glass vessel is chemically resistant to ammoniated latex and other compounding ingredients. After compounding the mixes were kept for maturation at room temperature for 24 hours.

Rheological study

The experimental mixes containing optimum dosage of AMT and the corresponding references were used for the rheological study. A Haake viscotester (VT 550) was used to study the effect of temperature and shear

Table 4.1 Formulation of the mixes.

Ingredients, parts by weight (wet)	Mixes																	
	A_0	A_1	A_2	A_3	A_4	A_5	C_0	C_1	C_2	C_3	C_4	C_5	E_0	E_1	E_2	E_3	E_4	E_5
60% Centrifuged latex	167	167	167	167	167	167	167	167	167	167	167	167	167	167	167	167	167	167
10% KOH solution	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
10%potassium oleate solution	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
50%ZnO dispersion	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
50%ZDC dispersion	7.2	3.6	3.6	3.6	3.6	3.6												
33% TMTD dispersion							7.2	3.6	3.6	3.6	3.6	3.6						
33% CBS dispersion													8	4	4	4	4	4
10% TU solution		3.8						3.8						3.8				
10%AMT solution			1.47	2.95	5.9	8.85			1.47	2.95	5.9	8.85			1.47	2.95	5.9	8.85
50% sulphur dispersion	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3

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

Latex is located in the measuring gap of the sensor system. Rotational speed, measuring time, number of measuring points and measuring temperature are preset. The rotor is rotated at the preset speed. The latex exerts a resistance to the rotational movement due to its viscosity, which becomes apparent as a torque value applied on the measuring shaft of the VT 550. From the measured variables of speed, torque and sensor geometry the computer attached to the system calculates the relevant values for the following factors: viscosity η in mPa.s, shear rate γ in s^{-1} and shear stress τ in Pa. The temperature T is measured in degree centigrade. In the present study measurements were taken at 25, 35 and 45°C at shear rate from 1 to 150 s^{-1}.

The rheological behavior of the latex has been analysed using power law equation,

$$\tau = k\gamma^{n}$$

where τ = shear stress (Pa)

k = viscosity index

γ = shear rate (s^{-1})

n = flow index

By plotting $\log\tau$ vs $\log\gamma$ the values k and n are obtained as slope and intercept by regression analysis. The apparent viscosity η is the ratio of shear stress to shear rate.

i.e $\eta = k\gamma^{n-1}$

Latex films were cast on glass cells using the matured compound. About 30 to 35 ml of the latex compound was poured and distributed so that a film of thickness 1 to 1.25 mm was obtained upon drying. In order to study the effect of temperature on vulcanization, these compounds were cured at two different temperatures, viz. 100 and 120°C for definite time intervals in an air oven. The optimum cure time was found out from the tensile strength– time graph (Figs. 4.1 - 4.6). From the graph the time taken for attaining optimum tensile strength is taken as the optimum cure time. The tensile properties of the vulcanizates were determined using a Zwick universal testing machine as per ASTM D 412-83. The aging resistance of the vulcanizates was determined by heating the samples in an air oven at 70°C for seven days. The tear strength of the samples was determined as per ASTM D 624-86. The total crosslink density and the polysulphidic linkages of the vulcanizates were determined using the equilibrium swelling method. The concentration of polysulphidic linkages was estimated from the change in the crosslink density of the vulcanizates before and after treatment with propane 2–thiol and piperidine, which cleaves the polysulphidic crosslinks in the net work[29,30].

4.2 RESULTS AND DISCUSSION

Cure and tensile properties

The tensile strength–time graphs at 100 and 120°C for various systems studied are given in Figs. 4.1 - 4.6. It can be seen that at 120°C ZDC-AMT mix (A_4) takes only 15.7 minutes to attain optimum tensile strength while similar system containing ZDC alone (A_0) takes 20 minutes and ZDC-TU (A_1) takes 20.5 minutes. At 100°C the optimum cure time for ZDC-AMT is lower than that for ZDC alone but is same as that for ZDC-TU. The optimum cure time value decreases as the concentration of secondary accelerator (AMT) increases in the mix. There is definite increase in tensile strength also with concentration of AMT. The percentage retention of tensile strength is also found to be higher for the experimental mixes compared to the reference formulations. Mix C_4 containing one molar equivalent of AMT with similar concentration of TMTD showed a

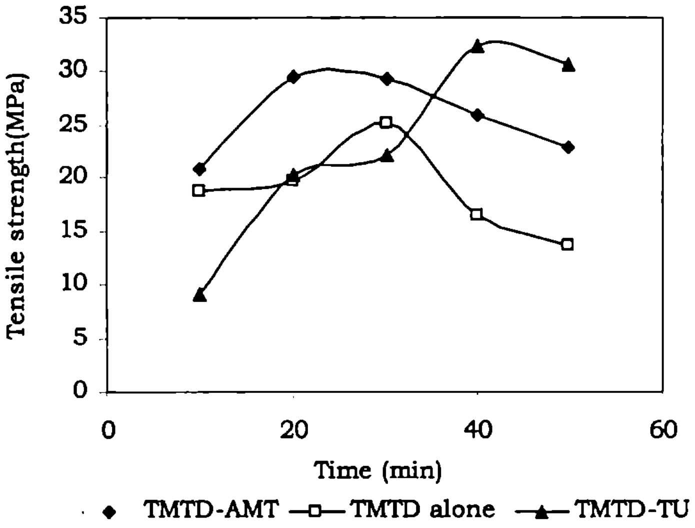

Fig.4.1 Variation of tensile strength with time for TMTD mixes (cured at120°C)

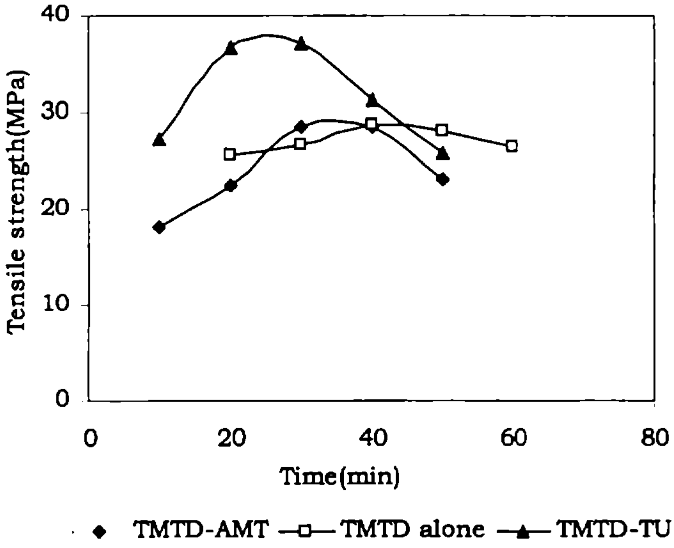

Fig.4.2 Variation of tensile strength with time for TMTD mixes (cured at100°C)

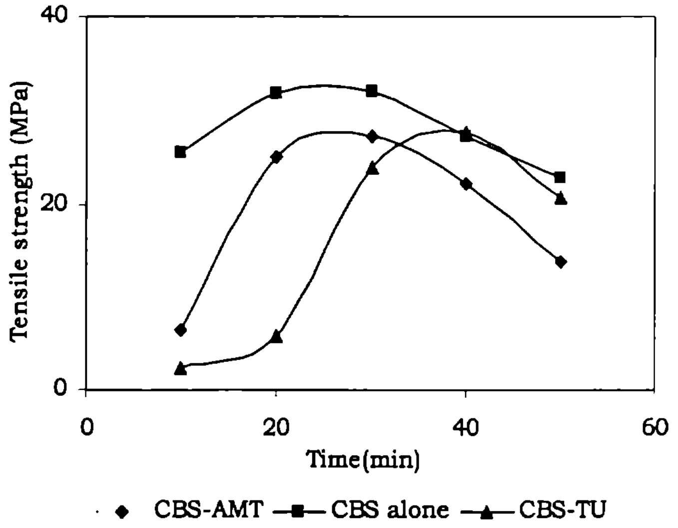

Fig.4.3 Variation of tensile strength with time for CBS mixes (cured at 120°C)

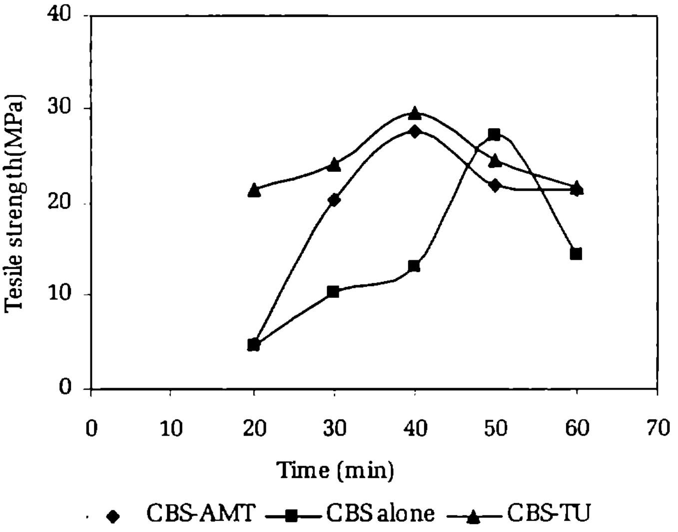

Fig.4.4 Variation of tensile strength with time for CBS mixes (cured at 100°C)

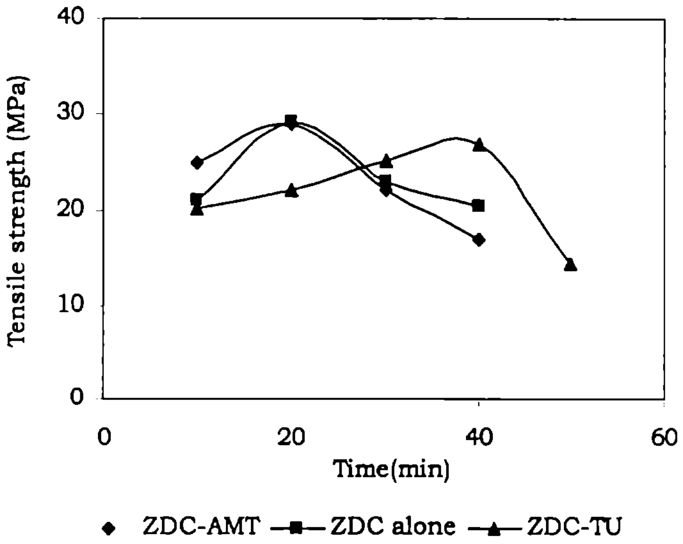

Fig.4.5 Variation of tensile strength with time for ZDC mixes (cured at 120°C)

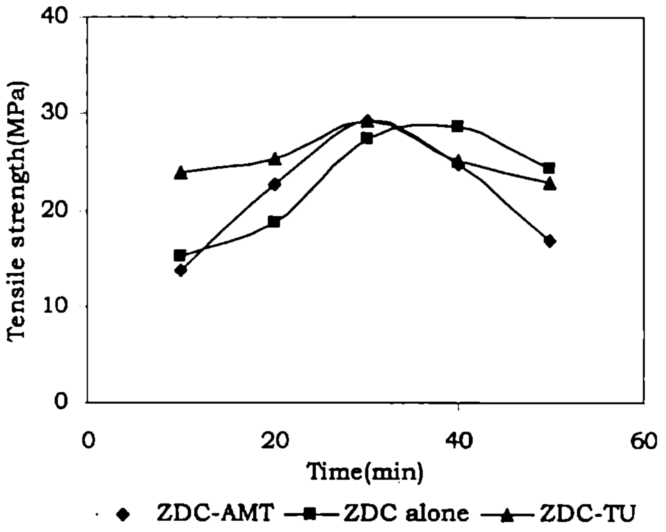

Fig.4.6 Variation of tensile strength with time for ZDC mixes (cured at 100°C)

cure time of 22.8 min. that is lower compared to TMTD-TU. At 100°C TMTD-TU mix takes 40 min. to cure while the system containing AMT takes 32.8 min. Taking the cure and the tensile strength values it can be inferred that the optimum dosage of the secondary accelerator (AMT) required is one molar equivalent along with one molar equivalents of the primary accelerators.

At 120°C mix E_0 containing CBS alone shows a cure time of 35.1 min. while mix E_4 containing CBS-AMT has a cure time of 26.4 min. Mix E_1 containing similar CBS-TU combination cures in 46.7 min. At 100°C the system containing CBS-AMT takes 39.2 min. to attain optimum tensile strength while the systems containing CBS alone and CBS-TU take 44.5 and 40 min. respectively. The lower optimum cure time exhibited with AMT in the above systems can be attributed to the nucleophilic attack by AMT which enhances the S–S bond cleavage in the primary accelerator leading to a faster cure. It has also been suggested that the higher the nucleophilic character of the attacking agent, the faster will be the cure. The optimum cure time obtained in the different systems under review and considering the fact that AMT is more nucleophilic than thiourea, these cure results point to a nucleophilic reaction mechanism in these latex vulcanization systems.

The tensile strength values obtained in the ZDC-AMT vulcanizates are given in Table 4.2. Considering the samples cured at 120°C, as the concentration of AMT increases, the tensile strength is also found to increase. The tensile strength values of mix A_4 (ZDC–AMT) is found to be higher than mix A_1 (ZDC–TU). For the samples cured at 100°C the tensile strength values of the experimental mixes containing AMT are found to be comparable to those of the control mixes. The aging resistance of the vulcanizates, given as the percentage retention of tensile strength, is found to be higher for the experimental mixes containing AMT compared to the reference formulations. The tensile strength values evaluated for the TMTD-AMT systems are given in Table 4.3. These values for the experimental mixes containing AMT are slightly less than the control mixes containing TU both at 100 and 120°C. For CBS-AMT systems also tensile strength values are less than the control mixes (Table 4.4).

Table 4.2 Properties of ZDC mixes.

Mixes cured at 120°C							
Mix No.	Optimum cure time (min)	Tensile strength (MPa)			Tear strength (N/mm)	Total crosslink density×10^5 (g.mol/cm^3)	Poly sulphidic linkages×10^5 (g.mol/cm^3)
		Before aging	After aging	Retention (%)			
A_0	20.0	29.2	20.9	71.5	45.7	5.64	2.02
A_1	20.5	26.8	18.5	69.0	42.0	5.66	2.32
A_2	28.0	28.6	21.1	72.2	30.7	4.34	
A_3	16.0	25.7	13.2	51.3	47.1	5.54	
A_4	15.7	29.0	25.4	87.0	51.6	5.50	2.47
A_5	12.0	29.3	27.2	92.8	69.1	4.34	
	Mixes cured at 100°C						
A_0	38.0	29.0	22.3	76.8	52.7	4.71	2.89
A_1	29.0	29.1	20.2	69.0	55.8	5.68	3.83
A_2	37.0	26.1	20.0	76.6	50.1	3.9	
A_3	35.0	26.0	20.6	79.0	54.8	4.07	
A_4	30.0	29.2	27.7	94.8	58.8	4.24	2.36
A_5	29.0	28.7	34.3	119.0	60.6	4.08	

However, the percentage retention of this property after heat aging is found to be higher for CBS-AMT systems. The tear strength values evaluated indicate that there is a definite increase in tear strength with increase in the concentration of AMT in the different combinations tried. Samples cured at 100°C also showed a similar trend.

Chemical characterization of the samples containing optimum concentration of AMT and corresponding control formulations was carried out.

Table 4.3 Properties of TMTD mixes

Mix No.	Optimum cure time (min)	Tensile strength (MPa)			Tear strength (N/mm)	Total crosslink density× 10^5 (g.mol/cm^3)	Poly sulphidic linkages× 10^5 (g.mol/cm^3)
		Before aging	After aging	Retention (%)			
	Mixes cured at 120°C						
C_0	30.0	25.2	17.3	68.6	46.3	4.84	2.27
C_1	41.2	32.3	18.4	56.9	50.3	4.92	2.73
C_2	39.0	24.9 ~~56.9~~	23.8	95.5	39.4	4.36	
C_3	30.4	24.5	16.8	68.5	54.8	4.6	
C_4	22.8	29.5	15.1	51.1	56.3	4.98	2.87
C_5	19.6	31.7	20.5	64.6	61.3	4.65	
	Mixes cured at 100°C						
C_0	40	28.7	29.6	103.0	48.7	4.80	3.34
C_1	42.4	37.1	15.9	42.8	46.8	4.65	3.30
C_2	43.2	20.7	19.8	95.0	54.6	4.2	
C_3	40	26.6	13.1	49.0	66	3.82	
C_4	32.8	28.6	20.7	72.3	53.2	3.43	2.88
C_5	31.2	32.3	17.0	52.6	52.3	4.47	

Tables 4.2-4.4 give the total crosslink density and polysulphidic linkages (mixes of optimum secondary accelerator combinations only) of these vulcanizates. In ZDC–AMT systems, both at 100 and 120°C, the total crosslink density and polysulphidic linkages are lower than that of control mixes. These results are generally in agreement with tensile strength values obtained. In TMTD-AMT mixes at 120°C the total crosslink density and polysulphidic linkages are higher than that obtained for control mixes. However, at 100°C these values are found to be lower. In CBS-AMT mixes total crosslink density and polysulphidic linkages are higher compared to control mixes containing TU. The percentage retention of tensile strength

is also higher than control mixes. This may be attributed to the higher amount of mono and disulphidic linkages in AMT mixes.

Table 4.4 Properties of CBS mixes.

Mixes cured at 120°C							
Mix No.	Optimum cure time (min)	Tensile strength (MPa)			Tear strength (N/mm)	Total crosslink density×10^5 (g.mol/cm^3)	Poly sulphidic linkages×10^5 (g.mol/cm^3)
		Before aging	After aging	Retention (%)			
E_0	35.1	31.9	14.3	45.0	42.6	5.76	3.17
E_1	46.7	27.6	17.8	64.4	41.2	4.47	2.81
E_2	50.7	28.4	25.1	88.0	39.5	5.5	
E_3	29.3	22.6	20.5	91.0	41.2	4.5	
E_4	26.4	27.2	18.0	66.0	48.1	5.38	3.51
E_5	22.4	29.7	26.0	87.5	46.6	3.78	
	Mixes cured at 100°C						
E_0	44.5	27.2	14.6	53.6	44.1	3.32	1.64
E_1	40	29.6	22.2	75	44.3	4.61	2.93
E_2	48.4	23.5	12.9	55	46	5.06	
E_3	48.1	19.9	14	70	41.9	5.35	
E_4	39.2	27.5	25.6	93	51.5	5.79	4.21
E_5	31	30.3	27.2	89	48.7	5.4	

Flow Behaviour

In the present investigations the viscosity and processability of the different natural rubber compounds under different shear rates and temperatures have been studied. Figures 4.7 - 4.9 show the effect of shear rate and temperature on the viscosity of TMTD mixes containing other secondary accelerators. On increasing the shear rate viscosity of the latex compounds is found to decrease in accordance to the pseudoplastic behaviour of these mixes.

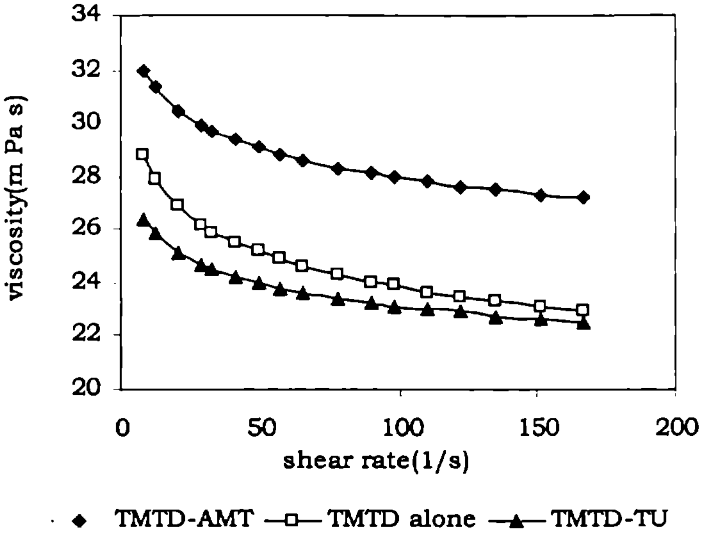

Fig. 4.7 Variation of viscosity with shear rate for TMTD mixes at 25°C

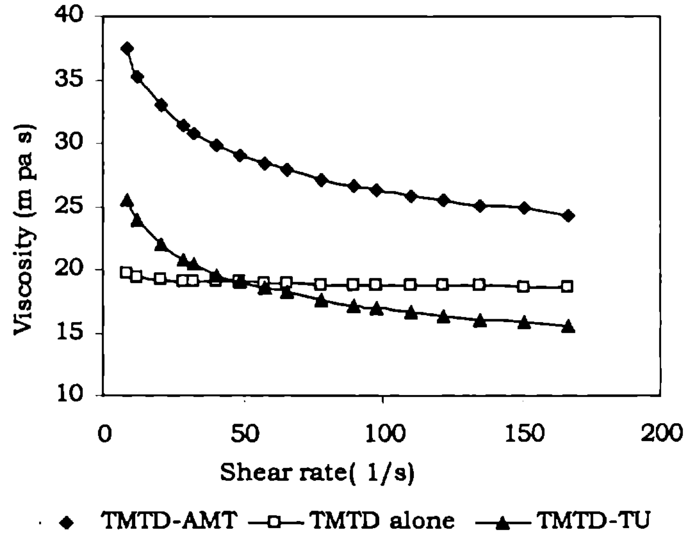

Fig. 4.8 Variation of viscosity with shear rate for TMTD mixes at 35°C

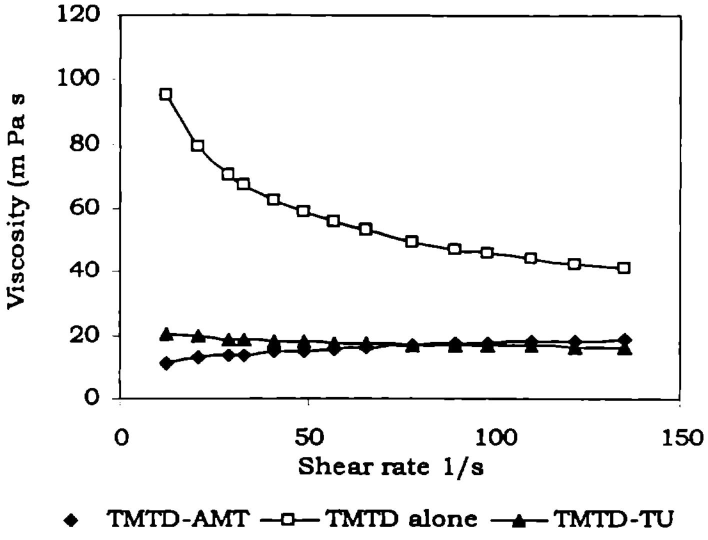

Fig. 4.9 Variation of viscosity with shear rate for TMTD mixes at 45°C

The effect is more pronounced at low shear rates, whereas it approaches near-Newtonian behaviour at high shear rates. As the temperature is increased from 25 to 35°C, viscosity is found to be decreasing in all the three systems under review. But as the temperature is increased to 45°C mix containing TMTD alone shows a sharp increase in viscosity causing the destabilization of latex. For TMTD alone, at a shear rate of 61.7 s^{-1}, viscosity is 59 mPa.s while that for TMTD-AMT it is 19 mPa.s at this temperature. A similar behaviour is observed in TMTD-TU and its viscosity is 20 mPa.s. Fig.4.10 shows the effect of temperature on the viscosity (at constant shear rate) of these mixes.

The effect of shear rate on viscosity of compounded latex for CBS systems at 25, 35 and 45°C is shown in Figs. 4.11- 4.13. In CBS-AMT combination the effect of shear rate on viscosity is found to be different from TMTD mixes. On increasing the shear rate viscosity of CBS-AMT mixes increased at all these three temperature ranges (Figs. 4.11 - 4.13). Similar trend is shown by thiourea systems also. In this case AMT and TU seem to destabilize the system. This indicates that when CBS systems are employed AMT and TU are not useful especially at temperatures above 35°C.

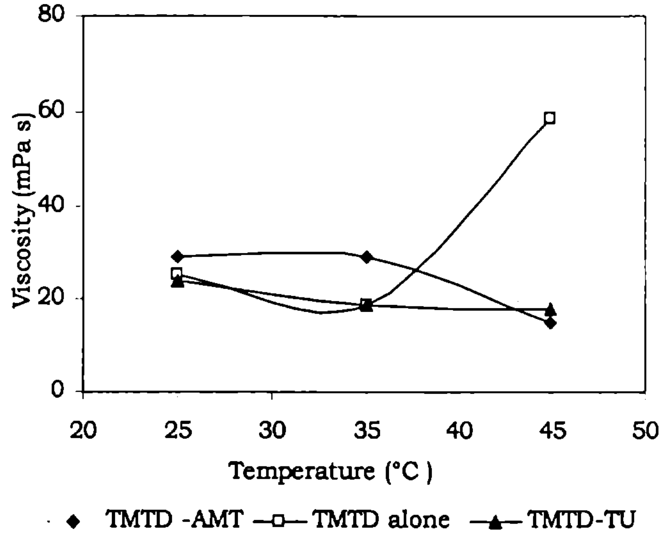

Fig 4.10 Variation of viscosity with temperature at shear rate 61.7 /s

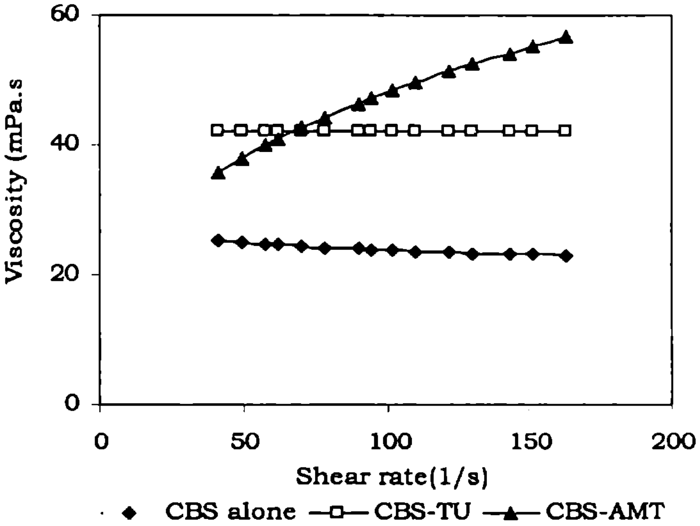

Fig.4.11 Variation of viscosity with shear rate for CBS mixes at 25°C

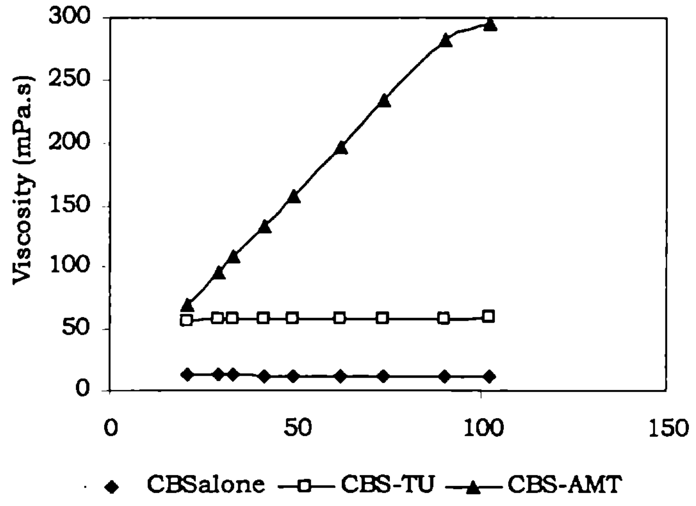

Fig.4.12 Variation of viscosity with shear rate for CBS mixes at 35°C

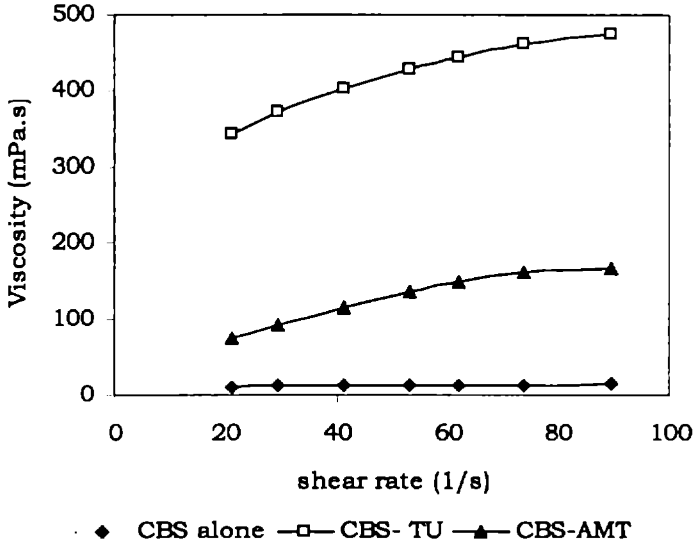

Fig. 4.13 Variation of viscosity with shear rate for CBS mixes at 45°C

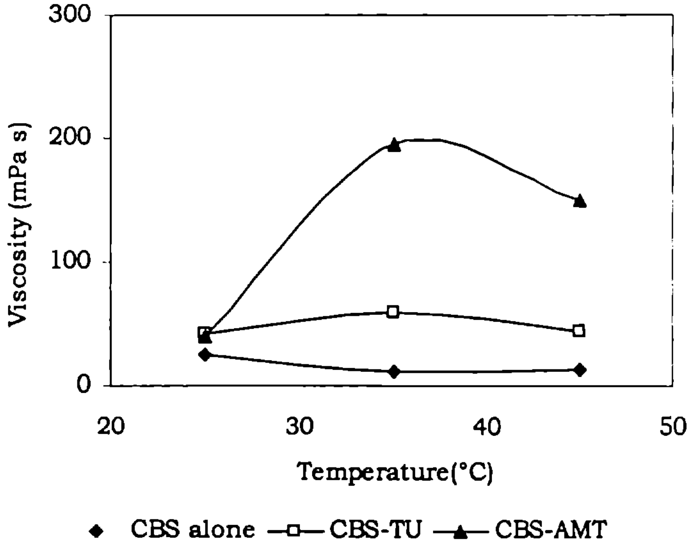

Fig.4.14 Variation of viscosity with temperature at shear rate 61.7 /s

Figures 4.15 to 4.17 give the effect of shear rate on the viscosity of the compounds containing ZDC as the primary accelerator. In these systems also viscosity increases with shear rate at the three different temperature

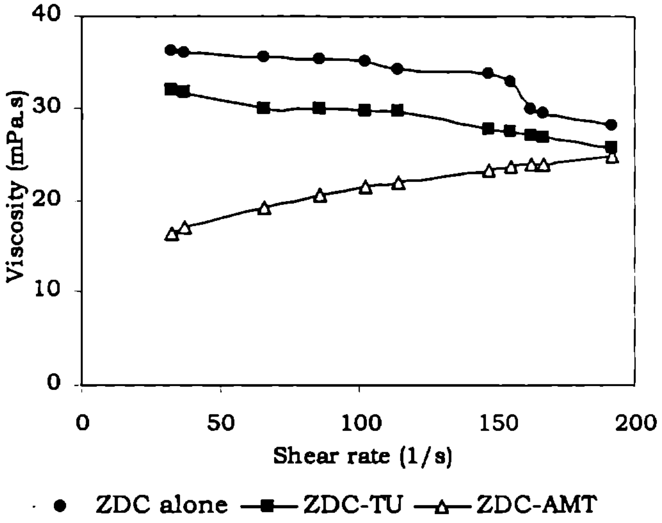

Fig. 4.15 Variation of viscosity with shear rate for ZDC mixes at 25°C

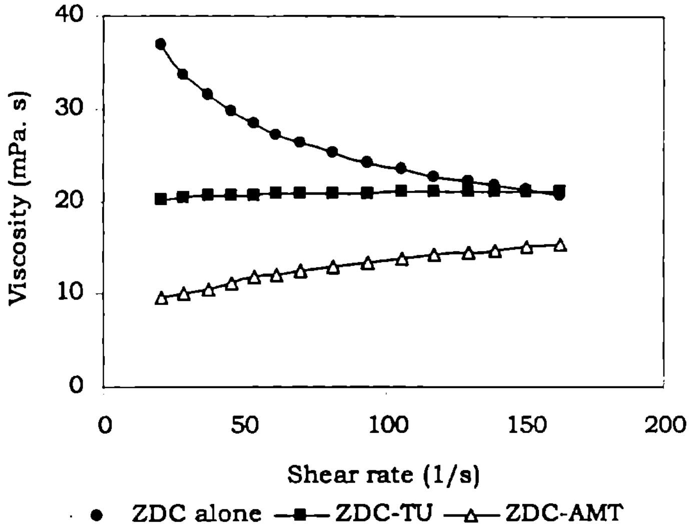

Fig. 4.16 Variation of viscosity with shear rate for ZDC mixes at 35°C

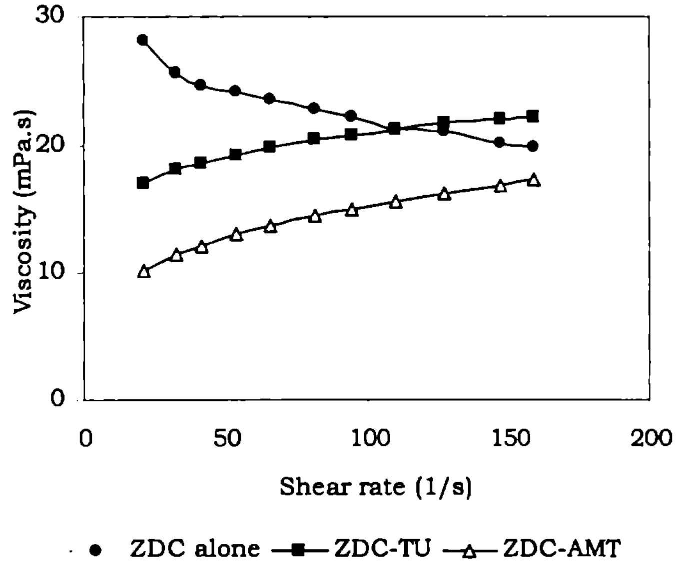

Fig. 4.16 Variation of viscosity with shear rate for ZDC mixes at 45°C

ranges studied. Fig. 4.18 shows the changes in viscosity with increase in temperature at constant shear rate for ZDC systems. From these studies it is clear that CBS-AMT and ZDC-AMT systems and the corresponding control formulations are comparatively unstable at higher shear rates and temperatures, while TMTD-AMT systems are reasonably stable.

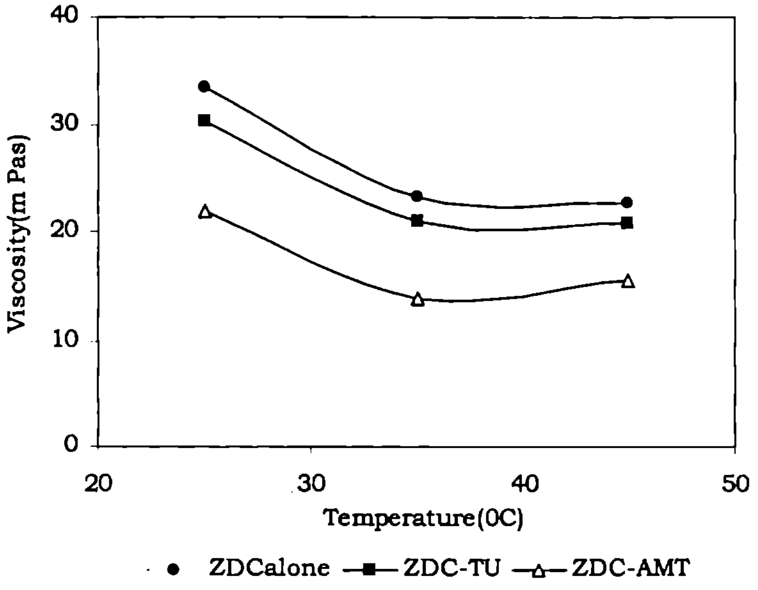

Fig. 4.18 Variation of viscosity with temperature at shear rate 61.7 /s

4.3 CONCLUSIONS

The results obtained in this study show that aminoiminomethyl thiourea can be used as an effective secondary accelerator in the sulphur vulcanization of NR latex with TMTD as primary accelerator. Based on the cure time values obtained, it can be inferred that AMT being more nucleophilic than TU, the results support a nucleophilic reaction mechanism in these binary systems of latex also. The systems containing optimum dosages of AMT give satisfactory values for mechanical properties like tensile strength and tear strength. It may be noted that at 100°C also these systems cure during a reasonable time period. The rheological studies of these mixes show that the addition of AMT does not adversely affect the processing characteristics especially when TMTD is used as the primary accelerator. At higher temperatures AMT is found to stabilize the TMTD mixes. However in ZDC and CBS mixes both AMT and TU are seen to destabilize the latex compounds. The advantageous point here is that AMT is a non-toxic chemical and is used in the pharmaceutical industry.

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Chapter 5

EFFECT OF AMINOIMINOMETHYL THIOUREA IN THE SULPHUR VULCANIZATION OF STYRENE-BUTADIENE RUBBER.

In view of the fact that we got encouraging results on the use of aminoiminomethyl thiourea (AMT) as secondary accelerator along with TMTD/MBTS/CBS in the sulphur vulcanization of NR, we thought it worthwhile trying this thiourea derivative in the vulcanization studies of a synthetic rubber also. It is to be noted that a lot of differences are encountered in the compounding and vulcanization of NR vis-a-vis synthetic rubbers. For example, compared with NR, 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 moulding. This provides savings in both energy consumption and time and hence on costs. It is also to be noted that mill mixing of some synthetic rubbers is more difficult compared to NR. Natural rubber is crystalline with a T_m in the range 50 to 60°C, while synthetic rubbers are more or less amorphous. Although crystallinity in NR is reduced by the presence of crosslinks and of fillers, it still crystallizes on extension giving a rubber of good tensile strength even with gum stocks. On the other hand, gum vulcanizates of synthetic rubbers are generally weak and it is essential to use reinforcing fillers such as fine carbon black to obtain products of high strength. The vulcanization characteristics and vulcanizate properties of NR differ from synthetic rubbers in many respects including variation of recipe for compounding. Compared to NR, synthetic rubbers require higher proportion of accelerator with a corresponding reduction in the amount of sulphur.

We used styrene-butadiene rubber (SBR 1502) for this investigation. It is a non-staining, non-discolouring cold rubber. Styrene-butadiene rubbers are the most commonly used general purpose synthetic rubbers. They are produced by the co-polymerization of butadiene and styrene under controlled conditions of reaction using different techniques of polymerization. Depending on the method of manufacture SBR is divided into emulsion or solution SBR, cold or hot SBR, etc. Cold SBR gives better abrasion resistance and dynamic properties. Not only does styrene butadiene rubbers have extrusion properties superior to those of NR, but also its stocks have less tendency to scorch in processing. Although cold SBR is often preferable to hot for optimum physical properties, hot SBR can be better for some processing and product properties. Both cold and hot polymerized SBR are marketed in numerous varieties under various trade names[1]. These brands differ from one another in the relative proportions of butadiene and styrene content, different initiating agents, emulsifiers, oils, fillers and temperature of polymerization.

Without reinforcing fillers such as carbon black or silica, the physical properties of SBR are much inferior to those of NR. Similarly its green strength is also inferior. The unsaturation in SBR is less than that in NR and the double bonds are less active chemically than the double bonds of the isoprenoid unit in NR. Hence SBR rubbers are slower curing than NR and either more accelerators or a more active accelerator system is required[2]. The compounding of SBR is done in a way more or less similar to that of NR and other unsaturated hydrocarbon rubbers. In SBR plasticization before mixing with other ingredients is not necessary. Zinc stearate or zinc oxide and stearic acid is the most common activator for SBR. The amount of activator used for SBR is same as that for NR whereas the concentration of accelerator and sulphur are varied for both rubbers. All types of SBR require less sulphur than NR does for curing. The usual range in NR is about 1.5 to 2 parts per hundred rubber. On the other hand, SBR requires more accelerator because of the lower unsaturation to achieve the same rate of cure. TMTD can be used as a primary accelerator in the sulphur vulcanization of SBR. It imparts the vulcanizates relatively high modulus and good mechanical and aging properties. The onset of vulcanization of compounds containing TMTD can be increased by adding small amounts of accelerators like DPG, dithiocarbamate, thiourea, etc. For soft vulcanizates thiazole and sulphenamides are used as primary accelerators while guanidines, thiurams and dithiocarbamates are used as secondary accelerators. Only guanidines have synergistic effect on thiazole and sulphenamides while other secondary accelerators have only additive effect[3]. For SBR mixes sulphenamides are the best for balanced rate of cure, safety and physical properties. Thiurams along with normal amount of sulphur are too scorchy. TMTD based SBR vulcanizates have a tendency to bloom and also impart odour.

In the present study we tried AMT as secondary accelerator in the sulphur vulcanization of SBR along with MBTS/TMTD/CBS as primary accelerators. Mixes containing TU and some other conventional binary systems were taken as reference formulations and the results obtained with AMT were compared with these control mixes. In order to see whether these vulcanization reactions follow a nucleophilic pattern, we prepared and studied the gum formulations first. To investigate the effect of AMT on filled systems, vulcanizates were also prepared with carbon black and precipitated silica. These mixes were studied at two different temperatures, viz. 120 and 150°C. The details of these studies are given under part I and II.

PART I

5.1 SBR GUM FORMULATIONS

5.1.1 Experimental

The formulations of SBR gum mixes prepared are given in Table 5.1. In these mixes all the accelerators are taken in molar concentrations and other compounding ingredients are taken in parts per hundred rubber (phr). Mixes A_2 to A_5 contain AMT ranging from 0.25 to 1.5 molar equivalents with one molar equivalent of MBTS. Mix A_0 contains two molar equivalents of MBTS and A_1 contains one molar equivalent of TU with one molar equivalent MBTS. Mixes B_2 to B_5 contain different concentrations of AMT ranging from 0.25 to 1.5 molar equivalents with one molar equivalent TMTD. Mix B_0 contains two molar equivalents of TMTD and B_1 contains one molar equivalent each of TU and TMTD. Similarly mixes C_2 to C_5 contain different concentrations of AMT with one molar equivalent of CBS. Mix C_0 contains two molar equivalents CBS and mix C_1 contains CBS and TU in the molar ratio 1:1. Mixes D_1 (TMTD-CBS) and D_2 (TMTD-MBTS) are the other two conventional binary systems tried for comparison of properties.

All the mixes were prepared on a laboratory size two-roll mill. Goettfert elastograph, model 67.85 was used to determine the cure characteristics (at 120 and 150°C) of the various mixes. The different cure characteristics studied are optimum cure time (t_{90}), scorch time (t_{10}), induction time (t_5), minimum torque, maximum torque and cure rate index. The rubber compounds were moulded in an electrically heated hydraulic press at a pressure of 12 MPa. Tensile properties of the vulcanizates were determined according to ASTM D412 using dumb-bell specimens using a Zwick universal testing machine at a crosshead speed of 500 mm/min. Aging was carried out at 100°C for 48 hours in a laboratory air oven (ASTM D 865-88). Tear resistance was determined as per ASTM D624-86. Test samples of 1.25 cm thickness and 2.8 cm diameter were used to determine the compression set (ASTM D395-89, method B). Shore A durometer was used to determine the hardness of vulcanizates (ASTM D2240-86). Abrasion resistance was measured using a DIN abrader (DIN 53516). The total crosslink density was calculated using equilibrium swelling data in toluene. (Details of the above experiments are described in chapter II)

Table 5.1 Formulation of SBR gum mixes

Ingredients	A_0	A_1	A_2	A_3	A_4	A_5	B_0	B_1	B_2	B_3	B_4	B_5	C_0	C_1	C_2	C_3	C_4	C_5	D_1	D_2
SBR	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
Stearic acid	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
TMTD							2.4	1.2	1.2	1.2	1.2	1.2							1.2	1.2
MBTS	3.32	1.66	1.66	1.66	1.66	1.66														1.66
CBS													2.64	1.32	1.32	1.32	1.32	1.32	1.32	
Thiourea		0.38						0.38						0.38						
AMT			0.147	0.295	0.59	0.885			0.147	0.295	0.59	0.885			0.147	0.295	0.59	0.885		
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

5.1.2 RESULTS AND DISCUSSION

Cure characteristics

Cure characteristics of the various mixes are given in Table 5.2 and corresponding cure curves are given in Figs. 5.1 - 5.5. The results obtained in this investigation clearly indicate the acceleration effect of AMT in the vulcanization of SBR. Considering the mixes cured at 150°C, cure time obtained for mix B_0 containing two molar equivalents of TMTD alone is 7.5 min. and the corresponding cure rate index is 17.8. The optimum cure time of the mix B_1 containing one mole equivalent of TU and TMTD each is 4.6 min. But mix B_4 containing one mole equivalent of AMT with one mole equivalent of TMTD shows a cure time of 4 min. and cure rate index is increased from 31.7 to 44.4. The mix B_4 showed lower cure time compared to B_0 and B_1 but have higher scorch safety. Hence considering the cure characteristics, mix B_4 containing one molar equivalent of AMT can be taken to be the optimum dosage. It is also observed that the maximum torque value decreases as the concentration of AMT increases.

The cure characteristics of the MBTS mixes also show the accelerating effect of AMT. The cure time obtained when two molar equivalents of MBTS alone is used as the accelerator (mix A_0) is 24.6 min. When one mole equivalent of TU is added with one mole equivalent of MBTS, the cure time obtained is 21.3 min. But when TU is replaced by one mole equivalent of AMT the cure time is reduced to 20.7 min. As the concentration of AMT is increased from 0.25 to1.5 molar equivalents an appreciable reduction in cure time is observed. MBTS mixes show comparatively higher cure times and cure rates are also low. This may be due to the fact that thiazole derivatives are slow curing with SBR as reported earlier[3].

There is considerable reduction in cure time in the case of CBS-AMT systems also as the amount of AMT is increased from 0.25 to 1.5 molar equivalents. Here also the optimum dosage of AMT required is found to be

Table 5.2. Cure characteristics of gum formulations

Mixes	Mixes cured at 150°C					
	Optimum cure time (min)t_{90}	Scorch time (min) t_{10}	Induction time (min) t_5	Cure rate index	Mini. Torque (Nm)	Maxi. Torque (Nm)
A_0	24.6	11.2	9.4	7.4	0.028	0.17
A_1	21.3	6.0	4.8	6.5	0.042	0.20
A_2	24.3	9.9	8.5	7.4	0.021	0.14
A_3	21.0	7.6	6.9	7.4	0.028	0.13
A_4	20.7	5.2	4.5	6.4	0.028	0.14
A_5	19.8	4.5	3.6	6.5	0.028	0.15
B_0	7.5	1.9	1.6	17.8	0.021	0.33
B_1	4.6	1.5	1.2	31.7	0.042	0.35
B_2	6.9	2.6	1.2	18.8	0.035	0.40
B_3	5.8	2.1	1.6	26.6	0.035	0.32
B_4	4.0	1.8	1.5	44.4	0.035	0.22
B_5	3.7	1.5	1.3	44.4	0.028	0.19
C_0	16.5	9.2	8.5	13.7	0.028	0.22
C_1	11.2	4.5	4.0	14.8	0.028	0.19
C_2	15.3	7.3	6.4	12.5	0.028	0.21
C_3	13.3	5.7	4.9	13.0	0.028	0.21
C_4	12.7	3.4	3.1	10.7	0.028	0.18
C_5	9.6	3.1	2.7	15.3	0.028	0.17
D_1	7.2	3.0	2.7	23.8	0.028	0.39
D_2	13.3	3.3	3.0	9.9	0.028	0.37
	Mixes cured at 120°C					
A_4	27.6	8.4	6.9	5.2	0.036	0.157
A_1	28.8	7.2	6.1	4.6	0.043	0.286
B_4	77.1	24.0	17.0	1.9	0.043	0.178
B_1	79.0	24.8	18.1	1.8	0.036	0.071
C_4	33.0	15.9	14.4	5.8	0.057	0.150
C_1	49.0	17.6	14.6	3.2	0.039	0.270

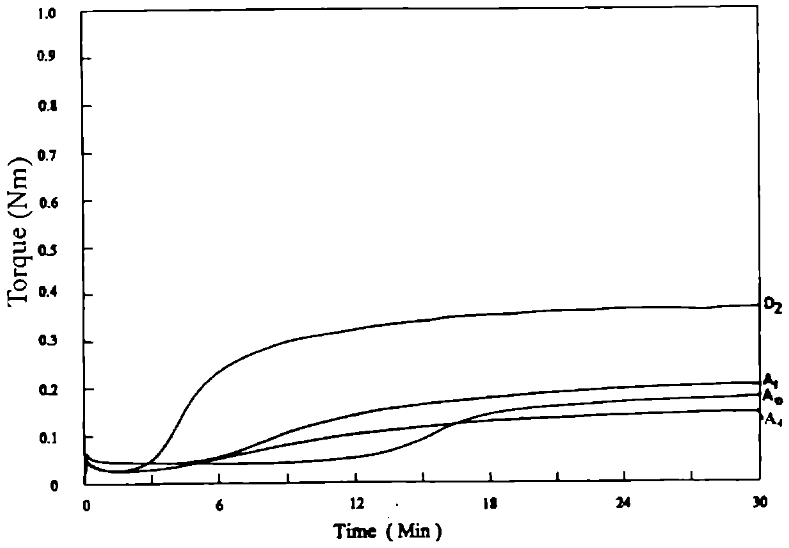

Fig. 5.1 Cure curves of SBR gum mixes with MBTS (cured at 150°C)

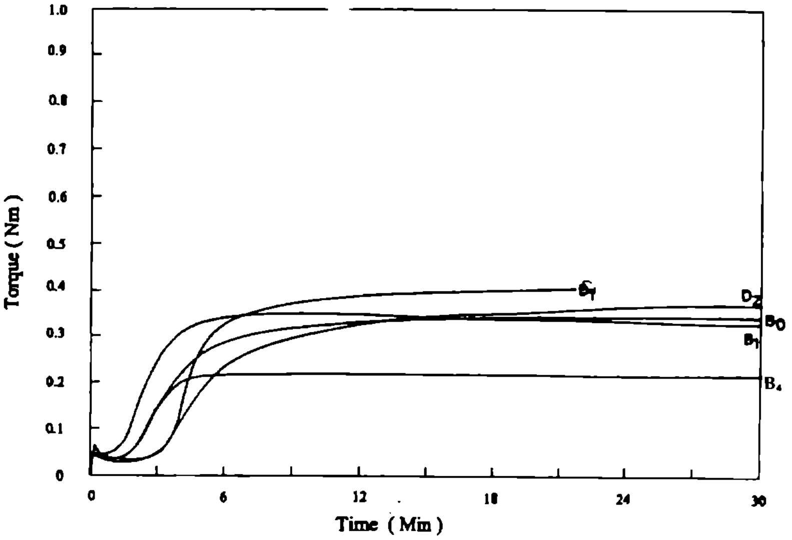

Fig. 5.2 Cure curves of SBR gum mixes with TMTD (cured at 150°C)

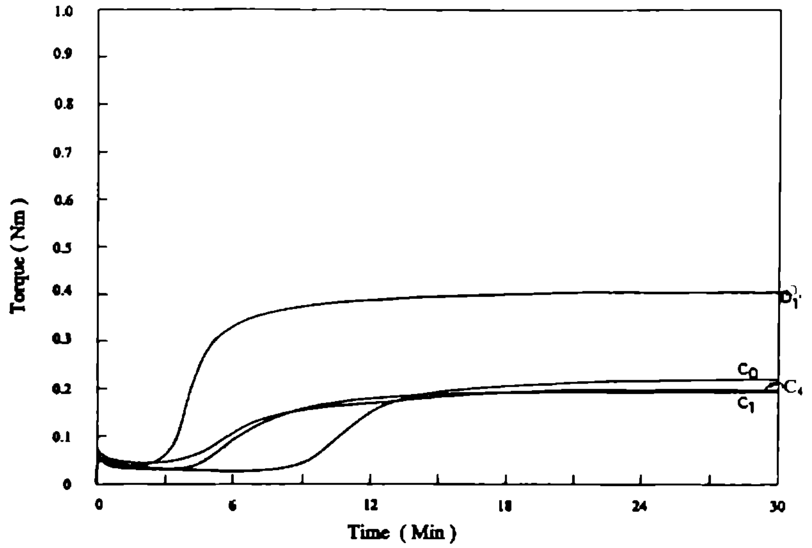

Fig. 5.3 Cure curves of SBR gum mixes with CBS (cured at 150°C)

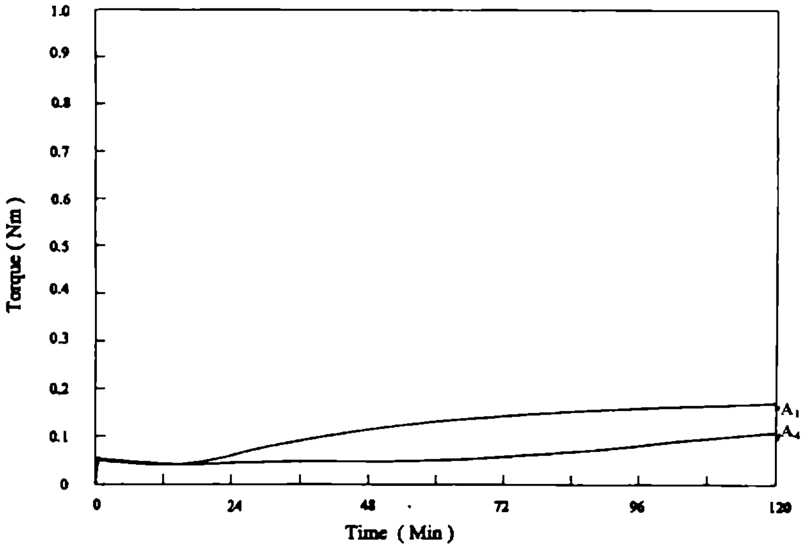

Fig. 5.4 Cure curves of SBR gum mixes with MBTS (at 120°C)

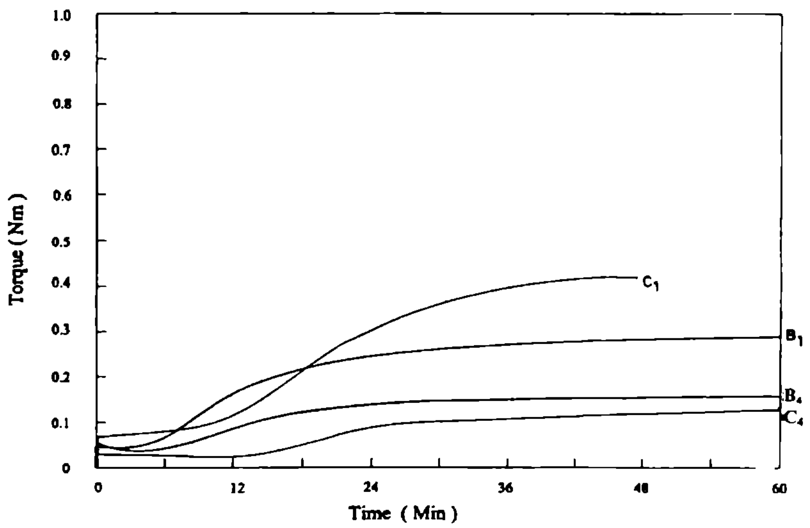

Fig. 5.5 Cure curves of SBR gum mixes with TMTD and CBS (at 120°C)

one molar equivalent with one molar equivalent of CBS. At this level the optimum cure time is brought down to 11 min. from 16.2 min when AMT is added. At 120°C also cure time values of AMT mixes are lower than that of TU mixes. There is a corresponding increase in the cure rate also. The above results indicate that AMT is more effective than TU as a secondary accelerator. Considering the cure characteristics of the above mixes and noting the fact that AMT is more nucleophilic than TU, these results point to a nucleophilic reaction mechanism in these binary systems under review.

Tensile and other Physical Properties

The tensile properties of the vulcanizates obtained from the various mixes are given in Table 5.3. SBR being a non-strain crystallizing rubber has poor gum strength. However we have determined the tensile properties of the gum formulations also for a comparative evaluation. Here the tensile strength of vulcanizates containing AMT is found to be comparable to that of control mixes. In the case of the mixes cured at 150°C, there is appreciable increase in the properties like tensile strength and modulus for the mix A_4 containing optimum dosage of AMT compared to vulcanizate containing TU (mix A_1).

Table 5.3. Tensile properties of SBR gum vulcanizates.

Mixes	Mixes cured at 150°C								
	Tensile strength (MPa)			100% Modulus (MPa)			Elongation at break (%)		
	Before aging	After aging	Retention (%)	Before aging	After aging	Retention (%)	Before aging	After aging	Retention (%)
A_0	1.57	1.37	87	1.20	0.54	45	284	174	61
A_1	1.60	1.40	90	0.53	0.73	135	338	277	82
A_2	1.71	1.57	92	1.02	0.78	76	262	194	74
A_3	1.97	1.69	86	0.98	0.80	81	267	247	92
A_4	1.81	1.79	99	1.06	1.43	135	235	244	104
A_5	1.53	2.29	149	0.82	1.10	134	274	243	88
B_0	2.20	1.95	89	1.30	1.40	107	171	182	106
B_1	2.60	2.06	79	1.10	1.30	118	297	170	57
B_2	2.40	2.40	100	0.55	1.60	290	577	167	29
B_3	2.40	3.40	141	0.89	1.20	135	215	173	80
B_4	2.30	1.90	84	0.62	1.20	192	392	198	50
B5	2.40	1.80	77	0.56	0.90	161	254	194	76
C_0	2.09	1.48	71	1.40	0.70	50	312	201	64
C_1	1.31	1.55	118	0.40	0.70	175	265	183	69
C_2	1.88	1.68	89	0.60	0.80	133	387	190	49
C_3	1.67	1.84	110	0.90	1.10	122	337	247	73
C_4	1.74	1.97	113	0.80	1.10	122	342	261	76
C_5	1.91	2.98	196	0.50	0.90	198	332	253	76
D_1	1.70	1.90	116	0.88	1.20	136	138	149	108
D_2	2.30	1.40	61	1.00	0.48	48	246	164	66
	Mixes cured at 120°C								
B_4	1.76	1.45	82	1.03	1.00	97	300	234	78
B_1	2.07	1.98	95	1.38	0.59	43	262	230	87
C_1	2.74	2.36	86	0.74	0.94	127	350	302	86
C_4	2.53	1.99	78	1.01	0.80	79	337	300	89

Table 5.4 Other physical properties of SBR gum vulcanizates.

Mixes	Mixes cured at 150°C				
	Hardness (Shore A)	Abrasion loss (cm^3/hr)	Compression set (%)	Tear strength (N/mm)	Total crosslink density X10^5 ($g.mol/cm^3$)
A_0	39.6	4.0	53.4	14.8	5.80
A_1	39.0	3.2	21.0	12.0	6.08
A_2	38.0	14.5	21.5	9.30	6.06
A_3	41.0	3.0	14.8	11.7	6.00
A_4	41.6	3.4	14.9	12.4	6.50
A_5	39.3	3.4	16.4	11.7	6.60
B_0	48.0	12.7	18.0	11.8	10.9
B_1	44.0	4.7	15.2	12.2	7.7
B_2	36.0	6.1	13.0	9.7	10.3
B_3	44.0	4.3	16.4	12.0	8.0
B_4	40.0	4.6	21.4	9.3	7.8
B_5	40.6	4.8	24.6	13.1	6.9
C_0	34.6	4.5	17.9	11.1	7.1
C_1	41.6	3.6	23.6	11.2	6.5
C_2	39.6	4.0	27.4	13.2	6.7
C_3	41.0	3.7	17.6	11.4	7.3
C_4	39.0	3.5	20.7	10.7	7.0
C_5	41.0	3.3	18.0	13.1	6.8
D_1	51.0	10.0	8.3	11.1	10.5
D_2	50.0	12.7	6.9	8.1	10.7
	Mixes cured at 120°C				
B_4	33.3	4.3	11.3	15.7	7.1
B_1	34.6	4.6	6.1	15.2	6.5
C_4	37.0	3.3	25.7	18.4	6.1
C_1	36.3	3.6	13.0	14.8	5.9

Also the aging behaviour of mix containing AMT is found to be satisfactory. The tensile strength of the vulcanizates containing TMTD–AMT are found to be higher than that of the other two systems, viz. MBTS-AMT and CBS-AMT. These properties are comparable to that of other control mixes. In the case of CBS-AMT binary systems the tensile strength values are higher compared to that of CBS-TU. In the AMT systems the percentage retention of tensile properties like tensile strength and modulus after heat aging is also found to be higher. The variations in the tensile properties are more or less in accordance with the crosslink density values estimated. For physical properties of vulcanizates cured at 120°C only those containing optimum dosages of the secondary accelerator were selected. The variations in these properties follow a more or less similar pattern for the vulcanizates cured at this temperature also.

Other physical properties studied are hardness, compression set, abrasion loss and tear strength. These values obtained are reported in Table 5.4. For MBTS-AMT systems hardness is found to increase with increase in the concentration of AMT up to a maximum and then decreases. At the optimum dosage of AMT the hardness is slightly higher than the corresponding control mixes. The abrasion resistance values are more or less comparable to the control mixes. Compression set values show a favourable decrease with increase in the concentration of AMT and these values are less than that of control mixes also. Total crosslink density values of experimental vulcanizates are in general higher than that of control mixes. For TMTD-AMT vulcanizates hardness values are less than that of control mixes. Abrasion loss values are also less (higher abrasion resistance) than that of control mixes. Compression set for AMT systems are however found to be higher. In CBS-AMT systems also more or less similar trend is observed. When cured at 120°C a similar behaviour is observed and these properties show improvement over those cured at 150°C. Compared to the TU mixes AMT mixes show lower abrasion loss and higher tear strength values.

PART II

5.2 FILLED FORMULATIONS OF SBR

Polymers filled with reinforcing fillers are important for most of the polymer industries because of economic reasons and property requirements. Gum vulcanizates of SBR exhibits low physical properties and the tensile strength of gum vulcanizates of SBR is much lower than that of NR. This is obviously due to the inability of SBR to crystallize on stretching[4]. 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. It is not uncommon for particulate fillers such as carbon black to increase the strength of vulcanized rubbers more than ten fold. Thus it is hardly surprising that relatively few applications of elastomers utilize the polymer in the unfilled state. Fillers are commonly employed to reduce the cost and improve the mechanical properties and to reduce the tackiness of highly plasticized compounds. Reinforcing fillers are necessary to achieve optimum properties with SBR and its blends.

The fundamental aspects of polymer-filler interaction have been studied in detail in a number of polymers[5]. Carbon blacks are the most affective reinforcing fillers used in rubber industry. The best reinforcing fillers are those having the smallest particle size. It is known that the reinforcing filler improves the failure properties, especially for rubbers which are non-crystallizing at room temperature. This is done at the cost of flex crack resistance, heat build up and set properties. Dinsmore[6] reported that the ratio of tensile strength of black filled to that of gum vulcanizate is 10 to 5 for SBR. SBR has some optimum filler loadings at which polymer-filler attachment may develop a balanced system with an optimum range of all technical properties. Porter[7]as well as Bhowmick and De[8] have discussed the role of reinforcing black in the sulphuration process in vulcanization. Non-black fillers like precipitated silicas are used in SBR to improve processing and to reinforce the polymer in the production of both white and coloured compounds[9]. Due to the highly absorptive nature of precipitated silica, more accelerators or a combination of accelerators, which is more active, is necessary.

Table 5.5 Formulation of SBR mixes containing carbon black

Ingredients	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8
SBR	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
Stearic acid	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
TMTD					1.2	1.2	1.2	1.2						2.4			1.2		1.2	1.2
MBTS	1.66	1.66	1.66	1.66									3.32			1.66				1.66
CBS									1.32	1.32	1.32	1.32			2.64			1.32	1.32	
Thiourea																0.38	0.38	0.38		
AMT	0.147	0.295	0.59	0.885	0.147	0.295	0.59	0.885	0.147	0.295	0.59	0.885								
Carbon black	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50
Aromatic oil	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
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

Table 5.6 Formulation of SBR mixes containing silica

Ingredients	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_9	S_{10}	S_{11}	S_{12}	P_1	P_2	P_3	P_4	P_5	P_6	P_7	P_8
SBR	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
Stearic acid	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
TMTD					1.2	1.2	1.2	1.2						2.4			1.2		1.2	1.2
MBTS	1.66	1.66	1.66	1.66									3.32			1.66				1.66
CBS									1.32	1.32	1.32	1.32			2.64			1.32	1.32	
Thiourea																0.38	0.38	0.38		
AMT	0.147	0.295	0.59	0.885	0.147	0.295	0.59	0.885	0.147	0.295	0.59	0.885								
silica	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50
Naphthenic oil	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
DEG	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
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

In the present study HAF black (N 330) and precipitated silica are used as fillers. We have investigated the filled mixes of SBR containing AMT as secondary accelerator along with MBTS/TMTD/CBS. The study covers different aspects like mixing, curing, evaluation of various physical properties of the vulcanizates and chemical characterization. Control mixes were also prepared and the properties of the experimental mixes were compared with those of the references.

5.2.1 EXPERIMENTAL

In this study both carbon black and precipitated silica are used at 50 phr level. Table 5.5 shows the formulation of different mixes with carbon black. Mixes C_1 to C_4 contain different concentrations of AMT ranging from 0.25 to 1.5 molar equivalents with one molar equivalent of MBTS. Mixes C_5 to C_8 contain different concentrations of AMT with one molar equivalent of TMTD and mixes C_9 to C_{12} contain different concentrations of AMT with one molar equivalent of CBS. Mixes R_1 to R_8 are other reference formulations. Table 5.6 gives the composition of mixes containing silica. Mixes S_1 to S_4 contain different concentrations of AMT with one molar equivalent of MBTS. Mixes S_5 to S_8 contain different concentrations of AMT with TMTD and mixes S_9 to S_{12} contain AMT with CBS. Mixes P_1 to P_8 are other reference mixes prepared. Two phr diethylene glycol (DEG) is used as an activator for formulations containing silica. Cure characteristics of the mixes and physical properties of the vulcanizates are evaluated as per relevant standards detailed in chapter II.

5.2.2 RESULTS AND DISCUSSION

Cure characteristics

The cure characteristics of carbon black filled systems are given in Table 5.7 and the corresponding cure curves are given in Figures 5.6 to 5.9.Carbon black has a favourable effect on the vulcanization reaction of SBR. In the case of MBTS systems, mix C_3 containing optimum dosage of AMT has lower cure time compared to other control mixes of equivalent concentrations and it is also found that there is definite decrease in cure time with increase in the concentration of AMT.

Table 5.7. Cure characteristics of mixes containing carbon black

Mixes	Mixes cured at 150°C					
	Optimum cure time (min)t_{90}	Scorch time (min)t_{10}	Induction time (min) t_5	Cure rate index	Mini. Torque (Nm)	Maxi. Torque (Nm)
C_1	14.8	2.90	2.50	8.4	0.070	0.48
C_2	12.9	2.70	2.10	9.8	0.070	0.50
C_3	11.5	2.20	1.50	10.8	0.070	0.54
C_4	9.0	2.40	1.60	15.0	0.070	0.45
C_5	2.8	1.30	1.05	66.0	0.078	0.43
C_6	2.6	1.30	0.90	77.0	0.080	0.42
C_7	2.4	1.20	0.90	83.0	0.078	0.41
C_8	1.6	0.90	0.75	133.0	0.078	0.37
C_9	7.8	2.70	2.40	19.0	0.071	0.50
C_{10}	6.7	2.70	2.40	24.0	0.085	0.43
C_{11}	6.1	2.10	1.80	24.0	0.085	0.43
C_{12}	5.8	1.90	1.60	26.0	0.078	0.37
R_1	12.4	3.00	2.50	10.0	0.085	0.59
R_2	2.9	1.50	1.05	71.0	0.078	0.61
R_3	7.9	3.30	3.00	21.0	0.078	0.57
R_4	13.5	2.20	1.50	8.0	0.090	0.56
R_5	2.4	1.00	0.75	74.0	0.078	0.48
R_6	6.3	1.80	1.50	22.0	0.071	0.47
R_7	3.3	1.90	1.60	74.0	0.078	0.50
R_8	6.6	2.10	1.60	22.0	0.085	0.72
	Mixes cured at 120°C					
C_1	53.4	18.00	15.50	2.80	0.099	0.320
C_2	51.6	14.40	11.10	2.70	0.100	0.336
C_3	51.0	14.40	12.60	2.70	0.107	0.393
C_4	49.8	14.70	9.90	2.80	0.100	0.371
C_5	18.5	7.35	5.80	8.90	0.100	0.471
C_6	14.7	4.35	1.05	9.60	0.093	0.343
C_7	12.7	4.05	2.20	11.50	0.093	0.300
C_8	10.4	4.05	3.00	15.70	0.100	0.328
C_9	44.0	18.30	16.20	3.90	0.100	0.428
C_{10}	35.4	16.50	13.50	5.30	0.100	0.350
C_{11}	32.1	10.80	6.60	4.70	0.093	0.314
C_{12}	30.6	11.10	9.00	5.10	0.100	0.285
R_4	51.8	7.20	5.00	2.20	0.096	0.384
R_5	17.0	4.50	3.30	8.00	0.100	0.542
R_6	33.0	10.50	8.40	4.40	0.100	0.443

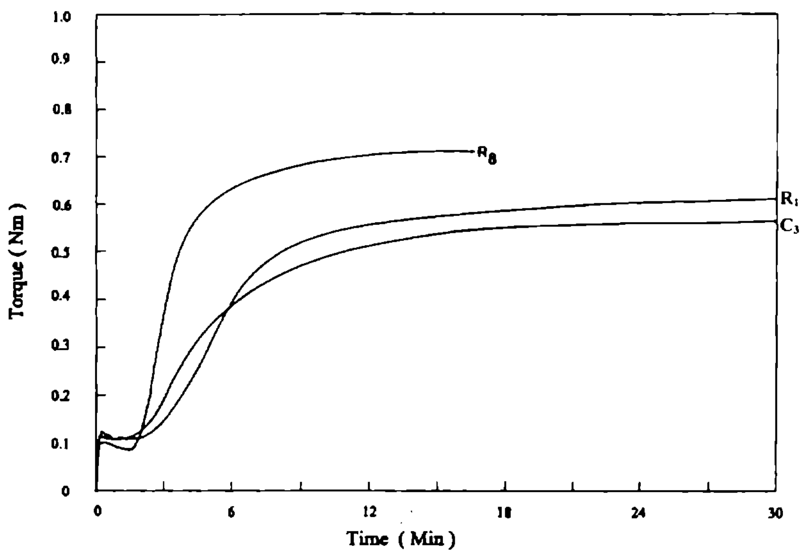

Fig. 5.6 Cure curves of carbon black filled mixes with MBTS (at 150°C)

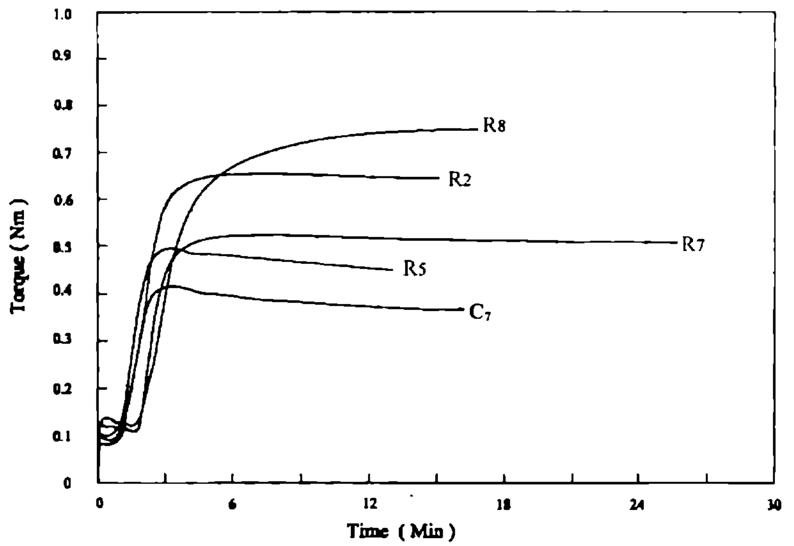

Fig. 5.7 Cure curves of carbon black filled mixes with TMTD (at 150°C)

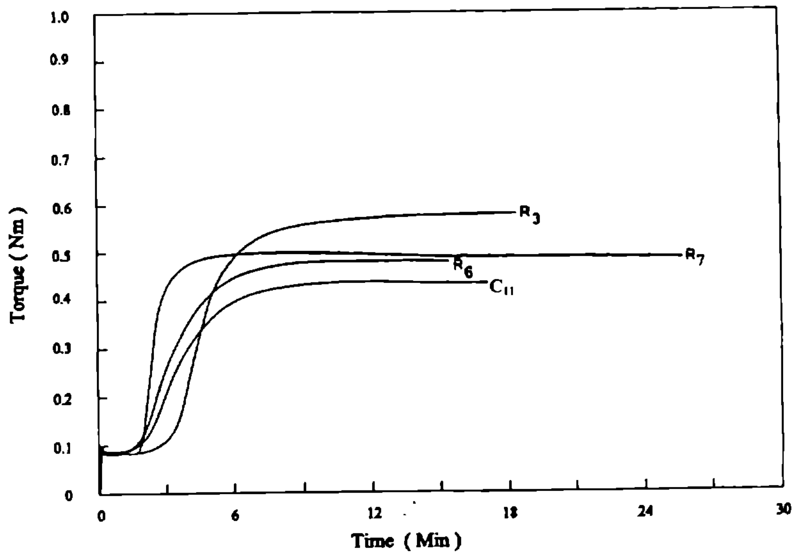

Fig. 5.8 Cure curves of carbon black filled mixes with CBS (at 150°C)

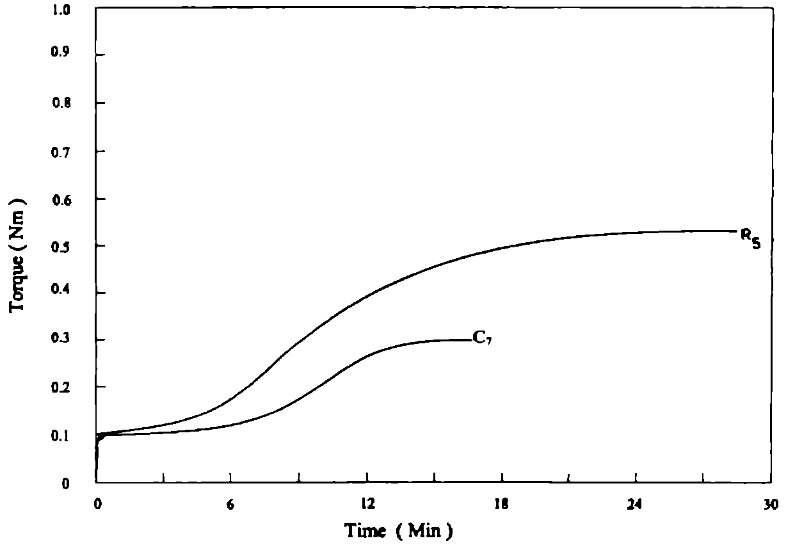

Fig. 5.9 Cure curves of carbon black filled mixes with TMTD (at 120°C)

The cure rate index values are higher for MBTS-AMT mixes, but torque value is found to decrease with the addition of AMT. In TMTD-AMT mixes also cure time decreases with the increase in the amount of the secondary accelerator and there is corresponding increase in the cure rate. Induction time and scorch time are also found to decrease with incorporation of AMT. In CBS systems also more or less similar trend is observed when AMT is added. Mix C_{11} containing one mole equivalent of AMT showed a cure time of 6.1 min. while mix R_6 (CBS-TU) shows a cure time of 6.3 min. Addition of 1.5 molar equivalents of AMT reduces the cure time to almost half and the cure rate is also increased considerably. In TMTD mixes a tendency for reversion was also observed. Considering the optimum cure time, scorch time, etc., the optimum dosage of the secondary accelerator (AMT) required can be taken to be one molar equivalent with one molar equivalent of the primary accelerator. At this level there is appreciable reduction in cure time, but scorch time and maximum torque are more or less satisfactory. When cured at 120°C also these three binary systems with AMT are found to be more effective than thiourea. MBTS systems exhibit longer cure time and the cure rates are also low. This is found to be in accordance with the behaviour of MBTS systems reported in literature[3]. The above results indicate the acceleration effect of AMT in the vulcanization systems of SBR under review. AMT being more nucleophilic than thiourea these results are also indicative of a nucleophilic reaction mechanism in these systems and this provides a supporting evidence for the postulate proposed by Philpott[10].

The cure curves of the silica filled mixes are given in Figs 5.10 to 5.13 and the corresponding cure characteristics are given in Table 5.8. In MBTS systems the system containing AMT has a cure time of 16.3 min. while corresponding mix containing TU has a cure time of 10.6 min. In the TMTD and CBS systems also a similar behaviour as with MBTS is observed. In all these silica filled systems, mixes containing TU show lower cure time values compared to those containing AMT. These observations are somewhat different from what we noticed in gum and filled systems of NR and also in gum formulations of SBR. Here the possibility is that instead of a pure nucleophilic mechanism there may be a mixed polar-radical type mechanism involved in these silica filled binary systems as suggested by Shelton and Mc Donel[11]. In the case of mixes cured at 120°C also, those containing AMT showed a reduction in the cure time with increase in the amount of AMT but the cure time values are lower when compared to TU-containing mixes.

Table 5.8. Cure characteristics of mixes containing silica

Mixes	Mixes cured at 150°C					
	Optimum cure time (min)t_{90}	Scorch time (min)t_{10}	Induction time (min) t_5	Cure rate index	Mini. torque (Nm)	Maxi. torque (Nm)
S_1	19.5	7.1	6.0	8.0	0.08	0.38
S_2	17.9	6.4	5.6	8.7	0.08	0.33
S_3	16.3	4.6	3.9	8.5	0.07	0.35
S_4	15.7	2.8	2.4	7.7	0.07	0.41
S_5	6.5	1.7	1.7	20.8	0.08	0.45
S_6	6.4	1.6	1.5	20.8	0.07	0.49
S_7	6.0	1.7	1.6	23.2	0.06	0.39
S_8	5.9	1.6	1.5	23.2	0.08	0.44
S_9	16.6	6.1	5.5	9.5	0.07	0.32
S_{10}	12.9	4.2	3.8	11.4	0.07	0.55
S_{11}	12.1	3.2	2.8	11.2	0.07	0.53
S_{12}	9.9	1.7	1.4	12.2	0.07	0.54
P_1	26.4	12.6	10.8	7.2	0.07	0.34
P_2	4.7	1.5	1.4	31.2	0.06	0.62
P_3	14.3	7.3	6.7	14.2	0.03	0.35
P_4	10.6	2.2	1.7	11.9	0.10	0.57
P_5	2.9	0.9	0.8	50.0	0.06	0.44
P_6	8.7	3.1	2.7	17.8	0.06	0.49
P_7	4.0	2.1	1.9	52.6	0.05	0.58
P_8	5.2	2.4	2.1	35.7	0.06	0.67
	Mixes cured at 120°C					
S_1	59.0	36.4	28.4	4.4	0.13	0.43
S_2	58.6	35.6	29.8	4.3	0.15	0.43
S_3	54.5	25.2	20.4	3.4	0.11	0.27
S_4	51.2	3.0	1.4	2.1	0.04	0.17
S_5	43.2	11.0	7.5	3.1	0.11	0.52
S_6	42.6	11.0	7.5	3.1	0.11	0.45
S_7	42.2	9.0	7.0	3.0	0.12	0.44
S_8	39.8	10.8	8.2	3.4	0.10	0.43
S_9	55.8	35.4	32.8	4.9	0.09	0.42
S_{10}	54.6	25.2	22.6	3.4	0.08	0.36
S_{11}	52.0	19.8	17.4	3.1	0.11	0.50
S_{12}	38.4	8.0	6.0	3.3	0.12	0.46
P_4	49.4	6.2	2.0	2.3	0.09	0.42
P_5	16.0	4.0	2.8	8.3	0.12	0.50
P_6	47.8	15.8	11.8	3.1	0.07	0.49

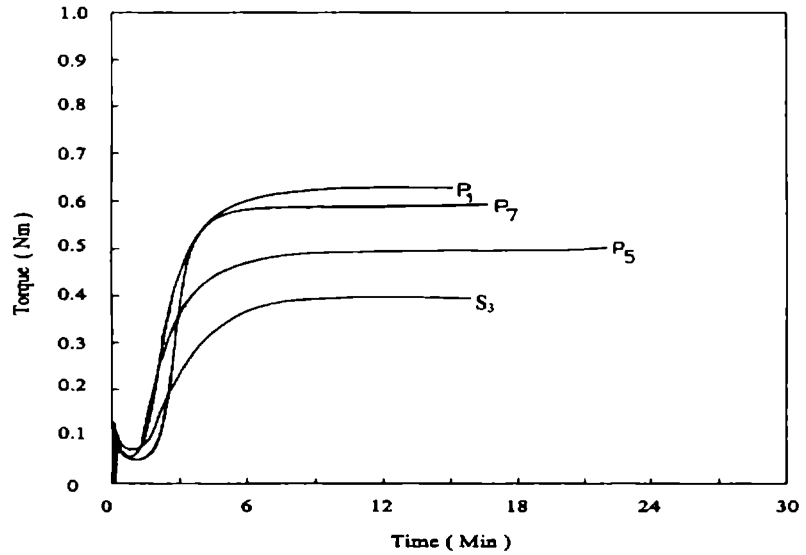

Fig. 5.10 Cure curves of silica filled mixes with MBTS (at 150°C)

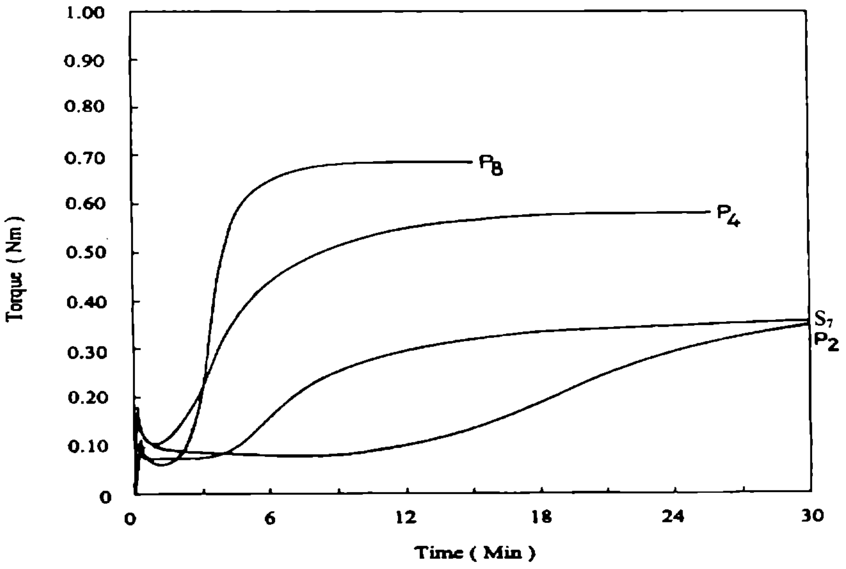

Fig. 5.11 Cure curves of silica filled mixes with TMTD (at 150°C)

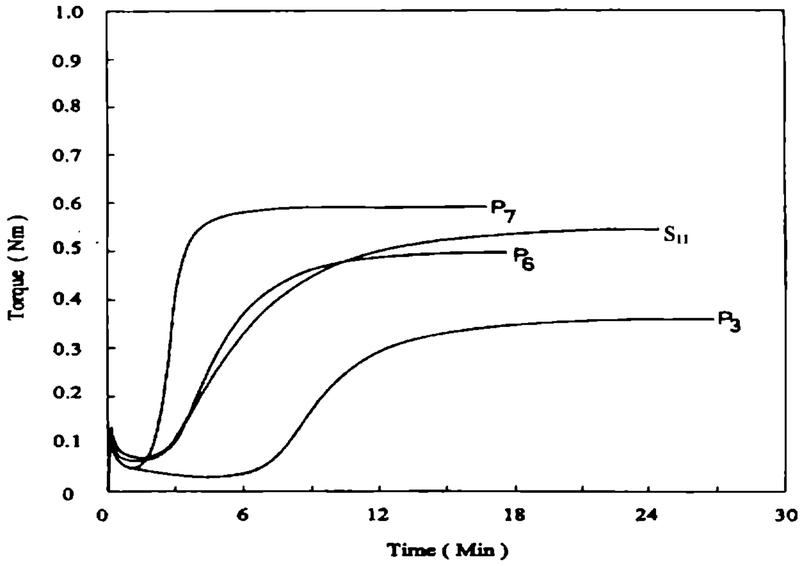

Fig. 5.12 Cure curves of silica filled mixes with CBS (at 150°C)

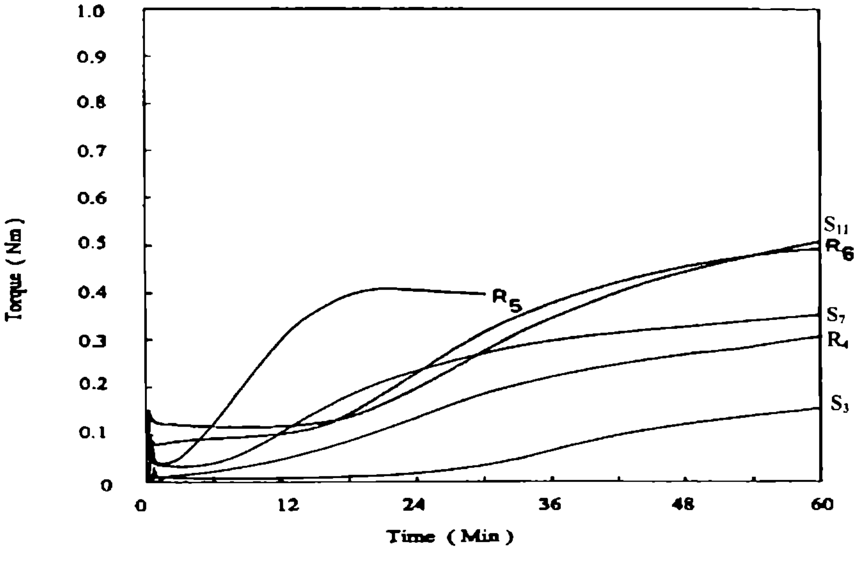

Fig. 5.13 Cure curves of silica filled mixes (at 120°C)

Tensile Properties

SBR is a non-strain crystallizing rubber and hence has poor gum strength. Carbon black and silica improve the tensile properties and resistance to failure of the SBR vulcanizates. The new secondary accelerator (AMT) we tried is found to improve many of the tensile properties of the vulcanizates in all these three binary systems. The values of the different tensile properties evaluated for the vulcanizates containing carbon black and silica are given in Tables 5.9 and 5.10 respectively. Considering the samples cured at 150°C, for TMTD-AMT systems the tensile strength values and the aging resistance are better/comparable to those of the control mixes in carbon black filled vulcanizates. In MBTS and CBS systems also, those containing AMT have higher tensile strength and modulus values. The percentage retention of these properties after heat aging is also better in these systems compared to control mixes. Compared to MBTS and CBS, TMTD systems show lower tensile strength values. It is known that the maximum strength of the vulcanizates is attained by mobile polysulphidic linkages. But with thiuram accelerators the sulphur linkages are reported to be mainly mono and disulphidic[12] and hence lower tensile strength for TMTD systems. The aged samples with these three systems also show a similar trend. However the retention of tensile strength after heat aging is better compared to reference samples.

Even though good tensile strength and abrasion resistance can be achieved with precipitated silica they are still inferior to carbon black. Cured at 150°C, silica filled TMTD-AMT systems showed tensile strength and elongation at break values higher than those of reference mixes. In MBTS-AMT systems tensile strength and elongation at break values remain more or less same as that for control mixes. At 120°C the cure time values of MBTS systems are found to be very high and so the physical properties of these vulcanizates were not further investigated. For CBS-AMT systems also tensile strength and elongation at break values are found to increase with increase in the dosage of AMT. In all the three systems 100% modulus values are comparatively lower than those of control mixes.

Table 5.9. Tensile properties of vulcanizates containing carbon black

Mixes	Mixes cured at 150°C.								
	Tensile strength (MPa)			100% Modulus (MPa)			Elongation at break (%)		
	Before aging	After aging	Retention (%)	Before aging	After aging	Retention (%)	Before aging	After aging	Retention (%)
C_1	20.2	19.0	94	2.6	2.5	96	629	570	91
C_2	21.5	20.9	97	3.1	2.5	80	521	477	91
C_3	22.2	20.6	93	2.8	2.6	93	558	482	86
C_4	23.2	21.2	91	2.8	2.8	100	568	495	87
C_5	12.2	11.2	92	1.9	3.8	200	201	282	140
C_6	11.8	11.6	98	1.9	2.6	136	264	290	110
C_7	16.4	17.6	107	2.1	2.6	123	331	280	85
C_8	15.6	11.9	77	2.9	5.0	172	239	236	99
C_9	21.4	20.3	95	2.7	3.0	111	642	527	82
C_{10}	22.4	19.2	86	2.5	2.9	116	632	505	80
C_{11}	24.4	18.9	77	2.7	2.7	100	767	515	67
C_{12}	28.7	23.4	81	2.3	2.9	126	685	587	85
R_1	21.1	18.4	87	1.9	2.7	142	557	410	74
R_2	10.1	10.6	105	3.1	2.8	90	110	320	290
R_3	20.3	12.0	59	2.7	3.1	114	477	322	67
R_4	18.7	16.7	89	1.9	2.7	142	517	405	78
R_5	15.1	14.4	95	3.7	3.9	105	210	355	169
R_6	20.4	18.5	91	2.2	2.7	122	672	545	81
R_7	14.4	9.9	69	2.8	3.0	107	407	265	65
R_8	16.1	15.0	93	3.2	3.8	118	315	305	96
	Mixes cured at 120°C								
C_3	19.5	19.7	101	2.4	2.7	112	288	268	93
R_4	17.8	11.2	63	1.8	1.6	88	286	315	110
C_7	14.5	15.6	107	2.7	4.3	159	232	229	98
R_5	13.4	12.2	91	2.7	2.8	103	181	160	88
C_{11}	24.4	20.5	84	2.7	2.8	103	333	260	78
R_6	21.3	17.2	81	2.7	3.1	114	279	213	76

Table 5.10 Tensile properties of vulcanizates containing silica

Mixes	Mixes cured at 150°C								
	Tensile strength (MPa)			100% Modulus (MPa)			Elongation at break (%)		
	Before aging	After aging	Retention (%)	Before aging	After aging	Retention (%)	Before aging	After aging	Retention (%)
S_1	8.9	7.1	79	1.7	2.3	137	822	525	64
S_2	11.2	7.3	65	1.6	2.1	131	977	587	60
S_3	11.4	6.8	60	1.2	1.9	158	1047	582	56
S_4	13.0	7.2	55	1.8	2.5	136	1077	620	57
S_5	6.6	6.6	100	1.7	1.9	117	717	582	81
S_6	7.1	6.3	88	2.0	2.5	120	685	465	68
S_7	7.7	4.9	64	1.5	2.5	170	877	415	47
S_8	8.2	7.5	91	1.7	1.8	106	775	521	67
S_9	7.8	6.4	82	1.5	2.5	166	852	487	57
S_{10}	11.9	7.6	64	1.5	1.9	126	947	537	57
S_{11}	12.9	7.3	56	1.5	1.9	126	1007	490	49
S_{12}	13.8	9.2	66	1.1	2.7	246	1120	567	51
P_1	11.1	6.8	62	2.0	2.1	103	927	527	57
P_2	4.6	4.4	96	2.1	3.1	149	350	230	66
P_3	10.5	6.6	63	2.2	2.4	109	857	460	54
P_4	12.5	6.6	53	0.7	2.2	314	1022	570	56
P_5	7.5	5.9	78	0.6	2.1	320	790	482	61
P_6	9.8	5.1	52	0.8	1.9	231	885	307	35
P_7	5.5	3.9	6.2	1.4	2.3	164	615	275	45
P_8	6.3	5.4	86	1.4	2.4	165	557	330	59
	Mixes cured at 120° C								
S_7	7.8	7.3	93	1.9	1.2	63	1100	907	82
P_5	7.5	6.6	88	1.0	1.4	135	1062	855	80
S_{11}	9.3	9.3	101	1.3	1.3	100	925	770	83
P_6	12.7	4.0	32	1.5	1.5	100	1000	790	79

Other Physical Properties

Other physical properties of the vulcanizates evaluated with carbon black filled systems are given in Table 5.11. Hardness, compression set, abrasion loss and tear strength were evaluated for the above vulcanizates. At 150°C, for TMTD-AMT systems hardness values are slightly lower than that of mix containing TMTD alone but these values are comparable to those containing TU. Compression set is found to be more or less comparable to the control mixes. Tear strength values increase with the incorporation of the secondary accelerator (AMT). For samples cured at 120°C, hardness and compression set values are higher for the vulcanizates containing optimum dosage of AMT. Other properties evaluated remain more or less similar to that of control mixes.

In MBTS-AMT systems compression set and abrasion loss decrease as the concentration of AMT increases. Tear strength is found to be higher at the lower dosages of AMT. Total crosslink density values also increase with increase in the concentration of AMT. Other physical properties evaluated gave values comparable with that of reference formulations. Mixes cured at 120°C, in general, show lower values for these physical properties. For CBS -AMT systems, hardness values increase and then decrease with the dosage of AMT. Compression set and abrasion loss decreases with AMT and there is a definite increase in tear strength with the amount of AMT.

Other physical properties evaluated for the vulcanizates containing silica (cured at 150°C) are given in Table 5.12. In TMTD-AMT systems the hardness values are lower than that of mix containing TMTD alone. Compression set values show an unfavourable increase with increase in the concentration of AMT. Abrasion loss is found to decrease (abrasion resistance increases) with increase in the amount of AMT. Tear strength values are found to be significantly higher for vulcanizates containing AMT and the increase is found to be proportional to the increase of the amount of AMT in the mix. Mixes containing AMT cured at 120°C also show better values for these physical properties. In MBTS-AMT systems hardness decreases while compression set increases with AMT. Cured at 120°C this binary system containing silica has comparatively better physical properties. CBS-AMT systems have higher hardness values than CBS alone and CBS-TU. For all these three binary systems studied carbon black filled vulcanizates showed higher crosslink density values and also better physical properties.

Table 5.11 Other physical properties of vulcanizates containing carbon black

Mixes	Mixes cured at 150°C				
	Hardness (Shore A)	Abrasion loss (cm^3/hr)	Compression set (%)	Tear strength (N/mm)	Total crosslink densityX10^5 ($g.mol/cm^3$)
C_1	64	2.8	25.3	80.0	6.9
C_2	62	2.1	16.4	75.0	8.4
C_3	60	1.9	12.9	74.3	8.1
C_4	66	1.9	10.8	74.6	8.4
C_5	61	3.5	9.4	81.0	10.6
C_6	65	2.9	8.1	64.0	9.3
C_7	60	3.2	11.6	77.0	8.2
C_8	59	3.1	10.7	76.0	10.1
C_9	57	2.2	23.5	64.0	7.9
C_{10}	60	2.2	16.1	69.0	7.8
C_{11}	63	2.2	14.6	71.0	7.5
C_{12}	59	1.9	16.5	77.0	8.3
R_1	66	1.8	16.3	72.0	8.8
R_2	69	3.2	10.9	76.0	8.3
R_3	65	2.2	16.1	62.0	9.8
R_4	63	2.7	16.2	61.0	8.7
R_5	60	3.0	11.6	70.0	10.1
R_6	64	2.2	27.1	76.0	8.4
R_7	61	2.4	6.4	51.0	8.7
R_8	68	2.0	7.5	60.0	9.7
	Mixes cured at 120°C				
C_3	64	2.4	26.0	56.0	9.5
R_4	63	2.5	28.0	54.0	8.7
C_7	63	3.1	13.1	74.0	8.6
R_5	67	3.2	17.0	65.0	10.4
C_{11}	59	2.3	32.8	77.0	10.0
R_6	60	2.2	35.2	74.3	11.1

Table 5.12 Other physical properties of vulcanizates containing silica

Mixes	Mixes cured at 150°C				
	Hardness (Shore A)	Compression set (%)	Abrasion loss (cm^3/hr)	Tear strength (N/mm)	Total crosslink densityX10^5 (g.mol. /cm^3)
S_1	48	18.8	10.4	46.3	2.5
S_2	43	21.4	11.5	41.8	2.2
S_3	44	22.5	11.2	48.0	2.2
S_4	42	26.1	10.9	48.2	2.3
S_5	46	22.4	11.4	44.0	2.6
S_6	54	23.8	6.5	43.6	2.7
S_7	50	30.3	9.4	45.0	2.4
S_8	50	29.7	9.3	44.9	2.9
S_9	51	15.6	9.8	35.8	2.6
S_{10}	46	16.9	10.8	39.2	2.5
S_{11}	47	27.0	9.8	45.0	2.6
S_{12}	51	36.1	10.2	47.2	2.5
P_1	51	13.5	10.6	49.0	2.4
P_2	64	19.0	12.7	38.0	3.5
P_3	41	28.0	9.9	39.0	2.9
P_4	54	27.3	10.8	44.0	2.2
P_5	46	26.2	10.3	41.0	2.8
P_6	48	22.0	10.6	44.0	2.8
P_7	56	19.7	10.3	43.5	3.3
P_8	52	17.6	10.8	33.8	3.9
	Mixes cured at 120°C				
S_7	52	16.9	8.8	53.4	1.7
P_5	48	18.3	9.3	54.9	1.4
S_{11}	51	16.0	7.2	57.5	2.7
P_6	49	15.9	7.5	52.3	2.7

CONCLUSIONS

From the results obtained in this study it is evident that AMT can be used as a secondary accelerator in the sulphur vulcanization of styrene-butadiene rubber. Considering the unfilled systems, there is found to have appreciable reduction in optimum cure time when AMT is used as a secondary accelerator. Comparing the mixes TMTD-AMT and TMTD-TU the former showed lower cure time and higher cure rate values. The results with MBTS and CBS are also more or less similar. At 120°C also cure time values of AMT mixes are lower than that of TU. This indicates that the nucleophilic reaction mechanism suggested in NR for the activity of these binary systems is applicable in unfilled SBR systems also.

AMT is found to be an effective secondary accelerator in filled systems also. This is equally true for the vulcanization reactions carried out at 120 and 150°C. In the filled systems of SBR studied, carbon black filled mixes are seen to follow a nucleophilic reaction pattern. The cure time values obtained for the AMT mixes are lower than that of TU mixes. In physical properties also these systems showed values that are better/ comparable to reference formulations. However silica filled systems of SBR do not seem to follow the nucleophilic reaction pattern. Considering the cure characteristics, especially the optimum cure time values, a mixed polar-radical mechanism is most probable here. In the filled systems tensile strength values showed a general improvement in the binary systems containing AMT while other properties like compression set, abrasion loss, tear strength, etc. gave more or less satisfactory values. Non-toxic nature of AMT can be considered to be an added advantage in this context.

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Chapter 6

STUDIES ON THE EFFECT OF AMT IN THE SULPHUR VULCANIZATION OF NR-SBR BLENDS

The use of blends of rubbers is widespread, the purpose being to obtain a balance of properties including cost, which one elastomer alone cannot give. One type of rubber may not posses all the physical properties desired in a finished product and so normally two or more rubbers are blended together. Blends are commercially useful because the synthesis of an entirely different elastomer can be avoided and technologically important because it is used to improve the properties of existing elastomers. Miscible blends of elastomers combine the higher tensile strength of the semi crystalline polymers and the favourable low temperature properties of amorphous polymers. Theoretically blends of chemically dissimilar elastomers can attain a wider variation in properties than blends of miscible, and thus chemically similar elastomers.

Each polymer possesses its own advantages and disadvantages in properties. For example, NR has excellent mechanical properties but relatively poor oil resistance and nitrile rubber (NBR) has the opposite. As a consequence, blending these two rubbers together is one of the best solutions to achieve good mechanical properties and oil resistance. Therefore on blending two rubbers it should be possible to obtain the right compromise in properties[1]. There are also considerable differences in price between rubbers and this is the economic reason for blending. The difficulties experienced in processing some rubbers also necessitate blending. Most blends of elastomers are immiscible because mixing is endothermic and the entropy contribution is small because of high molecular weight[2]. True miscibility is not required for good rubber properties even though adhesion between the polymer phases is necessary and the respective interfacial energies are important in this respect[3].

The physical properties of polymer blends are generally controlled by many factors including the nature of the polymer, the blend composition[4] and the blend morphology[5]. NR and SBR are the world's leading general purpose rubbers. They can be usefully blended if the fundamental differences and similarities between them are recognized. NR and SBR are unsaturated hydrocarbon polymers and hence unvulcanized compounds will dissolve in most hydrocarbon solvents and other liquids of similar solubility parameters, while cured stocks will swell extensively in these solvents[6]. NR may be added to a synthetic rubber compound to improve building properties, resilience, tear strength or under some circumstances, fatigue resistance. Conversely, a basically NR compound may have an admixture of synthetic rubber to improve wear or crack resistance under particular circumstances, or merely to reduce the cost of the compound while retaining adequate favourable properties. SBR is blended with NR to attain fairly constant cure characteristics and better abrasion resistance. Both rubbers may be reinforced by carbon black and neither can be classed as heat resistant rubber. Compared to NR, SBR is more uniform in many cases. NR is crystalline with a T_m of about 50°C while SBR is amorphous. Since NR is stress crystallizable, it gives good tensile strength to the gum stocks. On the other hand, SBR gum vulcanizates are weak and it is essential to use reinforcing fillers like fine carbon black. It has been recognized that when two polymers are insoluble, blends may be produced by intense mechanical mixing[7]. The high shearing forces required to blend high molecular weight elastomers are provided only by open-roll mills or internal mixers. Shundo[8] has compared the use of roll mill and internal mixer in the preparation of NR-SBR blends and found the mill to furnish more uniform compositions. When filler is added to a binary elastomer blend, it first goes to less viscous polymer and when viscosity becomes equal to that of higher viscous polymer, it would be taken up by both the polymers[9]. In the vulcanization of NR-SBR blends, NR phase takes a larger share of curatives leaving the SBR phase slightly under-crosslinked[10]. It has been reported that SBR requires less sulphur and more accelerator than NR because of the lower unsaturation of SBR[11]. This necessitates more active accelerator or binary accelerator system to obtain uniform curing.

The results obtained in the study of aminoiminomethyl thiourea (AMT) as a secondary accelerator in NR and SBR were found to be promising. In this context we thought it worthwhile to investigate its effect in a blend of NR and SBR. The accelerating effect of this thiourea derivative with primary accelerators like MBTS, TMTD and CBS in a 50:50 blend was investigated both in the filled and unfilled stocks. The cure properties of mixes with MBTS–AMT showed that this system could not constitute a practical formulation. So in further studies only TMTD-AMT and CBS-AMT were investigated. Mechanical properties like tensile strength, 100 % modulus, elongation at break, tear strength, etc. were also studied. Other physical properties evaluated include hardness, compression set, abrasion loss and tear strength. The total crosslink density values were also determined using the equilibrium swelling method.

6.1 EXPERIMENTAL

Table 6.1 gives the composition of the various unfilled formulations of the blends. In all the mixes zinc oxide (5 phr), stearic acid (2 phr) and sulphur (1.5 phr) were incorporated as activator, co-activator and curing agent respectively. Accelerators were added in molar equivalents. Binary systems containing thiourea in 1:1 molar combinations of MBTS-TU, TMTD-TU and CBS-TU were taken as reference formulations for comparing the cure properties and to see whether the reactions follow a nucleophilic pattern. Conventional accelerator systems like TMTD-CBS were also prepared for comparison. Mix R_1 contains two molar equivalents of TMTD alone, while R_4 contains one molar equivalent of TMTD with one molar equivalent of TU. Mixes A_1- A_4 contain different concentrations of AMT ranging from 0.25 to 1.5 molar equivalents with one mole equivalent of TMTD. Mix R_2 contains two molar equivalents of CBS and R_5 contains CBS and TU in 1:1 molar ratio. Mix R_3 contains two molar equivalents of MBTS and R_6 is a binary mix of MBTS and TU in the ratio 1:1. R_7 is a binary system of TMTD and CBS. Mixes A_5 to A_8 contain AMT ranging from 0.25 to 1.5 molar equivalents with one mole equivalent CBS. Similarly mixes A_9 to A_{12} contain different concentrations of AMT ranging from 0.25 to 1.5 mole equivalents in the MBTS system.

Table 6.1 Formulation of NR-SBR blends (unfilled mixes)

Mixes	NR	SBR	ZnO	Stearic acid	TMTD	CBS	MBTS	AMT	TU	Sulphur
A_1	50	50	5	2	1.2			0.148		1.5
A_2	50	50	5	2	1.2			0.295		1.5
A_3	50	50	5	2	1.2			0.590		1.5
A_4	50	50	5	2	1.2			0.885		1.5
A_5	50	50	5	2		1.32		0.148		1.5
A_6	50	50	5	2		1.32		0.295		1.5
A_7	50	50	5	2		1.32		0.590		1.5
A_8	50	50	5	2		1.31		0.885		1.5
A_9	50	50	5	2			1.66	0.148		1.5
A_{10}	50	50	5	2			1.66	0.295		1.5
A_{11}	50	50	5	2			1.66	0.590		1.5
A_{12}	50	50	5	2			1.66	0.885		1.5
R_1	50	50	5	2	2.4					1.5
R_2	50	50	5	2		2.64				1.5
R_3	50	50	5	2			3.32			1.5
R_4	50	50	5	2	1.2				0.38	1.5
R_5	50	50	5	2		1.32			0.38	1.5
R_6	50	50	5	2			1.66		0.38	1.5
R_7	50	50	5	2	1.2	1.32				1.5

The optimum dosage of AMT required in the vulcanization reaction was determined based on the cure characteristics.

The mixes were prepared on a laboratory two-roll mixing mill as per ASTM D 3182-89 as detailed in earlier chapter. Goettfert elastograph was used to determine the cure characteristics of the various compounds at 150°C. The cure characteristics at 130°C were also determined, but as the cure times were found to be too high they were not further investigated. The compounds were then vulcanized up to the optimum cure time in an electrically heated hydraulic press at a pressure of 12 MPa. The tensile properties, total chemical crosslinks, etc. were determined as per details given in chapter II.

6.2 RESULTS AND DISCUSSIONS

Cure Characteristics

The cure curves obtained for the various gum mixes are given in Figs. 6.1 to 6.3 and the corresponding cure characteristics such as optimum cure time (t_{90}), scorch time (t_{10}), induction time (t_5), cure rate index, minimum torque and maximum torque values obtained are given in Table 6.2. In the case of TMTD-AMT systems the optimum cure time is found to decrease with increase in the concentration of AMT from 0.25 to 1.5 molar levels. Considering the optimum cure time, scorch time and maximum torque values obtained, the optimum dosage of AMT required can be found to be one molar equivalent with a similar dosage of TMTD. Compared to the reference mixes like TMTD-TU (R_4) and TMTD alone (R_1) there is considerable reduction in cure time for the corresponding AMT mix (A_3). The optimum cure time for AMT mix is 5.3 min. and that for the TU mix is 5.5 min., while that for the conventional binary system TMTD-CBS is 7.7min.

In CBS-AMT systems also the cure time decreases with increase in the concentration of AMT. Compared to the control mix containing TU the mix containing AMT (A_7) has a lower cure time. In the case of MBTS mixes also a similar trend is observed in the mixes containing AMT. The above results are indicative of a nucleophilic reaction mechanism in these systems under

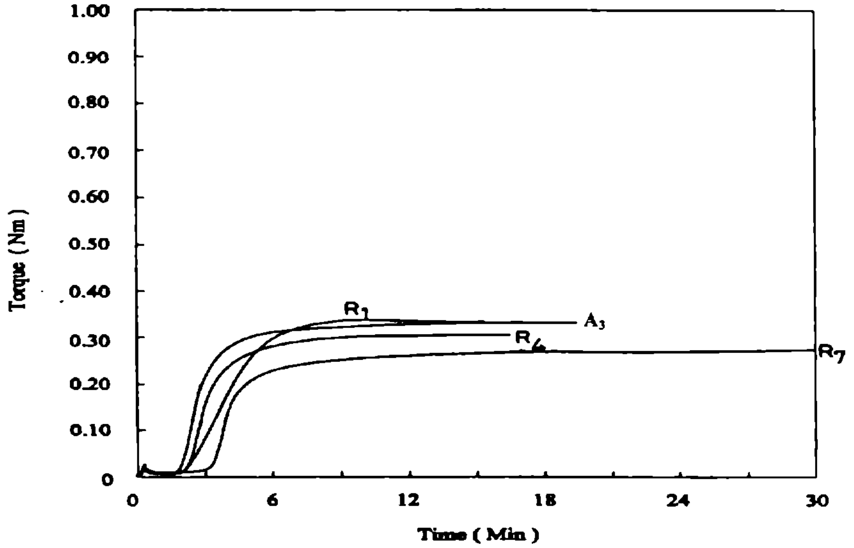

Fig. 6.1 Cure curves of NR -SBR blends (unfilled mixes containing TMTD)

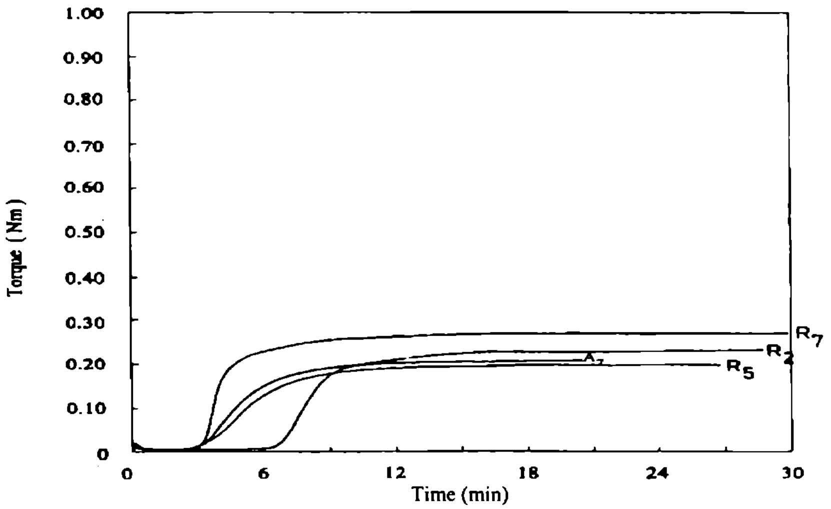

Fig. 6.2 Cure curves of NR -SBR blends (unfilled mixes containing CBS)

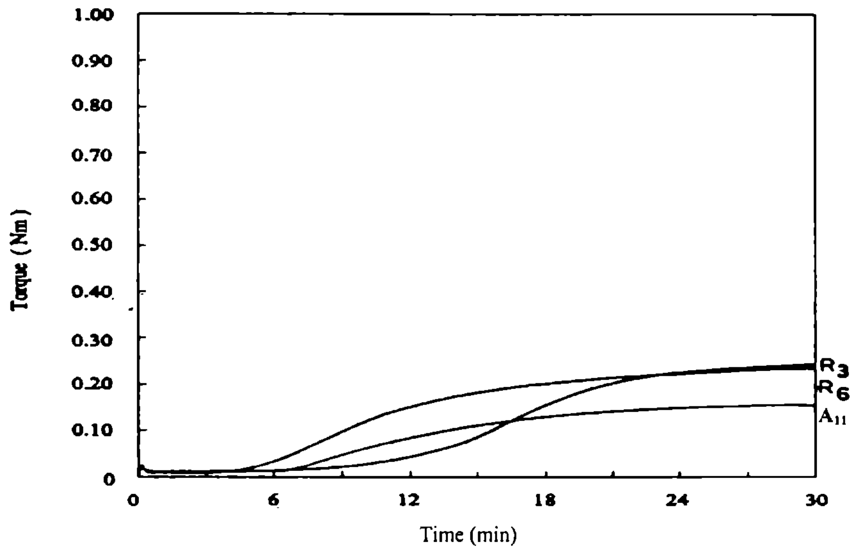

Fig. 6.3 Cure curves of NR -SBR blends (unfilled mixes containing MBTS)

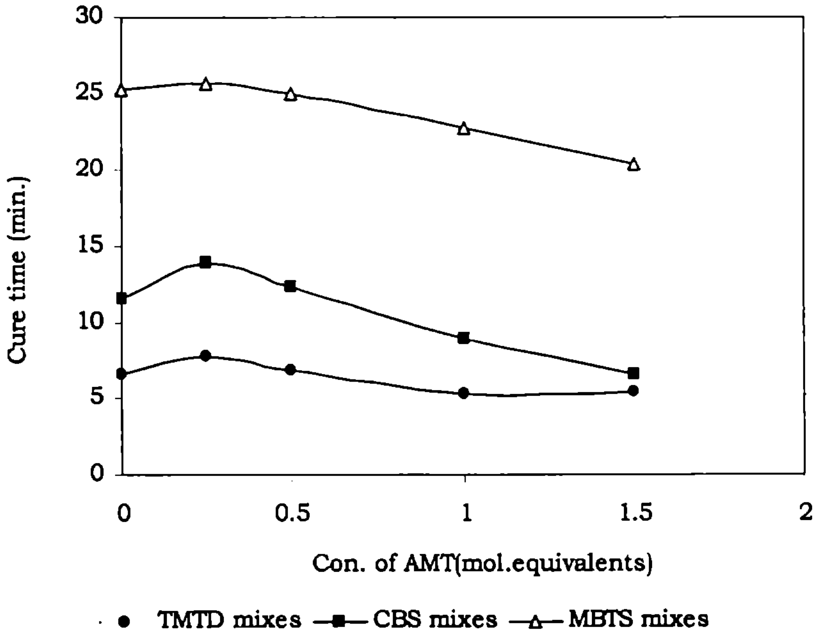

Fig. 6.4 Variation of cure time with concentration of AMT (gum mixes)

Table 6.2 Cure characteristics of NR-SBR blends (unfilled mixes)

Mixes	Optimum cure time (min) t_{90}	Scorch time (min) t_{10}	Induction time (min) t_5	Cure rate index	Minimum torque (Nm)	Maximum torque (Nm)
A_1	7.8	2.6	2.3	19.2	0.0054	0.23
A_2	6.8	2.6	2.3	23.8	0.0073	0.28
A_3	5.3	2.1	2.0	30.3	0.0073	0.28
A_4	5.4	2.2	2.0	31.2	0.0058	0.25
A_5	14.0	6.5	6.1	13.3	0.0058	0.19
A_6	12.4	5.4	5.1	14.3	0.0068	0.21
A_7	9.0	3.5	3.2	18.1	0.0054	0.20
A_8	6.6	2.3	2.1	23.2	0.0054	0.18
A_9	25.7	11.3	4.1	6.9	0.0044	0.15
A_{10}	25.0	11.0	9.3	7.1	0.0048	0.17
A_{11}	22.7	7.4	6.5	6.5	0.0054	0.15
A_{12}	20.4	5.5	4.8	6.7	0.0063	0.18
R_1	6.6	2.6	2.3	25	0.0063	0.34
R_2	11.6	6.9	6.6	21.2	0.0049	0.25
R_3	25..2	13.8	11.3	8.7	0.0058	0.19
R_4	5.5	2.1	1.9	33.3	0.0054	0.23
R_5	9.6	3.5	3.0	16.4	0.0058	0.19
R_6	23.0	5.7	4.4	6.1	0.0063	0.19
R_7	7.7	3.4	3.2	23.2	0.0044	0.27

review. But as the MBTS systems are very slow curing the mechanical and other physical properties are not studied in these systems. Fig. 6.4 explains the effect of the concentration of AMT on the cure time values.

Tensile and other Physical Properties

Tensile and other physical properties obtained for the vulcanizates from the various systems are given in Tables 6.3 and 6.4. In the case of TMTD-AMT systems, as the concentration of AMT is increased, the tensile strength value also increases and these values are better/comparable to those of control mixes. Modulus values are in general lower than that of the reference mixes. Elongation at break values remain comparable to the other formulations. A similar trend is observed in CBS-AMT systems also. Generally higher tensile strength and elongation at break values are noticed in the mixes containing AMT. The percentage retention of tensile properties after heat aging of the AMT mixes are higher than that of control formulations. Compared to the conventional systems like TMTD-CBS also the experimental mixes with AMT show higher tensile strength values.

Table 6.3 Tensile properties of NR-SBR blends (gum mixes)

Mixes	Tensile strength (MPa)			100% Modulus (MPa)			Elongation at break (%)		
	Before aging	After aging	Retention %	Before aging	After aging	Retention %	Before aging	After aging	Retention %
A_1	3.6	2.5	69	1.12	1.00	91	188	144	76
A_2	2.6	2.9	111	0.78	0.92	118	150	194	129
A_3	3.5	3.3	94	0.97	1.00	107	169	156	92
A_4	5.5	4.2	76	0.86	1.30	151	375	286	76
A_5	5.4	4.1	76	0.77	0.92	119	438	326	74
A_6	6.3	3.3	54	0.66	0.75	113	425	350	82
A_7	7.1	8.6	121	0.89	1.30	146	563	388	69
A_8	8.6	9.9	115	0.88	1.10	125	525	473	90
R_1	2.9	2.1	73	1.10	1.40	93	138	149	108
R_2	6.0	5.1	84	1.10	1.00	91	363	300	82
R_3	3.5	2.9	83	1.60	1.30	82	238	196	82
R_4	4.2	3.0	71	1.20	1.10	91	338	244	72
R_5	3.5	3.1	87	1.20	1.10	91	150	113	75

Table 6.4 Other physical properties of NR-SBR blends (gum mixes)

Mixes	Hardness (Shore A)	Compression set (%)	Abrasion loss (cm^3/hr)	Tear strength (N/mm)	Total cross link density $\times 10^{-5}$ $g.mol/cm^3$
A_1	37	19.3	11.6	20.7	3.30
A_2	37	18.9	10.7	23.5	5.75
A_3	35	23.1	11.3	20.5	6.37
A_4	35	18.5	13.0	33.2	6.05
A_5	29	17.7	15.4	17.5	4.21
A_6	27	21.8	10.2	20.3	4.29
A_7	30	23.1	8.2	26.8	6.08
A_8	31	32.8	8.1	29.1	5.56
R_1	43	20.3	15.2	16.2	9.10
R_2	33	12.5	9.1	33.3	6.70
R_3	35	18.3	13.1	22.8	6.30
R_4	28	11.5	13.5	20.5	4.29
R_5	37	12.3	13.8	21.9	8.19

Other physical properties evaluated are given in Table 6.4. In the vulcanizates of TMTD-AMT and CBS-AMT the physical properties like hardness, compression set and abrasion loss are found to decrease with increase in the concentration of AMT. The vulcanizates containing optimum concentration of AMT give comparable values to that of thiourea systems. The chemical characterization of the vulcanizates was carried out by determining the total cross link density. These results are also given in Table 6.4.

6.3 FILLED MIXES OF THE BLENDS

Even though gum vulcanizates of NR have high tensile strength, gum vulcanizates of a blend of NR and SBR show low physical properties. As in the case of individual rubbers, fillers are added to the blends for improved processability, reinforcement and/or cost reduction. The particle distribution of fillers in each polymer phase and the effects of their distribution on properties of the blends have been studied in detail[12].

Polymers are usually not miscible and blends consist of intermingled micro regions of individual polymers. When fillers are mixed into such a blend, a situation may develop in which the filler is unevenly distributed over the different phases and this distribution affects the compound properties[13]. During the mixing of the pre-blend with filler, the soft polymer will penetrate the voids between filler particles first so that there will be a higher concentration of filler in the softer rubber. Because of the uptake of filler, the viscosity of the softer rubber increases until it is equal to that of the more viscous polymer, after which the second polymer participates in the filler penetration so that the viscosity of the two phases is roughly the same[14]. The factors that dominate the partitioning of fillers are the degree of unsaturation of the polymers, their viscosities, polarities and the method of preparation[15].

In the study of aminoiminomethyl thiourea as a secondary accelerator in the filled mixes of NR-SBR blends, we used HAF black and precipitated silica as fillers.

Effect of carbon black

The formulations of the filled mixes of the blends are given in Table 6.5. Two binary systems with TMTD/CBS as primary accelerator were studied. In the carbon black filled mixes B_1 to B_4 contain different concentrations of AMT ranging from 0.25 to 1.5 molar equivalents with one molar equivalent of TMTD. Mixes B_5 to B_8 contain similar dosages of AMT with one molar equivalent of CBS. Mixes R_1 and R_2 contain two molar equivalents of TMTD/CBS each. Mixes R_3 and R_4 contain one molar equivalent of TU with similar concentrations of TMTD/CBS. Mix R_5 is a conventional system containing TMTD and CBS in the ratio 1:1.

The cure curves obtained for the above black-filled mixes are given in Fig. 6.5 and 6.6 and the cure characteristics calculated are given in Table 6.6. From the table it is clear that in the case of TMTD-AMT mixes there is decrease in scorch time and optimum cure time values. There is a corresponding increase in the cure rate. The maximum torque is also found to be less in these mixes. Compared to the control mixes containing TU, there is not much variation in optimum cure time for experimental

Table 6.5 Formulation of NR-SBR blends (filled mixes)

Ingredients	B_1	B_2	B_3	B_4	B_5	B_6	B_7	B_8	R_1	R_2	R_3	R_4	R_5	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	R_1	R_2	R_3	R_4	R_5
NR	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50
SBR	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50
ZnO	5	5	5	5	5	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	2	2	2	2	2
TMTD	1.2	1.2	1.2	1.2					2.4		1.2		1.2	1.2	1.2	1.2	1.2					2.4		1.2		1.2
CBS					1.32	1.32	1.32	1.32		2.64		1.32	1.32					1.32	1.32	1.32	1.32		2.64		1.32	1.32
Thiourea											0.38	0.38												0.38	0.38	
AMT	0.15	0.29	0.59	0.88	0.15	0.29	0.59	0.88						0.15	0.29	0.59	0.88	0.15	0.29	0.59	0.88					
Carbon black	50	50	50	50	50	50	50	50	50	50	50	50	50													
Aromatic oil	5	5	5	5	5	5	5	5	5	5	5	5	5													
Silica														30	30	30	30	30	30	30	30	30	30	30	30	30
DEG														1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2
Naphthenic oil														3	3	3	3	3	3	3	3	3	3	3	3	3
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	1.5	1.5	1.5	1.5	1.5

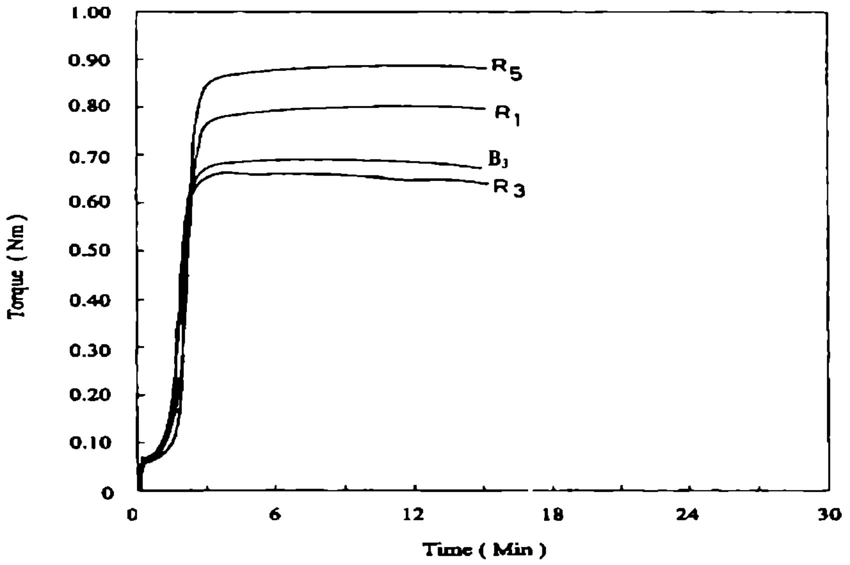

Fig. 6.5 Cure curves of NR-SBR blends (carbon black filled, containing TMTD)

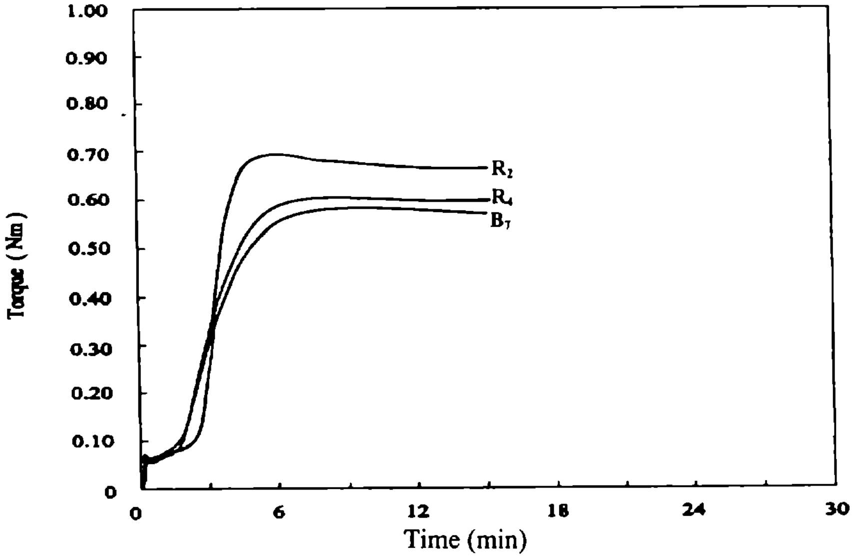

Fig. 6.6 Cure curves of NR-SBR blends (carbon black filled, containing CBS)

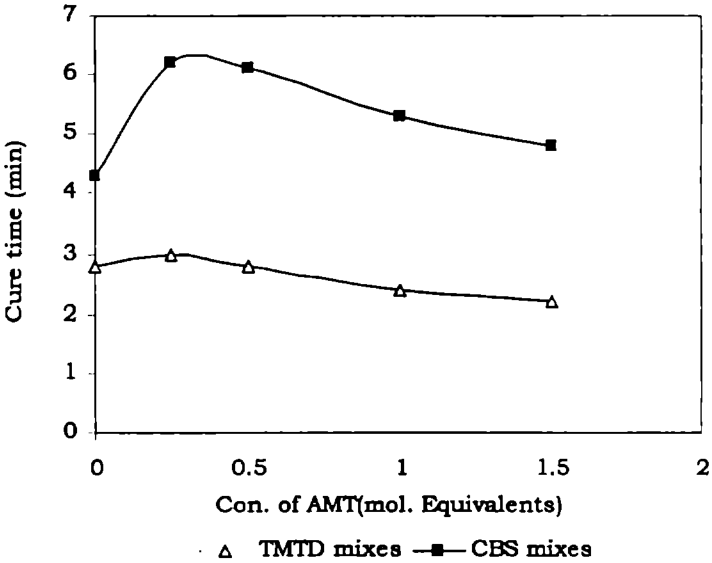

Fig. 6.7 Variation of cure time with concentration of AMT (carbon black filled)

Table 6.6 Cure characteristics of NR-SBR blends (carbon black filled)

Mixes	Optimum cure time (min) t_{90}	Scorch time (min) t_{10}	Induction time (min) t_5	Cure rate index	Minimum torque (Nm)	Maximum torque (Nm)
B_1	3.0	1.5	1.2	67	0.056	0.64
B_2	2.8	1.6	1.3	83	0.061	0.69
B_3	2.4	1.4	1.2	100	0.059	0.68
B_4	2.2	1.2	1.1	100	0.059	0.66
B_5	6.2	2.4	1.8	26	0.057	0.64
B_6	6.1	2.2	1.7	25	0.057	0.60
B_7	5.3	1.6	1.3	28	0.071	0.64
B_8	4.8	1.6	1.3	31	0.055	0.60
R_1	2.8	1.5	1.3	77	0.065	0.79
R_2	4.3	2.7	2.3	62	0.056	0.67
R_3	2.4	1.4	1.1	100	0.064	0.65
R_4	5.2	2.0	1.5	31	0.059	0.60
R_5	2.7	1.9	1.6	125	0.062	0.88

Table 6.7 Tensile properties of NR-SBR blends (carbon black filled)

Mixes	Tensile strength (MPa)			100% Modulus (MPa)			Elongation at break (%)		
	Before aging	After aging	Retention %	Before aging	After aging	Retention %	Before aging	After aging	Retention %
B_1	16.3	15.8	96	2.4	3.1	129	229	164	71
B_2	19.6	17.4	88	2.5	4.1	164	275	163	59
B_3	19.2	16.0	83	2.3	4.4	191	250	175	70
B_4	17.2	16.9	92	2.1	3.5	166	238	165	69
B_5	25.2	25.0	99	2.7	4.4	162	354	263	74
B_6	31.8	29.5	92	2.1	4.3	204	425	275	84
B_7	27.8	26.7	96	2.5	3.4	136	363	278	76
B_8	27.8	26.6	95	2.4	2.7	112	350	294	84
R_1	13.1	11.0	83	4.2	4.9	116	150	85	56
R_2	25.9	19.6	75	2.7	4.3	159	306	225	73
R_3	18.2	15.4	84	3.2	4.3	138	209	139	66
R_4	24.2	20.0	82	2.4	3.2	133	340	200	58
R_5	18.0	14.1	78	4.4	3.1	70	154	130	84

Table 6.8 Other physical properties of NR-SBR blends (carbon black filled)

Mixes	Hardness (Shore A)	Compression set (%)	Abrasion loss (cm^3/hr)	Tear strength (N/mm)	Total cross link density $\times 10^{-5}$ g.mol/cm^3
B_1	64	22.7	4.2	78.8	7.98
B_2	65	17.4	4.9	96.0	8.18
B_3	66	18.0	5.0	80.4	8.29
B_4	67	18.9	4.5	83.5	8.19
B_5	56	15.4	4.4	109.0	6.13
B_6	60	24.8	4.4	88.3	6.07
B_7	60	10.7	4.7	93.0	5.12
B_8	62	9.7	4.3	100.0	5.72
R_1	63	8.1	4.8	62.5	11.10
R_2	62	13.7	4.2	105.0	7.15
R_3	62	16.0	4.5	99.0	8.34
R_4	62	14.7	4.7	74.9	5.79
R_5	72	10.2	5.2	76.5	10.80

mixes containing AMT of the same concentration. The cure time of the experimental mix containing CBS-AMT is slightly higher than that for TU. These observations are somewhat different from what we observed in NR and SBR vulcanization systems. Here it is most probable that instead of a pure nucleophilic mechanism there may be a mixed polar-radical type reaction involved as suggested by Shelton and McDonel[16]. A similar trend is observed in the case of CBS-AMT systems also. But in these systems the mixes with AMT are found to be slower curing than those containing TMTD alone or TMTD with CBS. Fig. 6.7 shows the variation of cure time with concentration of AMT.

Table 6.7 shows the tensile properties of the vulcanizate samples obtained from the above mixes. The vulcanizates from binary systems containing AMT are found to give higher tensile strength values than control mixes. Elongation at break values are also higher for these systems. Other physical properties evaluated for the mixes are given in Table 6.8. For TMTD-AMT systems hardness, compression set and abrasion loss values are found to increase with increase in the amount of AMT. Compared to the TU mixes also, mixes containing AMT exhibit higher values for these properties. CBS-AMT mixes show lower compression set and abrasion loss (better abrasion resistance) and higher tear strength values compared to the control system with TU and the system containing TMTD and CBS.

Effect of Silica

Table 6.5 gives the formulations of different mixes containing silica also. Mixes C_1 to C_4 contain different concentrations of AMT ranging from 0.25 to 1.5 molar levels with one mole equivalent of TMTD. Similarly mixes C_5 to C_8 contain different concentrations of AMT with CBS. Mixes R_1 and R_2 contain two molar equivalents of TMTD and CBS respectively. R_3 and R_4 contain one molar equivalent of TU with one equivalent of TMTD or CBS. Mix R_5 is a system containing TMTD and CBS in the ratio 1:1.

The cure curves for these various silica filled systems are shown in Figs: 6.8 and 6.9 and the corresponding cure properties are given in Table 6.9. Fig. 6.10 gives the variation of cure time with concentration of AMT.

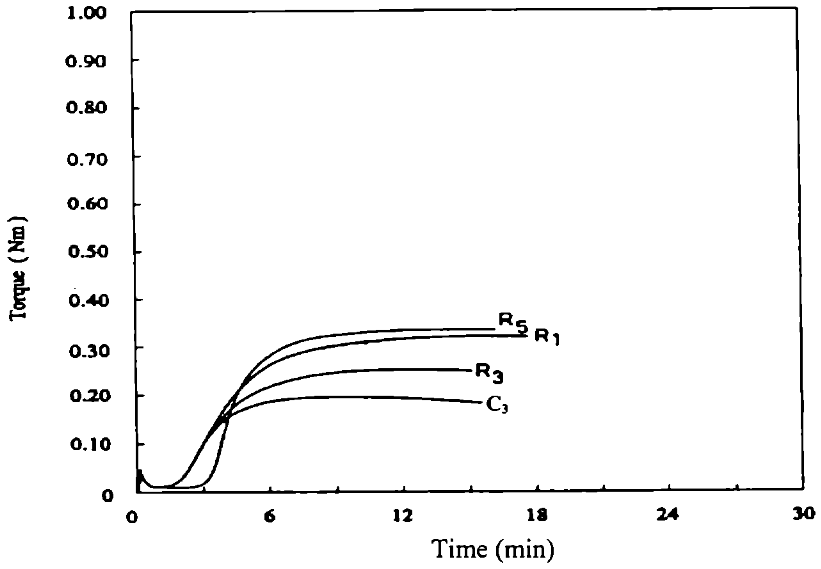

Fig. 6.8 Cure curves of NR-SBR blends (silica filled, containing TMTD)

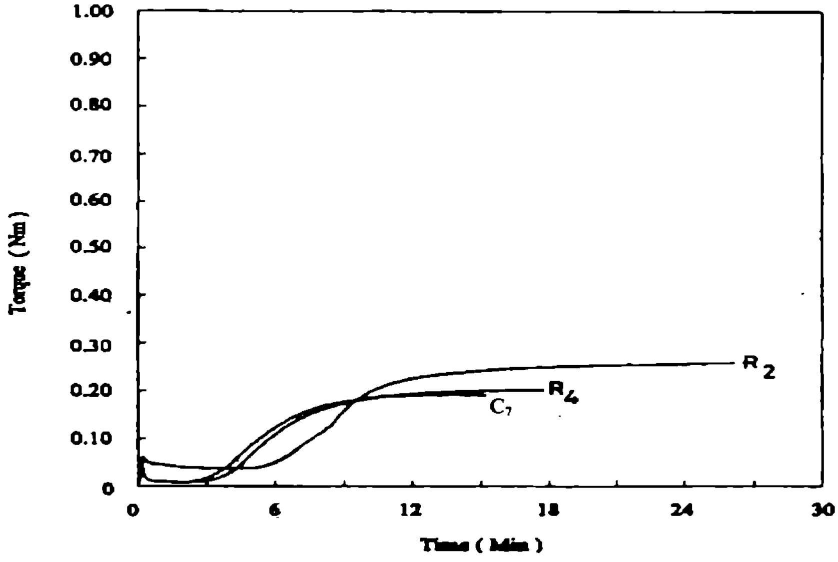

Fig. 6.9 Cure curves of NR-SBR blends (silica filled, containing CBS)

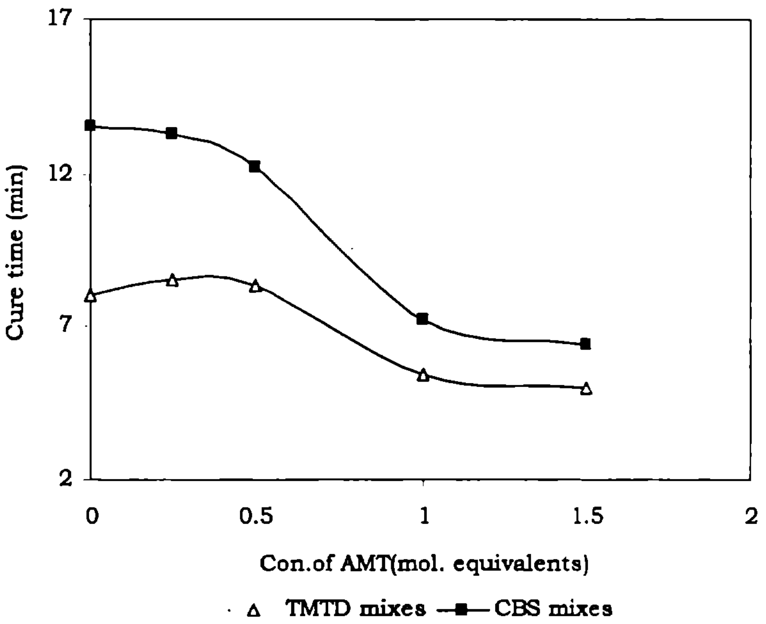

Fig. 6. 10 Variation of cure time with concentration of AMT (silica filled)

Table 6.9 Cure characteristics of NR-SBR blends (silica filled)

Mixes	Optimum cure time (min) t_{90}	Scorch time (min) t_{10}	Induction time (min) t_5	Cure rate index	Minimum torque (Nm)	Maximum torque (Nm)
C_1	8.5	2.8	2.5	17.5	0.007	0.21
C_2	8.3	2.5	2.2	17.2	0.009	0.21
C_3	5.4	2.0	1.8	21.7	0.012	0.19
C_4	5.0	1.9	1.7	24.4	0.014	0.21
C_5	13.3	6.4	5.9	14.5	0.008	0.20
C_6	12.2	5.6	5.2	15.1	0.008	0.19
C_7	7.2	2.5	2.2	16.1	0.010	0.23
C_8	6.4	2.1	1.9	23.2	0.009	0.22
R_1	8.0	2.5	2.2	18.1	0.009	0.33
R_2	13.5	7.6	7.4	16.9	0.034	0.25
R_3	6.8	2.2	1.9	21.7	0.015	0.25
R_4	8.8	3.5	3.0	18.8	0.008	0.19
R_5	7.3	3.4	3.2	25.6	0.007	0.33

Table 6.10 Comparison of cure characteristics of mixes containing NR, SBR and their blends

Parameters	Gum formulations			Carbon black filled			Silica filled		
	NR	SBR	Blend	NR	SBR	Blend	NR	SBR	Blend
TMTD mixes									
Optimum cure time (min.) t_{90}	1.92	4.05	5.30	1.90	2.40	2.40	2.30	6.00	5.40
Scorch time (min.) t_{10}	1.30	1.80	2.10	1.10	1.20	1.40	1.30	1.70	2.00
Cure rate index	166	44	30	122	83	100	96	23	22
CBS mixes									
Optimum cure time (min.) t_{90}	3.30	11.00	9.00	3.60	6.10	5.30	3.60	12.10	7.20
Scorch time (min.) t_{10}	1.70	3.40	3.50	1.20	2.10	1.60	1.30	3.20	2.50
Cure rate index	64	13	18	42	25	28	43	11	16

Table 6.11 Tensile properties of NR-SBR blends (silica filled)

Mixes	Tensile strength (MPa)			100% Modulus (MPa)			Elongation at break (%)		
	Before aging	After aging	Retention %	Before aging	After aging	Retention %	Before aging	After aging	Retention %
C_1	9.1	8.4	92	1.6	1.5	91	344	305	87
C_2	9.6	8.9	93	1.4	1.2	88	409	360	88
C_3	12.7	12.1	95	1.3	1.0	81	422	365	86
C_4	13.0	11.5	88	1.2	1.3	112	409	353	86
C_5	15.2	14.6	96	0.8	1.5	190	451	408	90
C_6	19.4	18.2	94	1.5	1.4	93	470	456	97
C_7	19.9	17.1	86	1.5	1.5	98	512	406	79
C_8	19.1	18.7	98	2.0	1.5	74	488	446	91
R_1	8.3	5.4	65	1.6	1.2	73	262	205	78
R_2	16.2	15.3	95	1.9	1.3	68	372	413	111
R_3	11.4	8.5	75	1.9	1.5	79	382	310	81
R_4	16.9	16.0	95	1.4	1.6	111	506	418	83
R_5	12.9	9.4	73	1.0	1.8	178	331	230	69

Table 6.12 Other physical properties of NR-SBR blends (silica filled)

Mixes	Hardness (Shore A)	Compression set (%)	Abrasion loss (cm^3/hr)	Tear strength N/mm)	Total cross link density $\times 10^{-5}$ g.mol/cm^3
C_1	45	15.7	8.5	32.6	2.91
C_2	49	10.6	7.2	37.7	2.89
C_3	50	18.9	7.8	40.6	2.96
C_4	47	21.1	7.9	39.3	3.04
C_5	43	40.5	7.7	41.8	2.48
C_6	42	32.4	7.9	45.9	2.48
C_7	47	28.4	6.3	44.4	2.59
C_8	47	24.3	8.5	42.6	2.75
R_1	52	20.7	8.5	30.7	4.01
R_2	51	28.0	7.3	40.4	3.26
R_3	45	21.7	8.5	33.3	2.91
R_4	40	37.3	7.4	37.0	2.18
R_5	49	27.3	6.6	34.9	4.06

There is a sharp decrease in cure time up to one molar equivalent of AMT in both binary systems. The synergistic effect of AMT as a secondary accelerator is evident from these results. Considering the TMTD systems, definite decrease in optimum cure time and scorch time with increase in concentration of AMT is noticed. As the concentration of AMT is increased from 0.25 to 1.5 level the t_{90} value decreases from 8.5 min. to 5 min. A corresponding decrease in scorch time and increase in cure rate is also observed (Table 6.9). Considering the cure values the optimum dosage of AMT required can be taken to be one molar equivalent. Comparing the systems containing equivalent amounts of AMT and TU, t_{90} values are found to be lesser for the former. A nucleophilic reaction mechanism can be envisaged in these systems under review. The cure time value for the mix containing optimum dosage of AMT (C_3) is lesser than that of other conventional mixes also. In the CBS systems also a similar trend is seen for the optimum cure time and scorch time values. The cure time for mix C_7 containing optimum dosage of AMT is 7.2 min. while the value for TU mix (R_4) is 8.8 min. Since we have analyzed the effect of AMT in the vulcanization reactions of NR, SBR and their blends we have made a comparative study of their cure characteristics. Table 6.10 gives a comparative evaluation of the cure properties of mixes of NR (ref. Tables 3.2, 3.13 and 3.15), SBR (ref. Tables 5.2, 5.7 and 5.8) and NR-SBR blends (ref. Tables 6.2, 6.6 and 6.9). Considering the unfilled mixes of NR, SBR and their blends, the optimum cure time for the blend is in between that of SBR and NR in CBS mixes. But in TMTD mixes cure time value for blend is higher than that for individual rubbers. The scorch safety of NR-AMT system is found to be improved in the blend formulation. In the case of filled systems containing CBS, cure time values for blends are lower than that for SBR and higher than that for NR. Scorch safety for NR–AMT systems is found to be increased in blends. One of the other advantages to be noted in the blend systems is that the reversion resistance in carbon black filled systems containing AMT is improved.

Tensile properties of the silica filled systems are shown in Table 6.11. In TMTD-AMT systems, the tensile strength values are found to increase with the amount of AMT. But 100% modulus decreases slightly with AMT. Compared to the control mix containing TU (R_3), AMT mix (C_3) has higher tensile strength and percentage retention of this property is also higher for the AMT mixes. In CBS-AMT systems also the tensile strength and elongation at break values are found to be higher compared to other mixes. Values for other physical properties evaluated are given in Table 6.12. Compression set and abrasion loss values show a favourable decrease in the vulcanizates containing AMT. It is to be noted that as the dosage of AMT increases, tear strength and hardness increase up to an optimum level. In CBS-AMT systems also, hardness increases with AMT and compression set decreases. The CBS-AMT system containing optimum dosage of AMT is better in these physical properties compared to those systems containing thiourea of equivalent concentrations.

CONCLUSIONS

The results obtained in this study on the effect of aminoiminomethyl thiourea in the vulcanization systems of NR-SBR blends indicate that AMT can act effectively as a secondary accelerator in the sulphur vulcanization of these blends also. The inclusion of AMT is found to reduce the optimum cure time of the mixes considerably. Compared to the mix with TU, AMT systems show lower cure time and correspondingly higher cure rates except in the carbon black filled systems. The cure properties of the silica filled mixes indicate that a nucleophilic reaction mechanism proposed for NR binary systems is applicable to these blend systems also. But the carbon black filled systems do not follow a similar pattern. A radical – polar mixed reaction mechanism is most probable here. The vulcanizates obtained from these binary systems showed satisfactory tensile properties and also good retention of these properties after heat aging. Aminoiminomethyl thiourea is a non-toxic chemical and our findings indicate that it can be advantageously used in rubber vulcanization reactions.

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Chapter 7

SUMMARY AND CONCLUSIONS

In rubber vulcanization the sulphide and sulphenamide accelerators in which sulphur is covalently linked to another sulphur, carbon or nitrogen are of the delayed action type, displaying little activity at or around 100°C. This is due to the inherent stability of the sulphur bonds. The cleavage of S - S, S - C or S - N bond is the preliminary step leading to a series of fast reactions in vulcanization. There should be some activators to favour the cleavage of these bonds. It was found that sulphur nucleophiles like thiourea enabled the accelerators like TMTD, CBS, MBTS etc. to operate at low temperatures. It is also reported that the mechanism of vulcanization reaction depends on the nature of the elastomer used, curing conditions, the nature of the accelerators used, etc. But convincing proof for these suggestions are lacking. Earlier investigations in our laboratory have indicated that different derivatives of thiourea can be used as effective secondary accelerators along with sulphide and sulphenamide type accelerators in rubber vulcanization. These results more or less support a nucleophilic reaction mechanism in these binary systems as suggested by Philpott and by Moore. In the present study we synthesized aminoiminomethyl thiourea (AMT) and tried this compound as secondary accelerator in the binary systems containing TMTD/MBTS/CBS in sulphur vulcanization of different elastomers and their blends. Necessary control formulations were also prepared for comparison of properties. One of the aims of this study is to give further proof with regard to the theory of nucleophilic reaction mechanism in such binary systems. Nowadays a lot of importance is given world wide for the use of non-toxic chemicals for rubber compounding. It is reported that many of the conventional accelerators used in sulphur vulcanization are toxic in nature. However AMT is a non-toxic chemical used in the pharmaceutical industry. The present study is also the result of the search for a safe and non-toxic accelerator.

The first chapter of the thesis gives an introduction on rubber compounding and curing, curing agents, accelerators and binary accelerator systems. Details of the mechanism of vulcanization reactions are also described in this chapter. It also includes the scope and objectives of the present work.

A detailed description of the experimental procedures adopted in the present study is given in chapter 2. It covers the materials used for this study, their specifications and procedures adopted. It also includes the methods adopted for compounding, vulcanization and determination of different physical properties. The method used for the estimation of total crosslink density is also given in this chapter. Also the methods for latex compounding and of determination of flow behaviour of latex compounds are described.

The study of the accelerator activity of AMT with TMTD/MBTS/CBS in sulphur vulcanization of natural rubber using standard procedures for compounding and vulcanization is described in chapter 3. The procedure adopted for the synthesis of aminoiminomethyl thiourea and its characterization is also given in this chapter. The first part of this chapter deals with the study in NR gum formulations. This study includes compounding, evaluation of different cure characteristics, and determination of various physical properties. In order to study the effect of AMT on the temperature of vulcanization cure characteristics of these mixes were evaluated at two different temperatures, viz. 120 and 150°C. There is appreciable reduction in optimum cure time for mixes containing AMT compared to thiourea, which is used as the control. Considering the nucleophilic character of AMT and TU, AMT is more reactive than TU. The lower optimum cure time exhibited by AMT in the above systems can be attributed to the higher nucleophilic attack by AMT which enhances the S-S bond cleavage in the primary accelerators leading to a faster cure. The results obtained on the cure characteristics of the different binary systems point to a nucleophilic reaction mechanism in the binary systems studied.

Based on the scorch safety and torque value obtained, one molar equivalent of AMT can be taken to be the optimum concentration of the secondary accelerator required. At 120°C also the accelerator activity of AMT is significant. The tensile strength, modulus and elongation at break values of vulcanizates with AMT are generally better than those of the control mixes. These vulcanizates also showed better retention in these properties after heat aging. Other physical properties such as hardness, abrasion resistance and tear strength were also estimated for the different formulations prepared.

The second part of this chapter investigates the effect of fillers in the vulcanization of NR with TMTD-AMT, MBTS-AMT and CBS-AMT. Carbon black, silica and china clay are used as fillers for this study. The optimum cure time obtained in the NR filled systems with AMT is found to be lower than that of the control mixes. This again is indicative of a nucleophilic reaction mechanism in these binary systems and is true for all the fillers used. At the relatively lower temperature of 120°C also, AMT is effective as a secondary accelerator in the binary systems under review. The optimum cure time is reduced nearly by 40 percent in the case of mixes with AMT compared to control mixes with TU. The physical properties evaluated, viz. tensile strength, modulus, elongation at break, hardness, compression set, abrasion resistance and tear strength values of all the three filled experimental systems gave values better than/comparable to those of reference mixes. In these systems also the optimum dosage of AMT required for the above binary systems has been derived as 1:1 molar combinations of AMT with TMTD/MBTS/CBS. Aging resistance of these vulcanizates with AMT is also found to be comparable to the reference formulations.

Investigations on the effect of aminoiminomethyl thiourea in NR latex systems are given in chapter 4. The vulcanization of latex and the use of accelerators are basically different from that of dry rubber. A wide range of organic accelerators for the sulphur vulcanization of dry natural rubber is available. But only those of the highest activity are important for the vulcanization of latices because latex vulcanization temperatures are low and there is no danger of scorching here. Moreover, some of the accelerators will affect the colloidal stability of latex systems. In the present study AMT is tried as secondary accelerator along with primary accelerators, viz. TMTD/CBS/ZDC. Thiourea binary systems are taken as controls. Different mixes with varying concentrations of AMT are prepared and the optimum dosage of AMT required is derived based on the cure characteristics and the tensile strength of the vulcanizates obtained. These mixes are cured at two different temperatures, viz. 100 and 120°C. Physical properties like tensile strength, tear strength, etc. of the different mixes are evaluated. Chemical characterization of the vulcanizates is also carried out using the swelling method. It is observed that the optimum cure time values decrease substantially as the concentration of AMT increases. Compared to the reference systems containing equivalent accelerator combinations, ZDC-AMT mix in 1:1 molar ratio shows substantially lower optimum cure time. In TMTD-AMT and CBS-AMT systems also the optimum cure time values are lower than that of the reference mixes. These observations are true for both the cure temperatures of 100 and 120°C. The cure results obtained in the different systems under review point to a nucleophilic reaction in these latex vulcanization systems also. AMT being more nucleophilic than TU, lower optimum cure time is exhibited by the former. The systems with the optimum dosage of AMT is found to give better values for mechanical properties like tensile strength and tear strength. The favourable effects of this non-toxic amidino thiourea as a secondary accelerator are noticeable more in NR latex systems than in dry NR formulations.

The flow properties of latices are of great practical relevance for the industrial applications of polymers in latex form. Therefore, the study of viscosity of a polymer as a function of shear rate and temperature is very important. Viscosity and the processability of the different latex compounds under different shear rates and temperatures have also been studied. On increasing the shear rate, viscosity of the latex compounds is found to decrease in accordance to the pseudoplastic behaviour of these mixes. This effect is more pronounced at low shear rates as the latex compound approaches near Newtonian behaviour at high shear rates. As the temperature is increased from 25 to 35°C, viscosity is found to decrease in all the three systems under review. However CBS-AMT and ZDC-AMT systems and the corresponding control mixes are comparatively unstable at higher shear rates and temperatures while TMTD-AMT are reasonably stable. The rheological studies of these compounded latex systems show that the introduction of AMT in these systems does not have adverse effects in processing, especially in comparison to the control mixes.

The fifth chapter describes the effect of AMT as a secondary accelerator in the sulphur vulcanization of a synthetic rubber, viz. styrene butadiene rubber (SBR1502). This elastomer was chosen for this study because SBR is a general-purpose synthetic rubber and there are differences in compounding and vulcanization of synthetic rubbers compared to NR, especially with regard to reaction mechanism. Binary systems containing AMT with different primary accelerators were studied and the properties were compared with reference formulations. The cure and mechanical properties and the network structure of the various vulcanizates under review were investigated in detail. Even though gum formulations of SBR are not industrially important, they will be of advantage for the study of reaction mechanism. Part I of this chapter describes the effect of AMT in SBR gum formulations. Considering the mixes cured at 150°C, it was found that TMTD-AMT mixes have lower cure time compared to the control mixes containing thiourea. As the concentration of AMT is increased appreciable reduction in cure time is observed. In MBTS-AMT and CBS-AMT systems also, a similar trend is observed. At 120°C also cure time values of AMT mixes are lower than that of control formulations containing TU. Considering the cure characteristics of these mixes and noting the fact that AMT is more nucleophilic than thiourea, these results point to a nucleophilic reaction mechanism in these binary gum systems of styrene butadiene rubber.

The second part of this chapter investigates the effect of fillers in these binary systems containing the amidino thiourea. The cure characteristics, tensile properties and chemical crosslink studies are carried out on filled mixes containing carbon black and silica. AMT showed promising results with filled systems of SBR also, especially in the cure characteristics. The cure time values obtained for the AMT mixes containing carbon black are lower than that of TU mixes and these mixes are seen to follow a nucleophilic reaction pattern for vulcanization. In physical properties also, these systems showed values that are better/ comparable to reference formulations. Comparing the optimum cure time, values of the experimental mixes containing filler with that of the control mixes, the silica formulations showed slight difference from that of filled and unfilled NR systems and SBR gum formulations. These silica systems do not seem to follow a purely nucleophilic reaction pattern, but a mixed polar-radical mechanism is most probable here. In the filled systems tensile strength values showed a general improvement in the binary systems containing AMT, while other properties like compression set, abrasion loss, tear strength, etc. gave more or less similar values as the control systems. This is equally true for the vulcanization reactions carried out at 120 and at150°C.

The use of a single rubber may not provide all the physical properties desired in a finished product and so normally two or more rubbers are blended together. Each polymer possesses its own advantages and disadvantages in properties. Therefore on blending two rubbers, it should be possible to obtain the right compromise in properties. The use of AMT as a secondary accelerator for the vulcanization of NR-SBR blends is attempted and details of this study is described in Chapter 6. TMTD-AMT and CBS-AMT binary systems are studied in the above blends. Cure characteristics and tensile properties of both gum and filled blends containing AMT are studied and these properties are compared with control mixes. In these blends also AMT is found to give appreciable reduction in cure time compared to the control formulations. The optimum dosage of AMT required is also derived based on the different cure characteristics of the mixes. Compared to the mixes containing thiourea, AMT systems show lower cure time and correspondingly higher cure rate values except in the carbon black filled systems. The cure properties of the silica filled mixes indicate that a nucleophilic reaction mechanism proposed for NR binary systems is applicable to these blend systems also. But in the carbon black filled systems a mixed polar-radical reaction mechanism is most probable. The vulcanizates from these binary systems of the blends containing AMT are found to give higher tensile strength and better results for other physical properties like abrasion resistance and tear strength.

List of Publications

1. "Studies on sulphur vulcanization of natural rubber using amidino thiourea." *J. Plastics, Rubber and Composites,*UK, **30**, (6) 263 (2001).
2. "A new secondary accelerator for the sulphur vulcanization of natural rubber latex." Proceedings of 14th Kerala Science Congress, Kochi, January 29-31, 2002.
3. "Studies in a new binary accelerator system in sulphur vulcanization of styrene – butadience rubber" (communicated)
4. "A new binary accelerator system containing aminoiminomethyl thiourea for the vulcanization of NR – SBR blends" (communicated).
5. "Amidino thiourea as a secondary accelerator in the sulphur vulcanization of filled natural rubber systems." (to be communicated).