# EFFECT OF N-BENZOYL-N$'$,N$'$-PYRROLIDINYLTHIOUREA AS A NOVEL SECONDARY ACCELERATOR IN THE VULCANIZATION OF ELASTOMERS

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*by*

**Molice Thomas**

**Department of Polymer Science and Rubber Technology**
**Cochin University of Science and Technology**
**Kochi- 682 022, Kerala, India**

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# Effect of N-Benzoyl-N',N'-Pyrrolidinylthiourea as a Novel Secondary Accelerator in the Vulcanization of Elastomers

*Ph.D. Thesis*

**MOLICE THOMAS**

*Author*

**Molice Thomas**
Research Scholar
Department of Polymer Science and Rubber Technology
Cochin University of Science and Technology
Kochi- 682 022, Kerala, India.
E-mail: molicethomas@gmail.com

*Supervising Teacher*

**Dr. Thomas Kurian**
Professor
Department of Polymer Science and
Rubber Technology
Cochin University of Science and
Technology (CUSAT)
Kochi- 682 022, Kerala, India.
E-mail: drtkurian@gmail.com

Department of Polymer Science and Rubber Technology
Cochin University of Science and Technology
Kochi- 682 022, Kerala, India

October 2017

**DEPARTMENT OF POLYMER SCIENCE AND RUBBER TECHNOLOGY**
**COCHIN UNIVERSITY OF SCIENCE AND TECHNOLOGY**
**Kochi- 682 022, Kerala, India.**

**Dr. Thomas Kurian**
Professor

Tel: 0484-2575723 (Off.)
E-mail: drtkurian@gmail.com

*Date:* .......................

# Certificate

This is to certify that the thesis entitled **"Effect of N-Benzoyl-N′, N′-Pyrrolidinylthiourea as a Novel Secondary Accelerator in the Vulcanization of Elastomers",** which is being submitted by Mrs. Molice Thomas, in partial fulfillment of the requirements of the degree of Doctor of Philosophy to Cochin University of Science and Technology (CUSAT), Kochi, Kerala State, India is a record of bonafide research work carried out by her under my supervision and guidance.

Mrs. Molice Thomas has worked on the research problem for about seven years (part-time) in the Department of Polymer Science and Rubber Technology of CUSAT. In my opinion, the thesis fulfills the requirements according to the regulations. The results embodied in this thesis have not been submitted for any other degree or diploma. All the relevant corrections and modifications suggested by the audience during the pre-synopsis seminar and recommended by the Doctoral committee have been incorporated in the thesis.

**Dr. Thomas Kurian**
(Supervising Guide)

# Declaration

I hereby declare that the thesis entitled **“Effect of N-Benzoyl-N',N'-Pyrrolidinylthiourea as a Novel Secondary Accelerator in the Vulcanization of Elastomers”** is the bonafide work carried out by me under the supervision of Dr. Thomas Kurian Professor, Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Cochin-22 and has never been included in any other thesis submitted previously for the award of any degree.

Kochi-22
13-10-2017

**Molice Thomas**

**Dedicated to**

*My beloved sister*

*Annie Verghese*

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# Preface

A great breakthrough in the history of vulcanization of rubber and its application happened through the discovery of an organic accelerator by Oenslager in 1906. The role of accelerators in the vulcanization of rubber is in the modification of induction time, scorch time and cure time. They can also enhance mechanical properties of rubber compounds. Studies on cure characteristics led to the introduction of combinations of accelerators to produce a synergistic effect in the system so that the final properties are somewhat better than those produced by either accelerator separately.

The present study deals with the synthesis of novel thiourea derivatives viz: N-benzoyl-$N^1$,$N^1$–pyrrolidinylthiourea (BPTU) and N-benzoyl-$N^1$,$N^1$–diphenylthiourea (BDPTU) as thiourea and its derivatives are well known secondary accelerators. The role of these new thiourea derivatives in the sulphur vulcanization of natural rubber as accelerator has been determined. Our intention was to find a new compound with more nucleophilic character than thiourea to increase rate of vulcanization. The new accelerator used shall be capable of imparting better rheometric properties in different elastomers and also in their blends as it is of prime importance to the industry. It is also desired that the proposed accelerator can bring out synergistic effect in combination with known other accelerators to produce vulcanizate of superior mechanical properties without compromising cure characteristics.

The thesis comprises of eight chapters. The first chapter includes a general introduction to various elastomers, compounding ingredients, rubber vulcanization reactions and different accelerator systems. Literature survey, scope and objectives of the present work are also included. The second chapter gives the specifications of different elastomers and compounding ingredients used in the study. It includes a detailed description of the experimental procedure adopted. The third chapter gives the synthesis and characterization of two new thiourea derivatives namely BPTU and BDPTU. Preparation and characterization of phenylthiazoles viz. (2-N,N-dialkylamino)-5-(indole-3-oyl)-4-phenylthiazole derivatives are also included. Investigation on the accelerating activity of BPTU, BDPTU and phenyl thiazoles in the sulphur vulcanization of natural rubber is described.

Fourth chapter narrates a detailed account of the effect of BPTU as a secondary accelerator along with MBTS/CBS in the NR gum and silica filled systems. The optimum concentrations of BPTU required for NR vulcanization are proposed. The fifth chapter describes the studies on sulphur vulcanization of SBR with BPTU as a secondary accelerator both in gum and silica filled systems. Chapter six is about the investigation on the role of BPTU along with MBTS/CBS on the vulcanization of gum and silica filled NR-SBR (50:50) blends.

The first part of the seventh chapter is about the accelerated curing of NR latex at low temperature using BPTU along with ZDC at two different temperatures. Second part of seventh chapter includes the role of BPTU as secondary accelerator in the carbon black filled elastomers. The conclusion and scope for further work are summarized in the eighth chapter.

# Abstract

Accelerators play a vital role in the vulcanization process of elastomers. The selection of accelerators in sulphur vulcanization determines the category of network structure produced and consequently the specific vulcanizate properties. The chosen accelerators affect the cure rate and scorch safety as well as the number and average length of cross links formed. A novel derivative of thiourea namely N-benzoyl-N$^{'}$,N$^{'}$-pyrrolidinylthiourea (BPTU) has been synthesized and characterized. BPTU accelerates the vulcanization of natural rubber. Binary accelerator formulations using BPTU as secondary accelerator along with conventional accelerators viz. MBTS or CBS in the vulcanization of natural rubber resulted in appreciable reduction of cure time as compared to the conventional accelerators. Natural rubber compounds based on varying dosage of BPTU as secondary accelerator showed improved cure characteristics and mechanical properties both in gum and filled systems.

Vulcanizates of SBR and NR/SBR blends, both gum and filled systems were prepared using BPTU in a binary accelerator formulation. These compounds containing the new accelerator systems showed better cure characteristics and reduction in cure time. Better mechanical properties and ageing properties were exhibited by their vulcanizates. Vulcanization of natural rubber latex using BPTU as a secondary accelerator along with ZDC also showed reduction of cure time at low temperature with improved mechanical properties. The variation in mechanical properties has been correlated to the crosslink formation in various vulcanizates.

BPTU as an accelerator is found to be effective in a binary system for the vulcanization of elastomers in gum and filled systems without much reversion tendency, better abrasion resistance, hardness and resilience. Appreciable reductions of optimum cure time, enhancement of cure rate and improvement in mechanical properties are the main outcome of newly investigated binary systems in the vulcanization of elastomers. Thus a synergistic behaviour is observed leading to better vulcanizate properties in the combined system of accelerators than expected for mixtures.

**Key words:** natural rubber, cure characteristics, mechanical properties, crosslinks, synergistic behaviour, thiourea derivatives, secondary accelerators

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# List of Abbreviations and Symbols

ASTM - American Society for Testing and Materials
ACN - Acrylonitrile
ADS - Air dried sheet
AMT - Aminoiminomethyl thiourea
APT - Amidino phenylthiourea
ATU - Amidinothiourea
BPTU - N-benzoyl-$N^1$,$N^1$-pyrrolidinylthiourea
BDPTU - N-benzoyl-$N^1$,$N^1$-diphenylthiourea
BR - Polybutadiene rubber
CBS - N-cyclohexyl-2-benzothiazolesulfenamide
CD - Crosslink Density
CRI - Cure rate index
CR - Polychloroprene rubber
CV - Conventional vulcanization
DEG - Diethylene glycol
DEIP - 2-(N,N-Diethylamino)-5-(indol-3-oyl)-4-phenylthiazole
DGP - Diphenyl guanidine
DMIP - 2-(N,N-Dimethylamino)-5-(indol-3-oyl)-4-phenylthiazole
DPNR - De-proteinised natural rubber
DRC - Dry rubber content
DTG - Derivative thermogravimetry
EBC - Estate brown crepe
ENR - Epoxidised natural rubber
ETU - Ethylene thiourea
EV - Efficient vulcanization
FTIR - Fourier-transform infrared spectroscopy
GPF - General purpose furnace black
HA - High-ammonia
HAF or N330 - High abrasion furnace
IR - Polyisoprene rubber
ISO - International organization for standardization
IR - Infrared spectroscopy

| | | |
|---|---|---|
| k | - | Cure reaction rate constant |
| LCM | - | Liquid curing medium |
| MBS | - | N-oxydiethylene 2-benzothiazolesulfenamide |
| MBT | - | 2-Mercaptobenzothiazole |
| MBTS | - | Mercaptodibenzothiazyl disulphide |
| MPa | - | Mega pascal |
| MPIP | - | 2-(N,N-Methylphenylamino)-5-(indol-3-oyl)-4-phenylthiazole |
| MST | - | Mechanical stability time |
| $M_w$ | - | Weight average molecular weight |
| NBR | - | Nitrile rubber |
| NMR | - | Nuclear magnetic resonance |
| NR | - | Natural rubber |
| NRS | - | Non-rubber solid content |
| OENR | - | Oil-extended rubber |
| PEG | - | Polyethylene glycol |
| PLC | - | Pale latex crepe |
| $Q_t$ | - | Mole percent solvent uptake |
| R | - | Universal gas constant |
| RPA | - | Rubber process analyzer |
| RSS | - | Ribbed smoked sheet |
| SBR | - | Styrene butadiene rubber |
| SEM | - | Scanning electron microscope |
| SEV | - | Semi efficient vulcanization |
| SP | - | Styrenated phenol |
| STU | - | Phenyl -(γ-triethoxysilane)-propyl thiourea |
| T | - | Absolute temperature |
| TBAB | - | Tetrabutylammonium bromide |
| TGA | - | Thermogravimetric analysis |
| TMTD | - | Tetramethylthiuramdisulfide |
| TQ | - | Polymerized 1,2-dihydro-2,2,4–trimethylquinoline |
| TSR | - | Technically specified rubber |
| TU | - | Thiourea |
| ZDC | - | Zinc dithiocarbamate |
| ZnO | - | Zinc oxide |

cc/hr - Cubic centimeter per hour
cSt - Centistokes
°C - Degree celsius
°C/min - Degree Celsius per minute
dNm - Deci newton meter
g/cc - Gram per cubic centimeter
$\Delta G$ - Gibbs free energy change
$\Delta H$ - Change in enthalpy
J/mol K - Joule per mole Kelvin
kg/$m^3$ - Kilogram per cubic meter
KJ/mol - Kilo joule per mole
KN - Kilo newton
KOH No: - Potassium hydroxide number
$M_H$ - Maximum torque
$M_L$ - Minimum torque
ml - Millilitre
nm - Nanometer
phr - Parts per hundred rubber
$\Delta S$ - Entropy change
$t_{10}$ - Scorch time
$t_{90}$ - Optimum cure time
VFA - Volatile fatty acid number
$V_r$ - Volume fraction of rubber
$V_s$ - Molar volume of the solvent
WTR - Waste tyre rubber
µm - Micrometer
$\varphi$ - Volume fraction of filler
$\chi$ - Interaction parameter

……

# Chapter 1

# GENERAL INTRODUCTION

## 1.1 Elastomers

Rubbers or elastomers form a class of compounds with diverse applications. It has such remarkable and desirable properties that it is being put to many engineering applications like bearings, springs and seals in addition to the manufacture of bulk products like tyres, tubes, belts, hoses, etc. Thus modern life would be unimaginable without these compounds. Raw rubber is an entanglement of high molecular weight hydrocarbon chains. It is not suitable for engineering applications. In 1839, Charles Goodyear [1] discovered that rubber heated with sulphur gave products which were far superior to the original material and were not so sensitive to temperature changes. He patented the process [2] in 1844. Almost at the same time (in 1843) Thomas Hancock independently patented a similar process. Vulcanization is the technique of transforming rubber, a substance of very low strength into a highly elastic material of considerable strength and not so sensitive to temperature changes by treatment with suitable chemicals. From the chemical point, vulcanization is the process whereby the flexible, discrete rubber molecular chains are joined together by crosslinking reactions giving a three dimensional network. Sulphur vulcanization of rubber is a chemical process by which individual polymer chains are united into a three dimensional network by sulphur linkages. The chemistry of the crosslinking reaction and the structure of the sulphur crosslinks have been studied extensively for natural rubber[3].Various studies on the chemistry of vulcanization were carried out on natural and synthetic rubbers as it has a central role in achieving better product performance [4,5] .

The oldest method of vulcanization was carried out by heating rubber with sulphur. But this form of ‘sulphur only’ vulcanization is a very slow process and takes several hours or even days to reach optimum curing, depending on the temperature of vulcanization and the nature of rubber used. This yields vulcanizates of very low mechanical properties. Also, they have a strong tendency to revert and their resistance to aging is poor. Thus this process does not have much technological importance. The ultimate goal of vulcanization is to produce vulcanizate with desired mechanical and chemical properties. These properties to a great extent depend on the network structure of the cured elastomers, which in turn depend on the chemistry of vulcanization. As a result of the network formation, the rubber becomes essentially insoluble in solvents and cannot be processed by any means that requires the flow of material. Thus vulcanization should start only after the rubber article is in its final form.

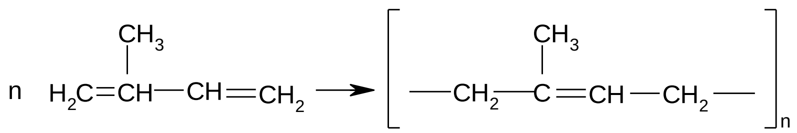
Vulcanization increases elasticity while it decreases plasticity. It should be noted that the modulus increases with vulcanization. Tear strength, fatigue life and toughness are increased as crosslinking proceeds. Therefore understanding the chemistry of vulcanization and its relationship with the resulting network is important to achieve the desired properties.

There are two interpretations about the general nature of chemical reaction of sulphur with rubber. Farmer and coworkers [6] proposed a free radical chain mechanism whereas Bateman and coworkers [7-11] favoured a polar mechanism for the vulcanization of rubber. Rubbers are broadly classified into natural and synthetic. Synthetic rubbers are further classified into two categories: general purpose rubbers (e.g., SBR and BR - used for the manufacture of tyres and general mechanical products) and special purpose rubbers (e.g., NBR and CR-intended for specialized applications).

### 1.1.1 Natural rubber

Natural Rubber (NR) is polyisoprene recovered from the sap of Hevea brasiliensis. Raw NR, in addition to rubber hydrocarbons, contains a certain amount of impurities, which precipitates out during the coagulation of the latex. The amount of impurities depends on the processing conditions. Raw rubber is a macromolecular material, amorphous at room temperature and has a glass transition temperature considerably below ambient temperatures. It can be crosslinked to form a network structure and thus it becomes elastomeric. Because of the highly coiled structure they exhibit a considerable amount of elasticity at room temperature. While at higher temperatures, they tend to creep and display thermoplastic properties. The hydrocarbon component of NR consists of over 99.99% of linear cis-1,4 polyisoprene. The chain structure of the polyisoprene depends to some extent on the biogenesis of NR [12].

In the polyisoprene chain of NR there is one double bond for each isoprene unit as given in Fig.1.1. These double bonds and the alpha methylene groups are reactive for vulcanization reactions with sulphur. Thus, the double bonds are a prerequisite for the sulphur vulcanization reaction.



$$n\ H_2C{=}\overset{CH_3}{\overset{|}{C}}H-CH{=}CH_2 \longrightarrow \left[-CH_2-\overset{CH_3}{\overset{|}{C}}{=}CH-CH_2-\right]_n$$

**Fig. 1.1 Structure of polyisoprene (NR)**

Since NR is an unsaturated hydrocarbon, it can readily react with oxygen, peroxides, ozone, peroxyacids, chlorine and other oxidizing agents. Therefore, the degradation process starts autocatalytically in NR even in the presence of small amounts of oxygen. It has to be prevented by special chemicals, stabilizers or antioxidants. NR is stable for longer storage periods in air at room temperature as it contains an innate amount of antioxidants. But at higher temperatures and on exposure to light, NR oxidizes by forming hydroperoxides through oxygen radicals.

### Physical properties

The specific gravity of raw dry NR is 0.92 and it increases if the rubber is frozen or stretched. The heat of combustion is 10547.04 cal/g, and the refractive index is 1.52. The electrical properties are determined by the presence of water soluble impurities. The extrudability and calenderability of NR is excellent. Another beneficial property of NR is its high rate of cure. When NR is stretched more than 80% of its original length, crystallization occurs due to the orientation of polymer chains. This crystallization enhances the intermolecular attractive forces and this reinforces the strength of the polymer. This strain orientation of the macromolecules gives reinforcement to the vulcanizates of NR, even without reinforcing fillers. NR vulcanizates have higher levels of tensile strength than vulcanizates of most of the synthetic rubbers. NR being non-polar can be readily blended with a great number of other non-polar rubbers [12].

In NR, cis-1,4 isoprene units are arranged in a highly stereo regular manner. The molecular weight of the polymer ranges from $10^5$ to $10^6$ and it varies widely [13]. This corresponds to about 3000 to 5000 isoprene units per polymer chain. Because of its broad molecular weight distribution, NR has an excellent processing behavior. NR is preferred in many areas of application because of its superior building tack, green stock strength, better processibility, high resilience and excellent dynamic properties.

### 1.1.2 Synthetic Rubber

The term synthetic rubber (SR) not only denotes the synthetic analogue of natural rubber, but also a great variety of other rubbery materials produced by chemical synthesis. There are different types of synthetic rubbers depending on the method used for their synthesis or polymerization. They are classified according to ASTM-D 1418-76 or ISO R1629, 1987 [14].

Styrene butadiene rubbers (SBR) are the most commonly used general purpose synthetic rubbers. They are produced by the copolymerization 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.

Polybutadiene comes under general purpose rubbers [1]. Nitrile rubber (NBR) is a copolymer of butadiene and acrylonitrile. NBR has good resistance to a wide variety of oils and solvents [15] and hence is widely used in products like oil seals. Properties of NBR depend on the acrylonitrile content (ACN) and usually it varies from 20-50% by weight. NBR shows no self-reinforcing effect as there is no crystallinity [16]. NR and synthetic rubbers differ in the degree of unsaturation, polarity, etc. [17].

Neoprene is the generic name for polymers of 2-chloro-1,3-butadiene (chloroprene-CR). The molecular structure of neoprene polymers are primarily trans-1,4 chloroprene units, but three other configurations viz. cis (1,4), (1,2) and (3,4) also occur. The degree of crystallinity in neoprene is largely dependent upon the amount of trans configurations in the polymer. CR is a polar rubber. CR has a better resistance to swelling in mineral, animal and vegetable oils and fats as compared to other non-polar diene rubbers. The chlorine atom also imparts to CR better flame, weather and ozone resistance than normally encountered with diene rubbers [18].

The elastomers should have a certain viscosity in order to incorporate fillers and other compounding ingredients easily and to disperse them uniformly. NR has high viscosity. The viscosity can be reduced by mastication. Compared to 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. However one type of rubber may not possess all the physical properties desired in a finished product. Therefore polymers are conveniently and economically modified by combining two or more of them. Elastomer blends are widely used in rubber products for a variety of reasons, which include improved physical properties, improved service life, easier processing and reduced production cost [19].

## 1.2 Natural rubber - processing

Nearly 2000 species of trees, shrubs or vines of the tropical and temperate regions produce latex from which natural rubber or a closely related substance can be obtained. However, the latex from the trees of *Hevea brasiliensis* is the only important commercial source of natural rubber [20]. The tree is indigenous to the Amazon valley. It is cultivated in South East Asia especially in Malaysia, Indonesia, Thailand, India and China. Rubber trees normally grow to a height of 60 feet in a warm, humid climate with fairly distributed rainfall of not less than 200cm. They have well-developed tap roots.

By the controlled cutting on the bark of the tree, fresh field latex is channelled into a container. The pH of the latex ranges from 6.5 to 7 and specific gravity 0.975 to 0.98 with variable viscosity [21]. The latex, when it comes out of the tree gets contaminated with microorganisms like bacteria and yeast [22]. As it has high water content and susceptible to bacterial attack, the latex gets coagulated within hours of leaving the tree unless a preservative is added. The microorganisms metabolise the non-rubber contents of the latex and produce volatile fatty acids such as formic, acetic and propionic acid. This causes coagulation of the latex [23]. This problem was solved by Johnson [24], when he discovered that addition of ammonia can prevent coagulation of the latex. Widely, ammonia is used as preservative in latex because ammonia can inhibit bacterial growth and can act as an alkaline buffer. It acts by raising the pH and by neutralizing the free acid formed in latex. Latex preserved with higher percentage of ammonia is known as high-ammonia (HA) latex. High percentage of ammonia causes processing problems and is also hazardous to the workers dealing with it. So the practice now is to use NR latex containing less percentage of ammonia and a secondary preservative [25]. Latex coagulation is prevented by the addition of small amounts of stabilizers, such as ammonia (0.01%), sodium sulphite (0.05%) or formaldehyde (0.02%).

For higher dry rubber content (drc), the normal latex is concentrated, so that a large portion of serum and some small rubber particles are removed. By doing this better uniformity in composition is also obtained. For most product manufacture, latex of 60% minimum drc is essential. There are different methods for concentrating the latex. The important methods used are (a) evaporation (b) creaming (c) centrifuging and (d) electro decantation. Among this, creaming and centrifuging are the most commonly used processes for the concentration of preserved field latex [25].

NR latex concentrate is a highly specified raw material. The significant latex properties are dry rubber content (DRC), non-rubber solid content (NRS), mechanical stability time (MST), volatile fatty acid number (VFA), potassium hydroxide number (KOH No:) and alkalinity [26]. Latex viscosity decreases with increasing shear rate and also depends considerably on its solid content and particle size distribution. The thickness of the film deposited during the manufacture of dipped rubber products depends on the viscosity of the latex concentrate [27].

### 1.2.1 Dry rubber production

The process of conversion of fresh latex and/or field coagula into a suitable marketable form of raw rubber is called primary processing as another stage of processing is necessary to convert the raw rubber into a finished product. The various marketable forms of raw rubber include preserved field latex, concentrated latex, ribbed smoked sheet (RSS), air dried sheet (ADS), block or technically specified rubber (TSR), pale latex crepe (PLC), estate brown crepe (EBC) and other lower grade crepes made from field coagula.

The conventional forms of NR such as RSS and crepes are graded according to the International Standards of Quality and Packing for Natural Rubber Grades. Grading is by visual examination based on the presence of dirt, bubbles, uniformity and intensity of colour. The advantages of TSR include assurance of quality for important technical parameters, consistency in quality, minimum space for storage and clean and easy to handle packing. This method enables NR producers to process both latex and field coagulum using almost the same set of machinery and to minimise the processing time to less than 24 hours.

### 1.2.2 Sheet rubber production

Field latex stabilized against coagulation is collected in bulk, screened to remove foreign matter, diluted and the rubber coagulated with acid. The coagulum, a white spongy mass, is squeezed between contra rotating rollers to remove much of water and serum and then dried to a moisture content of less than 1% by heat. During the squeezing operation coagulum is washed thoroughly with iron-free water on the roll mills. Iron-free water is used to prevent oxidative deterioration of the rubber in storage. The coagulum is then passed through successive two-roll mills and the last pair of rollers has rib that imparts a ribbed appearance to the sheet and finally dried to obtain sheet rubber. Depending on the drying method, sheet rubbers are classified into two: ribbed smoked sheets and air dried sheets [28].

**Crepe rubbers:** When coagulated latex or any form of field coagulum is passed several times in between a minimum of 3 mills with heavy rolls, a crinkly lace-like rubber is obtained. This lace like rubber when air dried is called crepe rubber. The different types of crepe rubbers are pale crepe, sole crepe, brown and blanket crepes.

**Technically specified natural rubbers (TSR):** These were developed in 1960s to make natural rubber more attractive in competition with synthetic rubbers. Consequently new methods of processing and presentation were developed to market natural rubber as TSR in compact bales, wrapped in polyethylene film.

### 1.2.3 Modification of NR

Nitrogen content of deproteinised natural rubber (DPNR) is only about 0.07%. It is made by treating natural rubber latex with a bio-enzyme to hydrolyse the protein present. It is useful when low water absorption is wanted and vulcanisates with low creep are needed.

Oil-extended rubber (OENR) can be made in three ways: (1) co-coagulation of latex with an oil emulsion, (2) Banbury mixing of the oil and rubber and (3) allowing the rubber to absorb the oil in pans until almost all is absorbed. Both aromatic and naphthenic oils are used. It is used where high black and oil contents are wanted in a natural rubber stock or blends with natural rubber. They make excellent flexible molds to release waxes, gypsums and ceramics easily with excellent surface reproduction and dimensional stability. Other uses include binders in grinding wheels and automotive sealants though they are not recommended for outdoor exposure.

Epoxidised natural rubber (ENR) is made by the partial epoxidation of rubber molecule. Commercially two grades were developed (i) 25 mol% epoxidized-ENR 25 (ii) 50 mol% epoxidized-ENR 50. It has improved oil resistance and lower gas permeability than natural rubber. It is used in adhesives and the protective systems against ozone attack [28].

### 1.2.4 Uses of natural rubber

**Mechanical Goods (Industrial Products):** These include a large variety of products such as hose, conveyor belts, rubber linings, gaskets, seals, rubber rolls, rubberised fabrics, etc. Natural rubber is preferred in some products because it has certain properties that cannot be matched by any other rubber.

**Tyres:** In passenger car, natural rubber is used in the carcass as well as in the side wall, due to the superior fatigue resistance and low heat build-up. In commercial vehicles, the amount of NR used increases with the size of the tyre. In large earth mover tyres, almost 100% NR is used due to the requirements of low heat generation and high cutting resistance. It is also used in blends with halobutyl rubbers and SBR in the inner liner of tubeless tyres.

**Engineering Products:** Rubber is a unique engineering material, unlike other engineering solids, as it has high elastic resilience. The stiffness of NR component in different directions may be varied independently by the judicious use of shape effects. High fatigue resistance, good strength and durability are additional properties in favour of NR in dynamic applications such as springs, antivibration mounting and bushings. In other applications such as bridge bearings, earthquake bearings and rocket nozzle bearings factors such as weathering, ozone resistance, and low-temperature flexibility are also important. NR is accepted as suitable for use in bridge bearings, in place of neoprene.

**Latex Goods:** The main use of latex is in dipped goods, foam, carpet backing, thread and adhesives.

**Footwear:** NR is extremely suitable for rubber footwear [29].

## 1.3 Processing and properties of SBR

Styrene butadiene rubber is a copolymer of styrene and butadiene. The mixture of these two monomers is polymerised by different process such as solution (S-SBR) or emulsion (E-SBR). E-SBR produced by emulsion polymerization is initiated by free radicals. S-SBR is produced by an anionic polymerisation process, with strict exclusion of water. S-SBR is favoured more than E-SBR because it offers improved wet grip and rolling resistance, which translate to greater safety and better fuel economy. Formulations of the monomers are 70-75% butadiene and 30-25% of styrene. Polymerisation may be done at 40-50 °C giving hot SBR or it may be conducted at lower temperature of 5 °C or even lower than this to give cold SBR rubber. SBR containing 30-50% bound styrene is useful as rubbers in the design of tread compounds for tyres with improved road grip. Although cold SBR is often preferred to hot for optimum physical properties, hot SBR can be better for both processing and product properties. Hot SBR breaks down more rapidly to a desirable molecular weight on the mill, develops less heat and accepts more filler in processing. These rubbers are seldom used alone and are blended with other rubbers like NR, NBR, etc. SBR is blended with NR in appropriate proportions for the production of hard vulcanisates. Copolymers with still higher bound styrene contents (up to 90%), known as high styrene resins, is used for imparting improved hardness and stiffness to NR and SBR vulcanisates.

The compounding of SBR is similar to that of NR and other unsaturated hydrocarbon rubbers [30]. The most convenient and effective compounding of SBR is based on fillers, extending oils, zincoxide, sulphur, accelerators such as mercaptobenzothiazole, and protective agents such as antioxidants, antiozonants, and waxes. Processing these complex mixtures, into smooth compounds, that can be quickly pressed, sheeted, calendered, or extruded is a most important step for manufacture of products. E-SBR, a “general-purpose” rubber, has ability to be blended, with any other such rubber into compounds. It is said to have “cure-compatibility” and “excellent processing” or “processability.” The good processing of SBR results from its favourable combination of molecular weight and molecular weight distribution and the considerable proportion of long branches in its molecules. The main advantages of S-SBR is that it can be constructed so as to have just enough branching and molecular weight distribution for adequate processing, with maximised molecular weight for rolling resistance and wear.

Compounding recipes with low sulphur or with only organically bound sulphur, as in thiozoles, lead to vulcanisates with better aging but slow curing. Zinc stearate or zinc oxide with stearic acid, is the most common activator for SBR. There are many accelerators that speed up slow-curing stocks and retards scorch. Recipes may also contain plasticisers, softeners, tackifiers and other ingredients that can solve compounding problems. The ingredients are mixed in internal mixers or on mills and may be extruded, calendered, moulded and cured in conventional equipment.

SBR is much superior to NR with respect to tyre tread-wear, aging properties and ozone resistance. Resistance to crack initiation is better. Building tack is poor and dynamic properties are such that heavy-duty tyres become too hot in use. Without reinforcing fillers, the physical properties of SBR are much inferior to those of NR. The tensile strength of the compound is distinctly inferior to those of NR. This is the principal reason for using higher proportion of NR in radial tyres. It is also characterised by relatively high heat build-up and poor resilience. The abrasion resistance of SBR is as good as NR or slightly better. SBR was originally developed for the production of tyre. A good balance of desirable properties, production economics of the raw rubber grades and easy processing characteristics made SBR popular. Different types of SBR blends with other rubbers were carried out by several researchers [31, 32].

### 1.3.1 Applications of SBR

Of all the SBR produced, about 75% goes into tyre manufacture. The rest goes into shoes and other footwear, mechanical goods, sponge and foamed products, water proofed materials, hose, belting, adhesives and other miscellaneous uses mostly carpet-back coating. The next larger use is in construction industry [29].

## 1.4 Vulcanizing (Curing) Agents

Substances that can bring out actual crosslinks between the chains of the rubber molecules are called vulcanizing agents. Charles Goodyear mixed sulphur with natural rubber and subjected it to heat to transform a plastic substance into an elastic substance. Years later, it was learned that the sulphur actually crosslinked the different chains of the rubber molecules.

Eventually chemicals other than sulphur were also used to crosslink elastomers, resulting in the term crosslinking to become synonymous with vulcanization. In addition to sulphur, various organic peroxides, quinines, metal oxides, bifunctional oligomers, resins, amine derivatives, etc. are used. Vulcanization can also be achieved by using radiations like gamma and X-radiation without any vulcanization chemicals. The saturated rubbers cannot be crosslinked by sulphur and accelerators. Organic peroxides are necessary for the vulcanization of these rubbers or those which do not contain any reactive groups capable of forming crosslinks. By the decomposition of peroxides free radicals are formed on the polymer chains, and these chains combine to form crosslinks of carbon to carbon bonds and they are quite stable. This type of linkages can be formed by radiations. Thus the importance of peroxide is the ability to crosslink saturated elastomers, silicone rubber, etc. which cannot be crosslinked by other vulcanizing agents.

The type of crosslinking agent required varies with the type of rubber to be used. They are usually grouped as (a) sulphur and related elements, (b) sulphur-bearing chemicals and (c) non -sulphur systems.

**Sulphur and Related Elements:** The most common agent used is sulphur. It enters into reaction with the majority of the unsaturated rubbers to provide a crosslinked network of molecular chains with visco-elastic properties. Selenium and tellurium in the same periodic family may also be used in place of sulphur when excellent heat resistance is required. They are capable of shortening the cure time and improving some vulcanizate properties.

**Sulphur-Bearing Chemicals:** Accelerators and similar compounds can be used as a source of sulphur for the vulcanization of natural and styrene-butadiene rubbers. Generally it is a low-sulphur curing system containing 3 to 4 phr of sulphur donor in combination with less than 1 phr of sulphur or without elemental sulphur. This form of vulcanization produces products that resist aging more effectively than normal curing systems. Sulphur-bearing accelerators make the sulphur-vulcanization process safer and more efficient.

**Non-sulphur vulcanization:** Most of these belong to one of three groups: a) metal oxides, b) difunctional compounds or c) peroxides. Carboxylated nitrile, butadiene and styrene-butadiene rubbers can be crosslinked by the reaction of zinc oxide with the carboxylated groups on the polymer chains. Formation of zinc salts by neutralization of the carboxylate groups takes place. Neoprenes and chlorosulfonated polyethylene are also vulcanized by reactions with metal oxides. Other metal oxides like litharge, litharge/ magnesia and magnesia/pentaerythritol combinations are also used [33].

Sulphur and non-sulphur systems have advantages and disadvantages of their own, but sulphur systems still remain versatile [34]. The use of sulphur alone for vulcanization is a very slow process, ineffective and requires 45 to 55 sulphur atoms per crosslink and tends to produce a large number of cyclic crosslinks [35]. Sulphur bloom is also very common in this process. Hence this type of vulcanization where sulphur alone is used is not of technological importance. A major breakthrough was the discovery of organic compounds containing nitrogen, called accelerators. Bases like aniline, thiocarbanilide, etc., were the first organic accelerators used in the vulcanization of rubber. Now a large number of compounds have been suggested as accelerators in the vulcanization of rubbers. In the vulcanization network sulphur is combined in a number of ways as in Fig.1.2. In the form of crosslinks it remains as (a) disulphide, (b) monosulphide or (c) polysulphide. It may be present as (d) pendent sulphides or accelerator terminated pendent group or (e) cyclic monosulphides / disulphides.

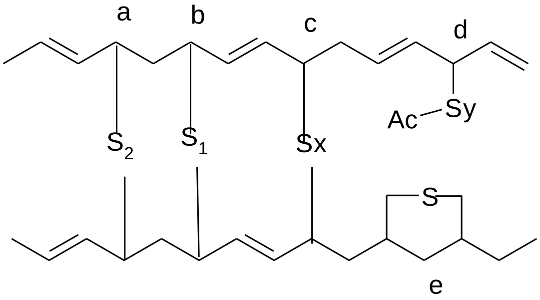


**Fig. 1.2 A Diagrammatic representation of the network**

The accelerator sulphur ratio determines the efficiency by which sulphur is converted into crosslinks, the nature of crosslinks and the extent of main chain modification. Depending on the sulphur accelerator ratio the sulphur vulcanizing system can be categorized as below [36].

| System | Sulphur (phr) | Accelerator (phr) | Accelerator /Sulphur |
|---|---|---|---|
| Conventional | 2.0 - 3.5 | 1.2 -0.4 | 0.1 - 0.6 |
| Semi-efficient | 1.0 - 1.7 | 2.5 - 1.2 | 0.7 - 2.5 |
| Efficient | 0.4 - 0.8 | 5.0 -2.0 | 2.5 - 1.2 |

As the conventional system (CV) has got higher amount of sulphur compared to the accelerator, the possibility for the formation of polysulphidic linkage is high. At higher temperature the polysulphidic linkage may break to mono and disulphidic linkages. This causes reversion at high temperature and which leads to low strength and modulus. Compression set and thermal stability are better for efficient systems (EV), due to the lower amount of polysulphidic linkages. Structural characterization of sulphur vulcanized rubber networks were done by B.Savilla et al. [37]. In EV systems, the network contains more of monosulphidic crosslinks, at least eighty percent of the total. The properties for semi-efficient system (SEV) are usually compromise between EV and CV systems. The vulcanization properties are not only the functions of crosslink density, but they are also affected by the type of crosslink, nature of polymer, type and amount of filler used, etc. [38].

## 1.5 Accelerators

In 1905 George Oenslager discovered that a derivative of aniline called thiocarbanilide accelerated the action of sulphur with rubber, leading to shorter cure time and reducing energy consumption [39, 40]. This discovery was almost as important as the invention of vulcanization of rubber by Goodyear. These accelerators made the curing process not only faster but also improved the reliability of the process and enabled vulcanization to be applied to synthetic polymers also.

Substances that are added in small amounts during compounding to accelerate the vulcanization reaction and to improve the physical and service properties of the finished products are called accelerators. They play an important role in vulcanization of rubber as they affect the scorch safety, the cure rate, the length of sulphur chain and the number of crosslinks formed [41]. They can increase the rate of vulcanization, aging resistance of the vulcanizate and reduce the amount of sulphur without compromising the optimum vulcanizate properties. The decrease in vulcanization time gives increased turnover and consequent reduction in the cost of production. Thus the role of accelerators is of great importance in economy of the industry. The first accelerators used in vulcanization of rubber were in fact inorganic compounds viz. magnesium oxide, litharge, and zinc oxide.

Large varieties of accelerators were developed during the first two decades of 20th century. The discovery of thiuram disulphide to enable vulcanization to proceed without sulphur around 1920 was an epoch making event in the history of rubber industry [42]. Granski and coworkers made a detailed study of the vulcanization of NR with TMTD [43]. In early

1920, Sebrell [44] and Bruni [45] discovered independently that 2-mercaptobenzothiazole, its homologues, its disulphides or its metal salts are very effective accelerators, which yield vulcanizates of improved physical properties. A detailed study was conducted by Chatterjee and Sircar about the reaction between MBT and rubber [46]. Mercaptodibenzothiazyl disulphide (MBTS) was the first delayed action accelerator, which gave great scorch safety at higher processing temperatures. Later more delayed action and yet fast curing vulcanization systems were made available from thiazole derivatives of sulphenamides. Thiocarbamyl sulphenamides were reported to be more productive than the corresponding benzothiazole derivative, due to the combined scorch delay of sulphinamides and the fast acceleration activity of the thiocarbamate both being present in their structure. With the discovery of ultra accelerators, vulcanization can be achieved even at room temperature [47]. A common feature in these accelerators is the presence of –N=C-S-H functional group in the tautomeric form. The time to onset of cure varies with the class of the accelerator used. Usually a long delay period before the onset of sulphur crosslinking occurs with sulphenimide accelerators. The role of accelerator is to react with elemental sulphur, metal oxide or rubber prior to crosslinking reaction. Accelerators can lower the cure temperature and shorten cure time, thus reducing thermal and oxidative degradation. Optimum physical properties could also be obtained with lower sulphur content.

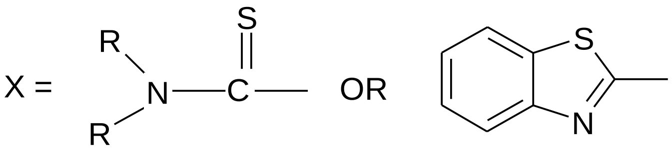
With the introduction of synthetic elastomers and the use of fine furnace blacks, delayed action accelerators like sulphenimide were developed for long processing safety and satisfactory cure rates. Attempts to modify the extra ordinary fast ammonium dithiocarbamate resulted in discovery of zinc dialkyl dithiocarbamates. Thus there are different classes of compounds, which can serve as accelerators in sulphur vulcanization. Following table gives main classes of compounds that are commercially useful either as primary or secondary accelerators in sulphur vulcanization of diene rubbers.

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

Accelerators are also classified as primary and secondary accelerators based on the role they play in a given sample. Generally, thiazole and sulfenamide accelerators play an important role as primary accelerator due to their characteristics of good processing safety, a broad vulcanization plateau and optimum cross link density as well as desired reversion delay. The primary accelerators are used at 0.5 to 1.5 phr dosages in most rubber compounds. The accelerators such as guanidines, thiurams, and dithiocarbamates, are used as secondary accelerators to activate the primary accelerators. The use of secondary accelerators increases the speed of vulcanization substantially but at the expense of scorch safety.

### 1.5.1 Single accelerator system

The nature of the vulcanizing system has a considerable influence on determining the structure of the crosslinks and the extent to which the polymer chains are modified chemically during vulcanization. The chemistry of single accelerator system is simple and therefore majority of the research work concentrates on single accelerator. The accelerated sulphur vulcanization of NR has been studied extensively. It is unclear how the accelerator catalyses the reaction of sulphur with rubber [3, 38]. It is considered to proceed by the following sequence. First, the curatives combine to form a zinc-sulphur-accelerator complex, which can attach sulphur to the rubber to form rubber-Sx-accelerator intermediate. This intermediate either reacts with rubber or combines with another intermediate to form the sulphide crosslink. As vulcanization continues, the initial polysulphidic crosslinks mature and become shorter or involve in a variety of other reactions, depending on the rubber. Considering the generally accepted scheme of vulcanization, it is observed that the zinc accelerator complex is formed continuously. Assuming a low 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. The initially formed polysulpidic crosslinks may be desulphurated or degraded, leading to the final network structure. Majority of accelerator used to assist the sulphur vulcanization of NR are thiozoles, thiuramdisulphides and sulphenamides. They can be represented as XSH, XSSX, XSZnSX, XSNRR, where



A schematic representation of a typical cure curve of the accelerated sulphur system [48] is shown in Fig.1.3. The curve illustrates three main regions [38]. The first region is the scorch delay period or the induction period in which majority of the accelerator chemistry takes place. During this period, various accelerator complexes are formed which are the active sulphurating agents. The extent of this region varies with different accelerators. For example, there is very little scorch time in thiuram types and very long scorch time in sulphenamide types. The second region is the crosslinking period, where the initial network structures are formed and the accelerator intermediate is consumed. The final stage is the over cure or reversion period, during which the property deterioration occurs.

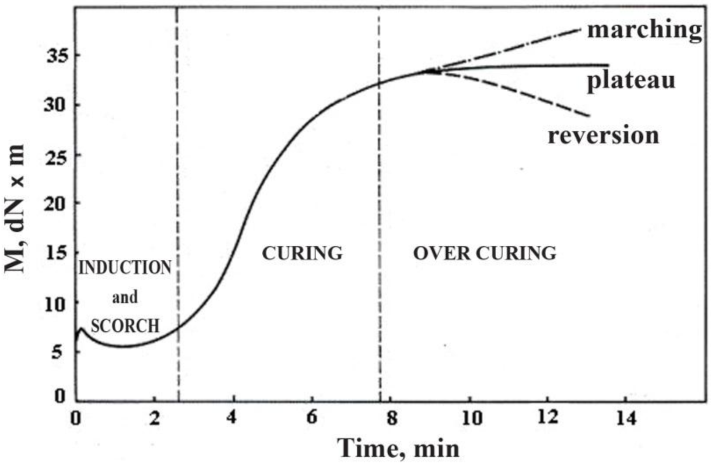


**Fig. 1.3 A typical cure curve obtained from a rheometer for accelerated sulphur vulcanization**

Though the single accelerator system is studied extensively, research on the chemistry of binary accelerator system has not picked up momentum.

### 1.5.2 Binary accelerator system

There is no ideal accelerator i.e., one that is absolutely safe at processing temperature and fast curing at vulcanizing temperature with desired properties. Vulcanization of rubber can be effectively modified by the combined action of two or more accelerators. When the accelerators are mixed in the proper proportions, they can lead to significant improvement in curing behaviour, mechanical properties and prevent pre-vulcanization [49]. Thus mixed accelerator systems find wide technological applications. Certain accelerators such as guanidines, thiurams, and dithiocarbamates, are used as secondary accelerators to activate the primary accelerators. The use of secondary accelerators increases the speed of vulcanization substantially but at the expense of scorch safety. Combination of two or more accelerators, can improve the properties of the vulcanizates. The dosages of the secondary accelerators are generally between 10-20% of the primary accelerator [33].

A binary accelerator system refers to the use of two accelerators in a given formulation. The binary system approaches ideal behavior to some cases [50-52]. 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 the synergistic effect [53]. Some of the more widely used accelerators for binary systems are given in the work of Layer [54]. Several authors [55-57] studied the synergistic behavior of different binary systems.

One of the motivations for the use of binary system is to achieve the mechanical properties of the vulcanizates superior to those produced by either accelerator separately [58].These systems are becoming increasingly popular because of the fact that such mixed systems can effectively prevent pre-vulcanization and permit vulcanization at lower temperature in a shorter time without compromising the mechanical properties [59]. The synergistic behavior of these systems is said to be due to the formation of new chemical moieties, which make the curing process easier [60, 61, 62]. So far a number of binary systems have been developed for industrial use [63].

In binary systems usually thiocarbamate derivatives and benzothiozoles are used. Thiurams generally show very little scorch safety hence with thiurams, sulphenamides or MBT are used in order to increase scorch delay period. Thiourea and its derivatives are also known to be good secondary accelerators in rubber vulcanization [64-66]. A eutectic mixture or a complex salt formed by the binary system has greater chemical reactivity and better solubility in elastomers. It is assumed that this formation of mixture or salt promotes the cure action [67, 68]. A number of accelerator combinations were investigated by Dogadkin and co-workers and found synergistic activities among many of them [69, 70].

They classified binary systems into three groups:

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

The active complex formed depends on the molar ratio of accelerators [71]. In systems with mutual activity such as MBTS with DGP or CBS, the reactions between the accelerators were observed to be higher in vulcanization conditions than when they are reacted alone [72]. Coran et al., reported the use of certain co-activators in delayed action of accelerators in sulphur vulcanization [73]. An effect of using a mixture of two different types of accelerators can be that each activates the other and crosslinking rates can be better than expected. Mixing accelerators of the same type gives intermediate or average results [38].

## 1.6 Accelerator activators

Geert Heideman et al. studied the role of activators in the sulphur vulcanization process using thiuram and sulphenamide accelerators and reported the ability to enhance the cure rate [74].

The activators are the substances used to enhance the vulcanization speed, the cross-link density and to increase reversion resistance, particularly when used in high doses. In most cases the dynamic properties of the vulcanizate products are also improved [75]. It is believed that they form effective intermediates to activate sulphur present in the mixture [76].

**Accelerator activators are grouped as:**

a) Inorganic compounds - mainly metal oxides, alkali carbonates, and hydroxides. Zinc oxide used in combination with a fatty acid to form rubber-soluble soap in the rubber matrix is the most common activator. ZnO is further activated by fatty acid or its salts and this leads to better processing and dispersion of fillers and chemicals [77]. Most of the metal oxides are used in coated or treated forms in order to disperse more readily in the rubber mixtures. Normal usages are 2 to 5 phr.

b) Organic acids - used in combination with metal oxides. They are generally high molecular weight monobasic acid or mixtures of stearic, oleic, palmitic, myristic acids and hydrogenated oils from palm, castor, fish and linseed oils. Usage depends on the type of accelerator used and the amounts of other compounding ingredients. Normal dosage is 1 to 3 phr.

c) Alkaline substances - this will increase the pH of rubber compound and thereby increase the cure rate. Any material that makes the compound more basic will increase the cure rate since acid materials tend to retard the effect of accelerators. Ammonia, amines, salts of amines with weak acids and reclaim rubbers made by the alkali process are some of the examples. Their usage depends on how the above materials are to be used [78]. Vulcanization activators, by favouring a decrease in the number of sulphur atoms in the sulphur bonds, increase the heat stability of the vulcanizates [79].

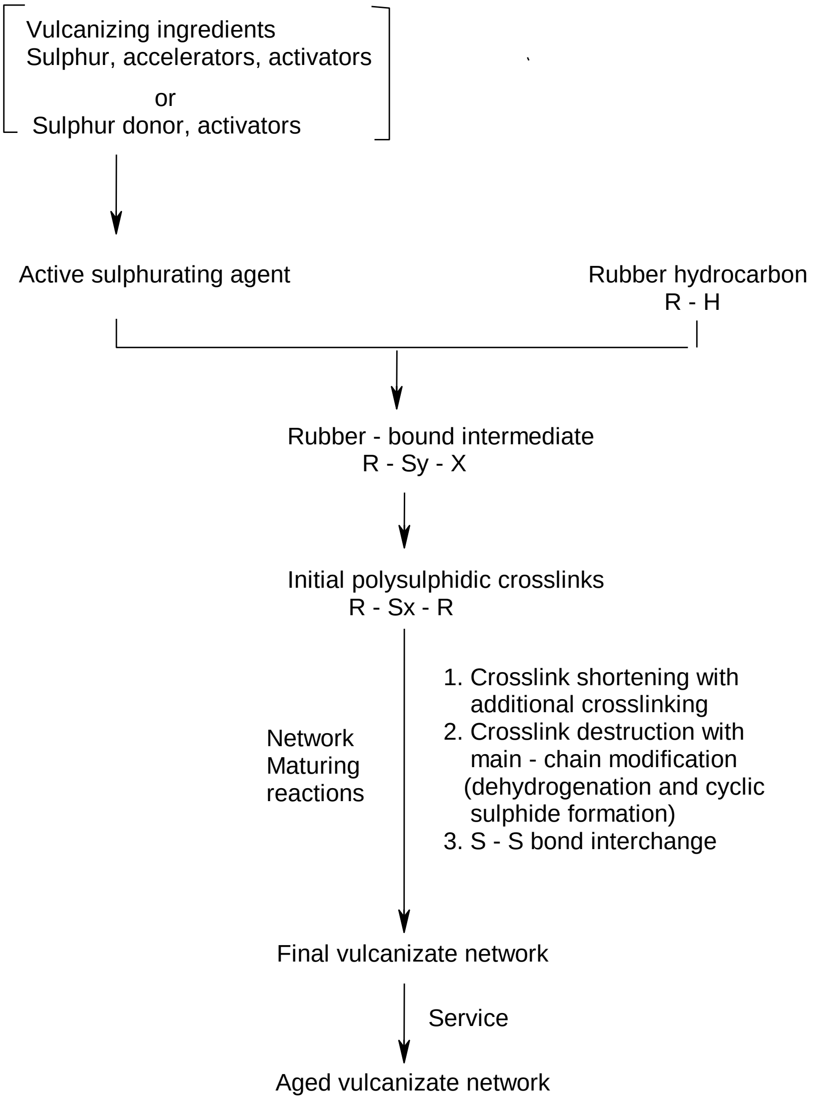
## 1.7 Mechanism of vulcanization

Vulcanization processes are not simple chemical reactions, but they involve complex chemical processes. The un-accelerated sulphur formulation consists of rubber and sulphur, while the accelerated sulphur system contains rubber, accelerator and sulphur. Both the formulations include zincoxide and stearic acid as activators. There is a third category in which elemental sulphur is not used; instead, the accelerator provides the sulphur for vulcanization. This system is generally referred as sulphur donor formulation.

The mechanisms of un-accelerated or the ‘sulphur only’ vulcanization involves reactions such as double bond migration, isomerization, chain cleavage, cyclization, formation of vicinal crosslinks, etc. [80-84]. The mechanism was studied using radical scavengers [85] and electron paramagnetic resonance techniques [86]. These studies revealed a polar (ionic) mechanism in these systems. However the possibility of the $S_8$ ring undergoing homolytic ring opening, producing a radical reaction is also possible [87]. Even though certain reactions proceed by radical mechanism, the general concept is that sulphur only vulcanization occurs via polar mechanism. Though extensive studies have been carried out on mechanism of accelerated vulcanization for the last few decades; there is still disagreement over exact mechanism [7-11,88].

Tsurugi and coworkers have suggested free radical mechanism to explain the result of accelerated sulphur vulcanization. Whereas Bateman [4] and Allen [84] suggested polar mechanism, to explain un-accelerated sulphur vulcanization. But Shelton, McDonel [85] and Coran [89] proposed mechanism involving both the free radical and ionic species. It can be believed that in a complex mixture of rubber, zinc oxide, sulphur, fatty acids and accelerators, both free radical and ionic reactions, may occur simultaneously at different stages of the vulcanization reaction depending on the system used [90].

Now it is generally accepted that vulcanization of natural rubber by sulphur and accelerator or sulphur donor follows simple reaction sequence. The overall course of accelerated sulphur vulcanization can be represented as in scheme 1.1[91].



**Scheme 1.1 Generalised mechanism of vulcanization**

The active sulphurating agent formed by a sequence of reactions from sulphur, accelerator, and activators or from a sulphur donor and activator reacts directly with rubber hydrocarbon to form C-S bonds. This gives a rubber-bound pendent group where the fragment (X), derived from the accelerator or sulphur donor is linked through two or more sulphur atoms to the rubber chain. These pendent groups are the immediate precursors to the crosslinks. The crosslinks are formed either by direct reaction with another rubber molecule or disproportionate with a second pendent group of a neighboring rubber chain. The polysulphidic crosslinks are formed first. These are thermally unstable and chemically reactive and can undergo a number of competing reactions, called maturing reactions, leading to the final network structure.

In radical mechanism of accelerated sulphur vulcanization, the accelerator cleaves to form a radical which then abstract proton from rubber hydrocarbon to form a free radical. The rubber radical reacts with another intermediate to form rubber-bound intermediates. Two such rubber-bound intermediates then form the actual crosslinks.

## 1.8 Fillers in rubber industry

The strong reinforcement effect of filler particles on the mechanical behaviour of elastomers is well known for decades and has significantly contributed to the use of rubber materials in the tyre industry. Fillers are usually inorganic powders of small particles incorporated during compounding for various purposes. Choice of the type and amount of the fillers to be used depends on the hardness, tensile strength and other properties required in the product. They are broadly classified as reinforcing and non-reinforcing fillers depending on the properties of the final product.

### 1.8.1 Non-reinforcing fillers

Fillers that are included mainly to make the product cheap and stiff are termed as non-reinforcing fillers. Some of them are china clay, barites (barium sulphate), calcium carbonates, mica, titanium dioxide ($TiO_2$) and silicates of calcium and zinc. These inactive fillers can bring out small increase in the viscosity of the compound and can cause deterioration to mechanical properties of the vulcanizate. The size of the filler particle is one of the most important parameters for reinforcing. Generally coarse particles are non-reinforcing.

### 1.8.2 Reinforcing fillers

These fillers are incorporated primarily to improve the strength of the product. Carbon blacks, silica, silicates, etc. belong to this class. In a broader sense the reinforcement in rubber industry means the improvement in abrasion, tear, stiffness, cutting and rupture resistance of the products. Reinforcement by filler leads to the enhancement of one or more properties of elastomers by making it more suitable for a given application [92, 93]. It is generally agreed that strong links exist between rubber molecular chain and reinforcing filler particles [94].

Organic fillers like resorcinol-formaldehyde resins added as an aqueous solution to rubber latex followed by drying and curing at low temperature gives a larger improvement (reinforcement) in tensile strength, modulus and elongation. Alkaline lignin and starch derivatives are reported to have certain reinforcing effect when added in the form of aqueous solution to natural or synthetic latex. None of these organic fillers is of commercial importance.

## 1.9 Polymer blends

A polymer blend or polymer mixture is a member of a class of materials analogous to metal alloys, in which at least two polymers are blended together to create a new material with different physical properties [95]. The blending of commercially available polymers provides the manufacturer with a new technique for the modification of already existing polymers, by an inexpensive route. Polymer blends are gaining technological importance due to their variability of properties. By blending two or more elastomers, it is possible to attain properties that are not available with a single elastomer. The most important concept in polymer blends is that, the resulting blend has a property which is the weighted average of the properties of the individual polymers. Polymer blends can be obtained by methods such as melt mixing, solution mixing, latex blending, etc. These methods do not involve the formation of chemical bonds between the polymers. The commercially used blends are usually made of NR, SBR, BR, NBR and EPDM.

### 1.9.1 Classification of polymer blends

Blends are classified in to three categories viz. miscible, partially miscible and immiscible or in a technological sense as compatible, semi-compatible and incompatible. The most important polymeric properties pertaining to elastomer blends are phase morphology (homogeneity of mixing) and cure compatibility. For complete miscibility of polymers the free energy of mixing should be negative and this can be achieved by exothermic mixing or large entropy of mixing [96]. Most blends of elastomers are immiscible as mixing is endothermic and the entropy contribution is small because of high molecular weights. Fortunately miscibility is not a criterion for most rubber applications.

To obtain the optimum compromise in the properties of a rubber blend, it is always better to use rubbers of closest solubility parameter values. The cured blends of dissimilar polymers having large differences in polarity and unsaturation for example EPDM and NBR, usually show inferior properties, well below the values anticipated from the additive property. Cured blends of polymers with similar polarity and unsaturation, frequently show additive properties as in cured blends of SBR and BR [97]. One advantage of heterogeneous polymer blends is the ability to alter the phase morphology for specific performance criteria [98]. This type of alteration is more difficult with homogeneous blends. Miscible (single phase) blends are usually optically transparent and are homogeneous to the polymer segmental level. Single-phase blends also undergo phase separation that is usually brought about by variations in temperature, pressure, or the composition of the mixture [99].

### 1.9.2 Effect of fillers in polymer blends

Generally speaking, all the phenomena regarding the morphology of polymer blends are governed by thermodynamic and kinetic effects, as well as the localization of particles. Concerning the kinetic effects, the final localization of fillers in a polymer pair is guided by the sequence of mixing of the components, viscosity ratio, composition, temperature, shear rate and the time of mixing. When the particles are placed at the interface between two polymers, they play the role of compatibilizers. In a ternary system the final properties of the material, such as mechanical, conductive, magnetic and thermal properties depend on (i) the shape of the particle (spheres, rods or “onions-shape”), (ii) the particle radius and (iii) the surface chemistry of the particles [100]. In an immiscible blend, the amount of each polymer in any phase can be modulated by changes in the viscosity and chemical identity of the elastomers, the surface chemistry of filler, the sequence of addition of the components and that of the mixing procedure. The mixing methods for preparing elastomer blends can be divided into two general categories viz. ‘pre-blending’ and ‘phase mixing’ [101]. In the first case, the compounding ingredients are added to the premixed polymers in a manner similar to the mixing of a single elastomer. In a phase mix, an attempt is made to control the specific location of filler, extender oil and curing agents. This is done by the preparation of separate master batches, which are then blended mechanically.

### 1.9.3 Applications of polymer blends

With increased academic and industrial research interest, application of polymer blend technology of commercial utility has grown significantly. Unique applications for polymer blends include immobilization of enzymes, permi-selective membranes, reverse osmosis membranes, selective ion-exchange systems and medical applications.

The applications of polymer blends have been commercialized by replacing traditional materials, generally metals. Although costlier than metals on weight basis, they are often more economical in terms of final manufacturing cost. It has more corrosion resistance, lighter than metals, which is especially important for fuel economy in automotive applications [102]. Nanostructured polymer blends and composites find applications across many sectors like electronics, coatings, adhesives, energy (photovoltaics), aerospace, automotive, and medical devices (biocompatible polymers). The reuse of polymer scrap is going to be a promising future application for polymer blends [103]. Incorporation of waste tyre rubber (WTR) into polymeric matrices in elastomer blends has shown the most promising properties, which is capable of commercialization and is also a viable solution to address polymeric waste problem [104].

## 1.10 Review/ Relevance of the present work

Among the binary accelerator systems, thiourea (TU) and its derivatives are favourable for making improvements in the vulcanization process and mechanical properties of rubber composites, [105,106]. Kurien et al. [107] synthesized a TU derivative, namely amidinothiourea (ATU) and studied the vulcanization properties of natural rubber (NR) with binary accelerator systems including tetramethylthiuram disulphide (TMTD), mercaptobenzothiazyl disulphide (MBTS), or cyclohexyl benzthiazolsulphenamide (CBS). The induction time and optimum curing time of the formulations with ATU or TU were shorter than those of the control mix without ATU or TU. Moreover the above author also found that the rubber compound with ATU presented the fastest curing rate. Some of the important members of thiourea accelerators are ethenylthiourea, N,N'-dimethylthiourea, syn-di-(o-tolyl)thiourea, 1-phenyl-N,N'-diphenyl-amidinothiourea, etc. Thiourea accelerators are almost exclusively used as organic accelerators in neoprene stocks. Ethenylthiourea (ETU) and

N,N'-diethylthiourea are particularly useful in injuction moulded stocks, sponge and liquid curing medium (LCM). Philpot has shown that, sulphur-containing nucleophiles enable accelerators like tetramethylthiuram disulphide (TMTD) to operate at lower vulcanization temperatures. He suggested an ionic mechanism for vulcanization reactions where the S-S bond in TMTD is cleaved by the nucleophile produced from thiourea [107].

The exact mechanism of the chemical reactions involved when binary accelerator systems are used in rubber vulcanization is not fully understood so far. Accelerators in which sulphur is combined as S-S, C-S-C or S-N are generally inactive at lower temperatures because of the high thermal stability of the sulphur bonds [108]. Investigations of Kuriakose et al. [109-113] found that the higher the nucleophilicity of the thiourea derivative, the greater is the rate of vulcanization. They found that N-amidino-N'-phenyl thiourea (APT) can be effectively used as a secondary accelerator in the binary systems containing MBTS, TMTD or CBS in NR vulcanization where carbon black or silica is used as filler. APT being more nucleophilic than thiourea, a nucleophilic reaction mechanism was suggested. Considering the non-reverting nature of some of the mixes containing APT, amidinothiourea derivative seemed to act as an anti-oxidant also. The percentage retention of tensile properties of the vulcanizates containing APT is also found to be satisfactory [114].

Shu-yanYang et al. [115] prepared N-phenyl-N′-(γ-triethoxysilane)-propyl thiourea (STU), and investigated its accelerator property with CBS. Compared to the references, the optimum curing time of NR compounds with STU was the shortest, indicating the presence of a more nucleophilic reaction. Accelerators like MBTS or CBS when used alone does not give much crosslinking in diene rubbers. But when used with thiourea rapid crosslinking occurs. Investigations made in this laboratory on secondary accelerators in the vulcanization of different elastomers, showed that the optimum cure time values in general decreased when the compound is more nucleophilic.

## 1.11 Scope of the Present Work

Technological importance of an accelerator in rubber industry is the ability to decrease vulcanization time and increase the production rate. Thus the role of accelerator in rubber industry acquires great importance. Therefore the processing of elastomers is governed by the type of accelerators or accelerating systems.

Binary accelerator systems are increasingly popular in rubber industry as it can effectively facilitate the vulcanization process at a lower temperature and in a shorter time. These binary systems can also provide better chemical properties, improvement in physical properties and finally bring in superior mechanical properties for the vulcanizate. Among these systems, thiourea (TU) and its derivatives are advantageous for improving the vulcanization process and mechanical properties of rubber composites. The ever increasing demand for vulcanized rubber in automobile and other industries necessitated the need to discover newer thiourea derivatives to give vulcanizates with varying mechanical properties. The reductions in energy and cost effectiveness are of prime importance in sustaining the growth of the industry. This prompted to investigate the viability of novel thiourea derivatives which can bring out vulcanization in shorter time with scorch safety, reversion resistance and vulcanizate with better mechanical properties. The intention was to find a new compound with more nucleophilic character than thiourea to increase cure rate. The new accelerator used shall be capable of imparting better rheometric properties in different elastomers and also in their blends as it is of prime importance to the industry. It is also desired that the proposed accelerator can bring out synergistic effect in combination with known other accelerators to produce vulcanizate of superior mechanical properties without compromising cure characteristics. The new accelerator is also expected to work in NR latex as it prefers low temperature for curing.

Thiazole moiety is present in commercially available accelerators such as MBT, MBTS and ZMBT. Thiazoles are medium-fast primary accelerators with only moderate processing safety. They are most widely used accelerators in the rubber industry for the production of wide variety of goods such as cycle tyres and tubes, footwear, beltings, hoses and other moulded and extruded goods. Thiazoles are activated by zinc oxide / stearic acid combination and produce flat cure with vulcanizates having very good reversion resistance.  On account of this, three derivatives of phenylthiazoles synthesised by Thomas et al. viz. a) 2-(N,N-Dimethylamino)-5-(indol-3-oyl)-4-phenylthiazole, b) 2-( N,N-Diethylamino)-5-(indol-3-oyl)-4-phenylthiazole and c) 2-(N,N-Methylphenylamino)-5-(indol-3-oyl)-4-phenylthiazole were investigated for their accelerator activity in sulphur vulcanization of natural rubber in a binary system containing conventional accelerator (MBTS).

**The specific objectives of the present investigations are:**

1) To synthesise thiourea derivatives viz.
    a) N-benzoyl-N$^{I}$,N$^{I}$-pyrrolidinylthiourea (BPTU)
    b) N-benzoyl-N$^{I}$,N$^{I}$-diphenylthiourea (BDPTU)
    and characterisation by IR, $^{1}$H NMR, $^{13}$C NMR, CHN & TG analysis and melting point.

2). Prepare three phenylthiazoles viz.
    a) 2-(N,N-Dimethylamino)-5-(indol-3-oyl)-4-phenylthiazole,
    b) 2-(N,N-Diethylamino)-5-(indol-3-oyl)-4-phenylthiazole and
    c) 2-(N,N-Methylphenylamino)-5-(indol-3-oyl)-4-phenylthiazole

3). To study the effect of
    a) thiourea derivatives as a accelerators in the vulcanization of NR gum.
    b) thiourea derivatives in the vulcanization of NR gum along with MBTS and CBS.
    c) phenylthiazole derivatives in the vulcanization of NR gum along with MBTS.

4). To study the effect of BPTU as an accelerator in the vulcanization of:
    a) silica filled NR along with MBTS and CBS.
    b) SBR gum and silica filled system along with MBTS and CBS.
    c) NR /SBR blends (gum) and silica filled system along with MBTS and CBS.
    d) carbon black filled NR, SBR and NR/SBR blends
    e) NR latex along with ZDC.

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Chapter 2

# EXPERIMENTAL TECHNIQUES AND MATERIALS USED

Contents

The specifications of the materials and details of the experimental techniques used in this study are given in this chapter.

## 2.1 Materials

### 2.1.1 Natural rubber (NR)

The natural rubber used in this study was ISNR-5 of Mooney viscosity (ML 1+4, 100 $^{o}$C) 85, obtained from the Rubber Research Institute of India, Kottayam. Rubber from the same lot has been used for the experiments since it is known that the molecular weight, molecular weight distribution and non rubber constituents of natural rubber are affected by clonal variation, season, use of yield stimulants and method of preparation [1]. The current ISO specifications for the grade of rubber are given in the Table 2.1 [2].

**Table 2.1 Specifications for ISNR – 5 (ISO 2000: 1989 (E))**

| Characteristics | Limit | Test method |
|---|---|---|
| Dirt content, % (m/m) retained on 45 μm sieve, max. | 0.05 | ISO 249 |
| Ash, % (m/m), max. | 0.60 | ISO 247 |
| Initial plasticity, min. | 30 | ISO 2007 |
| Plasticity retention index (PRI), min. | 60 | ISO 2930 |
| Nitrogen content, % (m/m), max. | 0.60 | ISO 1656 |
| Volatile matter content, % (m/m), max. | 0.80 | ISO 248<br>(Oven method at100±5 °C) |

### 2.1.2 Styrene Butadiene Rubber (SBR)

Styrene butadiene rubber used was TAIPOL 1502 of Mooney viscosity (ML 1+4, 100 °C) 46, obtained from Indian Synthetic Rubber Ltd., Delhi, India. The specifications of TAIPOL SBR 1502 are given in Table 2.2.

**Table 2.2 Specifications of TAIPOL SBR 1502**

| Characteristics | Limit | Test method |
|---|---|---|
| Bound styrene, (%) (max) | 24.5 | ASTM D 5775 |
| Ash, (% ) | 0.75 | ASTM D 5667 |
| Organic acid, (%) (min) | 4.75 | ASTM D 5774 |
| Soap, (%) | 0.50 | ASTM D 5774 |
| Volatile matter, (%) | 0.75 | ASTM D 5669 |

### 2.1.3 Centrifuged natural rubber latex

The specifications of the centrifuged natural rubber latex (high ammonia (HA) type as per ASTM D 1076-2010) collected from Central Experiment Station, Rubber Board, Chethackal, Ranni, Kerala are given in Table 2.3.

**Table 2.3 Properties of centrifuged natural rubber latex**

| Properties | Value |
|---|---|
| Dry rubber content (% by mass) | 60 |
| Non rubber solids (% by mass) | 1.0 |
| Sludge content (% by mass) | 0.04 |
| Ammonia content (% by mass) | 0.8 |
| Potassium hydroxide number | 0.5 |
| Mechanical stability time (s) | 1000 |
| Volatile fatty acid number | 0.01 |
| Coagulum content (% by mass) | 0.03 |
| Copper content (ppm) | 1 |
| Manganese content | Traces |

### 2.1.4 Compounding Ingredients

#### a. Vulcanizing agent - Sulphur

Sulphur with the specifications shown below was supplied by Standard chemicals Co. Pvt. Ltd., Chennai.

| Parameter | Value |
|---|---|
| Specific gravity | 2.05 |
| Acidity, max (%) | 0.01 |
| Solubility in $CS_2$ (%) | 98 |

### b. Accelerators

### (i) N-Cyclohexyl-2-benzthiazolsulphenamide (CBS)

CBS was obtained from Merchem Ltd., Cochin, India. The specification of CBS is as shown below.

| Parameter | | Value |
|---|---|---|
| Melting point (°C ) | Initial | 99 |
| | Final | 100 |
| Density (25 °C, kg/m$^3$) | | 650 |

### (ii) 2-Mercaptodibenzothiazyl disulphide (MBTS)

MBTS was obtained from Merchem Ltd., Cochin, India. The specification of MBTS is as shown below.

| Parameter | | Value |
|---|---|---|
| Melting point (°C ) | Initial | 164 |
| | Final | 168 |
| Density (25 °C, kg/m$^3$) | | 1550 |

### (iii) Tetramethylthiuram disulphide (TMTD)

TMTD was obtained from Merchem Ltd., Cochin, India. The specification of TMTD is as shown below.

| Parameter | | Value |
|---|---|---|
| Melting point (°C ) | Initial | 144 |
| | Final | 148 |
| Density (25 °C, kg/m$^3$) | | 1450 |

### (iv) Thiourea (TU)

TU was of AR grade supplied by Sisco Research Laboratory, Mumbai, India. It had specifications as shown below.

| **Parameter** | | **Value** |
|---|---|---|
| Melting point ($^oC$ ) | Initial | 172 |
| | Finial | 178 |
| Ash, max (%) | | 0.1 |

### (v) Zinc diethyldithiocarbamate (ZDC)

ZDC was obtained from Merchem Ltd., Cochin, India. The specification of ZDC is as shown below.

| **Parameter** | | **Value** |
|---|---|---|
| Melting point ($^oC$ ) | Initial | 176 |
| | Final | 178 |
| Density (25 $^oC$, $kg/m^3$) | | 350 |

## c. Anti-oxidants

### (i) Polymerized 1,2-dihydro-2,2,4–trimethylquinoline(TQ)

TQ was obtained from Merchem Ltd., Cochin, India. The specification of TQ is given below.

| **Parameter** | **Value** |
|---|---|
| Softening point ($^oC$ ) | 83 - 97 |
| Dimer content (%) | 45 |
| Bis aniline content (%) | 0.2 |
| Density (25 $^oC$, $kg/m^3$) | 1100 |

### (ii) Styrenated phenol (SP)

SP was supplied by Merchem Ltd., Cochin, India. The specifications are:

| Parameter | Value |
|---|---|
| Specific gravity | 1.08 |
| Flash point ($^{o}$C ) | 182 |
| Acidity (%) | 0.1 |

## d. Other chemicals

### (i) Zinc oxide (ZnO)

Zinc oxide was supplied by M/s Meta Zinc Ltd., Mumbai. The specifications are:

| Parameter | Value |
|---|---|
| Specific gravity | 5.5 |
| ZnO content (%) | 98 |
| Acidity (%) | 0.4 |

### (ii) Stearic acid

Stearic acid was supplied by M/s Godrej Soaps Pvt. Ltd., Mumbai. The specifications are as shown below.

| Parameter | Value |
|---|---|
| Specific gravity | 0.85 |
| Melting point ($^{o}$C ) | 50-69 |
| Acid number | 185-210 |

### (iii) Diethylene glycol (DEG)

DEG was obtained from M/s Merck Ltd., Mumbai, India. The specification of DEG are:

| Parameter | Value |
|---|---|
| Flash point ($^{o}$C ) | 140 |
| Boiling point ($^{o}$C ) | 245 |
| Density (at 20 $^{0}$C ) | 1.12 |
| Viscosity (at 40 $^{0}$C, cSt) | 43 |

### e. Fillers

### (i) High abrasion furnace black (HAF-black)

High abrasion furnace black (N330) used in the study was supplied by M/s Philips carbon black India Ltd., Kochi, India. The specifications of the black are:

| Parameter | Value |
|---|---|
| Appearance | Black granules |
| DBP absorption (cc/100g) | 102 ± 5 |
| Pour density (kg/m$^3$) | 376 |
| Iodine adsorption number (mg/g) | 82 |

### (ii) Precipitated silica

Precipitated silica of commercial grade supplied by Minar Chemicals, Kochi. The following are the specifications.

| Parameter | Value |
|---|---|
| pH(5 % aqueous solution) | 6.3 |
| Density(g/cc) | 2.03 |
| $SiO_2$ content (%) | 90 |

### f. Process Oils

### (i) Naphthenic oil

M/s. Hindustan Petroleum Ltd., India, supplied naphthenic oil. The specifications are:

| Parameter | Value |
|---|---|
| Aniline point ($^oC$) | 78 |
| Viscosity gravity constant | 0.85-0.9 |
| Aromaticity (%) | 20 |

### (ii) Aromatic oil

M/s. Hindustan Petroleum Ltd., India, supplied aromatic oil. The specifications are:

| Parameter | Value |
|---|---|
| Aniline point ($^oC$) | 43 |
| Viscosity gravity constant | 0.96 |
| Specific gravity | 0.98 |

**g.** **Dispersol F** was supplied from M/s Indian Explosives Ltd., Kolkata.

**h.** **Stabilizing agent** (Potassium Oleate)

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

### i. Other reagents used

Other reagents like toluene, benzoyl chloride, benzene, tetrabutyl ammonium bromide, potassium thiocyanate, petroleum ether, pyrrole, etc. were of analytical grade.

## 2.2 Experimental methods

### 2.2.1 Mixing and homogenization of the rubber compound

Mixes were prepared on a laboratory size two roll-mixing mill (15x33) as per ASTM D 3182 [3]. The mill opening was set at 0.2 mm and the elastomer was passed through the rolls twice without banding. This was then banded on the slow roll with mill opening at 1.4 mm and was increased to 1.9 mm as the band became smooth. The temperature of the rolls was maintained at 70 ± 5 °C. The compounding ingredients were added as per procedure given in ASTM D 3184 [4] in the following order: activators, fillers, accelerators and curing agents. Before the addition of accelerator and sulphur, 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 case of blends, natural rubber was masticated first so that its viscosity is comparable to that of SBR. These rubbers were pre-blended and then the additives were added.

After the completion of mixing, homogenization of the compound was carried out by passing the rolled stock endwise six times at a mill opening of 0.8 mm. The mill is opened to give a minimum stock thickness of 6mm and the stock was passed through the rolls four times folding it back on itself each time. Finally the stock was sheeted out at a nip gap of 3 mm. Mixing time and temperatures were controlled during the process.

### 2.2.2 Determination of cure characteristics of the compounds

Cure characteristics of the mixes were determined as per ASTM D 2084 [5] using Rubber Process Analyser (RPA 2000-Alpha Technologies, model - 90AJC2353). It uses two directly heated, opposed by conical dies that are designed to achieve a constant shear gradient over the entire sample chamber. The sample of approximately 5 gm was placed in the lower die that oscillated through a small deformation angle ($0.2^o$) at a frequency of 50 cpm. The torque transducer on the upper die senses the force being transmitted through the rubber. The torque was plotted as a function of time and the curve was called a cure graph. The important data that could be taken from the torque-time curve were minimum torque ($M_L$), maximum torque ($M_H$), and scorch time ($t_{10}$), optimum cure time ($t_{90}$) and cure rate. Optimum cure rate corresponds to achieve 90% of maximum torque increase, calculated using the equation given below.

Optimum cure time = time to achieve torque of $0.9\ (M_H-M_L) + M_L$

cure rate index (CRI) = $100/\ (t_{90} - t_{10})$

The kinetic study of vulcanization by Fujimoto et al. showed that cure activating nature of an accelerator in vulcanization of natural rubber follow first order kinetics [6]. The general equation for a first order chemical reaction can be written as $\ln(a-x) = kt + \ln a$, where a is the initial concentration of reactant, x is the reacted quantity at time t and k is the first order rate constant. For the vulcanization of NR the rate of crosslink formation is usually monitored by measuring the torque developed during vulcanization. The torque values obtained are proportional to the modulus of the rubber. So the change in a physical property such as modulus is measured rather than change in reaction concentration. The following substitution therefore can be made $(a-x) = M_H - M_t$ , $a = M_H - M_L$ where Mt is the modulus at time t. When $\ln (M_H - M_t)$ is plotted against t, a straight line graph obtained, proves that the cure reaction of the compounds follow first-order kinetics. The cure reaction rate constant, k is obtained from the slope of the straight line. Even though straight line is claimed for the plots theoretically, deviations are experimentally observed. Arrhenius equation is used to calculate the activation energy of the mixes,

$$(t_{90})^{-1} = Ce^{-E/RT}$$

$$-(\log t_{90}) = \log C - E/2.303RT$$

A plot of $-(\log t_{90})$ versus 1000/T gives a straight line and the activation energy can be calculated from the slope of the line. The lower the activation energy, the faster is the cure reaction initiation.

### 2.2.3 Moulding of test specimens

Vulcanization of various test samples was carried out in an electrically heated hydraulic press having 45 cm × 45 cm platen at 150 °C at a pressure of 200 kg /cm$^2$ on the mould up to optimum cure times. Moulded samples were conditioned for 24 hours before testing. For samples having thickness more than 6 mm (compression set, abrasion resistance, etc.) additional curing time based on the sample thickness was given to obtain satisfactory moulding.

## 2.3 Physical tests on vulcanizate

For the test described below at least 5 specimens per sample were tested for each property and mean values are reported.

### 2.3.1 Modulus, tensile strength and elongation at break

Tensile properties of the vulcanizates were determined according to the ASTM D 412[7] using dumb-bell specimens on a Shimadzu Universal Testing Machine, model– AG-1 series (10 KN) at a cross head speed of 500 mm/min. All the tests were carried out at ambient temperature. Samples were punched out from compression moulded sheets along the mill direction using a dumb-bell die (C-type). A bench thickness gauge was used to measure the thickness of the narrow portion. The sample was held tight by two grips, the upper grip of which was fixed. The gauge length between the jaws at the start of each test was adjusted to 40 mm. The tensile strength, elongation at break and modulus were evaluated. The modulus and tensile strength are reported in Mega pascal (MPa) unit and elongation at break in percentage (%).

### 2.3.2 Tear strength

Tear resistance of the samples was tested as per ASTM D 624 [8], using un-nicked $90^o$ angle test specimens that were punched out from the moulded sheets, along the mill grain direction. The measurements were carried out at a crosshead speed of 500 mm/min on a Shimadzu Universal Testing Machine (model- AG1). The tear strength was reported in N/mm.

### 2.3.3 Hardness

The hardness of the moulded samples was tested using Mitutoyohardmatic hardness tester in accordance with ASTM D 2240 [9]. The tests were performed on mechanically unstressed sample of 12 mm diameter and 6 mm thickness. A load of 12.5 Newton was applied and the readings were taken 10 seconds after the intender made firm contact with the specimen. The mean value of 3 measurements was reported. The hardness values are reported in Shore A unit.

### 2.3.4 Compression set

The samples of 6.5 mm thick and 18 mm diameter in duplicate, compressed to constant deflection (25%) were kept for 22 hours in an air oven at 70 $^{o}$C. After the heating period, the samples were taken out and cooled to room temperature for half an hour and the final thickness was measured. The compression set was calculated using the equation

Compression set (%) = $(t_{\text{initial}} - t_{\text{final}} / t_{\text{initial}} - t_{\text{spacer}})$ X 100

The procedure used was ASTM D 395 method B [10].

### 2.3.5 Abrasion resistance

The abrasion resistance of the samples was measured using a DIN abrader (DIN 53,516). Samples having s diameter of 6±0.2 mm and a thickness of 12 mm was kept on a rotating sample holder and 10 Newton load was applied. Abrasion loss was measured as per ASTM D 5963[11]. Initially a pre-run was given for the sample and its weight was taken. The sample was then given a complete run and weight after final run was also noted. The difference in weight is the abrasion loss. It is expressed as the weight of the test piece getting abraded away by its travel through 42cm on a standard abrasive surface and expressed as the weight loss in gram (g). The abrasion loss in $cm^3/h$ was calculated using the formula given below:

$$\text{Abrasion loss} = \frac{\text{Loss of weight} \times 60}{\text{Specific gravity} \times 2.2}$$

Abrasion resistance is the reciprocal of volume loss on abrasion.

### 2.3.6 Rebound resilience

The rebound resilience of the samples was determined as per ASTM D 2632 [12]. This test is used for the determination of impact resilience of solid rubber from measurement of vertical rebound of a dropped mass. Resilience is determined as the ratio of rebound height to drop height of a metal plunger of prescribed weight and shape, which is allowed to fall on the rubber specimen. Resilience is a function of both dynamic modulus and internal friction of rubber. The test specimen should have a thickness of 12.5 mm and the standard temperature is 23± 2 $^oC$. Resilience is tested as follows. The instrument is leveled and the plunger is raised to the top of the guide rod. The resilience scale is positioned so that its full weight rests upon the specimen. It is locked in that position. The plunger is then raised making sure it slides freely on its guide. The first three values are avoided. The next three values are recorded. Since resilience scale is divided into 100 parts, the rebound height is equal to the resilience in percentage.

### 2.3.7 Heat build- up

The Goodrich flexometer conforming to ASTM D 623 [13] was used for measuring the heat buildup. A cylindrical sample of 25 mm in height and 19 mm in diameter was used for the test. The oven temperature was maintained at 100 °C. The samples were placed in the preconditioned oven for 20 minutes at 100 °C. The test samples were subjected to a flexing stroke of 4.45 mm under a load of 10.9 kg and the temperature rise at the end of 20 minutes was taken as the heat buildup.

### 2.3.8 Density

Density of the sample was determined as per ASTM D 297 [14]. In this method the weight of the specimen in air was first noted and then specimen was immersed in water and its loss of weight in water was determined. The density of the sample was calculated as:

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

## 2.4 Chemical test methods

### 2.4.1 Determination of total crosslink density

$$\frac{(D - FT) / \rho_p^{-1}}{(D - FT) / \rho_p^{-1} + A_0 \rho_s^{-1}}$$

The crosslink density of vulcanized samples was determined by the equilibrium swelling method [15] using Florey-Rehner equation. Circular samples of approximately 0.3 g were accurately weighed and kept in toluene solvent taken in an air- tight container for 72 hours. The surface of the swollen samples was then gently wiped using filter paper and weighed in a weighing bottle to get equilibrium weight. The samples were heated at 60 °C for 24 hours in an oven to remove the solvent. The de-swollen weight was then determined. The volume fraction of rubber ($V_r$) in the de-swollen network was then calculated using the following equation as reported by Ellis and Welding [16].

T = weight of the specimen, D = de-swollen weight, F = weight fraction of insoluble component, $A_0$ = weight of the absorbed solvent corrected to the swelling increment, $\rho_p$= density of test specimen (polymer), $\rho_s$= density of the solvent. Knowing the value of $V_r$, the total crosslink density 1/2Mc was calculated using Flory-Rehner equation [17] given below.

$$Mc = \frac{-\rho_p \times V_s \times V_r^{1/3}}{[\ln(1-V_r) + V_r + \chi V_r^{2}]}$$

Where $\chi$ is the interaction parameter [18,19], *Vr* is the volume fraction, *Vs* is the molar volume of the solvent.

### 2.4.2 Swelling studies

In order to analyse the interaction between the components of the system, equilibrium swelling studies were carried out in toluene. Circular specimens of diameter 20 mm were punched from the vulcanized elastomer sheet and were allowed to swell in toluene at room temperature. At different intervals, the amount of solvent entering the sample was assessed gravimetrically until equilibrium was reached, as evidenced by the constant weight of the sample. The mole % uptake of the solvent was calculated using the equation given below [20].

$$Qt = \frac{Mc(m)/Mr(m)}{Mi(s)} \underset{t}{\times} 100$$

Where *Mc(m)* is the mass of solvent at a given time, *Mr(m)* is the molecular weight of solvent and *Mi(s)* is the initial weight of specimen. Sorption curves were obtained by plotting mole % (Qt) uptake against square root of time.

## 2.5 Thermal analysis

### 2.5.1 Thermogravimetric analysis

Thermogravimetric analysis was carried out on BDPTU, BPTU and vulcanized samples using a Thermo Gravimetric Analyser Q-50 (TA Instruments). It is a computer controlled instrument that permits the measurement of the weight changes in the sample material as a function of temperature or time. It is programmed in the required temperature range to measure the weight change resulting from chemical reaction, decomposition, solvent and water evolution, and oxidation of the sample materials. The temperature is scanned at a linear rate. The instrument has two components, an ultra sensitive microbalance and a furnace. The balance is sensitive to 0.1 microgram and the furnace could be heated from ambient to 800 $^{o}$C at the rates of 0.1 to 200 $^{o}$C per minute. The sample was placed in a temperature programmed furnace. It was then subjected to a temperature change from room temperature to 600 $^{o}$C with a heating rate of 20 $^{o}$C / minute in nitrogen atmosphere. The corresponding weight changes were noted with the help of an ultra sensitive microbalance. Thermograms were recorded from room temperature to 600 $^{o}$C. The onset of degradation, the temperature at maximum degradation and residual weight in percentage were noted.

### 2.5.2 Thermal ageing studies

Tests were carried out as per ASTM D 573 [21]. Dumb-bell shaped samples were punched out from the vulcanized rubber and exposed to the deteriorating influence of air at specified elevated temperature in an air oven, for known periods of time. Their physical properties like tensile strength, elongation at break, modulus, etc. were determined. These were compared with the properties determined on the original specimens and the changes noted.

## 2.6 Morphology Studies

Scanning electron microscope studies were found to be a very powerful tool in polymer research for studying morphology [22].The SEM observations reported in the present study were made on the fractured surface of tensile test specimen. A thin specimen of the samples was prepared by coating the conducting point with gold-palladium and the sample was observed in the SEM. Scanning electron microscope model TESCAN (VEGA 3 SBH) was used for the present investigation.

## 2.7 Compounding and testing of latex

### 2.7.1 Preparation of dispersions

The compounding ingredients were added to rubber latex as aqueous solution, dispersion or emulsion. The materials are made to disperse in water by grinding action and the dispersing agents prevent the dispersed particles from re-aggregating. The amount of dispersing agent needed for preparing dispersions depends on the nature of the materials to be dispersed. If the ingredients are of very fine particle size the quantity of dispersing agent required is about 1% by weight, but for materials like sulphur 2 to 3 % is required. There are different type of grinding equipments like ball mill, ultrasonic dispersion unit, and attrition mill. In the present study a ball mill was used for making the dispersions of the ingredients.

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

### (i) Sulphur dispersion (50%)

| Ingredients | Parts by weight |
|---|---|
| Sulphur | 100 |
| Dispersol F | 3 |
| De-ionised water | 97 |

Ball milled for 72 hours.

### (ii) ZnO dispersion (50%)

| Ingredients | Parts by weight |
|---|---|
| ZnO | 100 |
| Dispersol F | 2 |
| De-ionised water | 98 |

Ball milled for 48 hours.

### (iii) BPTU dispersion (10%)

| Ingredients | Parts by weight |
|---|---|
| BPTU | 10 |
| Dispersol F | 0.15 |
| De-ionised water | 89.85 |

Ball milled for 24 hours.

### (iv) ZDC dispersion (50%)

| Ingredients | Parts by weight |
|---|---|
| ZDC | 100 |
| Dispersol F | 2 |
| De-ionised water | 98 |

Ball milled for 48 hours.

### 2.7.2 De-ammoniation of latex

High ammonia (HA) type concentrated latex was de-ammoniated to 0.23% by stirring in a glass vessel using a mechanical stirrer for 3 hours. Otherwise the high ammonia content in latex will create problems during conversion to solid products or in the stability of the latex compound in presence of zinc oxide [23]. The concentration of ammonia in latex was estimated as per ASTM D 1076-88 [24].

### 2.7.3 Compounding

The mixing of ingredients was done as per the order given in the respective chapter. The stabilizers were first added as solutions, followed by the other ingredients. Mixing was done in a glass vessel and homogenized by stirring for 30 min, using a laboratory stirrer at 10-20 rpm. It was also stirred occasionally during storage too, in order to prevent settling of the ingredients.

### 2.7.4 Maturation

The latex compound was matured at ambient temperature for 24 hours. This ensures the compound to free itself of air entangled during the preparation and allows the stabilizers to distribute themselves uniformly throughout the aqueous and dispersed medium. During this maturation period important changes take place [25]. Adsorption of vulcanization ingredients into the rubber particle surface commences and becomes a continuous process with time and temperature. It also allows time for the reaction of ammoniated latex with zinc oxide for getting uniform physio-chemical properties.

### 2.7.5 Preparation of latex films

Latex films were casted on glass dishes using the latex compound as described by Flint and Naunton [26]. The size of the glass dishes was 6 × 6 inches and about 25 gm of the latex compound was poured and uniformly distributed so that a film of thickness 1-1.25 mm was obtained upon drying. These glass dishes with the latex compound were placed on leveled table and dried for 3 hours.

### 2.7.6 Vulcanization of latex films

The vulcanization of latex films was carried out in a laboratory type air oven at 120 and 100 $^{o}$C. The time for optimum cure was determined by vulcanizing the film for different duration of time and determining the tensile strength of the vulcanizate in each case. The optimum cure time was taken as the time for attaining maximum tensile strength.

### 2.7.7 Testing of the latex films

The tensile and tear properties of the latex film were determined as per ASTM D 412 and ASTM D 624 respectively using Shimadzu Universal Testing Machine (model- AG1). The chemical crosslink density was determined by equilibrium swelling method.

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## Chapter 3

# SYNTHESIS OF NEW THIOUREA AND PHENYLTHIAZOLE DERIVATIVES AND THEIR ROLE AS ACCELERATORS IN THE VULCANIZATION OF NATURAL RUBBER

Contents

## 3.1 Introduction

Natural rubber (NR) is the preferred polymer in many industrial applications because of its superior building tack, green stock strength, high resilience and excellent dynamic properties. The raw polymer, at room temperature has considerable strength, elasticity and resilience but is sensitive to hot and cold conditions. Compounding and vulcanization transform this raw rubber in to a material suitable for varied applications. During vulcanization the long chain rubber molecules are crosslinked by curing agents to form three-dimensional network. The vulcanization of NR can be affected with the aid of sulphur, organic peroxides, synthetic resins, other polyfunctional reagents and also by high energy radiations [1, 2]. The intermolecular crosslinks thus formed due to vulcanization restrict the mobility of molecules. This gives the product reduced tendency to crystallize, improved elasticity, sustainable modulus and hardness characteristic over a wide range of temperatures [2]. The extent of changes taking place is governed by the choice of the vulcanizing agents and also by the vulcanization conditions.

Sulphur is the principal vulcanizing agent used with NR. Sulphur vulcanization of NR is reported in a number of publications [4, 5, 6], is widely used for several reasons. Accelerated sulphur formulations are the most common vulcanization systems used in industrial applications. NR is usually vulcanized at the temperature range of 140 to 160 °C, with a combination of sulphur (1-3 phr), one or more accelerators (0.5-2.5 phr), ZnO (3-5 phr), a fatty acid (1-3 phr) and other special additives.

The different types of accelerators used in NR are thiazoles, thiocarbamates, thiuramsulphides, guanidines, etc. With these accelerators or combination of them, it is possible to vulcanize rubber at the desired time and temperature. Many of the physical properties of the vulcanizate can be controlled to a certain extent by the choice of the accelerators, the level of sulphur and the sulphur-accelerator ratio. The vulcanization obtained by conventional vulcanization systems (high sulphur, low accelerator) deteriorate when subjected to thermal ageing. Vulcanizates with high heat resistance are obtained by using a high ratio of accelerator to sulphur or vulcanization with thiurams using small proportion of sulphur [7]. When thiurams are used as accelerator the vulcanizates have a relatively high modulus, good mechanical properties and good resistance to ageing [8]. Among thiuram accelerators tetramethylthiuram disulphide (TMTD), but they have to be activated with ZnO. Inclusion of fatty acids improves the degree of vulcanization. Another class of widely used accelerators of high economic importance in NR vulcanization are thiazoles. Mercaptobenzothiazole and its derivaties belong to thiazole class of compounds. They give higher processing safety than the ultra accelerators and require high vulcanization temperatures. These thiazole accelerators can be sub divided into mercapto accelerators (e.g. MBT, MBTS, ZMBT, etc.) and benzothiazole sulphenamide accelerators (e.g. CBS, TBBS, MBS, etc.). Compared to thiuram accelerators mercapto accelerators give compounds with higher processing safety. Dibenzothiazole disulphide (MBTS) has a delayed onset of vulcanization as the MBTS has to decompose thermally to MBT before vulcanization begins and because of this, MBTS gives higher processing safety. Benzothiazole sulphenamide accelerators are considered as derivatives of mercaptobenzothiazole where an amine is oxidatively bound to the mercaptosulphur. These accelerators become active as the amines are split off during vulcanization and the base activates mercaptobenzothiazole as it is formed. Therefore sulphenamides produce a delay in vulcanization start and therefore improves processing safety. Addition of ZnO is necessary for the activation of all these accelerators.

Thiourea (TU) and its derivatives have also been developed as powerful secondary accelerators in the vulcanization of natural and synthetic rubbers. They give good synergistic behavior with thiazole and thiuram accelerators. For example, in NR vulcanization, the accelerator MBTS gives very slow crosslinking by itself, even if heavy dosage is given. But if substituted or unsubstituted thiourea is used, very rapid vulcanization occurs at normal temperature particularly in CR. The vulcanizates obtained have reasonably high tensile strength and good resistance to ageing [9]. Thiourea derivatives act as effective secondary accelerators with TMTD or CBS especially in latex vulcanization. Philpot suggested an ionic mechanism in these systems where S-S bond or S-N bond of the primary accelerator is cleaved by the nucleophile produced from thiourea [10] but no conclusive proof has been given.

Earlier work in our laboratory indicated that different derivatives of thiourea namely amidinothiourea (ATU), amidinophenylthiourea (APT) and aminoiminomethyl thiourea (AMT) can act as effective secondary accelerator in the sulphur vulcanization of natural and synthetic rubbers. It can be used in the manufacture of industrial rubber products [11, 12 & 13]. Resmi et al. has reported dialkyl/azacycloalkyl substituted benzoylthioureas as effective secondary accelerators with CBS, MBT & ZDC for the NR vulcanization [14]. This work has supported the nucleophilic mechanism of Philpot and also showed that highest tensile strength was given by the system containing the highest nucleophilic compound.

The present work envisages the synthesis of new thiourea derivatives that can be used as accelerators in the sulphur vulcanization of elastomers. The ever increasing demand for rubber valcanizates with varying properties by the industry necessitates more work to be done in this area. Two thiourea derivatives namely BPTU and BDPTU were synthesized and characterized using chemical, physical and spectroscopic techniques. Investigations on the effect of these compounds as accelerator in the NR gum vulcanization were carried out. The vulcanization of gum formulations were carried out in the beginning as it can give an insight into the reaction pattern. Attempts were also made to evaluate the synergistic effect of BPTU and BDPTU in a binary accelerator system for the sulphur vulcanization of elastomers with MBTS or CBS as primary accelerator. Their cure characteristics and mechanical properties were compared with that of systems containing conventional accelerators (MBTS or CBS) and also with an ultra accelerator (TMTD) in a binary system.

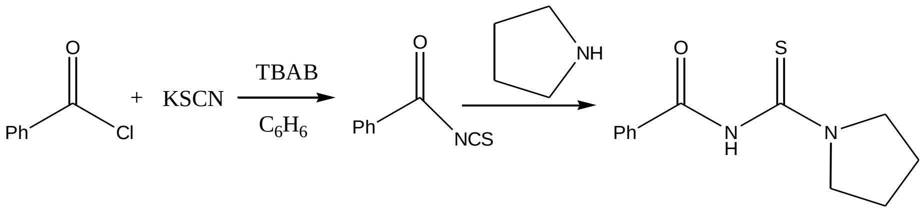
Organic compounds containing thiazole or benzothiazole moiety for example MBT, MBTS, ZMBT, ZBDP, TBBS etc. [15, 16, 17, and 18] are uesd as accelerators. The previous studies of the author on novel benzothiazolylthiazoles [19] further revealed the hidden potentials of these classes of compounds as secondary accelerator. These prompted the investigation on the binary accelerator properties of a new set of derivatives of the same family to meet the ever increasing demand for newer accelerators by the rubber industry.

## 3.2 Synthesis of accelerators

### 3.2.1 Synthesis of new thiourea derivatives and characterization

**a). Synthesis of N-benzoyl-N$^{I}$,N$^{I}$-pyrrolidinylthiourea (BPTU,1a)**

A solution of benzoylchloride (7.5 mmol, 0.8 mL) in 4 mL benzene was stirred well in presence of tetrabutylammonium bromide (TBAB (0.2 g)). To this mixture, aqueous solution of potassium thiocyanate (33%, 5.5 mL) was added slowly (in drops during 15 min.). Stirring was continued for another 30 min. The aqueous layer was then removed using a Pasteur pipette. This aqueous layer was extracted with benzene and added back to the main bulk. Pyrrole (7.5 mmol, 0.62mL) in benzene was added to the benzene layer with stirring. The mixture was stirred at room temperature for 30 min. It was then diluted slowly with petroleum ether under slow stirring until the precipitation of thiourea was complete. The product (yield: 76%; Scheme 1.) obtained was recrystallized from ethanol water system to get cream coloured microcrystalline powder of 1a viz. N-benzoyl-N$^{I}$,N$^{I}$–pyrrolidinylthiourea (BPTU; mp: 131$^{o}$C).

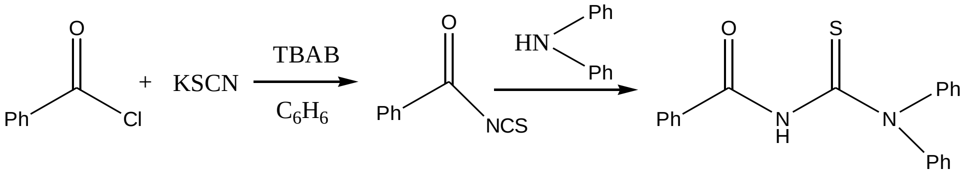


**Scheme 1**

Thin layer chromatography was performed for characterization of the newly synthesized BPTU using silica gel-G (E. Merck, India) coated on glass plates and spots were observed under UV-light. The infra-red spectrum of the sample was recorded between 4000 cm$^{-1}$ and 400 cm$^{-1}$ on Shimadzu IR-470 (Fig. 3.1). Brucker (400 MHz) spectrometer was used for $^{1}$HNMR and $^{13}$C NMR spectra of the compound (Fig. 3.2 & 3.3).

### b). Synthesis of N-benzoyl-N$^{I}$,N$^{I}$-diphenylthiourea (BDPTU,2a)

The synthesis BDPTU was carried out as in the case of BPTU with pyrrole replaced by diphenyl amine (7.5 mmol). The product (yield: 86%; Scheme 2.) obtained was recrystallized from ethanol water system to get pale yellow coloured powder of 2a viz. N-benzoyl-N$^{I}$,N$^{I}$–diphenylthiourea (BDPTU; mp: 122 °C).

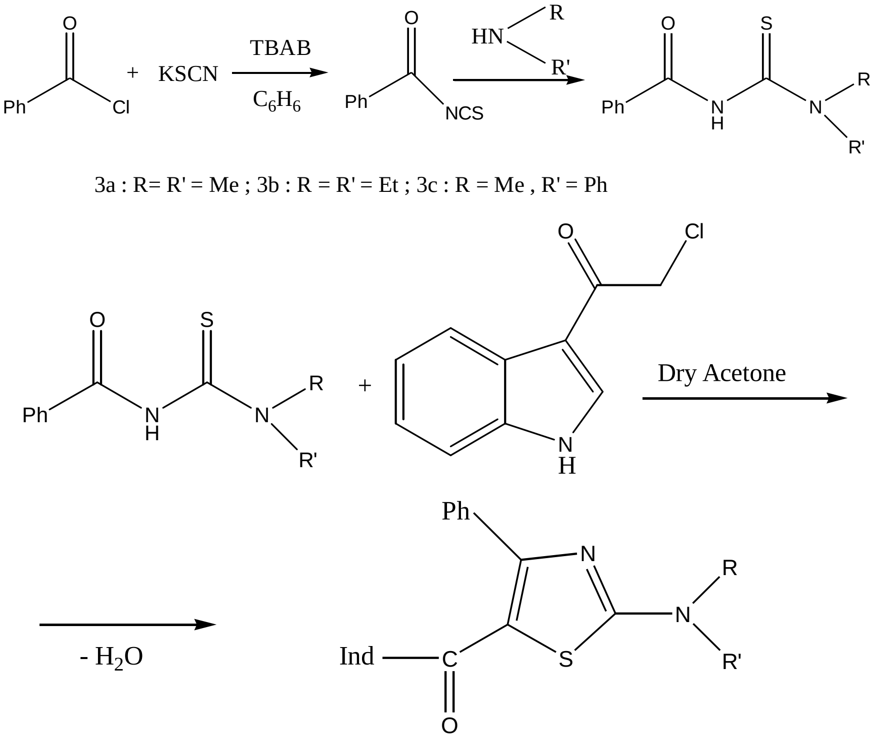


**Scheme 2**

Thin layer chromatography was performed for characterization of the newly synthesised BDPTU using silica gel-G (E. Merck, India) coated on glass plates and spots were observed under UV-light. The infrared spectrum of the sample (Fig.3.4) was recorded between 4000 $cm^{-1}$ and 400 $cm^{-1}$ on Shimadzu IR-470. Brucker (400 MHz) spectrometer was used for $^{1}H$ NMR and $^{13}C$ NMR spectra of the sample (Fig.3.5 & 3. 6).

### 3.2.2 Preparation of 2-(N,N-dialkylamino)-5-(indole-3-oyl)-4-phenylthiazoles[20]

Benzoylisothiocyanate was prepared by using phase transfer catalyst and reacted with dialkylamine in situ to get the required 3a-c.



3a : R= R' = Me ; 3b : R = R' = Et ; 3c : R = Me , R' = Ph

Ind = Indolyl ; 4a : R = R' = Me ; 4b : R= R' = Et ; 4c : R = Me , R' = Ph

**Scheme 3**

A solution of 3-chloroacetylindole (1 mmol, 0.184g) in dry acetone was refluxed with 3a-c (1 mmol, 0.248g) for 1.5 hour. The reaction mixture was then cooled and added to ice-cold water and the pH of the resulting solution was adjusted to approximately 6. The precipitate thus formed was filtered, washed with water, dried and crystallized from ethanol-water to obtain 2-(N,N-dialkylamino)-5-(indole-3-oyl)-4-phenylthiazole (4a-c) as in Scheme 3 and then characterized by their melting points and IR spectrum.

The three phenylthiozoles 4a, 4b and 4c obtained are listed below:

4a: 2-(N,N-Dimethylamino)-5-(indol-3-oyl)-4-phenylthiazole (DMIP) yield 68%, mp: 236 $^{o}$C.

4b: 2-(N,N-Diethylamino)-5-(indol-3-oyl)-4-phenylthiazole (DEIP) yield 71%, mp: 220 $^{o}$C.

4c: 2-(N,N-Methylphenylamino)-5-(indol-3-oyl)-4-phenylthiazole (MPIP) yield 89%, mp:132 $^{o}$C.

### 3.2.3 Results and discussion on characterization of derivatives

The synthesis and work up carried for the thiourea derivative (3.2.1a) yielded (76 %) cream microcrystalline powder, mp: 131$^{o}$C had the molecular formula $C_{12}H_{14}N_2OS$. The IR spectrum (Fig. 3.1) of the compound showed bands at 3145 , 1645 and 1532 cm$^{-1}$ characteristic of stretching frequencies of N-H, C=O and C=S. The $^1$HNMR spectrum (Fig. 3.2) showed a singlet at $\delta$: 10.8 which could be due to a N-H hydrogen and $\delta$: 1.89-1.97(m), 3.5 (t), 3.7(t) corresponding to four methylene groups of pyrroludine. Its $^{13}$C NMR spectrum (Fig. 3.3) showed $\delta$: 24.20($CH_2$), 25.57($CH_2$), 51.35($CH_2$), 53.61($CH_2$), 128.32 (2, Ar-C), 128.34 (2, Ar-C), 132.31 (Ar-C), 132.84(Ar-C), 163.81(C=S), 177.21(C=O), appeared to be in agreement with the structure assigned as N-benzoyl-N$^{\prime}$,N$^{\prime}$-pyrrolidinylthiourea. Thus IR, $^{1}$H NMR and $^{13}$C NMR spectrum of 1a confirms the structure of BPTU. The structure was further confirmed by CHN analysis as given in Table 3.1.

**Table 3.1 CHN analysis of BPTU ($C_{12}H_{14}N_2OS$) and BDPTU ($C_{20}H_{16}N_2OS$)**

| **Compound** | **Calculated** | | | **Obtained** | | |
|---|---|---|---|---|---|---|
| | **C%** | **H%** | **N%** | **C%** | **H%** | **N%** |
| $C_{12}H_{14}N_2OS$ | 61.5 | 6.02 | 11.96 | 61.2 | 5.96 | 11.87 |
| $C_{20}H_{16}N_2OS$ | 72.30 | 4.85 | 8.43 | 70.86 | 4.86 | 8.28 |

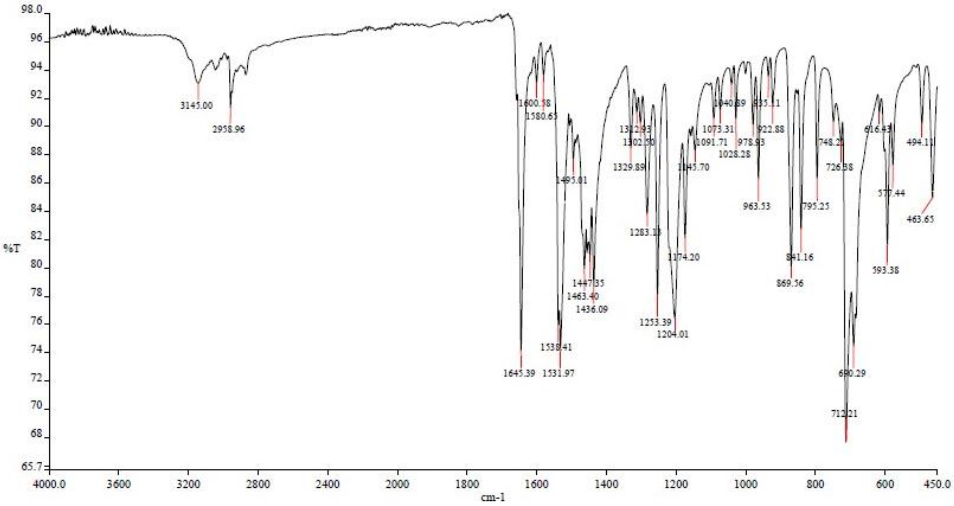


**Fig. 3.1 IR spectrum of N-benzoyl-N$^{\prime}$,N$^{\prime}$–pyrrolidinylthiourea (BPTU)**

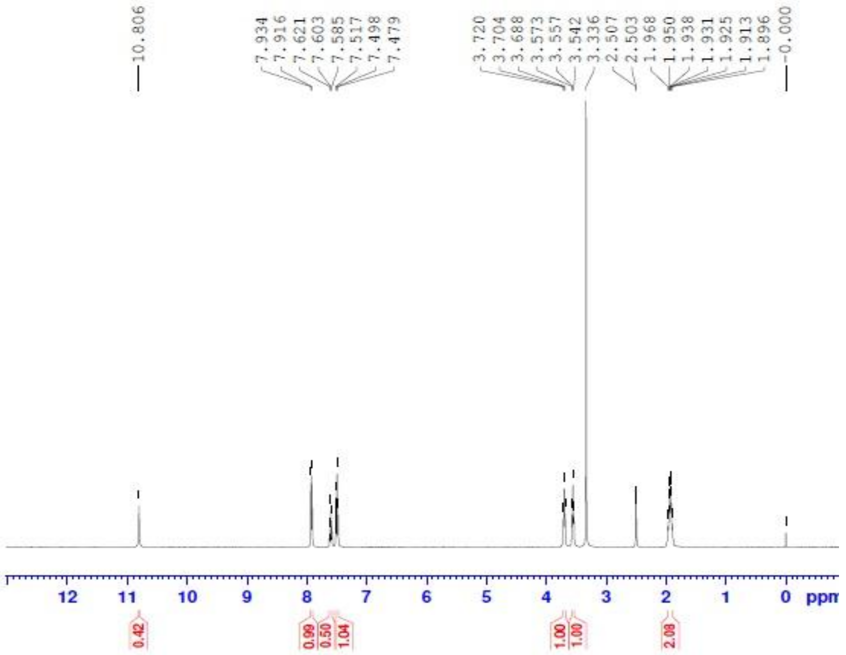


**Fig. 3.2 $^{1}$HNMR spectrum of N-benzoyl-N$^{'}$,N$^{'}$–pyrrolidinylthiourea (BPTU)**

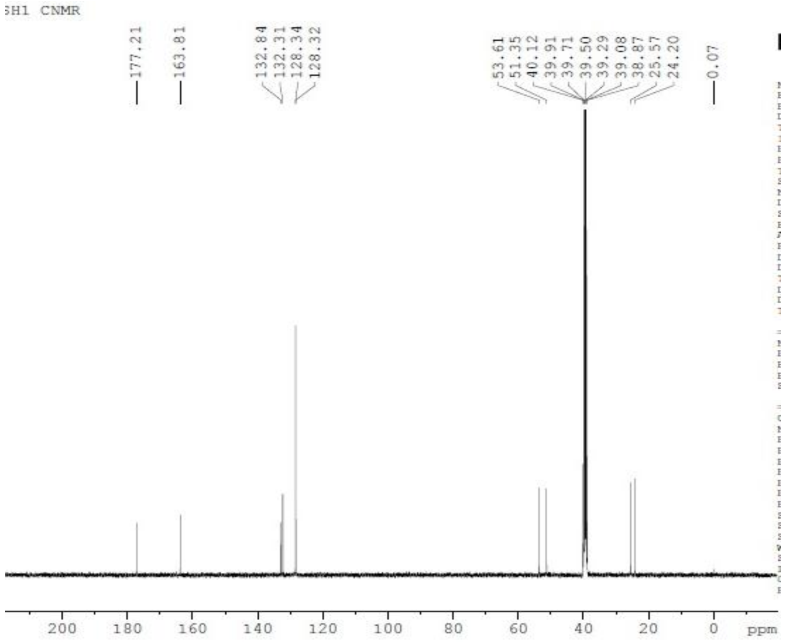


**Fig. 3.3 $^{13}$C NMR spectrum of N-benzoyl-N$^{'}$,N$^{'}$–pyrrolidinylthiourea (BPTU)**

The synthesis and work up carried for the thiourea derivative (3.2.1b) yielded (86 %) yellow powder, mp: 122 °C had the molecular formula $C_{20}H_{16}N_2OS$. The IR spectrum (Fig.3.4) of the compound showed bands at 2966,1692,1505,1254,713 & 692 $cm^{-1}$ characteristics of stretching frequencies of N-H, C=O,C=S, Ar C-C and Ar C-H. The $^1H$ NMR spectrum (Fig.3.5) showed a singlet at $\delta$: 11.175 which could be due to a N-H hydrogen and $\delta$: 7.2 – 7.7 (m), corresponding to15 Ar H. Its $^{13}C$ NMR spectrum (Fig.3.6) showed $\delta$: 116 - 146 (18, Ar-C), 184.45(C=O), 163.38 (C=S) appeared to be in agreement with the structure assigned as N-benzoyl-N$^{I}$,N$^{I}$-diphenylthiourea. Thus IR, $^1H$ NMR and $^{13}C$ NMR spectrum obtained for 2a confirms the structure of BDPTU. The structure was further confirmed by CHN analysis as in Table 3.1.

The three phenylthiozoles 4a, 4b and 4c prepared are also characterised by their melting points and IR spectroscopy.

4a: 2-(N,N-Dimethylamino)-5-(indol-3-oyl)-4-phenylthiazole(DMIP), yield 68%, mp: 236 °C. Molecular composition: $C_{20}H_{17}N_3OS$; IR (KBr) $cm^{-1}$: 3184, 2935, 1639, 1527, 1432, 1283, 1243, 1148, 1094, 953, 740, 643.

4b: 2-(N,N-Diethylamino)-5-(indol-3-oyl)-4-phenylthiazole (DEIP) yield 71%, mp: 220 °C. Molecular composition: $C_{22}H_{21}N_3OS$; IR (KBr) $cm^{-1}$: 2982, 2935, 2861, 1647, 1560, 1528, 1438, 1330, 1317, 1196, 1148, 1020, 899, 825, 757, 693, 670, 596, 427.

4c: 2-(N,N-Methylphenylamino)-5-(indol-3-oyl)-4-phenylthiazole (MPIP) yield 89%, mp:132 °C. Molecular composition: $C_{25}H_{19}N_3OS$; IR (KBr) $cm^{-1}$:3191, 2955, 1654, 1580, 1526, 1438, 1391, 1283, 1243, 1162, 960, 798, 764, 643.

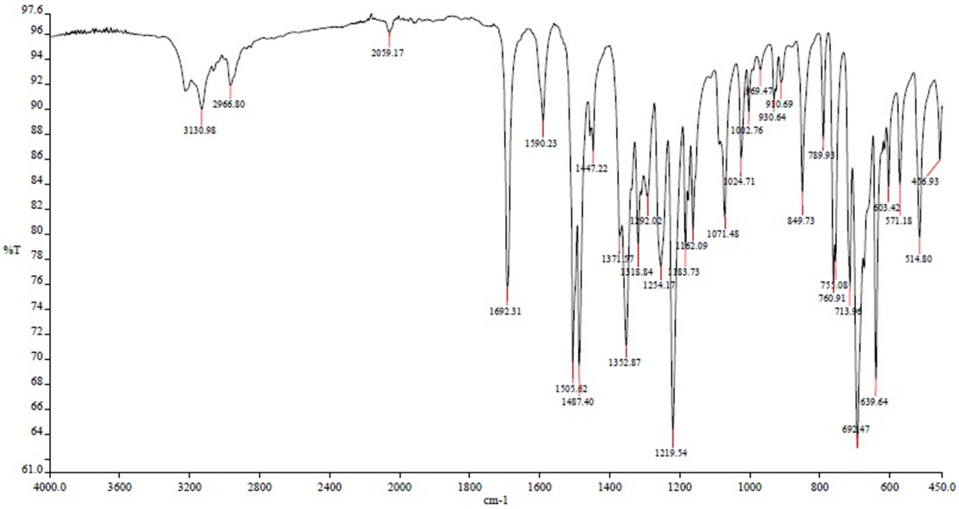


Fig. 3.4 IR spectrum of N-benzoyl-N$^{1}$,N$^{1}$–diphenylthiourea (BDPTU)

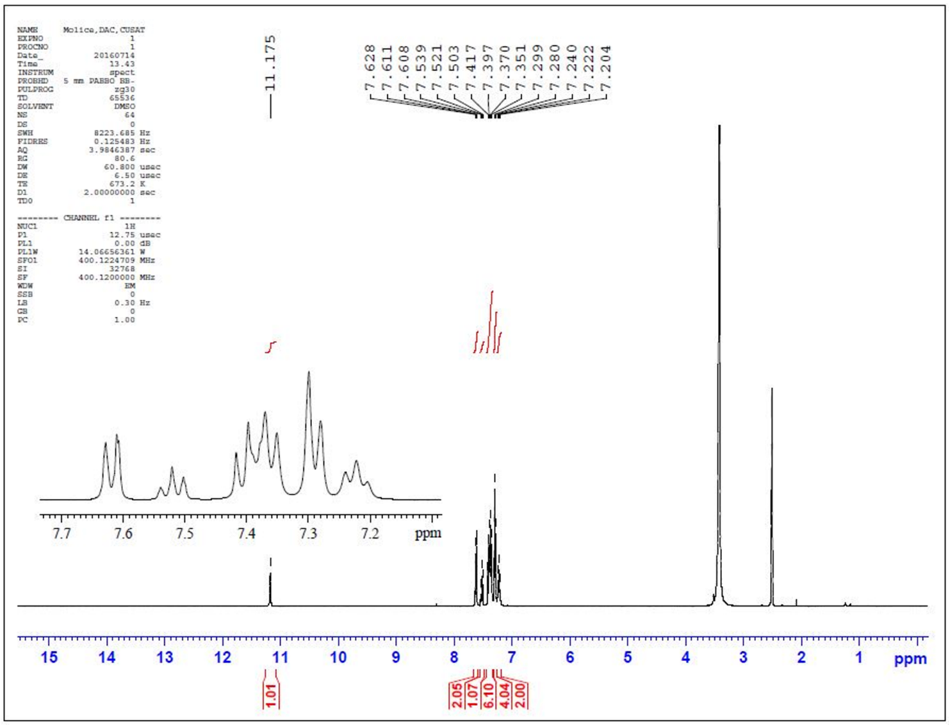


Fig. 3.5 $^{1}$H NMR spectrum of N-benzoyl-N$^{1}$,N$^{1}$–diphenylthiourea (BDPTU)

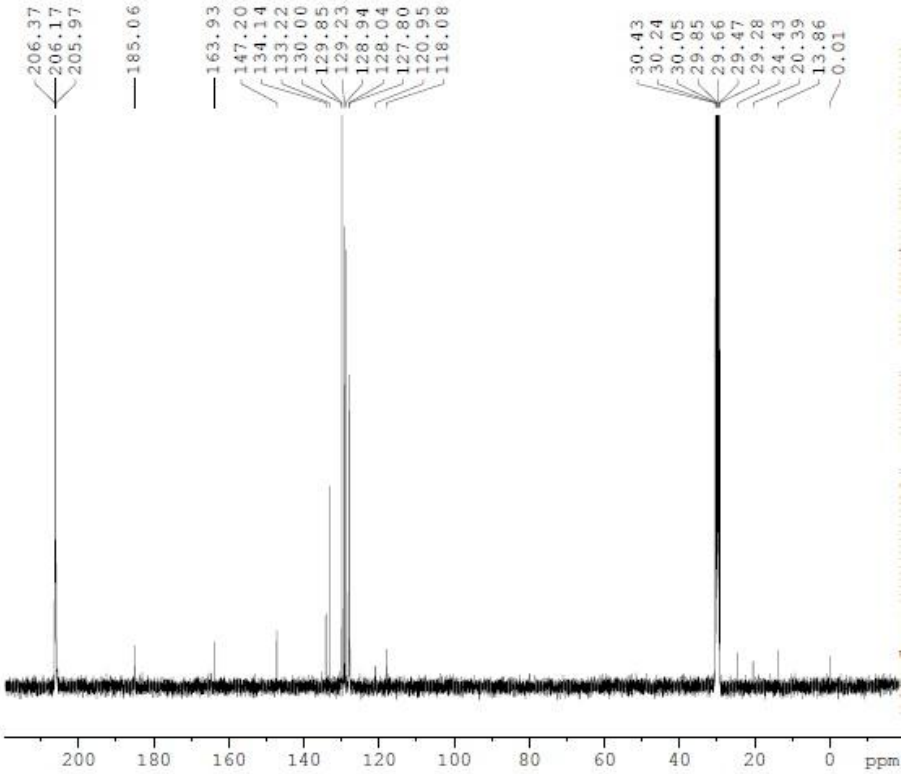


**Fig. 3.6 $^{13}$C NMR spectrum of N-benzoyl-N$^{\prime}$,N$^{\prime}$–diphenylthiourea (BDPTU)**

The thermogravimetric analysis of the compounds BPTU and BDPTU given in Figs. 3.7 and 3.8 respectively showed that onset of degradation for BPTU as 135 ±1 $^{o}$C and that of BDPTU as 105±1 $^{o}$C. Temperature at which maximum degradation takes place for BPTU and BDPTU are at 205±1 $^{o}$C and 140±2 $^{o}$C respectively. The thermogram shows that at 150 $^{o}$C the amount of accelerator available for vulcanization is 95% of BPTU and 76% of BDPTU. These results indicate that BPTU can be a better accelerator than BDPTU.

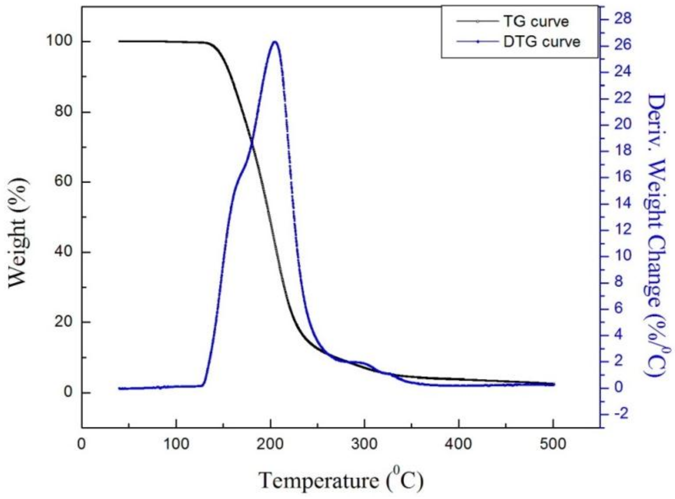


Fig. 3. 7 TG and DTG curves of N-benzoyl-N$^{I}$,N$^{I}$–pyrrolidinylthiourea (BPTU)

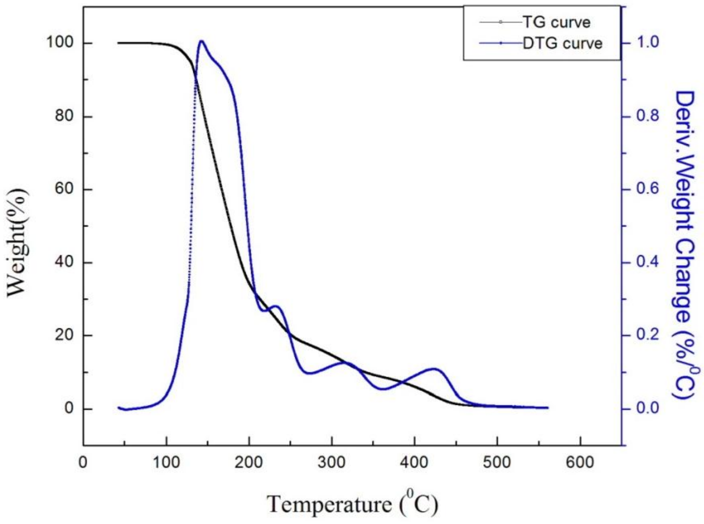


Fig. 3.8 TG and DTG curves of N-benzoyl-N$^{I}$,N$^{I}$-diphenylthiourea (BDPTU)

## 3.3 Investigations on NR gum formulations

### 3.3.1 Experimental

The composition of various mixes prepared is given in Tables 3.2- 3.5. Zinc oxide (5 phr), stearic acid (2 phr) and sulphur (1.5 phr) were incorporated as activator, co-activator and vulcanizing agent respectively in all these mixes. An attempt was made to find the optimum concentration of BPTU required for the vulcanization of NR at 150 $^{o}$C. $A_0$ and $B_0$ are the mixes containing conventional accelerators MBTS (1.0 phr) and CBS (1.0 phr) respectively. Mixes $B_1$, $B_2$, $B_3$, and $B_4$ are systems containing varying amounts of BPTU ranging from 1.0 to 2.5 phr and mixes $D_1$-$D_4$ contain varying amounts of BDPTU ranging from 0.25 - 1.5 phr along with 1.0 phr of CBS and $C_1$- $C_3$ contain BDPTU from 0.5 -1.5 phr along with 1.0 phr of MBTS respectively. Formulations containing BDPTU alone as accelerator for the vulcanization of NR in varying concentrations (1.0, 1.5, and 2.0 phr) were studied. It was found that curing does not take place even up to one hour at 150 $^{o}$C. Mixes $P_1$, $P_2$, and $P_3$ containing 0.5 phr each of phenylthiazoles (4a, 4b and 4c respectively), along with 1.0 phr of MBTS was examined.

**Table 3.2 Formulations of NR mixes containing CBS and BPTU (alone)**

| **Ingredients** | **$B_0$** | **$B_1$** | **$B_2$** | **$B_3$** | **$B_4$** |
|---|---|---|---|---|---|
| NR (g) | 100 | 100 | 100 | 100 | 100 |
| ZnO (phr) | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 |
| Stearic acid (phr) | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 |
| CBS(phr) | 1.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| BPTU (phr) | 0.0 | 1.0 | 1.5 | 2.0 | 2.5 |
| Sulphur (phr) | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 |

**Table 3.3 Formulations of NR mixes containing MBTS-BDPTU**

| Ingredients | $A_0$ | $C_1$ | $C_2$ | $C_3$ |
|---|---|---|---|---|
| NR (g) | 100 | 100 | 100 | 100 |
| ZnO (phr) | 5.0 | 5.0 | 5.0 | 5.0 |
| Stearic acid (phr) | 2.0 | 2.0 | 2.0 | 2.0 |
| MBTS(phr) | 1.0 | 1.0 | 1.0 | 1.0 |
| BDPTU (phr) | 0.0 | 0.5 | 1.0 | 1.5 |
| Sulphur (phr) | 1.5 | 1.5 | 1.5 | 1.5 |

**Table 3.4 Formulations of NR mixes containing CBS- BDPTU**

| Ingredients | $B_0$ | $D_1$ | $D_2$ | $D_3$ | $D_4$ |
|---|---|---|---|---|---|
| NR (g) | 100 | 100 | 100 | 100 | 100 |
| ZnO (phr) | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 |
| Stearic acid (phr) | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 |
| CBS(phr) | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| BDPTU (phr) | 0.0 | 0.25 | 0.5 | 1.0 | 1.5 |
| Sulphur (phr) | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 |

**Table 3.5 Formulations of NR mixes containing MBTS- phenylthiazole**

| Ingredients | $A_0$ | $P_1$ | $P_2$ | $P_3$ |
|---|---|---|---|---|
| NR (g) | 100 | 100 | 100 | 100 |
| ZnO (phr) | 5.0 | 5.0 | 5.0 | 5.0 |
| Stearic acid (phr) | 2.0 | 2.0 | 2.0 | 2.0 |
| MBTS (phr) | 1.0 | 1.0 | 1.0 | 1.0 |
| DMIP (phr) | 0.0 | 0.5 | 0.0 | 0.0 |
| DEIP (phr) | 0.0 | 0.0 | 0.5 | 0.0 |
| MPIP (phr) | 0.0 | 0.0 | 0.0 | 0.5 |
| Sulphur (phr) | 1.5 | 1.5 | 1.5 | 1.5 |

All the mixes were prepared on a laboratory size two- roll mixing mill according to ASTM D 3182 (details are as given in chapter 2). The determination of cure characteristics, equilibrium swelling data, physical and mechanical properties of the vulcanizates were carried out as described in chapter 2.

## 3.4 Results and discussion

### 3.4.1 Cure Characteristics

The rheographs of the mixes carrying BPTU cured at 150 $^{o}$C are shown in Fig. 3.9. Optimum cure time of NR vulcanizate using BPTU was found to decrease from $B_1$ to $B_3$ and then increase as shown in Table 3.6. $B_3$ has the lowest optimum cure time of 17.11min and the highest CRI value of 6.93. The maximum torque value increases with increase in concentration of BPTU. The optimum cure time for the vulcanization of NR, using one phr CBS is only 7.41min and for one phr MBTS is 16.38 min. This shows that the cure acceleration imparted by BPTU is lower than the conventional accelerators MBTS or CBS and optimum dosage was found to be 2 phr. But it is observed that on increasing the dosage of BPTU the $t_{90}$ values decreased and maximum torque increased as in the case of other known accelerators. These processing characteristics [5, 8] indicate that BPTU has some accelerating effect in the vulcanization of NR.

**Table 3.6 Cure characteristics of NR mixes containing CBS and BPTU (alone)**

| Cure Characteristics | $B_0$ | $B_1$ | $B_2$ | $B_3$ | $B_4$ |
|---|---|---|---|---|---|
| Scorch time, $t_{10}$ (min) | 2.72 | 3.44 | 2.86 | 2.69 | 3.14 |
| Optimum cure time, $t_{90}$ (min) | 7.41 | 21.84 | 18.09 | 17.11 | 19.04 |
| CRI (min$^{-1}$) | 21.32 | 5.43 | 6.57 | 6.93 | 6.29 |
| Torque Max. (dNm) | 4.86 | 1.26 | 1.45 | 1.65 | 3.42 |
| Torque Min. (dNm) | 0.31 | 0.07 | 0.07 | 0.05 | 0.19 |

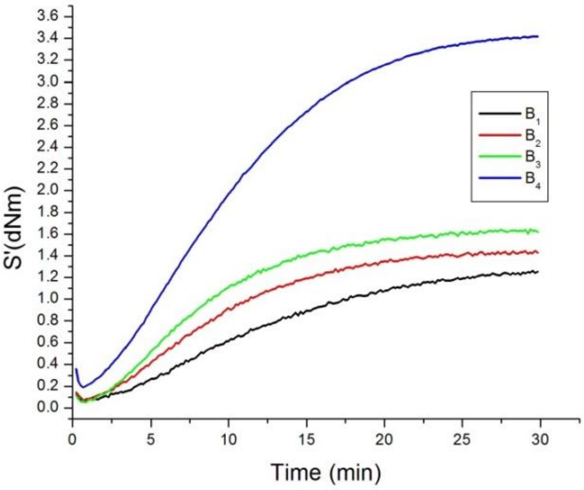


**Fig. 3.9 Rheographs of NR- BPTU mixes**

**Table 3.7 Cure characteristics of NR mixes containing MBTS- BDPTU**

| **Cure Characteristics** | **$A_0$** | **$C_1$** | **$C_2$** | **$C_3$** |
|---|---|---|---|---|
| Scorch time, $t_{10}$ (min) | 5.48 | 3.15 | 1.70 | 0.75 |
| Optimum cure time, $t_{90}$ (min) | 16.38 | 7.40 | 6.15 | 5.14 |
| CRI ($min^{-1}$) | 9.17 | 23.53 | 22.47 | 22.78 |
| Torque Max.(dNm) | 3.88 | 4.82 | 1.70 | 1.91 |
| Torque Min. (dNm) | 0.27 | 0.18 | 0.03 | 0.02 |

Accelerating effect of BDPTU in the vulcanization of NR was not observed even if 2 phr was used at 150 $^{o}$C for 60 min. But it shows cure accelerating property along with MBTS or CBS. BDPTU (1phr) with MBTS (1.5 phr) gives the lowest optimum cure time as 5.14 min as given in Table 3.7. This is only one third of the optimum cure time of $A_0$ which carries only MBTS as accelerator. The addition of 0.5 phr of BDPTU to 1.0 phr of MBTS reduced the optimum cure time from 16.38 min to 7.40 min, clearly indicates the effectiveness of BDPTU as accelerator in the sulphur vulcanization of NR using MBTS. The rheographs of the mixes containing BDPTU and CBS cured at 150 °C are shown in Fig.3.10. BDPTU (1 phr) with CBS (1phr) has the lowest optimum cure time, 5.38 min and is 70% of $B_0$ which carries only CBS. The cure properties of the system are presented in Table 3.8. The change in $t_{90}$ of $D_1$, $D_2$, $D_3$ and $D_4$ are only very small and CRI values are almost the same. But it is seen that there is a marked increase in cure rate by the addition of BDPTU to CBS. These results reveal that vulcanization of NR can be carried out by using BDPTU with MBTS or CBS.

**Table 3.8 Cure characteristics of NR mixes containing CBS-BDPTU**

| **Cure Characteristics** | **$B_0$** | **$D_1$** | **$D_2$** | **$D_3$** | **$D_4$** |
|---|---|---|---|---|---|
| Scorch time, $t_{10}$ (min) | 2.72 | 3.58 | 2.59 | 1.80 | 1.63 |
| Optimum cure time, $t_{90}$ (min) | 7.41 | 7.26 | 6.09 | 5.38 | 5.74 |
| CRI ($min^{-1}$) | 21.32 | 27.17 | 28.57 | 27.93 | 24.33 |
| Torque Max. (dNm) | 4.86 | 2.03 | 1.92 | 1.70 | 1.63 |
| Torque Min. (dNm) | 0.31 | 0.01 | 0.02 | 0.02 | 0.02 |

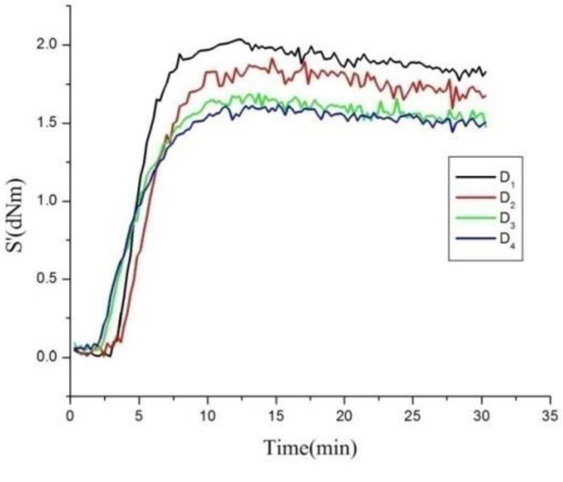


**Fig. 3.10 Rheographs of NR-CBS-BDPTU mixes**

Considering the cure accelerating property of phenylthiazoles (4a, 4b, 4c) to vulcanize NR, lowest optimum cure time and highest cure rate is shown by the mix $P_2$. The optimum cure time is in the order $P_2<P_3<P_1$ as reported in Table 3.9. The optimum cure time can be reduced by the addition of 0.5 phr of 4b or 4c along with one phr of MBTS. A reversal in cure time i.e. increase is observed when 0.5 phr of 4a is added and it is more than that of $A_0$. Addition of 0.5 phr of 4b to one phr MBTS increases the cure rate of vulcanization by 59% and 4c by 31%. This shows that 4b and 4c are better cure accelerating agents along with MBTS for the vulcanization of NR than 4a.

**Table 3.9 Cure characteristics of mixes containing NR with phenylthiazole & MBTS**

| Cure Characteristics | $A_0$ | $P_1$ | $P_2$ | $P_3$ |
|---|---|---|---|---|
| Scorch time, $t_{10}$ (min) | 5.48 | 7.03 | 3.25 | 6.45 |
| Optimum cure time, $t_{90}$ (min) | 16.38 | 22.54 | 10.10 | 14.72 |
| CRI ($min^{-1}$) | 9.17 | 6.36 | 14.60 | 12.09 |
| Torque Max.(dNm) | 3.88 | 1.66 | 1.81 | 1.88 |
| Torque Min. (dNm) | 0.27 | 0.10 | 0.09 | 0.09 |

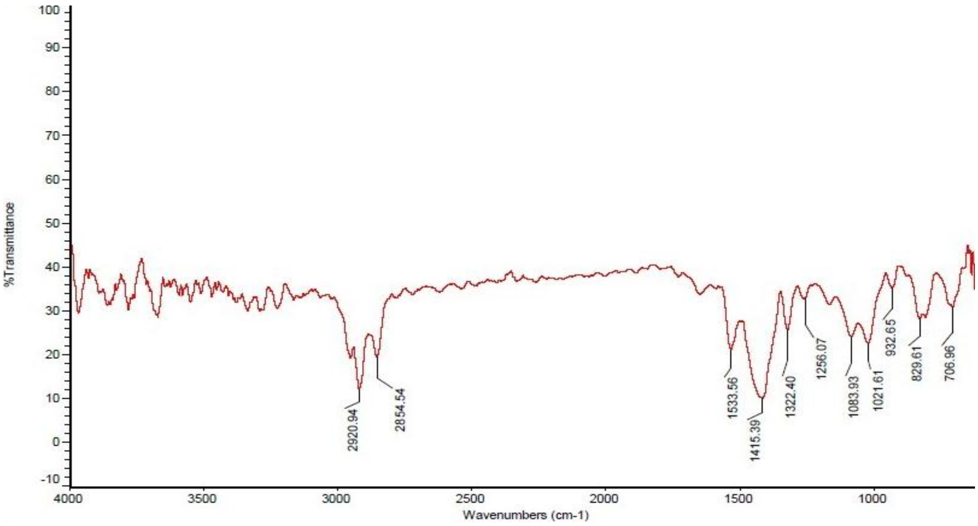


Fig. 3.11 FTIR of NR-BPTU vulcanizate

The FTIR spectrum of the NR vulcanizate using BPTU (Fig. 3.11) reveals that the characteristic IR peaks due to carbonyl and amide NH bonds which were present in the IR spectrum of BPTU (Fig. 3.1) are missing. However there is a characteristic peak due to thionyl group in the NR vulcanizate spectrum which shows that there is some unreacted C=S remains. The FTIR spectrum of the NR vulcanizate obtained by using BPTU along with MBTS (Fig. 3.12) shows the absence of all characteristic peaks due to BPTU. This indicates that BPTU has been fully utilized along with MBTS during vulcanization.

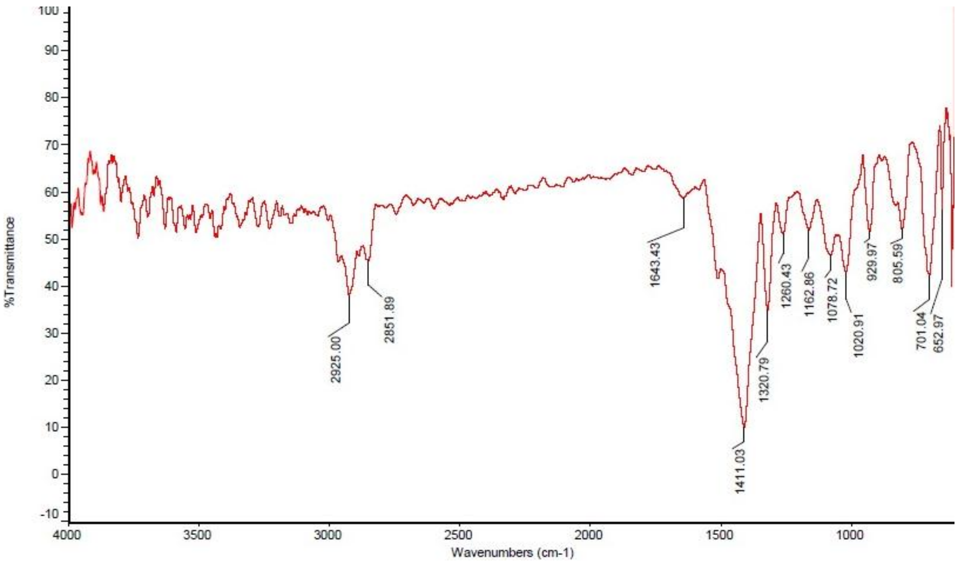


**Fig. 3.12 FTIR of NR vulcanizate using MBTS with BPTU**

### 3.4.2 Mechanical properties

Tensile strength and elongation at break values increase with increase in amount of BPTU as shown in Table 3.10. It is to be noted that the tensile strength values and tensile retention property of vulcanizates containing BPTU (alone) are not appreciable when compared to that of vulcanizates containing primary accelerators alone (MBTS or CBS).

**Table 3.10 Stress-strain properties of NR vulcanizates containing BPTU (alone)**

| Samples | Tensile Strength (MPa) | | | Elongation at break, (%) | | | Modulus at 300% (MPa) | | |
|---|---|---|---|---|---|---|---|---|---|
| | Un-aged | Aged | Retention % | Un-aged | Aged | Retention % | Un-aged | Aged | Retention % |
| $B_0$ | 20.10 | 19.49 | 97 | 1064 | 1104 | 104 | 1.48 | 1.51 | 102 |
| $B_1$ | 3.68 | 3.29 | 89 | 929 | 808 | 87 | 0.97 | 1.06 | 110 |
| $B_2$ | 6.60 | 5.14 | 78 | 980 | 750 | 77 | 1.92 | 1.91 | 99 |
| $B_3$ | 6.94 | 6.53 | 94 | 986 | 941 | 95 | 2.04 | 1.49 | 73 |
| $B_4$ | 9.88 | 10.03 | 101 | 1074 | 943 | 88 | 0.80 | 0.99 | 123 |

Variation in tensile strength on ageing is given in Fig. 3.13. Decrease of tensile strength on ageing can be due to desulphuration on ageing process [21].The values of 300% modulus increased first up to $B_3$ and then decreased on addition of BPTU. Other physical properties are shown in Table 3.11. Tear strength exhibited by the vulcanizates containing BPTU does not make any comparison to that of vulcanizates containing MBTS or CBS. However its values first increased and then decreased with increase in concentration of BPTU.

**Table 3.11 Physical properties of NR vulcanizates of CBS and BPTU (alone)**

| Property | $B_0$ | $B_1$ | $B_2$ | $B_3$ | $B_4$ |
|---|---|---|---|---|---|
| Tear strength(N/mm) | 36.11 | 23.25 | 24.57 | 20.38 | 19.08 |
| Resilience % | 55 | 55 | 53 | 51 | 55 |
| Hardness (Shore A) | 36 | 30 | 32 | 35 | 32 |
| Compression set (%) | 33.67 | 32.31 | 26.85 | 24.12 | 26.67 |
| Crosslink density x$10^5$ (gmol/mL) | 5.35 | 1.87 | 2.05 | 3.73 | 2.45 |

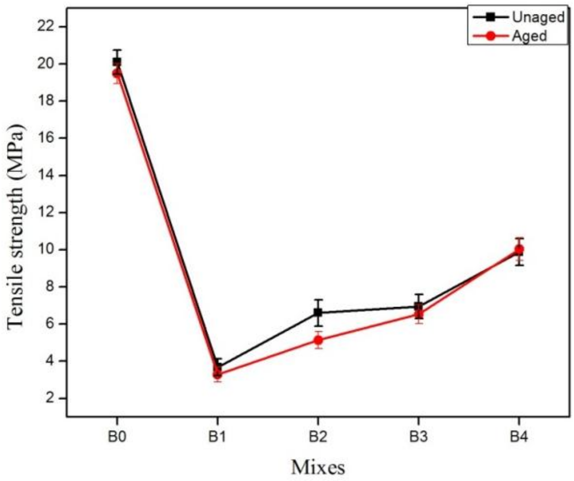


**Fig. 3.13 Tensile strength of NR- BPTU vulcanizates**

Compression set values are better than the vulcanizates of primary accelerator systems, $A_0$ and $B_0$. Compression set values first decreased up to $B_3$ and then increased. Hardness values first increased till $B_3$ and then decreased, but it is reverse in the case of resilience values. The total crosslink density values first increased and then diminished with increase of BPTU concentration and their values are lower than vulcanizates of NR containing conventional accelerator MBTS or CBS.

**Table 3.12 Stress-strain properties of NR vulcanizates containing MBTS- BDPTU**

| Samples | Tensile Strength (MPa) | Elongation at break, (%) | Modulus at 300% (MPa) |
|---|---|---|---|
| $A_0$ | 18.59 | 1365 | 0.94 |
| $C_1$ | 16.61 | 1374 | 1.18 |
| $C_2$ | 13.25 | 1357 | 1.17 |
| $C_3$ | 11.29 | 1244 | 1.51 |

Tensile strength of NR vulcanizates of MBTS-BDPTU system decreased from $C_1$ to $C_3$ as in Fig. 3.14. Elongation at break (%) and modulus at 300% also decreased as given in Table 3.12. Mix $C_1$ shows highest tensile strength and tear strength. Hardness of this system increased on enhancing the concentration of BDPTU, but resilience values decreased as shown in Table 3.13. Lowest value for compression set is obtained for $C_1$ and it also shows the maximum crosslink density. In MBTS-BDPTU-NR system $C_1$ can be considered the optimum concentration, which has the highest CRI value and better mechanical properties.

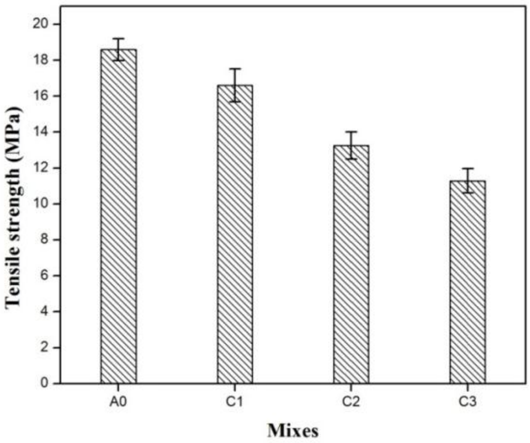


**Fig. 3.14 Tensile strength of NR vulcanizates containing MBTS- BDPTU**

**Table 3.13 Physical properties of NR vulcanizates containing MBTS-BDPTU**

| Property | $A_0$ | $C_1$ | $C_2$ | $C_3$ |
|---|---|---|---|---|
| Tear strength(N/mm) | 32.04 | 29.96 | 28.13 | 23.54 |
| Resilience % | 54 | 61 | 59 | 56 |
| Hardness (Shore A) | 30 | 32 | 35 | 35 |
| Compression set (%) | 30.89 | 35.15 | 36.39 | 37.71 |
| Crosslink density x$10^5$ (gmol/mL) | 3.62 | 5.66 | 5.45 | 5.14 |

In NR vulcanization of CBS-BDPTU system tensile strength first increased up to $D_3$ and then decreased as shown in Table 3.14. $D_3$ has highest value for tensile strength and modulus at 300% elongation. Tensile strength of $D_2$ is nearly the same as $D_3$. Increase of tensile strength and modulus at 300% elongation on ageing can be because of formation of additional crosslinks [22].

**Table 3.14 Stress-strain properties of NR vulcanizates containing CBS-BDPTU**

| Samples | Tensile Strength (MPa) | | | Elongation at break, (%) | | | Modulus at 300% (MPa) | | |
|---|---|---|---|---|---|---|---|---|---|
| | Un- aged | Aged | Retention % | Un- aged | Aged | Retention % | Un- aged | Aged | Retention % |
| $B_0$ | 20.10 | 19.49 | 97 | 1063 | 1103 | 104 | 1.48 | 1.51 | 102 |
| $D_1$ | 12.33 | 22.35 | 181 | 1034 | 1106 | 107 | 1.23 | 1.79 | 146 |
| $D_2$ | 17.81 | 22.08 | 124 | 1213 | 1171 | 97 | 1.40 | 1.64 | 117 |
| $D_3$ | 19.14 | 21.45 | 112 | 1153 | 1160 | 101 | 1.48 | 1.84 | 124 |
| $D_4$ | 9.73 | 15.43 | 159 | 1052 | 1041 | 99 | 1.17 | 1.46 | 125 |

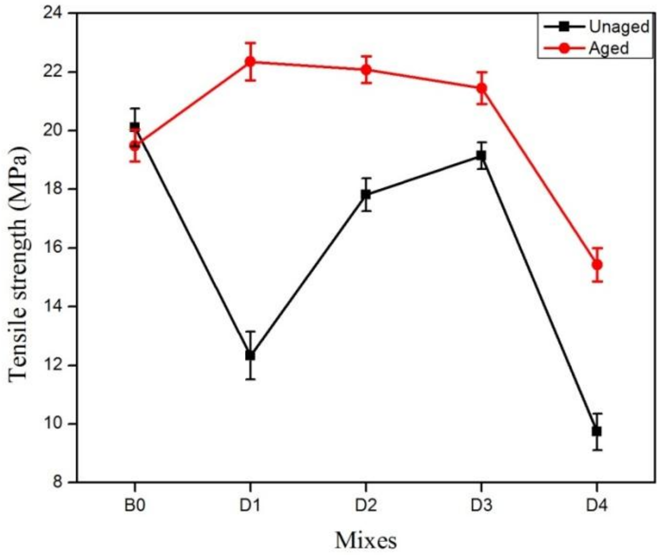


**Fig. 3.15 Tensile strength of NR vulcanizates containing CBS- BDPTU**

Tensile retention of this system is found to be better than the conventional system of CBS alone as in Fig. 3.15. Other physical properties in Table 3.15 show that, $D_2$ has the highest tear and resilience values among them. $D_3$ shows the lowest compression set value. Hardness values are almost the same and are less than $B_0$ and are in line with crosslink density. Considering cure properties and tensile strength, $D_3$ can be considered as the optimum concentration.

**Table 3.15 Physical properties of NR vulcanizates containing CBS- BDPTU**

| **Property** | **$B_0$** | **$D_1$** | **$D_2$** | **$D_3$** | **$D_4$** |
|---|---|---|---|---|---|
| Tear strength (N/mm) | 36.11 | 23.43 | 32.05 | 25.41 | 19.64 |
| Resilience % | 55 | 60 | 63 | 58 | 61 |
| Hardness (Shore A) | 36 | 32 | 31 | 31 | 30 |
| Compression set (%) | 33.67 | 42.63 | 35.91 | 30.32 | 45.65 |
| Crosslink density x$10^5$ (gmol/mL) | 5.35 | 3.36 | 3.68 | 3.91 | 2.54 |

**Table 3.16 Stress-strain properties of NR vulcanizates containing MBTS-phenylthiazole**

| samples | Tensile Strength (MPa) | Elongation at break, (%) | Modulus at 300% (MPa) |
|---|---|---|---|
| $A_0$ | 18.59 | 1365 | 0.94 |
| $P_1$ | 16.96 | 1410 | 1.27 |
| $P_2$ | 18.17 | 1312 | 1.34 |
| $P_3$ | 19.82 | 1003 | 1.99 |

Tensile properties of NR vulcanizates of phenylthiazoles, $P_1$- $P_3$ are given in, Fig. 3.16. This shows that $P_3$ has the highest tensile strength and $P_2$ has nearly the same strength. Highest value for modulus at 300% elongation and lowest value for elongation at break (%) are also given by $P_3$ as given in Table 3.16.

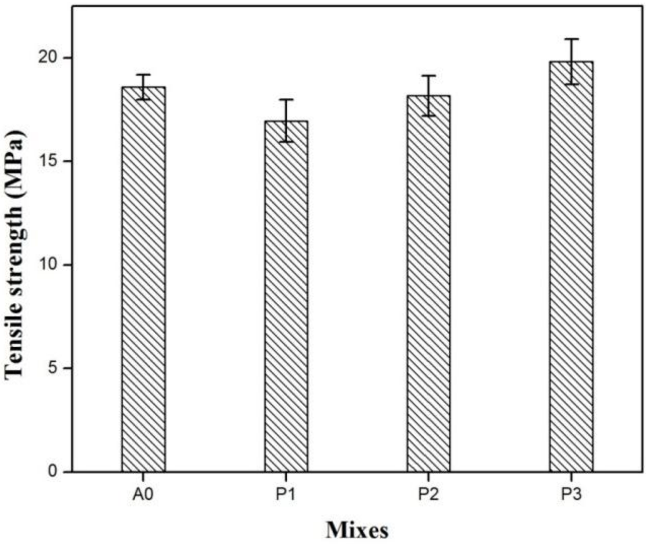


**Fig. 3.16 Tensile strength of NR vulcanizates containing MBTS-phenylthiazole**

**Table 3.17 Physical properties of NR vulcanizates containing MBTS-phenylthiazole**

| Property | $A_0$ | $P_1$ | $P_2$ | $P_3$ |
|---|---|---|---|---|
| Tear strength(N/mm) | 32.04 | 23.18 | 26.17 | 37.76 |
| Resilience % | 54 | 49 | 53 | 53 |
| Hardness (Shore A) | 30 | 35 | 39 | 39 |
| Compression set (%) | 30.89 | 29.17 | 27.07 | 24.50 |
| Crosslink density x$10^5$ (gmol/mL) | 3.62 | 4.50 | 4.96 | 5.17 |

Vulcanizate $P_3$ exhibits highest tear strength. Resilience and hardness values of $P_2$ and $P_3$ are the same (Table 3.17). Compression set value of $P_3$ is lowest and that of $P_1$ is comparable to $A_0$ (MBTS alone). Lowest crosslink density value is presented by $P_1$. These results show that the compound DEIP (4b) has better cure activating nature in NR vulcanization while MPIP (4c) gives better mechanical properties to NR vulcanizates.

## 3.5 Conclusion

The new organic molecule N-benzoyl-N$^{'}$,N$^{'}$–pyrrolidinylthiourea (BPTU) a derivative of thiourea synthesised can accelerate the vulcanization process in NR. Considering the cure and mechanical properties, $B_3$ (2.0 phr) can be taken as the best candidate. But its activity is not comparable to MBTS or CBS. Another derivative of thiourea BDPTU synthesized was found to be inactive in accelerating the NR vulcanization, but it is found to have accelerating activity with MBTS and CBS. Vulcanization of NR using MBTS and CBS systems $C_1$ (0.5 phr) and $D_3$ (1.0 phr) respectively are found to be the optimum dosage of BDPTU in them. Out of three phenylthiazoles DMIP, DEIP and MPIP examined, DEIP [2-(N,N-

Methylphenylamino)-5-(indol-3-oyl)-4-phenylthiazole] (i.e. mix $P_2$) is found to have more cure accelerating property with MBTS in the NR vulcanization. Further studies on phenylthaizoles could not be carried out due to the undesirable physical properties associated with the compound under normal conditions even though it has some accelerator properties. Therefore further studies were planned on the role of BPTU as an accelerator in the vulcanization of elastomers.

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# Chapter 4

# STUDIES ON THE EFFECT OF N-BENZOYL-N$^{1}$, N$^{1}$-PYRROLIDINYLTHIOUREA AS AN ACCELARATOR IN THE SULPHUR VULCANIZATION OF NATURAL RUBBER

Contents

## Part I

## STUDIES ON NR GUM COMPOUNDS

### 4.1.1 Introduction

In this study an attempt is made to evaluate the synergistic effect of benzoylpyrrolidinylthiourea in binary accelerator systems with MBTS or CBS in sulphur vulcanization of natural rubber. Different experimental mixes were prepared by changing the concentration of BPTU along with a primary accelerator MBTS or CBS. Mixes containing TMTD along with MBTS or CBS were studied as reference mix. To find the effect of BPTU in the vulcanization, cure characteristics of the mixes were evaluated. After curing the mixes at 150 $^{o}$C, vulcanizates were evaluated for various mechanical properties. These properties were compared with properties of vulcanizates obtained from conventional single accelerator system and also with binary system containing TMTD. The crosslink density of the vulcanizates was also determined using swelling method.

### 4.1.2 Experimental

The formulations of the different mixes prepared are given in Table 4.1 and 4.2. Accelerators and other ingredients were taken in parts per hundred rubbers (phr). Mixes $A_1$ to $A_5$ contain varying concentrations of BPTU ranging from 0.1 to 1.5 phr with one phr MBTS. Mix $A_0$ contains only one phr of MBTS (single accelerator system) while mix A contains only BPTU (2.5 phr, single accelerator system). Formulation of A is seme as that of $B_4$ in Table 3.2. Mix $A_6$ is a conventional binary system containing 1.0 phr MBTS with 0.2 phr TMTD. $B_1$ to $B_4$ are systems containing BPTU in varying concentrations, ranging from 0.1 to 1.0 phr along with 1.0 phr CBS. Mix $B_0$ contains only one phr CBS and $B_5$ contains conventional binary system containing 1.0 phr CBS with 0.2 phr TMTD. All the mixes are prepared in SEV systems.

**Table 4.1 Formulations of the NR mixes containing MBTS-BPTU & MBTS-TMTD**

| **Ingredients** | **A** | **$A_0$** | **$A_1$** | **$A_2$** | **$A_3$** | **$A_4$** | **$A_5$** | **$A_6$** |
|---|---|---|---|---|---|---|---|---|
| NR (g) | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| ZnO (phr) | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 |
| Stearic acid (phr) | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 |
| MBTS (phr) | 0 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| BPTU (phr) | 2.5 | 0 | 0.1 | 0.2 | 0.5 | 1.0 | 1.5 | 0 |
| TMTD (phr) | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.2 |
| Sulphur (phr) | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 |

**Table 4.2 Formulations of NR mixes containing CBS-BPTU & CBS-TMTD**

| Ingredients | $B_0$ | $B_1$ | $B_2$ | $B_3$ | $B_4$ | $B_5$ |
|---|---|---|---|---|---|---|
| NR (g) | 100 | 100 | 100 | 100 | 100 | 100 |
| ZnO (phr) | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 |
| Stearic acid (phr) | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 |
| CBS (phr) | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| BPTU (phr) | 0.0 | 0.1 | 0.2 | 0.5 | 1.0 | 0.0 |
| TMTD (phr) | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.2 |
| Sulphur (phr) | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 |

All the mixes were prepared on a laboratory size two-roll mixing mill. The determination of cure characteristics, equilibrium swelling data, physical and mechanical properties of the vulcanizates were carried out as described in chapter 2.

## 4.1.3 Results and discussion

### 4.1.3.1 Cure characteristics of NR mixes containing MBTS-BPTU

The role of accelerators is remarkable in reducing the cure time and improving the mechanical properties of the vulcanizate. The rheographs of the mixes carrying MBTS cured at 150 $^{o}$C are shown in Fig. 4.1a, 4.1b & 4.1c. The cure characteristics of NR gum using MBTS-BPTU is given in Table 4.3. The scorch time ($t_{10}$) decreased as the amount of BPTU increased. This, in fact, affects the scorch safety of the compound. The maximum torque, which is a measure of the stiffness of the compound, is found to increase with BPTU concentration. It is directly related to the modulus of the compound.

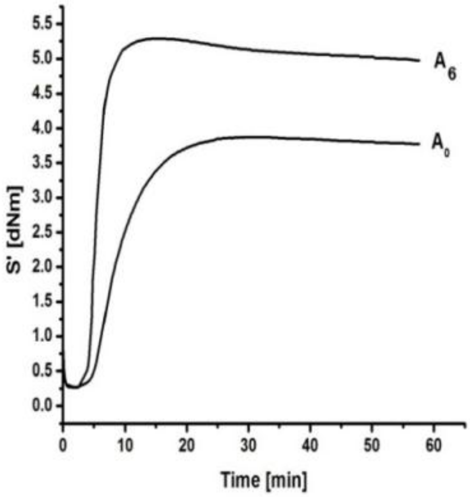

Fig. 4.1a Rheographs of NR mixes $A_0$ and $A_6$

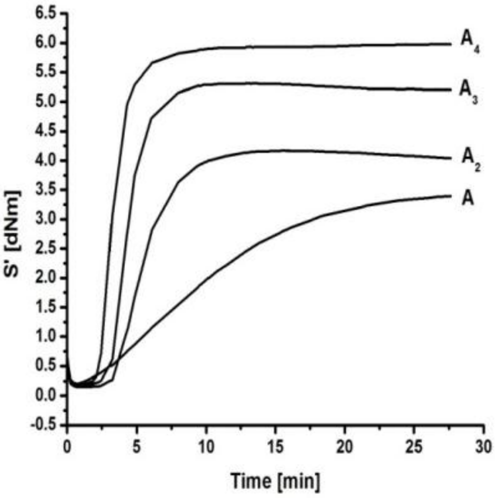

Fig. 4.1b Rheographs of the NR mixes A, $A_2$ -$A_4$

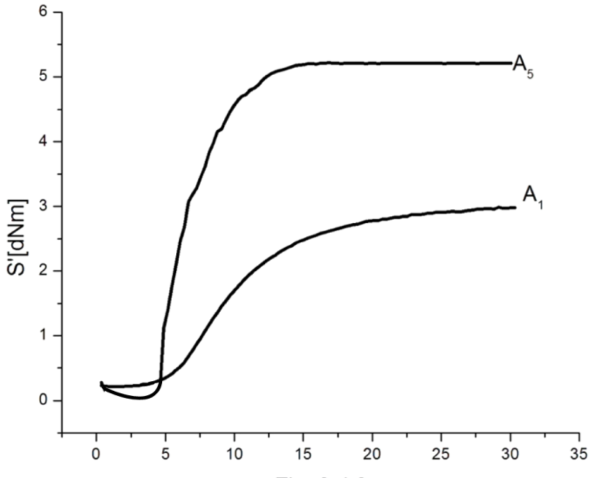

Fig. 4.1c Rheographs of the NR mixes $A_1$, $A_5$

**Table 4.3 Cure characteristics of NR mixes containing MBTS-BPTU and MBTS-TMTD (150 °C)**

| Cure Characteristics | A | $A_0$ | $A_1$ | $A_2$ | $A_3$ | $A_4$ | $A_5$ | $A_6$ |
|---|---|---|---|---|---|---|---|---|
| Scorch time, $t_{10}$(min) | 3.14 | 5.48 | 6.40 | 3.83 | 3.23 | 2.55 | 2.14 | 4.13 |
| Optimum cure time, $t_{90}$(min) | 19.04 | 16.38 | 16.19 | 8.57 | 6.17 | 5.10 | 5.53 | 7.49 |
| CRI ($min^{-1}$) | 6.29 | 9.17 | 10.21 | 21.10 | 34.01 | 39.21 | 29.50 | 29.76 |
| Torque Max. (dNm) | 3.42 | 3.88 | 4.02 | 4.18 | 5.31 | 5.98 | 5.68 | 5.29 |
| Torque Min. (dNm) | 0.19 | 0.27 | 0.26 | 0.14 | 0.19 | 0.19 | 0.14 | 0.26 |
| Torque difference, $M_H$-$M_L$ (dNm) | 3.23 | 3.61 | 3.76 | 4.04 | 5.12 | 5.79 | 5.54 | 5.03 |

The torque difference between maximum and minimum is highest for $A_4$. As the concentration of BPTU increases, the time needed for optimum cure ($t_{90}$) decreases significantly up to 1 phr ($A_4$).The vulcanization plateau obtained for MBTS-BPTU cure curves(except $A_1$) are broad and show resistance to reversion. The width of the plateau is a measure of the heat stability since it indicates the influence of the heat of vulcanization on the stress value of the vulcanizate [1].

The decrease in cure time is extremely beneficial because it increases the production rate. Among these mixes of the gum system, maximum cure rate is shown by $A_4$, but its scorch safety is less than $A_3$. It is also interesting to note that the cure rate of $A_4$ increased approximately by 33% to that of reference mix $A_6$ and six times that of reference mix $A_0$. The optimum concentration of BPTU required for vulcanization is based on the cure characteristics and tensile properties obtained. The cure rate index

(CRI) value is a measure of the rate of the vulcanization process. It increases significantly with the amount of BPTU. The straight line graph obtained by plotting ln($M_H$ - $M_t$) against time (t), (Fig. 4.2) shows that the vulcanization reaction follows first-order kinetics [2].

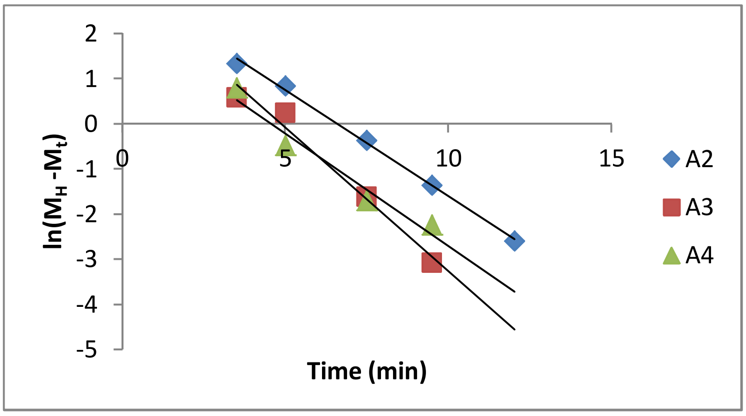

**Fig. 4.2 Plots of ln ($M_H$- $M_t$) versus time for NR-MBTS-BPTU mixes at 150 °C**

### 4.1.3.2 Cure characteristics of NR mixes containing CBS-BPTU

The rheographs of mixes ($B_0$-$B_5$) are given in Fig. 4.3a & 4.3b and the cure characteristics are given in Table 4.4.

**Table 4.4 Cure characteristics of NR mixes containing CBS-BPTU and CBS-TMTD (150 °C)**

| Cure Characteristics | $B_0$ | $B_1$ | $B_2$ | $B_3$ | $B_4$ | $B_5$ |
|---|---|---|---|---|---|---|
| Scorch time, $t_{10}$ (min) | 2.72 | 2.83 | 2.68 | 2.07 | 1.85 | 1.84 |
| Optimum cure time, $t_{90}$(min) | 7.41 | 8.77 | 5.81 | 4.45 | 4.39 | 4.05 |
| CRI (min$^{-1}$) | 21.32 | 16.83 | 31.95 | 42.02 | 39.37 | 45.25 |
| Torque Max. (dNm) | 4.86 | 4.10 | 4.89 | 5.32 | 5.16 | 5.73 |
| Torque Min. (dNm) | 0.31 | 0.25 | 0.17 | 0.22 | 0.16 | 0.24 |
| Torque difference, $M_H$-$M_L$ (dNm) | 4.55 | 3.85 | 4.72 | 5.1 | 5.0 | 5.49 |

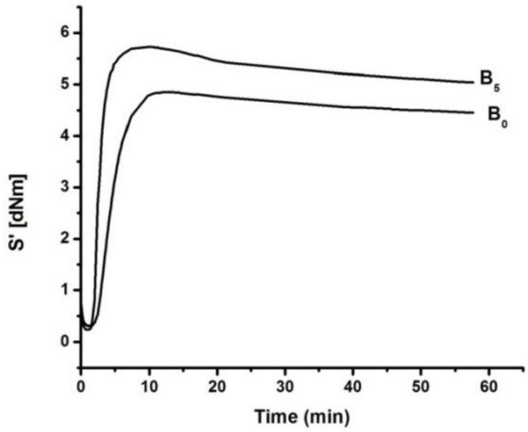

**Fig. 4.3a Rheographs of the mixes $B_0$& $B_5$**

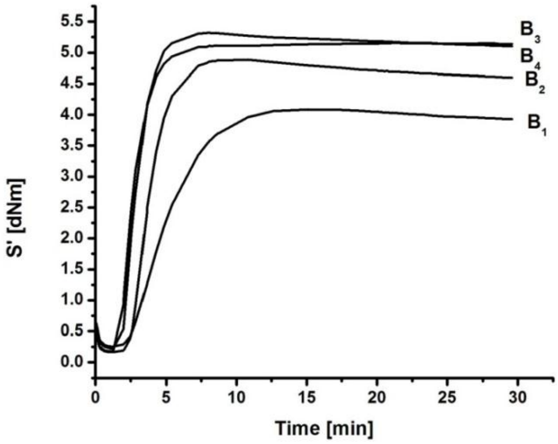

**Fig. 4.3b Rheographs of the mixes $B_1$, $B_2$, $B_3$ and $B_4$**

It is found that when BPTU is used along with CBS, the optimum cure time ($t_{90}$) diminishes as the amount of BPTU increases up to 0.5phr ($B_3$). The decrease in cure time is of prime importance in vulcanization as it leads to a faster end product formation. This could be due to a better cleavage of S-S bond in CBS due to the nucleophilic attack of BPTU, facilitating the availability of S-S chains to form crosslinks in NR. At the same time, the scorch time ($t_{10}$) is found to be decreasing. This affects the scorch safety of the compound. The maximum torque, which is a measure of the stiffness of the compound, is found to increase with the concentration of BPTU upto 0.5 phr ($B_3$). The torque difference between maximum and minimum is highest for $B_{3.}$ It is directly related to modulus of the compound.

The cure rate index (CRI) value, a measure of the rate of the vulcanization process, increases with the concentration of BPTU up to 0.5 phr **.** This reveals the cure activating nature of the accelerator BPTU in a binary system. The CRI value of $B_3$ is twice that of reference mix $B_0$ (CBS alone). Lowering of cure time can be assigned to the nucleophilic character of BPTU. When $\ln(M_H - M_t)$ is plotted against t, a straight line graph is obtained (Fig. 4.4). This proves that cure reaction of the compounds follows first-order kinetics. The vulcanization plateau obtained for $B_3$ is broad showing resistance to reversion. Thus from the cure characteristics, we infer that the new organic compound BPTU in combination with a known conventional accelerator CBS can act as an effective binary accelerator in the sulphur vulcanization of NR at 150 $^{o}$C. Though it shows appreciable reduction in cure time with MBTS or CBS in NR vulcanization, optimum cure time and CRI value of mix A which contains 2.5 phr of BPTU alone are not comparable to that of MBTS or CBS alone mixes. Thus a synergistic behavior [3, 4] is observed in the curing process of NR by using BPTU as an accelerator along with MBTS or CBS.

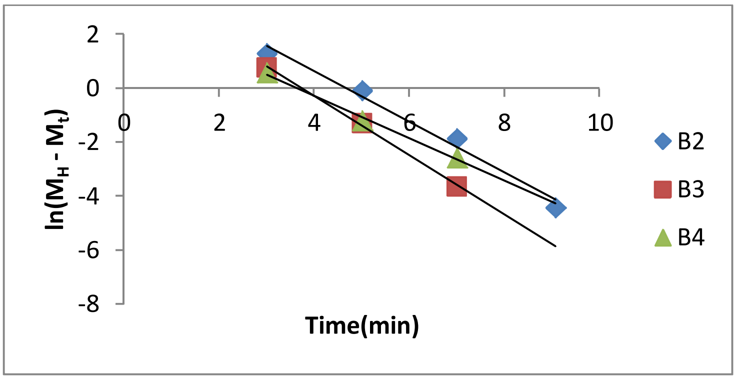

**Fig. 4.4 Plots of ln ($M_H$- $M_t$) versus time for NR-CBS-BPTU mixes at 150 °C**

### 4.1.3.3 Mechanical properties

Considering the NR vulcanizates of MBTS-BPTU system the tensile strength, tear strength, compression set % and hardness increased with increase in concentration of BPTU to an optimum value and then decreased. This is in correlation with the torque difference $M_H$-$M_L$ (Table 4.3).

The elongation at break values shows a negative trend, as the amount of BPTU increased. This can be due to the decrease in flexibility resulting from enhancement of crosslink density. Tensile and percentage of elongation at break before and after ageing (for 24 hours at 70 °C) are given in Figs. 4.5 & 4.6. It showed that tensile retention property of the vulcanizate was less when compared to the reference mixes ($A_0$, $A_6$). Decrease of tensile strength on ageing is due to less stable polysulphidic links converted to mono and disulphide links [5]. Modulus at 300% elongation increased on the addition of BPTU and also after ageing for 24 hours at 70 °C (Fig. 4.7). Increase of modulus with the increase of BPTU show increase of stiffness and thus elongation of break decreased [6].

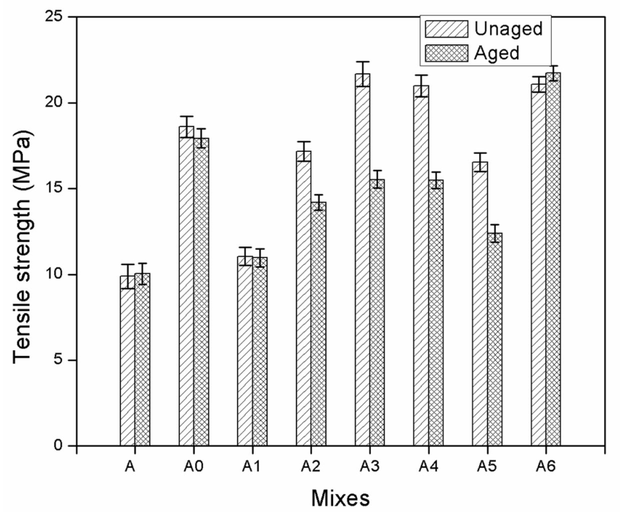

**Fig. 4.5 Tensile strength of NR-MBTS-BPTU vulcanizates**

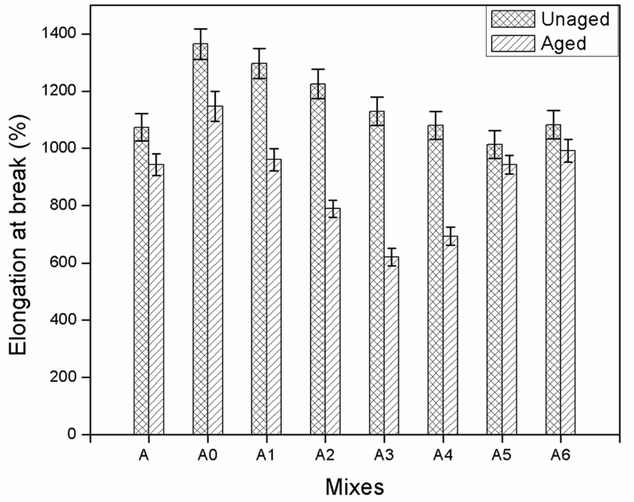

**Fig. 4.6 Elongation at break (%) of NR-MBTS-BPTU vulcanizates**

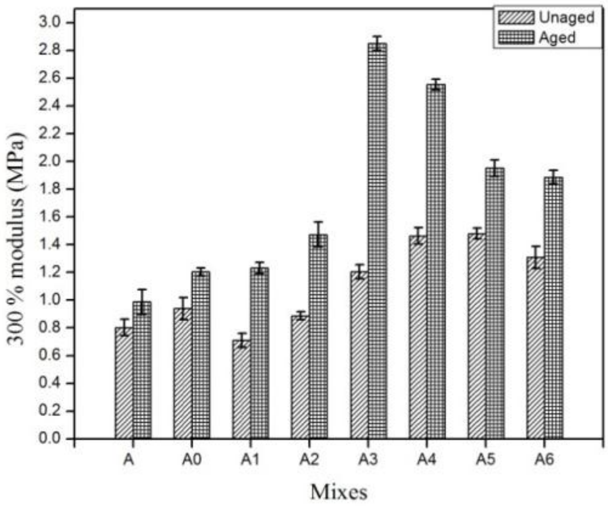

**Fig. 4.7 Modulus at 300% of NR-MBTS-BPTU vulcanizates**

**Table 4.5 Properties of NR-MBTS –BPTU vulcanizates**

| **Property** | **A** | **$A_0$** | **$A_1$** | **$A_2$** | **$A_3$** | **$A_4$** | **$A_5$** | **$A_6$** |
|---|---|---|---|---|---|---|---|---|
| Resilience % | 55 | 54 | 60 | 55 | 63 | 61 | 61 | 62 |
| Hardness (Shore A) | 32 | 30 | 32 | 35 | 39 | 38 | 36 | 39 |
| Crosslink density x$10^5$ (gmol/mL) | 2.45 | 3.63 | 2.38 | 4.09 | 5.10 | 5.54 | 4.31 | 5.07 |

Variation in tear strength and compression set values are given in Fig. 4.8. The physical properties of different NR vulcanizates with MBTS-BPTU are given in Table 4.5. Values of tear strength, resilience, hardness and crosslink density increased with the amount of BPTU. Compression set value of $A_4$ is at par with reference mixes $A_0$ and $A_6$. Resilience and hardness of $A_3$ were also better than the reference mixes ($A_0$ & $A_6$). These results show that the mixes $A_3$ and $A_4$ gave comparable tensile and retention properties even though $A_4$ gave significantly higher cure rate. Hence concentration of BPTU in $A_4$ can be taken as the optimum dosage considering cure characteristics. This is in correlation with the observed torque difference ($M_H - M_L$) and crosslink density.

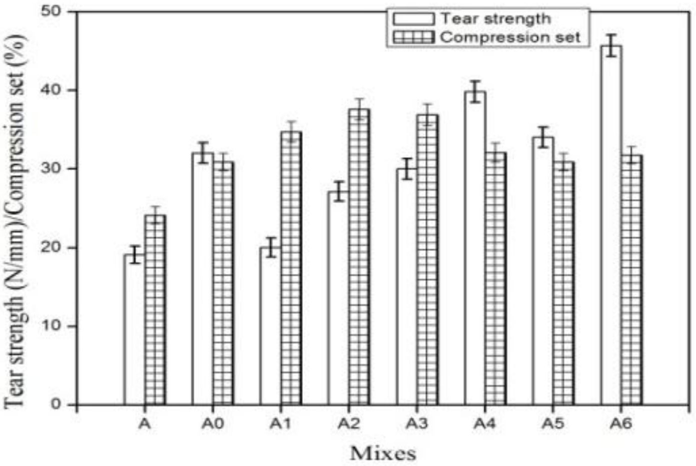

**Fig. 4.8 Tear strength and compression set of NR-MBTS-BPTU vulcanizates**

The stress-strain properties of the NR vulcanisates of CBS-BPTU before and after ageing for 24 hours at 70 $^{o}$C, shows marginal retention in the properties (Figs. 4.9-4.11). The tensile strength shows an upward trend with the increase in concentration of BPTU and reaches a maximum value at $B_3$ (0.5 phr BPTU), almost comparable to the reference mix ($B_5$). With further increase in concentration of BPTU the tensile strength diminishes. This may be due to desulphuration during vulcanization process which turns polysuphidic linkage to mono and disulphidic linkages [5]. For the mixes $B_1$ and $B_2$ the tensile strength decreases after ageing as expected from the thermal ageing process. But for $B_3$ and $B_4$ it increases and is comparable with the reference mix $B_5$ as shown in Fig. 4.9. This may be due to the additional crosslinking that occurs with the vulcanizates during ageing process [7]. The % of elongation at break shows an inverse relationship with concentration of BPTU as shown in Fig. 4.10. This is due to increase of modulus on increase of accelerator BPTU.

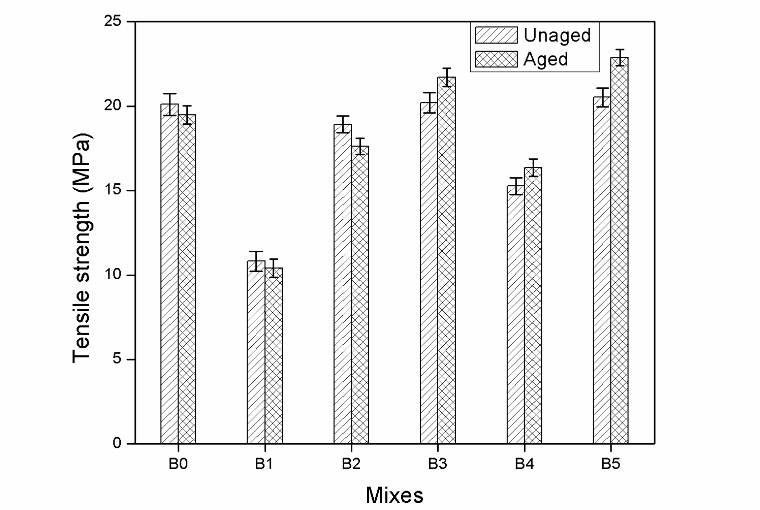

**Fig. 4.9 Tensile strength of NR-CBS-BPTU vulcanizates**

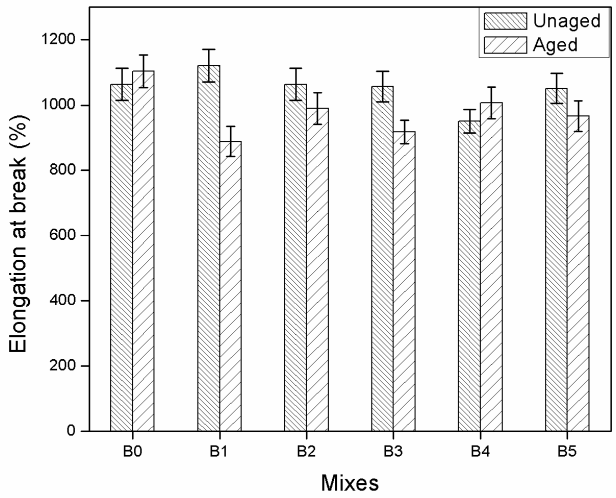

**Fig. 4.10 Elongation at break (%) of NR-CBS-BPTU vulcanizates**

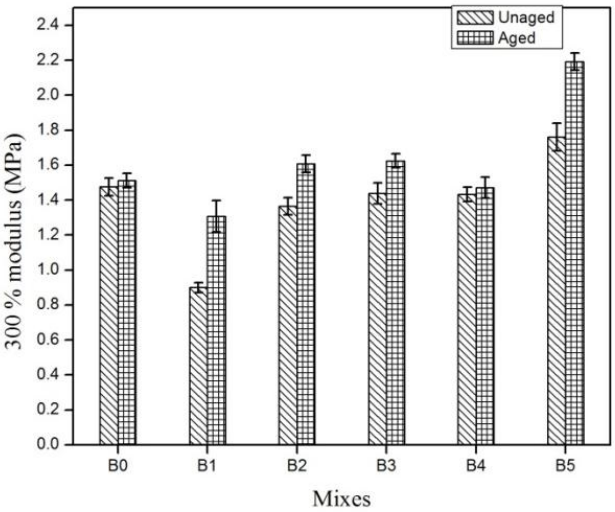

**Fig. 4.11 Modulus at 300% of NR-CBS-BPTU vulcanizates**

The resilience and hardness of the vulcanizate (Table 4.6) presents a pattern of increasing values from $B_1$ to $B_3$ and moves down to $B_4$. Hardness which is a measure of modulus of elasticity at low strain [8] is found to be highest for $B_3$ and is the same as that of reference mix $B_5$. Compression set of rubber vulcanizate depends on the type of the polymer, nature of cross links, type of filler, its quantity and vulcanization system [6, 9]. Measurement of set under compression gives an evaluation of either the creep or the stress relaxation of rubber.

**Table 4.6 Properties of NR–CBS-BPTU vulcanizate**

| **Property** | **$B_0$** | **$B_1$** | **$B_2$** | **$B_3$** | **$B_4$** | **$B_5$** |
|---|---|---|---|---|---|---|
| Resilience % | 55 | 60 | 60 | 67 | 58 | 63 |
| Hardness (Shore A) | 36 | 29 | 31 | 39 | 34 | 39 |
| Crosslink density x$10^5$ (gmol/mL) | 5.35 | 2.93 | 3.88 | 4.33 | 4.27 | 5.99 |

The compression set values of the vulcanizate show down ward trend where as $B_4$ is almost at par with reference mix $B_5$ (Fig. 4.12).

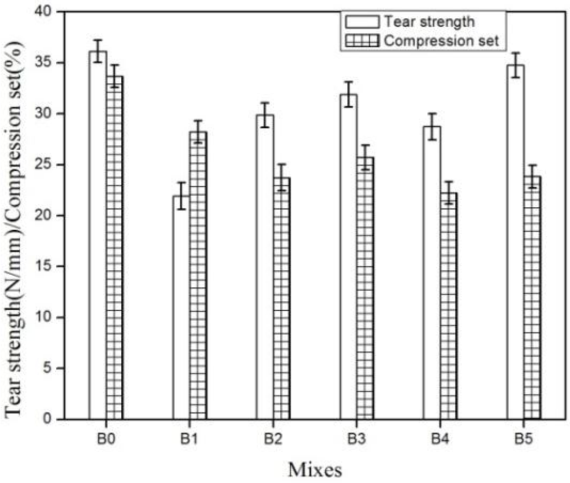

**Fig. 4.12 Tear strength and compression set of NR-CBS-BPTU vulcanizates**

The tensile and tear strength shown by the mix A (BPTU alone) is not appreciable. Other physical properties are also not comparable with that of MBTS or CBS alone, it can exhibit synergistic properties when combined with MBTS or CBS.

### 4.1.3.4 Crosslink density measurements

The effect of crosslinking is the most important and best understood in elastomers. The physically effective crosslink density includes contribution from the chemical crosslinks, chain entanglements and loose chain ends acting as crosslinks in the rubber [10, 11]. Crosslink densities of the NR vulcanizate MBTS-BPTU calculated from the equilibrium swelling measurements in toluene are given in Table 4.5. The crosslink density was found to increase with increase in concentration of BPTU upto $A_4$. For the gum system there is a pronounced increase in tensile strength with increase in the concentration of BPTU, but A3 and A4 are observed to have almost the same tensile strength, even though the crosslink density continuously increased up to $A_4$. A similar pattern is observed in the case of modulus also. The crosslink density improved with increase in concentration of BPTU up to 0.5 phr in NR vulcanizates containing CBS-BPTU (Table 4.6). The decrease in mechanical properties from $B_3$ to $B_4$ is well in agreement with the observed crosslink densities.

### 4.1.4 Conclusion

This study presents a new candidate, BPTU, a simple organic molecule as a novel accelerator in vulcanization of NR. A set of new, efficient and hitherto unknown binary accelerator systems viz. MBTS-BPTU (N-benzoyl-N',N'-pyrrolinidylthiourea) and CBS-BPTU in [SEV system] sulphur vulcanization of natural rubber is introduced. With the use of MBTS-BPTU system ($A_4$) the cure time is decreased to one third and cure rate increased six times when compared to the reference mix $A_0$ (MBTS alone) and better than NR mix containing MBTS-TMTD, leading to cost effectiveness and considerable improvement in productivity. Mechanical properties such as tensile strength, tear strength, resilience, hardness and compression set % were found to be better for the vulcanizates prepared using the BPTU as compared to the reference vulcanizates. This is in correlation with the cross link densities of the vulcanizates. This result supports the nucleophilic reaction mechanism of Philpott for binary accelerator system.

BPTU effectively acts as a secondary accelerator along with CBS. This system improves the processing characteristics and mechanical properties of the NR causing the process more economically viable and industrially useful. It is found that the optimum concentration of 0.5 phr BPTU with 1.0 phr CBS reduces the optimum cure time to almost half of that of reference mix $B_0$ and the rate of vulcanization doubled. The tensile and other mechanical properties (hardness, resilience, and tear strength) of above said vulcanizate ($B_3$) is found to be better than $B_0$ and comparable to reference mix $B_5$, containing the fastest accelerator TMTD. This work also supports the nucleophilic mechanism of the secondary accelerator in the sulphur vulcanization of natural rubber.

## Part II

## STUDIES ON SILICA FILLED SYSTEMS OF NR

### 4.2.1 Introduction

Rubber vulcanizates are usually reinforced with fillers. Incorporation of fillers can improve processability and reduce cost. Reinforcing fillers are used to enhance the properties like tensile strength, abrasion resistance, tear resistance, etc. Carbon black and silica are the most important reinforcing fillers. Silica is highly adsorptive and it is necessary to formulate NR compounds with more than normal quantity of accelerator or a combination of accelerators.

In the first part of this chapter it has been reported that BPTU is an effective secondary accelerator in NR gum vulcanization along with MBTS or CBS. So it is decided to extend the study to NR filled systems also. This part of the study includes aspects like mixing, curing and the evaluations of various physical and mechanical properties of silica filled NR vulcanizates. Cure characteristics and various properties of the experimental mixes were compared with the properties of mixes carrying conventional binary systems namely MBTS-TMTD and CBS-TMTD. They were also compared with mixes having single accelerator systems of MBTS and CBS. Kinetic study of vulcanization for experimental mixes was also carried out. To understand the variations in physical properties of the various vulcanizates, the total crosslink density was calculated from equilibrium swelling measurements. Thermal stability of vulcanizates were compared with those of vulcanizates obtained from conventional accelerators.

### 4.2.2 Experimental

The formulations of the different mixes prepared are given in Table 4.7. Accelerators and other ingredients were taken in parts per hundred rubbers. Mixes $AA_1$ to $AA_4$ contains varying concentrations of BPTU ranging from 0.1 to 1.0 phr with one phr MBTS. Mix $AA_0$ contains only one phr of MBTS (single accelerator system) while mix $AA_5$ is a conventional binary system containing 1.0 phr MBTS with 0.2 phr TMTD. The systems $BB_1$ to $BB_4$ contain 1.0 phr CBS with varying amounts of BPTU ranging from 0.1 to 1.0 phr. Mix $BB_0$ contains only one phr CBS while $BB_5$ contains conventional binary system containing 1.0 phr CBS with 0.2 phr TMTD. That only 30 phr of precipitated silica was loaded as higher loading was found to raise the temperature and can lead to pre-vulcanization. It is known that the shear heating during mixing goes up with increasing the silica loading due to the elevation of compound viscosity [12]. The compounding of NR was done on a two- roll mill. Details of the experiments conducted are given in chapter 2.

**Table 4.7 Formulations of different silica filled NR mixes**

| **Ingredients** | **$AA_0$** | **$AA_1$** | **$AA_2$** | **$AA_3$** | **$AA_4$** | **$AA_5$** | **$BB_0$** | **$BB_1$** | **$BB_2$** | **$BB_3$** | **$BB_4$** | **$BB_5$** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| NR (g) | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| ZnO (phr) | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 |
| Stearicacid(phr) | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 |
| Silica (phr) | 30 | 30 | 30 | 30 | 30 | 30 | 30 | 30 | 30 | 30 | 30 | 30 |
| DEG(phr) | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 |
| SP(phr) | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| Naphthenic oil(phr) | 6.0 | 6.0 | 6.0 | 6.0 | 6.0 | 6.0 | 6.0 | 6.0 | 6.0 | 6.0 | 6.0 | 6.0 |
| MBTS(phr) | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | - | - | - | - | - | - |
| CBS (phr) | - | - | - | - | - | - | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| BPTU (phr) | 0.0 | 0.1 | 0.2 | 0.5 | 1.0 | 0.0 | 0.0 | 0.1 | 0.2 | 0.5 | 1.0 | 0.0 |
| Sulphur (phr) | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 |
| TMTD (phr) | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.2 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.2 |

## 4.2.3 Results and discussion

### 4.2.3.1 Cure characteristics

The effect of a new compound BPTU along with MBTS as well as with CBS as binary accelerator system in the vulcanization of silica filled NR was investigated and compared with systems containing TMTD &MBTS and TMTD& CBS respectively. Cure characteristics of all the mixes are given in Table 4.8.

**Table 4.8 Cure characteristics of silica filled NR vulcanizates (150 $^oC$)**

| **Cure Characteristics** | **$AA_0$** | **$AA_1$** | **$AA_2$** | **$AA_3$** | **$AA_4$** | **$AA_5$** | **$BB_0$** | **$BB_1$** | **$BB_2$** | **$BB_3$** | **$BB_4$** | **$BB_5$** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Induction time $t_5$(min) | 2.89 | 2.16 | 1.70 | 1.53 | 1.34 | 1.74 | 1.58 | 1.48 | 1.36 | 1.24 | 1.00 | 1.27 |
| Scorch time $t_{10}$(min) | 3.18 | 2.31 | 1.83 | 1.63 | 1.42 | 1.83 | 1.75 | 1.60 | 1.48 | 1.34 | 1.08 | 1.34 |
| Optimum cure time $t_{90}$(min) | 8.04 | 5.72 | 4.15 | 3.52 | 2.94 | 3.46 | 5.67 | 4.75 | 4.25 | 3.55 | 2.85 | 3.01 |
| CRI ($min^{-1}$) | 20.58 | 29.32 | 43.10 | 52.91 | 65.79 | 61.35 | 25.51 | 31.75 | 36.10 | 45.25 | 56.50 | 59.88 |
| Torque Max. (dNm) | 5.00 | 5.22 | 5.69 | 6.28 | 6.94 | 5.75 | 4.85 | 4.89 | 5.21 | 5.40 | 6.10 | 5.52 |
| Torque Min. (dNm) | 0.20 | 0.10 | 0.25 | 0.22 | 0.25 | 0.16 | 0.08 | 0.09 | 0.15 | 0.15 | 0.14 | 0.13 |

The minimum torque can be taken as a measure of the viscosity of the masticated rubber. The only variable in the mixes was the amount of BPTU. As the amount of BPTU increases the optimum cure time ($t_{90}$) decreases in all the cases. The lowering of cure time is of high interest for the rubber industry. Rheometric induction time ($t_5$) is the minimum time needed for the start of vulcanization process. Induction time also decreases and follows the same trend as optimum cure time. BPTU reduces the induction time considerably and thereby starts the vulcanization process quickly as evident from Table 4.8. However the scorch time ($t_{10}$) was also found to be decreasing and can affect scorch safety of the compound. The maximum torque, which is a measure of the stiffness of the compound, was found to be increasing with the concentration of BPTU in both the systems.

Cure rate index, the kinetic parameter of vulcanization, was estimated [2]. The CRI value was found to increase significantly with increasing dosage of BPTU. The addition of 0.1phr BPTU to 1.0 phr of MBTS ($AA_1$) gives 42 % higher CRI value than $AA_0$ (1.0 phr MBTS alone) and similar change noticed for CBS system ($BB_1$ to $BB_0$) is 24%. This proves the cure activating nature of the secondary accelerator BPTU.

On comparing the cure characteristic of MBTS-BPTU and CBS-BPTU systems, we found that MBTS-BPTU system showed better scorch safety coupled with much higher CRI value. The induction time ($t_5$), scorch time ($t_{10}$) and maximum torque values of $AA_2$ are at par with $AA_5$ with the same amount of secondary accelerator (1.2 phr), the latter carrying the fastest accelerator TMTD. Rheographs of MBTS-BPTU and CBS-BPTU systems are given in Figs. 4.13 & 4.14 respectively.

The mixes $AA_4$ and $BB_4$ each containing 1:1 accelerators showed the highest cure rate and maximum torque value. Among them, $AA_4$ is better and has CRI value 13% higher than $BB_4$ and 7% higher than $AA_5$. The cure curves obtained for $AA_3$, $AA_4$ and $BB_4$ shows more resistance to reversion than the conventional mixes ($AA_5$ & $BB_5$) is evident from Figs. 4.13 & 4.14.

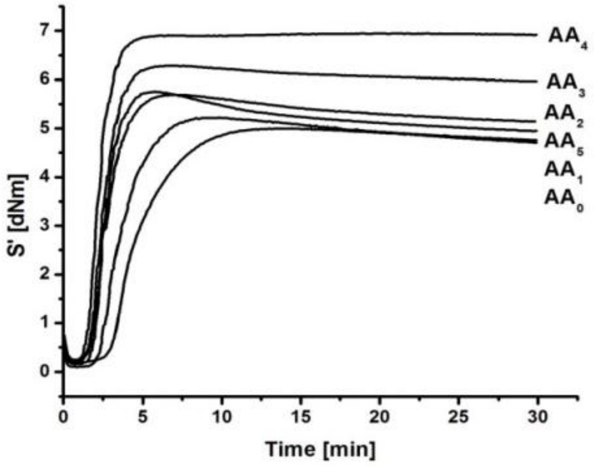

**Fig.4.13 Rheographs of mixes $AA_0$ - $AA_5$**

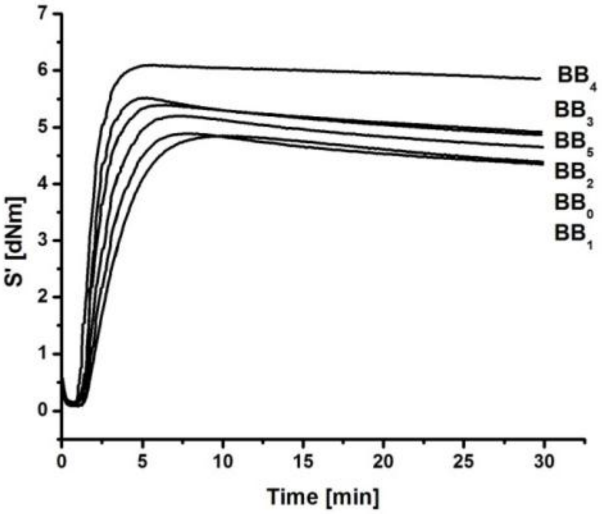

**Fig. 4.14 Rheographs of mixes $BB_0$ - $BB_5$**

Plots of ln($M_H$ - $M_t$) versus time for NR-MBTS and NR-CBS silica mixes at 150 °C are Figs. 4.15 & 4.16 respectively. A straight line obtained for various mixes reveals that the vulcanization reaction is of first order kinetics.

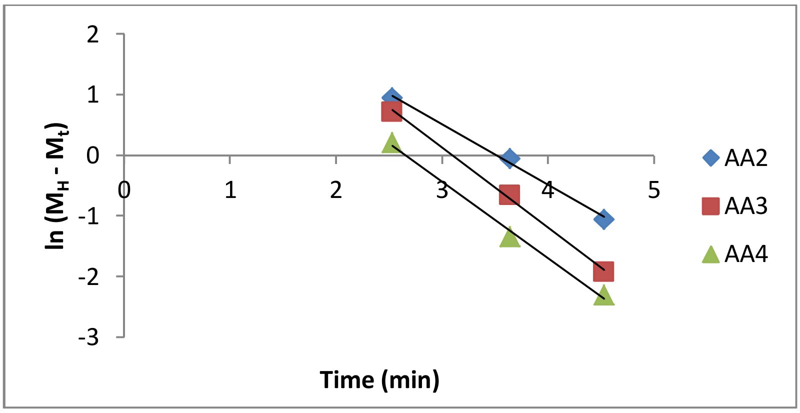

**Fig. 4.15** **Plots of ln($M_H$- $M_t$) versus time for NR-MBTS-BPTU silica mixes at 150 °C**

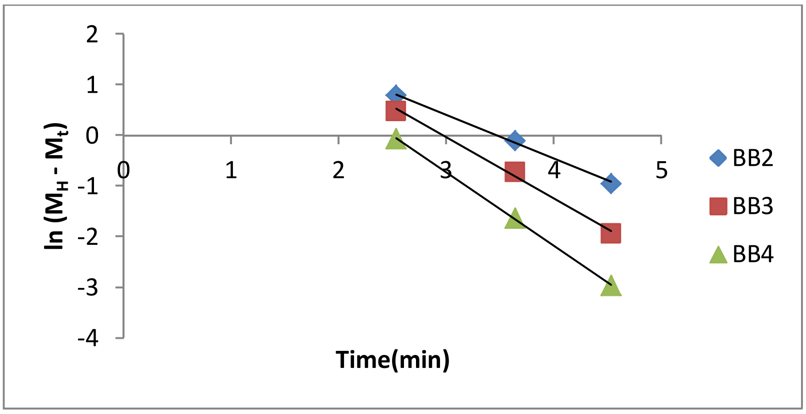

**Fig. 4.16** **Plots of ln($M_H$- $M_t$) versus time for NR-CBS-BPTU silica mixes at 150 °C**

### 4.2.3.2 Mechanical Properties

The mechanical Properties of the different vulcanizates are given in Table 4.9 and Figs. 4.17–4.24. The tensile strength, modulus at 300% elongation, tear strength of all the vulcanizates of both the systems were found to enhance with the amount of BPTU. This can be attributed to increase in crosslink density by the addition of BPTU. By the addition of 0.2 phr of BPTU to 1.0 phr of MBTS, tensile strength increased by 31% whereas 0.2 phr TMTD with 1.0 phr MBTS gave only 25% increase (Fig. 4.17). The addition of 0.1 phr of BPTU gives 13 % increase in tensile strength. In the case of CBS -BPTU system for 10:2 by weight ($BB_2$), there was an increase of 6% tensile strength of $BB_0$ (Fig.4.18). The elongation of break values depleted with addition of BPTU from $AA_1$to $AA_4$ and $BB_1$ to $BB_4$ as given in Figs. 4.19 and 4.20 respectively. This can be correlated to crosslink density, as flexibility decreases with increase of crosslink density.

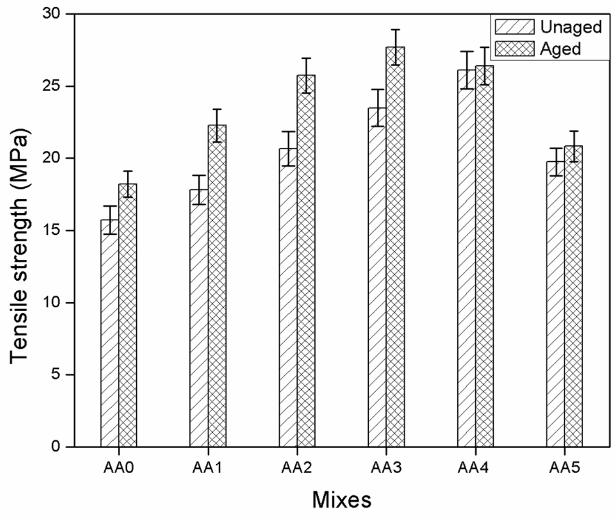

**Fig. 4.17 Tensile strength of silica filled NR-MBTS-BPTU vulcanizates**

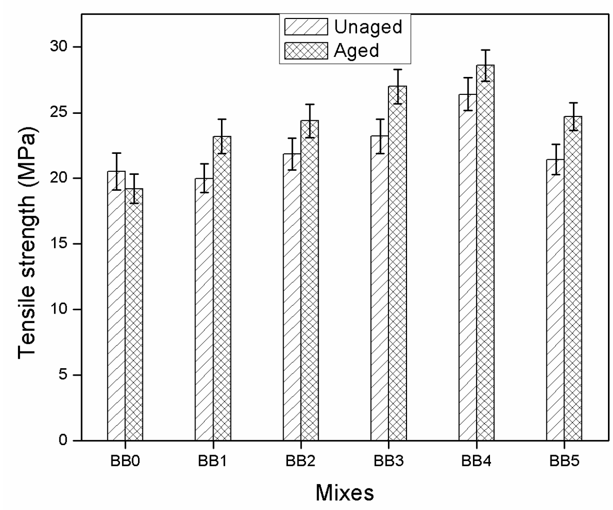

**Fig. 4.18 Tensile strength of silica filled NR-CBS-BPTU vulcanizates**

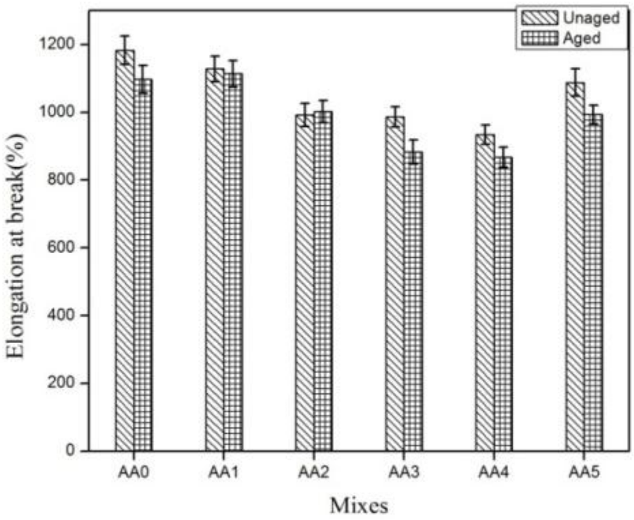

**Fig. 4.19 Elongation at break (%) of silica filled NR-MBTS-BPTU vulcanizates**

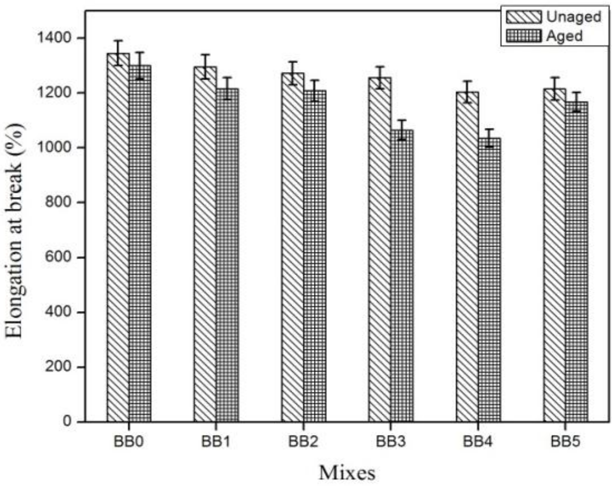

**Fig. 4.20 Elongation at break (%) of silica filled NR-CBS-BPTU vulcanizates**

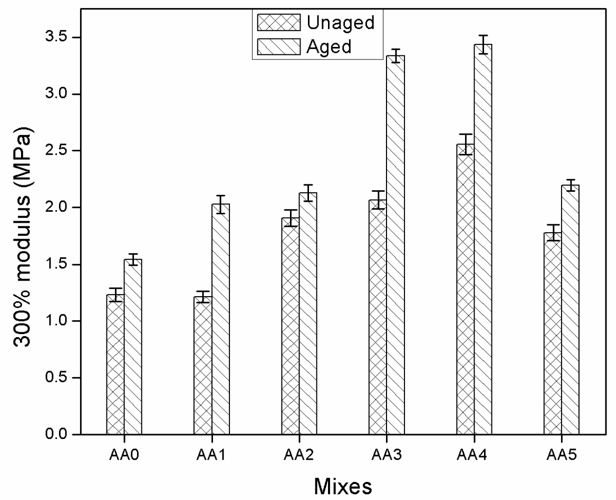

**Fig. 4.21 Modulus at 300% elongation of silica filled NR-MBTS-BPTU vulcanizates**

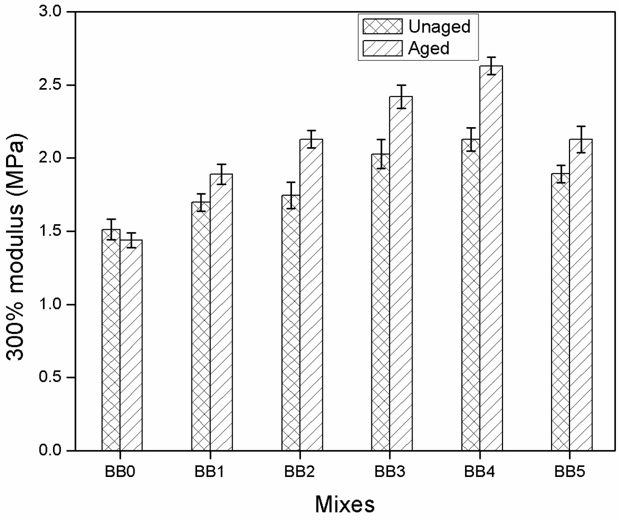

**Fig. 4.22 Modulus at 300% elongation of silica filled NR-CBS-BPTU vulcanizates**

Both MBTS-BPTU and CBS-BPTU systems showed improvement in tensile strength on ageing when compared to systems with primary accelerator alone and also with TMTD as in Figs.4.17 & 4.18. Considering increase in tensile strength, decreases in elongation at break and increase in modulus at 300% before and after ageing 24 hours at 70 $^{o}$C, in both the systems (MBTS-BPTU & CBS-BPTU) can be due to the formation of additional crosslinks that occur to the vulcanizates during heating [5] and subsequently the stiffness of the material increases. It can also be attributed to the presence of a higher concentration of mono and di-sulphidic linkages [13].

The hardness of the vulcanizates for both the systems were almost the same and higher values were obtained for enhanced dosage of BPTU. Lower compression set value is highly advantageous and is related to both the elastic recovery of the materials and the type of crosslinks [14].

Compression set values of MBTS and CBS systems were similar. Of the two systems studied, the MBTS-BPTU system showed better values as the amount of BPTU increased. The compression set values of $AA_3$ and $AA_4$ are almost the same. Compression set values and tear resistance of $AA_4$ are better than that of reference mixes $AA_0$ & $AA_5$ (Fig. 4.23). Compression set values and tear resistance of $BB_3$ and $BB_4$ are better than that of reference mixes $BB_0$ & $BB_5$ (Fig. 4.24). Resilience values improved with the dosage of BPTU in vulcanizates of MBTS-BPTU and are found slightly decreased in vulcanizates of CBS-BPTU (Table 4.9). $AA_3$ and $BB_3$ showed almost the same value for resilience. Resistance to tear increased with the concentration of BPTU in both the systems. Abrasion loss was found to decrease with the increasing concentration of BPTU and lower values were obtained for MBTS system. Lowest value for abrasion resistance was observed for $AA_3$ and was at par with MBTS-TMTD system.

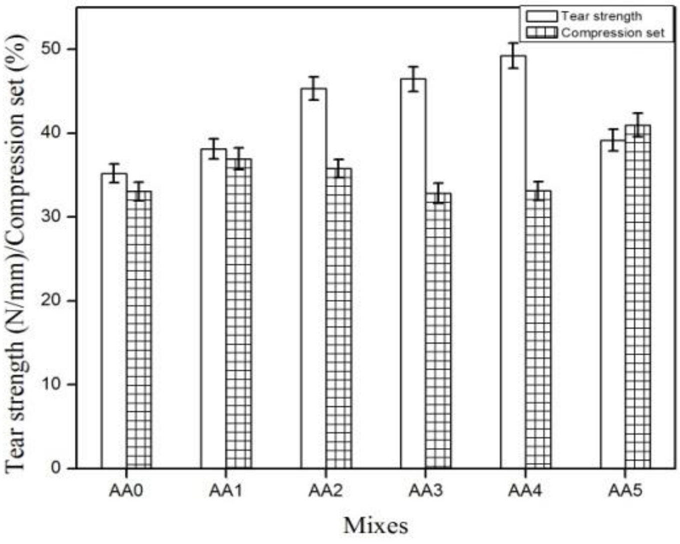

**Fig. 4.23 Tear strength and compression set of silica filled NR-MBTS-BPTU vulcanizates**

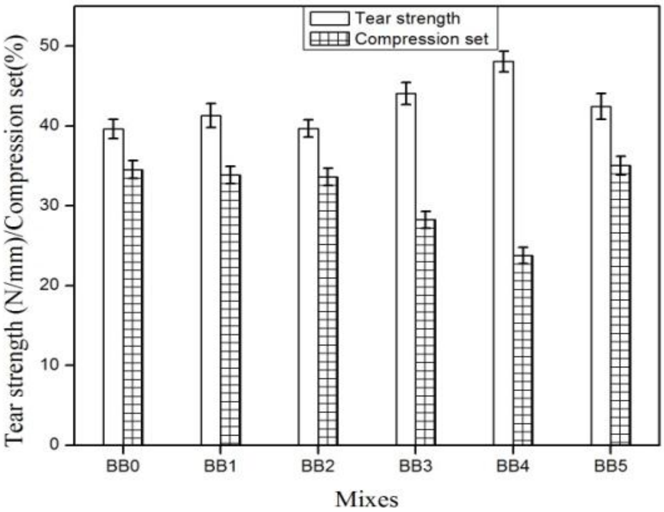

**Fig. 4.24 Tear strength and compression set of silica filled NR-CBS-BPTU vulcanizates**

**Table 4.9 Physical properties of different vulcanizates**

| **Property** | **$AA_0$** | **$AA_1$** | **$AA_2$** | **$AA_3$** | **$AA_4$** | **$AA_5$** | **$BB_0$** | **$BB_1$** | **$BB_2$** | **$BB_3$** | **$BB_4$** | **$BB_5$** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Resilience (%) | 45.00 | 50.00 | 56.00 | 53.00 | 56.00 | 51.00 | 56.00 | 55.00 | 52.00 | 54.00 | 50.00 | 58.00 |
| Hardness (Shore A) | 41.00 | 43.00 | 45.00 | 44.00 | 44.00 | 44.00 | 40.00 | 42.00 | 44.00 | 45.00 | 44.00 | 39.00 |
| Abrasion loss ($cm^3/h$) | 8.13 | 7.43 | 4.88 | 2.32 | 2.79 | 2.06 | 7.45 | 5.92 | 5.15 | 5.57 | 5.47 | 5.12 |
| Crosslink density $x10^5$ (gmol/mL) | 4.80 | 6.76 | 7.67 | 8.53 | 8.86 | 8.24 | 5.65 | 7.52 | 7.53 | 7.72 | 8.02 | 7.69 |

### 4.2.3.3 Crosslink density measurements

The chemical crosslink density of the vulcanizates increased with the increase in dosage of BPTU. These is the reason for increase of tensile strength, tear resistance, abrasion resistance and decrease of compression set %  in both MBTS-BPTU and CBS-BPTU systems with the increase of BPTU concentration. Sorption curves of these vulcanizates showed similar pattern and the penetration of solvent was more difficult in $AA_4$ and $BB_4$ as evident from Figs.4.25a and 4.25b respectively. This is in accordance with higher crosslink density obtained for $AA_4$and $BB_4$.

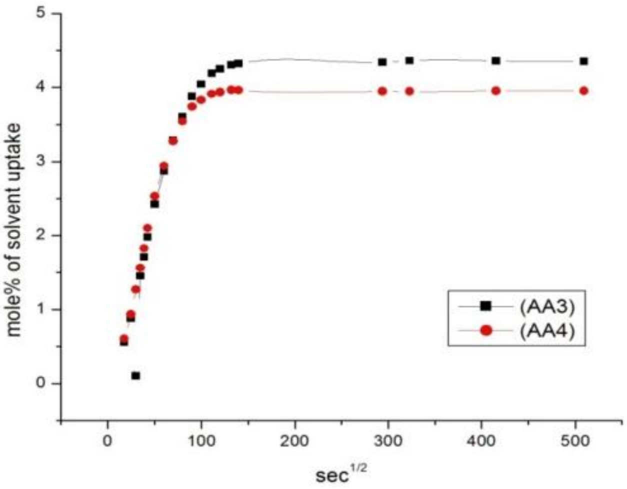

**Fig. 4.25a Solvent uptake of silica filled NR–MBTS-BPTU vulcanizates**

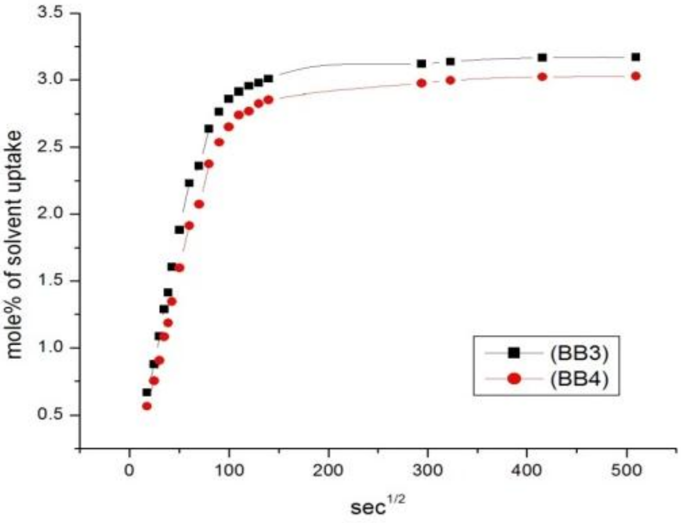

**Fig. 4.25b Solvent uptake of silica filled NR–CBS-BPTU vulcanizates**

### 4.2.3.4 Thermal analysis

Characteristics of thermograms are given in Table 4.10 and the thermograms (Figs. 4.26 & 4.27) showed that there were no appreciable changes in the onset of degradation, temperature at which 60% weight remains, maximum degradation temperature and residue content when compared to reference mixes in both the systems. The thermograms obtained were almost the same for both the systems. The temperature at maximum degradation for BPTU is 205 $^{o}$C. Onset of degradation of BPTU being 135±2 $^{o}$C, it can react with other accelerators when vulcanization takes place at 130 $^{o}$C or above. This shows that BPTU does not affect both the systems adversely.

**Table 4.10 Results of Thermogravimetric Analyses**

| Characteristics | BPTU | $AA_0$ | $AA_3$ | $AA_4$ | $AA_5$ | $BB_0$ | $BB_3$ | $BB_4$ | $BB_5$ |
|---|---|---|---|---|---|---|---|---|---|
| Onset of degradations ($^{o}$C) | 135±2 | 340±3 | 355±2 | 355±2 | 355±2 | 350±2 | 345±2 | 350±2 | 350±2 |
| End set of degradation ($^{o}$C) | 240±2 | 430±2 | 415±1 | 455±2 | 440±3 | 445±2 | 435±1 | 440±1 | 430±1 |
| Temperature at 60% retained ($^{o}$C) | 190±2 | 390±2 | 385±2 | 385±2 | 385±1 | 385±2 | 385±2 | 382±2 | 385±1 |
| Temperature at maximum degradation ($^{o}$C) | 205±1 | 390±1 | 390±1 | 390±1 | 390±1 | 390±1 | 390±2 | 390±1 | 390±2 |
| Residue ( %) at 550 $^{o}$C | 0.0 | 19.46 | 18.88 | 19.23 | 19.21 | 19.60 | 18.02 | 18.75 | 18.87 |
| Remaining at 300 $^{o}$C (%) | 0.0 | 91.01 | 89.80 | 89.71 | 88.09 | 90.53 | 88.01 | 87.56 | 88.89 |

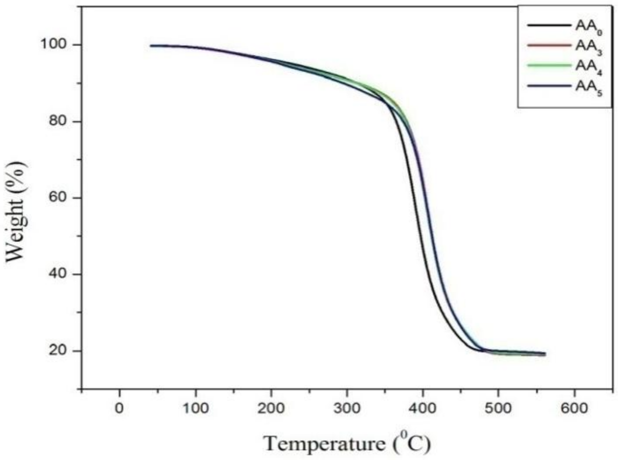

**Fig. 4.26 Thermogram of silica filled NR-MBTS-BPTU vulcanizates**

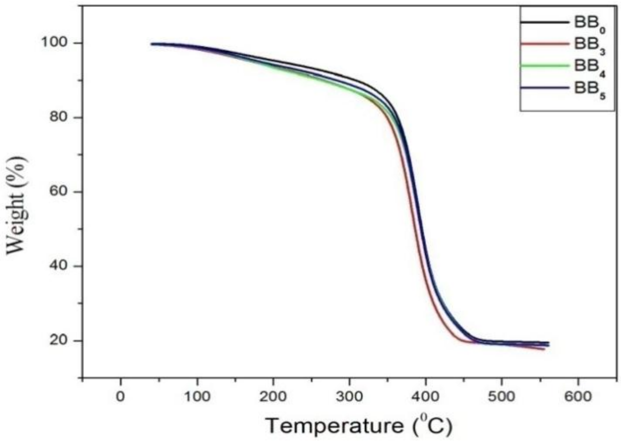

**Fig. 4.27 Thermogram of silica filled NR-CBS-BPTU vulcanizates**

### 4.2.3.5 SEM analysis

The SEM micrographs of tensile fractured surfaces of $AA_3$, $AA_4$, $BB_3$ and $BB_4$ at 750x magnification respectively are given in Figs 4.28(a-d). All the four figures showed uniform mixing, indicating that the incorporation of the silica filler in the rubber matrix was almost to the same extent in the vulcanizates obtained using BPTU with MBTS or CBS. This homogeneous dispersion depicts interfacial adhesion between the polymer and the filler.

More tear marks present in $AA_3$ and $BB_3$ and the nature of the stretch marks showed that the polymer exists in a high molecular state and this can prevent degradation. This could be the reason for the grater tensile retention property of $AA_3$ & $BB_3$.

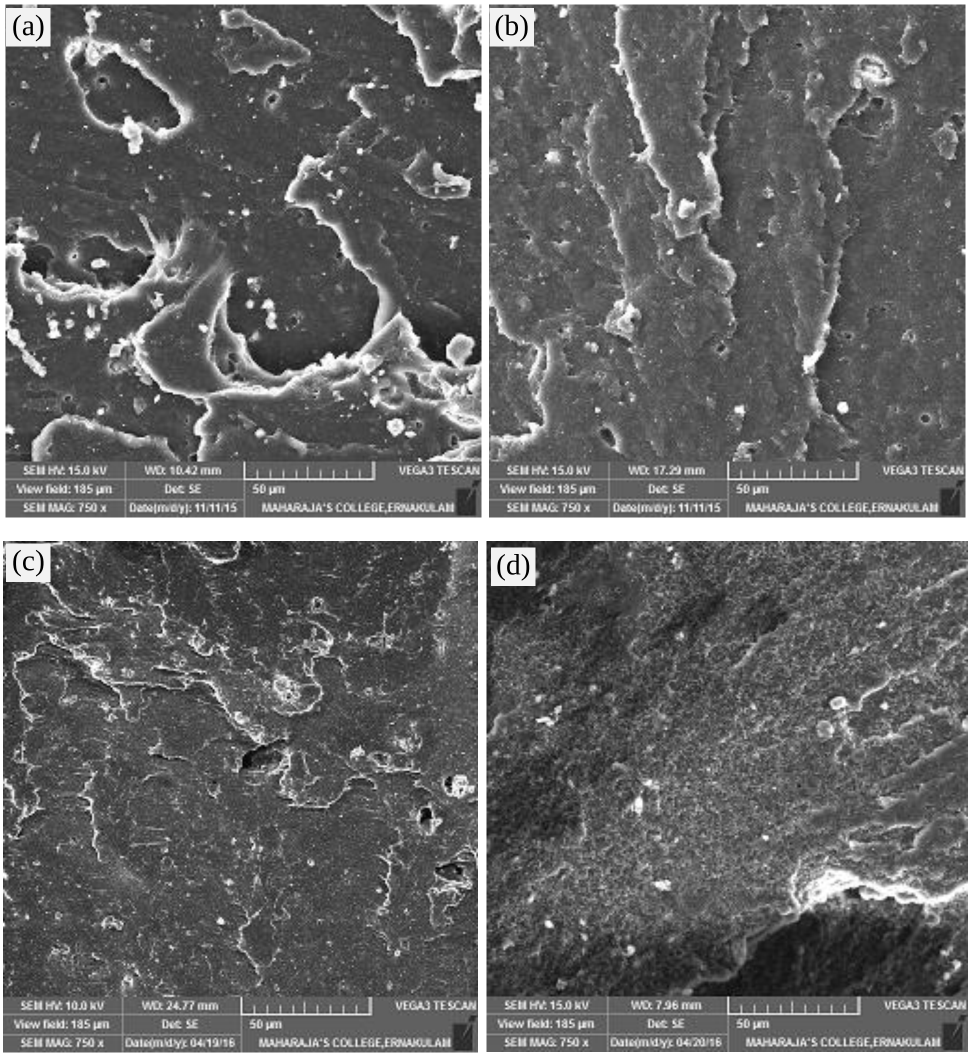

**Fig. 4.28 SEM pictures of different silica filled NR vulcanizates at 750x of (a)$AA_3$, (b) $AA_4$, (c) $BB_3$ and (d ) $BB_4$**

### 4.2.4 Conclusion

Here we present a novel accelerator viz. N-benzoyl-$N^{I}$,$N^{I}$-pyrrolidinylthiourea (BPTU) which can act as an accelerator along with MBTS or CBS in a binary system. These new binary systems can bring about a revolutionary change in vulcanization of natural rubber both in gum and silica filled systems. This can give a boost to the rubber industry, one of the major industries of the world. It is found that these systems can shorten the vulcanization time considerably and increase the mechanical properties to a good extent.

A study on vulcanization of NR using MBTS-BPTU and CBS-BPTU accelerator system showed the ability of BPTU to activate the curing process. The mechanical properties and crosslink densities of the experimental vulcanizates appeared to be better than primary accelerator systems or along with TMTD. The optimum cure time decreased with increase in dosage of BPTU with improvement in mechanical properties. The SEM analysis confirms the reinforcing of silica filler when the vulcanizate is formed with BPTU along with MBTS or CBS. The observed mechanical properties were in confirmation with observed crosslink density. The thermal stability of vulcanizates upon ageing was considerably good in both systems and better result was presented by MBTS-BPTU system. Resilience and abrasion resistance of vulcanizates of NR containing MBTS-BPTU were better than CBS-BPTU vulcanizates, but compression set values which are of prime importance to some industries were appreciable for CBS-BPTU vulcanizates. The solvent uptake and SEM analysis showed that the interaction of BPTU in two systems were almost the same. Thus the results clearly indicate that the BPTU can advantageously be used as a secondary accelerator in the sulphur vulcanization of silica filled NR. The optimum concentration that can be suggested is one phr BPTU along with one phr MBTS or CBS.

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Chapter 5

# N-BENZOYL-N$^1$,N$^1$-PYRROLIDINYLTHIOUREA IN THE SULPHUR VULCANIZATION OF SBR

Contents

## Part I

## INVESTIGATION ON SBR GUM COMPOUNDS

### 5.1.1 Introduction

The mechanism of vulcanization depends on the type and nature of elastomers [1]. So the study was extended to a synthetic rubber also. As they are made synthetically, they are available in different viscosity ranges and this facilitates better dispersion of ingredients and ease of flow in extrusion, calendaring, moulding, etc. Thus it saves time, energy and also the cost of production.

In this investigation styrene butadiene rubber (1502) was used. SBR has extrusion properties superior to those of NR, and its stocks have less tendency to scorch in processing. Cold SBR is often preferred to hot SBR for optimum physical properties whereas hot SBR is better for some processing properties [2]. Both hot and cold SBR are available in numerous grades, under various trade names. It depends on the type of polymerization, styrene content, emulsifier, stabilizer and temperature [3]. The vulcanization of SBR, compared to natural rubber requires higher amounts of accelerator and lower levels of sulphur. This is attributed mainly to the lesser number of double bonds, which are responsible for crosslinking with sulphur [4]. In synthetic rubber vulcanization, often equal parts of accelerator and sulphur give a useful vulcanizate [5]. SBR rubbers are slower curing than NR as the double bonds are less chemically active than the double bonds of the isoprenoid unit in NR. The retardation can be avoided by the use of combination of accelerators. Binary accelerator systems enhance the efficiency of sulphur intake during crosslinking and this in turn improves the mechanical, chemical and service properties of finished rubber goods. Compounding of styrene butadiene rubber can be done similar to that of natural rubber and other unsaturated hydrocarbon rubbers [6].

MBTS and sulphenamides provide good processing safety during vulcanization and these accelerators can be activated by the presence of thiurams or guanidines as secondary accelerator. Guanidines are used in order to get low modulus. Thiurams and dithiocarbamates are used for getting high modulus. Only guanidines have synergistic effect on thiazole and sulphenamides, while other secondary accelerators have only additive effect. Sulphenamide accelerators in the sulphur vulcanization of unsaturated rubber results in a longer scorch time and rapid rate of cure [7]. For SBR mixes sulphenamides are the best for balanced rate of cure, safety and physical properties [8].

Gum vulcanizates of SBR have a much lower tensile strength and resistance to tear when compared to the vulcanizates of NR. The activity of fillers is the same in SBR and NR, but the degree of reinforcement of the fillers is higher in the former [9]. Precipitated silica is the best reinforcing filler used in SBR to improve processing and to reinforce the polymer in the production of light coloured products [10]. Good strength and abrasion resistance can be achieved with precipitated silica, though they are inferior to carbon black in this respect [11]. Precipitated silica is having high adsorption nature and as a result retard cure at high loading. In order to balance the cure time, activators such as diethylene glycol have to be used during compounding.

The effect of BPTU as secondary accelerator in the sulphur vulcanization of SBR along with MBTS and also with CBS as primary accelerator was explored. Mixes containing MBTS or CBS alone and along with TMTD were taken as reference formulations. The binary systems of BPTU mixes were compared with those of the reference mixes. An attempt to bring down the optimum cure time and to reduce the amount of accelerators to be used to improve the properties of the vulcanizate was carried out.

Gum formulations and precipitated silica filled systems were studied. Different mixes with varying concentrations of BPTU with MBTS and also with CBS were prepared in standard recipes for gum and filled compounds. The study covered different aspects like mixing, curing and determination of various mechanical properties of vulcanizates. Thermogravimetric analysis was carried out for selected samples. To understand the variation in mechanical properties of the vulcanizates, chemical crosslinks were also estimated using the equilibrium swelling method. SEM analysis was carried out for selected silica filled samples.

### 5.1.2 Experimental

Different gum compounds were prepared by using BPTU along with MBTS/CBS as accelerator. The formulations are reported in Tables 5.1 & 5.2. Compounding ingredients are taken in parts per hundred rubbers (phr). Binary mixes $M_4$ and $S_4$ containing TMTD–MBTS and TMTD - CBS are conventional formulations for comparing the cure properties of experimental mixes where TMTD is one of the fastest accelerators known. All the mixes are prepared in SEV systems. Mix $M_0$ and $S_0$ contain 2.0 phr of MBTS and 2.0 phr of CBS respectively. These are the two conventional single accelerator systems for comparison. Mixes $M_1$ to $M_3$ contain different concentrations of BPTU ranging from 0.5 to 1.5 phr with 1.0 phr MBTS. $S_1$ to $S_3$ mixes contain 0.5 to 1.5 phr BPTU with 1.0 phr CBS. [Though the accelerator quantity was more than 2.5 phr for $M_3$* its cure property was studied].

All the mixes were prepared on a laboratory size two-roll mixing mill as detailed in chapter 2. RPA was used to determine the cure characteristics of various compounds at 150 °C. The compounds were vulcanized up to the optimum cure time in an electrically heated hydraulic press at 150 °C. The mechanical properties and total crosslink density were determined as described in chapter 2.

**Table 5.1 Formulations of SBR mixes containing MBTS-BPTU**

| Ingredients | $M_0$ | $M_1$ | $M_2$ | $M_3$ | $M_3$* | $M_4$ |
|---|---|---|---|---|---|---|
| SBR(g) | 100 | 100 | 100 | 100 | 100 | 100 |
| Zno(phr) | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 |
| Stearic acid(phr) | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 |
| MBTS(phr) | 2.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| BPTU(phr) | 0 | 0.5 | 1.0 | 1.5 | 2.0 | 0 |
| TMTD(phr) | 0 | 0 | 0 | 0 | 0 | 0.2 |
| Sulphur(phr) | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 |

**Table 5.2 Formulations of SBR mixes containing CBS-BPTU**

| Ingredients | $S_0$ | $S_1$ | $S_2$ | $S_3$ | $S_4$ |
|---|---|---|---|---|---|
| SBR (g) | 100 | 100 | 100 | 100 | 100 |
| Zno (phr) | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 |
| Stearicacid (phr) | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 |
| CBS(phr) | 2.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| BPTU(phr) | 0 | 0.5 | 1.0 | 1.5 | 0 |
| TMTD(phr) | 0 | 0 | 0 | 0 | 0.2 |
| Sulphur(phr) | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 |

## 5.1.3 Results and discussion

### 5.1.3.1 Cure characteristics

The cure curves obtained for MBTS systems and CBS systems are given in Figs. 5.1 & 5.2 respectively. Their cure properties are given in Tables 5.3 and 5.4. The cure characteristics and graphs reveal the accelerator activity of BPTU in the sulphur vulcanization of SBR. The plateau obtained for $M_1$ is less marching than $M_2$, $M_3$ and $M_4$. A similar trend is given by the experimental mixes of CBS systems also; i.e. cure curves of $S_1$ and $S_2$ show no reversion tendency and the plateaus are broader than $S_0$. Reversion resistance is observed in both the systems.

**Table 5.3 Cure characteristics of SBR mixes containing MBTS-BPTU (150 °C)**

| Cure Characteristics | $M_0$ | $M_1$ | $M_2$ | $M_3$ | $M_3$* | $M_4$ |
|---|---|---|---|---|---|---|
| Scorch time (min) | 17.06 | 6.81 | 5.01 | 3.92 | 3.57 | 9.08 |
| Optimum cure time (min) | 51.02 | 17.61 | 13.26 | 11.03 | 10.86 | 15.65 |
| CRI ($min^{-1}$) | 2.31 | 9.26 | 12.12 | 14.06 | 13.72 | 15.22 |
| Torque Max. (dNm) | 1.78 | 3.21 | 3.74 | 3.80 | 3.77 | 2.79 |
| Torque Min. (dNm) | 0.20 | 0.20 | 0.21 | 0.20 | 0.21 | 0.22 |
| Torque difference, $M_H$-$M_L$ (dNm) | 1.58 | 3.01 | 3.53 | 3.60 | 3.56 | 2.57 |

**Table 5.4 Cure characteristics of SBR mixes containing CBS-BPTU (150 °C)**

| Cure Characteristics | $S_0$ | $S_1$ | $S_2$ | $S_3$ | $S_4$ |
|---|---|---|---|---|---|
| Scorch time(min) | 9.29 | 5.89 | 4.67 | 4.33 | 7.91 |
| Optimum cure time(min) | 27.52 | 19.55 | 16.16 | 17.43 | 16.81 |
| CRI ($min^{-1}$) | 5.48 | 7.32 | 8.70 | 7.63 | 11.23 |
| Torque Max. (dNm) | 3.06 | 3.04 | 3.21 | 3.39 | 3.11 |
| Torque Min. (dNm) | 0.19 | 0.21 | 0.21 | 0.19 | 0.20 |
| Torque difference, $M_H$-$M_L$ (dNm) | 2.87 | 2.83 | 3.0 | 3.2 | 2.91 |

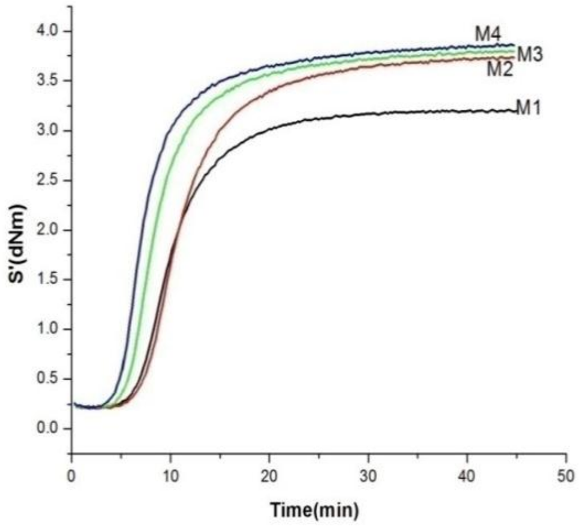

**Fig. 5.1 Rheographs of mixes $M_1$- $M_4$**

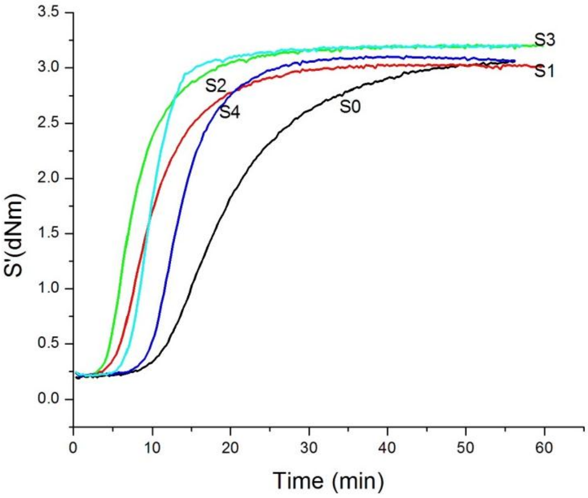

**Fig. 5.2 Rheographs of mixes $S_0$– $S_4$**

In the case of binary system of BPTU with MBTS, the optimum cure time ($t_{90}$) is reduced considerably as the amount of BPTU increases from 0.5 phr to 1.5 phr. But the decrease in $t_{90}$ from $M_3$ to $M_3$* is not that appreciable. The cure rate of all the BPTU mixes is found to be several times higher than $M_0$. Also a considerable decrease in scorch time is observed. Optimum cure time for $M_0$ (2phr MBTS alone) is 51.02 min where as for $M_2$ (1.0 phr BPTU with 1.0 phr MBTS) is only 13.26 min, that is, cure time is reduced nearly to 25% of $M_0$. But in comparison to $M_4$ which contains TMTD, the optimum cure time of $M_2$ is reduced to 84% of $M_4$. As the optimum cure time descended from $M_1$ to $M_3$ on increasing BPTU concentration, the cure rate index of $M_3$ is the highest. The advantage is that the optimum cure time of $M_3$ is reduced to 20% of $M_0$.

As the concentration of BPTU increases, it is seen that the maximum torque value also increases, which indicates an increase in stiffness of the compound. This may be due to increase in crosslink density. For $M_3$* the maximum torque value is showing a slight decrease from $M_3$. This may be because, as the concentration of BPTU is increased from 1.5 to 2.0 phr, the optimum concentration required for a synergistic combination is exceeded [12]. Both $M_3$ and$M_3$* concentration have almost the same cure characteristics. The total concentration of accelerator in $M_3$* is 3.0 phr. Therefore other physical properties of $M_3$* are not determined. Optimum concentration is the composition in which the best balance in vulcanizates properties is obtained.

When the binary system of CBS is considered the optimum cure time first decreased from $S_0$ to $S_2$ and then increased. Thus $S_2$ which contains 1.0 phr of CBS with 1.0 phr of BPTU has the lowest optimum cure time and it is at par with $S_4$ which contains the fastest accelerator TMTD. The optimum cure time of $S_2$ is 41% less than $S_0$ which contains 2.0 phr of CBS. $S_2$ has the highest value of CRI among the CBS mixes. The mixes containing CBS with BPTU have low scorch time than MBTS with BPTU. Scorch time is found to decrease with the enhancement of BPTU concentration in both the systems. The only disadvantage noted is the lower scorch time at higher dosage of BPTU. The $t_{90}$ value for the mix carrying MBTS alone is much higher than CBS alone [13] but a reversal in property is observed when BPTU is added.

It is observed that the value of minimum torque decreases and the maximum torque increases with the addition of BPTU in both the systems. Torque difference ($M_H - M_L$) is an indicator of crosslink density of the vulcanizates [14]. Thus, higher torque difference of $S_3$ indicates greater crosslink density. The optimum dosage of MBTS-BPTU system is found to be $M_3$ on considering CRI value, maximum torque and lowest $t_{90}$. In CBS-BPTU system $S_3$ has the highest torque difference and maximum torque. The above results indicate that BPTU can effectively accelerate vulcanization of SBR with MBTS and also with CBS. These observations support the nucleophilic reaction mechanism proposed by Mathew et al. [15].

### 5.1.3.2 Mechanical properties

Tensile properties of the SBR vulcanizates obtained for the various mixes of MBTS-BPTU are given in Fig. 5.3. SBR being a non-strain crystallizing rubber has poor green strength. However the tensile properties of gum formulations are determined for a comparative evaluation of the effect of BPTU in the vulcanization of SBR. Tensile strength of SBR vulcanizates of MBTS-BPTU systems were found to enhance with increase in the amount of BPTU. $M_3$ has the highest value for tensile strength and modulus at 100% elongation. This is in agreement with the highest torque difference of $M_3$.Tensile retention values decreased as the amount of BPTU is enhanced. This can be attributed to the conversion of less stable polysulphidic links to mono or di sulphidic links on ageing [16]. The elongation of break % decreased as shown in Fig. 5.4, when 100% modulus increased from $M_1$ to $M_3$ (Fig. 5.5). As the amount of accelerator increased stiffness increased and elongation decreased [17].

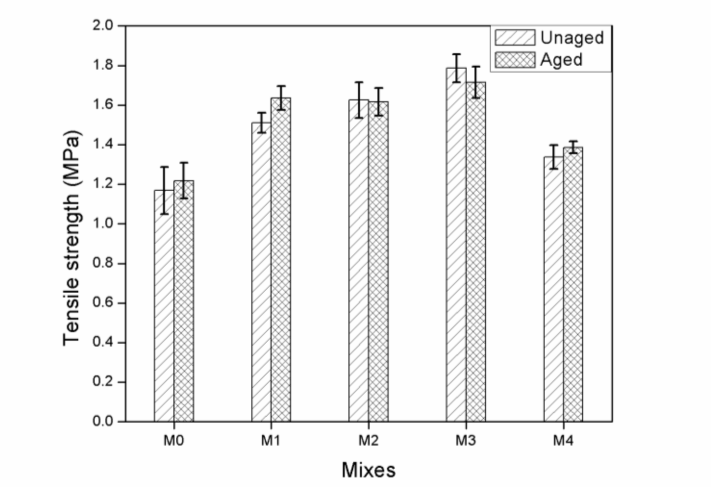

**Fig. 5.3 Tensile strength of SBR-MBTS-BPTU vulcanizates**

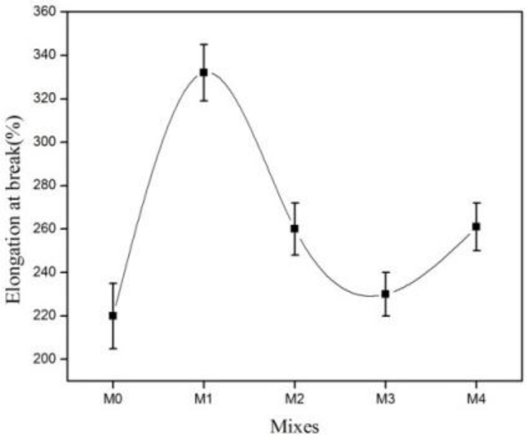

**Fig. 5.4 Elongation at break (%) of SBR-MBTS-BPTU vulcanizates**

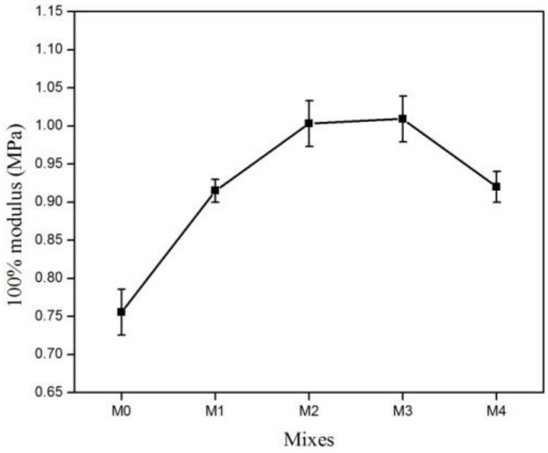

**Fig. 5.5 Modulus at 100% elongation of SBR-MBTS-BPTU vulcanizates**

Tensile retention after thermal ageing is found to be better for lesser concentration of BPTU. Compression set and hardness values are better than those of reference mixes ($M_0$&$M_4$) and resilience is at par with them. Lowest compression set value is obtained for $M_{3,}$ which has the highest torque difference (Fig. 5.6). Considering some of the properties such as tear strength, tensile strength retention after thermal ageing, hardness and crosslink density, are better for $M_2$ as in Table 5.5. $M_3$ has appreciable values for compression set and resilience than $M_2$. Crosslink density of $M_2$ and $M_3$ are nearly the same. Both $M_2$ and $M_3$ have almost the same value of maximum torque and difference of torque ($M_H – M_L$). By the addition of BPTU to MBTS, there is considerable improvement in total crosslink density, cure and physical properties of the vulcanizate in comparison to the systems of MBTS alone and also with TMTD. Thus BPTU with 1.0 phr of MBTS in the vulcanization of SBR imparts better mechanical properties with increased cure rate.

**Table 5.5 Properties of SBR-MBTS-BPTU vulcanizates**

| Property | $M_0$ | $M_1$ | $M_2$ | $M_3$ | $M_4$ |
|---|---|---|---|---|---|
| Hardness (shore A) | 33 | 32 | 41 | 39 | 33 |
| Resilience (%) | 56 | 51 | 49 | 55 | 56 |
| Crosslink density x10 $^5$(gmol/mL) | 4.12 | 7.24 | 9.46 | 9.19 | 5.20 |

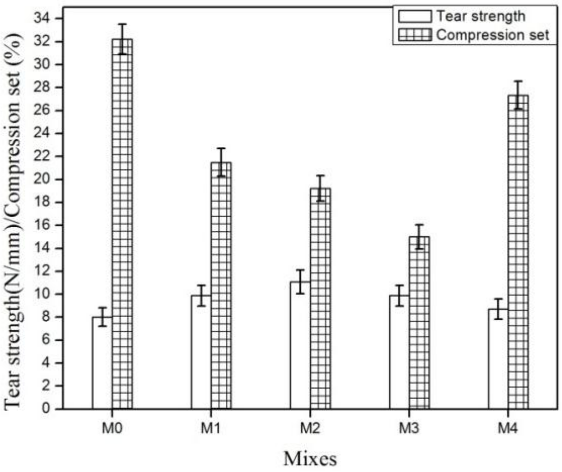

**Fig. 5.6 Tear strength and compression set of SBR-MBTS-BPTU vulcanizates**

The addition of BPTU increased tensile strength of SBR vulcanizates of CBS-BPTU as given in Fig. 5.7. But values of elongation at break % were found to enhance, as the amount of BPTU increased (Fig. 5.8) and modulus at 100% elongation of CBS-BPTU vulcanizates also increased (Fig. 5.9). This implies that vulcanizate could be stretched easier with less resistance [18]. Tensile strength values from $S_1$ to $S_3$ are higher than $S_0$ (CBS alone) but lesser than $S_4$ (CBS with TMTD). Tensile strength of the vulcanizate of $S_2$ is 17% more than that of $S_0$ though both the mixes contain same amount of accelerators. Among the CBS-BPTU vulcanizates,

$S_2$ has grater tensile retention after thermal aging (Fig. 5.7). On thermal ageing, lower dosage of BPTU shows slight increase in tensile strength and this can be due to formation of additional crosslinks on ageing [19].

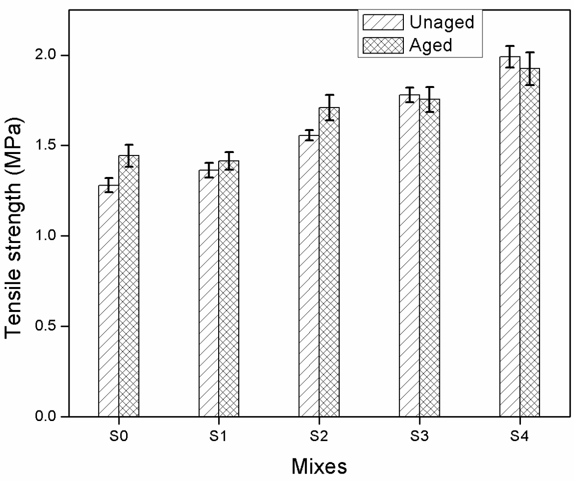

**Fig. 5.7 Tensile strength of SBR-CBS-BPTU vulcanizates**

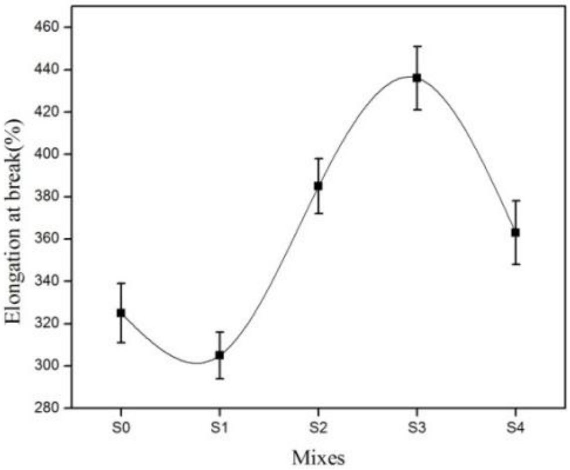

**Fig. 5.8 Elongation at break (%) of SBR-CBS-BPTU vulcanizates**

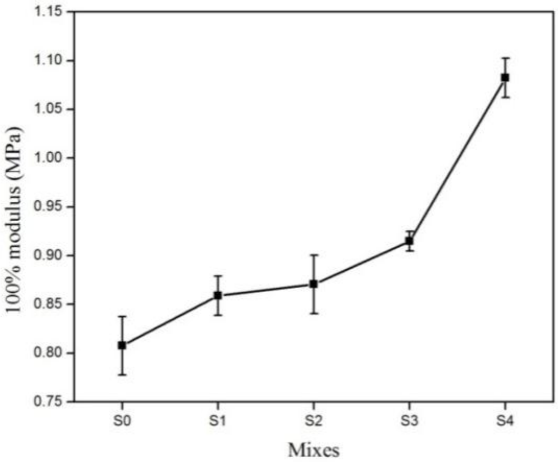

**Fig. 5.9 Modulus at 100% elongation of SBR-CBS-BPTU vulcanizates**

Increase in tensile strength and hardness from $S_1$ to $S_3$ are in correlation with total crosslink density given in Table 5.6. Tear strength and compression set values of CBS-BPTU are reported in Fig. 5.10. Tear value of $S_2$ is at par with $S_4$ and $S_1$ and found to be 37% more than $S_0$. $S_3$ has a highly appreciable value for compression set with highest crosslink density. $S_2$ has the highest resilience value.

**Table 5.6 Properties of SBR-CBS-BPTU vulcanizates**

| **Property** | **$S_0$** | **$S_1$** | **$S_2$** | **$S_3$** | **$S_4$** |
|---|---|---|---|---|---|
| Hardness(shore A) | 40 | 33 | 44 | 46 | 45 |
| Resilience (%) | 50 | 53 | 56 | 50 | 47 |
| Crosslink density x10 $^5$(gmol/mL) | 6.57 | 6.86 | 7.44 | 8.37 | 8.54 |

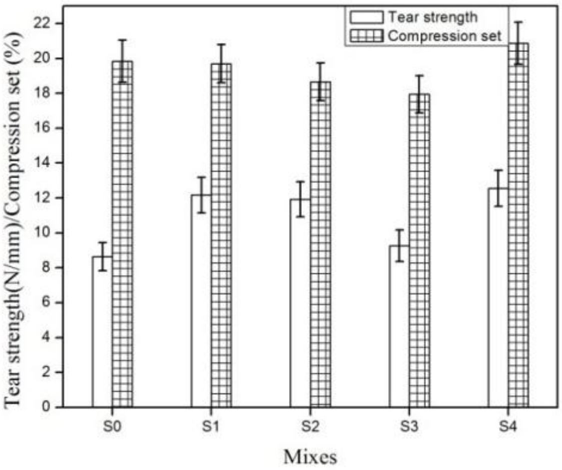

**Fig. 5.10** **Tear strength and compression set of SBR-CBS-BPTU vulcanizates**

### 5.1.3.3 Thermal analysis

Thermal properties of the vulcanizates are given in Table 5.7. The degradation of vulcanizates of both MBTS and CBS lies within the range of 340 – 500 $^{o}$C. Onset of degradation temperature is high for MBTS vulcanizates. Temperature at which 60% retained is almost the same for all vulcanizates and is above ~ 440 $^{o}$C. Temperature at which maximum degradation takes place is ~ 470 $^{o}$C for all except $S_2$ (465 $^{o}$C). At 300 $^{o}$C nearly 95% of all vulcanizates remains unchanged. This shows that, thermal properties of MBTS and CBS vulcanizates of SBR are almost similar irrespective of the dosage of BPTU. This indicates that there is no adverse effect in the thermal properties of the vulcanizate on using the new binary accelerator system containing BPTU.

**Table 5.7 Results of Thermogravimetric analyses**

| **Characteristics** | **$M_1$** | **$M_2$** | **$M_3$** | **$S_1$** | **$S_2$** | **$S_3$** |
|---|---|---|---|---|---|---|
| Onset of degradations (°C) | 385±1 | 395±2 | 390±1 | 365±2 | 340±2 | 360±2 |
| End set of degradation (°C) | 510±2 | 505±2 | 510±2 | 505±2 | 500±2 | 505±1 |
| Temperature at 60% retained (°C) | 450±2 | 450±1 | 450±1 | 450±1 | 450±2 | 450±2 |
| Temperature at maximum degradation (°C) | 475±1 | 475±2 | 475±1 | 475±2 | 465±2 | 475±2 |
| Residue (%) at 550 °C | 5.957 | 6.019 | 5.946 | 6.339 | 6.889 | 6.037 |
| Remaining at 300 °C(%) | 96.81 | 96.64 | 96.43 | 96.72 | 95.83 | 95.72 |

## 5.1.4 Conclusion

The influence of BPTU in accelerating the curing process of SBR using MBTS or CBS in SEV system is well pronounced in this study. Even 0.5 phr of BPTU with 1.0 phr MBTS/CBS can shorten the cure time nearly 2.9 times in MBTS and 1.4 times in CBS system when compared to MBTS or CBS alone. The physical properties of both the systems are better than the single accelerator systems. The tensile and tear properties of experimental mixes of both the systems are found to be almost the same. Tensile retention of the vulcanizates, on ageing was better than reference mixes in both the systems especially for the lower dosage of BPTU. BPTU as a secondary accelerator along with MBTS/CBS shows almost the same effect in thermal analysis of their vulcanizates.

## Part II

## STUDIES ON SILICA FILLED SYSTEM OF SBR

### 5.2.1 Introduction

Polymers filled with reinforcing fillers are important for most of the polymer industries for economic reason and to get required property. Tensile strength and physical properties of SBR gum vulcanizate are much lower than that of NR, as SBR does not crystallize on stretching [20]. Therefore there are only very few applications for unfilled elastomers. Fillers can reduce cost, improve mechanical properties and can also reduce tackiness of highly plasticized compounds. Reinforcing fillers are necessary to achieve optimum properties with SBR and also with its blends. Precipitated silica is used in SBR to improve processing and to reinforce the polymer in the production of white and coloured compounds [21]. Since higher loading of silica can contribute to high temperature development and processing problems, only 30 phr of silica was used in this investigation. The increase in silica loading leads to an increase in the silica-silica interaction. Hence, a decrease in filler-rubber interaction takes place which leads to decrease in crosslink density [22]. Precipitated silica has high adsorptive nature and so more accelerators or mixers of accelerators are needed [23].

The present study is an investigation on the effect of BPTU in vulcanization of silica filled SBR using BPTU along with MBTS/ CBS.

### 5.2.2 Experimental

Formulations of silica filled SBR systems are given in Table 5.8. Mixes $MM_1$ and $MM_2$ contain 0.5phr and 1.0phrof BPTU respectively along with 1.0 phr MBTS. Mixes $SS_1$ and $SS_2$ contain 0.5 phr and 1.0 phr BPTU respectively with 1.0 phr CBS. $MM_0$, $MM_3$, $SS_0$ and $SS_3$ are reference mixes. 1.5 phr diethylene glycol as an activator and 6.0 phr naphthenic oil as processing aid are used with silica formulations. Procedure for mixing, vulcanization, determination of cure characteristics of the compounds, evaluation of physical properties, chemical characteristics, TGA and SEM analysis were all carried out as per relevant standards described in detail in chapter 2.

**Table 5.8 Formulations of silica filled SBR vulcanizates**

| **Ingredients** | **$MM_0$** | **$MM_1$** | **$MM_2$** | **$MM_3$** | **$SS_0$** | **$SS_1$** | **$SS_2$** | **$SS_3$** |
|---|---|---|---|---|---|---|---|---|
| SBR(g) | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| ZnO(phr) | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 |
| Stearic acid(phr) | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 |
| Silica(phr) | 30.0 | 30.0 | 30.0 | 30.0 | 30.0 | 30.0 | 30.0 | 30.0 |
| DEG(phr) | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 |
| SP(phr) | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| Naphthenic oil (phr) | 6.0 | 6.0 | 6.0 | 6.0 | 6.0 | 6.0 | 6.0 | 6.0 |
| MBTS(phr) | 2.0 | 1.0 | 1.0 | 1.0 | 0 | 0 | 0 | 0 |
| CBS(phr) | 0 | 0 | 0 | 0 | 2.0 | 1.0 | 1.0 | 1.0 |
| BPTU(phr) | 0 | 0.5 | 1.0 | 0 | 0 | 0.5 | 1.0 | 0 |
| TMTD(phr) | 0 | 0 | 0 | 0.2 | 0 | 0 | 0 | 0.2 |
| Sulphur(phr) | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 |

## 5.2.3 Results and discussion

### 5.2.3.1 Cure Characteristics

Cure curves obtained for the various silica filled systems of SBR are shown in Figs. 5.12 – 5.15 and their cure characters are given in Table 5.9.

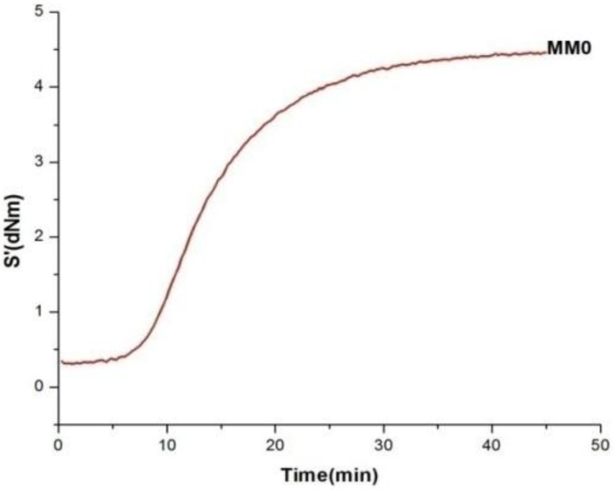

Fig. 5.11 Rheograph of mix $MM_0$

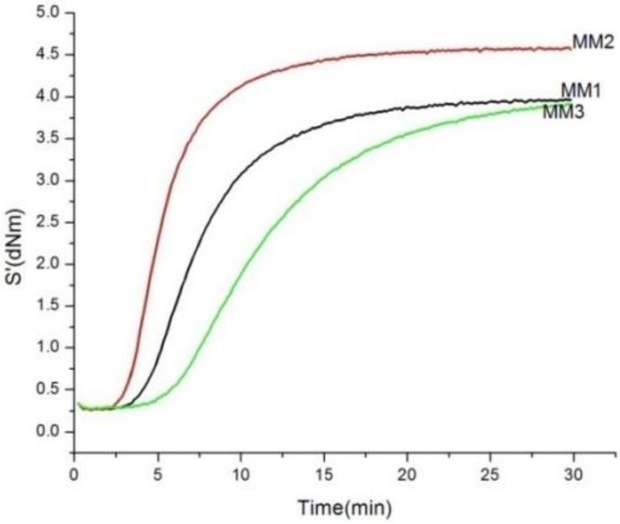

Fig. 5.12 Rheographs of mixes $MM_1$ - $MM_3$

The effect of BPTU in the vulcanization of SBR is significant in the cure graphs. The optimum cure time of $MM_2$ is 60% less than $MM_0$ though both the mixes contain the same quantity of accelerator. On addition of 0.5 phr and 1.0 phr BPTU to 1.0 phr of MBTS, gives decrease of scorch time and optimum cure time as in the case of SBR gum vulcanizates.

**Table 5.9 Cure characteristics of silica filled SBR vulcanizates (150 $^o$C)**

| **Cure characteristics** | **$MM_0$** | **$MM_1$** | **$MM_2$** | **$MM_3$** | **$SS_0$** | **$SS_1$** | **$SS_2$** | **$SS_3$** |
|---|---|---|---|---|---|---|---|---|
| Scorch time $t_{10}$ (min) | 8.29 | 4.49 | 3.38 | 6.39 | 7.07 | 3.46 | 2.83 | 5.0 |
| Optimum cure time $t_{90}$ (min) | 25.28 | 14.02 | 10.22 | 20.05 | 15.01 | 11.72 | 9.91 | 14.04 |
| CRI (min$^{-1}$) | 5.88 | 10.49 | 14.62 | 7.32 | 12.59 | 12.11 | 14.12 | 11.06 |
| Torque Max. (dNm) | 4.468 | 3.982 | 4.586 | 3.923 | 4.507 | 3.978 | 4.132 | 4.138 |
| Torque Min. (dNm) | 0.294 | 0.268 | 0.258 | 0.275 | 0.261 | 0.284 | 0.271 | 0.290 |

The addition of 0.5 phr BPTU with 1 phr of MBTS, there is 40% decrease in optimum cure time which is beneficial as it saves time, energy and chemicals. The cure rate of $MM_1$ is double that of $MM_0$ which carries the conventional accelerator 2.0 phr MBTS alone and it is 30% more than $MM_3$ which has the fastest accelerator TMTD with MBTS. The cure rates of $MM_2$ is three times that of $MM_0$ and double that of $MM_3$ ,the reference mix as shown in Table 5.9. The cure curves obtained for $MM_1$ and $MM_2$ with broad plateau shows the complete picture of the overall kinetics of crosslink formation without reversion. Maximum torque increased with increase in concentration of BPTU though scorch time decreased. This proves the cure accelerating nature of BPTU with MBTS in the vulcanization of silica filled SBR.

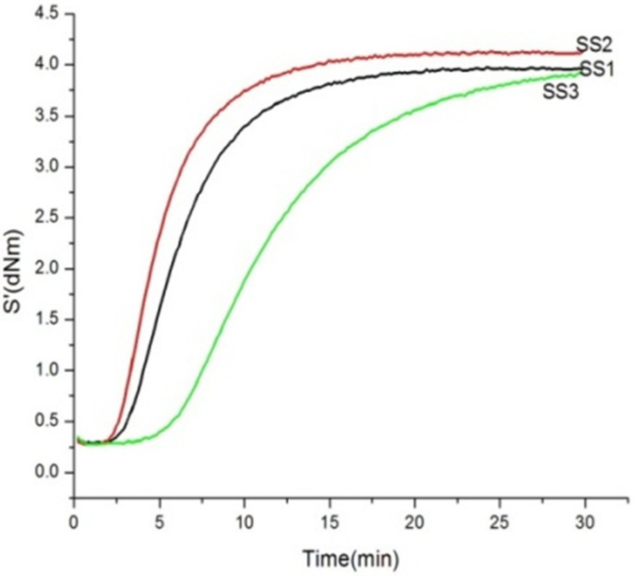

Fig. 5.13 Rheographs of mixes $SS_1$ - $SS_3$

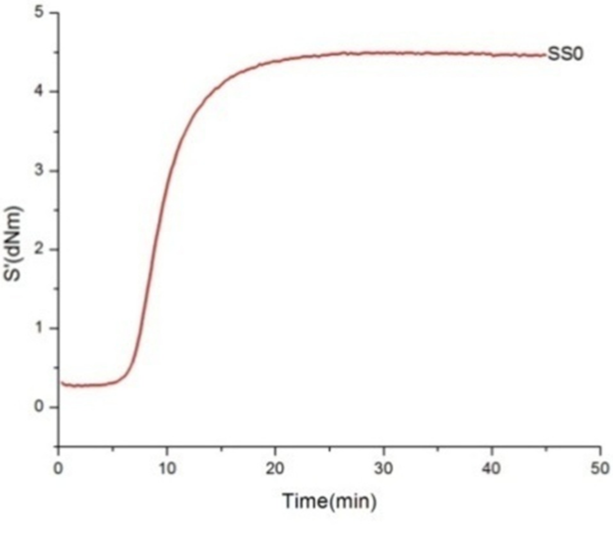

Fig. 5.14 Rheograph of mix $SS_0$

Cure characteristic of BPTU with CBS shows that $SS_0$, $SS_1$ and $SS_3$ have almost the same CRI values (Table 5.9). But the optimum cure time of $SS_1$ is 22% less than $SS_0$ and 16% less than $SS_3$. This is highly beneficial for rubber industry. The synergistic effect of BPTU is clearly seen in the cure properties of $SS_1$ and $SS_2$. The optimum cure time of $SS_2$ is 33% less than $SS_0$, where both contain the same amount of accelerator and it is 29% less than $SS_3$. Synergistic effect is also revealed as the addition of 0.5 phr BPTU to 1.0 phr CBS ($SS_1$) reduced the $t_{90}$ by 22% in comparison to $SS_0$. From $SS_1$ to $SS_2$ the minimum torque decreased while maximum torque increased. Thus the incorporation of BPTU with CBS can decrease energy loss and time in the vulcanization of SBR. The plateau obtained for $SS_1$ and $SS_2$ in cure graphs shows reversion resistance. Absence of marching of the cure curve denotes that they have reached constant torque. Plots of ln ($M_H$- $M_t$) versus time for silica filled SBR-MBTS-BPTU (Fig. 5.16) and SBR-CBS –BPTU (Fig. 5.17) giving straight lines prove that curing of SBR using BPTU follows first-order kinetics.

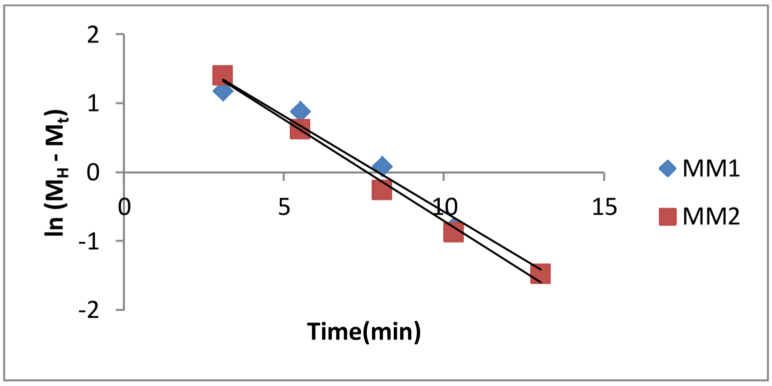

**Fig. 5.15 Plots of ln ($M_H$- $M_t$) versus time for silica filled SBR-MBTS-BPTU silica mixes at 150 °C**

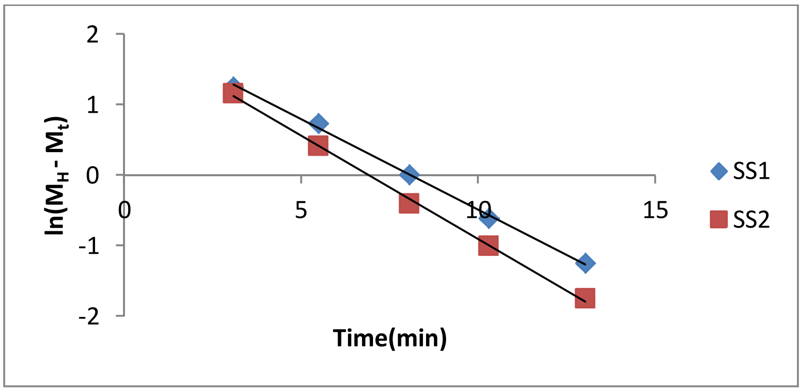

**Fig. 5.16** **Plots of ln ($M_H$- $M_t$) versus time for silica filled SBR-CBS-BPTU mixes at 150 °C**

### 5.2.3.2 Mechanical Properties

Mechanical properties of SBR vulcanizates of MBTS-BPTU and CBS-BPTU are given in Figs. 5.17 to 5.22. MBTS-BPTU system shows that tear value of $MM_2$ is 28% more than $MM_0$ and 20% more than $MM_3$. Compression set values of this MBTS- BPTU systems are much less than those of the reference mixes and it is attractive for certain applications of rubber products like seals. Compression set value of $MM_2$ is 21% less than $MM_0$ and 28% less than $MM_3$. Hardness and resilience values of vulcanizates of this MBTS-BPTU system are all comparable. Abrasion resistance of $MM_2$ is 40% more than $MM_3$ and at par with $MM_0$. Total crosslink density increased by the addition of BPTU and $MM_2$ shows the highest value. Thus $MM_2$ exhibits the highest value of tear, tensile strength and lowest value for compression set and abrasion loss. Tensile strength of the filler system of SBR is better when compared to its gum systems. Decrease of tensile strength on ageing can be due to conversion of less stable polysulphidic links to mono and disulphide links [24]. Tensile strength of

$MM_2$ is 20% more than $MM_0$. 300% modulus and tensile strength increased from $MM_1$ to $MM_2$ with increase in concentration of BPTU and elongation at break values decreased as expected (Fig. 5.18). This can be attributed to increase in crosslinking with increase of BPTU concentration.

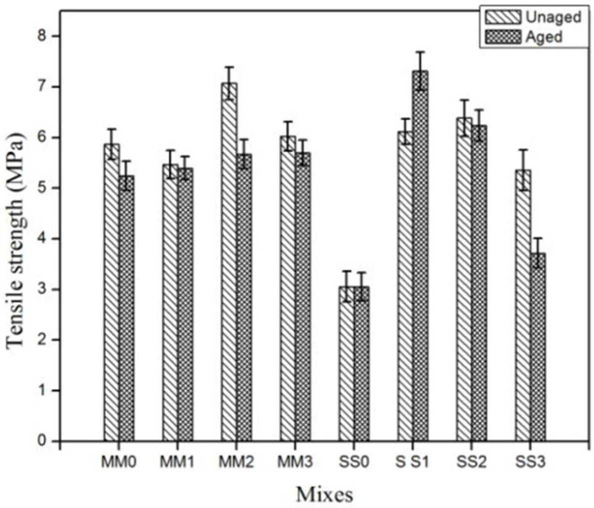

**Fig. 5.17 Tensile strength of silica filled SBR vulcanizates**

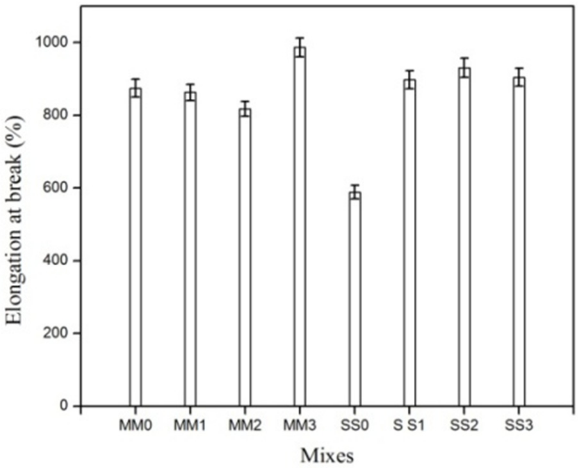

**Fig. 5.18 Elongation at break (%) of silica filled SBR vulcanizates**

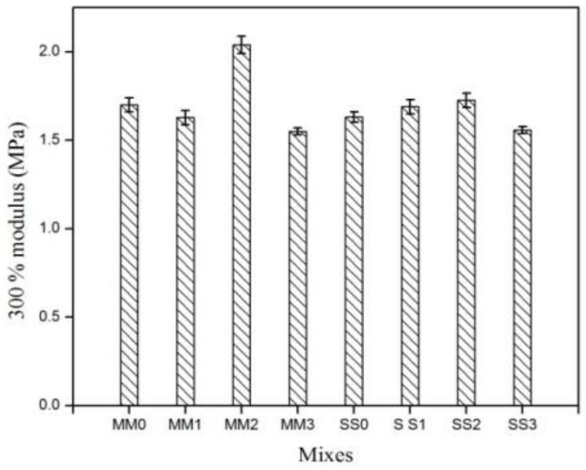

Fig. 5.19 Modulus at 300% elongation of silica filled SBR vulcanizates

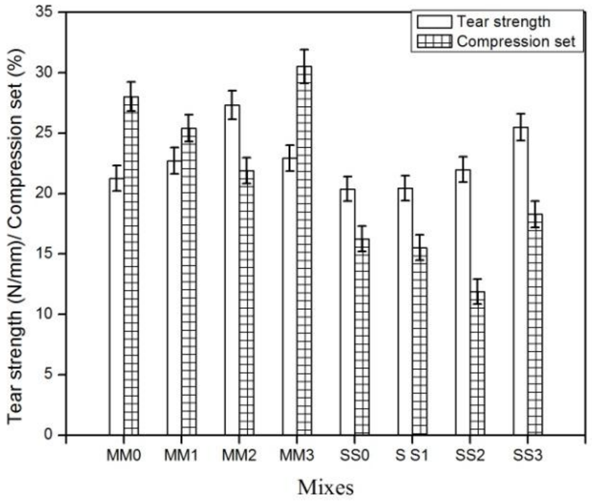

Fig. 5.20 Tear strength and compression set of silica filled SBR vulcanizates

Mechanical properties of CBS-BPTU system show that tensile strength of $SS_2$ is 50% more than $SS_0$ and 20% more of $SS_3$. Tensile strength, elongation at break (%) and modulus at 300% elongation increased by the addition of BPTU as reported in Figs 5.17, 5.18 & 5.19 respectively. Tensile retention after ageing is better for lower dose of

BPTU. The tensile retention of $SS_2$ is better than $SS_0$ and $SS_3$. Tear values of the experimental mixes are at par with $SS_0$ and less than $SS_3$ (Fig. 5.20). But the compression set values are much better than the reference mixes $SS_0$ and $SS_3$.

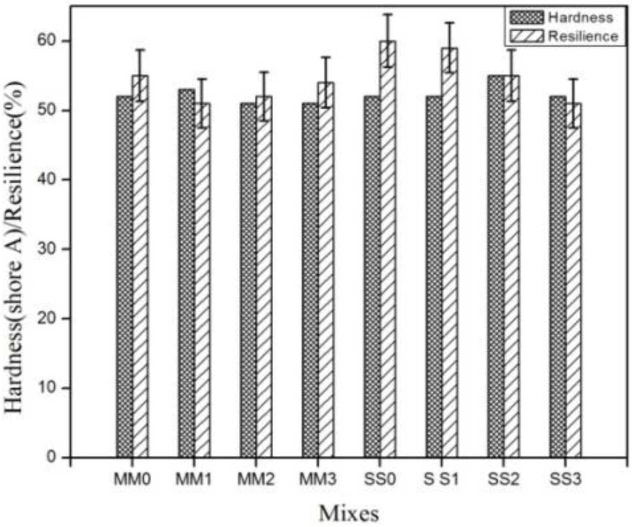

**Fig. 5.21 Hardness and resilience of silica filled SBR vulcanizates**

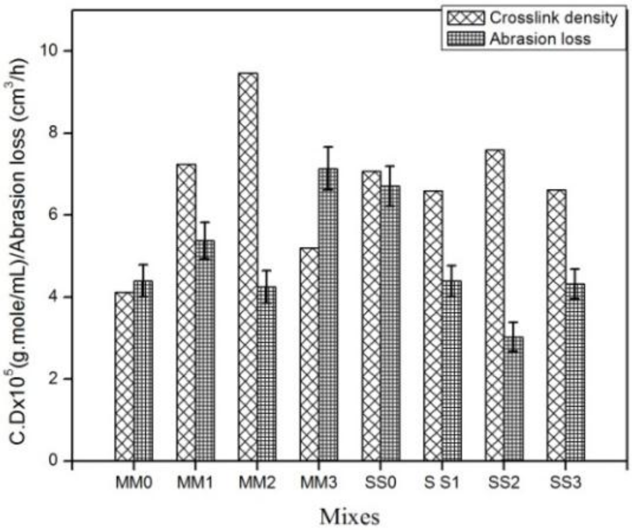

**Fig. 5.22 Crosslink density and abrasion loss of silica filled SBR vulcanizates**

The compression set value of $SS_2$ is 30% less than $SS_0$ and 35% less than $SS_3$. Values of hardness for all the experimental mixes are almost the same (Fig. 5.21). But abrasion resistance of $SS_2$ is 50% more than $SS_0$, though both the mixes carry the same amount of accelerator. Abrasion resistance of $SS_1$ and $SS_3$ are at par (Fig. 5.22). Resilience value of $SS_2$ is more than $SS_3$ but less than $SS_0$. $SS_2$ has the highest crosslink density (Fig.5.22) and hence exhibits highest tensile strength, 300 % modulus, and hardness. But it has lowest values for compression set and abrasion loss. Lower compression set value shows the presence of more of monosulphidic crosslinks than polysulphidic crosslinks [7]. And this can be the reason for better retention in tensile strength for $SS_2$ on ageing. Considering the overall properties of the vulcanizates of CBS-BPTU system mix $SS_2$ is better than $SS_1$. Thus BPTU not only accelerates the rate of cure but also the formation of crosslink density and there by increases the mechanical properties of SBR vulcanizates.

### 5.2.3.3 SEM analysis

Tensile fractured samples of $MM_1$, $MM_2$, $SS_1$ and $SS_2$ were scanned and are reported in Figs. 5.23(a-d) respectively in 3000x magnification. The smooth fracture surfaces, smooth filler dispersion and unidirectional tear path oriented along the direction of flow are seen in all the samples. The micrograph of $MM_1$ is characterized by a smooth, rubbery failure without the formation of necking and the additives are seen to some extent. This appearance is associated with a low tensile strength [13]. In $MM_2$ there is fatigue type of failure showing more tensile strength than $MM_1$. Dispersion of silica in the rubber matrix is found to be uniform except for few agglomerates. Pull-outs and holes seen in the picture reveal that the silica particles are better distributed and have good interaction with the rubber matrix. Fewer agglomerates are seen in $SS_2$ compared to $SS_1$ and so it is expected to have more tensile strength than $SS_1$.

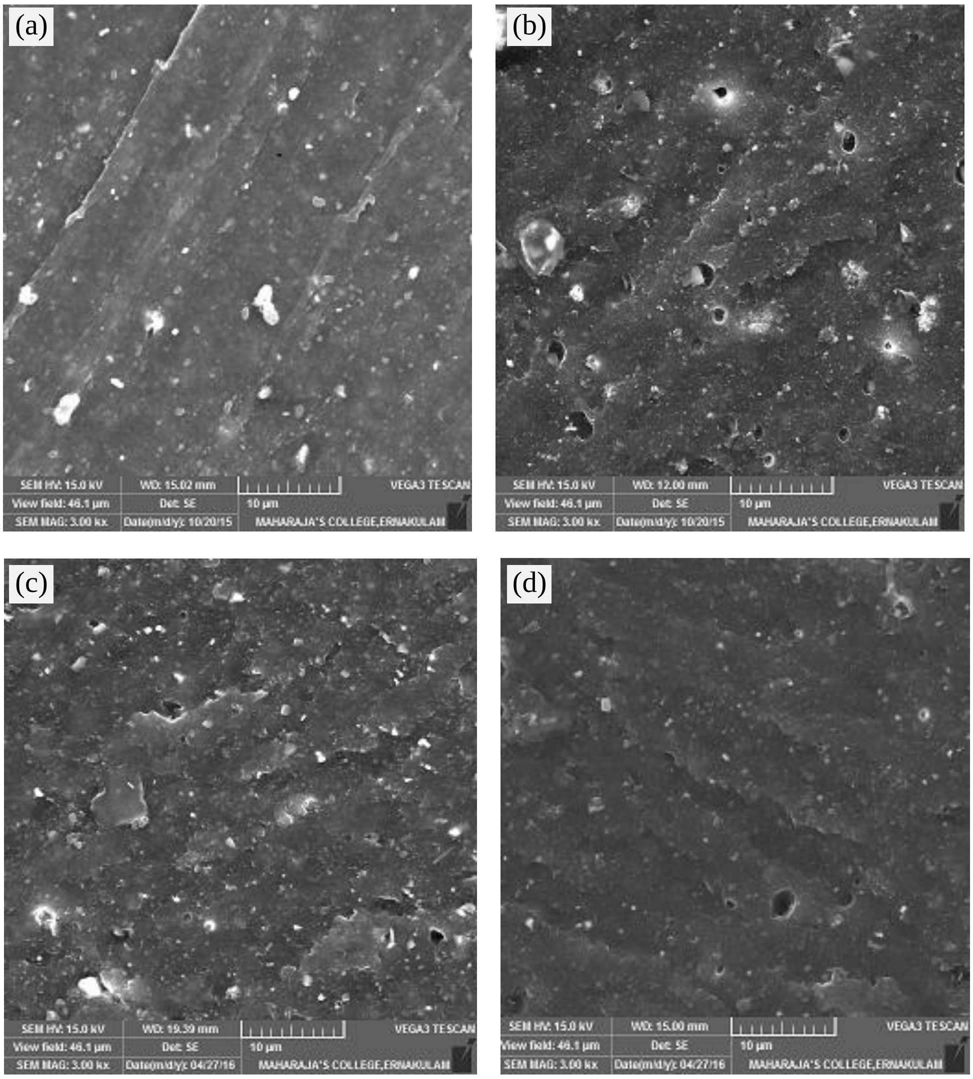

**Fig. 5.23 SEM pictures of different silica filled SBR vulcanizates at 3000 x of (a) $MM_1$, (b) $MM_2$, (c) $SS_1$and (d) $SS_2$**

### 5.2.4 Conclusions

The new secondary accelerator BPTU, developed can be used along with MBTS and CBS as an efficient binary system for the vulcanization of SBR gum and silica filled SBR. In both MBTS and CBS systems the cure characteristics improved by the addition of BPTU. The reduction in optimum cure time is highly advantageous as far as the production of finished products is concerned. All the physical properties of MBTS-BPTU and CBS-BPTU systems are more appreciable than MBTS / CBS alone. In both the systems lower dosage of BPTU showed better tensile retention on ageing. Presence of BPTU with MBTS / CBS shows almost the same effect in thermal analysis. Decrease of cure time and increase of torque for silica loaded mixes by the addition of BPTU show the cure accelerating nature of BPTU.

Of the two systems MBTS-BPTU and CBS-BPTU, the former is found to be better on considering the crosslink density, physical properties (except compression set and abrasion resistance). All the properties of MBTS-BPTU system are much better than those of the reference mix (MBTS-TMTD). Abrasion resistance and compression set values of CBS-BPTU systems are more advantageous than the other systems discussed here. The optimum cure time and CRI values of $MM_2$ (1:1) and $SS_2$ (1:1) are almost the same but $MM_2$ has better scorch safety.

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Chapter 6

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

Contents

## Part I

## STUDIES ON NR/SBR BLENDS (GUM)

### 6.1.1 Introduction

An epoch making polymer modification was introduced by Thomas Hancock, based on a simple mechanical process of mixing natural rubber and Gutta-percha. This process generated a new polymer class called Polymer blends. The ever-increasing demand for high performance polymers shifted the focus of studies in the area of polymer science and this led to the development of new blends. New polymer blends can bring significant reduction in cost through the dilution of high cost polymers with low cost polymers or fillers. Polymer blending is a simple idea of combining two or more different polymers to get desired properties in a single system. But it is not always successful or readily feasible due to the inherent incompatibility between polymers to be blended. If two polymers are mixed, the most frequent result is a system that exhibits a complete phase separation due to the repulsive interaction between the components (i.e. the chemical incompatibility between the polymers).

Complete miscibility in a mixture of two polymers requires the condition: $\Delta Hm - T\Delta Sm = \Delta Gm < 0$($\Delta Gm$, $\Delta Hm$, and $\Delta Sm$ are the Gibb's free energy of mixing, the enthalpy of mixing and entropy of mixing). This implies that, there should be an increase in the entropy on mixing. Therefore, the sign of $\Delta Gm$ always depends on mixing temperature T. Miscible polymer blend is a polymer blend which is homogeneous on a nanometer level, if not possible, at least to the molecular level. Miscible blends of elastomers consist of a single elastomeric phase with microscopically uniform crosslinking. This distribution of reinforcing agents reflects a compositionally weighted average of the intrinsic properties of the constituents [1].

Processability and mechanical properties of polymer blends depend mainly on their compatibility and miscibility. Depending on the polymer miscibility, the blends can be classified as miscible, partially miscible and immiscible or as compatible, semi compatible and incompatible in a technological sense. M.Shundo et al. studied the relationship between the properties and the blend ratios of NR and SBR by using four blending methods [2]. Roll blending was found to be more effective for obtaining uniform blends compared to Banbury mixer blending. In solution and latex blending, very uniform blends are easily obtained. Regardless of blending method, the properties of NR/SBR blends showed a direct relation to their blend ratios.

R. Joseph et al. [3] conducted different studies on the blends of 50/50 NR and SBR using several conventional and semi EV systems. They reported that by designing suitable formulations for attaining desired vulcanizate properties, blends could be compounded as in the case of the single rubbers. K. E. George and coworkers [4] reported that, compatible blends show a definite pattern of curing whereas the incompatible blends show no such pattern. The blending of two or more rubbers is a useful technique to improve certain properties. Fatigue and mechanical failure tests had been performed by Ismail and coworkers [5] to evaluate the behaviour of blend vulcanizates of NR/SBR and found that the fatigue life and the strain energy varies linearly with blend composition in the compatible NR/SBR blend, using a semi-efficient vulcanization system. Indra Surya and Syahrul Fauzi Siregar [6] reported that, maximum values of torque difference and crosslink density was obtained for a blend ratio of 75/25 of NR/SBR. As SBR requires less sulphur and more accelerators [7], it necessitates more active accelerator or binary system to obtain uniform curing.

The results of the study of BPTU as a secondary accelerator in NR and SBR reported in the earlier chapters of this work motivated the investigation of the effect of BPTU in the formulations based on the blends of NR and SBR. Thus the study on the accelerating effect of BPTU in a binary accelerator system with primary accelerators like MBTS and CBS in (50: 50) NR / SBR blends was conducted both in the filled and unfilled stocks. The cure properties of mixes along with mechanical properties like tensile strength, 300% modulus, elongation at break, tear strength, etc. was studied. Other physical properties evaluated include hardness, compression set, abrasion loss and resilience. Total crosslink density was determined by equilibrium swelling method. Kinetic study, thermal and SEM analysis were also carried out.

### 6.1.2 Experimental

The compositions of the various unfilled formulations of the blends are given in Table 6.1. 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. Binary systems containing MBTS-TMTD and CBS-TMTD in the ratio (1: 0.2) were taken as reference mixes. Lower doses (< 0.5phr) of BPTU were avoided as their optimum cure time was much higher in the pilot study.

**Table 6.1 Formulations of NR/ SBR blends (unfilled mixes)**

| **Ingredients** | **$P_0$** | **$P_1$** | **$P_2$** | **$P_3$** | **$Q_0$** | **$Q_1$** | **$Q_2$** | **$Q_3$** |
|---|---|---|---|---|---|---|---|---|
| NR (g) | 50 | 50 | 50 | 50 | 50 | 50 | 50 | 50 |
| SBR (g) | 50 | 50 | 50 | 50 | 50 | 50 | 50 | 50 |
| Zno (phr) | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 |
| Stearic acid (phr) | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 |
| MBTS (phr) | 2.0 | 1.0 | 1.0 | 1.0 | 0 | 0 | 0 | 0 |
| CBS (phr) | 0 | 0 | 0 | 0 | 2 | 1.0 | 1.0 | 1.0 |
| BPTU (phr) | 0 | 0.5 | 1.0 | 0 | 0 | 0.5 | 1.0 | 0 |
| TMTD (phr) | 0 | 0 | 0 | 0.2 | 0 | 0 | 0 | 0.2 |
| Sulphur (phr) | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 |

The mixes were prepared on a laboratory two- roll mixing mill as in earlier chapter 2. Cure characteristics of the various compounds at 150 °C were determined. The compounds were then vulcanized up to the optimum cure time in an electrically heated hydraulic press. Specifications of all the ingredients used and the experimental details are given in chapter 2. The kinetic study was also carried out.

## 6.1.3 Results and discussion

### 6.1.3.1 Cure characteristics

The effect of BPTU as an accelerator in a binary system is commendable in reducing the cure time and improving the rheometric properties of the vulcanizate. The rheographs of the mixes cured at 150 °C were shown in Figs. 6.1 & 6.2.

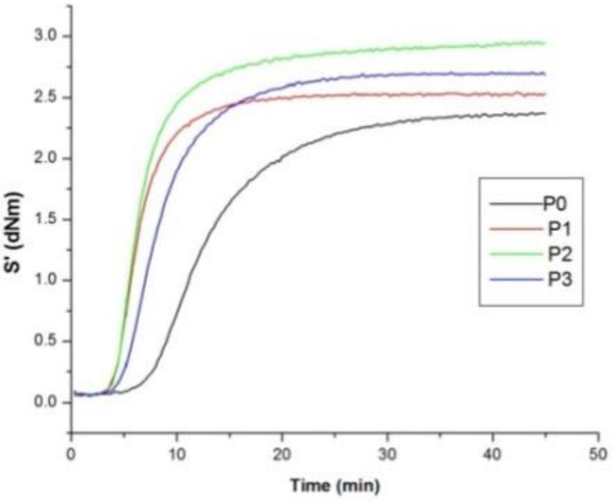

**Fig. 6.1 Rheographs of mixes $P_0$-$P_3$**

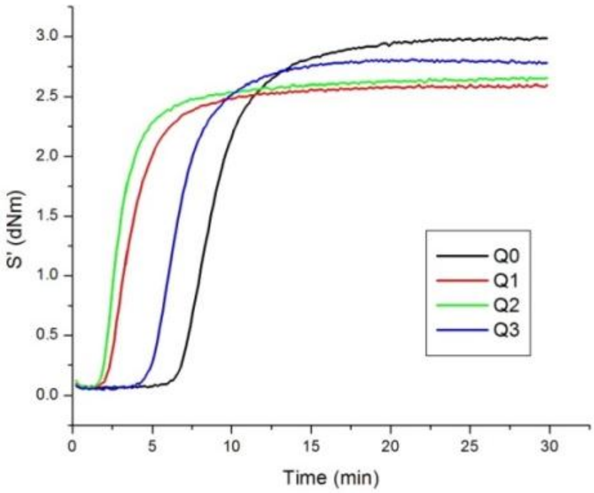

**Fig. 6.2 Rheographs of mixes $Q_0$-$Q_3$**

The corresponding cure characteristics such as optimum cure time, scorch time, cure rate, minimum torque and maximum torque values obtained are given in Table 6.2.

**Table 6.2 Cure characteristics of NR- SBR blends (unfilled mixes) (150 °C)**

| **Cure Characteristics** | **$P_0$** | **$P_1$** | **$P_2$** | **$P_3$** | **$Q_0$** | **$Q_1$** | **$Q_2$** | **$Q_3$** |
|---|---|---|---|---|---|---|---|---|
| Scorch time $t_{10,}$(min) | 7.83 | 4.37 | 3.01 | 5.17 | 7.03 | 2.44 | 2.04 | 5.11 |
| Optimum cure time$t_{90,}$ (min) | 23.03 | 11.21 | 8.88 | 15.39 | 13.09 | 6.94 | 6.01 | 10.24 |
| CRI ($min^{-1}$) | 6.58 | 14.62 | 17.04 | 9.80 | 16.50 | 22.22 | 25.19 | 19.49 |
| Torque Max. (dNm) | 2.38 | 2.54 | 2.96 | 2.71 | 3.01 | 2.61 | 2.66 | 2.81 |
| Torque Min. (dNm) | 0.05 | 0.07 | 0.06 | 0.05 | 0.06 | 0.06 | 0.07 | 0.05 |

In the case of MBTS-BPTU systems the optimum cure time of $P_1$ is 50% less than $P_0$, though $P_0$ carries more accelerator. Mixes $P_2$ and $P_0$ both contain same amount of accelerator while $P_2$ is a binary system and $P_0$ is a single accelerator system. The optimum cure time of $P_2$ is much less than $P_0$ and is only 38 % of $P_0$. On increase of BPTU concentration maximum torque increased. The CRI value of $P_2$ is 2.6 times more than $P_0$, while $P_1$ is 2.2 times more than $P_0$. The CRI value of $P_1$ is 1.5 times that of $P_3$ , and $P_2$ is 1.7 times more of $P_3$.

In the CBS-BPTU systems the optimum cure time of $Q_1$ is only 53% of $Q_0$ and 67% of $Q_3$. Eventhough $Q_2$ and $Q_0$ carry the same quantity of accelerator, the optimum cure time of $Q_2$ is only 46% of $Q_0$ and 58% of $Q_3$. Thus CRI value of $Q_1$ and $Q_2$ are much higher than $Q_0$ and $Q_3$. Though maximum torque increased on increasing the amount of BPTU, scorch time decreased in both the systems..

The cure reaction of $P_1$ and $P_2$ follows first order kinetics like that of $P_0$ and $P_3$ (Fig.6.3), where $\ln(M_H - M_t)$ plotted against time gives straight line. The observed linearity in the plots confirms that the cure reaction of the samples follow first order kinetics [8, 9,]. The cure reaction of CBS-BPTU also follows the same order evidenced as in Fig. 6.4. Thus by the addition of BPTU, decreases in optimum cure time and increases in maximum torque in both the systems are noticed. Moreover in the cure graphs, the plateaus obtained for the experimental mixes are broad and reveal the secondary accelerator property of BPTU in these binary systems.

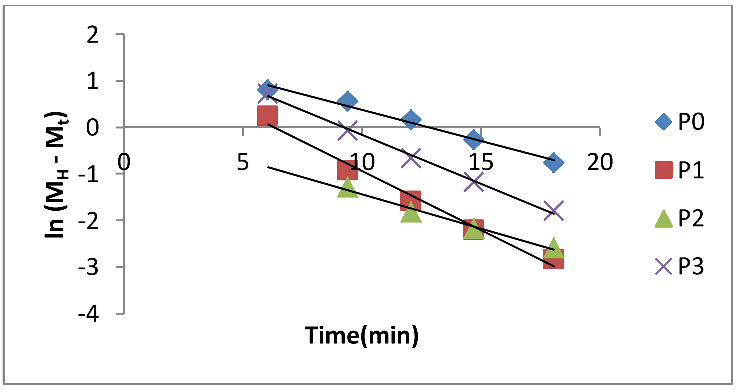

Fig. 6.3 Plots of ln($M_H$ – $M_t$) versus time for $P_0$ – $P_3$ mixes at 150 °C

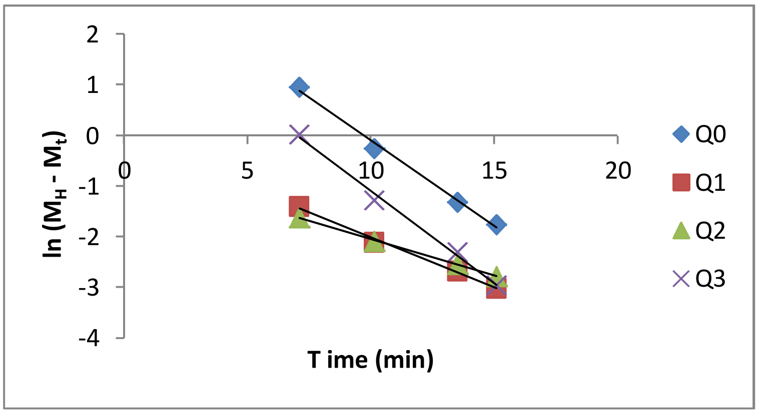

Fig. 6.4 Plots of ln($M_H$ – $M_t$) versus time for mixes $Q_0$ – $Q_3$ at 150 °C

### 6.1.3.2 Mechanical properties

The stress-strain properties of the various systems are given in Tables 6.3 & 6.4. The tensile strength of the vulcanizates MBTS-BPTU and CBS-BPTU systems is found to be increasing by the incorporation of BPTU. In MBTS system the tensile strength of $P_1$ is 1.6 times that of $P_0$ and 66% of $P_3$. Even though $P_0$ and $P_2$ have the same amount of accelerator, tensile strength of $P_2$ is twice that of $P_0$ and 74% of the reference mix $P_3$ (Fig.6.5). Modulus values are in general higher than the reference mixes. 300% modulus of the vulcanizates decreased on increasing the BPTU concentration while elongation at break percentage increased as expected as shown in Figs.6.6 and 6.7 respectively

**Table 6.3 Stress-strain properties of blend NR/ SBR-MBTS-BPTU vulcanizates**

| Sample | Tensile strength (MPa) | | Tensile retention (%) | Elongation of break (%) | Modulus at 300%(MPa) |
|---|---|---|---|---|---|
| | Unaged | Aged | | | |
| $P_0$ | 5.30 | 4.10 | 77 | 802 | 1.41 |
| $P_1$ | 8.95 | 8.29 | 93 | 847 | 1.78 |
| $P_2$ | 10.04 | 7.59 | 76 | 979 | 1.69 |
| $P_3$ | 13.45 | 12.48 | 93 | 1166 | 0.97 |

The CBS system of the NR/SBR blends also follow the same trend as MBTS system. Tensile strength of $Q_1$ is 2.6 times that of $Q_0$ and 1.3 times of $Q_3$. Tensile strength value of $Q_2$ is much higher than $Q_0$ though they carry the same quantity of accelerator (Table 6.4). The effect of binary accelerator system is well understood from the tensile strength values. Modulus at 300% elongation decreased from $Q_1$ to $Q_2$ and so the elongation at break percentage increased from $Q_1$ to $Q_2$.

**Table 6.4 Stress-strain properties of blend NR/ SBR-CBS-BPTU vulcanizates**

| Sample | Tensile strength (MPa) | | Tensile retention (%) | Elongation of break (%) | Modulus at 300%(MPa) |
|---|---|---|---|---|---|
| | Un-aged | Aged | | | |
| $Q_0$ | 5.25 | 4.14 | 79 | 705 | 1.69 |
| $Q_1$ | 13.81 | 8.90 | 64 | 923 | 1.81 |
| $Q_2$ | 19.90 | 18.04 | 91 | 993 | 1.70 |
| $Q_3$ | 10.43 | 9.87 | 95 | 956 | 1.56 |

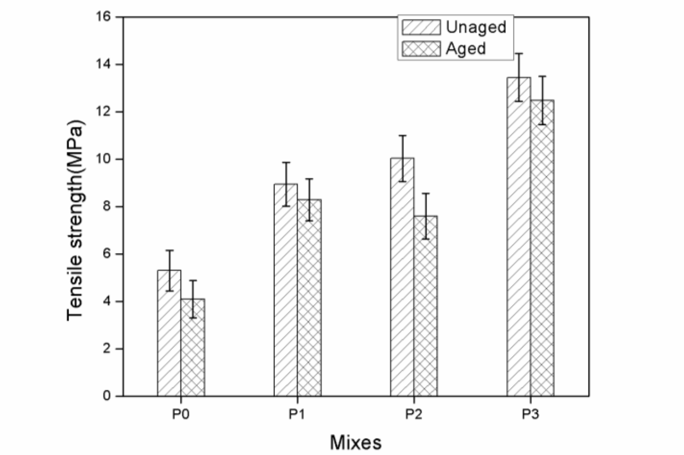

**Fig. 6.5 Tensile strength of blend NR/SBR-MBTS-BPTU vulcanizates**

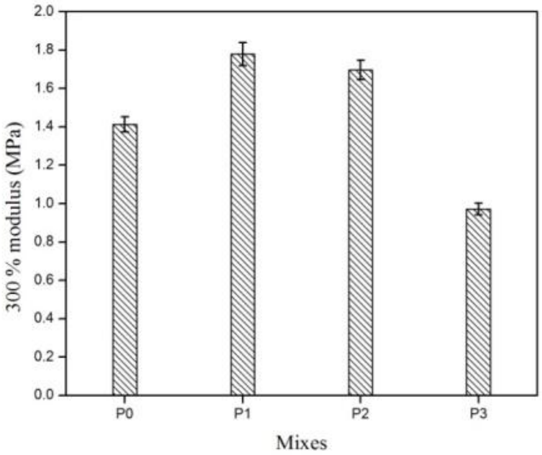

**Fig. 6.6 Modulus at 300% in blend of NR/SBR-MBTS-BPTU vulcanizates**

The variations of tensile properties are given in Figs. 6.8-6.10. Vulcanizate $P_1$ in the MBTS system and $Q_2$ in the CBS system have better retention of tensile strength on ageing.

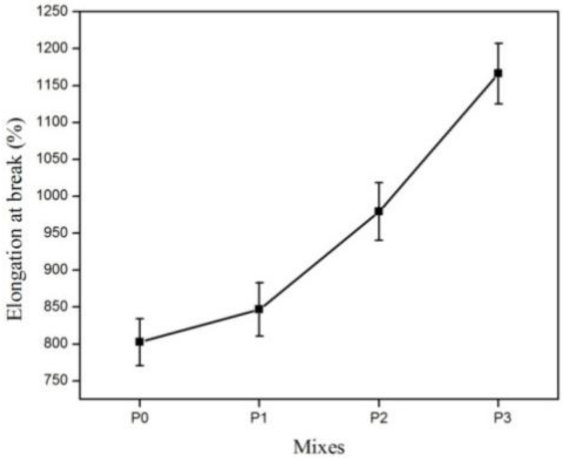

**Fig. 6.7 Elongation at break of blend NR/SBR-MBTS-BPTU vulcanizates**

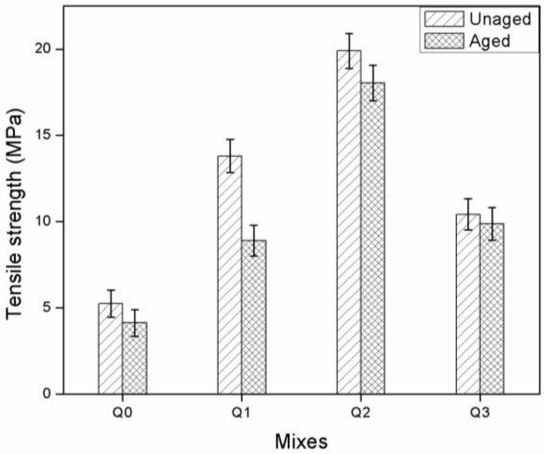

**Fig. 6.8 Tensile strength of blend NR/SBR-CBS-BPTU vulcanizates**

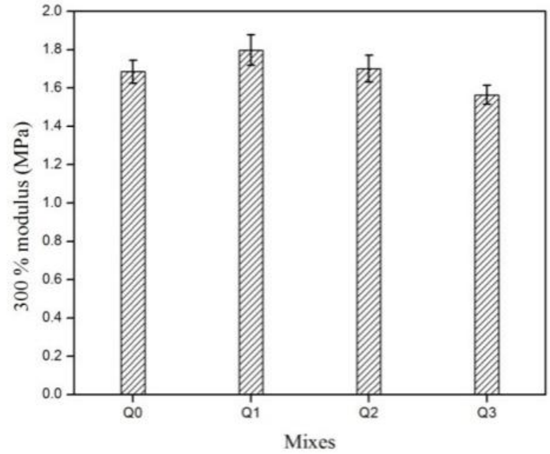

**Fig.6.9 Modulus at 300% in blend of NR/SBR-CBS-BPTU vulcanizates**

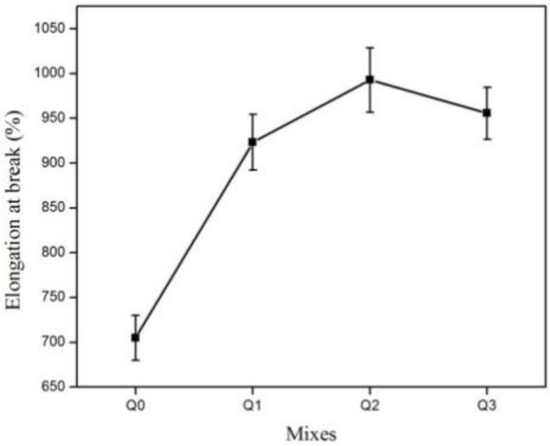

**Fig. 6.10 Elongation at break of blend NR/SBR-CBS-BPTU vulcanizates**

Other physical properties of vulcanizates of MBTS are given in Table 6.5. Tear strength of $P_1$ and $P_2$ are at par with the reference mix $P_3$ and 19% more than $P_0$ (Fig.6.11). But the tear strength of CBS vulcanizates are (Fig. 6.12) almost the same. The compression set value of $P_2$ is the lowest among the MBTS system and is beneficial. The compression set values of CBS system are higher than MBTS vulcanizates. Among the vulcanizates of CBS, $Q_2$ has the lowest compression set value. Other physical properties of CBS vulcanizates are given in Table 6.6. In both MBTS and CBS system, hardness and resilience increased with increase in the amount of BPTU. This is in correlation with total cross-link density obtained. The swelling resistance of $P_2$ and $Q_2$ are more than $P_1$ and $Q_1$ respectively and are evident from the sorption studies given in the Figs. 6.13a & 6.13b.

**Table 6.5 Properties of blend NR/SBR-MBTS-BPTU vulcanizates**

| **Proprerty** | **$P_0$** | **$P_1$** | **$P_2$** | **$P_3$** |
|---|---|---|---|---|
| Tear Strength (N/mm) | 19.92 | 23.80 | 23.67 | 23.09 |
| Compression set (%) | 19.13 | 16.13 | 12.87 | 18.92 |
| Hardness(shore A) | 34 | 36 | 39 | 35 |
| Resilience (%) | 49 | 57 | 66 | 51 |
| Crosslink density x $10^5$(gmol/mL) | 4. 39 | 5.27 | 6.16 | 5.16 |

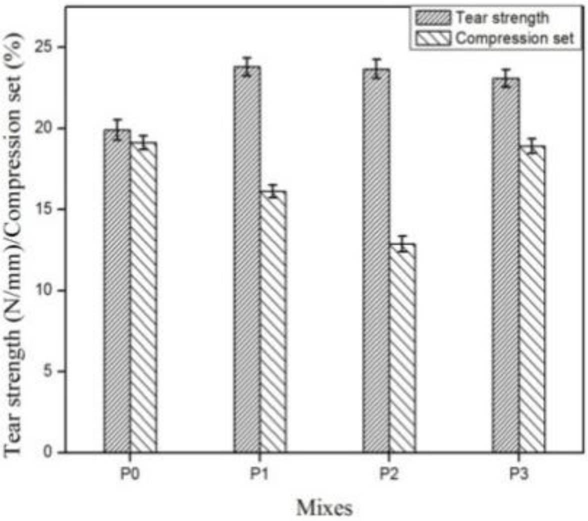

**Fig. 6.11** **Tear strength and compression set of blend NR/SBR-MBTS-BPTU vulcanizates**

**Table 6.6 Properties of blend NR/SBR-CBS-BPTU vulcanizates**

| **Property** | **$Q_0$** | **$Q_1$** | **$Q_2$** | **$Q_3$** |
|---|---|---|---|---|
| Tear strength(N/mm) | 23.77 | 24.74 | 24.32 | 24.54 |
| Compression set (%) | 24.59 | 19.06 | 16.54 | 20.0 |
| Hardness(shore A) | 36 | 40 | 42 | 39 |
| Resilience (%) | 61 | 43 | 55 | 60 |
| Crosslink density x $10^5$(gmol/mL) | 5.18 | 5.54 | 5.98 | 5.57 |

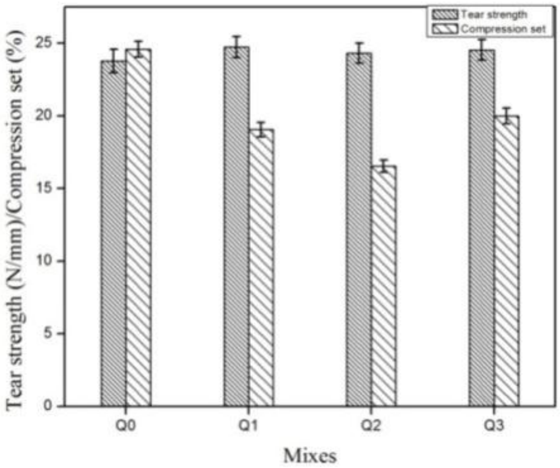

**Fig. 612 Tear strength and compression set of blend NR/SBR-CBS-BPTU vulcanizates**

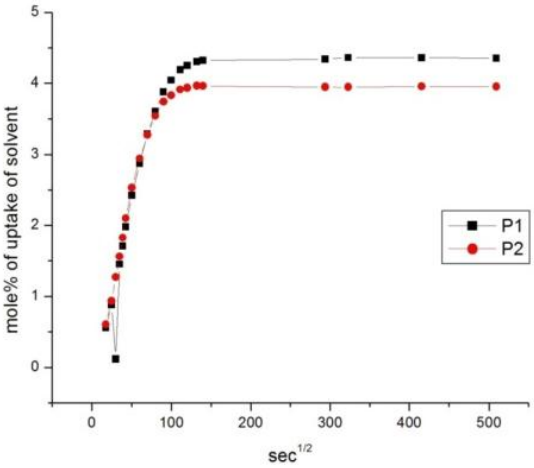

**Fig. 6.13a Sorption studies of $P_1$ and $P_2$ in toluene**

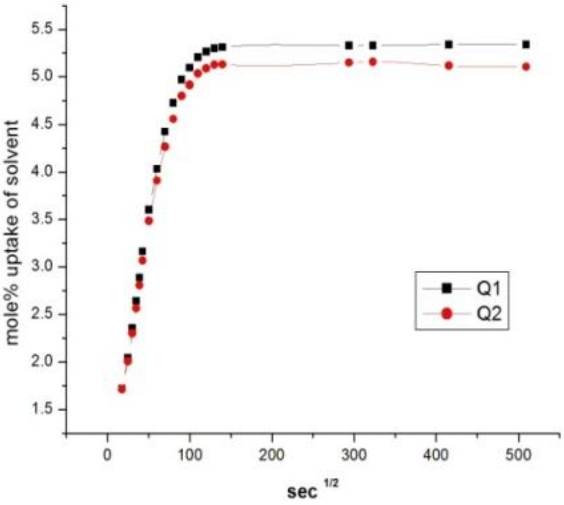

Fig. 6.13b Sorption studies of $Q_1$ and $Q_2$ in toluene

## 6.1.4 Conclusion

The vulcanization of NR/SBR (gum) blends using BPTU as an accelerator in a binary accelerator system reduced the optimum cure time. Curing can be carried out at 150 °C even with lesser amount of accelerator. The cure characteristics and some of the mechanical properties of the vulanizates under consideration are either comparable or better than the reference mixes.

## Part II

## STUDIES ON SILICA FILLED NR/SBR BLENDS

### 6.2.1 Introduction

Gum vulcanizate of NR / SBR blends show low physical properties compared to gum vulcanizates of NR and better than gum vulcanizates of SBR. Fillers are added to the blends for the improvement of processability, reinforcement and reduction of cost. During the mixing of filler with pre-blend, the soft polymer will enter into the voids between filler particles until the viscosity of the soft polymer reaches the viscosity of the more viscous polymer. Then the second polymer enters into the filler, so that the viscosity of the two phases is nearly the same [10].

### 6.2.2 Experimental

The composition of the various filled formulations of the blends is given in Tables 6.7 & 6.8. In all the mixes zinc oxide, stearic acid and sulphur were incorporated as activator, co-activator and curing agent respectively. Each mix also contains silica, DEG, SP and naphthenic oil. Mix $T_1$ to $T_4$ contains various amounts of BPTU with 1.0 phr of MBTS. These experimental mixes are compared with $R_1$, $R_2$ and $R_3$. $R_1$ and $R_2$ are single accelerator systems containing 1.5 phr and 2.0phr MBTS respectively. Reference mix $R_3$ is a binary accelerator system containing 1.0 phr MBTS with 0.2 phr TMTD.

In CBS system $S_1$, $S_2$, $S_3$ and $S_4$ contains various amounts of BPTU with 1.0phr of CBS. The experimental mixes of CBS are compared with $O_1$, $O_2$ and $O_3$ where $O_1$ and $O_2$ are single accelerator systems containing 1.5 phr and 2.0 phr of CBS respectively. Reference mix $O_3$ is a binary system containing 1.0 phr CBS with 0.2 phr TMTD. All the experimental procedures adopted are described in chapter 2. The compounding ingredients are added to the premixed NR and SBR in a manner similar to mixing in single elastomers.

**Table 6.7 Formulations of silica filled NR/SBR blends containing MBTS**

| **Ingredients** | **$T_1$** | **$T_2$** | **$T_3$** | **$T_4$** | **$R_1$** | **$R_2$** | **$R_3$** |
|---|---|---|---|---|---|---|---|
| NR (g) | 50 | 50 | 50 | 50 | 50 | 50 | 50 |
| SBR(g) | 50 | 50 | 50 | 50 | 50 | 50 | 50 |
| ZnO (phr) | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 |
| Stearic acid (phr) | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 |
| Silica (phr) | 30 | 30 | 30 | 30 | 30 | 30 | 30 |
| DEG(phr) | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 |
| SP(phr) | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| Naphthenic Oil(phr) | 6.0 | 6.0 | 6.0 | 6.0 | 6.0 | 6.0 | 6.0 |
| MBTS (phr) | 1.0 | 1.0 | 1.0 | 1.0 | 1.5 | 2.0 | 1.0 |
| BPTU (phr) | 0.25 | 0.5 | 0.75 | 1.0 | 0.0 | 0.0 | 0.0 |
| TMTD(phr) | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.2 |
| Sulphur (phr) | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 |

**Table 6.8 Formulations of silica filled NR/SBR blends containing CBS**

| **Ingredients** | **$S_1$** | **$S_2$** | **$S_3$** | **$S_4$** | **$O_1$** | **$O_2$** | **$O_3$** |
|---|---|---|---|---|---|---|---|
| NR (g) | 50 | 50 | 50 | 50 | 50 | 50 | 50 |
| SBR(g) | 50 | 50 | 50 | 50 | 50 | 50 | 50 |
| ZnO (phr) | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 |
| Stearic acid (phr) | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 |
| Silica (phr) | 30 | 30 | 30 | 30 | 30 | 30 | 30 |
| DEG(phr) | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 |
| SP(phr) | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| Naphthenic Oil(phr) | 6.0 | 6.0 | 6.0 | 6.0 | 6.0 | 6.0 | 6.0 |
| CBS (phr) | 1.0 | 1.0 | 1.0 | 1.0 | 1.5 | 2.0 | 1.0 |
| BPTU (phr) | 0.25 | 0.5 | 0.75 | 1.0 | 0.0 | 0.0 | 0.0 |
| TMTD | - | - | - | - | - | - | 0.2 |
| Sulphur (phr) | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 |

## 6.2.3 Results and discussion

### 6.2.3.1Cure characteristics

The cure curves for the silica filled systems are shown in Figs. 6.14 & 6.15. The cure characteristics are given in Tables 6.9 & 6.10. In MBTS system $T_3$ mix shows the lowest optimum cure, highest maximum torque and highest cure rate.

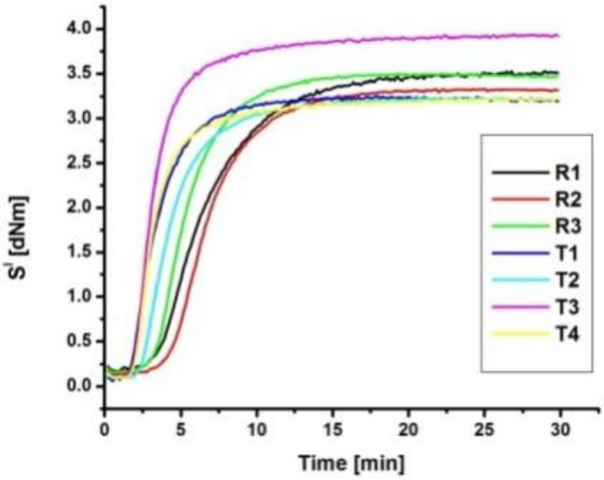

**Fig. 6.14 Rheographs of silica filled NR / SBR blends- MBTS mixes**

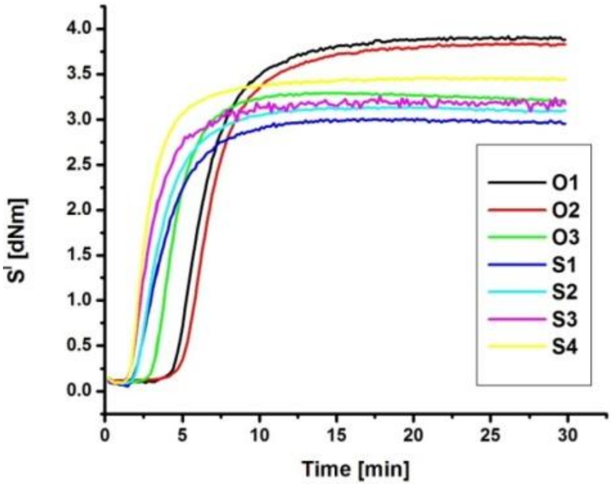

**Fig. 6.15 Rheographs of silica filled NR / SBR blends-CBS mixes**

**Table 6.9 Cure Characteristics of silica filled NR/SBR blends containing MBTS (150 °C)**

| Cure Characteristics | $T_1$ | $T_2$ | $T_3$ | $T_4$ | $R_1$ | $R_2$ | $R_3$ |
|---|---|---|---|---|---|---|---|
| Scorch time, $t_{10}$(min) | 2.87 | 2.67 | 2.14 | 2.14 | 3.83 | 4.48 | 3.54 |
| Optimum cure time, $t_{90}$(min) | 8.58 | 8.31 | 6.58 | 6.85 | 12.40 | 11.36 | 9.30 |
| CRI ($min^{-1}$) | 17.51 | 17.73 | 22.52 | 21.23 | 11.67 | 14.53 | 17.36 |
| Torque Max. (dNm) | 3.23 | 3.25 | 3.94 | 3.23 | 3.53 | 3.34 | 3.50 |
| Torque Min. (dNm) | 0.06 | 0.09 | 0.09 | 0.09 | 0.17 | 0.13 | 0.15 |

**Table 6.10 Cure characteristics of silica filled NR/SBR blends containing CBS (150 °C)**

| Cure Characteristics | $S_1$ | $S_2$ | $S_3$ | $S_4$ | $O_1$ | $O_2$ | $O_3$ |
|---|---|---|---|---|---|---|---|
| Scorch time, $t_{10}$(min) | 2.10 | 2.25 | 1.82 | 1.81 | 4.74 | 5.24 | 3.30 |
| Optimum cure time, $t_{90}$(min) | 7.27 | 6.87 | 6.15 | 5.39 | 10.36 | 10.83 | 6.92 |
| CRI ($min^{-1}$) | 19.57 | 21.64 | 23.09 | 27.93 | 17.79 | 17.89 | 27.62 |
| Torque Max. (dNm) | 3.02 | 3.15 | 3.27 | 3.47 | 3.93 | 3.85 | 3.31 |
| Torque Min. (dNm) | 0.04 | 0.08 | 0.08 | 0.09 | 0.07 | 0.11 | 0.09 |

The cure graph obtained for MBTS system is broad and shows reversion resistance. This supports the accelerator activity of BPTU. A plot of $-\log(t_{90})$ versus 1000/ T gave a straight line for all the mixes. The activation energy (E) can be calculated from the slope of this line. The CRI values and activation energies of the cure reactions of MBTS system are given in Table 6.11. It is noteworthy to mention that the activation energy required for the single accelerator systems namely $R_1$ and $R_2$ are the highest. In fact, this reaction requires much more energy and therefore will start and proceed slowly. The mixes $T_1$ and $T_3$ (binary systems) have lowest activation energy. The lower the activation energy, the faster is the cure reaction.$T_3$ has the highest CRI value among the MBTS systems.

**Table 6.11 Cure kinetics parameters of silica filled NR/SBR blends containing MBTS**

| **Parameters** | **$T_1$** | **$T_2$** | **$T_3$** | **$T_4$** | **$R_1$** | **$R_2$** | **$R_3$** |
|---|---|---|---|---|---|---|---|
| CRI ($min^{-1}$) | 17.51 | 17.73 | 22.52 | 21.23 | 11.67 | 14.53 | 17.36 |
| K value at 140 °C | 0.25 | 0.22 | 0.26 | 0.24 | 0.13 | 0.15 | 0.13 |
| K value at 150 °C | 0.38 | 0.31 | 0.32 | 0.32 | 0.26 | 0.28 | 0.34 |
| K value at 160 °C | 0.53 | 0.63 | 0.46 | 0.39 | 0.41 | 0.66 | 0.73 |
| Energy of activation (kJ/mol) | 91.83 | 99.30 | 92.92 | 94.53 | 103.97 | 106.07 | 97.32 |

In the CBS-BPTU system mix $S_4$ gives the lowest optimum cure time, highest maximum torque and highest cure rate. The vulcanization plateau obtained for $S_4$ in the cure graph is broad and parallel to time axis.

The straight line graph obtained by plotting $\ln(M_H - Mt)$ against different temperatures of both the systems as in Figs 6.16 & 6.17, (graph for $T_3$ an $S_2$ are shown, similar graphs are obtained for other mixes) show that the cure reaction of the compounds follows first- order kinetics [8]. For different mixes, same type of graph is obtained at 140°, 150° and 160 °C. Regardless of the temperature and concentration of BPTU, all vulcanization reactions proceed according to first-order kinetics. The rate constant k of the cure reaction is obtained from the slope of the respective straight lines. The k values and CRI values for MBTS systems are given in Table 6.11. Values of k are found to increase with temperature in MBTS system. Arrhenius plots for MBTS systems are presented in Figs. 6.18 and activation energies are calculated from these straight lines [11].

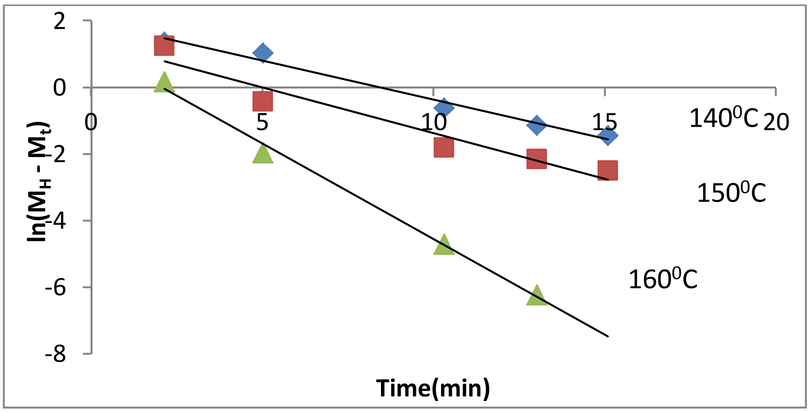

Fig. 6.16 Plots of ln($M_H$-$M_t$) versus time for mix $T_3$ at different temperatures

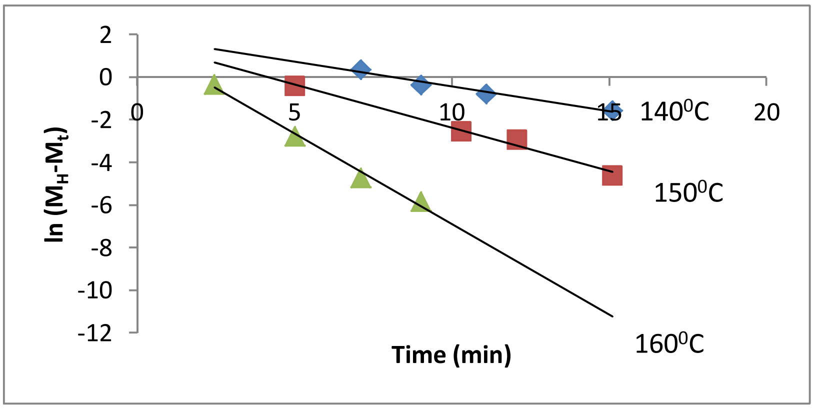

Fig. 6.17 Plots of ln($M_H$-$M_t$) versus time for mix $S_2$ at different temperatures

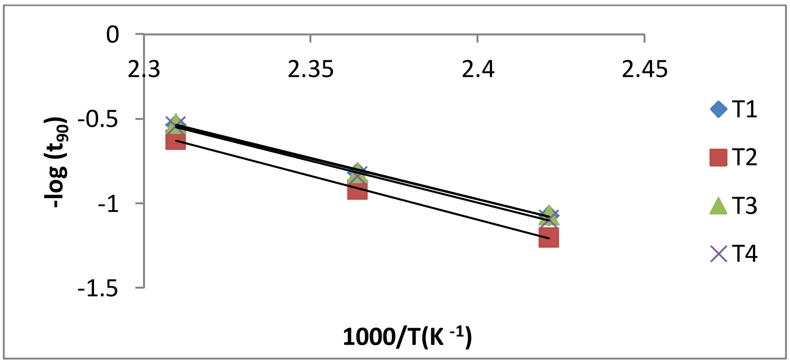

Fig.6.18 Arrhenius plots of the (MBTS-BPTU) mixes showing effect of temperature on curing

### 6.2.3.2 Mechanical properties

Tensile strength of various NR/SBR blend vulcanizates is given in Table 6.12. Among the mixes of MBTS, $T_4$ shows the highest tensile strength even though the mix$T_3$ has the highest CRI value. Tensile strength of $T_3$ and $T_4$ are almost the same.$T_3$ has the highest 300% modulus. In CBS system there is no appreciable variation in tensile strength from $S_1$ to $S_3$ but $S_4$ has the highest and is more than $T_4$. With the increasing amount of BPTU tensile strength increased in MBTS system. The effect of BPTU on the tensile properties of the vulcanizates before and after ageing is presented in Figs. 6.19 & 6.20. It is interesting to note that tensile retention property decreases as the concentration of accelerator increases, indicating the higher possibility of desulphuration on ageing with higher amount of accelerator [12].

**Table 6.12 Stress-strain properties of different silica filled NR-SBR blend vulcanizates**

| Samples | Tensile strength (MPa) | | Tensile retention (%) | Elongation at break (%) | | Modulus 300% (MPa) | |
|---|---|---|---|---|---|---|---|
| | Un-aged | Aged | | Un-aged | Aged | Un-aged | Aged |
| $T_1$ | 14.45 | 17.92 | 124 | 914 | 757 | 2.02 | 3.75 |
| $T_2$ | 16.36 | 14.22 | 87 | 974 | 746 | 2.09 | 2.62 |
| $T_3$ | 16.76 | 15.69 | 94 | 970 | 762 | 3.01 | 3.49 |
| $T_4$ | 17.19 | 12.72 | 74 | 969 | 798 | 2.15 | 2.66 |
| $R_1$ | 14.43 | 16.53 | 115 | 1094 | 1056 | 1.85 | 2.50 |
| $R_2$ | 16.95 | 15.27 | 90 | 1011 | 764 | 2.07 | 2.81 |
| $R_3$ | 16.28 | 15.33 | 94 | 936 | 812 | 2.22 | 2.37 |
| $S_1$ | 15.76 | 17.61 | 112 | 950 | 807 | 2.31 | 3.02 |
| $S_2$ | 16.96 | 19.82 | 117 | 957 | 879 | 2.30 | 3.03 |
| $S_3$ | 16.85 | 14.85 | 88 | 951 | 855 | 2.35 | 2.85 |
| $S_4$ | 20.30 | 15.41 | 76 | 965 | 700 | 2.66 | 3.42 |
| $O_1$ | 16.14 | 19.97 | 124 | 899 | 881 | 2.05 | 3.13 |
| $O_2$ | 15.97 | 14.50 | 91 | 770 | 626 | 2.14 | 2.23 |
| $O_3$ | 21.85 | 16.73 | 77 | 1089 | 749 | 2.10 | 2.66 |

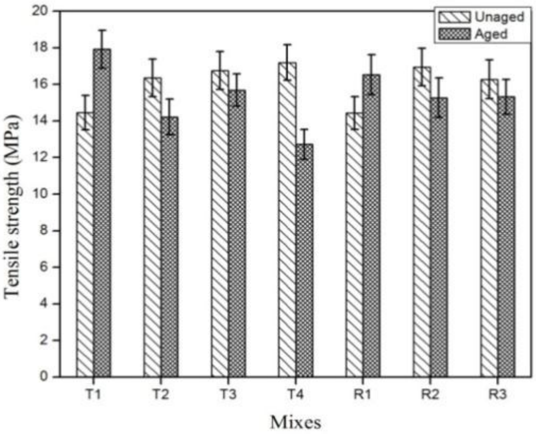

**Fig. 6.19 Tensile strength of silica filled NR/SBR blend - MBTS vulcanizates**

Mixes $T_1$, $S_1$, $R_1$& $O_1$ have the lowest amount of accelerators in each system and they have the maximum tensile retention. This may be due to the additional crosslinking that occurs to the vulcanizates during the ageing process.

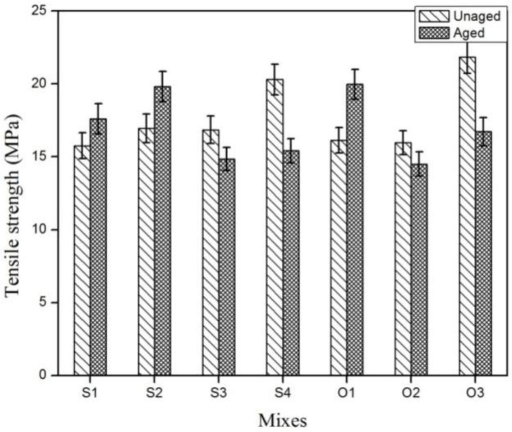

**Fig. 6.20 Tensile strength of silica filled NR/SBR blend - CBS vulcanizates**

But in the case of other vulcanizates except $S_2$ tensile strength decreases as expected on thermal ageing, being a natural phenomenon.

This can be due to desulphuration during the ageing process, which can convert the polysulphidic linkages into mono and disulphidic links [13 ]. Among the vulcanizates of CBS-BPTU $S_1$ has the highest elongation at break with lowest value for 300% modulus and $S_4$ has the lowest elongation at break with highest value of 300% modulus and highest tensile strength.

Other physical properties of MBTS systems investigated are reported in Table 6.13. Tear strength of vulcanizates of MBTS, $T_1$ - $T_4$ are almost the same with very little variation and are at par with (references) $R_2$ and $R_3$ (Fig.6.21). Mix $T_4$ has the lowest value for abrasion loss, which is beneficial in applications such as tyres and its crosslink density is nearly to that of the highest, $T_3$. Abrasion resistance and compression set values of $T_3$ are at par with $T_4$. Hardness of this system first diminishes and then increases, but the resilience values increased with increase in concentration of BPTU. Considering the cure characteristics, $T_3$ can be considered as the optimum dosage for NR/SBR blends along with MBTS for silica filled system. But the mechanical properties of $T_3$ and $T_4$ are almost similar.

**Table 6.13 Properties of silica filled NR/SBR (blends)-MBTS-BPTU vulcanizates**

| **Property** | **$T_1$** | **$T_2$** | **$T_3$** | **$T_4$** | **$R_1$** | **$R_2$** | **$R_3$** |
|---|---|---|---|---|---|---|---|
| Resilience (%) | 47 | 53 | 55 | 53 | 41 | 48 | 50 |
| Hardness (Shore A) | 44 | 43 | 47 | 49 | 46 | 44 | 42 |
| Abrasion loss ($cm^3/h$) | 8.39 | 7.67 | 6.19 | 6.10 | 9.49 | 6.01 | 9.09 |
| Crosslink density $x10^5$ (g mol/mL) | 6.31 | 7.44 | 7.96 | 7.56 | 6.13 | 7.71 | 7.47 |

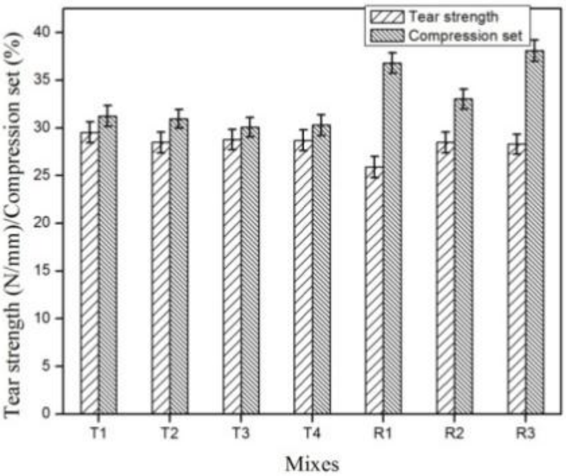

**Fig. 6.21 Tear strength and compression set of silica filled blend NR/SBR-MBTS vulcanizates**

Mechanical properties like resilience, compression set and abrasion loss of the CBS vulcanizates show appreciable changes on varying the concentration of the accelerators as shown in Table 6.14. Though there is only marginal change in tear strength, $S_3$ has the highest value (Fig. 6.22). There is an overall trend of increase in the values of resilience and hardness, while the phenomenon is reversed in the case of compression set and abrasion loss. Among the vulcanizates of CBS, $S_4$ shows the highest tensile strength and hardness with lowest values for compression set and abrasion loss which are advantages for a vulcanizate. The crosslink density, a key factor which controls the mechanical properties of a vulcanizate is also the highest for $S_4$, attesting to the above observed facts and hence making it the best candidate. The mechanical properties of $S_4$ are better than the references $O_1$, $O_2$ and even $O_3$ carrying the ultra accelerator TMTD.

**Table 6.14 Properties of silica filled NR/SBR (blends)-CBS –BPTU vulcanizates**

| **Property** | **$S_1$** | **$S_2$** | **$S_3$** | **$S_4$** | **$O_1$** | **$O_2$** | **$O_3$** |
|---|---|---|---|---|---|---|---|
| Resilience (%) | 41 | 50 | 49 | 51 | 49 | 50 | 47 |
| Hardness (Shore A) | 44 | 49 | 46 | 52 | 46 | 48 | 48 |
| Abrasion loss ($cm^3/h$) | 8.45 | 7.47 | 7.06 | 5.80 | 7.63 | 8.13 | 7.67 |
| Crosslink density $x10^5$ (g mol/ mL) | 6.67 | 7.01 | 7.23 | 8.67 | 7.49 | 7.38 | 7.41 |

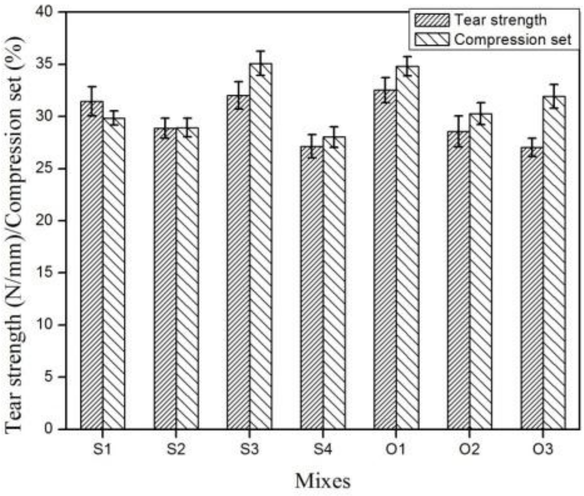

**Fig. 6.22 Tear strength and compression set of silica filled NR/SBR-CBS vulcanizates**

The mechanical properties of $S_4$ and $T_4$ are found to be almost similar with slight upper edge for $S_4$ as it has more resistance to abrasion loss and a small increase in crosslink density which is also evident from the solvent uptake of $T_4$ and $S_4$ (Fig. 6.23). The solvent uptake of $T_4$ and $S_4$ shows that the molecules in $S_4$ vulcanizates are held more tightly than in $T_4$ and this gives evidence for the higher tensile strength of $S_4$ than$T_4$.

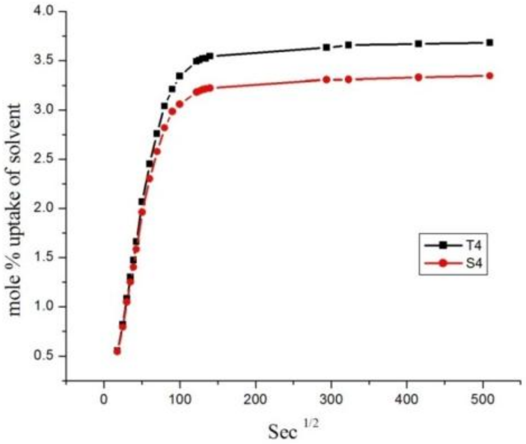

**Fig. 6.23 Comparison of solvent uptake**

### 6.2.3.3 Thermal analysis

Thermal degradation studies reveal that there are no appreciable changes among the various vulcanizates under study [Tables 6.15 & 6.16)]. The different thermal characteristics of experimental mixes are almost that of reference mixes. This indicates that there is no adverse effect in the thermal properties of the vulcanizate on using the binary accelerator system containing the new accelerator BPTU when compared to MBTS or CBS alone and also with TMTD as secondary accelerator. Among MBTS systems $T_3$ has the highest temperature for onset of degradation and also the temperature at which 60% remains. In CBS system $S_4$ has the highest temperature for end set of degradation and temperature at which 60% remains. Thermal properties of $S_4$ are more similar to the reference mix $O_3$.

**Table 6.15 Results of thermogravimetric analyses for blends of NR/SBR containing MBTS**

| Characteristics | $T_1$ | $T_2$ | $T_3$ | $T_4$ | $R_1$ | $R_2$ | $R_3$ |
|---|---|---|---|---|---|---|---|
| Onset of degradations (°C) | 340±1 | 345±2 | 350±2 | 350±1 | 340±3 | 345±3 | 345±2 |
| End set of degradation (°C) | 490±1 | 490±3 | 500±2 | 500±3 | 500±1 | 500±3 | 500±4 |
| Temperature at 60% retained (°C) | 415±2 | 410±3 | 420±1 | 410±2 | 415±1 | 415±2 | 415±1 |
| Temperature at maximum degradation (°C) | 470±1 | 465±1 | 466.17 | 465±1 | 465±1 | 465±2 | 465±2 |
| Residue (%) | 20.99 | 20.17 | 20.97 | 18.37 | 20.38 | 19.77 | 20.47 |
| Remaining at 300 °C (%) | 90.31 | 88.80 | 91.46 | 89.88 | 88.12 | 89.8 | 89.28 |

**Table 6.16 Results of thermogravimetric analyses for blends of NR/SBR containing CBS**

| Characteristics | $S_1$ | $S_2$ | $S_3$ | $S_4$ | $O_1$ | $O_2$ | $O_3$ |
|---|---|---|---|---|---|---|---|
| Onset of degradations (°C) | 330±1 | 345±2 | 335±3 | 345±1 | 325±2 | 345±2 | 350±1 |
| End set of degradation (°C) | 485±3 | 495±3 | 475±2 | 505±1 | 485±3 | 488±2 | 504±1 |
| Temperature at 60% retained (°C) | 403±2 | 398±2 | 405±1 | 410±2 | 405±1 | 410±2 | 410±3 |
| Temperature at maximum degradation (°C) | 455±2 | 465±2 | 455±3 | 465±2 | 453±3 | 470±1 | 465±1 |
| Residue (%) | 19.76 | 18.95 | 20.43 | 19.61 | 20.48 | 17.62 | 19.89 |
| Remaining at 300 °C (%) | 87.84 | 86.78 | 88.84 | 88.17 | 88.65 | 89.07 | 89.80 |

### 6.2.3.4 SEM analysis

SEM morphology studies of the tensile fractured samples of $T_3$, $T_4$, $S_3$ and $S_4$ at 3000x magnification are shown in Fig. 6.24 (a-d). Observation of the tensile fractured surface was done to investigate the filler dispersion and the interfacial adhesion between the filler and rubber matrix. $S_3$ and $S_4$ showed rougher surfaces than $T_3$ and $T_4$ indicating better stress transfer and improved tensile properties. Some pull-out and fatigue type failures are observed in $T_3$ and $T_4$. Though all the samples have agglomeration to a small extent, they show uniform mixing.

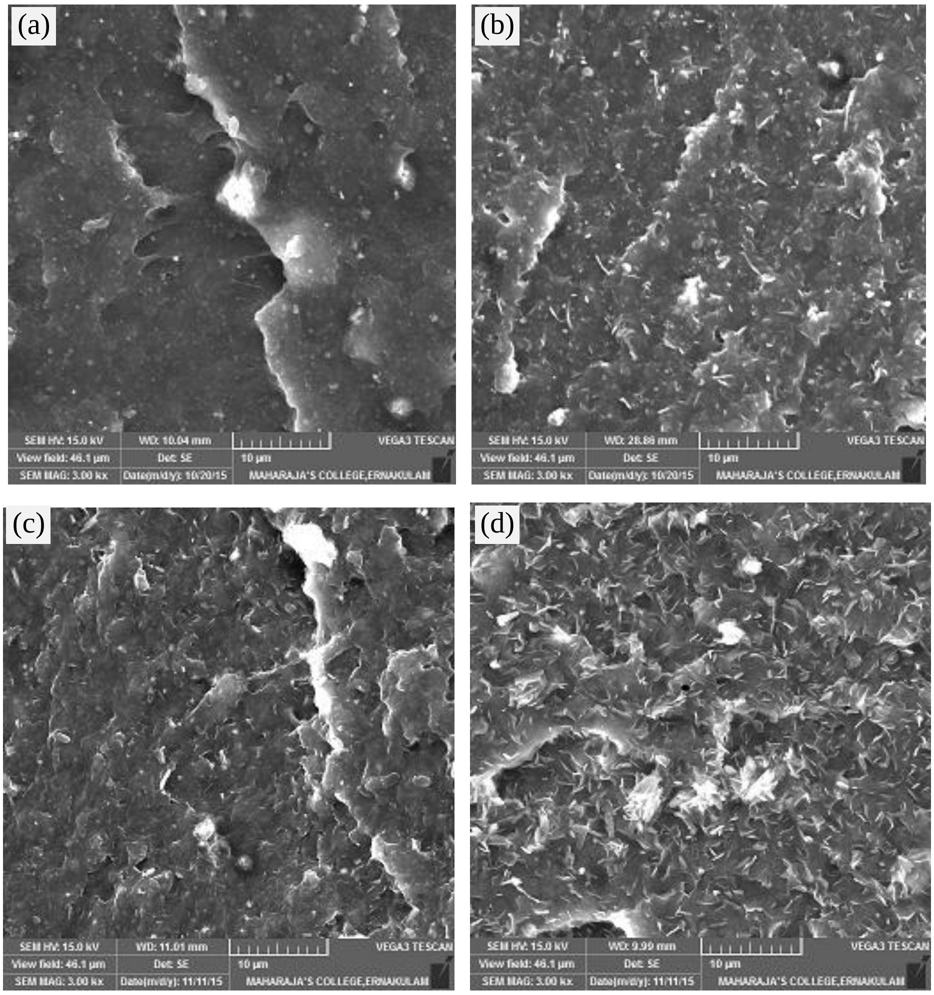

**Fig. 6.24 SEM micrograph of the tensile fractured surface of (a) $T_3$, (b) $T_4$, (c) $S_3$and (d) $S_4$ at 3000x magnification.**

### 6.2.4 Conclusion

BPTU as secondary accelerator along with MBTS or CBS has been investigated giving emphasis to the processing characteristics, mechanical properties and swelling behaviour. It is found that even 0.25 phr of BPTU with one phr of MBTS or CBS can improve the production rate of vulcanizate without adversely affecting the scorch safety of the compound. This new secondary accelerator does not adversely affect the kinetics of the cure reaction and it follows first order kinetics, even with changes in its concentration and temperature. In addition to this on thermal ageing there is improvement of tensile strength at lower concentrations of BPTU. Addition of BPTU improves the tear strength of the vulcanizate only to a small extent.

In the MBTS system, the mix with 0.75 phr of BPTU and 1.0phr of MBTS ($T_3$) can be taken as the optimum dosage on considering cure characteristics. Both $T_3$ and $T_4$ have almost the same mechanical properties.

Among the CBS binary accelerator systems, $S_4$ carrying BPTU and CBS (1:1) is observed to be the best candidate since it shows the highest hardness and resilience with lowest compression set and abrasion loss in comparison with reference mix $O_2$. The tensile strength is also at par with reference mixes $O_1$ and $O_2$. $S_4$ has the lowest optimum cure time and highest cure rate index which makes the system more economical. Thermal degradation temperature of all the vulcanizates, ranges from 300 to 450 $^oC$. Morphology study shows that the filler (silica) is uniformly dispersed in both MBTS and CBS systems. Though the mechanical properties of $T_3$, $T_4$ and $S_4$ are almost the same, the tensile retention, tensile strength, compression set and abrasion resistance of $S_4$ are better than $T_3$ and $T_4$. But $T_3$ and $T_4$ have better scorch safety. Thus CBS-BPTU system is better for mechanical properties while MBTS-BPTU system for the cure properties in the vulcanization of NR/SBR blends.

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Chapter 7

# INVESTIGATIONS ON THE ROLE OF N-BENZOYL-$N^1,N^1$-PYRROLIDINYLTHIOUREA IN THE VULCANIZATION OF NR LATEX AND CARBON BLACK FILLED SYSTEMS

## Part I

## STUDIES ON NR LATEX SYSTEMS

### 7.1.1 Introduction

Natural rubber latex is obtained from *Havea brasiliensis*. It is a colloidal dispersion of negatively charged rubber particles suspended in an aqueous medium [1]. The amount of rubber particles present depends on the type of tree, the tapping intensity, soil condition, season, etc. It is a white opaque liquid and its density is between 0.975 – 0.98 g/cm$^3$. Its pH ranges from 6.5 – 7 and has variable viscosity. The rubber hydrocarbon in latex is 1,4 cis-poly isoprene. It occurs as molecular aggregates with an average diameter ranging from 0.25 to 0.3 microns. These rubber particles are surrounded by a protective layer of proteins and phospholipids which imparts the prophyllic colloidal nature of latex and the stability of the latex is due to the negative charge present on the protective layer [2]. NR latex contains 30-40% rubber, 2-2.5% proteins, 1-2% resins, 1-1.5% sugar, 55-66% water and 0.7-0.9% ash. The rubber hydrocarbon in latex is a polymer with wide distribution of molecular weight ranging between $10^5$ to$10^6$ and the major part has high molecular weight ranges [3].

The latex, when it comes out of the tree gets contaminated with microorganisms like bacteria and yeast [4]. As it has high water content and is susceptible to bacterial attack, the latex gets coagulated within hours of leaving the tree unless preservatives are added. The microorganisms metabolize the non-rubber contents of the latex and produce volatile fatty acids such as formic, acetic and propionic acid. This causes coagulation of the latex [1]. Widely ammonia is used as preservative in latex because it can inhibit bacterial growth and acts as an alkaline buffer by raising the pH and neutralizing the free acid formed in latex. Latex preserved with higher percentage of ammonia is known as high-ammonia (HA) latex. High percentage of ammonia causes processing problems and is also harmful to the workers dealing with it. So the practice now is to use NR latex containing less percentage of ammonia and a secondary preservative. For higher wet gel, the normal latex is concentrated, so that a large portion of serum and some small rubber particles are removed. By doing this better uniformity in composition is also obtained. For most product manufactures, latex of 60% minimum rubber is essential. There are different methods for concentrating the latex. The important methods used are (a) evaporation (b) creaming (c) centrifuging and (d) electro decantation. Creaming and centrifuging are most commonly used for the concentration of preserved field latex [5].

NR latex concentrate is a highly specified raw material. The significant latex properties are dry rubber content (DRC), non-rubber solid content (NRS), mechanical stability time (MST), volatile fatty acid number (VFA), potassium hydroxide number (KOH number) and alkalinity [6]. Latex concentrate is a non-Newtonian fluid that exhibits pseudoplastic flow pattern. Its viscosity decreases with increasing shear rate and also depends considerably on its solid content and particle size distribution. The thickness of the film deposited during the manufacture of dipped rubber products depends on the viscosity of the latex concentrate.

Compared to dry rubber, latex processing requires relatively simple machinery. Capital outlay (initial expense) and power requirements are also relatively low. As Polymer degradation step or mastication is not needed, it not only saves time and energy but also gives the vulcanizate greater resistance to deterioration.

Natural rubber latex is extensively employed in the manufacture of dipped goods such as gloves, balloons, catheters, teats, contraceptives, etc. NR latex gives outstanding properties exceptionally for tensile strength and elongation, coupled with relatively low modulus values. Latex is also used in large quantities for the production of foam rubber. Service performance of the articles made out of latex is superior to those of rubber solutions [7].

### 7.1.2 Vulcanization of latex

Compounding Ingredients

Vulcanization of latex is the result of colloidal chemical reactions taking place in the homogeneous system. NR latex can be converted into products by different methods, but the colloidal system should be maintained stable until it is converted into a solid product [7]. The different ingredients used in the latex compound are (i) surface active agents (ii) curing agents (iii) accelerators (iv) activators (v) antioxidants (vi) fillers and (vii) special additives. The water soluble minerals are added as solutions, immiscible liquids as emulsions and insoluble solids as dispersions as latex is an aqueous colloidal system with poor wetting ability [8].

The particle size of the ingredients should be reduced to that of the rubber particles in latex so that uniform distribution of the latex compound can be obtained [9]. Ball milling is the most common technique used to produce dispersions for latex compounding. In this the size of the particle material is reduced to the colloidal range.

The surface active agents are those substances which can bring out marked modifications in the surface properties of aqueous media, even though they are added in small amounts (in the order of 1% or less) [10]. They can be classified as wetting agents, viscosity modifiers, protective colloids, dispersing agents, dispersion stabilizers, emulsifiers, etc. as per their function.

Compounding with curing agents is necessary so that a vulcanized product can be obtained. The ease of incorporation as aqueous dispersions or solutions and the absence of risk of pre-vulcanization by heat permit the use of very rapid accelerators. In latex the particles are vulcanized and the product obtained from it does not require any heat treatment apart from that to remove moisture [10]. The universal vulcanizing agent for natural rubber latex is sulphur. Sulphur should be of the required quality and should be finely ground. It is used as dispersion. In sulphur less vulcanization systems TMTD may be used, but the vulcanization proceeds at a useful rate only at relatively higher temperature (140 $^{o}$C). Organic peroxides and hydro peroxides may be used to vulcanize natural rubber latex for getting products of a high order of translucency [10]. A wide range of organic accelerators for the sulphur vulcanization of natural rubber is available. But, only those which are highly active are important for the vulcanization of latex. It is because latex vulcanization temperatures are relatively low and there is no danger of scorching [11]. Hence the use of accelerators in latex is basically different from their use in dry rubber [12]. Vulcanization speed of the dithiocarbamates is so high that it can be used alone as an accelerator in open cures [8].

Accelerators which contain S-S, C-S or S-N bonds are inactive below 100 $^{o}$C, due to the thermal stability of the sulphur bonds. Philpott has suggested that sulphur containing nucleophiles like thiourea (TU) can enable such accelerators to become active even at lower temperatures [13]. He has also observed that sulphenamide accelerators which are unable to vulcanize NR latex in the absence of sulphur are also activated by TU to such an extent that it can effect cure to useful rate. Mary Kurien [11] has found aminoiminomethylthiourea (AMT) as an effective secondary accelerator in the sulphur vulcanization of NR latex. Reshmy et al. [14] investigated the effect of different benzoylthiourea as secondary accelerator in the vulcanization of NR and found that as the nucleophilic character increases, their activity as secondary accelerator also increases. Moore has proposed that accelerative effect of thiourea is attributed to its interaction with TMTD in basic conditions to form thiurampolysulphides [15].

The author [16] examined the effect of BPTU in the vulcanization of NR, SBR and their blends and found it to be effective as a secondary accelerator with MBTS or CBS. The present study is to evaluate its effect in the vulcanization of NR latex. In this investigation BPTU is used along with primary accelerator ZDC for the vulcanization of NR latex. Different mixes with varying concentrations of BPTU were prepared and the optimum dosage of BPTU required was determined based on the tensile properties obtained. The mixes were cured at two different temperatures, viz.100 and 120 $^{o}$C. The different properties of the vulcanizates were evaluated and chemical characterization of vulcanizates was also carried out. These properties are compared with those of mixes containing ZDC alone and ZDC with TU.

### 7.1.3 Experimental

Formulations of NR latex containing BPTU as secondary accelerator along with ZDC were prepared as in Table 7.1. The amount of various ingredients is given as wet weight in grams calculated on dry rubber content. Mixes $Z_1$, $Z_2$ and $Z_3$ contains 2.0, 5.0 and 8.0 gm of 10% BPTU dispersion with one molar equivalent of ZDC. Mix $R_1$ contains ZDC alone and $R_2$ contains ZDC and TU in 1:1 molar proportion. Centrifuged NR latex of 60% drc was used in this study. One part by weight of 10% KOH and 0.5 parts by weight of potassium oleate (10%) were added to stabilize the latex throughout the compounding and processing stages. These were added as aqueous solutions. The insoluble compounding ingredients such as ZnO, ZDC, BPTU and sulphur were added as dispersions. TU was added as aqueous solution. BPTU dispersion was obtained by sonicating the mixture of BPTU and water in presence of dispersing agent (Dispersel F).

The ingredients in the given order (Table 7.1) were added with continuous and slow stirring, to the latex taken in a glass vessel. After compounding the mixes were kept for maturation at room temperature for 24 hours.

**Table 7.1 Formulations of the NR latex mixes**

| Ingredients parts by weight (wet) | $R_1$ | $R_2$ | $Z_1$ | $Z_2$ | $Z_3$ |
|---|---|---|---|---|---|
| 60% Centrifuged latex | 167 | 167 | 167 | 167 | 167 |
| 10% KOH solution | 1 | 1 | 1 | 1 | 1 |
| 10% potassium oleate solution | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| 50%ZnO dispersion | 1 | 1 | 1 | 1 | 1 |
| 50% ZDC dispersion | 7.2 | 3.6 | 3.6 | 3.6 | 3.6 |
| 10% TU solution | - | 3.8 | - | - | - |
| 10% BPTU dispersion | - | - | 2 | 5 | 8 |
| 50% Sulphur disperson | 3 | 3 | 3 | 3 | 3 |

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 $^{o}$C for definite time intervals in an air oven. The optimum cure time was obtained from the tensile strength - time graph as shown in Figs. 7.1-7.4. The optimum cure time is the time at which the maximum tensile strength obtained as per the graph. The tensile properties of the vulcanizates were determined using Shimadzu Universal Testing Machine according to ASTM D 412. Ageing resistance was determined by heating the samples in an air oven at 70 $^{o}$C for 24 hours in a laboratory air oven. Tear resistance was determined as per ASTM D 624. The total crosslink densities of the vulcanizates were determined using the equilibrium swelling method.

### 7.1.4 Results and discussion

The cure time values and physical properties of the latex formulations cured with ZDC- BPTU as accelerators are given in Table 7.2 & 7.3. At 100 °C there is a definite decrease in optimum cure time with increase in concentration of BPTU when compared to reference mixes $R_1$ and $R_2$ (Fig. 7.1 & 7.2). The mix $Z_2$ containing the concentration 5 g (10%) of BPTU gives the highest tensile strength (23% higher than reference $R_2$) and can be taken as the optimum dosage. There is only a small variation in the cure time for the mixes cured at 120 °C by the addition of secondary accelerator (BPTU).

**Table 7.2 Properties of NR (latex) vulcanizates (mixes cured at 100 °C)**

| Mixes | Cure time (min) | Tensile strength (MPa) Un- aged | Aged | Retention (%) | Tear strength (N/mm) | Total crosslink density x$10^5$ (g mol/mL) |
|---|---|---|---|---|---|---|
| **$R_1$** | 40.7 | 21.93 | 21.72 | 99 | 53.68 | 3.25 |
| **$R_2$** | 38.8 | 21.70 | 16.47 | 76 | 48.57 | 3.22 |
| **$Z_1$** | 32.97 | 21.75 | 24.15 | 111 | 48.27 | 3.51 |
| **$Z_2$** | 31.52 | 26.73 | 26.86 | 100 | 58.13 | 4.87 |
| **$Z_3$** | 31.60 | 23.26 | 24.75 | 106 | 65.69 | 3.55 |

**Table 7.3 Properties of NR (latex) vulcanizates (mixes cured at 120 °C)**

| Mixes | Cure time (min) | Tensile strength (MPa) Un-aged | Aged | Retention (%) | Tear strength (N/mm) | Total crosslink density x$10^5$ (g mol/mL) |
|---|---|---|---|---|---|---|
| **$R_1$** | 21.30 | 23.11 | 21.71 | 94 | 56.27 | 3.31 |
| **$R_2$** | 22.58 | 22.89 | 15.96 | 70 | 44.60 | 3.71 |
| **$Z_1$** | 21.48 | 23.4 | 20.67 | 88 | 56.12 | 3.61 |
| **$Z_2$** | 20.70 | 27.16 | 23.76 | 87 | 75.24 | 5.20 |
| **$Z_3$** | 18.02 | 22.25 | 24.57 | 110 | 70.66 | 3.42 |

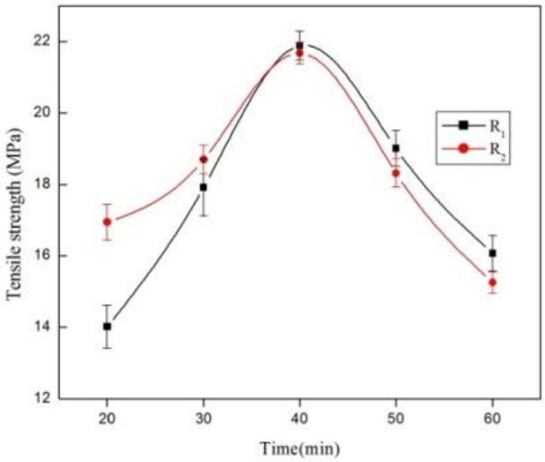

**Fig. 7.1 Variation of tensile strength with time for mixes $R_1$ & $R_2$ cured at 100 °C**

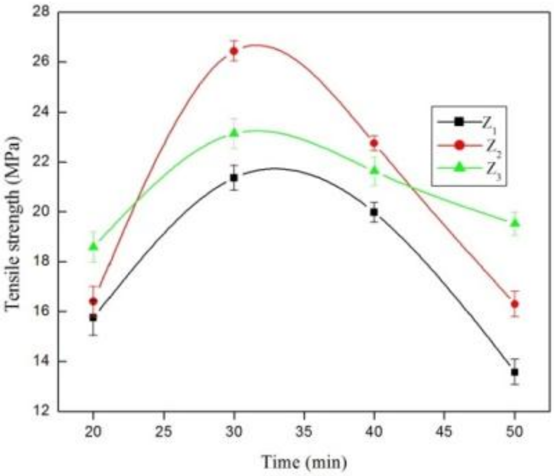

**Fig 7.2 Variation of tensile strength with time for mixes containing BPTU cured at 100 °C**

Variation in tensile strength of different vulcanizates with time cured at 120 °C is given by Figs. 7.3 & 7.4. The tensile strength of $Z_2$ has the highest value and is 18% more than reference mix $R_2$ and hence BPTU dosage in $Z_2$ can be taken as optimum dosage. The tensile retention of vulcanizates cured at 100 °C reveals that BPTU containing vulcanizates gives much better tensile strength than the references as shown in Fig. 7.5. The tensile retention after thermal ageing for mix $Z_1$ and $Z_2$ cured at 120 °C are almost the same and are in between the values of mixes $R_1$ and $R_2$. The optimum cure time of mix $Z_3$ is the lowest, and has the highest tensile retention after ageing and is greater than the reference mixes (Fig 7.6).

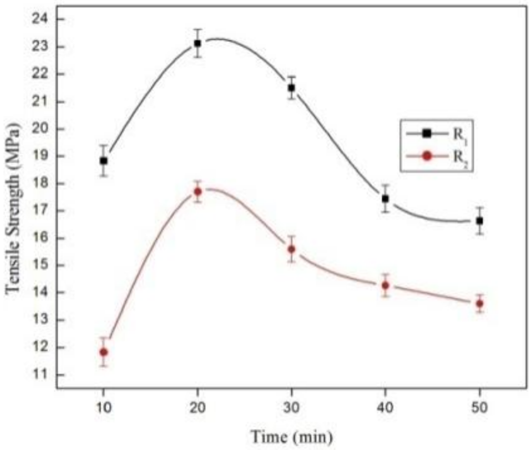

**Fig. 7.3 Variation of tensile strength with time for mixes $R_1$ and $R_2$ cured at 120 °C**

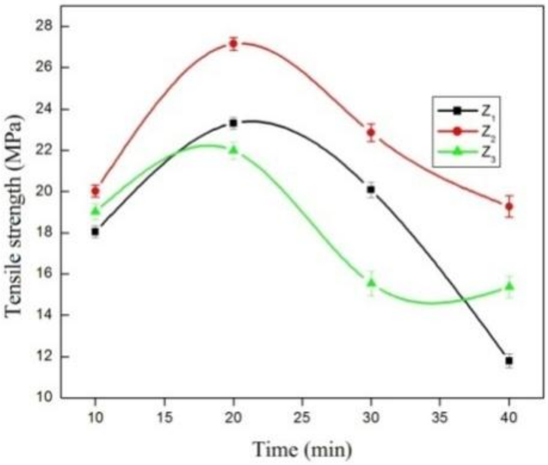

**Fig. 7.4 Variation of tensile strength with time for mixes containing BPTU cured at 120 °C**

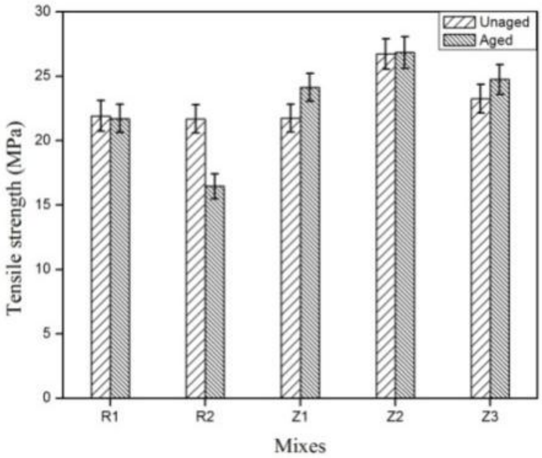

**Fig. 7.5 Variation in tensile strength of NR vulcanizates cured at 100 °C on ageing**

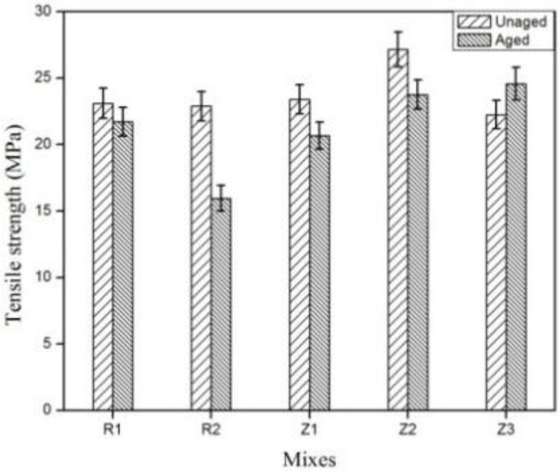

**Fig. 7.6 Variation in tensile strength of NR vulcanizates cured at 120 °C on ageing**

Tear resistance of these experimental mixes increased on the addition of BPTU, as seen in Fig. 7.7. Mixes $Z_3$ and $Z_2$ showed the highest tear resistance in the case of the samples cured at 100 and 120 °C. In both cases mix $Z_2$ showed the highest total crosslink density. Crosslink density values of both the systems are generally in agreement with tensile strength values obtained. The optimum cure time obtained in these systems showed that BPTU is more nucleophilic than thiourea. These results point to a probable nucleophilic reaction mechanism in the case of NR latex as suggested by Philpott [13].

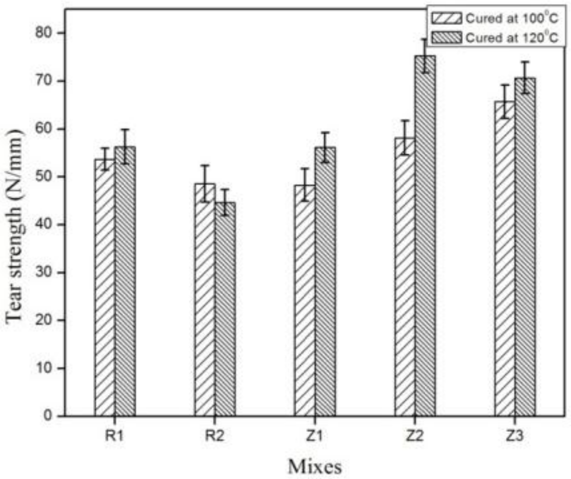

**Fig. 7.7 Variation in tear strength of vulcanizates cured at 100 °C and 120 °C**

### 7.1.5 Conclusions

BPTU can be used along with ZDC as a novel binary accelerator in the sulphur vulcanization of NR latex. The lower cure time values compared to the reference mixes reveals that it can vulcanize NR latex at a lower temperature than the commercially available accelerators. The new binary system gives vulcanizates with better tensile and tear properties. The tensile retention quality is also better and can attract the interest of the industry. The system containing optimum dosage of ZDC: BPTU in the ratio 3.6: 1 gives better values for tensile, tear and percentage of tensile retention (on thermal ageing) in comparison to reference mixes. It has to be noted that even at 100 °C curing takes place in a reasonable time and mechanical properties of the vulcanizates are comparable to the reference mixes.

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## Part II

# STUDIES ON THE EFFECT OF BPTU IN CARBON BLACK FILLED ELASTOMERS

## 7.2.1 Introduction

Carbon black is a material known and produced since olden days. But only a century ago i.e. January 1904 Mote and coworkers [1] discovered the effect of reinforcement of rubber by carbon black. Carbon black improves mechanical properties of rubber vulcanizates. Filling carbon blacks in elastomers and plastics also reduces the cost of the end product and modifies the electrical and optical properties of the polymer matrix [2]. Carbon black (CB) refers to a group of industrial products consisting of furnace blacks, channel blacks, thermal blacks and lampblacks. They are materials composed essentially of elemental carbon nearly in the form of spherical particles of colloidal sizes, combined mainly into particle aggregates obtained by partial ignition or thermal decomposition of hydrocarbons. Furnace black is made in a furnace by partial ignition of hydrocarbons. Thermal black and acetylene blacks are produced by thermal decomposition of natural gas and acetylene, respectively. Channel blacks are manufactured by impingement of natural gas flames on channel irons. Lampblack is made by burning hydrocarbons in open, shallow pans. Furnace and thermal decomposition processes are of commercial importance [3]. The increase in strength of the rubber containing carbon black led to many practical applications of the rubber throughout the world. The ability of tyres to last longer is primarily due to the wear resistance imparted to rubber from carbon black [4].

The use of fillers in rubber is almost as old as the rubber industry [1]. Hardness and modulus are normally increased by the use of particulate fillers and the higher effect is obtained by the reinforcing types. Reinforcing filler is the one that improves the modulus and failure properties (tensile strength, tear resistance and abrasion resistance) of the final vulcanizate [5]. Reinforcement of rubber by carbon black has been intensively studied by large number of researchers [6-9].

Carbon black is essentially elemental carbon composed of aggregated particles. The particles are partly graphitic in structure and are of colloidal dimensions. The particle size ranges from 10 nm to 400 nm in diameter. The smaller ones are less graphitic [3]. The degree of reinforcement provided by filler depends on a number of variables; the most important is the development of a polymer-filler interface. In general, the finer the particle size, the greater is the increase of modulus and strength. The quantity required varies from one polymer to another. Though high tensile strength can be obtained from NR gum vulcanizates, for most of the applications, the use of fillers is desirable or necessary. Effect of fillers on the mechanical properties of elastomers is of great interest because fillers can be used very effectively to enhance the ultimate properties. Porter [10] studied the effect of reinforcing carbon black and silica on the sulphuration process during vulcanization. Carbon black appeared to catalyze the formation of the active sulphurating agent. This explains the beneficial effect of carbon black in rubber vulcanization [11].

Carbon black (CB) is one of the most widely used conductive fillers. In a binary immiscible polymer blend, CB was found to have different affinity for each polymer in the blend; thus, it will disperse in one of the two phases or accumulate at the interface [12,13]. The increase in strength of the rubber containing carbon black led to many practical applications of the rubber throughout the world.

With general purpose elastomers like NR and SBR, high abrasion furnace (HAF) blacks with particle size in the range 24-28 μm are mostly used. It is known that carbon black contains active functional groups like -OH, -COOH, C=C, etc. [14]. Carbon black is known to have significant effect on the network structure of filled vulcanizates while semi-reinforcing fillers such as silica do not have similar effect on the rubber-network [15]. A pure gum vulcanizate of SBR has a tensile strength of not more than 2.2 MPa whereas by mixing 50 phr of a reinforcing black, this value can be easily raised to 25MPa. Thus the reinforceing strength of carbon black is obvious [5].

Furnace black is the most preferred reinforcing black for SBR compounding. The relative order of activity of fillers is the same in SBR and NR, but the degree of reinforcement of the fillers is higher in the former [16]. Among the commonly used fillers and reinforcing agents, carbon black gives the most potential reinforcement. It contributes much to increase the desirable properties of the vulcanized rubber and is a universal compounding ingredient for quality stocks [17].

The most common use (70%) of carbon black is as reinforcing filler in automobile tyres. It also helps to conduct heat away from the tread and belt area of the tyre, reducing thermal damage and increasing tyre life. Carbon black particles are also employed in some radar absorbent materials used in the reduction of the radar crosssection of aircraft, photocopier, laser printer toner, other inks and paints. About 20% of the world production of carbon black goes into belts, hoses and other non-tyre rubber goods used often in the aerospace industry and in elastomers for aircraft vibration control components such as engine mount.

### 7.2.2 Experimental

The formulations of the mixes are given in Table 7.4. The amount of primary and secondary accelerator used in the binary system is 1:1 by weight in experimental mixes ($CC_1$, $CC_2$, $CC_3$, $CC_4$, $CC_5$ and $CC_6$). Reference mixes are single accelerator systems MBTS/ CBS. These are $C_1$, $C_3$ and $C_5$ containing two phr MBTS each, while $C_2$, $C_4$ and $C_6$ contain two phr CBS each. The loading of carbon was limited to 40 phr.

All the mixes were prepared on a laboratory size two- roll mixing mill as given in chapter 2. The determination of cure characteristics, equilibrium swelling data, physical and mechanical properties of the vulcanizates were carried out as described in chapter 2. Thermal and SEM analysis of the experimental mixes are also reported.

Table 7.4 Formulations of the mixes

| **Ingredients** | **$C_1$** | **$CC_1$** | **$C_2$** | **$CC_2$** | **$C_3$** | **$CC_3$** | **$C_4$** | **$CC_4$** | **$C_5$** | **$CC_5$** | **$C_6$** | **$CC_6$** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| NR (g) | 100 | 100 | 100 | 100 | - | - | - | - | 50 | 50 | 50 | 50 |
| SBR(g) | - | - | - | - | 100 | 100 | 100 | 100 | 50 | 50 | 50 | 50 |
| ZnO (phr) | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 |
| Stearic acid (phr) | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 |
| Carbon black (phr) | 40 | 40 | 40 | 40 | 40 | 40 | 40 | 40 | 40 | 40 | 40 | 40 |
| Aromatic oil (phr) | 4.0 | 4.0 | 4.0 | 4.0 | 4.0 | 4.0 | 4.0 | 4.0 | 4.0 | 4.0 | 4.0 | 4.0 |
| TQ (phr) | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| MBTS(phr) | 2.0 | 1.0 | - | - | 2.0 | 1.0 | - | - | 2.0 | 1.0 | - | - |
| CBS (phr) | - | - | 2 .0 | 1.0 | - | - | 2.0 | 1.0 | - | - | 2.0 | 1.0 |
| BPTU (phr) | - | 1.0 | - | 1.0 | - | 1.0 | - | 1.0 | - | 1.0 | - | 1.0 |
| Sulphur (phr) | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 |

## 7.2.3 Results and discussion

### 7.2.3.1 Cure characteristics

The incorporation of BPTU as secondary accelerator can very well decrease the cure time of rubbers even in the presence of carbon black. It is evident from the cure data provided in the Tables 7.5 & 7.6 and the cure curves (Figs 7.8 & 7.9). The onset of vulcanization for BPTU incorporated mixes ($CC_1$ - $CC_6$) is not delayed as in the cases of single accelerator systems ($C_1$ -$C_6$). But there is a lowering of scorch time for mixes containing BPTU when compared to single accelerator systems and this can affect the scorch safety. The cure curves of $C_3$ and $C_5$ show increase of modulus (marching curve) with time, but not for $CC_3$and $CC_5$.This shows the effect of BPTU with MBTS in the sulphur vulcanization of SBR and SBR/NR blends. The cure curves obtained for binary systems are more advantageous (an excellent vulcanization plateau, low reversion tendency and good stability) than of single accelerator systems, as the cure can result in a constant equilibrium modulus. Blend systems are found to have the scorch time and optimum cure time in between NR and SBR systems. The cure rates of silica filled systems are better than carbon black filled systems in the case of NR (Table 7.7). The cure rates of carbon black or silica filled SBR systems are almost the same and for the blend systems also there is no appreciable change. The optimum cure time ($t_{90}$) of silica and carbon black filled systems are almost the same. Curing a NR compound at 130 $^{o}$C leads to no reversion, while curing at high temperature leads to reversion [18]. It is interesting to note that this reversion is not observed in this new binary accelerator system. It is worth noting that the optimum cure time of carbon black filled system of NR and SBR are reduced approximately to 50% of the respective gum systems. The reduction in optimum cure time for binary system is well depicted in Fig. 7.10.

**Table 7.5 Cure characteristics of carbon black filled reference mixes (150 °C)**

| Cure Characteristics | $C_1$ | $C_2$ | $C_3$ | $C_4$ | $C_5$ | $C_6$ |
|---|---|---|---|---|---|---|
| Scorch Time($t_{10}$ ) min | 1.80 | 2.73 | 3.80 | 5.70 | 2.70 | 3.70 |
| Optimum cure Time($t_{90}$ ) min | 6.94 | 6.14 | 23.31 | 14.19 | 15.29 | 8.15 |
| CRI( $min^{-1}$) | 19.45 | 29.32 | 5.12 | 11.78 | 7.94 | 22.47 |
| Torque Max. (dNm) | 3.677 | 3.942 | 5.485 | 5.953 | 5.174 | 6.348 |
| Torque Min. (dNm) | 0.137 | 0.124 | 0.373 | 0.446 | 0.278 | 0.297 |

**Table 7.6 Cure characteristics of carbon black filled BPTU incorporated mixes (150 °C)**

| Cure Characteristics | $CC_1$ | $CC_2$ | $CC_3$ | $CC_4$ | $CC_5$ | CC6 |
|---|---|---|---|---|---|---|
| Scorch Time($t_{10}$ ) min | 0.97 | 1.16 | 2.45 | 2.19 | 1.70 | 1.41 |
| Optimum cure Time($t_{90}$ ) min | 2.96 | 3.31 | 10.06 | 9.43 | 6.96 | 5.55 |
| CRI ($min^{-1}$) | 50.25 | 46.51 | 13.14 | 13.81 | 19.01 | 24.15 |
| Torque Max. (dNm) | 5.007 | 5.240 | 6.561 | 5.605 | 5.900 | 5.324 |
| Torque Min. (dNm) | 0.121 | 0.124 | 0.366 | 0.317 | 0.280 | 0.278 |

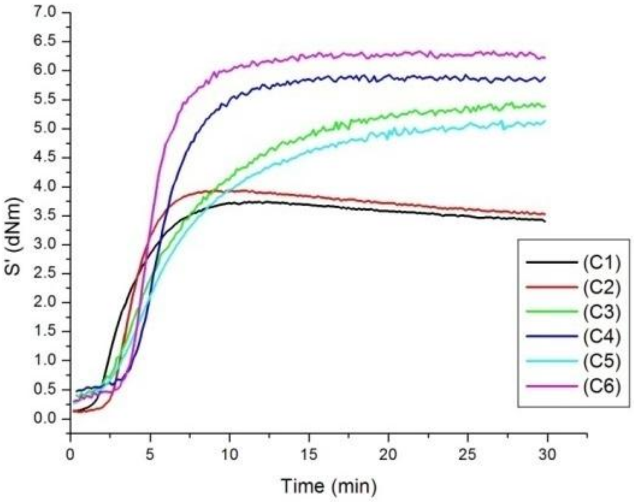

Fig. 7.8 Rheographs of reference mixes

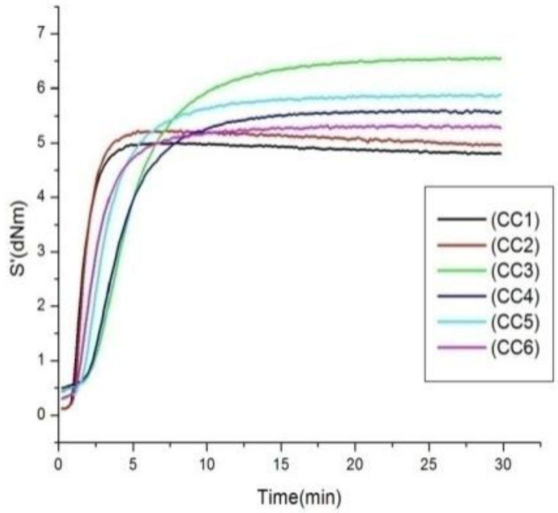

**Fig. 7.9 Rheographs of experimental mixes incorporating BPTU**

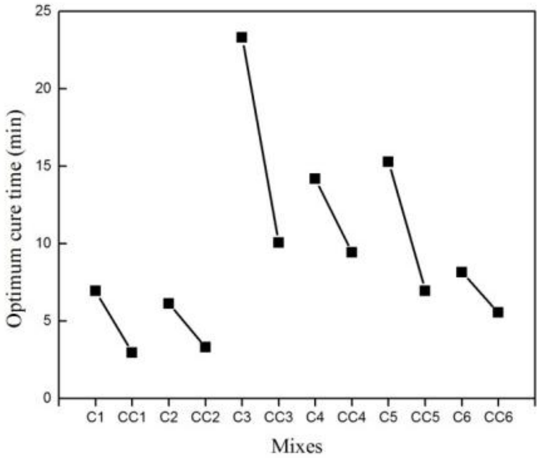

**Fig. 7.10 Optimum cure time for single and binary accelerator systems of CB filled vulcanizates**

**Table 7.7 Comparison of cure characteristics of gum, silica filled and CB filled mixes of NR, SBR and their blends (150 °C)**

| Parameters | Gum formulations |  |  | Silica filled |  |  | Carbon black filled |  |  |
|---|---|---|---|---|---|---|---|---|---|
|  | NR | SBR | Blend | NR | SBR | Blend | NR | SBR | Blend |
| MBTS mixes |  |  |  |  |  |  |  |  |  |
| Optimum cure time (min) | 5.10 | 13.26 | 8.88 | 2.94 | 10.22 | 6.25 | 2.96 | 10.06 | 6.96 |
| Scorch time (min) | 2.55 | 5.01 | 3.01 | 1.42 | 3.38 | 2.14 | 0.97 | 2.45 | 1.70 |
| Cure rate index ($min^{-1}$) | 39.21 | 12.12 | 17.04 | 65.79 | 14.62 | 21.23 | 50.25 | 13.14 | 19.01 |
| CBS mixes |  |  |  |  |  |  |  |  |  |
| Optimum cure time (min) | 4.39 | 16.16 | 6.01 | 2.85 | 9.91 | 5.39 | 3.31 | 9.43 | 5.55 |
| Scorch time (min) | 1.85 | 4.67 | 2.04 | 1.08 | 2.83 | 1.81 | 1.16 | 2.19 | 1.41 |
| Cure rate index ($min^{-1}$) | 39.37 | 8.70 | 25.19 | 56.50 | 14.12 | 27.93 | 46.51 | 13.81 | 24.15 |

### 7.2.3.2 Mechanical Properties

The stress-strain properties of various vulcanizates are presented in Table 7.8. Tensile strength of $CC_1$ and $CC_2$ are considerably higher than $C_1$ and $C_2$ respectively. Tensile strength of $CC_1$ and $CC_2$ are found to be better than silica filled $AA_4$ and $BB_4$ which contain the same amount of binary accelerator (1:1).

**Table 7.8 Stress-strain properties of CB filled vulcanizates**

| Samples | Tensile strength (MPa) |  | Tensile retention (%) | Elongation at break (%) |  | 300% modulus(MPa) |  |
|---|---|---|---|---|---|---|---|
|  | Un-aged | Aged |  | Un-aged | Aged | Un-aged | Aged |
| **$C_1$** | 20.74 | 18.06 | 87 | 689 | 764 | 6.01 | 6.60 |
| **$CC_1$** | 28.80 | 31.17 | 110 | 905 | 737 | 6.78 | 8.24 |
| **$C_2$** | 25.26 | 23.05 | 91 | 780 | 743 | 5.85 | 7.18 |
| **$CC_2$** | 29.47 | 31.69 | 108 | 902 | 758 | 6.24 | 7.98 |
| **$C_3$** | 22.21 | 19.95 | 90 | 832 | 851 | 5.84 | 6.03 |
| **$CC_3$** | 29.11 | 28.23 | 97 | 907 | 701 | 6.06 | 4.86 |
| **$C_4$** | 20.41 | 18.52 | 91 | 881 | 734 | 5.70 | 6.72 |
| **$CC_4$** | 27.57 | 27.74 | 101 | 731 | 812 | 8.20 | 6.97 |
| **$C_5$** | 25.42 | 22.72 | 89 | 963 | 810 | 4.96 | 6.05 |
| **$CC_5$** | 27.66 | 27.55 | 100 | 772 | 734 | 7.73 | 8.40 |
| **$C_6$** | 24.76 | 20.20 | 82 | 776 | 568 | 6.55 | 8.56 |
| **$CC_6$** | 26.44 | 24.75 | 94 | 832 | 668 | 6.54 | 8.18 |

The 300% modulus of $CC_1$ and $CC_2$ are much greater than silica filled systems. This can be attributed to the catalytic activity given by carbon black in the formation of the active sulphurating agent, which can improve the mechanical properties of vulcanizate [11]. The tensile strength of $CC_3$ is 31% more than that of $C_3$ and in the case of $CC_4$ it is 35% more than $C_4$. The above observation indicates that CB filled binary systems have better tensile properties in the case of NR and SBR as given in Fig.7.11.

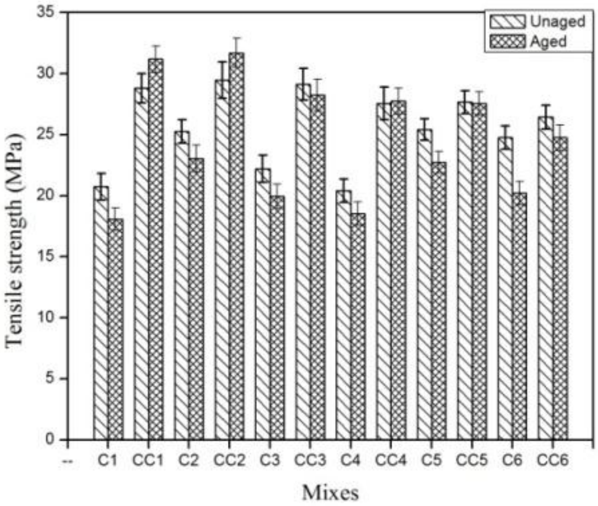

**Fig. 7.11 Tensile strength of $C_1$-$C_6$ and $CC_1$-$CC_6$vulcanizates**

The tensile strength of carbon black filled systems of SBR is much higher than corresponding silica filled systems and in fact it is four fold. This illustrates that, the reinforcing property of carbon black in SBR system is better than that of silica. This is in agreement with the findings of Porter [19] and Bhowmick et al. [20]. Ageing property of binary systems are better than single accelerator systems and is more pronounced in the case of natural rubber ($CC_1$ and $CC_2$) as given in Fig.7.11. In general the 300% modulus of the binary systems is higher than single accelerator systems. The elongation at break (%) is higher for $CC_1$, $CC_2$, $CC_3$ and $CC_6$ than the corresponding single accelerator systems.

Thermal ageing resistance is reported in terms of tensile retention. NR vulcanizates show more than 100% tensile retention indicating higher tensile strength of aged specimen than un-aged ones. But in the case of SBR and NR/SBR blends it is lower than 100% and deterioration in tensile strength of vulcanizates after ageing is normally found in polysulphidic linkages.

The various physical properties of the carbon black filled vulcanizates are given in Table 7.9. Tear strength, hardness, compression set %, abrasion loss and heat build-up for the above vulcanizates were evaluated.

Tear strength values increased with the incorporation of secondary accelerator and are much better than silica filled system. Just like tensile strength, tear resistance of binary systems are greater than single accelerator systems as given in Fig.7.12. The highest tear resistance is observed with $CC_2$ and the next highest is for $CC_6$. Considering the hardness values of the various vulcanizates one can find that there is improvement in the property on changing from single accelerator system to binary system.

### Table 7.9 Properties of CB filled vulcanizates

| Property | $C_1$ | $CC_1$ | $C_2$ | $CC_2$ | $C_3$ | $CC_3$ | $C_4$ | $CC_4$ | $C_5$ | $CC_5$ | $C_6$ | $CC_6$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Tear strength (N/mm) | 57.46 | 84.10 | 67.25 | 92.56 | 58.33 | 71.64 | 58.43 | 74.02 | 71.80 | 87.77 | 85.71 | 91.79 |
| Resilience (%) | 49 | 50 | 55 | 56 | 40 | 42 | 42 | 41 | 44 | 48 | 44 | 46 |
| Hardness (Shore A) | 50 | 53 | 52 | 58 | 60 | 66 | 63 | 62 | 56 | 63 | 56 | 59 |
| Heat build-up ($^0$C) | 36 | 20 | 30 | 22 | 35 | 31 | 38 | 36 | 37 | 32 | 40 | 36 |
| Crosslink density x $10^5$(gmol/mL) | 3.40 | 5.57 | 5.04 | 6.02 | 7.81 | 8 .43 | 6.05 | 6.64 | 6.63 | 8.48 | 6.29 | 7.52 |

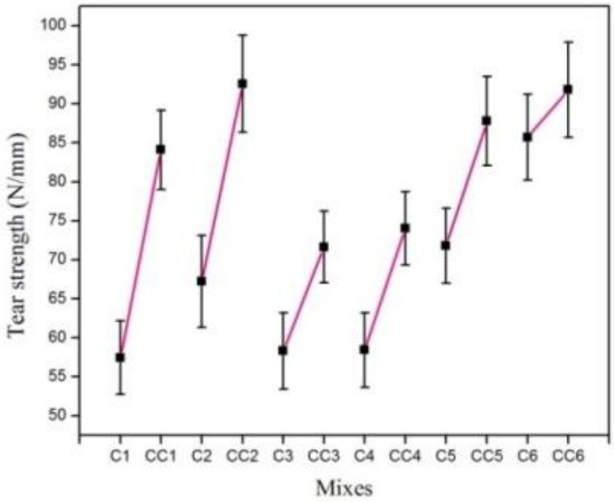

**Fig. 7.12 Tear strength of $C_1$-$C_6$ and $CC_1$-$CC_6$vulcanizates**

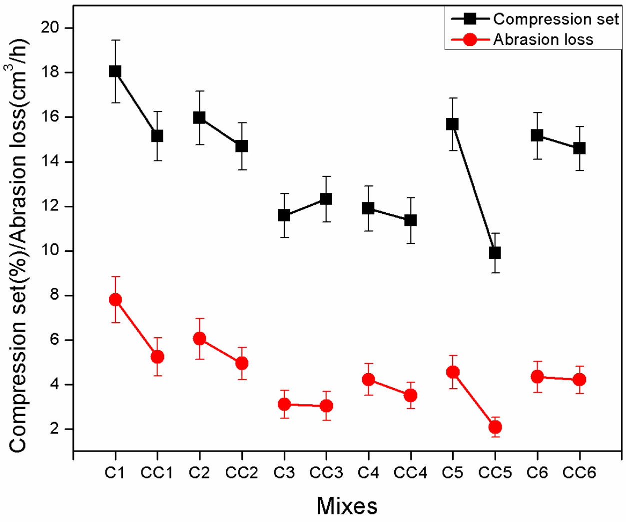

**Fig. 7.13 Compression set and Abrasion loss of $C_1$-$C_6$ and $CC_1$-$CC_6$ vulcanizates**

The compression set % values of all the binary systems except $CC_3$, are less than single accelerator systems. But $C_3$ and $CC_3$ have almost the same value for compression set. Lower values for compression set are considered better. The vulcanizate $CC_5$ has the lowest value for compression set and highest abrasion resistance (Fig. 7.13). Binary systems show more abrasion resistance. The heat build-up value of all binary systems have less value than single accelerator system but it is more pronounced in NR than in SBR and NR/SBR blends. Lower value of heat build-up is beneficial as it can resist abrasion.

Resilience values are nearly the same for binary and single accelerator systems with an upper edge for binary system and the difference is considerable for blends. The total crosslink density of all the binary systems is higher than corresponding single accelerator systems. It is worth noting that $CC_5$ has the highest crosslink density, and as a consequence it shows highest hardness.

**Table 7.10 Comparison of mechanical properties of vulcanizates of NR, SBR and their blends containing BPTU**

| Parameters | Gum formulations | | | Silica filled | | | Carbon black filled | | |
|---|---|---|---|---|---|---|---|---|---|
| | **NR** | **SBR** | **Blend** | **NR** | **SBR** | **Blend** | **NR** | **SBR** | **Blend** |
| **MBTS mixes** | | | | | | | | | |
| Tensile strength (MPa) | 20.98 | 1.63 | 10.04 | 26.12 | 7.07 | 17.09 | 28.80 | 29.11 | 27.66 |
| 300 % modulus (MPa) | 1.46 | 1.01* | 1.70 | 2.56 | 2.04 | 2.56 | 6.78 | 6.06 | 7.73 |
| Tear strength (N/mm) | 39.83 | 11.09 | 23.67 | 49.26 | 27.32 | 28.70 | 84.01 | 71.64 | 87.77 |
| Hardness (Shore A) | 38 | 41 | 39 | 44 | 54 | 49 | 53 | 66 | 63 |
| Compression set (%) | 32.12 | 19.23 | 12.87 | 35.81 | 21.90 | 30.28 | 15.14 | 12.31 | 9.89 |
| **CBS mixes** | | | | | | | | | |
| Tensile strength (MPa) | 15.26 | 1.56 | 19.90 | 26.40 | 6.38 | 16.30 | 29.47 | 27.57 | 26.44 |
| 300 % modulus (MPa) | 1.43 | 0.87* | 1.70 | 2.13 | 1.73 | 2.37 | 6.24 | 8.20 | 6.54 |
| Tear strength (N/mm) | 28.72 | 11.92 | 24.32 | 48.08 | 21.98 | 27.14 | 92.56 | 74.02 | 91.79 |
| Hardness (Shore A) | 34 | 44 | 42 | 44 | 55 | 52 | 58 | 62 | 59 |
| Compression set (%) | 22.22 | 20 | 16.54 | 23.77 | 11.88 | 28.03 | 14.68 | 11.35 | 14.59 |

*100% modulus

The crosslink density of $CC_3$ is almost same as $CC_5$ and its abrasion resistance is next to $CC_5$. Comparative study of mechanical properties of NR, SBR and their blends in gum and filled systems are given in Table 7.10. It reveals that mechanical properties of carbon black filled systems of SBR and NR/SBR blend systems are superior than their silica filled systems.

### 7.2.3.3 Thermal analysis

Thermogravimetric studies give three set of values, each one for different kind of elastomers and are given in Figs. 7.14-7.16. The thermogravimetric properties such as, temperature at onset of degradation, 60%weight remains, maximum degradation are almost the same for each set of elastomers viz. NR, SBR and NR/SBR blends. The remaining amount of vulcanizate left out at 300 $^{o}$C and % residue left out, are almost the same for all mixes.

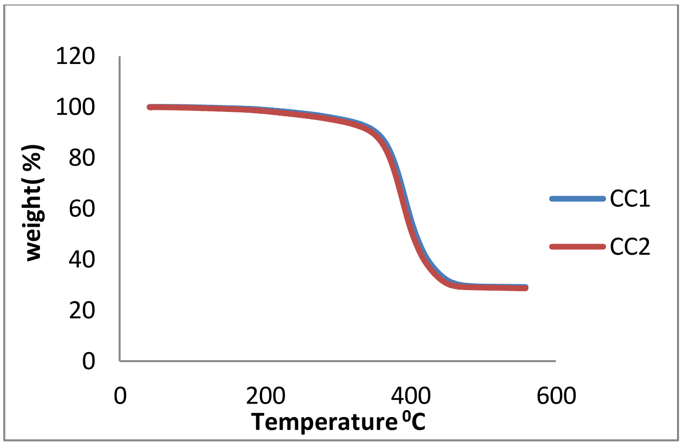

Fig. 7.14 Thermogram of CB filled vulcanizates of NR

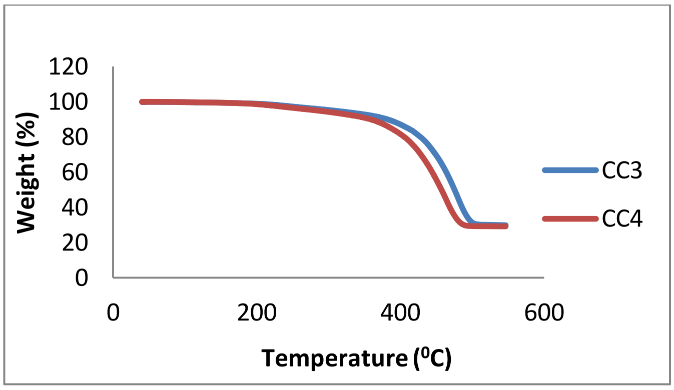

Fig. 7.15 Thermogram of CB filled vulcanizates of SBR

It is observed that the onset of degradation temperature for each vulcanizate is different and $CC_4$ has the highest temperature at which degradation starts. The end-set of degradation temperature is lower in the case of NR samples probably due to a decrease in crosslink density [21]. This is in line with the reported observation that increase in crosslink density increased the rigidity of the system, and there by increased the thermal stability. The rate of degradation was almost the same up to 90% degradation for all the samples. Thermal analysis data are given in Table 7.11.

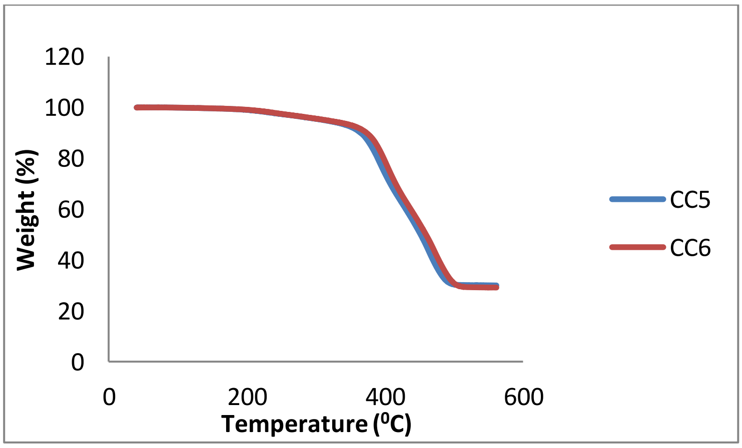

Fig. 7.16 Thermogram of CB filled vulcanizates of NR/SBR blends

**Table 7.11 Results of thermogravimetric analyses for CB filled vulcanizates**

| **Characteristics** | **$CC_1$** | **$CC_2$** | **$CC_3$** | **$CC_4$** | **$CC_5$** | **$CC_6$** |
|---|---|---|---|---|---|---|
| Onset of degradations(°C) | 340±1 | 345±2 | 355±1 | 360±2 | 340±3 | 330±3 |
| End set of degradation(°C) | 470±1 | 465±2 | 505±3 | 510±1 | 500±1 | 500±1 |
| Temperature at 60% retained (°C) | 395±1 | 395±1 | 465±2 | 460±2 | 430±1 | 425±2 |
| Temperature at maximum degradation (°C) | 390±2 | 390±2 | 480±1 | 480±1 | 465±2 | 460±1 |
| Residue ( %) | 29.07 | 28.65 | 29.83 | 29.24 | 30.07 | 29.19 |
| Remaining at 300 °C (%) | 95.34 | 94.71 | 95.27 | 94.97 | 95.45 | 95.09 |

### 7.2.3.4 SEM analysis

The SEM micrographs of the tensile fractured surfaces of carbon black (40 phr) filled vulcanizates at 750x and 3000x magnification are shown in Figs. 7.17-7.19. The tensile fractured surface was studied to investigate the filler dispersion and the interfacial adhesion between the filler and rubber. The smooth fracture surfaces, smooth filler dispersion and unidirectional tear path oriented along with the direction of flow were observed for all the samples. All figures of 750x magnifications showed rougher surface, indicating that the incorporation of filler in the matrix had enhanced the reinforcement in the rubber vulcanizates and had allowed for better stress transfer, leading to increased tensile properties [22]. Fatigue type of failure is observed in all figures of SEM and is associated with good tensile strength. At a higher magnification agglomeration seen is due to very little bad dispersion of filler in the rubber matrix. Further, more pull-outs and holes observed reveals that they have good interaction with rubber matrix.

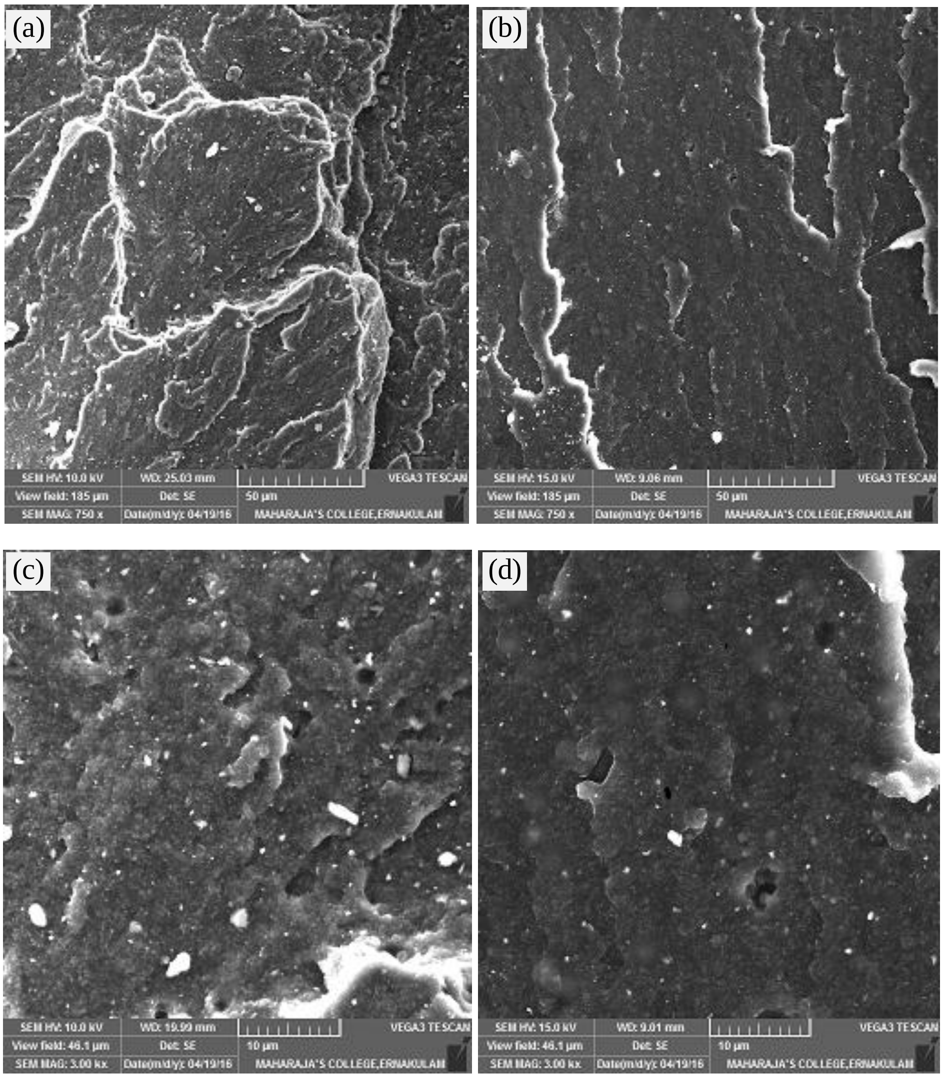

**Fig.7.17 SEM micrographs of the tensile fractured surface of carbon black filled NR (a) $CC_1$ and (b) $CC_2$ at750x magnification; (c) $CC_1$and (d) $CC_2$ at 3000x magnification**

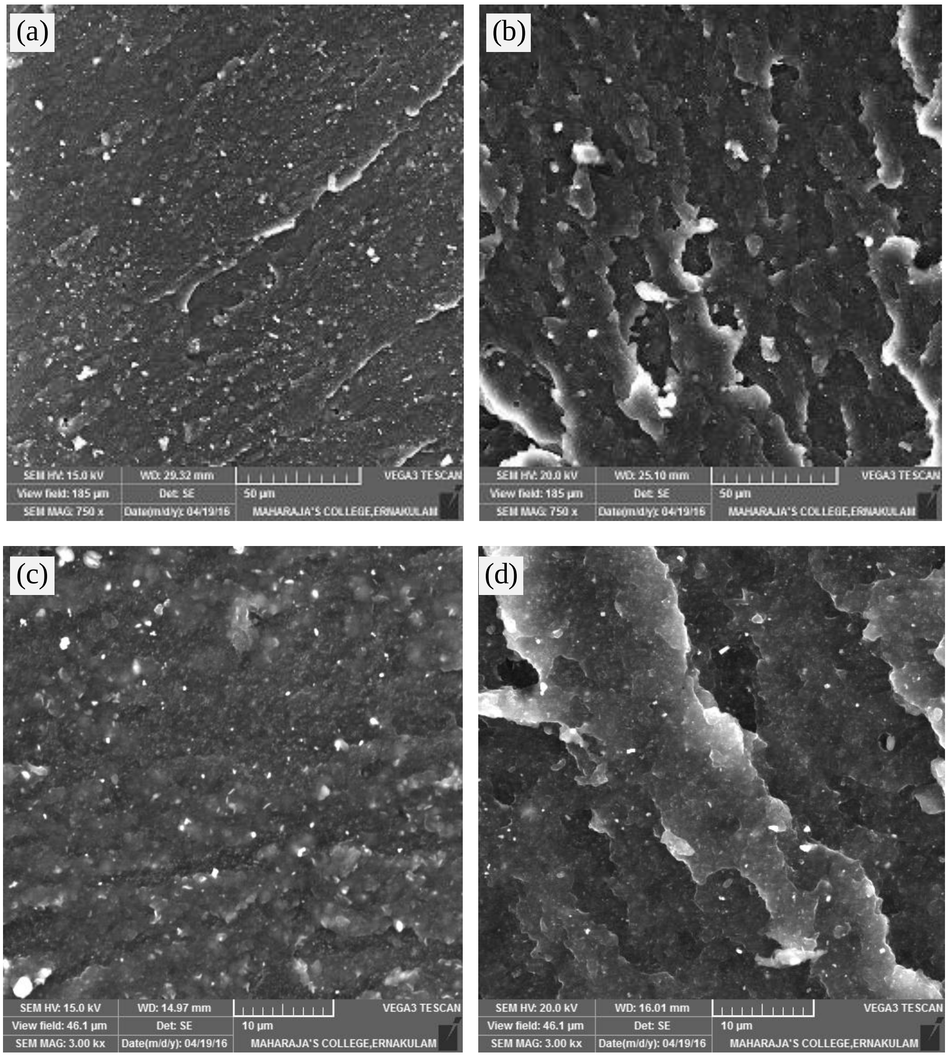

**Fig. 7.18 SEM micrographs of the tensile fractured surface of carbon black filled SBR (a) CC$_3$and (b) CC$_4$ at750x magnification; (c) CC$_3$ and (d) CC$_4$ at 3000x magnification**

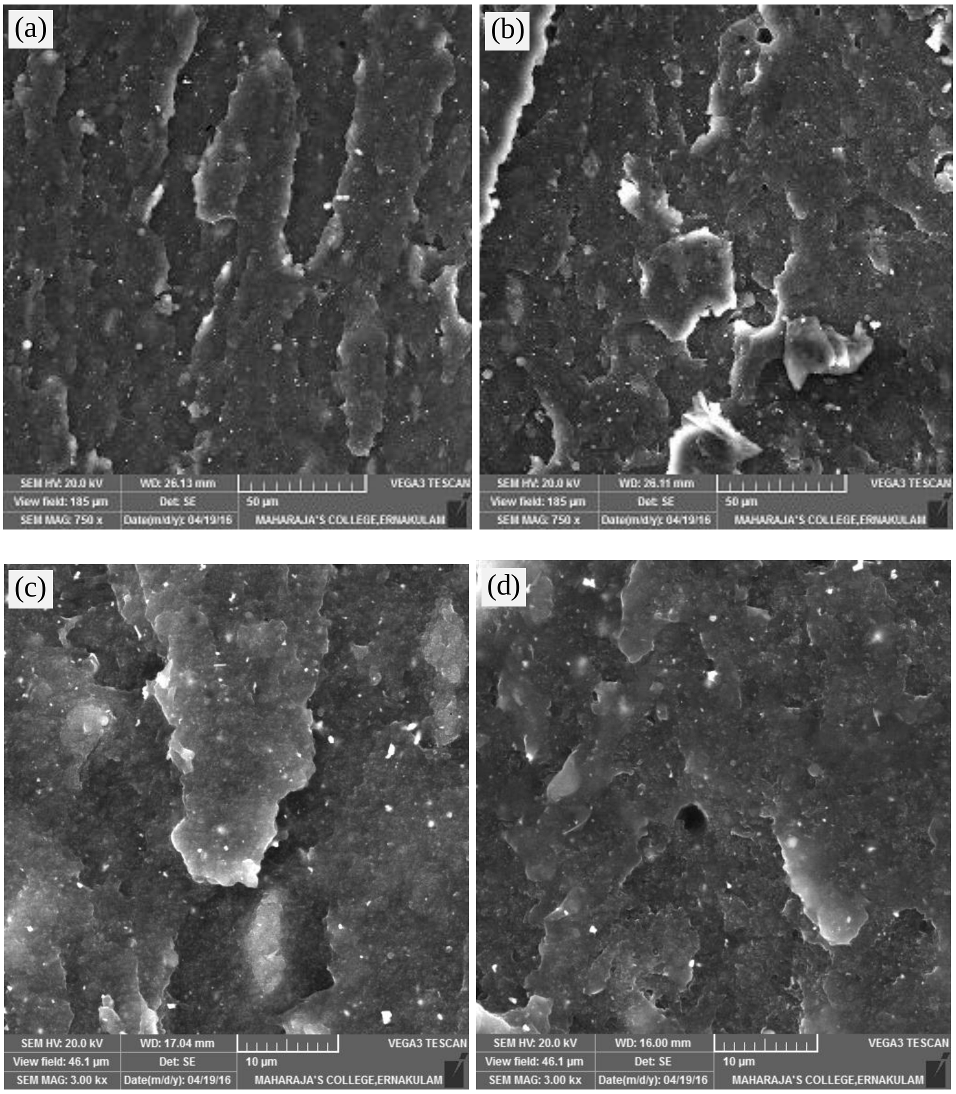

**Fig.7.19 SEM micrographs of the tensile fractured surface of carbon black filled NR/SBR blends (a) $CC_5$ and (b) $CC_6$ at750x magnification; (c) $CC_5$ and (d) $CC_6$ at 3000x magnification**

### 7.2.4 Conclusion

The result obtained reveals that BPTU effectively acts as a secondary accelerator along with MBTS and CBS in the sulphur vulcanization of elastomers. Incorporation of BPTU results in the reduction of optimum cure time in the case of carbon black filled elastomers by40%. The cure rates of all the carbon black filled systems are lower than silica filled systems. Carbon black filled elastomers show tensile strength much better than silica filled elastomers. The tear resistance exhibited is three fold of silica filled systems. These binary systems not only show satisfactory tensile strength but also good retention after thermal ageing. SEM and thermogravimetric studies support the strength of vulcanizates. The newly introduced binary system of BPTU is more effective in producing carbon black filled vulcanizates of NR, SBR and NR/SBR blends with better resilience, lower heat build-up, lower compression set better abrasion resistance and hardness than the vulcanizates prepared using single accelerator system. Thus these accelerators may be recommended for tyre repairing and retreading.

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# Chapter 8

# CONCLUSIONS

The ever increasing demand for natural rubber or synthetic rubbers by automobile industry and other elastomer-based consumer products used by modern man leads to research in this branch of science. As elastomers could not be used as such, they need modifications called curing or vulcanization. Hence researchers have interest in the field of compounding and curing. The author’s earlier interest in this area coupled with expertise in synthesizing thiazoles, thiourea and their derivatives led to the scientific study of their effect as accelerators. It forms the main focus of this work. Accelerators play a vital role in the vulcanization process of elastomers. It controls the time of vulcanization and properties of the products. When single accelerator system alone is not sufficient, mixture of accelerators are generally used to enhance the rate of vulcanization at lower temperature and to improve the mechanical properties of the vulcanizates. Nowadays binary accelerator systems are of great demand in rubber industry since it can give synergistic activity coupled with energy efficiency.

The thesis is divided into eight chapters. C**hapter 1** includes a general introduction to various elastomers, compounding ingredients, rubber vulcanization reactions and different accelerator systems. Literature survey on the mechanism of vulcanization reactions and the importance of binary accelerator systems are included. The scope and objectives of the present work are also presented.

**Chapter 2** gives the specifications of different elastomers and compounding ingredients used. It also includes a detailed description of the experimental procedures adopted. The methods used for compounding, vulcanization, determination of physical properties of vulcanizates, estimation of total crosslink density and determination of cure time for NR latex are also explained.

**Chapter 3** narrates the synthesis of two novel thiourea derivatives and also preparation of three phenylthiazole derivatives. These compounds were characterized by physical and spectroscopic methods. Further studies were carried out to find out the accelerator nature of these compounds alone and along with known primary accelerators in a mixed system. The best compound out of the five, namely N-benzoyl-N$^{I}$,N$^{I}$–pyrrolidinylthiourea (BPTU) was selected as the eligible candidate for further studies and its effect as a secondary accelerator was studied along with MBTS and CBS in the vulcanization of NR.

**Chapter 4** consists of two parts. The first part deals with the study of NR gum formulations using BPTU as accelerator in a binary system containing MBTS or CBS. The cure behaviour obtained for NR gum formulations gave supporting evidence to the nucleophilic reaction mechanism suggested by Philpott. The optimum concentrations required was found to be 1:1 for MBTS: BPTU and 2:1 for CBS: BPTU in the NR vulcanization. The only disadvantage is lowering of scorch time for higher dosage of BPTU. The tensile properties before and after thermal ageing were found to give satisfactory results compared to the reference formulations.

The second part of this chapter demonstrates the efficiency of BPTU as a secondary accelerator in the silica filled systems containing MBTS/ CBS. The kinetics of cure reaction proves that it is of the first order. The mechanical properties like tensile properties, hardness, compression set, abrasion resistance and tear strength values are commendable. Based on the cure characteristics and tensile strength, optimum dosage of the above binary systems was found to be 1:1of MBTS/CBS and BPTU. The optimum cure time obtained for silica filled systems was much lower than gum systems. This system also provides satisfactory properties even after thermal ageing. SEM results confirm the uniform mixing and tensile strength of vulcanizates.

**Chapter 5** describes the effect of BPTU as a secondary accelerator in the sulphur vulcanization of a synthetic rubber, namely styrene butadiene rubber (SBR 1502). The first part of this chapter gives SBR gum formulations using MBTS/CBS as primary accelerator with BPTU. The optimum cure time reduced considerably in both MBTS and CBS systems with concentration of BPTU. With the incorporation of BPTU the cure characteristics of SBR gum vulcanization were improved even with lesser amount of the accelerator compared to single accelerator systems.

The second part is about vulcanization of silica filled SBR. Higher concentration of BPTU improves the tensile strength and tensile retention properties more than the reference mix. It was found that tensile strength was five times that of gum vulcanizate and tear values improved twice in this system.

**Chapter 6** is about the effect of BPTU along with MBTS/CBS on the NR-SBR (50:50) blend vulcanization. The first part of the chapter deals with the gum vulcanization of blends and the properties of the vulcanizates. Cure and mechanical properties of the blends are in between that of NR and SBR alone but compression set values are remarkably good.

Second part deals with the silica filled blend systems. Cure characteristics of the silica filled blend systems are better than those of their gum systems. Rheometric and mechanical properties of this system are also found to be better than those of SBR system. One phr MBTS with 0.75 phr BPTU and one phr CBS with one phr BPTU systems are found to be the optimum concentration for NR/SBR (50/50) blends. Vulcanization of this blend system also follows the first order kinetics.

The first part of **chapter 7** is about curing of NR latex system using BPTU along with ZDC, at low temperatures viz. 120 and 100 $^{o}$C. Though the decrease in cure time with quantity of BPTU is not appreciable, the tensile strength was considerably enhanced. Tensile strength of experimental mix is 21% more than that of reference mixes vulcanized at100 $^{o}$C and 17 % more for mixes cured at 120 $^{o}$C. The optimum cure time for experimental mix is 23% less than the reference mix cured at 100 $^{o}$C but only 9% less at 120 $^{o}$C curing. That the variation in cure time is not according to the amount of BPTU points to the fact that the reaction mechanism is not purely nucleophilic.

Second part briefly deals with the effect of BPTU along with MBTS/CBS (1:1) on the carbon black filled (CB) elastomers. The optimum cure time of NR mix is reduced much at the expense of scorch safety compared to their reference mixes. In SBR system though there is reduction of $t_{90}$, scorch time is not reduced much and is better for MBTS system. The same trend is followed in NR/SBR blends also. The cure rate index of all the mixes under consideration was appreciable with very low reversion tendency. The cure rate of all these CB filled systems is lower than silica filled systems. Carbon black filled elastomers show tensile strength much better than silica filled elastomers with good retention after thermal ageing. The tear resistance exhibited is three fold of silica filled systems.

To sum up, the newly introduced **N-benzoyl-N$^{I}$,N$^{I}$-pyrrolidinylthiourea (**BPTU) is reported as an accelerator. It is also very effective as a secondary accelerator for the vulcanization of NR, SBR, their blends in gum and filled systems without reversion tendency. It is also reported that there is no adverse effect in curing and mechanical properties for the system. It was found that the carbon black filled vulcanizates of BPTU are capable of giving satisfactory result to the tyre industry. The newly introduced binary system of BPTU is proved to be more efficient in producing carbon black filled vulcanizates of NR, SBR and NR/SBR blends with better resilience, lower heat build-up, lower compression set, lower abrasion resistance and improved hardness compared to the vulcanizates prepared using single accelerator system. So these accelerators may be considered for tyre repairing and retreading rubber formulations. Thus the whole work throws light on the upbringing of a new compound **N-benzoyl-N$^{I}$,N$^{I}$-pyrrolidinylthiourea (**BPTU) which can bring out an innovative change in producing an efficient and cost effective growth to the rubber industry.

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# List of Publications

## List of conferences presentations:

[1] International conference on recent advances in chemical science (Dec., 28-30, 2015) Organized by Indian Chemical Society, Hosted by JECRC University, Jaipur, Rajasthan. Title: “ Benzoylpyrrolidinylthiourea: A new binary accelerator for the vulcanization of natural rubber”.

[2] International conference IC- AMMN- 2K16. Organized by FISAT (Jan. 7-9, 2016) Angamaly, Kerala. Title**: “**Effect of N-(pyrrolidine-1-carbithioyl) benzamide as a new secondary accelerator in the Sulphur vulcanization of Natural Rubber”.

[3] International conference on Advances in Polymer Technology -APT’ 16 (Feb.25&26, 2016). Organized by CUSAT & IRI, Kochi, Kerala. Title: “The influence of N-benzoyl-N$^{I}$,N$^{I}$-pyrrolidinylthiourea-a novel secondary accelerator- in the sulphur vulcanization of NR/SBR blends”.

[4] International conference on Science & Technology: Future Challenges and Solutions (STFCS -2016). Organized by JSPS & University of Mysore, Mysuru. Title: “N- (Pyrrolidine-1-carbithioyl)- benzamide- a novel secondary accelerator- in the sulphur vulcanization of NR/SBR blends”

[5] International conference on Crystal Ball Vision on Science and Engineering for Societal upliftment (IJAA Goa 2017) August 7-8, 2017, Title; “Effcet of a novel secondary accelerator N-benzoyl-N$^{I}$,N$^{I}$-pyrrolidinylthiourea with MBTS/CBS in the sulphur vulcanization of silica filled SBR”.

## List of International/ National Journal Publications:

[1] "The Effect of N-benzoyl- N$^{\prime}$,N$^{\prime}$-pyrrolidinylthiourea-a novel secondary accelerator- in the sulphur vulcanization of NR/SBR blends". IJSRD Vol. 3, Issue 11, (825-829), 2016.

[2] "N-benzoyl-N$^{\prime}$,N$^{\prime}$-pyrrolidinylthiourea/cyclohexylbenzthiazyl sulfenamide a superior Binary Accelerator for the sulphur vulcanization of Elastomers" IJESC Vol. 6 issue 8, (2230-2235), Aug 2016.

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# Curriculum Vitae

**Molice Thomas**
Associate Professor (Rtd)
Christian College,
Chengannur Pin: 689122.
Kerala. INDIA

Mob: +91(0) 9446503954
Email: molicethomas@gmail.com

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## Academic Profile

| **Course** | **University** | **College /University** | **Grade/Class** | **Year of Passing** |
|---|---|---|---|---|
| M.Phil (Environmental Science) | Kerala University | Department of Environmental Science, Kerala University, Kerala. | Grade A | 2002 |
| MSc (Physical Chemistry) | Kanpur University | Christ church College, Kanpur University, Kanpur, UP. | 1st Class | 1979 |

## Professional Experience

- Joined Dept. of Chemistry as a lecturer in Christian College, Chengannur, in 1982.
- Worked as Associate Professor from 1998 till retirement
- Worked as Head of Department of Chemistry from 2011 to 2013.

## Research Experience

- Doing Ph D (part time) from October 2010 in the Department of Polymer Science and Rubber Technology, CUSAT under the supervision of Prof. (Dr) Thomas Kurian.

## Personal Details

Age and Date of Birth : 60 years, 11th May 1957
Sex : Female
Nationality : Indian
Marital status : Married
Permanent Address Kaipuraidom House,
Angadical P O
Chengannur. 689122
Kerala

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# ANNEXURE BASED ON THE SUGGESTIONS OF THE EXAMINERS

1. **Explain each signal corresponding to the representative chemical structure in the $^{1}$H and $^{13}$C NMR spectra (Figures 3.2, 3.3, 3.5 and 3.6).**
   Signals corresponding to representative chemical structures for the Figures 3.2 & 3.3 are given in page no: 78 and for 3.5 & 3.6 in page no: 81.

2. **Is there any structure-property relation for lowering of scorch time for higher dose of BPTU?**
   The functionality "(N=C-S)" found in most of the accelerators used in rubber vulcanization is present in BPTU. The N atom of pyrrole ring gives basic nature and thus higher dose of BPTU lowers scorch time with decrease of cure time.

3. **The role of silica in comparison with the earlier silica based reports cure time and evaluate the role of your accelerator.**
   It has been reported that silica adsorbs the accelerators on its surface resulting in increase of cure time [1]. Thus it is necessary to use higher quantity of accelerator. Moreover the acidic nature of silica causes increase of cure time [2]. BPTU being basic increases the cure rate.

4. **Cure and mechanical properties of the blends were in between that of neat NR and SBR, however, compression values were remarkably good, why?**
   Compressions set values of vulcanizates are related to both the elastic recovery of the materials and the type of crosslinks. [3]. Type of crosslinks may be the reason for better compression set values.

5. **How BPTU works as an accelerator along with MBTS and CBS?**
   Moore et al., suggested probable mechanism for the synergistic activity of Thiourea in binary accelerator system. This theory gives the formation of polysulfidic intermediates by the accelerators during the vulcanization process. Then they react with the rubber chain to yield further intermediates. These rubber intermediates finally react to yield sulfurated crosslinks [4]. Mechanism suggested for the formation of polysulphidic intermediates and formation of crosslinks between rubber chains are given in schemes 1, 2 & 3

CBS in presence of sulphur on heating gives MBT and cyclohexylamine. MBT in presence of CBS gives MBTS and cyclohexylamine.

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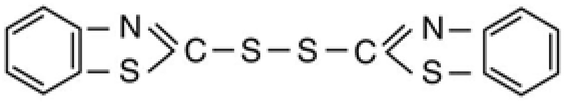
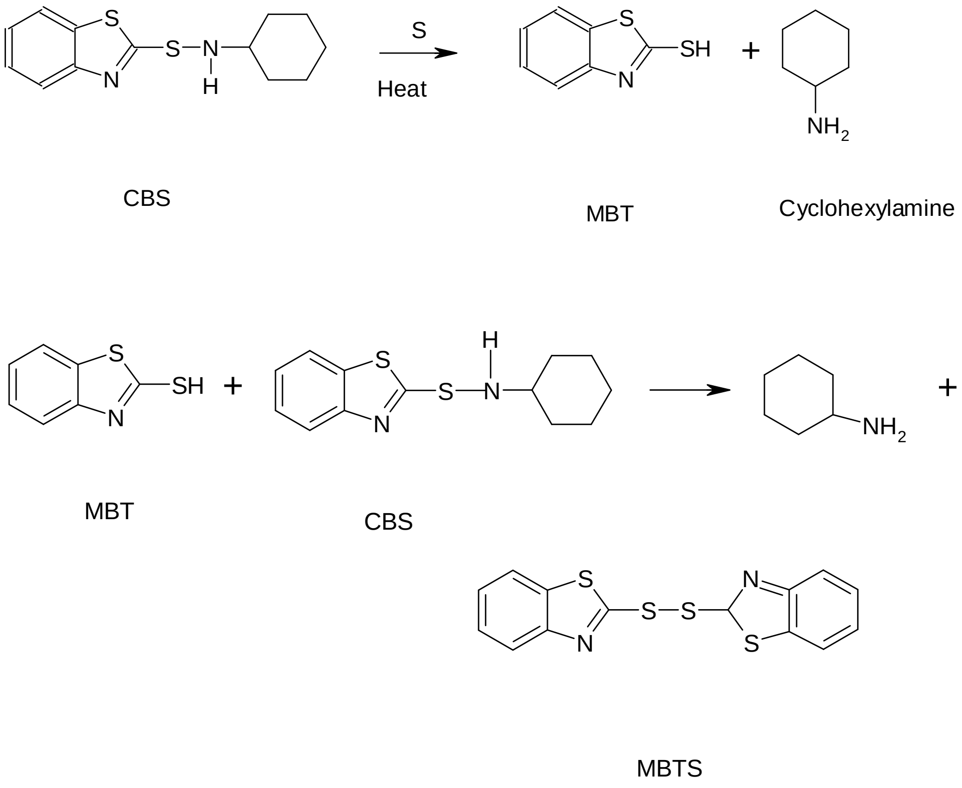
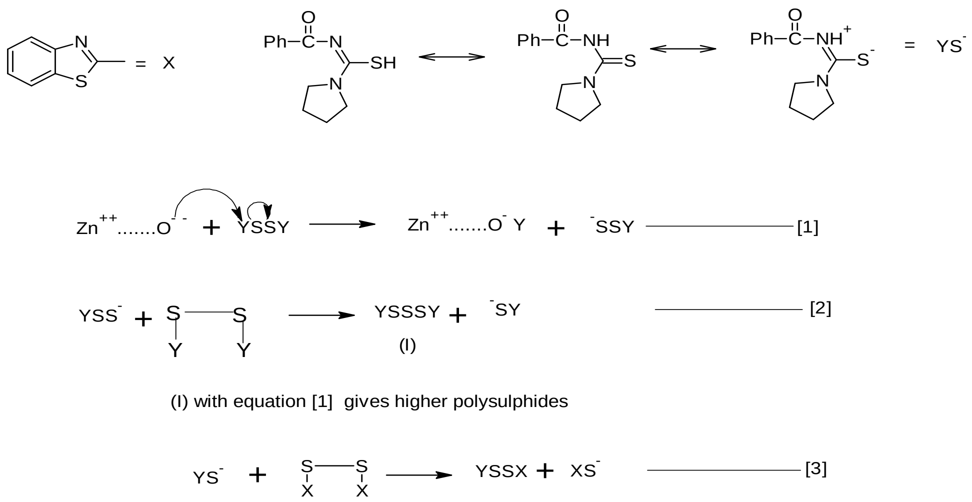


MBTS



**Scheme 1**


(I) with equation [1] gives higher polysulphides

Scheme 2

$$(m\text{-}1)\ \mathrm{YSSX} \xrightarrow{\mathrm{ZnO}} \mathrm{YS_mX} + \frac{(m-2)}{2}\{(\mathrm{XO})_2\mathrm{Zn} + (\mathrm{XS})_2\mathrm{Zn}\}$$

$$\mathrm{RH} + \mathrm{YS_mX} \xrightarrow{\mathrm{ZnO}} \mathrm{RS_{m-1}X} + \frac{1}{2}\{(\mathrm{YS})_2\mathrm{Zn} + \mathrm{H_2O}\}$$

$$\mathrm{RH} + \mathrm{RS_{m-1}X} \xrightarrow{\mathrm{ZnO}} \mathrm{RS_{m-2}R} + \frac{1}{2}\{(\mathrm{XS})_2\mathrm{Zn} + \mathrm{H_2O}\}$$

Scheme 3

6. **It is observed that in NR – SBR blend, CBS-BPTU is showing better properties than MBTS-BPTU. What may be the reason for that? It is also observed that the enhancement of properties of CBS-BPTU compared to MBTS-BPTU is not that evident in the silica filled system.**

The type and amount of accelerators have influence on the properties of NR-SBR vulcanizates. The reason for the difference in properties may be due to type of accelerators [5]. The marginal difference in properties between CBS-BPTU and MBTS-BPTU vulcanizates may be attributed to the difference in the mechanism of action of the accelerator systems.

The type of accelerators used influence the cure rate and properties of the silica filled vulcanizates. Thiazole accelerators show faster cure rate compared to the sulphenamides in the silica filled NR compounds [6] and hence their properties.

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