STABLE FREE RADICAL ASSISTED MECHANICAL DEVULCANISATION OF CARBON BLACK FILLED RUBBERS

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In partial fulfillment of the requirements for the award of the degree of

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By

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PhD. Thesis

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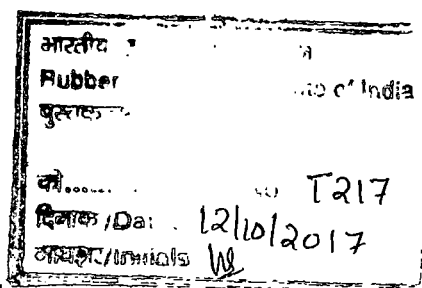Anu Mary Joseph

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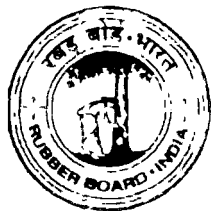Sr. Scientist   Jt. Director (Rtd.)

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Certificate

This is to certify that the thesis entitled "STABLE FREE RADICAl ASSISTED MECHANICAL DEVULCANISATION OF CARBON BLACK FILLED RUBBERS" which is being submitted by Ms. Anu Mary Joseph in partial fulfilment of the requirements of the degree of Doctor o Philosophy, to Cochin University of Science and Technology (CUSAT) Kochi, Kerala, India is a record of bonafide research work carried out by he under our guidance and supervision. She has worked on the topic for fiv years (2011-2016) at Rubber Technology Division of Rubber Researcl Institute of India, Kottayam. In our opinion, the thesis has fulfilled all th requirements according to the regulations. The relevant recommendation and suggestions made by the experts during pre-synopsis presentation ar incorporated while compiling the thesis. The results embodied in this thesi have not been submitted for any other degree or diploma.

Dr. Benny George   Dr. Rosamma Alex

Declaration

I hereby declare that the thesis entitled "STABLE FREE RADICAl ASSISTED MECHANICAL DEVULCANISATION OF CARBOⱤ BLACK FILLED RUBBERS" is the original research work carried out b: me under the supervision of Dr. Rosamma Alex, Joint director (Rtd.) Rubber Technology Division, Rubber Research Institute of India (RRIⱤ Rubber Board, Kottayam and Dr. Benny George, Senior Scientist, Rubbe Technology Division, Rubber Research Institute of India (RRII), Rubbe Board, Kottayam. No part of this thesis has been presented for any othe degree from any other institution.

RRII   Anu Mary Joseph

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Preface

Utilization and disposal of used tires represent an enormous challenge due to its three dimensional -cross linked- structure. The major global recycling practices involve energy recovery ($\approx$38%), which uses end-of- life tyres and other rubber products as fuel, and material recovery ($\approx$40%) which mainly involves grinding of the used rubber products to crumb rubber powder. The majority of crumb rubber powder generated is consumed by civil engineering applications, road surfacing *etc.* and only a marginal fraction of it is used by the rubber industry. The concept of devulcanisation – selective scission of crosslinks with minimum main chain scission – was coined with the intention of bringing more regenerated rubber back to rubber industry itself. Among the various devulcanisation technologies developed, mechano-chemical devulcanisation processes working through the combined action of mechanical shear and solid phase modifiers at ambient reaction conditions envisaging minimum main chain and better retention of revulcanisate properties are most viable. The devulcanisation agents used in mechano-chemical devulcanisation are claimed to induce targeted crosslink scission and /or subsequent stabilization of broken crosslinks. But, the similar mode of action to accomplish comparable revulcanisate properties by these un-related chemicals arouse suspicion regarding the capability of thus claimed devulcanising agents in targeted crosslink cleavage and subsequent radical stabilization under ambient conditions. Therefore it is hypothesized that, any shear induced devulcanisation process should be a dynamic process in which cross link breaking and reformation are competitive and any

chemical/process which can effectively and instantaneously block the recombination of the radicals formed can significantly improve the devulcanisation.

The present work addresses the issue of recombining of the radicals formed by crosslink scission and consequent reformation of once cleaved crosslinks under shear devulcanisation is using stable free radical. The various aspects of stable free radical assisted mechanical devulcanisation and the factors which can affect the per cent devulcanisation and revulcanisate properties of devulcanised rubbers were investigated in detail.

The thesis consists of eleven chapters. An abridged introduction to the subject, review of relevant literature and the scope and objectives of the present work are described in Chapter one. A review of the chemistry of sulphur vulcanisation and devulcanisation was presented together to explore the possibility of utilizing the sulphur vulcanisation chemistry to develop a more efficient devulcanisation process as well as to address the issues related to revulcanisation of devulcanised rubber such as low scorch. Chapter two describes the various analytical techniques and test methods used for this study.

Chapter three describes the systematic study of mechanical devulcanisation of carbon black filled natural rubber vulcanisates (both aged and un-aged) with known properties in a laboratory two roll mill at ambient conditions and the incorporation of the same in a virgin compound in the ratios 85/15, 75/25 and 60/40 with and without applying a filler correction during the compounding of blends. The logic behind working on a simple

mechanical devulcanisation process is that it is simple, economical, environmentally safe and easily adaptable by the rubber industry.

Chapter four discusses the comparative study of the industrially practiced mechano-chemical devulcanisation processes like, De Link and Lev Gum processes with mechanical devulcanisation.

Chapter five presents a logical analysis of the observations and results of the study conducted in chapter 4 to derive a hypothesis and propose the concept of 'stable free radical assisted mechanical devulcanisation'. A brief introduction to stable free radicals is also presented in this chapter. The chapter presents the results of 1phr 4-Hydroxy Tempo (stable free radical) assisted mechanical devulcanisation of CV, semi EV and EV cured carbon black filled NR vulcanisates (both aged and un-aged).

Chapter six deals with the systematic study of the effect of concentration of stable free radical 4-Hydroxy TEMPO (0-6 phr) and the effect of cure system i.e. CV, semi-EV and EV systems used for vulcanisation of original sample on the efficiency of devulcanisation of carbon black filled natural rubber (NR) vulcanisates. The results obtained for the extension of comparison study of devulcanisation processes described in chapter 4 to stable free radical assisted devulcanisation are described.

In Chapter seven the effect of carbon black type and carbon black concentration present in the original sample on the mechanical and 4-

Hydroxy Tempo assisted devulcanisation of natural rubber vulcanisates is described.

Chapter eight deals with the mechanical devulcanisation of blends of natural rubber and polybutadiene rubber (BR). The effect BR content, cure system used for preparation of original blend and crosslink density of the virgin blends upon the devulcanisation efficiency of the blends are investigated both in the absence and presence of stable free radical.

Chapter nine describes the effect of 4-Hydroxy Tempo upon the devulcanisation of commercial samples of waste rubber such as ground tyre rubber (GTR) and tyre tread buffings (buffing dust). The effect of the incorporation of buffing dust devulcanised with and without the assistance of stable free radical into a similar tread formulation and the factory scale trials of 4-Hydroxy Tempo assisted devulcanisation of buffing dust are presented in this chapter.

The possible reasons or causes behind the observed low scorch time during revulcanisation of devulcanised samples are investigated in chapter ten.

Chapter eleven includes the summary and conclusions of the work and the future perspectives.

Abstract

Stable free radical assisted mechanical devulcanisation of carbon black filled rubber vulcanisates is described in this work. Revulcanisate properties comparable with mechanical devulcanisation were obtained for samples devulcanised using contemporary industrial mechano-chemical processes like De Link process and Lev Gum process. This doubts the capability for targeted crosslink cleavage and broken crosslink stabilization by these devulcanisation agents. Since free radicals are formed from shear induced crosslink scission, any chemical or moiety that could effectively and instantaneously block the re-crosslinking of once cleaved crosslinks can act as a devulcanisation aid which is not possible with currently used devulcanisation agents. Chemical probe analysis of the devulcanised rubber in comparison with the crosslink distribution pattern of the corresponding original samples proved that stable free radical effectively prevented the recombination of once cleaved crosslinks resulting in significant improvement of per cent devulcanisation and revulcanisate properties.

Results of the devulcanisation of NR vulcanisates prepared using CV, semi EV and EV cure systems also suggested that, not only the bond energies of the crosslinks to be cleaved, but also the recombining capacities of these bonds might critically influence the per cent devulcanisation and corresponding revulcanisate properties of a sample. Concentration of 4-Hydroxy Tempo (stable free radical), crosslink density, amount and type of filler, cure system and the rubber used for the preparation of original sample plays decisive roles in devulcanisation. In all the cases under study, 4-Hydroxy Tempo was found to be a promising devulcanisation aid giving

significantly higher retention of vulcanisate properties than the mechanical and/or contemporary industrial devulcanisation processes. Devulcanisation studies using samples aged in laboratory conditions, buffing dust and GTR supported by the results of factory scale trials of the process confirmed the practical feasibility of stable free radical assisted mechanical devulcanisation in real world.

Investigations on the issue of low scorch indicated that, the low scorch associated with the revulcanisation of devulcanised rubber or the reduced scorch safety when ground rubber vulcanisates is blended with fresh rubber compound are not per se associated with these materials but is solely related to the cure system used for the preparation of the original sample from which these materials are sourced.

Key words: Devulcanisation, stable free radical, 4-Hydroxy Tempo, per cent devulcanisation, revulcanisation, revulcanisate properties, cure system, crosslink distribution, Horikx plot, scorch safety

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Chapter 1

INTRODUCTION AND LITERATURE SURVEY

1.1 RUBBERS

The modern life history of natural rubber[1-3] can be dated back to 11 June 1496, the day on which Christopher Columbus returned from his second voyage, bringing back the first rubber balls from the West Indies. The next landmark was the Spanish discovery of the use of latex for the water proofing of leather and fabrics in 1615. The rubber industry in Europe really started with Charles Macintosh in 1818, when he started exploiting the naphtha-based rubber solution as a water proofing layer between two fabrics. Two years later, in 1820, Thomas Hancock discovered mastication. The contributions of Sir Henry Wickham and Henry Ridley in rubber plantation also added on to the vast development and fast growth of rubber industry. The final landmark in the early history of rubber was the discovery of vulcanisation by Charles Goodyear in 1839 which revolutionized the use and applications of rubber, and changed the face of the industrial world. Dunlop's patenting of the pneumatic tire in England in 1888 led to the age of the bicycle as a prologue to the era of automobiles. However, synthetic alternatives remained mostly of academic interest till World War I during which Germany instituted programs to develop synthetic alternatives[4].

Rubbers might be general purpose "diene" elastomers like styrene-butadiene rubber (SBR), Butadiene rubber (BR) and isoprene rubber [both natural (NR) and synthetic (IR)] which are hydrocarbons with significant chemical unsaturation in their backbones primarily used in automobile and truck tyres[5]. The incapability of these general purpose rubbers in dealing with the higher demands of chemical, environmental and temperature resistance, led to the development of specialty elastomers such as

polychloroprene (CR), acrylonitrile-butadiene rubber (NBR), hydrogenated nitrile rubber (HNBR), butyl rubber (IIR), ethylene-propylene rubber (EPDM), silicon rubber, etc.

A thermosetting resin is a prepolymer in a soft solid or viscous state that changes irreversibly into an infusible, insoluble polymer network by curing by forming three-dimensional network of bonds (crosslinking)[5]. Curing is induced by the action of heat or suitable radiation, often under high pressure. A thermoset cannot be melted and re-shaped after curing which restricts its reprocessing/ recycling for the same purpose, except as filler material. Vulcanised rubbers also belong to this class of materials[6]. In the case of thermoplastics, molecules are joined by physical aggregation of molecules and hence are susceptible to easy reprocessing. Both thermosets and thermo plastics can be used interchangeably in many applications, but thermoset rubbers alone are considered for demanding applications such as tyres, engine mounts, springs, etc on account of their elasticity, durability and resistance to set[7]. This work and hence this chapter deals with general purpose thermoset rubbers.

1.2 VULCANISATION

None of the elastomers could have been made useful without proper compounding with various ingredients. Vulcanisation, named after Vulcan - Roman god of fire- is the chemical process of interlinking of rubber molecules to change the predominantly plastic/viscous properties to elastic properties. The vulcanisation system is mainly a collection of additives required to transform the essentially linear polymer molecules into a three dimensional network by the insertion of crosslinks[8]. Though, various curing systems are used for different rubbers, sulphur vulcanisation remains most favoured vulcanisation route for general purpose rubbers. Sulphur vulcanisation of natural rubber is discussed in some detail as it formed the

majority share of this work. The process of vulcanisation is also described in detail though the work is centered on devulcanisation based on the belief that understanding the chemistry of vulcanisation is important to develop a devulcanisation process and further vulcanisation of devulcanised rubber and dealing with the issues therein.

1.3 SULPHUR VULCANISATION OF NATURAL RUBBER

Sulphur vulcanisation is usually carried out industrially by heating the mechanically plasticized rubber with sulphur and auxiliary vulcanising agents such as organic accelerators, ZnO, long chain fatty acids or the zinc soaps of these acids (activators) along with additional ingredients like antioxidants, anti-ozonants, fillers and reinforcing agents such as carbon black.

1820 ——— Discovery of mastication (Thomas Hancock)

1839 ——— Discovery of vulcanization (Charles Goodyear)

1905 ——— Started to use ZnO as filler

1906 ——— Discovery of first organic accelerator (Oenslager)

1912 ——— Started to use carbon black as filler

1920 ——— Role of activators invented

1925 ——— MBT and its homologues invented

1970 ——— Started to use PVI
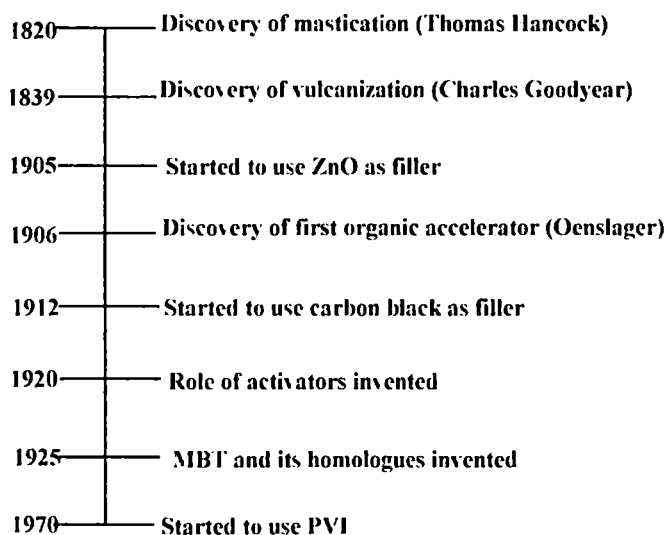
Figure1.1 Timeline showing various developmental stages in the history of vulcanisation of rubber

Major effects of vulcanisation on use related properties include increased elastic recovery, tear strength, tensile strength, fatigue life,

toughness, low hysteresis and compression set, $etc^{9\text{-}11}$. The timeline of various developmental stages in the history of sulphur vulcanisation is given in Figure 1.

1.3.1 Accelerators

Accelerators are added with sulphur in the rubber industry to increase the rate of vulcanisation by activating sulphur. The most important characteristics of accelerators are scorch time, cure time and vulcanisation time as illustrated in Figure 1.2[12]. The scorch time is the time available at a given temperature before the stock begins to vulcanise where much of the accelerator chemistry is involved[13]. Cure time is the time a stock must be heated in a press at a given temperature until it reaches a technically correct cure (optimum cure time). Vulcanisation time is the time required to reach a satisfactory technical cure. After vulcanisation time, the torque may increase further (marching), or decrease (reversion), or level off.
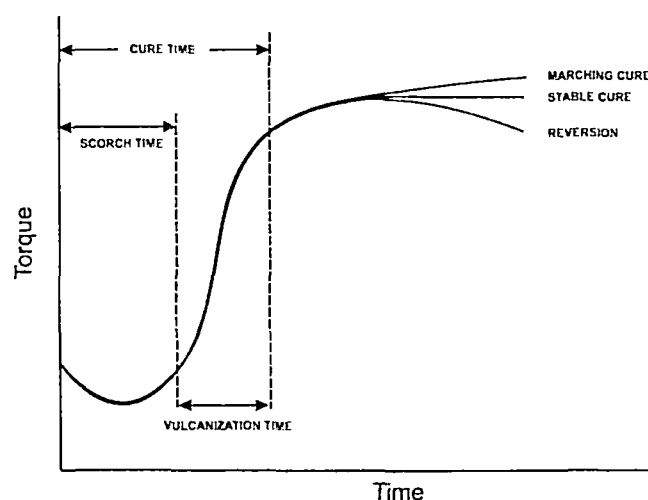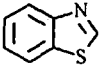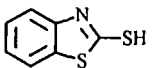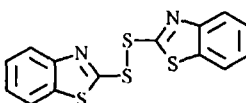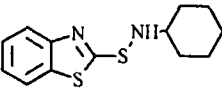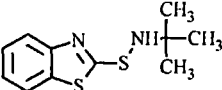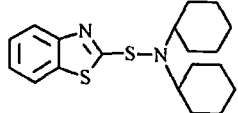
Figure 1.2 A typical rheograph showing different stages of cure
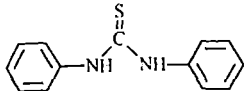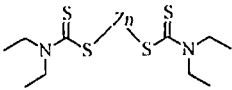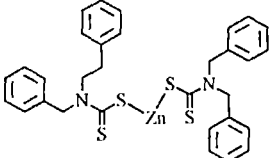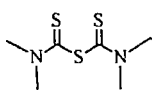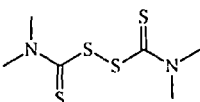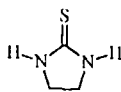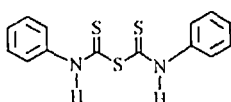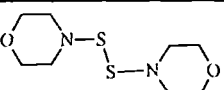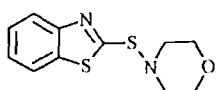
The two major classes of vulcanisation accelerators based on vulcanisation rate, are (i) primary accelerators or fast accelerators (semi-

ultra) like sulphenamides and thiazole derivatives and (ii) secondary accelerators or ultra-accelerators like thiurams and dithiocarbamates. Primary accelerators are characterized by very good scorch time and fast curing in the main vulcanisation phase. Secondary accelerators are used as small addition to primary accelerators to boost the speed and state of cure during vulcanisation. In addition to these, guanidines form a class of slow (medium) accelerators with short induction period and broad vulcanisation plateau[14,15]. Classification of accelerators based on structure and their important features are given in Table. 1.1

Table 1.1. Classification and properties of sulphur vulcanisation accelerators

BASIC GROUP : BENZOTHIAZOLE			
TYPES	**EXAMPLES**	**STRUCTURE**	**PROPERTIES**
MERCAPTO ACCELERATORS *Used along with secondary accelerators*	2-Mercapto Benzothiazole (MBT)		Semi-ultra accelerator, scorchy
	2-2' dithiobenzothiazole (MBTS)		Delayed action semi ultra accelerator
SULPHENAMIDES *Widely used scorch safe accelerators*	N-cyclohexylbenzothiazole 2-sulphenamide (CBS)		Semi ultra accelerator, delayed action
	N-t-butyl benzothiazole 2-sulphenamide (TBBS)		Delayed action
	Benzothiazyl dicyclohexyl sulphenamide (DCBS)		Extremely delayed onset of cure, best scorch resistance

BASIC GROUP : THIO CARBANILIDE			

DITHIOCARBAMATES *Salts of carbamic acid used as ultra accelerators*	**Zinc diethyl dithio carbamate (ZDEC)**		Ultra accelerator
	Zinc dibenzyl dithio carbamate (ZDBC)		Nitrosamine free ultra accelerator
THIURAMS *Highly process safe reversion free secondary accelerators and sulphur donors*	**Tetramethyl thiuram monosulphide (TMTM)**		Ultra accelerator
	Tetramethyl thiuram disulphide (TMTD)		Ultra accelerator and vulcanization accelerator
	Ethylene thiourea (ETU)		Accelerator for synthetic rubber production and for epichlorohydrin elastomers
	N,N diphenyl thiourea (ETU)		Medium speed accelerator. useful as 1° and 2° accelerator

BASIC GROUP : MORPHOLINE			

MORPHOLINE ACCELERATORS *Delayed action with safe accelerators*	**N,N dithio dimorpholine (DTDM)**		Sulphur donor. used along with thiurams, thiazoles, etc
	N-oxodienthylene 2 benzothiazole sulphenamide (MBS)		Excellent delayed accelerator

Three special types of cure systems *viz.* conventional vulcanisation (CV), semi-efficient vulcanisation (semi EV), and efficient vulcanisation (EV) systems are the commonly employed vulcanisation systems for sulphur vulcanisation. In the conventional curing systems, the sulfur dosage

is high together with low levels of accelerator giving rise to polysulphidic crosslink dominated vulcanisate network with better flex and dynamic properties but worse thermal and reversion resistance[15] (Datta). Semi EV systems provide vulcanisates with intermediate levels of heat and reversion resistance, flex and dynamic properties. EV systems are those where a low level of sulfur and a correspondingly high level of accelerator (or sulphur-less curing) are employed. The resulting vulcanisates would be high heat and reversion resistant. The levels of accelerator and sulfur in CV, semi EV and EV systems are shown in Table 1.2[16].

Table 1.2 Curative dosage level for CV, semi-EV and EV vulcanisation systems

Type of cure	Sulphur	Accelerator	Accelerator/sulphur ratio
CV	2.0-3.5	1.2-0.4	0.1-0.6
Semi-EV	1.0-1.7	2.4-1.2	0.7-2.4
EV	0.4-0.8	5.0-2.0	2.5-12.5

1.3.2 Activators

The ability of metal oxides in improving the efficiency of sulphur based cure systems has been discovered early in the history of vulcanisation, and the most useful metal oxide applied in the "activating" role is zinc oxide. Zinc stearate, the most popular activator used today is necessarily formed *in-situ* for optimum effect. Vulcanisation systems that contain zinc oxide (ZnO) lead to very high crosslink densities as ZnO assist the effective conversion of pendent groups into crosslinks[16] thereby increasing the fraction of the sulphur used for crosslink formation in the vulcanisate influencing the heat stability and reversion effects of the vulcanisates. ZnO has a significant effect on the number and nature of crosslinks between the

molecular rubber chains and can there by change physical properties[11,18-21]. Zinc oxide is claimed to benefit aged properties in certain formulations by acting as an acid scavenger[22,23]. Zinc complexes such as zinc dimethyldithiocarbamate (ZDMC) appeared to be homogeneous catalysts[24] for the processes of crosslink formation[25,26], crosslink shortening[9,26,27] and crosslink breaking[28,29].The role of metal oxides in the process of rubber vulcanisation by thiuram disulphide lies mainly in the binding of dithiocarbamic acid (DMDCA) whose decomposition products accelerate oxidative degradation of the vulcanisate network[30].

Fatty acids or zinc salts of fatty acids are generally regarded as indispensible activators in conjunction with ZnO to solubilize the ZnO and the accelerator to form the actual catalyst[20,31]. The role of activators also depends on the type of rubber, vulcanisation accelerator and active filler used[31]. ZnO has the greater influence on the degree, while stearic acid has the greater influence on the rate of the crosslinking reaction[20].

1.3.3 Stages of vulcanisation

The reactive sites—"cure sites"—during the process of vulcanisation are allylic hydrogen atoms lying adjacent to carbon-carbon double bonds. In natural rubber (NR), the hydrogen atoms at positions 4 and 5 are most preferred (Figure 1.3). During sulphur vulcanisation, some of these C-H bonds are replaced by chains of sulphur atoms (one to eight) that link with a cure site of another polymer chain to form a crosslink. The crosslinks that are formed initially are usually polysulphides with high sulfur rank, which subsequently can undergo two competing reactions. They are crosslink desulphuration which involves rearrangement of the polysulphidic crosslinks to the more stable mono and di-sulphidic crosslinks and crosslink decomposition/degradation where polysulphidic crosslinks degrades to

elastically ineffective cyclic sulphides, inactive pendant groups or other main-chain modifications[32].
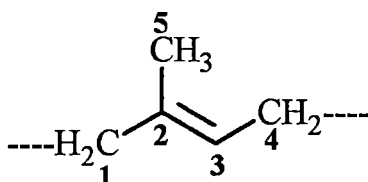
Figure 1.3 The reactive allylic carbon atoms (C4 and C5) in NR

Accelerated sulphur vulcanisation is a multidisciplinary field involving the aspects of radical, ionic and organo-sulphur chemistry, reactions in heterogeneous phase, homogeneous catalysis as well as coordination chemistry[24]. Many researchers proposed free radical mechanisms for the accelerated sulphur vulcanisation of unsaturated elastomers[11,19,33-35] while many others suggested a polar mechanism[9,32]. It is very difficult to generalize the discussion on accelerated sulphur vulcanisation as there are many unanswered questions and many reasons to believe that both free radical and ionic reactions take place at different stages of the vulcanisation reaction[36,37].

Despite the uncertainties regarding many processes taking place during the sulphur vulcanisation, the widely accepted basic steps during the vulcanisation reactions can be divided into (i) accelerator chemistry which includes the formation of activator-accelerator complex and the active sulphurating agent, (ii) crosslinking chemistry including the formation of crosslink precursors and reactions leading to the formation of crosslinks and (iii) post crosslinking chemistry dealing with the network maturing reactions such as crosslink degradation and crosslink desulphuration (Figure 1.4).

1.3.3.1 *Accelerator chemistry*

Active accelerator complex

The formation of an active accelerator complex *via* a reaction between the activator and the accelerator is generally regarded as the first step in the vulcanisation process[1]. This might in fact be the formation of active form of accelerator under the influence of the vulcanisation temperature through ionic and radical path ways as observed in benzothiazole-sulphenamide accelerated sulphur vulcanisation[38,39].

Accelerator + Activators

↓

Active Accelerator Complex   OR   **Sulphur donor & activators**   Accelerator Chemistry

| S_8

↓

Active Sulphurating Agent (XS-Sx-Zn-SX) ◄─────

↓

Crosslink Precursor (XS-Sx-R)   Crosslinking Chemistry

↓

Initial Polysulphidic Crosslinks (R-Sx-R)

(i)Crosslink shortening with additional crosslinking

(ii) Crosslink destruction with mainchain modifications   Post crosslinking Chemistry

(iii) S-S bond interchange

↓

Final Vulcanizate Structure

Where,
R- rubber chain
XS-Accelerator moiety
Sx-sulphur atoms in crosslink

Figure 1.4. Outline diagram showing different stages of vulcanisation

Active sulphurating agent

Active sulphurating agents are accelerator polysulphides formed at the beginning stages of vulcanisation process[40] through sulphur intake of the active accelerator[9, 10] by various mechanisms and are better sulphurating species than molecular sulphur. In the absence of an activator such as ZnO these polysulphides of the type XS-S_x-SX (X is a group derived from accelerator) are formed by a radical pathway while ZnO present as an activator in the vulcanisation system catalyzes the formation of complexes resulting in structures XS-S_x-Zn-SX through polar pathways[41].

1.3.3.2 Crosslinking chemistry

The crosslink precursor

Once the sulphurating agents are being formed, they react directly with the rubber molecule to give a rubber bound pendent group of structure R-S_x-SX (R denotes the rubber chain) which act as precursors to crosslink formation and hence the name[42]. The existence of such species which was first proposed by Scheele and Franck[43] were later confirmed later by many scientists[44-46].

Crosslink formation

Formation of crosslinks is an inevitable and immediate consequence of crosslink precursor formation. Various mechanisms have been proposed for the conversion of the crosslink precursors into crosslinks. Crosslink formation *via* precursor-precursor interaction[20], interaction involving precursor, sulphurating agent and rubber molecule[9] and through direct reaction of the crosslink precursor with rubber molecule[9,11,47] were proposed. Free radical mechanism is advocated for activator free systems whereas polar mechanisms are supposed to give rise to crosslinks in presence of activators like ZnO. Based on various experimental observation

made by various researchers, crosslink formation through the exchange of groups between precursor and rubber appear be the prominent pathway of crosslink formation in both cases[19,41,47].

A simplified version of crosslink formation during sulphur vulcanisation of NR through the involvement of different intermediate species is illustrated in Figure 1.5[48].
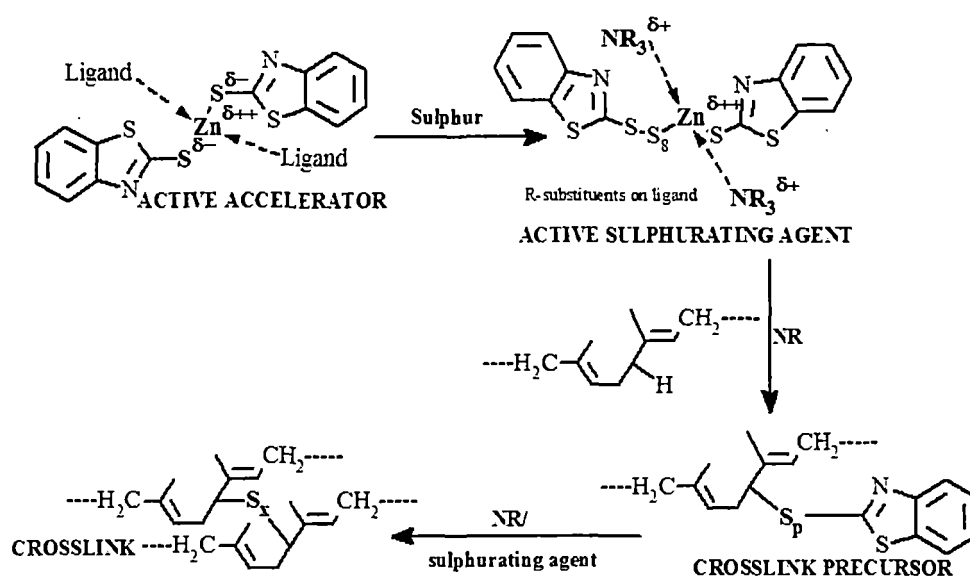
Figure 1.5 Crosslink formation in sulphur vulcanisation of NR

Scorch delay reactions

This section is reviewed in detail with an intention to understand the chemical reactions involved during the scorch delay period in sulphur vulcanisation which might be useful in tackling the problem of low scorch associated with the revulcanisation of devulcanised rubber. The long delay periods encountered in accelerated sulfur vulcanisation, especially when

scorch delay accelerators are used was explained by a model scheme proposed by Coran[49] as given in Figure 1.6.

Based on the scheme, crosslink formation will be minimum if the reaction $k4$ is much faster than $k3$, until A is essentially depleted. Both the reaction through $k3$ and that through $k4$ are assumed to be much faster than the reaction through $k2$ and hence, after the delay required for the depletion of A, crosslink formation will proceed in a first order fashion. Thus the formation of crosslinks is indeed inhibited by the starting materials and/or their initial reaction products. With respect to the scheme, the scorch delay observed with sulphenamide accelerators might be due to the formation of amine terminated precursors[41,50,51], the effect of zinc-accelerator complex[52,53], exchange reactions between various accelerator derived intermediates[46,49,51], etc.

$$A \xrightarrow{k_1} B \xrightarrow{k_2} B^* \xrightarrow{k_3} \alpha Vu$$

$$A + B^* \xrightarrow{k_4} \beta B$$

A- Accelerator and/or its reaction products

B- Crosslink precursor

B*- Activated form of B

Vu- Crosslink α and β adjust stoichiometry
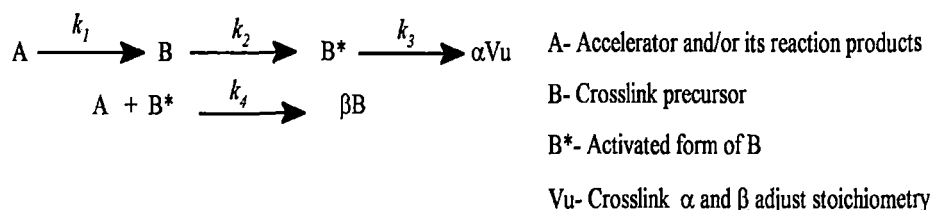
Figure 1.6 Coran's model scheme for scorch delay

The delay period before actual curing provided by the various accelerators through aforementioned mechanisms can further be increased by the introduction of a pre-vulcanisation inhibitor (PVI) while retaining other aspects of cure such as rate of cure, time to maximum cure, maximum crosslink density, etc[54-56]. The most widely used PVI is N-(cyclohexyl thio) phthalimide (CTP) introduced by Monsanto in 1970[57].
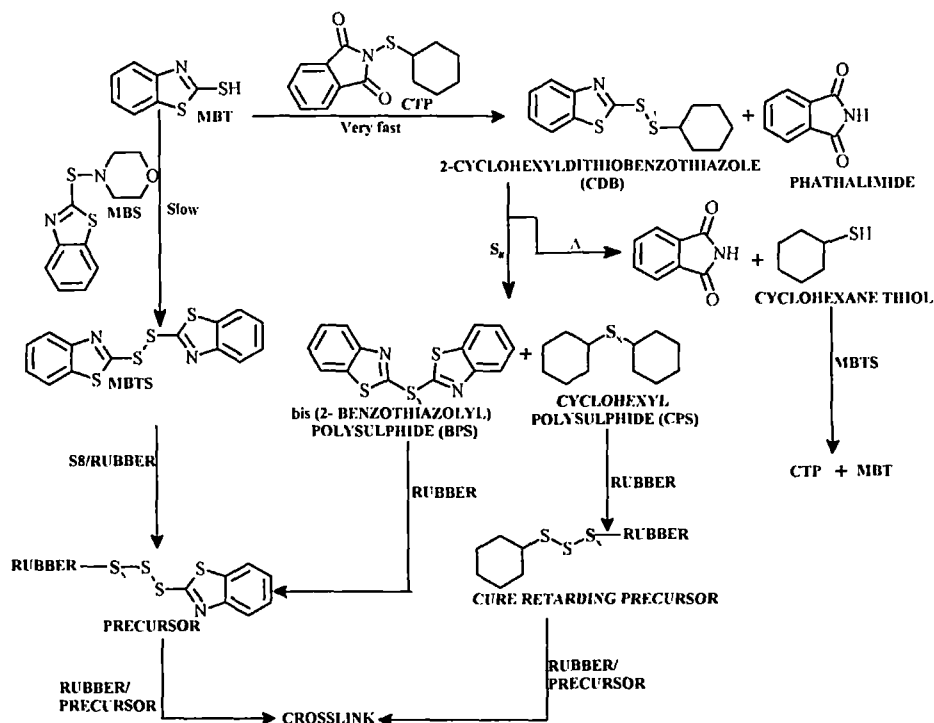
Figure 1.7 Mechanism of action of CTP in sulphenamide accelerated sulphur vulcanisation

The mechanism of action of PVI is based on the fact that, MBTS formation is the key step towards crosslinking and hence if its formation can be arrested, the whole crosslinking mechanism can be checked. MBTS formation is being blocked by CTP by consuming MBT thereby preventing any chance of MBT further reacting with sulphenamides to form MBTS. Kinetic factors also favour this reaction as MBT has greater affinity for CTP than to sulphenamides and hence it will react with CTP alone until all the CTP has been consumed[39,58-62]. The by-product of CTP action 2-cyclohexyldithiobenzothiazole (CDB), has been proved to be a lesser scorch

vulcanisation accelerator than N-oxydiethylene-2 benzothiazole sulphenamide (OBTS or MBS or MOR), but with slower cure rate will accelerate the vulcanisation process when actual curing begins[62]. The mechanism of action of PVI is outlined in Figure 1.7.

1.3.3.3 Post-crosslinking chemistry

As already mentioned, crosslink desulphuration and crosslink decomposition reactions dominate the post-crosslinking chemistry[13,29]. If the desulphuration proceeds rapidly the final network will be highly crosslinked with mainly monosulphidic bonds and there will be relatively few modifications of the cyclic sulphides or conjugated triene type (efficiently crosslinked)[63, 64] or else there will be opportunities for thermal decompositions leading to reversion or loss of crosslinks and to network modifications (inefficiently crosslinked)[63].

Desulphuration reactions[65-68] involve the extraction of sulphur atoms from higher ranked sulphur bonds, followed by insertion of the extracted sulphur atoms into the lower ranked sulphur crosslinks. Crosslink decomposition processes, either radical or polar in character, generally operate at high temperatures will lead to a net loss in crosslink density and hence impart reversion[69]. Radical decomposition is governed by bond dissociation energies of the bond that is broken and hence polysulphides of higher lengths are easily dissociated due to their lower bond dissociation energies (approx.150kJ/mol) whereas dissociation of di and tri sulphidic crosslinks are more difficult due to their higher bond dissociation energies (289 and 193kJ/mol respectively).

The various processes involved in the accelerated sulphur vulcanisation are being summarized are being summarized in Figure 1.8[48].
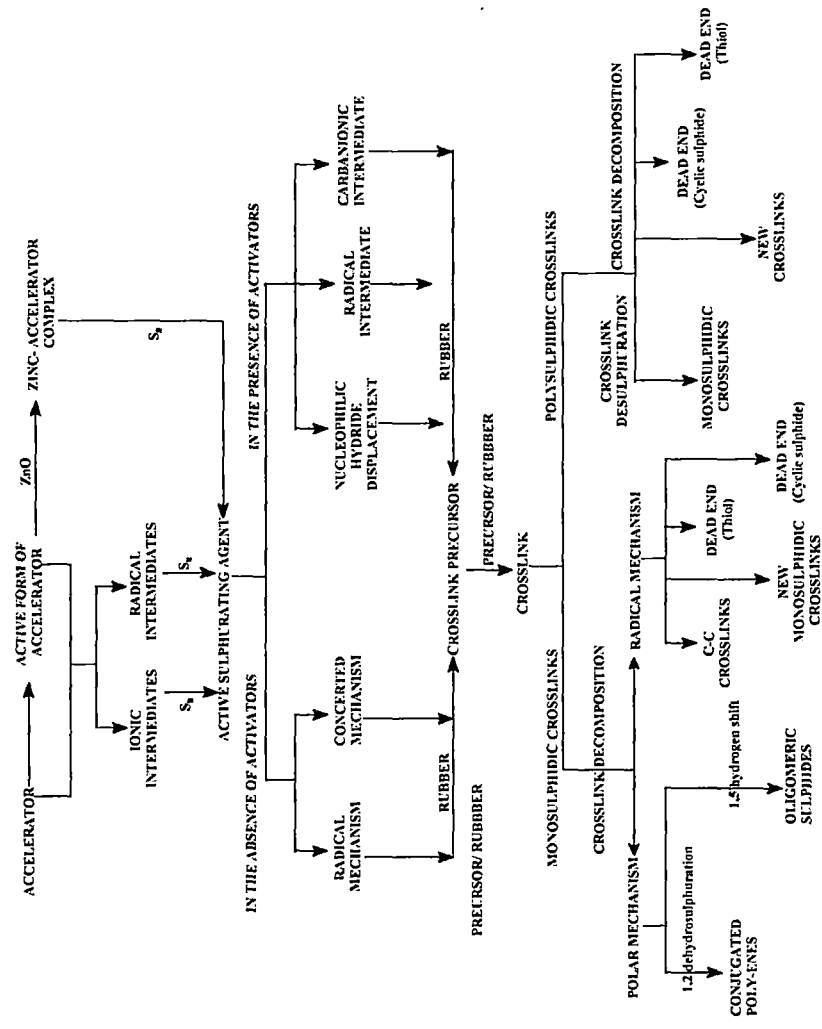
Figure 1.8. Summary of steps and processes involved in accelerated sulphur vulcanisation

1.4 NEED FOR DEVULCANISATION

1.4.1 Rubber in everyday life

Rubber products touch all realms of human lives though a few people recognize rubber in all of its applications. The broad categories of applications of rubber include[70]

- automotive industry *(tyres, tubes, dampers, o-rings, etc)*

- civil engineering applications *(bridge bearings, flexible parts in flyovers, bitumen modifier, sound vibration dampers, flooring, etc.)*

- industrial applications *(conveyor belting, transmission belting, hoses, joints, flexible couplings, vibration dampers for machines, corrosion resistant coatings etc.)*

- agriculture *(tyres, manufacture of harness, collars, horse-shoes, and rubber saddles, etc.)*

- clothing *(foot wears, elastic threads for garments, artificial leather, etc.)*

- latex goods *(gloves, catheters, draw sheets, finger stalls, hot water bottles, etc.)*. (Rehan Ahmed)

The use of rubber in so many applications results in a growing volume of rubber waste all over the world. Since at least 65% of worldwide rubber production, and likely an even higher percentage of rubber disposal consists of car and truck tyres, used tyres are a challenging problem owing to their virtually unlimited life span. The most obvious hazard associated with the uncontrolled disposal and accumulation of large number of tyres is the potential for large fires which are extremely detrimental to the environment. Even if large outside tyre piles do not catch fire, they still pose a serious problem for human health and the environment by being an ideal

breeding ground for mosquitoes and other water-incubating insects and bacteria[70,71,75].

1.4.2 Used rubber recycling scenario

In response to the environmental problems and health hazards caused by countless illegal scrap tyre piles around the globe, most developed countries have developed legal guidelines addressing this issue. These legislations to ensure environmental safety, resulted in radical shift of the reclamation dominated recycling industry to rubber powder based recycling methods focused on material and energy recovery as evident from Figure 1.9. These recycling methods primarily aim in converting end of life tyres into a useful form for reuse in many applications not in the rubber industry alone[76-91].
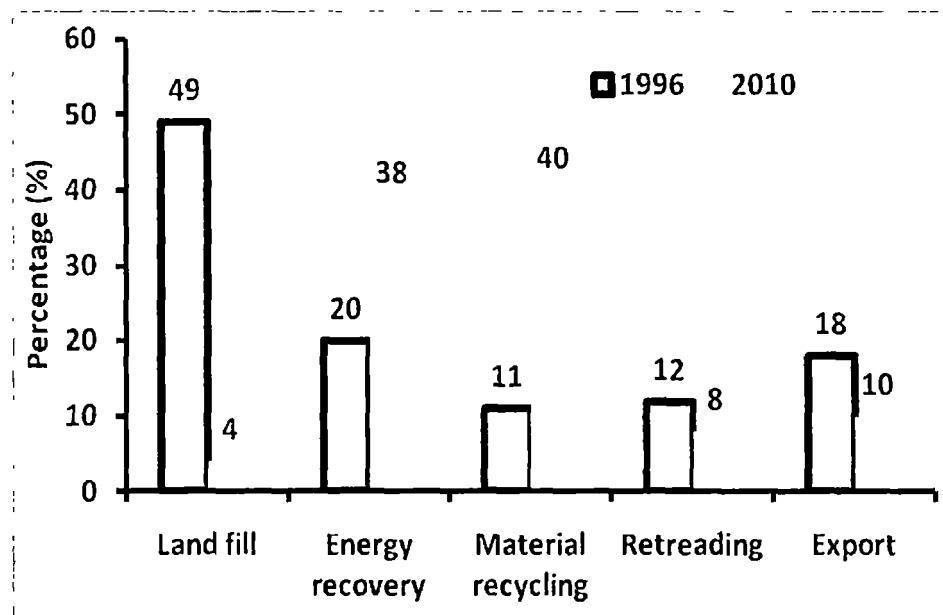
Figure 1.9 Change in pattern of end-of-life tyre reuse in European Union (1996-2010)

The concept of devulcanisation - selective scission of crosslinks with negligible main chain scission - was coined to reuse more amounts of recycled rubber in the rubber industry itself. Early methods of devulcanisation, described as reclamation significantly reduced the molecular weight of rubber as the process employed cleaved all bonds indiscriminately, thus limiting the amount of reclaim that can be used in new products without deteriorating the physical properties[92].

These methods employed environmentally hazardous production techniques also. In most of the later innovations, devulcanisation was achieved by applying high temperature and pressure, mechanical, mechano-chemical, microwave or ultrasonic energies and using biotechnological interventions with all processes having inherent advantages and disadvantages[93-95]. Though large scale commercial utilization of these new innovations are not reported, attempts have been initiated by many firms for small to medium scale production of devulcanised rubber using these technologies[96-99]. The various stages in the lifecycle of tyres are outlined in Figure 1.10.

Basel Convention is an international treaty that was designed to reduce the movements of hazardous waste between nations, and specifically to prevent transfer of hazardous waste from developed to less developed countries (LDCs). Basel Convention calls for an overall reduction of waste generation and encourages countries to keep wastes within their boundaries and to ensure environmentally sound management as close as possible to its source of generation. Accordingly, a recycling strategy for used tyres has been approved which is listed in Table 1.3[100-103].

Tyre raw materials (%)

Tyre raw materials	Car	Truck
Rubber	45	42
Filler	23	24
Metal	16	25
Textile	6	-
Zinc oxide	1	2
Sulphur	1	1
Additives	8	-

Material	Size (mm)
Cut	>300
Shreds (large)	75-300
Shreds (small)	40-75
Chips	10-50
Buffings	0-40
Granulate	1-10
Powder	0-1

Pyrolysis (%)

Pyrolysis products	500°C	900°C
Residue	41.6	55.3
Heavy oil	44	13.2
Light oil	3.6	6
Liquor	2.9	2.2
Ammonia	0.2	0.1
Gas	5	19.4
Total	97.9	96.3

Flowchart boxes:

Raw materials → Tyre manufacturing → Tyre in use → Used tyre → Retreading/ reuse (Waste prevention)

Discarded tyre → Shredding / Whole tyre storage

Material Recovery → Devulcanization/ reclamation, Pyrolysis, Grinding

Energy recovery → Fuel source, Power plants, Electric arc furnace

Industrial and consumer products, Civil engineering

Environmentally sound waste management

Energy content and CO$_2$ emission of fuels			
Fuel	Energy (GJ/t)	Emission KgCO$_2$/t	KgCO$_2$/GJ
Tyres	25-35	2.2	85
Carbon		2.43	90
Petroleum coke	32.4	3.24	100
Diesel oil	46	3.22	70
Natural gas	39	1.939	51
wood	12.2	1.122	110

Industrial/ consumer products	Civil engineering
Artificial turf, Playgrounds and sports grounds, Train and tram rail beds in door safety flooring, Shipping container liners, Conveyer belts, Footwear, Carpet and underlay, Roof tiles, Floor tiles, Activated carbon, Thermoplastic elastomers	Landfill, Erosion control, Rubber modified concrete, Road applications, Soil enforcement, Noise barrier, Thermal insulation

Figure 1.10 Stages in the life of tyres

Table 1.3 Recycling strategies of used tyres/rubber products as per Basel
Convention regulations

Recycling strategy	Features	Advantages/disadvantages
Reuse	• Partly worn tyres used for original purpose • Permitted in some countries	• Risky as the previous usage history unknown
Retreading	• Replacing the wearing surface of tyre • Restrictions on the number of times of retreading • Temporary recycling option	• Economical: 40-50% cheaper than new tyre • Environmental: crude oil consumption for new tread is ~7gallon against ~22 gallons for new tyre

Scrap tyre/ end of life tyre: Tyres that can no longer be used for the purpose for which it was originally manufactured but can be used for material recovery or energy recovery.

Energy recovery	**Fuel in cement kilns**: Direct utilization of inherent energy content • Tyres burnt for their calorific value (32.6 MJ/Kg) • Method of disposal rather than recycling	• Expensive: New feed system for fuel and methods to check air pollution***
	In electric arc furnace: Carbon from scrap tyres used as reducing agent in electric arc furnaces making steel. • Act as reactant, fuel and alloy element	• Increase combustion efficiency when co-injected with metallurgical coke
	Power plants: Used as supplementary fuel source Similar to application in cement kilns	• Needs methods to check air pollution

Material recovery	**Grinding:** Size reduction of scrap tyres through multi stage sequential processes based on requirements
	
	• De-beading → Shredding to coarse material →cutting to chips → powdering
	
	• For industrial and consumer products and civil engineering applications
	
	• *Ambient grinding*
	
	   • Grinding by cutting, tearing, shearing
	
	   • Ambient temperature
	
	   • Spongy and rough particle
	
	• *Cryogenic grinding* .
	
	   • Grinding by breaking cryogenically embrittled rubber
	
	   • Temperature below -80°C
	
	   • Even and smooth particles
		• Environment friendly
		
		• Activation techniques for compatibilization of blends
		
		• Higher power consumption
		
		• High specific surface and wide particle size range
		
		• Lower power consumption
		
		• 0.5-1Kg liquid nitrogen/kg tyre input
		
		• Low specific surface and narrow particle size range

	Pyrolysis: Ground tyre is thermally decomposed (120°C to 920°C) in the absence of oxygen to Produce oil, synthetic gas, carbon black and steel*	• Mixture of carbon black: low commercial value • Steel: Low market value
	Reclamation: Unrestricted cleaving of bonds in the crosslinked rubber by temperature, pressure and chemicals.	• Highly degraded product of low properties owing to severe main chain degradation
	Devulcanisation: Selective crosslink scission of vulcanised rubber with no or negligible main chain scission.	• Product of higher properties owing to minimum main chain degradation

1.4.3 Conventional reclamation processes

Ever since the invention of vulcanisation in 1839, efforts have been made to break the crosslinks formed during vulcanisation and to retrieve the rubber chains to obtain a material similar to the virgin rubber compound. Almost all such efforts produced a material of increased plasticity which has been identified as reclaim since the intention was to reuse the material.

Reclaiming is a procedure in which scrap tyre rubber or vulcanised rubber waste is converted (using mechanical and thermal energy and chemicals) into a state in which it can be mixed, processed, and vulcanised again through cleaving of covalent bonds (both crosslinks and main chain) existing in the vulcanised rubber. As previously mentioned, reclaiming processes generate environmental problems besides de-polymerization of the crosslinked polymer resulting in poor retention of the virgin rubber properties. In reclaiming processes, bond scission occurs due to free radicals producing hydroperoxides by the decomposition of oxygen. As oxygen is available in all of the reclamation processes, hydroperoxides can do form but the rate of attack by these species would be different for different polymers due to the difference in their molecular structure. Therefore, if different polymers are present together each will be reclaimed to different extends which would lead to processing problems and eventually poor revulcanisate properties[104]. Anyway, conventional reclamation processes of any type have been banned in US and whole of Europe and all nations with positive environmental policies. The major reclaiming processes are listed in Table 1.4.

The general aspects involved in the process of reclaiming are size reduction, separation of fibers and metals, incorporation of reclaiming chemicals and oils, heat treatment, mechanical processes, *etc*[105, 106]. In many rubber products, 5 to 10 per cent reclaim can be added to the new rubber content, without seriously harming the physical properties, but where the

performance requirements are toughened, use of reclaimed rubber is highly restricted. The advantages such as lower polymer cost, shorter mixing time, lower power consumption during mixing, low mixing, calendaring and extrusion temperature, improved building tack, improved green strength and reduced swelling and shrinkage during extrusion encourage the compounder to use reclaim[107]. Several studies have been carried out on the various aspects of reclamation processes, reclaimed rubber properties and incorporation of various types of reclaim in blends with virgin compounds[108-117].

Table 1.4 Conventional reclamation processes

Thermal process	• Oldest process • Heating crumb using steam in a pan • Pressure: 60psi; Temperature: 260°C; Time: 3-4 hours • Rubber in contact with air and steam • Washed, dried and sheeted through two roll mill

Heater/Pan process	• Carried out in a single shell steam autoclave
	• Two step process
	   o Fabric removal by boiling in strong acid solution
	   o Devulcanisation by 100-300psi pressure steam
	• Reclaiming, charring and wetting agents used
	• Time: 3 hours and 15 minutes
	• Cooled, dried, massed, strained through 40 mesh screen

Digester process/ alkaline process	- Carried out in double jacked autoclave - Devulcanisation and de-fibering in single step - Crumb submerged in aqueous sodium hydroxide minimizing oxygen contact except that is dissolved in water. - The hydroxyl anion (OH⁻) is supposed to attack and break crosslinks. (Not applicable with SBR) - Pressure: 150 psi steam pressure; Time: 10-15 hours - Washed, dried, massed, strained and sheeted
Neutral process	- Improvement of digester process to avoid hardening problem associated with SBR reclamation - Sodium hydroxide was replaced with zinc chloride or calcium chloride and pine oil to hydrolyse textile
Reclaimator process	- Continuous process carried out in an extruder - Fine ground rubber and the various reclaiming agents are subjected to a controlled amount of high heat and pressure in a continuously moving environment - Residence time of rubber in the machine is less than 5 minutes

1.4.4 Concept of devulcanisation

Rubber products like tyres are high-end engineering goods that are designed to last long and hence difficult to devulcanise and reuse. Unless complete or higher degree of crosslink scission is achieved with minimum

polymer chain degradation, there are fewer uses for the recycled product in the rubber industry. Ideally, contemporary devulcanisation strategies move in this direction and aims at recycling vulcanised rubber through selective cleaving of crosslinks to retrieve the linear polymer chains to reuse the rubber hydrocarbon by the rubber industry[82]. The concept of devulcanisation –selective scission of crosslinks – with the expected minimum main chain scission aims to ensure better retention of virgin rubber properties after devulcanisation.

The various contemporary devulcanisation processes make use of any of the typical methods such as opening by oxidation, opening by heat or shear, opening with nucleophilic reagents, opening by rearrangement and opening by substitution for selective rupturing the sulphur crosslinks of rubber. In the history of devulcanisation though several methods are being advocated and developed, only a handful of them succeeded in proving their credibility to be industrially viable. Most of them were relatively dry processes that can be carried out on normal rubber processing equipment and can be done quickly and belonged to either of the two categories namely, mechanical devulcanisation or mechano-chemical devulcanisation[104,118]. Irrespective of their industrial viability, several studies have been carried out on the various aspects of devulcanisation processes and the vulcanisate properties of devulcanised rubber and its blends with virgin compounds in various ratios[89,119]. Various devulcanisation processes are discussed below emphasizing on the reactions involved and proposed mechanisms along with the revulcanisate properties associated with them.

1.5 METHODS OF DEVULCANISATION

1.5.1 Chemical/Thermo-chemical devulcanisation

Chemical agents have been used to devulcanise scrap tyres since 1960s. Initially, most chemical devulcanisation processes involved mixing

of size reduced rubber particles and chemical reagents in a temperature and pressure controlled mixer which resembled the reclamation processes to a greater extent. Generally speaking, rubber is fed into a mixer with a devulcanising agent and heated. But, the higher temperature and pressure conditions employed result in severe degradation of the polymer along with crosslink scission that made the processes less attractive. Later, chemical assisted devulcanisation carried out under ambient conditions were put forth, some of which are discussed below.

1.5.1.1 *Using ferrous chloride and phenyl hydrazine*

A process that regenerates vulcanised rubber by treating the material at room temperature and atmospheric pressure for several hours with ferrous chloride ($FeCl_2$) and phenyl hydrazine, in which phenyl hydrazine is the main reagent and $FeCl_2$ acts as catalyst, is reported[120,121]. Although claimed to be a devulcanisation method, this process is essentially a reclamation method in which devulcanisation is achieved by the oxidative degradation of rubber chain in the presence of oxygen through Bolland oxidation mechanism[122].

1.5.1.2 *Using the principles of phase transfer catalysis*

The principles of phase transfer catalysis also have been used to devulcanise cured rubbers with an onium salt dissolved in an organic solvent, which exchanges its anions for a hydroxyl ion when exposed to the alkali[123,124]. The onium salt carrying the hydroxyl ion from water is claimed to diffuse into the rubber and react with sulphur, breaking the crosslinks with little main chain scission. Figure 1.11a illustrates the equation describing the transport of an anion X^- from water into an organic phase by a quaternary ammonium chloride catalyst, Q^+Cl^-. The anion X^- is made soluble in organic phase because of its association with Q^+, which is usually

substituted with large hydrocarbon radicals. Crosslinked rubber particles can be considered as viscous hydrocarbon phase.
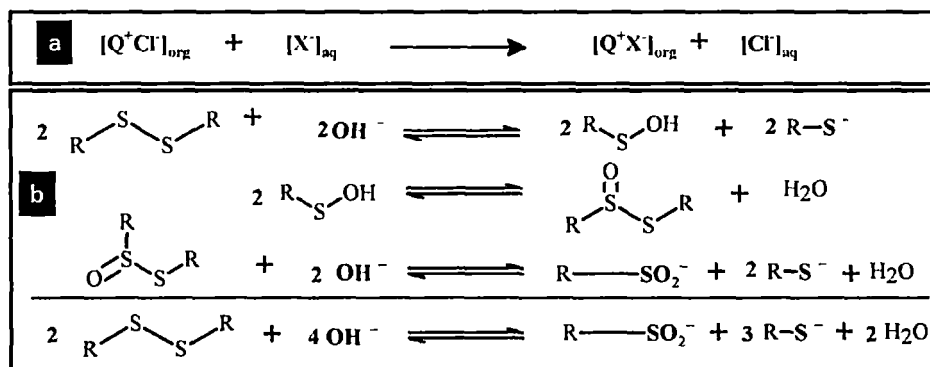
Figure 1.11 a: General representation of phase transfer of ions; **b:** Selective scission of sulphidic crosslinks by hydroxyl ions

According to this method, if hydroxide ions could be transported in this way at acceptable rates, then polysulphidic crosslinks may be selectively cleaved as in the case of alkali reclamation depicted in Figure 1.11b. Monosulphidic crosslinks are also expected to be cleaved with little, if any main chain scission through a beta elimination path way but the scission of monosulphidic crosslinks did not happen as the prominent reaction in the case of crosslinked rubber in which, deprotonation was the more feasible reaction[124]. Though the process was claimed to cleave 70 to 75 per cent of the crosslinks, only comparable mechanical properties with control blends with untreated samples was achieved when blended with virgin rubber.

1.5.1.3 *Using solvent swelling methods*

A method to devulcanise rubber crumb by desulphurization of solvent swollen crumb using metallic sodium[125,126] preferably in an oxygen free environment is also reported. Molecular hydrogen is supplied which

caps the radicals that are formed when the sulphur crosslinks are removed by metal. This method is not practically viable and advisable to swell the scrap tyres in solvent containing metallic sodium. Similar approaches involving swelling of crumb in solvents is reported elsewhere[127-132]. Though these references are found in literature, none of them had successfully emerged as a viable route for devulcanisation probably due to the inefficiency associated with large scale trials.

1.5.1.4 Using chemical probes

Chemical probes used in the structural study of rubber vulcanisates[133] can be used for devulcanisation as they can selectively cleave the crosslinks in the vulcanised rubber network and can thereby cause partial or selective devulcanisation. A chemical probe is being defined as an analytical reagent, which will react in some useful way with a specific network feature, which is capable of being homogeneously introduced to the network, and which can be easily extracted after chemical reaction has been completed without side reactions. Major probes employed are triphenyl phosphine, sodium di-n-butyl phosphite, thiol-amine reagent, lithium aluminium hydride, phenyl lithium, methyl iodide and sodium sulphite. This method is also not used for large scale devulcanisation as the method involves several swelling processes which cannot be made practical in large scale. In addition, the reagents employed do not belong to the category of safe chemicals and are hence used primarily for structural characterization of vulcanisates.

Triphenyl phosphine is known to open the sulphur crosslinks and convert the polysulphide links into disulphide links and in most cases further to monosulphides[134]. Sodium di-n-butyl phosphite cleaves di and polysulphide crosslinks but leaves monosulphide and carbon-carbon crosslinks intact[135]. The process of crosslink cleavage proceeds until monosulphidic crosslinks alone remains. Thiols in combination with organic

bases can selectively cleave sulphur crosslinks[136]. Hexane thiol was found to cleave di- and polysulphidic crosslinks, while 2-propane thiol selectively cleaves polysulphidic crosslinks in a nucleophilic displacement reaction with piperidine as base. Methyl iodide reacts with organic sulphides to form trimethylsulphonium iodide and there by removes the combined sulphur in crosslinks[137, 138]. Lithium aluminium hydride (LAH) has been used for qualitative and quantitative analysis of the polysulphide content of various types of rubber vulcanisates[139, 140]. The reactions of polysulphidic crosslinks with phenyl lithium occurs rapidly at room temperature and the monosulphidic crosslinks remain intact[141].

1.5.2 Thermo-mechanical / Mechanical devulcanisation

Thermo-mechanical devulcanisation employs just heat and/or shear in the absence of chemical agents to devulcanise rubber. The negative aspect of thermo-mechanical regeneration of scrap rubber is that, with the entire shear that is used and the temperature attained, chances are high for much main chain scission leading to considerable loss of physical properties. Meanwhile, mechanical devulcanisation envisages devulcanisation of vulcanised rubber under the influence of shear alone based on stress induced chemical reactions and structural changes of materials. Under induced stress, polymer bonds are distorted and bond angle and distance are extended. When the imposed stress exceeds the chemical bonding energy, bond rupture occurs. As the reaction conditions are ambient without the use of any chemical reagents the process appears to induce minimum chain degradation under nominal shear rates.

1.5.2.1 High pressure high temperature sintering

High Pressure High Temperature Sintering (HPHTS) is a novel recycling technique that makes it possible to recycle vulcanised rubber powder made from waste rubber through the application of heat and

pressure alone[142, 143]. The authors claim that recycled rubbers produced *via* HPHTS have the potential to replace virgin rubber in numerous applications. According to the suggested mechanism of particle adhesion, the applied pressure (0.5MPa to 26MPa) compress the particles to intimate contact while the temperature (80°C to 240 °C) provides the energy necessary to break the crosslink bonds and likely some main chain bonds. This in turn allows chemical exchange reactions to occur at the particle interfaces and within the particles, which reforms the crosslinks thereby fusing or sintering the particles into a single piece. A similar approach is applied in the direct powder moulding technology for rubber recycling also[144, 145].

1.5.2.2 Devulcanisation using twin screw extruder

Several studies on mechanical devulcanisation by breaking the crosslinking points in the rubber matrix selectively in a twin screw extruder[146-152]. The mechanism of this continuous recycling process claims that, various chemical reactions corresponding to selective breakage of crosslinking points can be efficiently controlled by optimizing the parameters in the reactor such as shear, stress, reaction temperature and internal pressure[153]. The reactor consists of three zones *viz.* pulverizing zone, devulcanising zone and cooling zone. In the pulverizing zone the crushed rubber material is converted into fine particles by shear stress and heated to devulcanisation reaction temperature quickly. The residence time assured is to be long enough to complete the devulcanisation reaction under shear flow in the following devulcanisation zone in which, fine particles of crosslinked rubber become highly elongated by filling and shearing with the kneading disc elements and are thus eventually plasticized.

According to the theory proposed, as the bond energy difference between carbon - carbon (C-C), sulphur - sulphur (S-S) and carbon - sulphur (C-S) bonds are small, simple heating of vulcanised rubber in a pressure vessel as in the case of reclamation will result in unselective bond cleavage

leading to poor physical properties of thus regenerated rubber. At extremely higher shear stresses induced by filling and kneading in the reactor, most of the rubber molecules may become fully elongated to their limited extensibility. But as the elastic constant value (k) for the S-S bonds are about 1/30th of that for the C-C bonds, the S-S bonds with lower k value may become more extended in comparison with bonds having higher elastic constant (C-C bonds) thereby causing selective scission of S-S bonds of crosslinking points as represented in Figure 1.12[153].
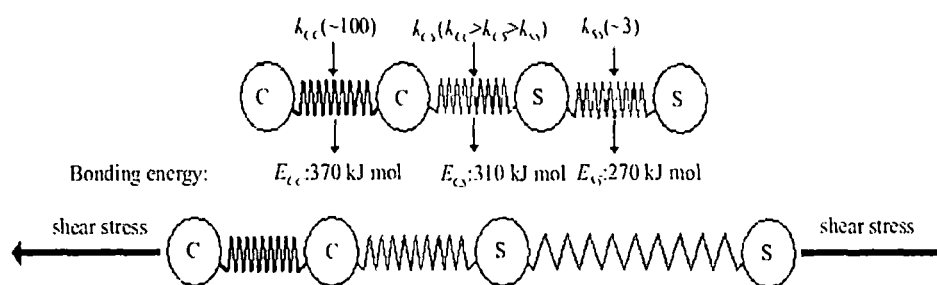
Figure 1.12 Scheme of decomposition of sulphur crosslinking bonds under a shear field in twin screw extruder

Revulcanisate properties of waste ground rubber tyre (GRT) powder devulcanised using a twin screw extruder with and without devulcanising chemicals in comparison with the mechanical properties of a commercial devulcanised GRT (reclaim) (Table 1.5) was found to have comparable results except for the higher elongation and the associated lower modulus of revulcanised commercial reclaim[154].

1.5.2.3 Devulcanisation using HSM technology

The objective of patented HSM devulcanisation technology is to devulcanise rubber production scraps and reintroduce them into the production chain through a 100% mechanical process[155]. The essence of this approach is the use of mechanical stresses to selectively break crosslinking

bonds, thereby returning a previously cured viscoelastic material to a soluble state for recycling into existing or new formulations. For sulphur bonded system, examination of the bond strengths indicates that under certain conditions, the sulphur bonds are weaker than the carbon-carbon bonds. The bonds within the crosslink should therefore break before the carbon backbone. It can therefore be reasoned that if stress is correctly applied across the total network, then the crosslinks should break preferentially.

Table 1.5 Comparison of revulcanisate properties of GRT powder devulcanised using a twin screw extruder with commercial devulcanised rubber

Properties	Without chemicals	With chemicals	Commercial reclaim
Tensile strength, MPa	6	7.5	7
Elongation at break,%	120	140	205
Modulus at 100%, MPa	5	5	2.6
Hardness, Shore A	65	62	70

Formulation: Devulcanised rubber - 100; ZnO - 5; stearic acid - 3; Accinox-TQ - 0.8; CBS - 0.8; Sulphur – 1.5

A new class of machine has been developed to apply the stresses required to rupture the crosslink bonds. This process is claimed to be applicable to any kind of used rubber product in which devulcanisation is achieved by a special rotor / stator design with variable parameters such as temperature regulated at a maximum of 80°C to protect the compound and maintain properties. The machine geometry moves the material through a series of high-stress and relaxation zones whilst the integrated cooling system ensures that the material remains at controlled temperatures during the mixing cycle.

1.5.2.4 Other methods

Solid state milling[156-159] and mechanical grinding in a two roll mill[160] appear to be a simple, low cost method for the devulcanisation of crosslinked rubber vulcanisates at ambient temperature without the use of any chemicals. The mechanical properties of revulcanised samples after mechanical devulcanisation of a tread formulation are given in Table 1.6[160].

Table 1.6 Revulcanisate properties of retread compound after mechanical devulcanisation

Properties	Virgin	Revulcanised
Tensile strength, MPa	23.8	16.5
Elongation at break,%	630	355
Modulus at 300%, MPa	7.9	12.3
Tear strength, N/mm	103.6	35.5
Hardness, Shore A	60	65

Revulcanisation formulation (phr) : Devulcanised rubber - 100; Virgin rubber – 10; ZnO - 2.5; MBTS - 0.9; Sulphur – 1.5

Some other methods like straining of solvent swollen rubber through the tiny pores of a metallic plate[161], and impinging vulcanised rubber by ultra-high-speed fluid jet[162] were also reported. Some of these methods, especially the mechanical grinding at ambient temperatures point to the possibility of devulcanisation of in-house waste of any manufacturing unit with the existing facilities and capabilities.

1.5.3 Mechano-chemical devulcanisation

Most of the mechano-chemical devulcanisation processes like the De Link process[163,164] and the Lev Gum process[165] uses mechanical shear along with chemical modifiers for devulcanisation. Since the processes take place on a two roll mill in the presence of air, there would be a reduction in polymer molecular weight which will in turn increase the plasticity of the

devulcanised sample along with the plasticity increase brought in by the crosslink scission. This point to the fact that assessment of efficiency of mechano-chemical devulcanisation based on the initial viscosity of the devulcanised samples might sometimes be misleading. In earlier studies of mechano-chemical devulcanisation, combinations of accelerator, ZnO, softening agents and peptizing agents were used as devulcanisation agents. Later, processes employing various other devulcanising agents also came to picture.

1.5.3.1 Devulcanisation using disulphides

Disulphides are widely employed class of devulcanisation agents. Several reports on the use of various disulphides for devulcanisation studies[166-169] were found in literature. The proposed mechanism through a four step sequence is demonstrated in Figure 1.13.

Step I.	Thermal degradation of diphenyl disulphide into reactive radicals which would then attack the crosslinks to bring about the actual devulcanisation.
Step II.	Breaking of sulphur crosslinking bond under the action of the reactive radicals
Step III.	Formation of new active crosslinking site to ensure good revulcanisation of the devulcanised sample
Step IV.	Revulcanisation process in which the regenerated rubber can be revulcanised alone or mixed with fresh rubber as per the product requirements

. The revulcanisate properties of mechano-chemically devulcanised unfilled natural rubber using 1 phr diaryl disulphide on a two roll mill, cured with high, medium and low sulphur formulations[169] (Table 1.7) reveal that, the per cent retention of tensile strength is higher for the revulcanisates

whose initial vulcanisates are cured with medium and low sulphur formulations.
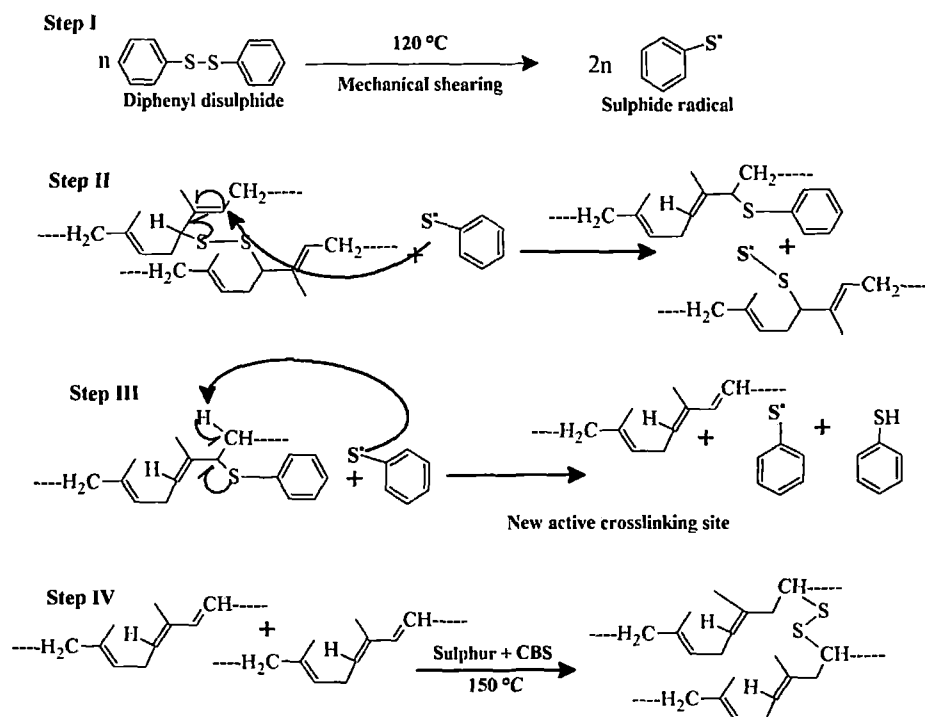
Figure 1.13 Mechanism of devulcanisation using disulphides

Also, the per cent retention of tear strength of revulcanisates from low sulphur cured original sample is the highest whereas the other two have comparable tear strength retention upon revulcanisation. As the results are in contradiction with the existing understanding that, high sulphur cures leading to predominantly polysulphidic linkages which are easier to break, it might be an indication of the role of the cure system employed for the vulcanisation of original compound as well as the revulcanisate, and the crosslink densities of these samples on the revulcanisate properties.

Table 1.7 Mechanical properties natural rubber vulcanisates and its revulcanisates after devulcanisation using diaryl disulphide

ᵔroperties	High Sulphur		Medium sulphur		Low sulphur	
	Original	Revulc	Original	Revulc	Original	Revulc
ensile strength (MPa)	16.82	9.4	15.34	12.11	16.87	14.44
longation at break (%)	1048	1006	1333	1065	1300	1011
[100 (MPa)	0.51	0.64	0.62	0.62	0.53	0.56
[300 (MPa)	0.81	0.96	0.93	0.95	0.85	0.85
ear strength (N/mm)	23.23	18.1	22.5	17.1	18.26	16.57
hore A hardness	40	38	36	37	32	36
rosslink density (mole $cm^{-3} \times 10^4$)	0.7	0.42	0.63	0.44	0.58	0.4

Vulcanisation/revulcanisation formulation (phr):Sulphur-2.2 & CBS-0.6(high sulphur); sulphur – 1.4 & CBS- 1.2 (medium sulphur); sulphur – 0.6 & CBS – 2 (low sulphur)

1.5.3.2 The De Link process

De Link process[163,164,170] envisages a mechano-chemical devulcanisation process in which mechanical shear exposes fresh rubber surfaces which is being reacted upon by the De Link reactant - a mixture of rubber accelerators and activators – which uncouples the sulphur crosslinks in a vulcanised network. The De Link system is claimed to be a novel recycling method which leads to rejuvenation or reincarnation of scrap tyre employing a unique Sekhar-Kormer-Sotnikova (SKS) reaction.

The reactant *viz.* De Link R, together with mechanical shearing causes the uncoupling of the sulphur crosslinks of the vulcanised rubber in Step I of the process, providing a final compound which is ready to be moulded and vulcanised without further addition of any vulcanising agents (Step II) as illustrated in Figure1.14. Though the mechanism of SKS reaction is shear mediated, the concept of inducing changes in degree of crosslinking of vulcanisates containing polysulphidic crosslinks in the presence of free accelerators were previously reported[171]. According to this study, exchange reactions take place between the polysulphidic crosslinks of the vulcanisate and the free accelerator containing S-S or S-N bonds.
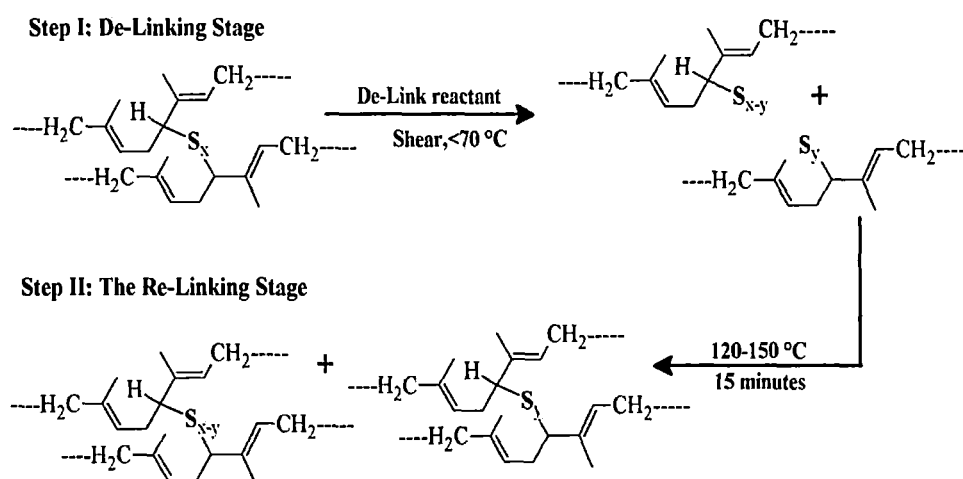
Figure 1.14 Reaction mechanism proposed for De Link process

Vulcanisate properties obtained for blends of virgin rubber and different types of vulcanised scrap devulcanised using De Link master-batch[164] (Table 1.8) show that the nature of scrap used for devulcanisation and quantity of devulcanised rubber incorporated plays an important role in determining the vulcanisates properties of the end product.

Table 1.8. Vulcanisate properties obtained by devulcanisation using De Link masterbatches.

Type of vulcanised scrap	NR : De Link, 10:90		NR : De Link, 50:50	
	Tyre tread	Gloves	Tyre tread	Gloves
Tensile strength, MPa	11.5	17	11	10
Elongation at break,%	250	860	250	610
Elongation set ,%	5	10	6	15

1.5.3.3 Devulcanisation using benzoyl peroxide

Devulcanisation of natural rubber compounds by means of addition of different amounts of benzoyl peroxide at temperature of 80°C (BPO) as a devulcanising agent in a sigma mixer (at a rotor speed of 60 rpm) have also been investigated and a plausible reaction mechanism was suggested[172]. The proposed reaction mechanism involving the following three steps is illustrated in Figure 1.15.
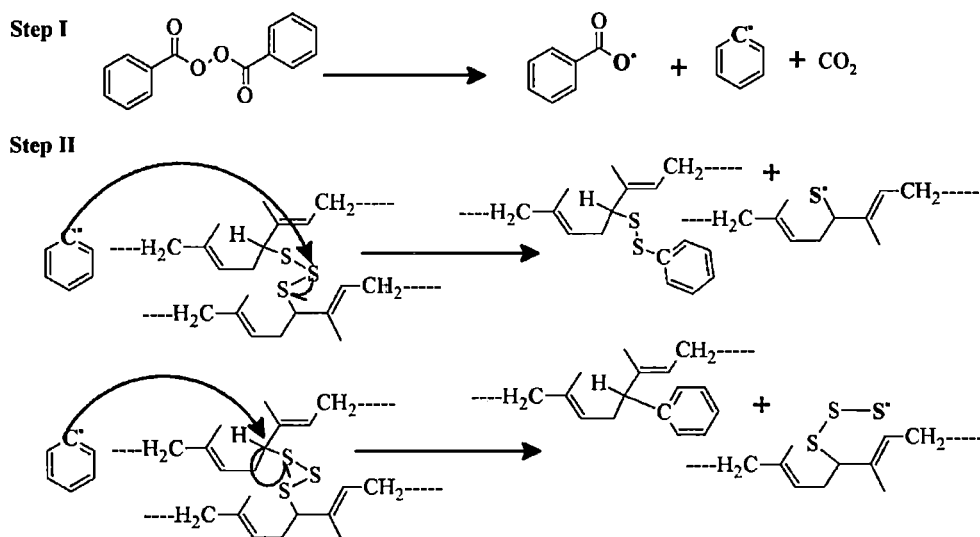
Step III
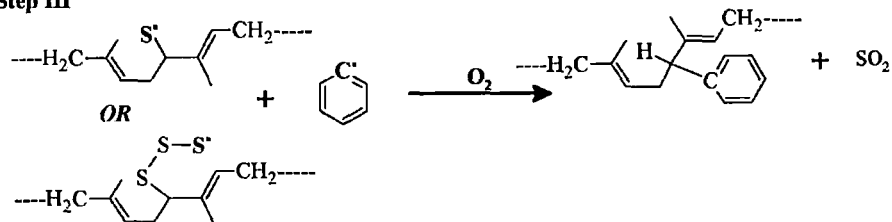
Figure 1.15 Mechanism of devulcanisation by benzoyl peroxide

Step I: Homolytic clevage of benzoyl peroxide to form benzoyl radical which gets converted into phenyl radical

Step II: Phenyl radical reacting with the weakest S-S bonds causing crosslink scission

Step III: Generation of sulphur dioxide

The mechanical properties of revulcanised gum samples after chemical and mechano-chemical devulcanisation using benzoyl peroxide as devulcanisation aid is given in Table 1.9.

Table 1.9 Revulcanisate properties of natural rubber devulcanised using benzoyl peroxide

Properties	Original	Chemical*	Mechano-chemical
Tensile strength (MPa)	15.01	13.72	11.15
Elongation at break (%)	1200	1151	1101
M100 (MPa)	1.01	0.92	1.04
M300 (MPa)	1.50	1.23	1.43

*Devulcanisation in xylene at 80°C using BPO as devulcanising agent
Revulcanisation formulation (phr): ZnO - 5; stearic acid – 2; Antioxidant - 1; sulphur – 2; CBS - 1

1.5.3.4 Lev Gum process

Lev Gum process is an industrially practiced mechano-chemical devulcanisation method carried out at room temperature and involves pouring the shredded rubber and a modifying composition in between two rollers that further crush the particles[173]. The process claims that the superior nature of the recycled rubber obtained by Lev Gum process ensures up to 30% replacement of the total rubber used for each tyre, thereby helps to drastically reduce the cost of the product[174]. The modifying composition is a mixture of (i) a chemical substance, which is disposed towards dissociation and formation of an organic cation and amine and (ii) another chemical as promoter of dissociation of the first chemical substance, and containing a functional group constituting an acceptor of the said amine. The modifier contains urea or a mono, di or tri-substituted derivative of it as the first substance and a dicarboxylic acid with two to four carbon atoms in the main chain as the second chemical substance in the molar ratio ranging from about, 0.5:1 to 2.5:1 added to the cured elastomer in an amount ranging from 0.25 to 4 per cent. A general representation of the interaction scheme of the modifier's components and the scheme of interaction between urea or its derivative with dicarboxylic acid to form ionic compound which will in turn react with the polymer network along the inter-chain bonds leading to its destruction, is outlined in Figure 1.16.

The patent claims that ionic compound containing the ions A+ and ⁻Y-BXH attacks chemical bonds of the polymer network. Cation A+ appears to be the main attacking agent, however it is not inconceivable that anion ⁻Y-BXH can also break down the bonds C-S and S-S. As per the claim by the inventers, the energetical level of cation (A+) is lower than the energetical level of proton, and owing to this fact the process claims selective break down of the C-S and S-S bonds with much less effect on the C-C bonds
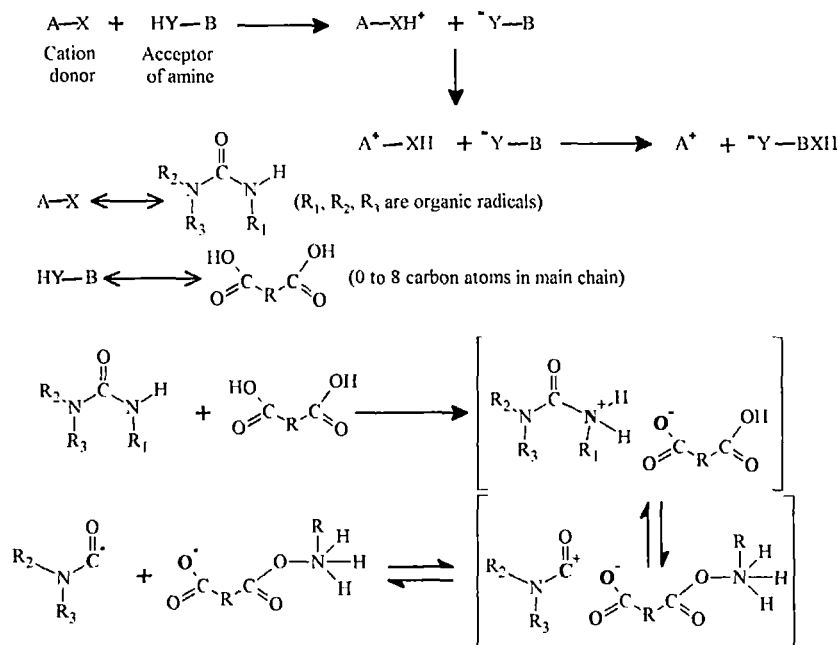
Figure 1.16 Devulcanisation mechanism proposed for Lev Gum process

The 300 per cent modulus, elongation at break and tensile strength of car tyre buffings devulcanised using 4 per cent of the Lev Gum modifier (urea and adipic acid) followed by blending with 23per cent virgin natural rubber was reported as 13.8MPa, 350per cent and 18.5MPa respectively[173]. As the corresponding results for a control vulcanisate was not provided, the efficiency of the process cannot be ascertained.

1.5.3.5 Devulcanisation using thiuram disulphides

A method of mechano-chemical devulcanisation of waste natural rubber using thiuram disulphides [tetramethyl thiuram disulphide (TMTD) and tetrabenzyl thiuram disulphide (TBzTD)] on a two roll mixing mill in which, the thiuram compound acts as the devulcanising agent during the

devulcanising process and as a curing agent during revulcanisation, are found in literature[175,176]. The proposed mode of action of the devulcanisation agent involves three steps as outlined in Figure1.17

Step I : Breaking of thiuram disulphide into radicals

Step II : Combination of reactant radicals with broken crosslink or polymer radicals

Step III : Chain extension during final part of millling

The mechanical properties of revulcanised GRT samples after mechano-chemical devulcanisation on a two-roll mill in the presence of varying concentrations of TBzTD indicate that the tensile strength of the revulcanised samples are not influenced by the concentration of thiuram disulphide[175] (Table 1.10). The changes in per cent elongation and modulus observed with the results seem to be related to the general response of the variation of these properties to curative dosage during vulcanisation rather than any effect of devulcanisation.

Table 1.10. Revulcanisate properties of GRT devulcanised with TBzTD

Properties	Concentration of TBzTD (phr)			
	2	3	4	5
Tensile strength (MPa)	6.17	5.35	5.59	5.25
Elongation at break (%)	180	155	140	125
Modulus at 100 % (MPa)	2.94	3.34	3.79	4.24
Shore A hardness	69	70	72	75

Revulcanisation formulation (phr): ZnO - 5; stearic acid – 2; sulphur – 0.5

Step I

Step II

Step III
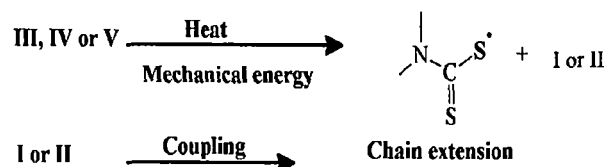
Figure1.17 Mechanism of devulcanisation assisted by thiuram disulphides

1.5.3.6 High pressure high temperature sintering with incorporated additives

A mechano-chemical devulcanisation process in which various organic compounds of different chemical structures such as dienophiles, dipolarophiles and organic acids are incorporated along with HPHTS process is also reported[177]. The additives are expected to slow/ stop conjugated diene formation either by reacting directly with zinc complex or to the rubber backbone during the sintering process resulting in an increase in mechanical properties of the devulcanised samples after revulcanisation. The action of maleic anhydride on rubber was previously reported and the reaction is proposed by the formation of links between double bonds either in the same chain or in adjacent molecules[178].

Figure 1.18 demonstrates the proposed scheme for crosslink scission and the interactions of the additives with the polymer. Three cases are represented denoting the crosslink scission taking place during the sintering process and the consecutive rearrangements leading to the formation of poly-ene structures from case I: polysulphidic crosslinks, case II: monosulphidic crosslinks, case III: the Diels Alder reaction and thionyl cycloaddition of these structures with the additives. The influence of various additives on the tensile properties of sintered gum natural rubber suggests that the mechanical properties of sintered materials can be improved by incorporating small amounts of dienophiles or dipolar organic additives[177].
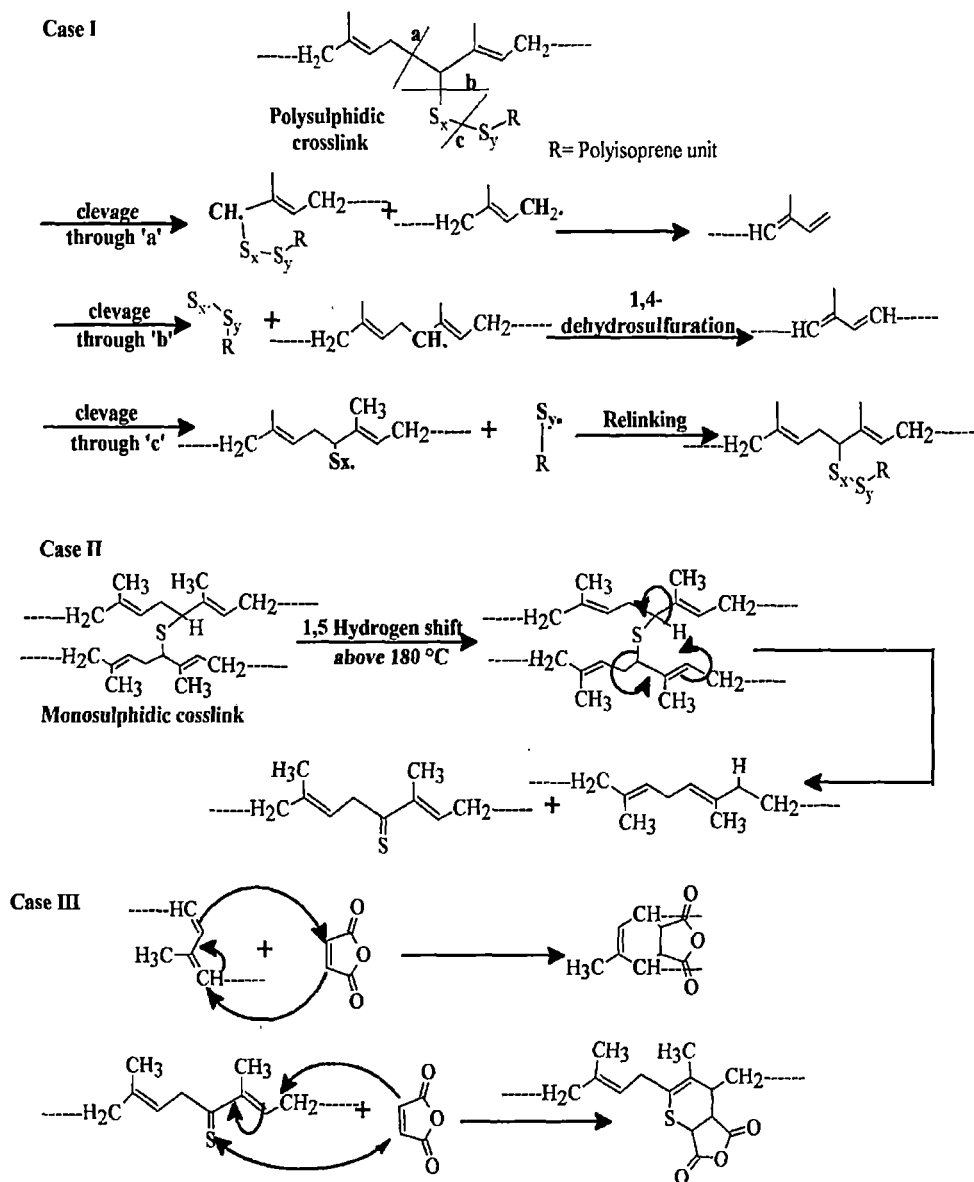
Figure 1.18 Breaking of crosslinks during sintering (case I and case II), Diels Alder reaction and thionyl cycloaddition of the derived products.

The influence of various additives on the tensile properties of sintered gum natural rubber as given in Table 1.11, claim that the mechanical properties of sintered materials can be improved by incorporating small amounts of dienophiles or dipolar organic additives.

Table 1.11 Effect of additives on sintered natural rubber

Properties	NR original	NR sintered	NR sintered with	
			2% phthalic anhydride	4% phthalimide
Tensile strength, MPa	12.9	5.3	8.9	9.6
Elongation at break,%	417	516	499	534
M100, MPa	1.8	0.9	1.1	1.4

1.5.3.7 Other processes

The mechanism of devulcanisation of sulphur vulcanised natural rubber with aromatic disulphides and aliphatic amines under various temperature conditions through model compound studies showed that higher ranks of the sulphide crosslinks are devulcanised quite easily whereas the lower trisulphidic and disulphidic crosslinks reacted slowly[179]. The monosulphidic crosslinks did not devulcanise at all in the temperature range used for the study.

Another patented process of mechano-chemical devulcanisation in a two-roll mill at ambient conditions employs a novel devulcanising agent containing two types of constituents *viz.* (i) a reactant species which can penetrate the rubber matrix and destabilize the sulphur - sulphur and carbon – sulphur bonds leading to their delocalization and (ii) an anti-stick material serving as an ash-less solid, preferably inorganic crystalline filler whose role is to promote deformational tension between rubber polymers during the mechanical action in devulcanisation and coat the fragmented rubber

particles in order to inhibit their sticking[180]. The reactant component is selected from organic compounds which contain carbonyl and amine or amide functional groups, specifically aminoacids, carbamates, isocyanurates, carboxylic acid amides and similar compounds. The comparison of vulcanisate properties obtained by incorporation of buffing dust devulcanised by this method to those cases where untreated buffing dust is incorporated as such, made the observation that the devulcanisation of the buffing dust by the said process allows incorporation of higher loadings of the same into new products with better retention of vulcanisate properties[180].

The results of comparison of four different devulcanisation techniques for the mechanochemical devulcanisation of ground tyre rubber (GTR) *viz.* low temperature mechanical shearing (LTSR, <40°C), high temperature mechanical shearing (HTSR, 180°C), shearing in a twin screw extruder (TSER, 200-240°C) [all three processes in the presence of rubber regeneration activator, RA 420] and reclaiming by high pressure super critical carbon dioxide in the presence of diphenyl disulphide (SCO2R, 180°C) is reported[181]. The study pointed that, low temperature shear devulcanisation is superior to other processes under comparison with regard to revulcanisate properties. Many similar process making use of different devulcanisation agents, and devulcanisation equipments are also found in literature[182-189].

1.5.4 Ultrasonic devulcanisation

Ultrasonic devulcanisation of rubbers is based on the use of high power ultrasound electromagnetic radiation and was most extensively studied by Isayev and coworkers[190-207]. Ultrasonic waves at certain levels, in the presence of pressure and heat can quickly break up three dimensional networks in vulcanised rubber. An ultrasonic field creates high frequency extension - contraction stresses in various media. High oscillation amplitude

can cause cracking in solids and cavitation in liquids. Acoustic cavitation of a solvent accompanied by fast movement of tiny resonating bubbles is considered to be responsible for the breakage of the macromolecules. The acoustic cavitation mechanism can be used to concentrate the ultrasonic energy at local sites of the molecular chains. It would allow the transformation of the relatively low energy density of the ultrasonic field to a high energy density in the proximity of the collapsing cavity. This local energy concentration will lead to drastic effects, such as the breaking of chemical bonds according to their energy level. The characteristics of ultrasonic waves that generate local effects are proposed to be most suitable to initiate the devulcanzation process since the bonds at crosslink sites have lower bond energy than the carbon - carbon (C-C) bonds of the main chain.

The process of ultrasonic devulcanisation appears to be very fast, simple, efficient and free of solvents and chemicals. Experiments have been carried out on ultrasound devulcanisation of several types of rubbers and their blends. Structural studies of ultrasonically treated rubber show that the breakup of chemical crosslinks is accompanied by the partial degradation of the rubber chains, *i.e.*, the C-C bonds. The degree of degradation of C-C bonds can be substantial depending on the conditions. Ultrasonic devulcanisation also alters the revulcanisation kinetics of rubbers. The specialized technological requirements needed for the conduct of the process challenges large scale application of ultrasonic devulcanisation.

1.5.5 Microwave devulcanisation

Microwave technology has also been proposed to devulcanise waste rubber employing microwave electromagnetic energy to break the S-S or C-S bonds[208-211]. The material absorbs the microwave radiation through molecular interaction with the electromagnetic field and gets converted to heat thereby raising the temperature of the material rapidly to about 260-350°C. Microwave heating is based on the interaction of the oscillating

electrical field of microwaves with the molecular dipoles and/or charged ions present in the sample. Microwave irradiation triggers heating by three main mechanisms: dipolar polarization, ionic conduction and interfacial polarization. However, the material to be used in microwave process must be polar enough to accept energy at a rate sufficient to generate the heat necessary for devulcanisation. Microwave energy at 915-2450 MHz is sufficient to cleave crosslink bonds but insufficient to cleave polymer chains and hence believed that, as microwave energy can allow heat propagation inside the material, devulcanisation efficiency can be improved at reduced processing time with cost savings. Study on the chemical modifications in SBR by microwave devulcanisation pointed that the high temperature applied during the process causes degradation of polymer backbone and induce chemical modifications generating devulcanised rubber with inferior properties[212]. To improve devulcanisation efficiency and reduce treatment energy, promising new approaches consisting of combined microwave irradiation with the effect of diphenyl sulphide[213], impregnation of the waste rubber with ionic solvent and then heat treating the impregnated material with microwave radiation[211], were also attempted

1.5.6 Biological/Biotechnological devulcanisation

Biological devulcanisation of vulcanised rubber has been used in some cases, although vulcanised materials are resistant to normal microbial attack. Several researchers have reported the use of different types of micro organisms to attack the sulphur bonds in vulcanised elastomers[214-221].

Irrespective of all these innovations large space and time requirements challenge the industrial expansion of biotechnological devulcanisation processes among which the innovations by Recyclatech group were an exception which envisages the reprocessing of used tyres into reusable rubber, economically, profitably and without any negative environmental impact[216,22-224].

1.6 SCOPE AND OBJECTIVES OF THE PRESENT WORK

It is well clear from the review that, the reclamation/ devulcanisation processes delivers either highly degraded or partly devulcanised products whereas products of other recycling strategies are favored consumables for industries like civil engineering or power generation rather than the rubber industry. Hence the current recycling methods centered on energy and material recovery renders only a minute fraction of the total annual output of used rubber brought back to the rubber industry.

The mechano-chemical processes, which are hailed to be the most effective and practical of the numerous devulcanisation strategies were found to have a common mechanism irrespective of the variations in the devulcanisation agent used and resulted in devulcanised samples with comparable revulcanisate properties. The generally accepted mechanism of the mechano-chemical devulcanisation processes claims to involve chemical attack of the devulcanising chemical on cross links leading to its scission and/or arresting of the recombination of free radicals which are generated during the crosslink scission under the influence of shear. On the other hand it is interesting to note that the revulcanisate properties of both mechanically and mechano-chemically devulcanised rubbers are comparable. These facts points towards the incapability of these chemicals either to induce crosslink scission reactions or to arrest the recombining of the radicals generated from crosslink scission by shear force.

Hence, it could be assumed that any species which could instantaneously and efficiently react with the free radicals generated from crosslink scission thereby preventing their recombination could improve the per cent devulcanisation associated with any devulcanisation processes taking place under the influence of shear. In this context, the capability of stable free radicals as an aid for mechanical devulcanisation seems relevant.

Since, stable free radicals exist in the free radical form itself, and are stable at room temperature and above; these species could possibly act as apt agents for instantaneous and effective stabilization of free radicals generated from crosslink scission. The advantage associated with these stable free radicals are that, the initial step for the generation of free radical from the chemicals employed as devulcanisation agents (as in the case of other mechano-chemical devulcanisation processes) is not necessary for stable free radicals. The absence of such an instantaneous stabilization of free radicals generated from crosslink scission during devulcanisation processes might be the limiting factor in the contemporary mechano-chemical devulcanisation processes.

Thus, the main objective of the present work is to analyze the role of stable free radical as an aid for mechanical devulcanisation and to address the possibilities and limitations associated with the process. In order to achieve this target, the following studies were carried out.

- Mechanical devulcanisation of carbon black filled natural rubber vulcanisates of known composition and properties
- Examine and compare the current mechano-chemical devulcanisation processes with mechanical devulcanisation
- Use of stable free radicals to aid mechanical devulcanisation process and comparison of the process with mechanical and the current mechano-chemical devulcanistion processes
- Influence of various factors on stable free radical assisted mechanical devulcanisation such as
  - o stable free radical concentration
  - o cure system employed for the vulcanisation of original sample
  - o type and amount of filler present in the sample to be devulcanised

- o type of rubber vulcanisate to be devulcanised
- o crosslink density of the sample to be devulcanised
- Stable free radical assisted mechanical devulcanisation of ground tyre rubber (GTR) and tyre tread buffing dust
- Studying the effects of incorporation of devulcanised rubber into new compounds
- Investigations on the reasons of the low scorch on revulcanisation of devulcanised rubbers

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Chapter 2

Experimental

This chapter includes a detailed description of the materials used, test methods employed for experiments and the various analytical techniques conducted for testing.

2.1 MATERIALS

Natural rubber (ISNR 5) was obtained from Pilot Crumb Rubber Factory (PCRF), Rubber Research Institute of India (RRII), Kottayam; Styrene butadiene rubber (SBR), Acrylonitrile butadiene rubber (NBR), Poly butadiene rubber (BR), Ethylene propylene diene rubber (EPDM) are the elastomers used. Carbon blacks of different particle size such as intermediate super abrasion furnace black (ISAF), general purpose furnace black (GPF), high abrasion furnace black (HAF), and fast extrusion furnace black (FEF) were used as filler. Commercial rubber chemicals such as zinc oxide (ZnO), stearic acid, process oil [naphthenic oil and paraffinic oil, Di octyl phthalate (DOP)], antioxidant [1.3- dimethylbutyl N' phenyl p-phenylenediamine (mernox 6 C), 2,2,4-trimethyl1,2-dihydroquinoline (TDQ)], accelerators [2-mercaptobenzothiazole (MBT), Zinc dimethyldithiocarbamate (ZDMC), N-Oxydienthylene-2-benzothiazole sulphonamide (MOR), 2,2'dibenzothiazyldisulphide (MBTS), Tetrabenzylthiuramdisulphide (TBzTD), 4,4'-dithiodimorpholine(DTDM), N-cyclohexyl-2-benzothiazolesulpenamide (CBS)] and sulphur was used to prepare carbon black filled rubber vulcanisates of known composition and properties in the laboratory. Dicumyl peroxide (DCP) of 100% activity was used for peroxide curing of vulcanisates.

Propane-2-thiol and hexane thiol were purchased from Sigma Aldrich Chemicals pvt. Ltd. and piperidine was bought from Merck, Germany. Laboratory grade solvents such as toluene, acetone and petroleum spirit were also used. Commercial tyre tread buffings supplied by Midas Mileage Private Limited, Kottayam, Kerala was characterized by thermogravimetric (TG) analysis as given in Table 2.1. Stable free radical 4-hydroxy-2, 2, 6, 6-tetramethylpiperidine-N-oxyl (4-Hydroxy TEMPO, abbreviated as 4HT) purchased from Mereck, Germany was used as devulcanisation aid.

Table 2.1. Composition of buffing dust and GTR from TG analysis

Components		Buffing dust		GTR	
		Per cent	Phr	Per cent	Phr
Polymer	NR	40	70	25.9	48
	BR	17.2	30	26.1	50
Carbon black		31.4	55	33.8	33.8
Acetone extractable		6.9	12	5.2	5.2
Ash		5	8	9	9

2.2 METHODS

2.2.1 Preparation of carbon black filled rubber vulcanisates

Carbon black filled rubber vulcanisates with known composition and properties were prepared in the laboratory following respective formulations. The master batches were prepared using an internal mixer one litre capacity. The curatives were added into the master batch on a two roll laboratory mixing mill of 15cm x 30cm. The mixing protocol is outlined in Table 2.2. The formulation adopted for the preparation of carbon black filled natural rubber (NR) vulcanisates are given in Table 2.3.

2.2.2. Preparation of aged samples

Carbon black filled natural rubber (NR) vulcanisates aged in laboratory oven under different conditions were devulcanised to simulate the devulcanisation of commercially available used rubber products which have undergone different levels of degradation in their service lives. The tensile sheets prepared were aged in the laboratory oven. Two ageing conditions were practised *viz.* ageing at 70°C for 7 days and ageing at 100°C for 3 days. The vulcanisate properties of the aged samples were determined. The aged samples were devulcanised and the percentage retention of properties on revulcanisation was calculated.

Table 2.2 Mixing schedule of compounds prepared in the laboratory

Mixing equipment	Description	Mixing time, min
Internal mixer**	Rubber	0
	½ carbon black	0.5
	½ carbon black	1.5
	Oil	3.5
	Anti oxidant	4
	Activators*	4.5
	Dump	6
Two roll mill***	Mastication of material from internal mixer	7
	Accelerator	8
	Sulphur*	9.5
	Compound finishing	12

*For sulphur curing;

**70rpm & 40°C;

***ambient temperature, & friction ratio 1:1.25

2.2.3. Devulcanisation and revulcanisation

Devulcanisation was carried out in a laboratory two roll mixing mill of 15cm x 30cm size manufactured by David Bridge & Company (Model 172) Castleton Rochdale, England and at a friction ratio 1:1.25 (12:15 rpm). Cold water was circulated through the rolls during devulcanisation to prevent the increase in temperature during the shearing process thereby ensuring minimal thermal degradation of polymer. The devulcanisation of commercial tyre tread buffing sample was carried out by passing it directly through the tight nip (approx.05mm) of two roll mill. In the case of compounds prepared in the laboratory, the tensile sheets moulded were cut into chips of about 1cm^2 size, made into crumb by passing through the two roll mill. The crumb thus produced was devulcanised by passing through the tight nip of two roll mill. 10g of virgin rubber was added per 100g of the crumb for consistency and easy handling after devulcanisation.

Table 2.3 Formulations used for preparation of original NR vulcanisates

Ingredients	Quantity (phr)		
	CV	Semi EV	EV
Natural Rubber	100	100	100
HAF black	40	40	40
Aromatic oil	4	4	4
CBS	0.6	1.5	5
Insoluble sulphur	2.5	1.5	0.5

Common ingredients: TDQ - 1.5; Zinc oxide – 5; Stearic acid -2

Mechanical devulcanisation was carried out by passing the crumb through the tight nip without adding any devulcanising agent or aid. In the

case of mechano-chemical devulcanisation, the crumb rubber mixed with the required amount of devulcanising agents/ aid was passed through the tight nip of two roll mill. Curatives are added according to the respective revulcanisation formulation and moulded in an electrically heated hydraulic press for their respective cure times.

2.2.3.1 Optimization of devulcanisation parameters

Various devulcanisation parameters were optimized using pre-cured tyre tread buffing dust as described below.

Dosage of curatives

Devulcanisation of buffing dust was carried out and revulcanised with three different formulations as given in Table 2.4. The time for devulcanisation was arbitrarily fixed as 7 minutes observing the behaviour of the crumb on the mill. The buffing dust began to form a band on the roll at about 5 minutes of passing through the tight nip which was then passed for additional two minutes.

Table 2.4 Formulations used for optimising curatives for revulcanisation

Ingredients	Quantity (phr)		
	High sulphur	Medium sulphur	Low sulphur
Devulcanised rubber	100g	100g	100g
Virgin rubber	10	10	10
TDQ	1.5	1.5	1.5
Zinc oxide	5	5	5
Stearic acid	2	2	2
MOR	0.8	0.8	0.8
Insoluble sulphur	2.5	1.5	0.5

10g virgin rubber was added to the devulcanised sample, homogenized by passing through the tight nip for 8 times followed by the addition of revulcanising agents. All other ingredients except curatives were provided as if in the case of a normal CV cure system considering that devulcanised rubber has a rubber content of 50%. The dosage of accelerator was kept constant and amount of sulphur was varied. The devulcanised samples were then moulded in a hydraulic press for their respective cure times, evaluated the physical properties and the curative dosage was optimized.

Number of passes through the mill

100g of the buffing dust was passed through the tight nip of the two-roll mill for 25, 30, 35, 40, 45, 50, 55 and 60 numbers of passes. After respective numbers of passes10g of virgin rubber was added followed by curatives as per the optimized dosage. The cure characteristics and the vulcanisate properties of the devulcanised samples were evaluated. The experiments revealed that optimum number of passes is highly dependent on the type of the sample employed and can be ascertained to a greater extend from the changes in the behaviour of sample during devulcanisation process.

Amount of Virgin rubber added

After optimising the number of passes required to obtain the best revulcanisate properties, the minimum amount of virgin rubber required per 100g of the buffing dust was optimized by varying the amount of virgin rubber added.

The optimized revulcanisation formulation for the devulcanised rubber is given in Table 2.5.

Table 2.5 Optimised revulcanisation formulation

Ingredients	Quantity (phr)
Devulcanised rubber	100g
Natural Rubber	10g
TDQ	1.5
Zinc oxide	5
Stearic acid	2
MOR	0.8
Insoluble sulphur	1.5

Rubber hydrocarbon of devulcanised rubber = 50%

2.2.3.2 Preparation of blends of devulcanised rubber and virgin rubber

Blends of devulcanised rubber and virgin rubber were prepared in a laboratory two roll mill. The virgin rubber was initially masticated for about 5 minutes followed by incorporation of devulcanised rubber. Once a smooth band was formed on the roll, carbon black was incorporated along with process oil followed by other ingredients.

2.3 CHARACTERIZATION

Characterization of devulcanised samples was carried out by different tests as discussed below.

2.3.1 Crosslink density

The crosslink densities (CLD) of the original samples and the residual crosslink densities of the devulcanised samples were determined by swelling in toluene applying Flory Rhener equation[1,2] given below. Correction for filler[3] is not applied for volume fraction (φ) calculation in the case of chemical probe analysis, as the carbon black of samples ooze out of the vulcanisate after probe treatment making the amount of filler a variable

(Equation 3). In other cases the Equation 4 with filler correction was used for calculating the volume fraction of rubber.

$$Mc = \frac{\rho r \times V \left(\varphi^{1/3} - \frac{\varphi}{2}\right)^2}{\{\ln (1 - \varphi) + \chi\varphi^2\}} \quad \text{----------(1)}$$

$$\nu = \frac{1}{2Mc} \quad \text{----------(2)}$$

$$\varphi = \frac{\dfrac{Dw}{\rho r}}{\left\{\dfrac{Dw}{\rho r} + \dfrac{(Sw - Dw)}{\rho s}\right\}} \quad \text{----------(3)}$$

$$\varphi = \frac{(D - FH)/_{\rho r}}{\left\{(D - FH)/_{\rho r}\right\} + \left\{(Sw - Dw)/_{\rho s}\right\}} \quad \text{----------(4)}$$

φ = Volume fraction of rubber in swollen gel

Dw = Deswollen weight of sample

ρr = Density of rubber

ρs = Density of solvent

Sw = Swollen weight of sample

F = Weight fraction of the insoluble components

H = Initial weight of the sample

Mc = Molecular weight between crosslinks

V = Molar volume of solvent

χ = Polymer solvent interaction parameter

ν = Crosslink density in molecm^{-3}

The determination of crosslink density was carried out as follows. About 0.5g test piece of the sample was swollen by dipping it in excess amount of toluene for 48 hours in a closed container. The completely swollen test piece was taken out (drained to a pre-weighed metallic gauze in the case of devulcanised samples), excess toluene was wiped off, and then weighed in a pre-weighed sealed container to obtain the swollen weight. Then, the swollen test piece was dried for 24 hours at room temperature or three hours at 60°C to remove toluene. The resultant dried test piece was weighed to obtain the de-swollen weight. The average value of two test specimens was taken as the result in the case of original samples and revulcanisates, while the average of four specimens were accepted as the result in the case of devulcanised samples.

2.3.2 Per cent devulcanisation

The percent devulcanisation was calculated following ASTM standard D 6814-02 as,

Per cent devulcanisation   =

$$\left(1 - \left(\frac{\text{crosslink density of devulcanised sample}}{\text{crosslink density of original sample}} \right) \right) \times \ 100 \ \text{--------(5)}$$

2.3.3 Horikx analysis

Horikx equations[4,5] provide a theoretical relationship between the soluble fraction generated after degradation of a polymer network and the relative decrease in the crosslink density, as a result of either main chain scission or crosslink scission which can very well be applied to devulcanised rubber also[2]. Horikx theory can be used for tracking the extent of main chain scission during devulcanisation process. The Horikx theory specifies how the crosslinks are broken selectively[6]. For crosslink scission, almost no sol is produced until most of the crosslinks have been removed. In

the case of main chain scission much more sol is produced for the same decrease in crosslink density[7]. When only main chain scission takes place, the relative decrease in crosslink density is given by Equation 6, whereas for crosslink scission, the relation is given in Equation 7. In directed scission, only those monomer units that are the nearest neighbours to a crosslink can undergo scission. As a result of this directing influence, the formal interchange of the crosslinking and scission reactions cannot be applied in the same manner as in random scission and an approximate relation as given in Equation 8 is also introduced.

$$1 - \frac{\vartheta f}{\vartheta i} = 1 - \frac{\left\{1 - Sf^{1/2}\right\}^2}{\left(1 - Si^{1/2}\right)^2} \qquad \text{------------(6)}$$

ϑi = crosslink density of original sample

Si = sol fraction of the original sample

ϑf = crosslink density of the devulcanised sample

Sf = sol fraction of the devulcanised sample

$$1 - \frac{\vartheta f}{\vartheta i} = 1 - \frac{\gamma f \left\{1 - Sf^{1/2}\right\}^2}{\gamma i \left(1 - Si^{1/2}\right)^2} \qquad \text{----------------(7)}$$

γf = average number of crosslinked units per main chain after devulcanisat

γi = average number of crosslinked units per original chain

$$1 - \frac{\vartheta f}{\vartheta i} \cong 1 - \frac{\left\{1 - (2Sf)^{1/2}\right\}^2}{\left(1 - si^{1/2}\right)^2} \qquad \text{----------------(8)}$$

The extra parameter γ in the Equation 7 is calculated from the Mc value in the crosslink density calculation and is related to the sol fraction of the respective samples as given in Equation 9 to Equation 11.

$$\gamma = \frac{Mc}{N} \quad\text{--------------(9)}$$

$$N = McS^{\frac{1}{2}} \quad\text{--------------(10)}$$

$$\gamma = \frac{1}{S^{\frac{1}{2}}} \quad\text{--------------(11)}$$

M = molecular weight between crosslinks

N = No. of primary molecules per gram of polymer

S = sol fraction of the sample

As Horikx theory defines the crosslink density of the devulcanised samples with the sol fraction still present, the crosslink density calculated by swelling test has to be corrected for the extracted sol part[4]. In order to include the extracted sol part in the calculation of the real crosslink density, the correction was made according to equation 12.

$$\vartheta_{real} = \vartheta_{actual} \times (1 - \text{sol fraction}) \quad\text{--------(12)}$$

ϑ_{real} = final corrected crosslink density for the revulcanisate

ϑ_{actual} = crosslink density obtained by swelling studies

Samples of the devulcanisates were initially extracted with acetone for 48 hours in a soxhlet extractor. FT IR analysis of the acetone extract of the devulcanised samples were carried out to check for the possibility of small molecular weight fragments of rubber getting extracted in acetone and thus getting excluded from the sol fraction calculated from the toluene

extract[8]. It is clear from Figure 2.1 that there are no significant characteristic peaks in the wave number range 800cm^{-1} to 850 cm^{-1} in the IR spectrum of acetone extract of any sample. The absence of peak around 830cm^{-1} which is the characteristic peak for cis-isoprene arising from the - CH$_3$ wagging mode rules out the possibility of the acetone extractable low molecular weight polymer fragments in these devulcanised samples. The acetone extracted samples were weighed and swollen in toluene for seven days in dark, swirling the flask at daily intervals using a laboratory shaker. The swollen rubber was then filtered off washing with fresh toluene. The excess solvent was evaporated off and the sol percent was calculated as the rubber soluble in toluene[9].
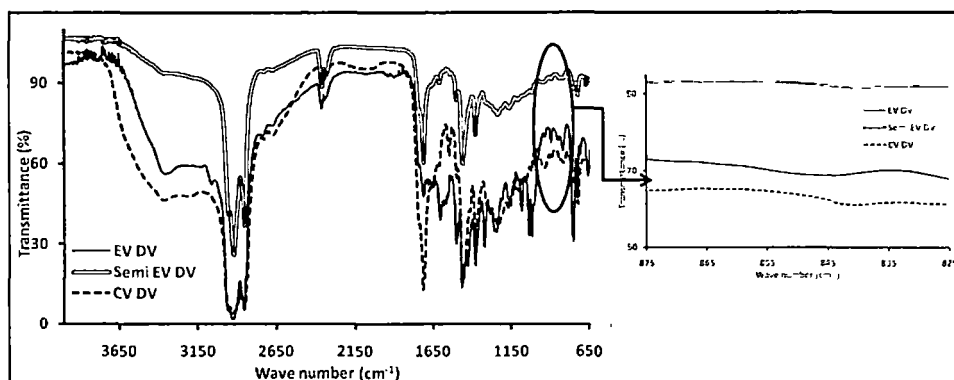
Figure 2.1   FT IR spectrum of the acetone extract of the devulcanised samples

Sol fraction of devulcanised samples against the relative decrease in crosslink density was plotted along with the standard Horikx plot. The calculated curves corresponding to main chain scission, directed scission and crosslink scission were constructed with the help of Equations 6, 7 and 8 respectively using the predefined values as parameters[5]. The nature of

bond scission that might have taken place during the devulcanisation process was thus analysed.

2.3.4 Crosslink distribution

2.3.4.1 Preparation of chemical probes

Mixture of propane-2-thiol and piperidine (0.4M) in toluene was prepared as follows. 0.4M solutions of propane-2-thiol and piperidine were prepared in toluene separately and equal volumes of both the reagents were mixed to prepare the probe. 1M hexane thiol in piperidine was prepared and used as such to cleave disulphidic crosslinks. Details of reagent preparation are given in Table 2.6

2.3.4.2 Determination of crosslink distribution

Chemical probes were used to determine the crosslink distribution pattern of the samples. The initial total crosslink density of the sample was determined by swelling in toluene and by applying Flory Rhener equation. These samples were pre-swelled in toluene for 16hours and treated with a mixture of propane-2-thiol and piperidine (0.4M) each in toluene for selective cleavage of polysulphidic crosslinks. Crosslink density of the samples was further determined after selective cleavage of polysulphidic crosslinks. This residual crosslink density of the treated sample is equivalent to the crosslink density contributed by the di and mono sulphidic crosslinks together. Crosslink density for polysulphidic bonds was calculated as the difference between total crosslink density and the residual crosslink density of the treated sample.

The samples obtained after selective cleavage of polysulphidic crosslinks were treated with 1M hexane thiol in piperidine for cleaving disulphidic crosslinks[10]. The residual crosslink density of these samples was again determined by swelling in toluene. This residual crosslink density is

equivalent to the crosslink density contribution by the mono sulphidic crosslinks. The crosslink density difference of the sample after disulphidic bond cleavage and polysulphide bond cleavage gave the crosslink density for disulphidic bonds. Prior to crosslink density determination after each probe treatment, the samples were cleaned off the reagent by washing in excess petroleum spirit four times (each standing for one hour).

Table 2.6 Procedure for preparation of chemical probes

Reagent	2-propane thiol	**0.4M solution**
Molecular weight	76.16	3.05g in 100ml toluene
Density	0.82g/ml	3.05/0.82 = 3.8 ml in 100 ml
solvent	Toluene	toluene
Reagent	Piperidine	**0.4M solution**
Molecular weight	85.15	3.4g in100ml toluene
Density	0.862g/ml	3.4/0.862 = 3.96ml in 100 ml
solvent	Toluene	toluene
Probe to cleave polysulphidic crosslinks	Mixture of propane-2-thiol and piperidine	**0.4M solution** 3.8 ml 2- propane thiol in 100 ml toluene + 3.96ml in 100 ml toluene
Reagent	Hexanethiol	**1M solution**
Molecular weight	118.24	11.824g in 100ml piperidine
Density	0.838	11.824/0.838 = 14.1ml in 100ml
solvent	Piperidine	piperidine
Probe to cleave disulphidic crosslinks	Hexanethiol in piperidine	**1M solution** 14.1 ml hexane thiol in 100ml piperidine

If T, P, D, and M denotes the total crosslink density, number of polysulphidic crosslinks, number of disulphidic crosslinks and number of

monosulphidic crosslinks respectively, the calculation of crosslink distribution pattern using chemical probe treatment could be represented as given in equations 13, 14 15.

$$T = [P + D + M] --------- (13)$$
$$P = [T - (D + M)] --------(14)$$
$$M = [(D + M) - D] --------(15)$$
$$D = [T - (P + M)] ---------(16)$$

As the reactivity of the reagents are sensitive to the factors such as concentration of the reagent, reaction time, reaction temperature, dimensions of the sample and structure of the rubber[11], optimum conditions were established initially. The optimum time for the treatment was determined by treating the samples with the respective reagents and checking the crosslink densities of the treated samples at definite intervals. The time required to attain a constant crosslink density for a treated sample was accepted as the optimum time for treatment. Accordingly, the treatment time for propane -2 thiol for poly sulphidic bond cleavage was assigned as 3 hours and that for hexane thiol treatment to cleave disulphidic crosslinks as 24 hours.

2.3.5 Processability analysis

The processability of devulcanised samples was ascertained based on the tan delta values of the devulcanised samples in the uncured state at $60°C$[12,13] (without adding virgin NR). Rubber Process Analyzer RPA 2000 (M/s Alpha Tech, USA) was used to monitor the strain sweep studies of the devulcanised raw samples at $60°C$ at a frequency of 6CPM. During strain sweep studies, the frequency was kept constant while varying the angle of rotation of the die to increase the strain per cent. The rotation angle was increased as $0.05°$, $0.11°$, $0.26°$, $0.61°$, $1.4°$, $3.22°$, $7.4°$, $17.02°$ and $39.12°$.

The strain versus tan delta plots of the samples were drawn and the processability was compared.

2.3.6 Cure characteristics

Monsato Rheometer and Rubber Process Analyzer RPA 2000 (at a frequency of 1.67Hz at an angle 0.5°) were used to monitor the cure characteristics at 150°C. Cure curve of a sample is a plot of torque versus time as illustrated in Figure 1.2. The scorch time (t_{S2}) is the time available at a given temperature before the stock begins to vulcanize[14]. Cure time (t_{c90}) is the time a stock must be heated in a press at a given temperature until it reaches a technically correct cure (optimum cure time) and calculated as the time required to attain 90% of the maximum torque. After attaining the maximum torque (M_H), it may increase further (marching), or decrease (reversion), or level off (stable cure)[15].

2.3.7 Thermogravimetric analysis

Thermogravimetry was employed to analyze the devulcanised rubber obtained by mechanical devulcanisation with and without the aid of stable free radical[16]. A Shimadzu thermo gravimetric analyzer TGA-50 was used for thermal characterization of the samples within the temperature range 0°C to 800°C at a heating rate of 10°C per minute. Nitrogen atmosphere (flow rate 30ml/min) was preserved till 550°C after which the atmosphere was switched to oxygen. All the analyses were carried out using 15 mg samples in platinum pan.

2.3.8 Scanning electron microscopy

The tear fracture surfaces of the revulcanisates were observed by a scanning electron microscope (SEM)[17,18] after coating with an ultra thin layer of gold to make the sample conductive.

2.4 ESTIMATION OF VULCANISATE PROPERTIES

The vulcanisate properties of the original samples and the revulcanisate properties of the devulcanised samples were determined by different tests and the per cent retention of the properties were estimated. The details of the physical testing are described below.

2.4.1 Tensile strength

Tensile Strength is defined as a measure of the ability of a material to withstand a longitudinal stress, expressed as the greatest stress that the material can stand without breaking. Tensile properties are key indicators of the strength of a material. ASTM D412 covers the tensile properties of thermoset rubbers. Stress-strain measurements were carried out using dumb-bell shaped specimens. Stress-strain curves represent the response of materials subjected to mechanical load. Stress is the force per unit area from the initial specimen dimensions while strain denotes the ratio of the extension divided by the initial specimen length. Young's modulus is the ratio of stress to strain. Stress-strain curves are mostly non linear indicating that modulus is changing with increasing strain and hence modulus is measured in the elastic region as the slope from the stress versus strain graph[19,20]. Percent elongation is calculated as

Percent elongation
$$= \frac{(Final\ gauge\ length - Initial\ gauge\ length)}{Initial\ gauge\ length} \times 100$$

$$-------------- (17)$$

Tensile strength was measured with a Zwick universal testing machine (UTM) at a test speed of 460 mm/min or Instron UTM at a test speed of 500 mm/min. Dumb-bell shaped test samples were punched out from the moulded sheets along the grain direction. The thickness of the specimen was recorded before testing. The tensile strength, elongation at break, stress at 100%, 200% and 300% of elongation are recorded. At least

five specimens were tested for each sample and the average value was taken.

2.4.2 Tear strength

The tear strength of thermoset rubbers can be measured according to specification ASTM D624. The test measures the strength required to initiate a tear in a material. Tear strength was measured using Zwick UTM at a test speed of 460 mm/min or Instron UTM at a test speed of 500 mm/min. Trouser shaped samples were used for tear measurements.

2.4.3 Heat Build-up

Heat build-up in a rubber material occurs as it is exposed to any of a variety of compressive stresses in service. Heat build-up testing is generally conducted by exposing a rubber sample of a specified size and shape to oscillating compressive stresses in a controlled environment. During this process, heat will be generated by the stress. The increase in temperature through the procedure is measured as either an increase to a specific equilibrium temperature or as a total rise in temperature over a given period of time[21].

Heat Build Up test was carried out using Goodrich Flexometer as per ASTM D 623 method. The samples were 25 mm in height and 19 mm in diameter. The oven temperature was kept constant at 50°C. The stroke was adjusted to 4.45 mm and the load to 10.05 kg/cm. The samples were preconditioned at the test temperature in the oven for 20 minutes prior to the test. The heat development at the base of the sample was sensed by a thermocouple and relayed to a temperature indicator. The temperature rise ($\Delta T°C$) at the end of the specific time interval (20 minutes) was taken as the heat buildup.

2.4.4 Abrasion loss

The ASTM method for testing the abrasion resistance of rubber is ASTM D5963 – 04 (2015). This test method covers the measurement of abrasion resistance of rubbers that are subjected to abrasive/frictional wear in actual service. The abrasion resistance is measured by moving a test piece across the surface of an abrasive sheet mounted to a revolving drum, and is expressed as volume loss in cubic millimetres or abrasion resistance index in percent. For volume loss, a smaller number indicates better abrasion resistance, while for the abrasion resistance index, a smaller number denotes poorer abrasion resistance.

Abrasion resistance of the samples was measured using a DIN abrader. Samples having a diameter of 12 ± 0.2 mm and a thickness of 16-20mm were placed on a rotating holder and a load of 10 N was applied. A complete run through the rotating surface is equal to a distance of 40m. A pre-run was given for conditioning the sample and the sample weight was taken. Weight after the test was also noted. The volume loss is calculated based on the weight loss and density of the sample as given in equations 18 and 19.

$$Abrasion\ loss\ = \frac{Weight\ loss}{Density\ of\ sample} \times 1000 \quad ------- (18)$$

$$Density = \frac{Weight\ in\ air}{Weight\ loss\ in\ water} \times density\ of\ water \quad ----(19)$$

2.4.5 Hardness

Shore hardness, using either the Shore A or Shore D scale, is the preferred method for determining the hardness of rubbers. The Shore A scale is used for 'softer' rubbers while the Shore D scale is used for 'harder' ones. The Shore hardness is measured with an apparatus known as a Durometer and consequently is also known as 'Durometer hardness'. The

hardness value is determined by the penetration of the Durometer indenter foot into the sample. The indentation hardness is inversely related to the penetration and is dependent on the elastic modulus and visco-elastic behavior of the material. The Shore A hardness of all samples were done as per the ASTM D2240-15[22, 23].

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Chapter 3

Incorporation of Mechanically Devulcanised NR in Virgin Compounds

3.1 INTRODUCTION

Among the various processes developed for devulcanisation, each with inherent advantages and disadvantages, mechanical/mechano-chemical devulcanisation processes were mostly adopted by the industry owing to the expected highest level of property retention associated with the minimum main chain degradation ensured by ambient reaction of conditions. On the other hand, the health and environmental credentials some the chemicals used as devulcanisation agents is a concern. Besides, most reported cases of mechano-chemical devulcanisation fails to provide the results obtained for a corresponding control experiment in which no chemical devulcanisation agents are used. Though several studies on the devulcanisation of commercial sources of waste rubber such as ground tyre rubber (GTR), whole tyre reclaim (WTR), buffing dust etc. and the incorporation of the same in virgin compounds have been found in literature[1-9], the efficiency of these processes could not be ascertained as the properties of the source material used in these studies are unknown.

Devulcanisation studies using vulcanisates of known composition and properties were also investigated to some extent. Gibala and Hamed reported the cure behaviour of SBR compounds containing ground vulcanisates of known composition and cure state[10,11]. Decrease in scorch times and maximum rheometer torques were observed when ground vulcanisates were added to the SBR compounds which was attributed to the migration of sulfur from the matrix rubber to the ground vulcanisate

(causing torque reduction) and migration of accelerator fragments from the ground vulcanisate to the matrix (causing decreased scorch time). Jana et al.[12-14] carried out devulcanisation of gum natural rubber vulcanisates cured with three different sulfur/accelerator ratios in an open two-roll cracker cum mixing mill at 90°C for 10 min, in presence and absence of thiol acid as a devulcanising agent. The results showed that, vulcanisate properties markedly depended on devulcanising agent and devulcanisation techniques. Devulcanisation of sulphur-cured filled natural rubber using a renewable resource material (RRM) and diallyl disulfide (DADS) at 60°C in an open two-roll mixing mill was carried out by De et al[15,16] and the effect of carbon black loading was studied in NR/regenerated rubber (50/50) blends.

Few studies on the property enhancement achieved by the addition of carbon black in the blends of ground rubber and NR were already reported. Phadke et al. observed that addition of cryo-ground rubber (CGR) causes changes in curing characteristics (decrease in Mooney scorch time, optimum cure time, and reversion time) and shows a detrimental effect on most of the vulcanisate properties[17]. Higher doses of curatives and addition of reinforcing carbon black make up the losses in physical properties owing to the fact that addition of carbon black overshadows the detrimental effect of CGR due to its minimal adhesion to natural rubber. Devulcanisation of GRT powder using a counter-rotating twin screw extruder followed by blending with 30phr virgin natural rubber (NR) and HAF carbon black added in various proportions were reported by Mariadass et.al[18]. The evaluation of mechanical properties suggested that optimum properties were obtained with a 15phr HAF addition. The continuous ultrasonic devulcanisation of natural rubber filled with various concentrations of carbon black followed by an attempt of adding fresh carbon black into

devulcanised compound were being made by Hong and Isayev[19]. But the mechanical properties were not found to improve in this case.

This chapter describes the systematic study of mechanical devulcanisation of carbon black filled natural rubber vulcanisates using a laboratory two roll mill at ambient conditions and the incorporation of the same in a virgin compound. A new concept considered in the present study is the introduction of filler correction (FC) during the compounding stage of blends of virgin rubber and mechanically devulcanised rubber. Since the devulcanised rubber is already a filled system, the amount of filler that has to be added for optimum vulcanisate properties of the blends of virgin rubber and devulcanised rubber is an issue. Since no filler migration is possible between the two phases of the rubbers in a blend[20-22], the filler present in devulcanised rubber might not lead to uniform reinforcement of the compound. But, when the filler present in the devulcanised rubber is neglected during the compounding stage of the blends, the total amount of filler in the system increases as the blend ratio rises, and may affect the vulcanisate properties in turn. In such a case, a comparative study of such blends, where the filler present in the devulcanised rubber is also considered active and corresponding reduction is made in the formulation (filler correction, FC) and the other case where the filler present in the devulcanised rubber is rendered passive (no filler correction, No FC) seems relevant.

The devulcanisation of rubber vulcanisates with known vulcanisate properties (both un-aged and aged) was carried out in a two roll mill at ambient temperatures and the devulcanised rubber was then incorporated into fresh compound in different ratios as 85/15, 75/25 and 60/40 with and without applying a filler correction during the compounding of blends.

3.2 EXPERIMENTAL

3.2.1 Devulcanisation of NR vulcanisates

Carbon black filled natural rubber vulcanisates (CV cured) with known composition and properties (Table 2.3) were mechanically devulcanised by shearing in a laboratory two roll mill as described in chapter 2. In order to simulate the end-of-life rubber products, mechanical devulcanisation of samples aged at standard laboratory conditions were also carried out. Tensile sheets (15cm x 15cm) moulded from the original compound were aged at standard laboratory conditions (70°C for seven days and 100°C for three days) in an oven. The devulcanised rubber obtained from un-aged original sample was designated as DVR and that obtained from samples aged at 70°C and 100°C are designated as DVR70 and DVR100 respectively. In order to ascertain the efficiency of the mechanical devulcanisation, the residual crosslink densities of the gel part of the devulcanised rubber was compared with the crosslink density of the original sample and per cent devulcanisation was calculated. Revulcanisation of devulcanised rubber was carried out using the revulcanisation formulation given in Table 2.5 and the revulcanisate properties were compared. Also, the effect of varying the revulcanisation formulation and that of the residual chemicals present in the devulcanised rubber upon the revulcanisate properties of the devulcanised rubber was also analyzed.

3.2.2 Effect of revulcanisation formulation

In order to study the effect of revulcanisation formulation, the accelerator sulphur ratio was varied keeping the total amount of curative constant. The revulcanisation formulation given in Table 2.5 was employed with varying curative dosage as given in Table 3.1.

Table 3.1 Formulations used to study the effect of revulcanisation system
on the revulcanisate properties

Ingredients	Quantity (phr)		
	I	**II**	**III**
Devulcanised rubber	100g	100g	100g
Virgin rubber	10	10	10
TDQ	1.5	1.5	1.5
Zinc oxide	5	5	5
Stearic acid	2	2	2
MOR	**0.8**	**1.1**	**1.5**
Insoluble sulphur	**1.5**	**1.1**	**0.8**

3.2.3 Effect of residual chemicals

For analyzing the effect of residual chemicals (remaining from vulcanisation of original sample), upon the revulcanisate properties of ddevulcanised samples, revulcanisation of devulcanised NR vulcanisates which was subjected to acetone extraction prior to devulcanisation was carried out. The devulcanised rubber was revulcanised using the revulcanisation formulation given in Table 2.5 with the exception that 2.5phr sulphur was used. In the revulcanisation formulation given in Table 2.5, the amount of sulphur used was lower than that used for normal CV curing considering the residual sulphur present in the devulcanised rubber. Since this residual sulphur was removed during acetone extraction, 2.5phr sulphur was used during revulcanisation of devulcanised rubber prepared from acetone extracted original sample. The results were then compared with that obtained for the non-extracted samples.

3.2.4 NR/Devulcanised rubber blends

All the three sets of devulcanised samples (DVR) obtained from the mechanical devulcanisation of un-aged and aged NR vulcanisates were

blended with fresh NR in the ratio 85/15, 75/25 and 60/40 and compounded with the same formulation as for the original vulcanisates (CBS/sulphur: 0.6/2.5). The blends were prepared in such a way that for 85/15 formulation, 85g virgin rubber was blended with an equivalent amount of devulcanised rubber to provide 15g rubber hydrocarbon. The same protocol is followed for other blends also. With regard to the incorporation of filler for the blend compound, three approaches were practiced *viz.*

(i) neglecting the filler content of the devulcanisate and adding the amount of filler as required in the formulation (no filler correction, No FC)

(ii) adjusting the filler loading so that the amount of filler already present in the devulcanisate is taken into account and the amount of filler added additionally is adjusted in such a way that, together they satisfy the quantity required by the formulation (filler correction, FC).

(iii) applying varying percentage of filler correction

Table 3.2 Distribution of virgin NR, devulcanised NR and carbon black in NR/DVR blends

Blend ratio		Devulcanised rubber (g)	NR(g)	HAF black
100/0		0	100	40
85/15	No FC	25	85	40
	With FC	25	85	31
75/25	No FC	33.5	75	40
	With FC	33.5	75	25
60/40	No FC	66.7	60	40
	With FC	66.7	60	16

The distribution of filler and devulcanised rubber in blends is given in Table 3.2 and the varying percentage of filler correction is detailed in Table 3.3.

Table 3.3. Distribution of carbon black in 75/25 NR/DVR blends with varying percentage of filler correction

Percentage of filler correction (%)		Devulcanised rubber (g)	NR (g)	HAF black (g)
	0% FC			40
	25%FC			36.25
75/25	50% FC	41.7	75	32.5
	75% FC			28.75
	100% FC			25

While preparing the blends, devulcanised rubber was added to the masticated virgin rubber followed by other compounding ingredients, which were then moulded and the vulcanisate properties were determined as per the respective ASTM standards.

3.3 RESULTS AND DISCUSSIONS

The devulcanisation of both aged and un-aged samples were carried out using a laboratory two roll mill and the devulcanised rubber was characterized by determining the residual crosslink density and associated per cent devulcanisation which was correlated with the revulcanisate properties. The devulcanised rubber was then blended with virgin NR in varying ratios and varying percentages of filler correction and the vulcanisate properties of these blends were analyzed.

3.3.1 Devulcanisation of original vulcanisates

3.3.1.1 Residual crosslink density and percent devulcanisation

The reduction in crosslink density upon mechanical shearing is a clear indication of the devulcanisation brought in by the process which is reflected in the percent devulcanisation also.

Table 3.4 Crosslink densities of original and devulcanised samples with corresponding per cent devulcanisation

Vulcanisate	Crosslink density$\times 10^4$ (molecm^{-3})		Percent devulcanisation (%)
	Virgin	Devulcanised	
Original	1.2	0.93	22.5
Aged 70°C for 7 days	1.5	0.26	82.6
Aged 100°C for 3 days	1.4	0.16	88.6

Table 3.4 shows the residual crosslink density of the devulcanised samples in comparison with the crosslink density of the original sample and the per cent devulcanisation. It can be observed that, the per cent devulcanisation of the aged samples are considerably higher compared with that of the un-aged samples irrespective of the higher crosslink densities of the aged virgin vulcanisates than that of the un-aged original vulcanisate.

Generally, it is expected that the crosslink density of sulphur cured vulcanisates increases with increase of ageing temperature[19-21]. The observed low crosslink density after ageing at 100°C for 3 days might be due to the main chain degradation taken place during thermal ageing causing increased swelling thereby lowering the calculated crosslink density value. The higher percent devulcanisation associated with vulcanisates

devulcanised after ageing might also be related to the degradation effects if not reflected as high revulcanisate properties.

3.3.1.2 Cure characteristics

The cure characteristics of the original samples as well as the devulcanised samples (DVR) during revulcanisation are listed in Table 3.5. The minimum torque (M_L) values of the devulcanised samples were much higher than the corresponding original vulcanisate. Also, the maximum torque (M_H) values of the devulcanised samples were lower compared with the original sample leading to a net reduction in the total torque (M_H- M_L) value of the devulcanised samples during revulcanisation. The similar M_L values of all devulcanised samples might also be indicating that, the higher percent devulcanisation of the vulcanisates devulcanised after ageing might not be an indication of higher crosslink scission of the corresponding vulcanisate as already mentioned. It is also observed that the scorch time (t_{s2}) of the revulcanised samples were reduced significantly compared with the original vulcanisate which will be discussed in detail in chapter 9.

Table 3.5 Cure characteristics of the original and devulcanised samples

Vulcanisate	Torque (dNm)			Scorch Time, min	Cure time (min)
	Minimum M_L	Maximum M_H	M_H- M_L		
Original	1.3	14.6	13.3	3.8	10.6
DVR	4.6	10.1	5.5	2.1	6
DVR70	4.5	9.6	5.1	2.2	7.5
DVR100	4.2	7.7	3.5	1.8	8.3

3.3.1.3 Revulcanisate properties

Revulcanisate properties of the devulcanised samples in comparison with the corresponding original vulcanisates are listed in Table 3.6 and the representative stress-strain curves are given in Figure 3.2. A comparative representation of tensile strengths, elongation at break and tear strengths of the original samples, aged samples and the corresponding revulcanised samples were illustrated in Figure 3.1.

It can be observed that, the mechanical properties of the original vulcanisate lowered significantly after ageing at 100°C for three days (CV100). Ageing at 70°C (CV70) did not affect the properties detrimentally except for the increase in modulus values associated with aged vulcanisates. Hence, these samples might be considered as the representatives of the different grades of NR based crumb rubber powder that has to be devulcanised in the real world scenario.

Table 3.6 Vulcanisate properties of the virgin, aged and revulcanised samples

Properties	Un aged		Aged at 70°C for 7 days		Aged at 100°C for 3 days	
	CV	CV DV	CV70	CV70 DV	CV100	CV100 DV
Tensile Strength,MPa	29.9	19.7	27.9	16	14.6	6.9
Elongation at Break,%	756	533	644	595	339	339
M100, MPa	1.9	1.9	3	1.6	3.2	1.6
M200, MPa	4.2	4.3	6.7	3.3	7.6	3.4
M300, MPa	7.6	7.8	11.3	5.8	12.6	5.8
Tear strength, N/mm	115	37	80	28	31	16
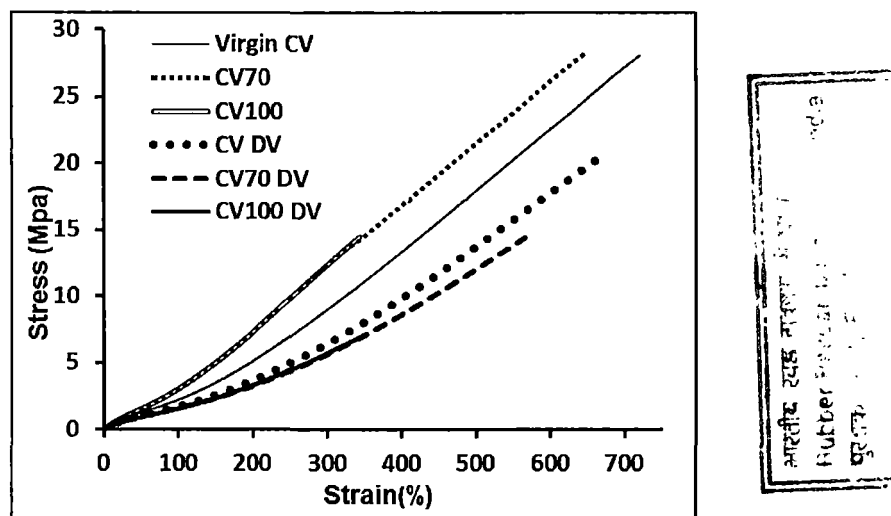
Figure 3.1 Stress-strain curves of virgin, aged and revulcanised CV vulcanisates.

The revulcanisate properties of the devulcanised samples are lower than the corresponding original samples which might be due to the combined effect of two factors viz. (i) low percent devulcanisation and (ii) possibility of higher main chain scission taken place during mechanical shearing and/or ageing. The low revulcanisate properties of the samples prepared from the devulcanisation of aged NR vulcanisates indicates that, the higher per cent devulcanisation associated with these samples might be attributed to the higher per cent of main chain degradation suffered by these vulcanisates.

The revulcanisate properties of the devulcanised samples also pointed that, mechanical devulcanisation alone can bring about 23 percent devulcanisation which is well enough to retain almost 60 percent of the original tensile properties but only with around 30 percent retention of original tear properties. Hence, it might be misleading to access the efficiency of devulcanisation based on tensile properties alone as observed

in most of the studies on devulcanisation since tear strength appear to be more sensitive to the efficiency of devulcanisation.
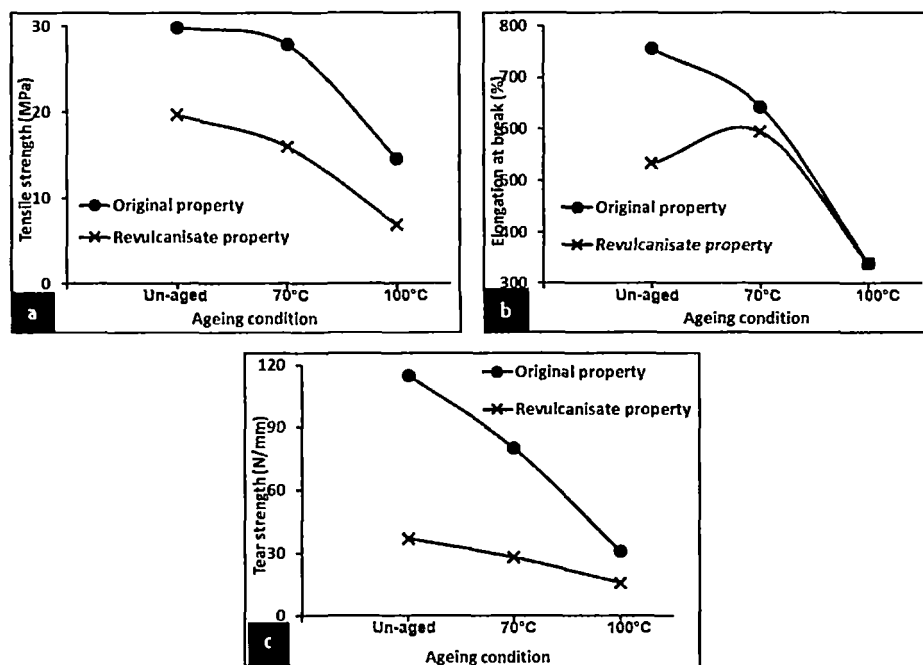
Figure 3.2 Comparison of revulcanisate **a:** tensile strength **b:** elongation at break and **c:** tear strength of un-aged and aged CV vulcanisates with corresponding original properties

3.3.1.4 Role of revulcanisation formulation

In order to study the effect of the cure system used for the revulcanisation on mechanical properties, the devulcanised samples prepared originally from CV cured NR vulcanisates were revulcanised by varying the accelerator/ sulphur ratio. The cure characteristics obtained from Monsanto rheometer upon revulcanisation is given in Table 3.7. Although the minimum torque and maximum torque of the samples varied

considerably with the cure system employed during revulcanisation, the total torque remained comparable.

The lowering of minimum torque of the devulcanised sample with varying the revulcanisation cure system might be due to the varying viscosity of the devulcanised sample corresponding to the amount of curatives added for revulcanisation. The scorch time and cure time during revulcanisation remained comparable. Hence, it might be assumed that, the cure characteristics of the devulcanised samples are not significantly affected by the change in cure system, provided the total amount of curatives is kept the same.

Table 3.7 Cure characteristics of mechanically devulcanised NR revulcanised by different MOR/S ratios

Cure system (MOR/S)	Torque (dNm)			Scorch Time, min	Cure time (min)
	Minimum, M_L	Maximum, M_H	M_H- M_L		
0.8/1.5	48.6	78	29.4	1.9	7.5
1.1/1.1	42.8	68.7	25.9	2.1	8.2
1.5/0.8	36.8	72.8	36	1.8	7.7

The crosslink densities of the devulcanised samples after revulcanisation using different cure systems is given in Table 3.8 points to the comparable revulcanisate crosslink densities irrespective of the cure system used. It can be observed that optimum revulcanisate properties of the devulcanised samples could be achieved by adjusting the revulcanisation formulation used. On the other hand, since significant variation of revulcanisate properties were not associated with the revulcanisation formulation employed, optimization of revulcanisation formulation might be considered to be requirement specific during product manufacture.

Table 3.8 Revulcanisate properties of devulcanised samples cured by different MOR/S ratios

Cure system (MOR/S)	Crosslink density x 10^4, mole/ cm^3	Tensile Strength, MPa	Elongation at Break, %	M100, MPa	M200, MPa	M300, MPa
0.8/1.5	1.3	17.3	563	1.7	3.6	6.45
1.1/1.1	1.14	19.4	694	1.6	3.2	5.6
1.5/0.8	1.2	18.2	581	1.7	3.7	6.6

3.3.1.5 Role of residual chemicals in the devulcanised sample

The effect of residual chemicals in the devulcanised samples, remaining after the vulcanisation of original sample is studied by acetone extraction of original samples prior to devulcanisation and subsequent revulcanisation. The revulcanisate properties of the samples were compared with that of the devulcanised samples prepared from original samples which were not subjected to acetone extraction. The comparison of the cure characteristics of the samples are given in Table 3.9.

Table 3.9 Cure characteristics of devulcanised samples prepared from acetone extracted and non- acetone extracted NR vulcanisates

Sample	Torque (dNm)			Scorch Time, min	Cure time (min)
	Minimum, M_L	Maximum, M_H	M_H- M_L		
CV DV	48.6	78	29.4	1.9	7.5
Ace. Ex. CV DV	39.6	79	39.4	1.8	11

The minimum torque of the samples devulcanised after acetone extraction was lower than those without acetone extraction. The maximum torque of both the samples remained comparable. Though the scorch time during revulcanisation were comparable for both the samples, the cure time of increased significantly when devulcanisation was carried out after acetone extraction.

Comparison of revulcanisate properties of the samples re given in Table 3.10 indicates that, residual chemicals present in the devulcanised samples are not significantly influencing the revulcanisate properties of the devulcanised samples. The marginal improvement in the tensile strength and modulus of the revulcanised samples when devulcanisation is carried out after acetone extraction might be attributed to the additional 1phr sulphur included in the revulcanisation formulation of samples devulcanised after acetone extraction on account of absence of residual sulphur in the devulcanised sample as previously stated.

Table 3.10 Revulcanisate properties of devulcanised samples prepared from acetone extracted and non- acetone extracted NR vulcanisates

Sample	Tensile Strength, MPa	Elongation at Break, %	M100, MPa	M200, MPa	M300, MPa
CV DV	17.3	563	1.7	3.6	6.5
Ace Ex CV DV	17.9	573	1.9	4	7

3.3.2 Blends of virgin rubber and devulcanised rubber

The mechanically devulcanised rubber was blended with virgin natural rubber in different proportions (85/15, 72/25 and 60/40) to evaluate the effect of incorporation of devulcanised rubber on the ultimate properties of the vulcanisates. The blends were prepared with and without applying filler correction and the characteristics of the blends were evaluated in

comparison with a control NR vulcanisate which does not contain devulcanised rubber.

3.3.2.1. Processability analysis

Tangent delta (tan δ) is the ratio of the viscous modulus to elastic modulus. The tan δ ratio for a rubber compound is always relatively high in the uncured state and low in the cured state and is related to processability of rubber in the uncured state[22,23]. Representative log-log plots of tan delta versus applied strain for various blends of virgin rubber and devulcanised rubber is given Figure 3.3.
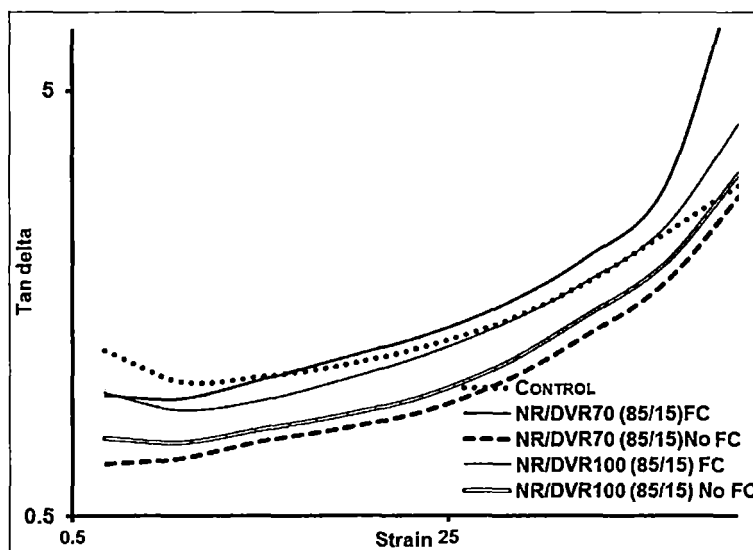
Figure 3.3. Processability variation of NR/DVR blends

The tan δ values of the blends without applying filler correction are lower than the control compound, denoting comparatively lower processability. Also, the tan delta values of the NR/ DVR100 blends were lower than that of the corresponding NR/DVR70 blends indicating better processability of the latter in comparison with the former. The tan δ values of those blends with filler correction were comparable with the tan δ value

of the control, indicating comparable processability, hysteresis or heat build-up of these blends with the control vulcanisate.

3.3.2.2 Cure characteristics

Cure characteristics of the blends of virgin rubber and devulcanised rubber (DVR) of both un-aged and aged vulcanisates are given in Table 3.11 and representative cure curves are shown in Figure 3.4.
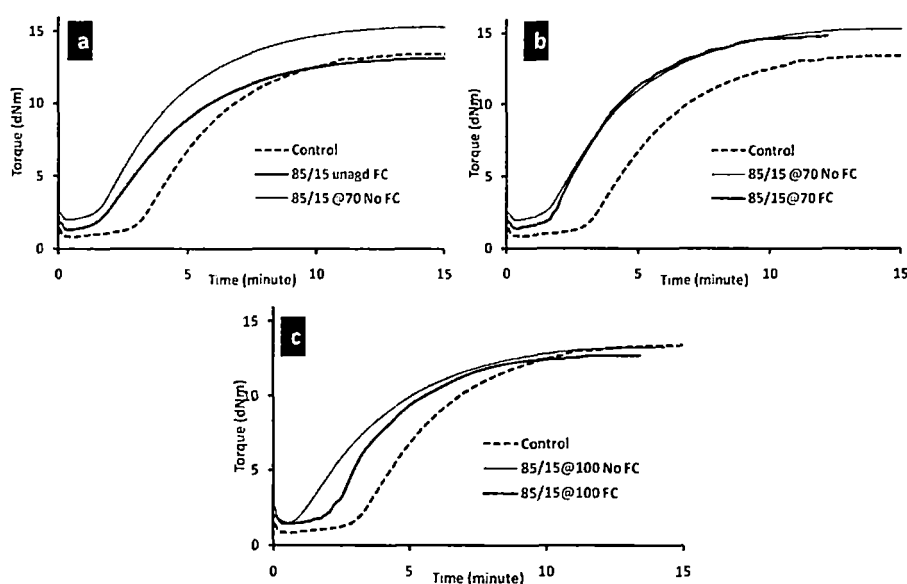
Figure 3.4 Cure curves of **a:** 85/15; **b:** 75/25 and **c:** 60/40 NR/DVR blends

The cure characteristics of the devulcanisates remain comparable with the original compound, except for the lower scorch time of the blends in comparison with the control compound. The scorch time reduced correspondingly with the increase in the amount of devulcanised rubber in the blend. The minimum torque of the control vulcanisate was lower than all the blends which increased with increase in filler content in the vulcanisate. Hence, the minimum torque of the blends without FC was higher than the

corresponding blend with an applied FC and increased in the order of blend ratio 85/15, 75/25 and 60/40.

Table 3.11 Cure characteristics of NR/DVR (unaged aged) blends

Sample	M_H	M_L	$M_H- M_L$ (dNm)	t_{c90} (Min)	t_{s2} (Min)
Control	13.5	0.9	12.6	9.4	3.5
NR/DVR					
85/15*	13.7	1.5	12.2	7.3	2.1
85/15#	13.1	1.3	11.8	8.6	2.2
75/25*	15.9	2.6	13.3	7.2	1.3
75/25#	12.4	1.3	11.1	8.2	2
60/40*	16.7	4.3	12.4	7	1.1
60/40#	11.6	1.4	10.2	7.6	1.9
NR/ DVR70					
85/15*	15.3	2	13.3	8.3	2
85/15#	14.9	1.4	13.9	7.7	2.2
75/25*	16	3.1	12.9	7.5	1.7
75/25#	12.6	1.4	11.2	8.1	2.1
60/40*	14.5	3.4	11.1	6.9	1.6
60/40#	11.8	1.7	10.1	7.6	2
NR/ DVR100					
85/15*	13.3	1.4	11.9	7.9	1.5
85/15#	12.7	1.2	11.5	8	2.5
75/25*	14.6	2.6	12	8.3	1.6
75/25#	11.6	1.8	9.8	8.5	2.4
60/40*	15.3	4	11.3	8.4	1.7
60/40#	10	1.6	8.4	8.6	2.7

*without filler correction; #with filler correction

The maximum torque for the blends with FC ranged from 10dNm to 13dNm while that for blends without an applied filler correction ranged

from 13dNm to 17dNM respectively. The blend without an applied filler correction had a higher total torque than the corresponding blend without FC. The total torque of the blends was comparable with that of the control vulcanisate. Scorch time and cure times of the blends were lower than the control vulcanisate and it lowered marginally with increase in the amount of devulcanised rubber in the blend. The scorch time and cure time of the blend with applied filler correction is marginally higher than the corresponding blend without filler correction applied.

3.3.2.3 Vulcanisate properties

NR/DVR blends

Variations in important vulcanisate properties of the blends of natural rubber and mechanically devulcanised NR vulcanisates with and without filler correction are plotted in Figure 3.5and given in Table 3.12. The hardness of the NR/DVR blends with an applied filler correction is comparable with the control compound and incresed significantly with amount of the devulcanised rubber in the blend increases if filler correction is omitted. The tensile strength showed a systematic reduction with the amount of devulcanised rubber in the blend and was not significantly influenced by whether the filler amount is corrected or not.

Tear strength also showed a systematic decrease with the increase in devulcanised rubber content in the blend. However, among the two approaches tried, the tear strengths of the blends were significantly higher when filler correction is not applied in comparison with the corresponding blends with an applied filler correction at equal blend ratio. Abrasion loss is higher at the lower blend ratio (85/15) in the absence of filler correction whereas it remains comparable for all other blends.

Table 3.12 Vulcanisate properties of NR/DVR (unaged and aged) blends

Sample	Hardness,Shore A	Tens. str., MPa	EB (%)	M100, MPa	M200, MPa	M300, MPa	Tear str., N/mm	Abr. Loss, mm^3	Heat build-up (°C)
Virgin NR	60	29.9	756	1.9	4.2	7.6	115	101	13
NR/ DVR									
85/15*	62	27.6	682	2.3	5.1	8.9	110	127	15
85/15#	61	29.6	701	2.1	4.8	8.5	70.5	115	12
75/25*	66	25.1	655	2.6	6	10	104	137	18
75/25#	59	27.5	685	2	4.4	7.8	69.6	139	9
60/40*	68	23.7	571	3	6.8	11.3	94.2	136	19
60/40#	57	28	693	1.8	4	7.2	56.6	134	10
NR/ DVR70									
85/15*	62	28	645	2.5	5.8	10	107.6	118	16
85/15#	55	27.7	703	2.1	4.7	8.4	78	130	13
75/25*	66	25.3	598	2.7	6.1	10.5	100.5	125	17
75/25#	59	27.4	683	2	4.4	7.8	63.4	122	11
60/40*	70	23.5	537	3	6.9	11.7	63.6	131	19
60/40#	58	27.3	697	1.8	4`	7.2	56.8	128	12
NR/ DVR100									
85/15*	58	25.9	635	2.3	5.4	9.6	86	122	15
85/15#	55	27	694	2.1	4.6	8.1	82.6	135	12.7
75/25*	62	23.3	553	2.7	6.3	10.8	50.9	136	18.5
75/25#	60	25.4	665	1.8	4	7.4	55.4	154	12.5
60/40*	66	19.5	443	3.2	7.4	12.3	36.2	146	21.5
60/40#	60	18.8	573	1.7	3.8	6.8	32.8	171	14

*without filler correction; #with filler correction
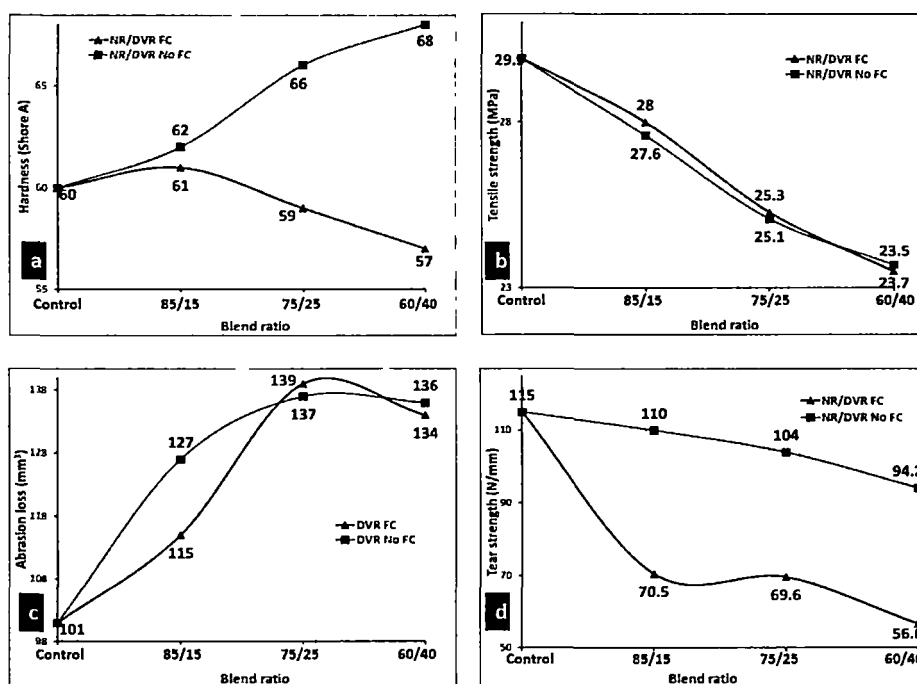
Figure 3.5 Variation in **a:** Hardness; **b:** Tensile strength; **c:** Abrasion loss and **d:** Tear strength of NR/DVR blends with and without filler correction

NR/DVR70 blends

Vulcanisate properties of blends of virgin rubber and mechanically devulcanised samples prepared after ageing at 70°C (DVR70) given in Table 3.11 are plotted in Figure 3.6

The figure shows the positive influence of the presence of extra filler on the tear strength and abrasion resistance in the case of blends without an applied filler correction prevails in this case also. Hence it can be understood that incorporation of moderately aged devulcanised rubber into virgin rubber is comparable with the incorporation of un-aged devulcanised rubber.
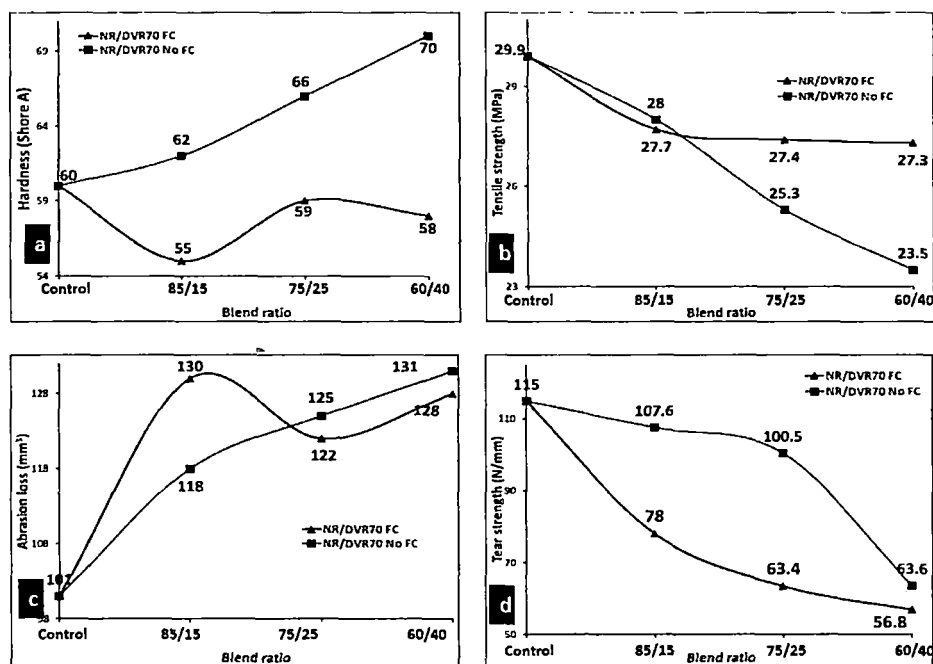
Figure 3.6. Variation in **a:** Hardness; **b:** tensile strength; **c:** Abrasion loss and **d:** Tear strength of NR/DVR70 blends with and without filler correction

NR/DVR100 blends

The vulcanisate properties of the blends of virgin rubber with devulcanised rubber from vulcanisates aged at 100°C (NR/DVR100) given in Figure 3.7 and Table 3.11.

The Shore A hardness of the 60/40 blend without filler correction is higher and those of the other blends were comparable with the control. Tensile strength of the blends systematically decreased with the DVR100 content and was not influenced by the filler correction or without filler correction. The elongation at break of samples with an applied filler correction is visibly higher than those without, and the difference increases

as the blend ratio increases. The positive influence of the presence of extra filler upon the tear strength in the blends without an applied filler correction was not observed in this case, while that in the case of abrasion loss was significantly observed. The heat build-up of the blends with applied filler correction are comparable with the control whereas, it is higher for the blends without filler correction.
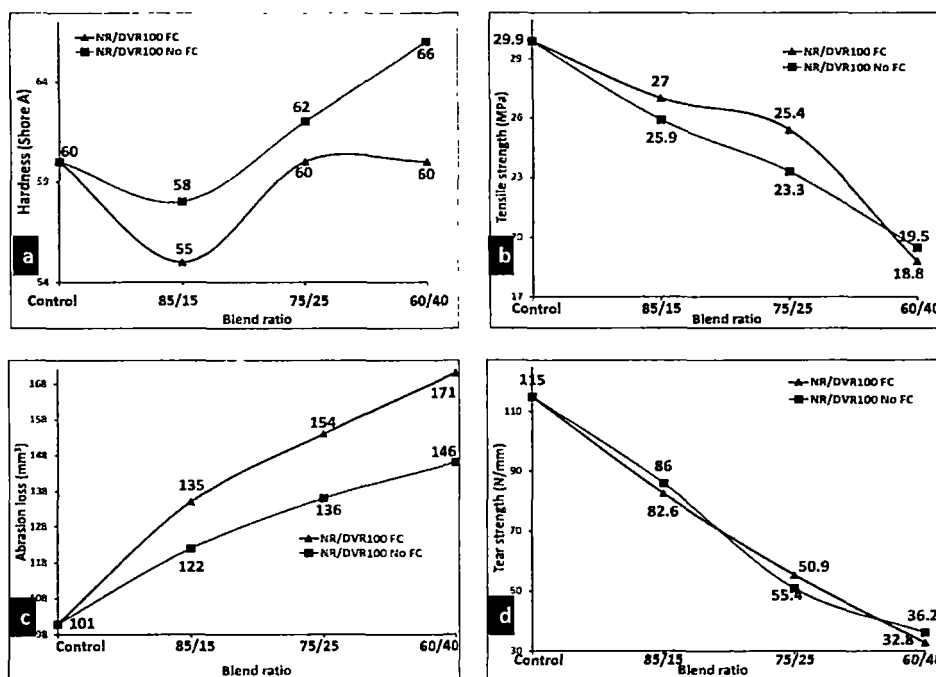
Figure 3.7 Variation in **a:** Hardness; **b:** tensile strength; **c:** Abrasion loss and **d:** Tear strength of NR/DVR100 blends with and without filler correction

Effect of ageing upon the vulcanisate properties of the blends

The effect of further ageing upon the vulcanisate properties of the blends of virgin rubber and devulcanised rubber (DVR) was monitored by

ageing the blend vulcanisate in laboratory oven at 70°C for seven days and the corresponding vulcanisate properties were listed in Table 3.13.

It can be noticed that, the tensile properties of the blends (without or with FC) are comparable with the control NR vulcanisate after ageing at 70°C for seven days except at higher DVR concentration. The elongation at break of all the blends are lowered compared with the control which might be due the increased modulus values resulted from the post-crosslinking reactions taken place during ageing conditions. The superiority in tear properties obtained for blends without an applied filler correction over the corresponding blends with FC applied were retained after ageing at 70°C for seven days also.

Vulcanisate properties of blends of mechanically devulcanised rubber from vulcanisates aged at 70°C and virgin rubber (NR/DVR70 blends) also showed comparable results with the blends with un-aged vulcanisates (NR/DVR blends) after ageing at 70°C for seven days. It is observed that, the tensile strength of the blends is comparable with the control after ageing both in the cases where FC is applied or not. But, the elongation at break of the samples with applied filler correction was higher than the corresponding vulcanisates without filler correction. The tear strength of blends without filler correction was significantly higher than the corresponding vulcanisates without filler correction. But, the absolute value of tear strength of the blends after ageing were lower than the control vulcanisate especially for 60/40 blends.

The tensile strength of the blends of virgin rubber and DVR from vulcanisates aged at 100°C (NR/DVR100) at the blend ratio 85/15 were comparable with the control when aged at 70°C, whereas those of the other blends are lower than the control especially for the blends without an applied filler correction.

Table 3.13 Vulcanisate properties of NR/ DVR(unaged and aged) blends after ageing at 70°C

Sample	Tensile Strength (MPa)	Elongation at Break (%)	M100 (MPa)	M200 (MPa)	M300 (MPa)	Tear strength (N/mm)
Control	27.6	645	2.7	6.2	10.6	109
NR/DVR						
85/15*	27.6	637	2.8	6.2	10.6	95.7
85/15#	28.3	594	2.8	6.6	11.4	68.3
75/25*	25.9	551	3.3	7.4	12.7	96
75/25#	27.1	566	2.7	6.3	11.3	62.4
60/40*	24	484	3.8	8.5	14.1	74.7
60/40#	25.9	558	2.5	5.9	10.6	54.7
Control70	27.9	644	3	6.7	11.3	80
NR/DVR70						
85/15*	28.2	550	3.5	8.1	13.8	92.4
85/15#	26.7	607	2.8	6.4	11	72.5
75/25*	25.8	502	3.8	8.8	14.5	91.09
75/25#	27.4	580	2.7	6.3	11.1	66.2
60/40*	24.1	450	4.3	9.8	15.6	68.4
60/40#	23.9	532	2.5	5.8	10.4	49.2
Control100	14.6	339	3.2	7.6	12.6	31
NR/DVR100						
85/15*	26.8	546	3.2	7.4	12.6	81.4
85/15#	26	585	2.8	6.4	10.9	73.1
75/25*	22.1	441	3.8	8.6	14.3	84.6
75/25#	24.9	561	2.6	6.1	10.7	56.2
60/40*	19.8	390	4.2	9.3	15	36.5
60/40#	21.6	530	2.6	5.6	9.9	43.5

*without filler correction; #with filler correction

The higher modulus of the blends without filler correction resulted in lower elongation at break of those blends in comparison with the corresponding blends with filler correction. The dominance of tear strength of blends without applied filler correction over those with filler correction sustains with 85/15 blend alone in this case. For 75/25 and 60/40 blends, those blends with filler correction had higher value for tear strength than those without, though significantly lower than the control vulcanisate.

Effect of varying the extend of filler correction upon vulcanisate properties of blends

Based on the results obtained for the blends of virgin rubber and devulcanised rubber and the effects of applying filler correction or not during the preparation of blends, investigation was carried out to optimize the percentage of filler correction that could be applied while preparing the blends so as to optimize vulcanisate properties of the blends. NR/DVR blends at 75/25 ratio were prepared with zero per cent (No FC), 25per cent, 50per cent, 75per cent and 100per cent filler correction using the formulation given in Table 3.3 and respective cure characteristics are given in Table 3.14.

Table 3.14 Cure characteristics of 75/25 NR/DVR blends with varying percentage of filler correction

Percentage of filler correction	Torque (dNm)			t_{c90} (Min)	t_{s2} (Min)
	Maximum, M_H	Minimum, M_L	Total, M_H- M_L		
0%	15.56	1.38	14.18	7.9	1.6
25%	14.49	1.23	13.26	7.8	1.7
50%	13.74	1	12.74	7.52	1.6
75%	12.87	0.84	12.03	7.61	1.7
100%	12	0.63	11.37	7.67	1.8

It can be observed from the table that the variation in filler content of the blend owing to the variation in percentage of filler correction applied affect the modulus properties while the scorch time and optimum cure time remain unchanged. The variation in vulcanisate properties of these blends with the varying percentage of filler correction is given in Table 3.15. There was a marginal decrease in tensile strength while elongation at break showed a systematic reduction with increase in filler content in the blend vulcanisates. On the other hand, the hardness and modulus were improved as the filler content in the blend was increased. The profound effect of increase in filler content was observed in tear strength of the blends. Hence, it might be assumed that the percentage of filler correction needed can be decided based on the product requirements.

Table 3.15 Vulcanisate properties of 75/25 NR/ DVR blends with varying percentage of filler correction

Properties	100% FC	75% FC	50% FC	25% FC	0% FC
Hardness (Shore A)	60	62	64	66	67
Tensile Strength (MPa)	25.1	24.8	23.6	22.1	22.3
Elongation at Break (%)	624	588	542	534	532
M100 (MPa)	2.0	2.1	2.3	2.5	2.6
M200 (MPa)	4.4	4.8	5.4	5.8	6.1
M300 (MPa)	7.8	8.6	9.6	10.1	10.7
Tear strength (N/mm)	65	71	78	88	107

Comparison of vulcanisate properties of the NR/DVR blends with and without filler correction (FC)

Comparison of the tensile strength and tear strength of the blends at equal blend ratio with and without filler correction are given in Figure 3.8 and Figure 3.9 respectively.
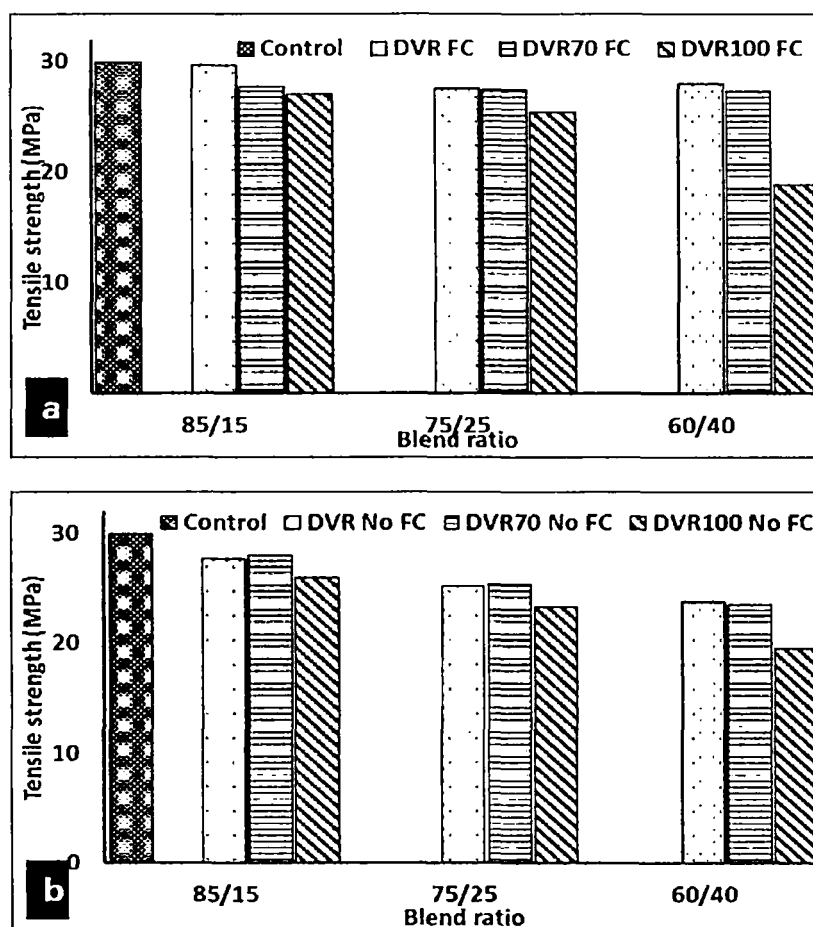
Figure 3.8 Comparison of tensile strength of NR/DVR (unaged and aged) blends at equal blend ratio **a:** with filler correction **b:** without filler correction

The observations regarding the filler correction approach indicated that, some vulcanisate properties are positively influenced if a filler correction is applied whereas, some other vulcanisate properties prefer the extra filler present in the system when filler correction is not applied. Generally, tensile strength and elongation at break are slightly favoured when filler correction is applied. On the other hand, heat build-up remained

at par with the control system when filler correction is applied. But, the tear strength of the blends were significantly improved when filler correction was not applied. The improvement brought in the tear strength is significantly higher so that, the negative influence of the presence of extra filler upon some other vulcanisate properties appears to be within an acceptable range in cases where tear strength plays a decisive role.
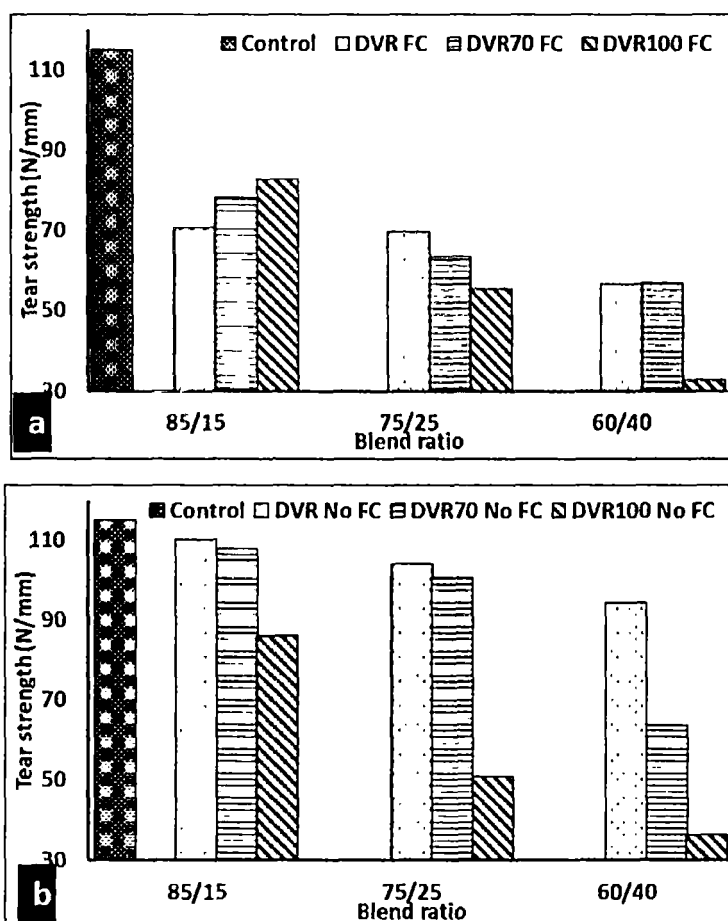
Figure 3.9   Comparison of tear strength of NR/DVR (unaged and aged) blends at equal blend ratio   **a:** with filler correction **b:** without filler correction

This might be because of the uniform distribution of the sufficient amount of carbon black required for the total rubber hydrocarbon of the system ensuring the reinforcing effect, which over shadows the non-reinforcing characteristics of vulcanised moieties present in the system acting as stress concentrators[24]. Since carbon black specifically improves the rubber's resistance to tearing the influence of extra filler might have well reflected directly in the tear strength values rather than on other vulcanisate properties[25].

The positive influence of extra filler upon tear strength appeared to be marginalized in the case of aged samples, specifically for the blends of virgin rubber and devulcanised rubber prepared from vulcanisates aged at 100°C for three days prior to devulcanisation (NR/DVR100), probably due to the highly degraded nature of devulcanised rubber. Hence, it might be considered that, the degradation level of original sample from which the devulcanised rubber is prepared plays the most important role in determining the vulcanisate properties and the level of influence of other factors when blended with virgin rubber/fresh compounds.

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Chapter 4

Comparison of Mechanical Devulcanisation with Contemporary Industrial Mechano-Chemical Devulcanisation Processes

4.1 INTRODUCTION

The concept of devulcanisation – selective scission of crosslinks – envisaged larger volumes of recycled rubber brought back into the rubber industry itself due to improved revulcanisate properties they could attain owing to minimum main chain degradation. Even with the various upgradation and innovations in the field of devulcanisation[1], the consumption of devulcanised rubber is limited to lower end products and in lower levels due to the inherent advantages and disadvantages of these processes.

Severe polymer degradation brought in by thermal effects makes thermal and microwave assisted devulcanisation less favorable whereas complication of the method stands against ultrasonic devulcanisation. Large space and time requirements challenges the biotechnological devulcanisation processes. Hence, mechano-chemical devulcanisation processes like the De Link process[2,3] and the Lev-Gum process[4] carried out at ambient reaction conditions were industrially taken up due to time, cost, and energy savings along with better revulcanisate properties due to minimum main chain scission. On the other hand, studies about the mechanical devulcanisation process in which mechanical shear alone devulcanise the rubber in the absence of any chemicals is also reported[5].

De Link process is a mechano-chemical devulcanisation process in which, mechanical shear expose fresh rubber surfaces which is being

reacted upon by the De Link reactant - a mixture of rubber accelerators and activators - which uncouples the sulphur crosslinks in a vulcanised network. Lev Gum process introduced a modifier, which is a mixture of two chemical substances one of which is a proton donor that will promote the dissociation of the other to generate an amine (such as a mixture of di-carboxylic acid or its derivatives and urea or its derivatives) which is being accepted by the proton donor to generate an ionic compound which will attack the chemical bonds of crosslinked network (preferentially the crosslinks). In both cases, the modifier acts on the crumb brought into a high stressed condition by means of transmission of the rubber mixed with the modifier through a narrow nip between the two rolls of a two roll mill.

Tun Abdul Rassak Research Centre (TAARC) London, conducted a detailed investigation on the mechano-chemical devulcanisation of rubber in which they have tried to find out the best combination of rubber chemicals (accelerator/activator) that could act as the best devulcanising agent to give maximum revulcanisate properties[6]. As a part of this investigation, they included the De Link and Lev Gum process of devulcanisation also in their trials, along with the various combinations they have tried. Interestingly, the revulcanisate properties of all mechano-chemical devulcanisation processes reported were comparable except for the fact that they haven't evaluated the revulcanisate properties of Lev Gum process due to some processing problems.

Madhusoodanan et al. reported a simple mechanical devulcanisation process of carbon black filled NR vulcanisates by shearing in a two roll mill[5] without using any devulcanising agent. A comparative data of the revulcanisate properties of devulcanised samples gathered from these literature[5,6] is tabulated in Table 4.1.

Table 4.1 Revulcanisate properties of rubber samples after devulcanisation by different processes (from literature)

	Mechano-chemical devulcanisation			Mechanical devulcanisation
	Lev-Gum process	De Link Process	TAARC Method	
Devulca-nisation agents	Urea + adipic acid	MBTS + ZDEC + Stearic acid+ZnO	ZDMC + CBS + ZnO + stearic acid	-
Tensile strength, MPa	Not revulcanised	10.27	10.77	11.5

It can be observed that, all mechano-chemical devulcanisation processes, though using different types of devulcanising chemicals are proposed to act in a similar manner. An ambient solid phase modifier is claimed to attack the sulphidic crosslinks (polysulphidic mostly) bringing about the required devulcanisation under the influence of provided shear. In some cases a subsidiary agent will also be present which is claimed to block the re-crosslinking of cleaved crosslinks by attaching to the broken fragments of crosslinks[2-5]. The general mechanism advocated for mechano-chemical devulcanisation is outlined in Figure 4.1

The similarity in mode of action and the comparable accomplished revulcanisate properties obtained by various mechano-chemical devulcanisation methods questions the capability of thus claimed devulcanising agents in targeted crosslink cleavage and subsequent radical stabilization under ambient conditions. If chemicals which are related in no way can bring about same result through similar processes, it may be assumed that it is the process that is, the mechanical shearing and not the chemical that bring about the result.
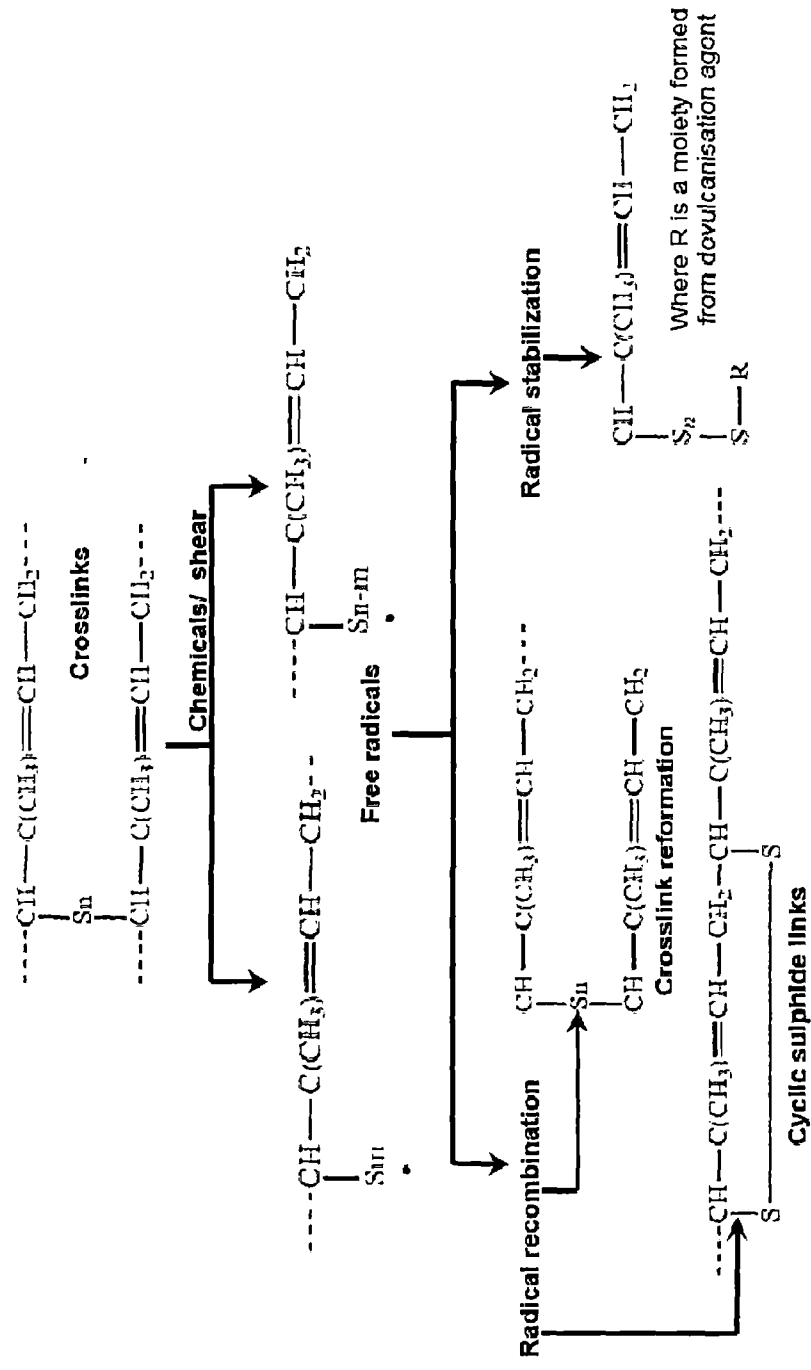
Figure 4.1 General mechanism proposed for mechano-chemical devulcanisation

This chapter describes a comparison of industrial mechano-chemical devulcanisation processes like the De Link process and Lev Gum processes with simple mechanical devulcanisation process. In order to verify the data from literature, an initial comparative study was carried out between these three processes using commercial pre-cured tyre tread buffing powder. Based on the experimental results of these trials, a detailed comparative study was carried out using carbon black filled NR vulcanisates of known formulation and properties.

4.2 EXPERIMENTAL

4.2.1 Materials

Commercial tyre tread buffings was obtained from M/s Midas Mileage Private Limited, Kottayam, Kerala, India. The composition of the material obtained from thermogravimetric (TG) analysis is given in Table 4.2.

Table 4.2 Composition of buffing dust from TG analysis

Components	Per cent	Phr
NR	40%	70
BR	17.2%	30
Carbon black	31.4%	55
Acetone extractable	6.9%	12
Ash	5%	8

4.2.2 Methods

4.2.2.1. Devulcanisation of tyre tread buffings

As stated in chapter 2, the devulcanisation was carried out at ambient temperature by passing the buffing dust through the tight nip of a laboratory two-roll mill in the presence of respective chemicals given in

Table 4.3 (as reported in patents/literature). The devulcanised buffing dust was revulcanised using the formulation given is also given in Table 4.3. For samples devulcanised by De Link method, no additional curatives are provided for revulcanisation.

Table 4.3 Formulations used for devulcanisation and revulcanisation of buffing dust

Process	Devulcanisation agent composition	Revulcanisation formulation, phr
De Link process*	MBT- 20g ZDMC – 6g Stearic acid – 2g Zinc oxide – 2g Sulphur -1.5g Diethylene glycol -12g	-
Lev Gum process**	Urea – 2g Oxalic acid – 1g	Zinc oxide – 5 Stearic acid – 2
Mechanical devulcanisation	-	TDQ – 1.5 MOR – 0.8 Sulphur – 1.5

* 10g of devulcanising agent used per 100g of crumb
** 2g of devulcanising agent used per 100g of crumb

4.2.2.2. Devulcanisation of NR vulcanisates

The virgin NR vulcanisates were prepared using the semi EV cure system given in Table 2.3. The devulcanisation and revulcanisation of carbon black filled NR vulcanisates were carried out as per the formulation given in Table 4.4. In this case, the revulcanisation formulation described in the respective patents were used as such for the revulcanisation of samples devulcanised by De Link and Lev Gum process whereas the mechanically

devulcanised samples were revulcanised using a previously optimized (Table 2.5) cure system with lower sulphur dosage than the normal CV cure formulation.

Table 4.4 Formulations used for devulcanisation and revulcanisation of NR samples

	Devulcanisation agent	Revulcanisation formulation
De Link process*	MBTS – 27.8g ZDEC – 7.6g Stearic acid – 5.1g Zinc oxide – 2.5g	-
Lev Gum process**#	Urea - 2g Oxalic acid – 1g	Zinc oxide – 1% Stearic acid – 1% CBS – 0.2% Sulphur – 0.9%
Mechanical devulcanisation##	-	Zinc oxide – 2.5phr Stearic acid – 0.5phr CBS – 0.5phr Sulphur – 2phr

* 10g of devulcanising agent used per 100g of crumb
** 2g of devulcanising agent used per 100g of crumb
# Revulcanisation formulation per 100g of crumb
Rubber hydrocarbon is regarded as 50% during revulcanisation

4.2.2.3. Preparation of NR/devulcanised rubber blends

Blends of virgin rubber and devulcanised rubber were prepared after mixing 10g of virgin rubber per 100g of the devulcanised crumb for consistency and easy handling. This devulcanised rubber was then incorporated with 75 parts of virgin NR and compounded using the formulation (CV) given in Table 2.4 to obtain 75/25* blends of virgin NR and devulcanised rubber (*rubber hydrocarbon, RH). A control compound

with no devulcanised rubber incorporated was also prepared with the same formulation.

Amount of devulcanised rubber was determined based on the rubber hydrocarbon (RH) requirement of the blend whereas the amount of filler added was adjusted considering the filler present in the devulcanised rubber as described in chapter 3 (filler correction). The amount of devulcanised rubber and carbon black added for each blend is tabulated in Table 4.5.

Table 4.5 Distribution of rubber and carbon black NR/devulcanised rubber blends

Devulcani-sation process	NR	Devulcanised rubber for 25 RH (g)	HAF in devulcani-sed rubber (%)	HAF (g)	
				From DVR	Added
De Link	75	42.7 (58.5 % RH)	33.3	14.2	25.8
Lev Gum	75	39.7 (63.03% RH)	35.7	14.2	25.9
Mechanical	75	38.9 (64.3% RH)	36.4	15.6	24.4

4.3 RESULTS AND DISCUSSION

4.3.1 Comparison of devulcanisation using commercial buffing dust
4.3.1.1 Cure characteristics

The cure characteristics of buffing dust after devulcanisation by different methods are given in Table 4.6 and the respective cure curves are given in Figure 4.2.

Table 4.6 Cure characteristics of buffing dust devulcanised by different methods

Devulcanisation process	Torque (dNm)			Scorch Time, (min)	Cure time (min)
	Minimum, M_L	Maximum, M_H	M_H-M_L		
Mechanical (BD DV)	5.1	12.6	7.5	2.9	7.6
De Link (BD DL)	4.5	18.9	14.4	1.7	7.2
Lev Gum (BD LG)	4.8	14.3	9.5	2	6.8

The cure characteristics of buffing dust devulcanised by all methods are similar except for the higher torque attained by the sample devulcanised by De Link process. This is because of the presence of high amounts of residual curatives left from the devulcanisation process. Cure characteristics also indicates that all the mechano-chemically devulcanised samples are re-cured with lower scorch time than the mechanically devulcanised samples.
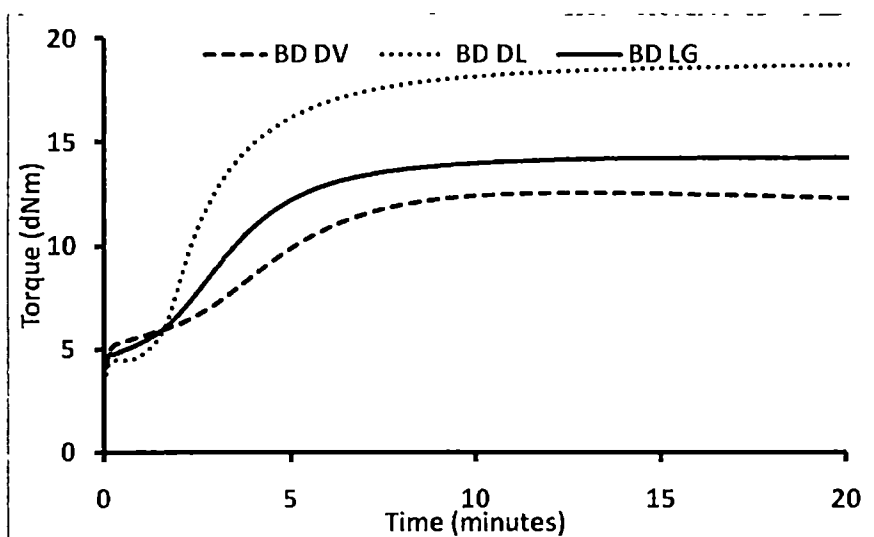
Figure 4.2 Cure curves of buffing dust devulcanised by different methods

4.3.1.2 Revulcanisate properties

Revulcanisate properties of the buffing dust devulcanised by different methods and the original properties of the pre-cured tread (provided by the pre-cured tread manufacturer) from which buffing dust is generated are given in Table 4.7. The results show that the revulcanisate properties of the buffing dust devulcanised using De link method and Lev Gum methods are comparable with that of the mechanical devulcanisation. The marginal differences in the revulcanisate properties appear to be related to the differences in the state of cures attained by these devulcanised samples rather than the effect of devulcanisation processes. The higher torque attained by the samples devulcanised by De Link process is reflected in the modulus values of revulcanised samples also. The sample devulcanised by De Link process have significantly higher modulus and lower elongation at break.

Table 4.7 Revulcanisate properties of devulcanised buffing dust

Sample	Tensile Strength, MPa	Elongation at Break, %	M100, MPa	M200, MPa	M300, MPa	Tear strength, N/mm
Original tread	19.6	570	-	-	8.3	95.6
Mechanical	13.8	318	2	4.7	8.9	25.2
De Link	9.6	219	3.2	8.2	-	21
Lev Gum	10.5	321	2.3	5.3	9.7	27

The obtained results substantiate the literature data. The important point to be noted is that, the industrial mechano-chemical devulcanisation methods do not provide any superior results and therefore indicate the incapability of the chemicals employed in these processes to induce chemical scission of the crosslinks. For further confirmation, a detailed

study was conducted using NR vulcanisates of known composition and properties.

4.3.2 Comparison of devulcanisation using carbon black filled NR vulcanisates

As stated above, HAF filled NR vulcanisates were prepared as per the formulation given in Table 4.4. The vulcanisates were devulcanised by passing through the tight nip of a two-roll mill using De Link, Lev Gum and mechanical devulcanisation processes. The devulcanised rubbers were characterized by determining the residual crosslink density[7,8], crosslink distribution by chemical probe method[9], Horikx analysis[10,11] and processability analysis by RPA[12,13]. The devulcanised rubbers were revulcanised and the per cent retention of vulcanisate properties were compared.

4.3.2.1 Characterization of devulcanised rubber

Residual crosslink density and per cent devulcanisation

The efficiency of devulcanisation was estimated by determining the residual crosslink density of the devulcanised samples and the per cent devulcanisation calculated in comparison with the initial crosslink density of original sample as given in Table 4.8.

It is found that the residual crosslink densities of samples obtained after De-Link process were comparable to the mechanically devulcanised samples $(0.8 \times 10^{-4} \text{mole/cm}^3)$ whereas that obtained by Lev-Gum process was $1 \times 10^{-4} \text{mole/cm}^3$ which is higher than that of the mechanically devulcanised samples. This observation is again reflected in the percent devulcanisation attained by the devulcanised samples. These values of residual crosslink densities and percent devulcanisation of the same NR vulcanisate devulcanised by three different processes points to the fact that, the De Link and Lev-Gum processes of devulcanisation are in no way superior to

mechanical devulcanisation. The crosslink distribution pattern of the devulcanised samples further confirms this observation.

Table 4.8 Crosslink densities and percent devulcanisation of devulcanised samples

Sample	Crosslink density x 10^4, mole/cm^3	Per cent devulcanisation (%)
Original	1.3	-
Mechanical DV	0.81	37.7
De Link DV	0.82	36.9
Lev Gum DV	1	23.1

Horikx analysis

For tracking the extent of main chain scission during devulcanisation process, Horikx analysis was carried out comparing the per cent devulcanisation and sol fraction of the devulcanised samples. The Horikx theory specifies how the cross-links are broken selectively[14]. If the devulcanisation follows through crosslink scission only, almost no sol is produced until most of the crosslinks have been removed. In the case of main chain scission, much more sol is produced for the same decrease in crosslink density[15] compared with the former. A plot of sol fraction of the samples devulcanised by different methods are plotted against the relative decrease in crosslink density along with the standard Horikx curves is given in Figure 4.3. According to Horikx theory, the data below the chain scission curve means that devulcanisation process has occurred by selective breakage of crosslinks (different from chain scission) whereas, data above and very close to the chain scission curve relate to devulcanised samples with higher degree of main chain scission[16].
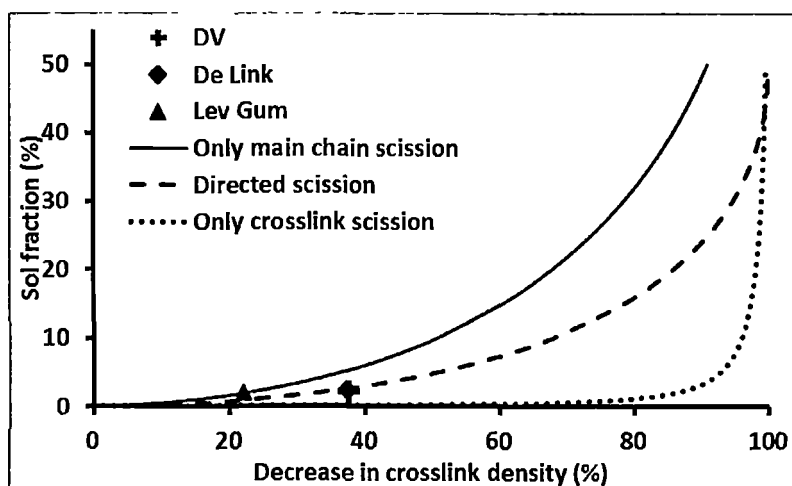
Figure 4.3 Horikx plot of NR samples devulcanised by different methods

It can be understood from Figure 4.3 that the devulcanisation of samples by different methods are not alike. The data of the sample devulcanised using Lev Gum method lies on the main chain scission curve owing to higher sol fraction resulting from higher extend of main chain scission for a small reduction in crosslink density. The data of the samples devulcanised by mechanical devulcanisation and the De Link process lies close to each other around the directed scission curve indicating that devulcanisation has taken place through the combination of directed scission and crosslink scission. No severe main chain degradation of rubber has occurred in the case of mechanical devulcanisation and devulcanisation by De Link method. As these samples were associated with comparable percent devulcanisation and comparable sol fraction it may be assumed that both these processes are alike.

Crosslink distribution

Chemical probe analysis of the devulcanised samples revealed the nature of bond scission involved in the devulcanisation process. The

crosslink distributions of various types of crosslinks in the devulcanised samples and that of the original vulcanisate are listed in Table 4.9. The results further consolidate the inferences obtained from the crosslink density measurements and Horikx analysis. As mentioned in chapter 2, for the crosslink density calculations during chemical probe analysis the volume fraction of rubber is calculated without applying the correction factor for the filler present in the sample. Also, the rounding off of values might result in slight variation of percent devulcanisation calculated using the residual crosslink densities of Table 4.9 in comparison with the earlier result.

Table 4.9 Crosslink distribution pattern of original and devulcanised NR vulcanisates

Sample	Crosslink density x 10^4, mole/cm^3	Polysulphidic bonds x 10^4, mole/cm^3	Di + mono -sulphidic bonds x 10^4, mole/cm^3
Original	2.4	1.9	0.8
Mechanical DV	1.5	1	0.5
De Link DV	1.5	1	0.5
Lev Gum DV	1.9	1.6	0.3

It is observed that the residual crosslink distribution pattern of all devulcanised samples follows similar trend. Further, it can be observed that the difference in the residual amount of polysulphidic crosslinks in the devulcanised samples is the reason behind the variation in percent devulcanisation of various devulcanised samples, since the residual number of crosslinks contributed by mono and disulphidic crosslinks is comparable for all the devulcanised samples. Also, the mechanical and/ or mechano-chemical devulcanisation of rubber is expected to proceed mostly *via* polysulphidic crosslink cleavage, owing to its least bond energy. The

residual crosslink density of sample devulcanised by Lev Gum process was higher due to the higher residual number of polysulphidic crosslinks. This is reflected in the Horikx analysis also.
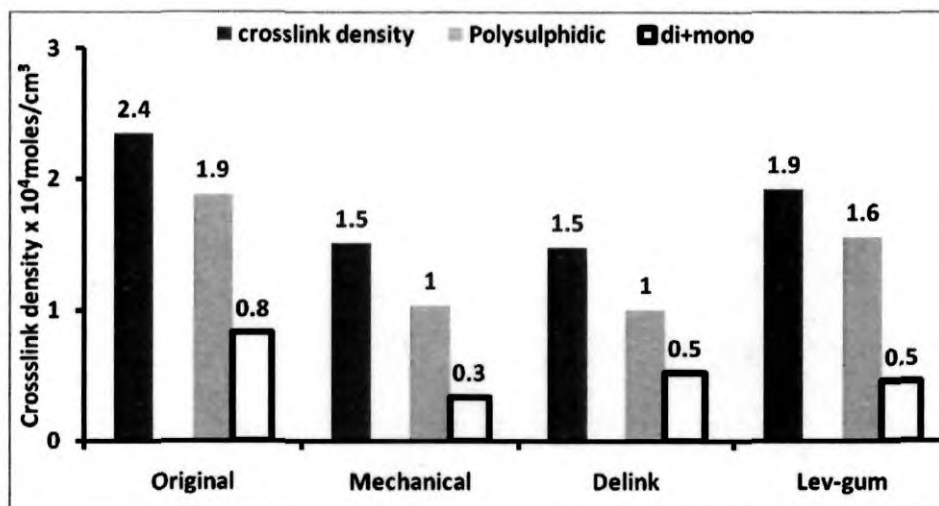
Figure 4.4 Crosslink density and crosslink distribution pattern of NR samples

Examining the crosslink distribution pattern of the original and the corresponding devulcanised samples given in Figure 4.4, it can be found that the reduction in the absolute number of majority crosslink type, ie. polysulphidic crosslinks is the reason behind better devulcanisation. As the sample under study and the applied shear was common to all the samples and the samples used were same it has to be assumed that the net number of cleaved crosslinks should be almost the same for all the devulcanisation processes under this study. But the comparative reduction in the number of polysulphidic bonds cleaved in the case of Lev Gum process of devulcanisation might be due to the effect of predominant main chain scission producing more sol (Horikx analysis), which in turn induce a

plasticised effect which lowers the shear experienced by the rubber thereby lowering the crosslink scission. Besides, the residual poly sulphidic crosslink densities of both mechanically devulcanised sample and samples devulcanised by De Link are similar correlating with the comparable residual crosslink densities of both samples indicating that both the processes are more or less the same.

Processability analysis

The processability analysis of devulcanised samples are carried out using RPA at 100°C (uncured state)and the plot of strain versus corresponding tan delta values of the devulcanised samples (before adding virgin NR) is given in Figure 4.5.
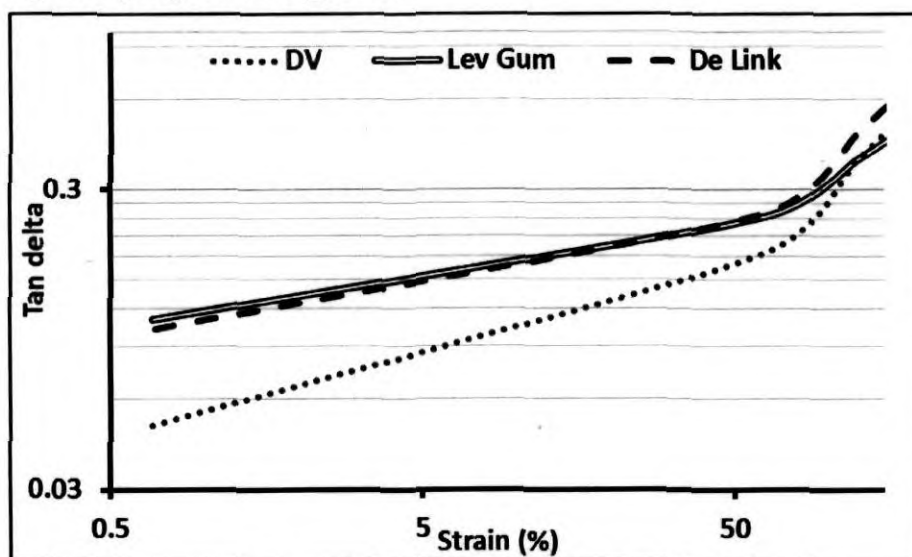
Figure 4.5 Processability of devulcanised samples

The higher tan delta values at lower strains of the samples devulcanised using *de Link process* and *Lev Gum process indicates higher* processability of those samples compared with the mechanically devulcanised (DV) sample with a lower tan delta value. The processability

analysis results are in correlation with the minimum torque (M_L) values except for the Lev Gum sample with a higher M_L value than the De link sample but with comparable processability as per the tan delta values. The comparable processability of sample devulcanised by Lev Gum method with that of the sample devulcanised by De Link method might be due to the higher degree of main chain scission as it has undergone observed from the Horikx analysis irrespective of its lower per cent devulcanisation.

4.3.2.2 Revulcanisation of devulcanised rubber

Cure characteristics

The cure characteristics of the devulcanised samples in comparison with the corresponding original samples are given in Table 4.10 and the respective cure curves are given in Figure 4.6.

Table 4.10 Cure characteristics of original and devulcanised NR samples

Devulcanisation process	Torque (dNm)			Cure time (min)	Scorch Time, min
	Minimum, M_L	Maximum, M_H	M_H-M_L		
Original	0.9	14.4	13.5	7.8	3.4
Mechanical	8.7	14	5.3	4.1	1.9
De Link	5.1	17.7	12.6	10.3	1.9
Lev Gum	6.7	13.4	6.7	4.7	1.3

The cure characteristics during the revulcanisation of devulcanised samples shows similar cure kinetics with short induction times and fast vulcanisation compared with the original sample. On revulcanisation, the scorch time of the devulcanised samples reduced considerably as in the case of the revulcanisation of any devulcanised sample[17]. Several reasons are

being advocated for this which are discussed in chapter 9 in detail. As evident from the cure characteristics and the cure curves, the minimum torque (M_L) values of the devulcanised samples are significantly higher than the original compound[18].
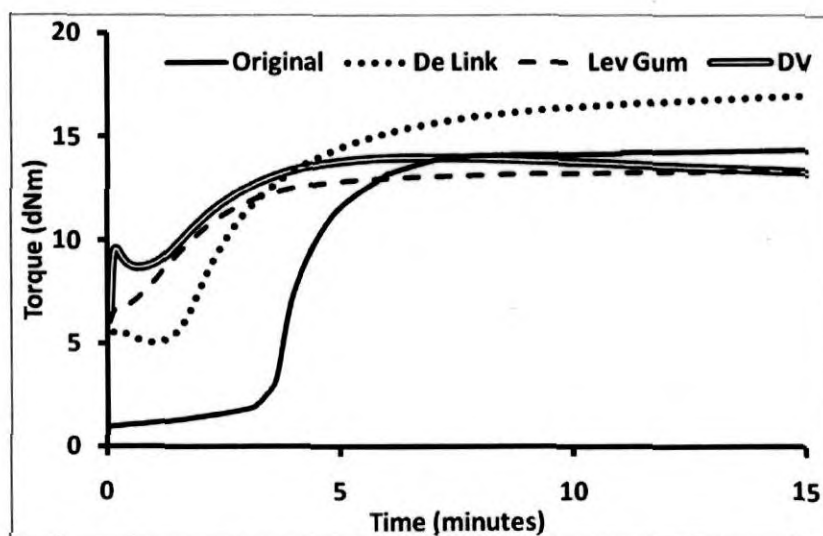
Figure 4.6 Revulcanisation cure curves of devulcanised NR samples

Among the devulcanised samples, the minimum torque of the sample devulcanised by De link process is the least, followed by sample devulcanised by Lev Gum process and the highest for mechanically devulcanised (DV) sample. The maximum torques of all samples are about 14dNm except for the sample devulcanised by De link process with a maximum torque value of 17.7dNm. Hence, the total torque (M_H-M_L) attained by the system is significantly lower than the original vulcanisate for all devulcanised samples except those devulcanised by De Link process. The higher torque might be due to the higher crosslink density attained by the devulcanised sample upon revulcanisation on grounds of the presence of high loadings of curatives as devulcanisation agent.

Crosslink density of revulcanised sample

The crosslink densities of the revulcanised samples are given in Table 4.11. The crosslink densities of the revulcanised samples might be having contributions from the residual crosslinks of the devulcanised samples and the newer crosslinks formed during revulcanisation. Hence, samples with low percent devulcanisation (higher residual crosslink density) indicate the higher gel content in the devulcanised part which will contribute to the total revulcanisate crosslink density.

Table 4.11 Revulcanisate crosslink density of NR samples devulcanised by different methods

Sample	Crosslink density x 10^4, mole/ cm^3
Original	1.3
Mechanical	1.97
De Link	2.14
Lev Gum	1.94

The crosslink densities of all revulcanised samples are higher than that of the original vulcanisate. This might be due to the influence of the residual crosslink density of the devulcanised sample during revulcanisation as mentioned before. The samples devulcanised using De Link system had the highest crosslink density upon revulcanisation in correlation with the highest torque attained by this sample which might adversely affect the revulcanisate properties of these samples.

Revulcanisate properties

The mechanical properties of the revulcanised samples positively correlated with the percent devulcanisation. The revulcanisate properties of

the devulcanised samples in comparison with that of the original vulcanisates are given in Table 4.12 and the corresponding stress strain curves are given in Figure 4.7.

Table 4.12 *Revulcanisate properties of the devulcanised samples*

Sample	Tensile strength (MPa)	Elongation at break (%)	M100 (%)	M200 (%)	M300 (%)	Tear strength (N/mm)
Original/virgin	26.1	605	2.1	4.8	8.9	114
DV	11.9	328	2.3	4.8	9.5	34.6
De Link	11.1	207	4.5	11.7	--	24.2
Lev Gum	9.3	285	2.3	5.3	10.5	30.7

The results show that, the revulcanisate properties of mechanically devulcanised samples are better than that of the revulcanised samples obtained by the industrial mechano-chemical devulcanisation processes. The elongation at break is significantly better for the mechanically devulcanised samples while tear properties are comparable with Lev Gum process. The modulus values of revulcanised samples were higher than the original vulcanisate, and were significantly higher for the revulcanised De Link sample.

Even though, the percent devulcanisation of both mechanically devulcanised samples and sample devulcanised by De Link process were comparable, the significantly lower revulcanisate properties of the latter might be due to the higher crosslink density attained by this sample during revulcanisation. The least revulcanisate tensile strength associated with the Lev gum process may be attributed to the higher main chain degradation undergone and lower percent devulcanisation attained during devulcanisation process. These data indicate the importance of optimizing

the cure system on revulcanisation. Had the crosslink density of the De Link devulcanised sample was adjusted to a comparable crosslink density of the other devulcanised samples, it is expected that the revulcanisate properties would have been comparable with that of the mechanically devulcanised samples. Another observation is that, the vulcanisate property upon which devulcanisation process has the most adverse effect is tear strength.
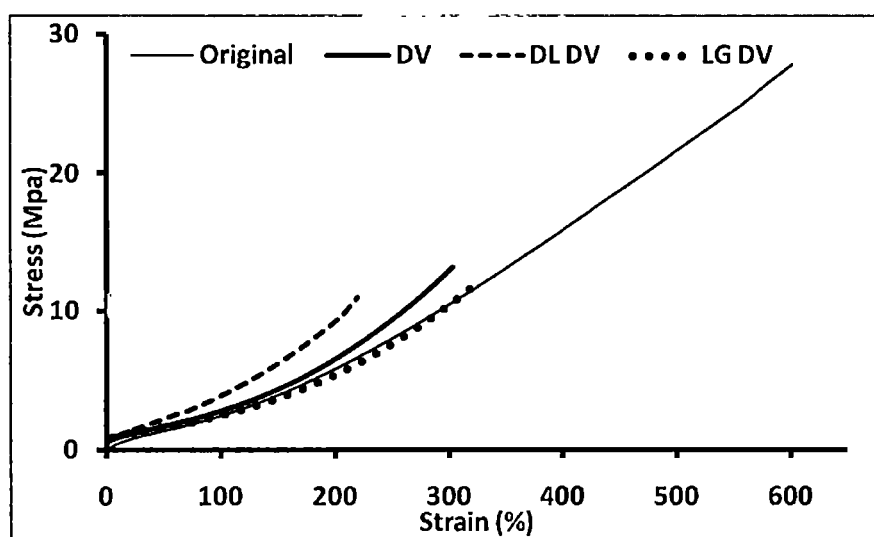
Figure 4.7 Stress strain curves of original and revulcanised NR samples

Comparison of devulcanisation of carbon black filled NR vulcanisates indicates that, the residual crosslink densities and the revulcanisate properties were comparable. Also, the chemical probe analysis of the devulcanised samples further confirmed that, the crosslink distribution pattern of all the devulcanised samples were comparable suggesting that all these samples have undergone similar pattern of bond scission during devulcanisation. Since the same virgin vulcanisate was devulcanised under the influence of same shear force but in the presence of different chemicals to attain a comparable crosslink distribution pattern for

the devulcanised rubber, it might be regarded that the mechano-chemical devulcanisation processes under current study are comparable with the mechanical devulcanisation. Hence, the variation in revulcanisate properties of the devulcanised samples of De Link process might be due to the variation in revulcanisation cure system rather than the effect of devulcanisation process. The low per cent retention of vulcanisate properties associated with Lev Gum process is supposed to be attributed to the comparatively low per cent devulcanisation and higher per cent of main chain scission with both having a complementing influence on each other.

In short, the chemicals employed as devulcanisation agents in mechano-chemical devulcanisation processes like De Link process and Lev Gum process are not found to exert any positive influence on the devulcanisation process under any of the investigated criteria. Hence blends of virgin rubber and devulcanised rubber obtained by different methods (with 10g virgin NR rubber per 100g devulcanised rubber) was prepared in the ratio 75/25 and the cure characteristics and revulcanisate properties are evaluated to ascertain the behaviour of vulcanisates devulcanised by different methods when blended with virgin rubber.

4.3.3 Blends of virgin natural rubber and devulcanised rubber

In order to evaluate the effect of incorporating devulcanised rubber in virgin rubber, blends of virgin rubber and devulcanised rubber obtained by different methods (with 10g virgin rubber added per 100g of devulcanised rubber) at 75/25 ratios were prepared as per the formulation given in Table 2.4 using CV cure system and following the devulcanised rubber and carbon black distribution pattern given in Table 4.5. The cure characteristics and the vulcanisate properties of the blends were determined and compared.

4.3.3.1 Cure characteristics

The cure curves of the blends of devulcanised rubber and virgin NR is given in Figure 4.8 and the cure characteristics are listed in Table 4.13.
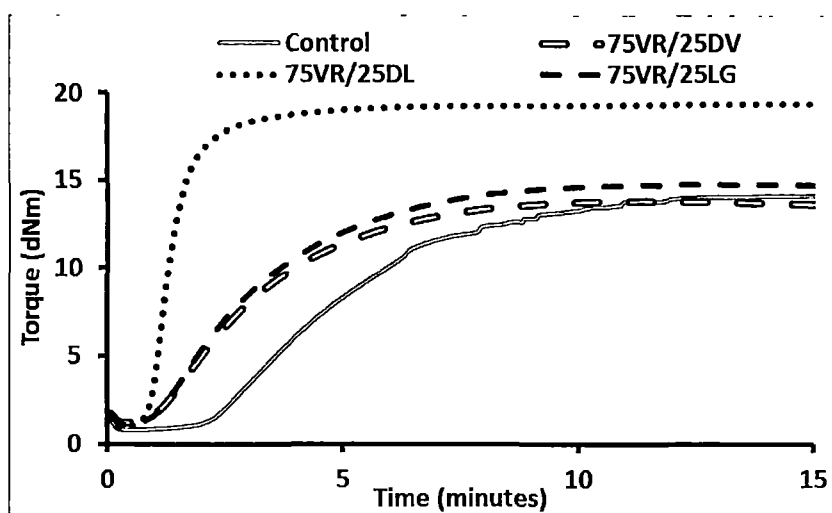
Figure 4.8 Cure curves of the 75/25 NR/ devulcanised rubber blends

It is clearly evident from the curves and the cure characteristics that, the scorch times of the blends are lower than that of the control compound. There is a significant reduction in the scorch time of the blends especially in the case of blends of virgin rubber with sample devulcanised by De Link process. The scorch time of the blends were lower than the control with a corresponding reduction in cure time. The maximum and minimum torque of the blends are comparable with that of the control except for the blend with NR devulcanised with De Link method having a considerably higher M_H value owing to the presence of higher fraction of residual accelerators, used as devulcanisation agents.

Table 4.13 Cure characteristics of 75/25 NR/devulcanised rubber blends

Devulcanisation process	Torque (dNm)			Cure time (min)	Scorch Time, min
	Minimum, M_L	Maximum, M_H	M_H- M_L, dNm		
100VR(control)	0.8	14.1	13.3	9.1	2.8
75VR/25DV	1.2	13.8	12.6	6.3	1.5
75VR/25DL	0.98	19.4	18.4	2.4	0.98
75VR/25LG	1.1	14.8	13.7	6.5	1.5

4.3.3.2 Vulcanisate properties

The vulcanisate properties of 75/25 blends of virgin rubber and devulcanised rubber are listed in Table 4.14 and the respective stress strain curves are outlined in Figure 4.9

Table 4.14 Vulcanisate properties of 75/25 NR/ devulcanised rubber blends

Sample	100VR/ 0DV	75VR/25 DV	75VR/25 DL DV	75VR/25 LG DV
Hardness	59	57	70	62
Tensile strength, MPa	25.8	25.7	11.3	24.2
Elongation at break, %	615	570	266	528
M100, MPa	2.1	1.8	3.3	2.4
M200, MPa	4.6	4.4	7.5	5.3
M300, MPa	8.6	8.3	-	9.7
Tear strength, N/mm	109.6	66.5	39.7	68.6
Abrasion loss, mm³	104	123	140	117
Heat build-up, °C	14.5	12	14	13

The stress strain curves indicate that, the visco-elastic behavior of the control and the blends with sample devulcanised with mechanical process and Lev Gum process are comparable as indicated by the closely

lying curves especially at the low strain region at the beginning. The higher modulus and lower elongation of the blends of devulcanised rubber and sample devulcanised by De Link process makes its stress strain curve vividly different from others.
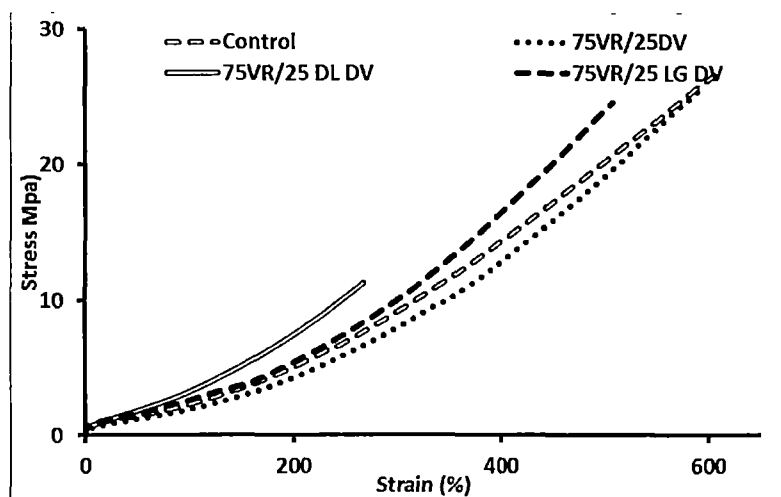
Figure 4.9 Stress strain curves of the control and NR/ devulcanised rubber blends

The vulcanisate properties of the blends (Table 4.14) show that, the blend prepared by incorporating devulcanised rubber from De Link process have significantly lower mechanical properties while the vulcanisate properties of the other two blends are comparable. This might be due to the higher crosslink density attained by the blend as indicated by the higher torque owing to the residual curatives as mentioned earlier. Even though, the sample devulcanised by Lev Gum method was associated with low revulcanisate properties owing to main chain degradation, the vulcanisate properties of 75/25 blends of virgin rubber and devulcanised rubber by Lev Gum method are comparable indicating that when blended with virgin rubber, the small differences in the level of devulcanisation are not that relevant in deciding the vulcanisate properties of blends. But there are chances that, at higher blend ratios the per cent devulcanisation attained by

the devulcanised samples used for making the blends play decisive roles regarding the vulcanisate properties of the blends.

The data in Table 4.14 also indicates that, the adverse effect of devulcanisation upon the tear strength of the vulcanisates prevails even after blending with virgin rubber, whereas the tensile properties of the blends with sample devulcanised by mechanical method and Lev Gum method are comparable with the control. The tear strength of the control sample was 109.6N/mm, whereas those of the blends of virgin rubber with NR devulcanised by mechanical and Lev Gum processes were 66.5N/mm, and 68.6N/mm respectively. The higher crosslink density of the samples devulcanised by De Link process has not detrimentally affected the heat build-up of the blend as heat build-up might be mostly attributed to the filler-polymer and/or filler-filler interactions of the vulcanisates rather than the vulcanisation state[19]. From the observations, abrasion resistance seems to be the second vulcanisate property that was highly influenced by the process of devulcanisation next to tear strength.

The present study indicates that, the contemporary industrial mechano-chemical devulcanisation processes give devulcanised rubber of comparable residual crosslink density, similar crosslink distribution pattern and comparable revulcanisate properties with mechanically devulcanised rubber. These observations point to the fact that, the chemicals employed in these processes might not be capable of targeted crosslink scission as claimed by these processes. Also, tear strength and abrasion resistance appear to be the limiting parameters in association with the devulcanised rubbers, both when revulcanised alone or after blending with virgin rubber.

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Chapter 5

Stable Free Radical Assisted Mechanical Devulcanisation of Carbon Black Filled NR Vulcanisates

5.1 INTRODUCTION

The results of the investigations presented in Chapter 4 substantiated that the mechano-chemical devulcanisation processes studied were in no-way different from mechanical devulcanisation process. Hence, it can be assumed that, during devulcanisation processes carried out under the influence of shear, it is the process of mechanical shearing and not the added chemical that bring about the devulcanisation. The crosslink scission induced by mechanical shearing would generate free radicals which can potentially recombine if not stabilized. Therefore, any shear induced devulcanisation process should be a dynamic process in which crosslink breaking and reformation are competitive.

As discussed in the previous chapter, mechanical devulcanisation carried out under ambient conditions can also lead to chain shortening reactions which however, cannot reduce crosslink density. It might also be assumed that, along with the chain shortening reactions, some of the polysulphidic crosslinks might have converted into cyclic sulphides which can reduce crosslink density, but may not be sufficient enough to significantly contribute to the total reduction in crosslink density. Therefore, during mechanical devulcanisation, the reduction in crosslink density might be achieved by arresting the recombining of the shear generated radicals by some species present in the system which may include atmospheric oxygen also. However the extent to which these species can arrest the radical recombining cannot go beyond a limit. The added chemicals in mechano-chemical devulcanisation processes carried out under ambient reaction

conditions cannot disintegrate to form free radicals and hence may not be able to prevent the reunion of radicals formed by crosslink scission. Even if these chemicals do disintegrate to form free radicals under ambient conditions, the kinetics might not favour these radicals to combine with the radicals generated from crosslink scission at the required rates. These might be the reasons behind the comparable percent devulcanisation associated with both mechanical and mechano-chemical devulcanisation processes investigated and their consequent comparable revulcanisate properties.

Based on these observations, a hypothesis is proposed that during shear induced devulcanisation processes crosslink breaking and reformation are competitive and any chemical/process which can effectively and instantaneously block the recombination of the radicals formed by bond scission can significantly improve the efficiency of devulcanisation process. Based on this hypothesis, the issue of recombining of the radicals formed by crosslink scission and consequent reformation of once cleaved crosslinks under shear devulcanisation is being addressed by the addition of a stable free radical which can instantaneously and effectively block the radical recombination under ambient conditions thereby increase the percent devulcanisation substantially.

Cyclic nitroxide free radicals are a class of free radicals that are stable at room temperature and also higher temperatures. 2, 2, 6, 6-Tetramethylpiperidine 1-oxyl free radical is one such nitroxyl radical, commonly also known as TEMPO. The stability of the radical has been proposed to be due to the steric influence of the methyl groups which flank the nitroxyl group. TEMPO and its derivatives (Figure 5.1) finds frequent use in organic synthesis as a catalytic oxidant for the synthesis of aldehydes from primary alcohols,oxidation of secondary alcohols to ketones[1] primary alcohols to carboxylic acids[2] and the oxidation of other functional groups including amines, phosphines, phenols, anilines, sulfides and organometallic

compounds[3,4] TEMPO also participates in numerous synthetically and analytically useful radical reactions as a radical scavenger[5] and as a carbon-radical trapping reagent in cascade and cyclisation reactions[6]. TEMPO mediated living free radical polymerisation procedures[7,8], induction of scorch safety in peroxide crosslinking[9-14] were also being investigated.
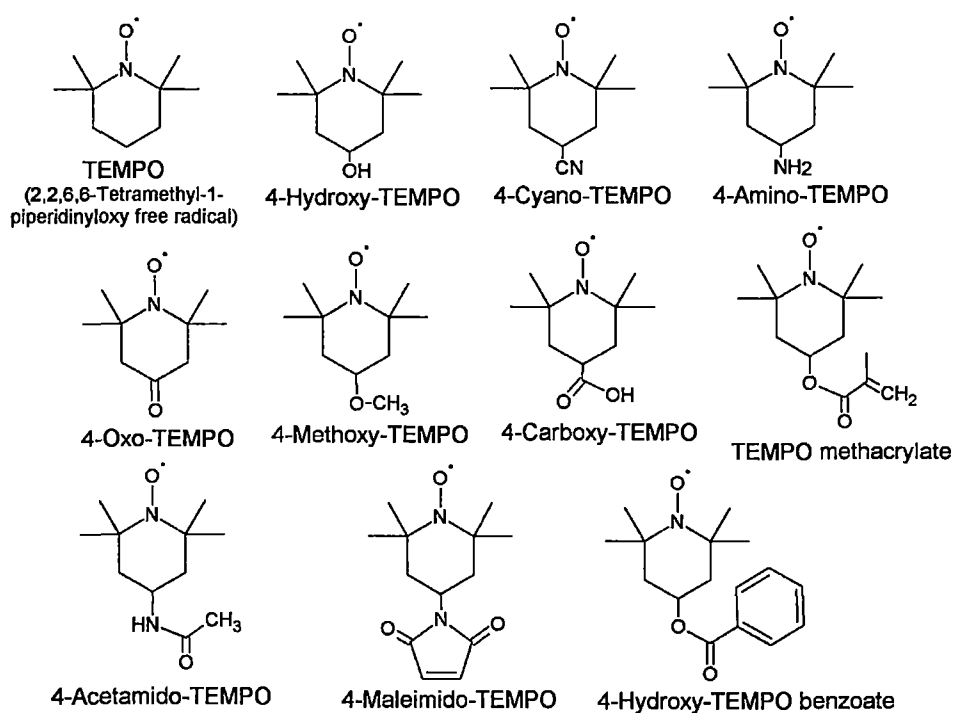
Figure 5.1. Structure of TEMPO and some of its derivatives

It is expected that, mechanical devulcanisation of crosslinked rubber with the aid of any stable free radical like 2, 2, 6, 6-tetramethylpiperidinoxyl (TEMPO) radical, 4-hydroxy-2, 2, 6, 6-tetramethylpiperidine-N-oxyl (4-Hydroxy TEMPO), etc. can positively influence the devulcanisation process and give better revulcanisate properties of devulcanised rubbers.

The effect of 1phr 4-Hydroxy TEMPO (4HT) on mechanical devulcanisation of carbon black filled NR vulcanisates (both aged and un-aged) initially cured with CV, semi EV and EV cure systems in a two roll mill is discussed in this chapter. Devulcanisation of samples aged in laboratory oven under different conditions were carried out to simulate the devulcanisation of commercially available used rubber products which have undergone different levels of degradation in their service life.

5.2 EXPERIMENTAL

5.2.1 Stable free radical assisted devulcanisation

Effect of 1phr 4HT stable free radical on the mechanical devulcanisation of carbon black filled NR vulcanisates are investigated in a two roll mill as described in chapter 2. The formulation given in Table 2.3 was used for the preparation of original CV and semi EV vulcanisates whereas for EV cured original vulcanisates, the cure system employed was CBS - 2.5phr and sulphur - 0.6 phr. Samples aged an oven at 70°C for seven days and at 100°C for three days were prepared and devulcanised as described in chapter 2. The designations used for different samples are given in Table 5.1.

It has been observed that the time requirement for devulcanisation in the tight nip of the two roll mill were different for different samples. The incorporation of stable free radical 4HT further reduced the devulcanisation time (Table 5.2). The devulcanisation time increased when samples were aged and devulcanised samples resisted band formation on the roll and to form a sheet in comparison with the samples devulcanised from un-aged NR vulcanisates.

Table 5.1 Designations used to denote samples devulcanised under different conditions

Conditions	CV	Semi EV	EV
Un-aged	CV	SEV	EV
Aged at 70°C for seven days	CV70	SEV70	EV70
Aged at 100°C for three days	CV100	SEV100	EV100
Mechanically devulcanised	CV DV	SEV DV	EV DV
4HT assisted devulcanised	CV 4HTDV	SEV 4HTDV	EV 4HTDV
Mechanically devulcanised after aged at 70°C for seven days	CV70 DV	SEV70 DV	EV70 DV
4HT assisted devulcanisation after aged at 70°C for seven days	CV70 4HTDV	SEV70 4HTDV	EV70 4HTDV
Mechanically devulcanised after aged at 100°C for three days	CV100 DV	SEV100 DV	EV100 DV
4HT assisted devulcanisation after aged at 100°C for three days	CV100 4HTDV	SEV100 4HTDV	EV100 4HTDV

The crosslink density of the vulcanisates were determined as described in chapter 2 using Flory Rhener equation[15,16,17] and the percent devulcanisation was determined.

Table 5.2 Time required for devulcanisation of NR samples with and without stable free radical

Vulcanisate	Time for devulcanisation, min	
	Mechanical	4HT assisted
CV	7.5	7
Semi EV	9	8
EV	6.5	4.5

5.2.2. Revulcanisation of devulcanised samples

The revulcanisation formulation given in Table 2.5 was used for the revulcanisation of devulcanised samples in all cases. The cure characteristics of the samples are determined using a Monsanto rheometer and moulded using a hydraulic press to respective cure times at 150°C. The revulcanisate properties were determined as per the respective ASTM standards.

5.3 RESULTS AND DISCUSSION

5.3.1 Devulcanisation of un-aged samples
5.3.1.1 Characterization of devulcanised rubber
Crosslink density and per cent devulcanisation

Crosslink densities of the original and corresponding devulcanised samples are given in Table 5.3. The residual crosslink density of the devulcanised samples denote that, mechanical devulcanisation of samples with the assistance of stable free radical resulted in lower residual crosslink density and higher percent devulcanisation compared with the corresponding mechanically devulcanised samples.

Table 5.3 Crosslink densities and per cent devulcanisation of devulcanised NR samples

Sample	Crosslink density x 10^4, mole/ cm^3			Percent devulcanisation		
	CV	Semi EV	EV	CV	Semi EV	EV
Original	1.41	1.36	0.76	-	-	-
Mechanical devulcanisation	1.07	0.87	0.21	29.1	36	72.4
4HT assisted devulcanisation	0.66	0.6	0.18	53.2	55.9	76.3

The percent devulcanisation of CV, semi EV and EV cured NR vulcanisates are given in Figure 5.2. The significant improvement in the percent devulcanisation by 4HT assisted devulcanisation indicates the capability of stable free radical as a devulcanisation aid. The low impact of 4HT upon the devulcanisation of EV samples may be due to the low original crosslink density of the EV sample enabling higher degree of devulcanisation even by mechanical devulcanisation alone. But in the case of devulcanisation of other vulcanisates, simple mechanical devulcanisation cannot ensure higher per cent of devulcanisation which is achieved with the aid of 4HT.
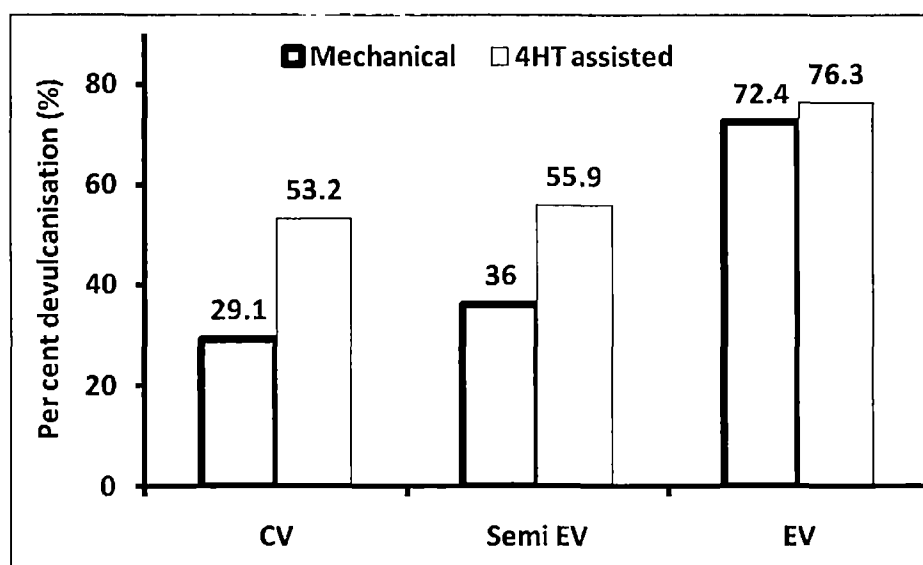
Figure 5.2 Comparison of per cent devulcanisation by mechanical and 4HT assisted devulcanisation

5.3.1.2 Revulcanisation of devulcanised samples

Cure characteristics

The cure characteristics of the original compound, and the devulcanised samples are given in Table 5.4 and the respective cure curves

are outlined in Figure 5.3. The cure characteristics and the cure curves make it clear that, the minimum torque of the devulcanised samples is significantly higher than the original compounds[18]. In all the cases, the minimum torque of the samples devulcanised with the assistance of 4HT are lower than the corresponding mechanically devulcanised samples. As minimum torque of the rheometer reading is an indirect indication of the compound viscosity and processability, the lower M_L value can be assumed as a symbol of better processability and low viscosity of the devulcanised sample. Hence, it is clear from the rheometer data that stable free radical assisted devulcanisation of NR vulcanisates improves the processability of the devulcanised sample by lowering its viscosity, compared with the corresponding mechanically devulcanised sample.

Table 5.4 Cure characteristics of original and devulcanised NR samples

Devulcanisation process	Torque (dNm)			Scorch Time, min	Cure time (min)
	Minimum, M_L	Maximum, M_H	M_H- M_L		
Virgin CV	9.22	77.29	68.07	4.59	12.43
CV DV	48.64	78.01	29.37	1.92	7.54
CV 4HT DV	34.02	78.29	44.27	1.24	6.55
Virgin semi EV	10.57	84.82	74.25	5.76	7.87
Semi EV DV	47.89	83.63	35.74	1.88	5.22
Semi EV 4HT DV	33.94	79.14	45.2	1.36	5.09
Virgin EV	10.79	69.69	58.88	5.76	10.19
EV DV	18.58	78.97	60.39	1.54	4.56
EV 4HT DV	9.46	75.47	66.01	1.45	5.04
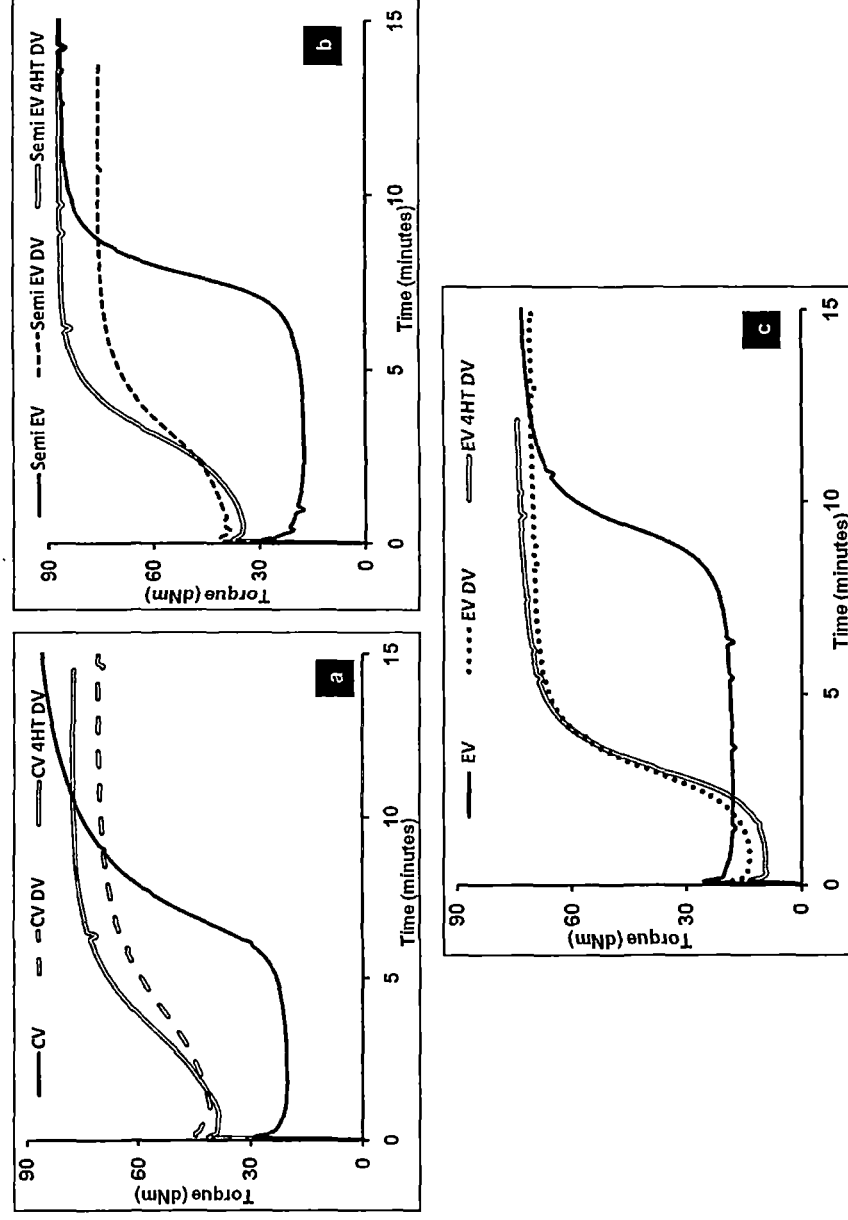
Figure 5.3 Cure curves of original and devulcanised **a:** C V; **b:** semi EV and **c:** EV cured vulcanisates

As viscous nature of rubber is associated with raw polymer it might be assumed that, stable free radical assisted devulcanisation lowers the elastic part imparted on the rubber by vulcanisation. In other words, the lower minimum torque of the stable free radical assisted devulcanised sample might be related to its higher degree of devulcanisation[19].

Both in the case of mechanical and stable free radical assisted devulcanisation, the lowest minimum torque was associated with EV samples. Also, the 4HT assisted devulcanised EV sample had comparable minimum torque with the original EV compound. The total torque attained by the devulcanised EV samples during revulcanisation is also comparable with that of the original compound, whereas the corresponding values were much lower for devulcanised CV and semi EVsamples[18]. The total torque of the EV compound was the lowest among the original samples corresponding to its lower crosslink density. This lower crosslink density of the original EV vulcanisate might have led to still lower residual crosslink densities and associated lower viscosity and minimum torque to the devulcanised EV samples. This better devulcanisation might have enabled devulcanised EV sample to attain comparable revulcanisation cure characteristics with original EV compound.

The cure time and scorch time of the all the devulcanised samples were considerably lower than those of the virgin compounds[19,20] as reported earlier. The possible reasons for is presented in detail in chapter 10.

Revulcanisate properties

The revulcanisate properties of the devulcanised samples in comparison with the respective original vulcanisates are given in Table 5.5 and the corresponding stress-strain curves are given in Figure 5.4, Figure 5.5 and Figure 5.6 respectively.

Table 5.5 Mechanical properties of un-aged NR vulcanisates before and after devulcanisation

Sample	Tensile Strength, MPa	Elongation at Break, %	M100 MPa	M200 MPa	M300 MPa	Tear strength, N/mm
CV	27.4	731	2.1	4.7	8.3	110
CV DV	17.3	563	1.7	3.6	6.45	41.4
CV 4HTDV	19.8	630	1.8	3.9	6.7	48.3
SEV	28.6	745	2.3	5.1	8.8	115
SEV DV	18.3	634	1.7	3.4	5.8	39
SEV 4HTDV	22.2	687	1.8	3.6	6.3	49
EV	24.7	801	1.6	3.5	6.2	105.4
EV DV	22.1	714	1.6	3.5	6.1	69
EV 4HTDV	23.5	725	1.7	3.6	6.3	80.1

It is observed from Table 5.5 that, the revulcanisate properties of all the devulcanised samples are improved by using stable free radical as devulcanisation aid. Significantly higher tear strength was obtained in all revulcanisates prepared from 4HT assisted devulcanisation. In all the cases, the per cent retention of tensile strength was significantly higher than that of the tear strength after revulcanisation. The influence of 4HT upon the revulcanisate properties is more prominent in the tear strength of vulcanisates.

For 4HT assisted devulcanised CV samples, there was a net increase of 2.5MPa on tensile strength, 67per cent on elongation at break and 7N/mm on tear strength on revulcanisation compared to the mechanically devulcanised sample. Similarly, 4HT assisted devulcanisation of semi EV samples resulted in a net increase of 4MPa, 53per cent and 10N/mm in revulcanisate tensile strength, elongation at break and tear strength

respectively than the corresponding mechanically devulcanised samples. The positive influence of 4HT upon devulcanisation is marginal in all revulcanisate properties except tear strength for devulcanised EV samples. It may be noted that, the per cent retention of tear strength was significantly higher for both mechanically and 4HT assisted devulcanised EV samples in comparison with CV and semi EV samples.

It is observed from the stress strain-curves and the vulcanisate properties that, the elastic modulus of the revulcanised samples are marginally lower than the corresponding virgin vulcanisate in the case of CV and semi EV samples. The modulus values of the revulcanised EV cured samples are comparable with the original EV vulcanisate. The elastic modulus of the revulcanised CV and semi EV vulcanisates could be made equivalent to the corresponding virgin vulcanisates by adjusting the cure system used for revulcanisation. However, the effect of such an adjustment upon other revulcanisate properties is not predictable. But, it is obvious that, modification of revulcanisation cure system can influence the revulcanisate properties of devulcanised rubber to some extent. Irrespective of the common revulcanisation formulation used, EV samples retained the modulus of the original vulcanisate after revulcanisation probably due to the low initial modulus of the vulcanisate. It can be observed from Table 5.2 that, the revulcanisate modulus of all the devulcanised samples are comparable. This low initial modulus due to lower crosslink density leading to lower residual crosslink density after devulcanisation might be the reason behind the exceptionally good revulcanisate properties of EV cured vulcanisates.
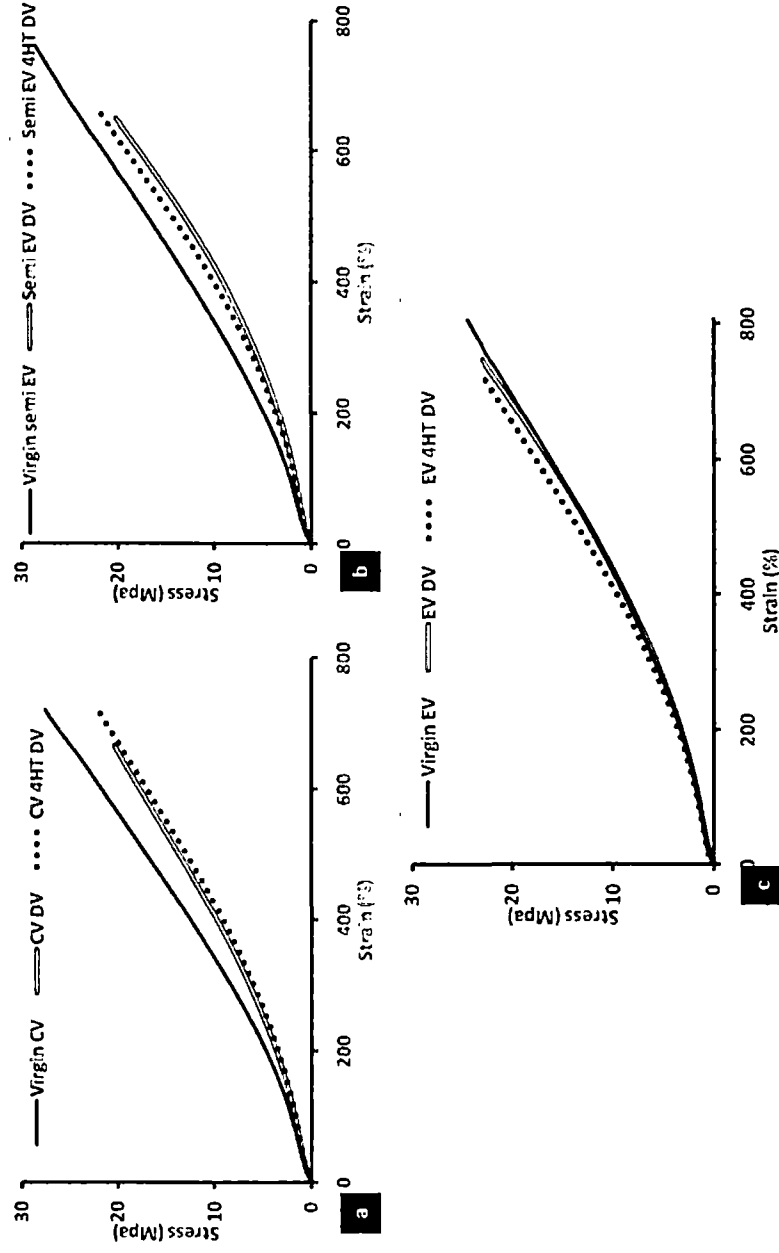
Figure 5.4 Stress strain curve of the original and revulcanised **a:** CV **b:** semi EV **c:** EV cured NR vulcanisates

5.3.2 Devulcanisation of aged samples

5.3.2.1 Aged at 70 °C for seven days

Cure characteristics

The cure characteristics of NR vulcanisates devulcanised after ageing at 70°C for seven days is given in Table 5.6 and the respective cure curves are given in Figure 5.5. The cure characteristics of the NR vulcanisates prepared from devulcanisation of samples aged at 70°C is similar to those of samples devulcanised without ageing in which the minimum torque, maximum torque and the total torque of the devulcanised samples were influenced by the ageing conditions.

Table 5.6 Cure characteristics of NR samples devulcanised after ageing at 70°C for seven days

Devulcanised sample	Torque (dNm)			Scorch Time, min	Cure time,min
	Minimum, M_L	Maximum, M_H	M_H-M_L		
CV70 DV	45.1	67	21.9	2.6	9
CV70 4HTDV	41.6	76.5	34.8	2.1	7.8
SEV70 DV	43.9	78.5	34.6	1.7	6.5
SEV70 4HTDV	38.2	81	42.8	1.6	6.1
EV70 DV	22	69.4	47.4	2.5	7.7
EV70 4HTDV	13.6	73.2	59.6	1.5	5.1

Table 5.7 gives the comparison of cure characteristics of devulcanised samples prespared from NR vulcanisates aged at 70°C for seven days with that of the corresponding samples prepared from un-aged vulcanisates. It is worth notable that, the cure characteristics of devulcanised semi EV vulcanisates were the least influenced by ageing whereas CV cured and EV cured vulcanisates were significantly affected.
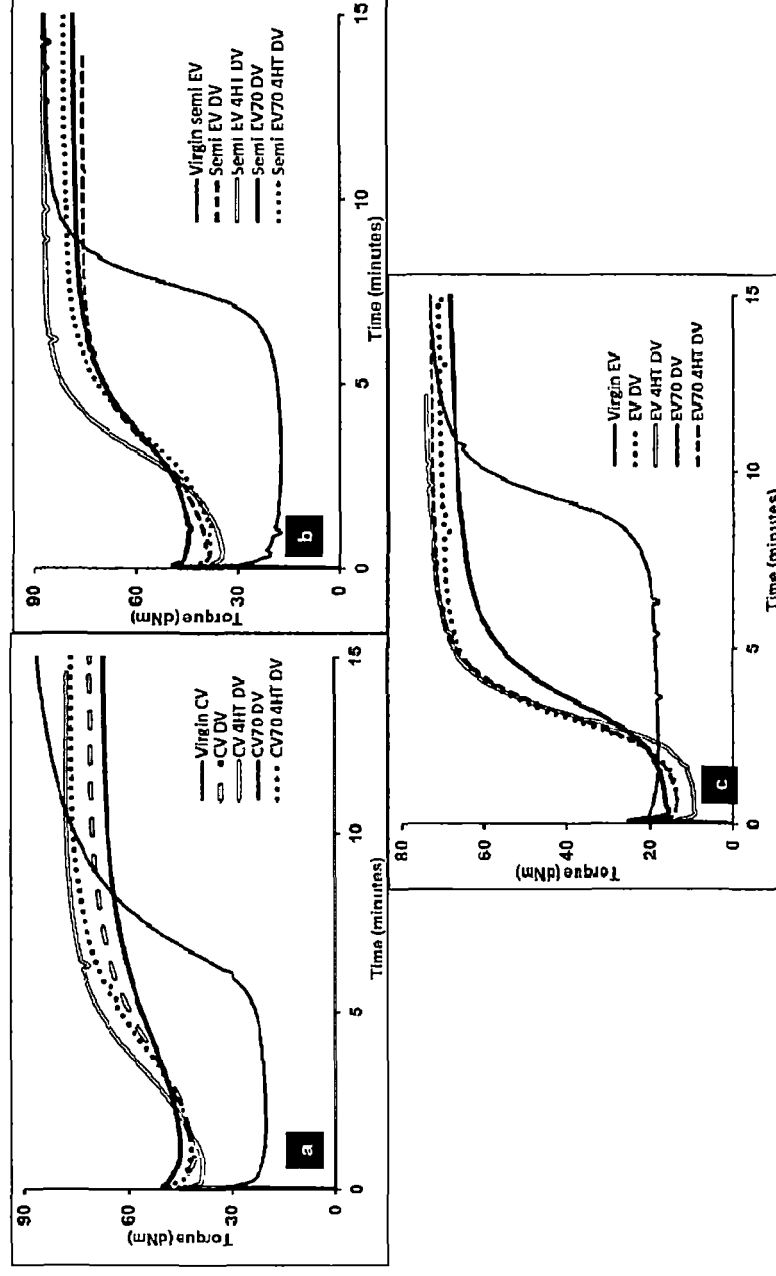
Figure 5.5 Cure curves of samples devulcanised after aging at 70°C in comparison with corresponding samples devulcanised without ageing

Table 5.7 Comparison of cure characteristics of samples devulcanised with and without ageing at 70^0C

Sample		Torque (dNm)					
		Unaged			Aged at 70°C for seven days		
		Minimum, M_L	Maximum, M_H	M_H-M_L	Minimum, M_L	Maximum, M_H	M_H-M_L
CV	DV	48.6	78	29.4	45.1	67	21.9
	4HT DV	34	78.3	44.3	41.6	76.5	34.8
Semi	DV	47.9	83.6	35.7	43.9	78.5	34.6
EV	4HT DV	33.9	79.1	45.2	38.2	81	42.8
EV	DV	18.6	79	60.4	22	69.4	47.4
	4HT DV	9.5	75.5	66	13.6	73.2	59.6

For devulcanised samples prepared from 70°C aged vulcanisates, a decrease in the extent of lowering of minimum torque in the presence of stable free radical was observed. Also, the maximum torque attained by the devulcanised samples during revulcanisation was less than the corresponding devulcanised sample prepared from un-aged samples. Scorch time and cure time of the devulcanised samples prepared from 70°C aged vulcanisates were marginally higher than the corresponding sample from un-aged vulcanisate.

Revulcanisate properties

Comparison of tensile strength and tear strength of the virgin vulcanisates, aged vulcanisates and the corresponding revulcanisates is illustrated in Figure 5.6a and Figure 5.6b respectively.
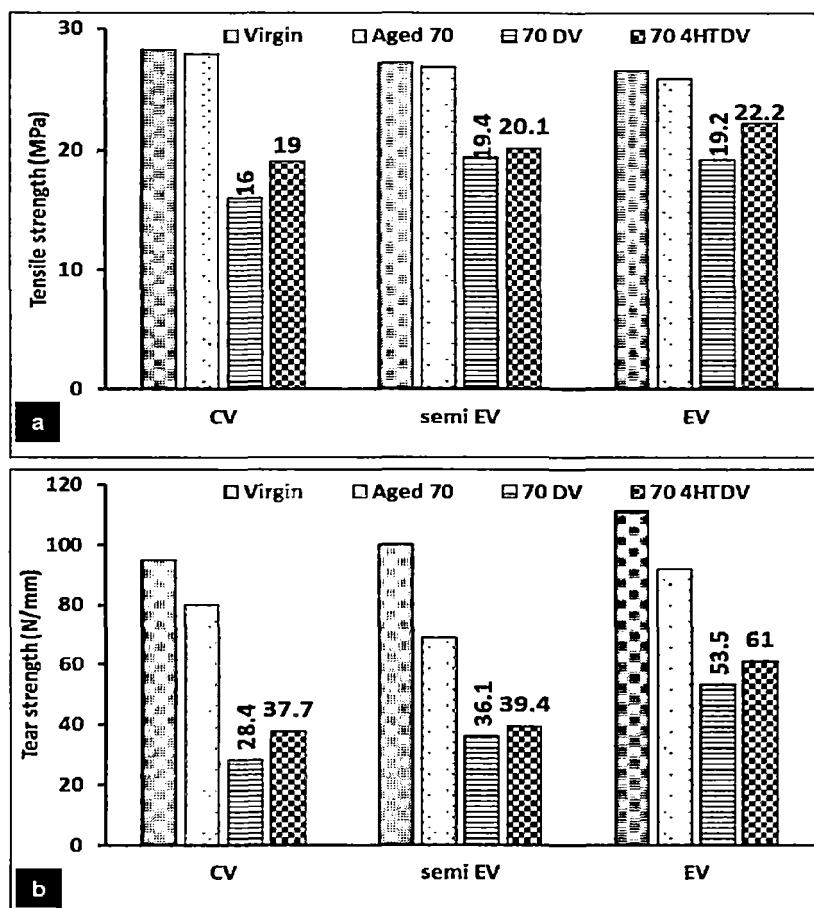
Figure 5.6 Comparison of **a:** tensile strength and **b:** tear strength of the revulcanisates (devulcanised after aging at 70^0C) with corresponding original samples

The revulcanisate properties of the NR vulcanisates devulcanised after ageing at 70°C for seven days in comparison with the corresponding virgin vulcanisate (with and without ageing) and the aged vulcanisates are given in Table 5.8 and the respective stress-strain curves in Figure 5.7. It

could be observed that, both the tensile strength and the tear strength of the revulcanised samples were improved for 4HT assisted devulcanisation.

Ageing at 70°C for seven days in an air oven did not severely deteriorate the vulcanisate properties of the NR vulcanisates. After ageing at 70°C for seven days, the elongation at break of the vulcanisates decreased with a corresponding increase of modulus values. The stress-strain curves given in Figure 5.7 shows that, this increase in modulus is the least in the case of EV cured samples. But, the modulus values of all the revulcanisates were comparable.

Table 5.8 Revulcanisate properties of samples devulcanised after ageing at 70°C for seven days

Sample	Tensile Strength, MPa	Elongation at Break, %	M100, MPa	M200, MPa	M300, MPa	Tear strength , N/mm
CV	28.2	719	2.3	5.2	9.1	95
CV70	27.9	644	3	6.7	11.3	80
CV70 DV	16	595	1.6	3.3	5.8	28.4
CV70 4HTDV	19	627	1.8	3.7	6.4	37.7
SEV	27.2	734	2.3	5.1	8.8	100
SEV70	26.8	614	3	6.7	11.1	69
SEV70 DV	19.4	625	1.8	3.7	6.4	36.1
SEV70 4HTDV	20.1	624	1.9	3.9	6.7	39.4
EV	26.5	754	1.8	4.1	7.3	111
EV70	25.9	678	2.1	4.9	8.6	92
EV70 DV	19.2	776	1.5	3.1	5.4	53.5
EV70 4HTDV	22.2	742	1.6	3.4	5.8	61

Stable free radiacal assisted mechanical devulcanisation
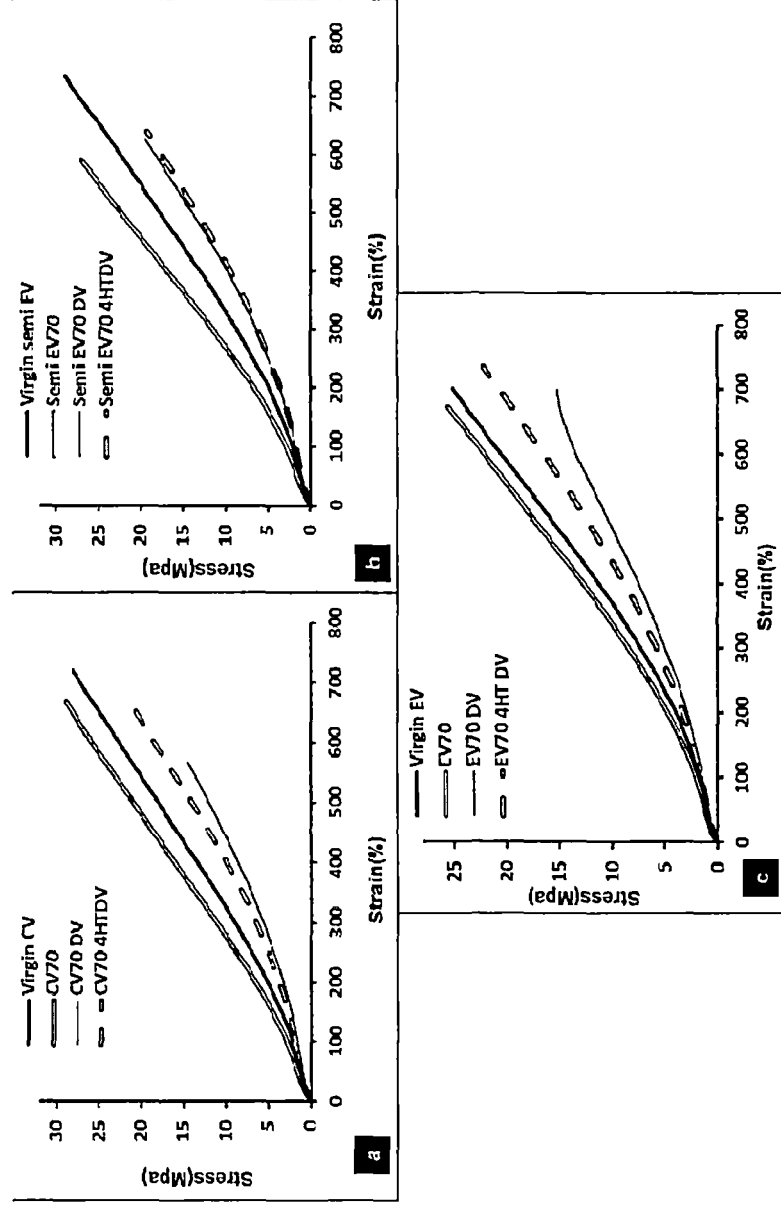
Figure 5.7 Stress strain curves of a: CV; b: Semi EV and c: EV cured NR samples devulcanised after ageing at 70°C in comparison with corresponding un-aged samples

5.3.2.2 Aged at 100 °C for three days

Cure characteristics

The cure characteristics during revulcanisation of devulcanised samples prepared from NR vulcanisates aged at 100°C for three days are listed in Table 5.9 and the corresponding cure curves are given in Figure 5.8.

Table 5.9 Cure characteristics of NR samples devulcanised after ageing at 100°C for three days

Devulcanised sample	Torque (dNm)			Scorch Time, min	Cure time, min
	Minimum M_L	Maximum , M_H	M_H-M_L		
CV100 DV	41.9	53.5	11.6	1.9	10
CV100 4HTDV	40.6	57.8	17.2	2.1	7.8
Semi EV100 DV	43.3	67.2	23.9	1.4	8
Semi EV100 4HTDV	42.6	71.1	28.5	1.1	7.1
EV100 DV	22.1	64.4	42.3	1.9	6.2
EV100 4HTDV	25.5	67	41.5	1.7	5.2

In this case, the minimum torque of the devulcanised samples are higher when stable free radical was used for devulcanisation. Also, the total torque attained by the system is significantly low especially in the case of CV and semi EV cured vulcanisates in comparison with the former cases. Though the lowering of minimum torque in the presence of 4HT is absent, a higher maximum torque is attained by the samples during revulcanisation after 4HT assisted devulcanisation except for EV samples. Comparison of cure characteristics of devulcanised samples prepared from NR vulcanisates aged at 100°C for three days with the corresponding characteristics of devulcanised samples prepared from un-aged vulcanisates is given in Table 5.10.
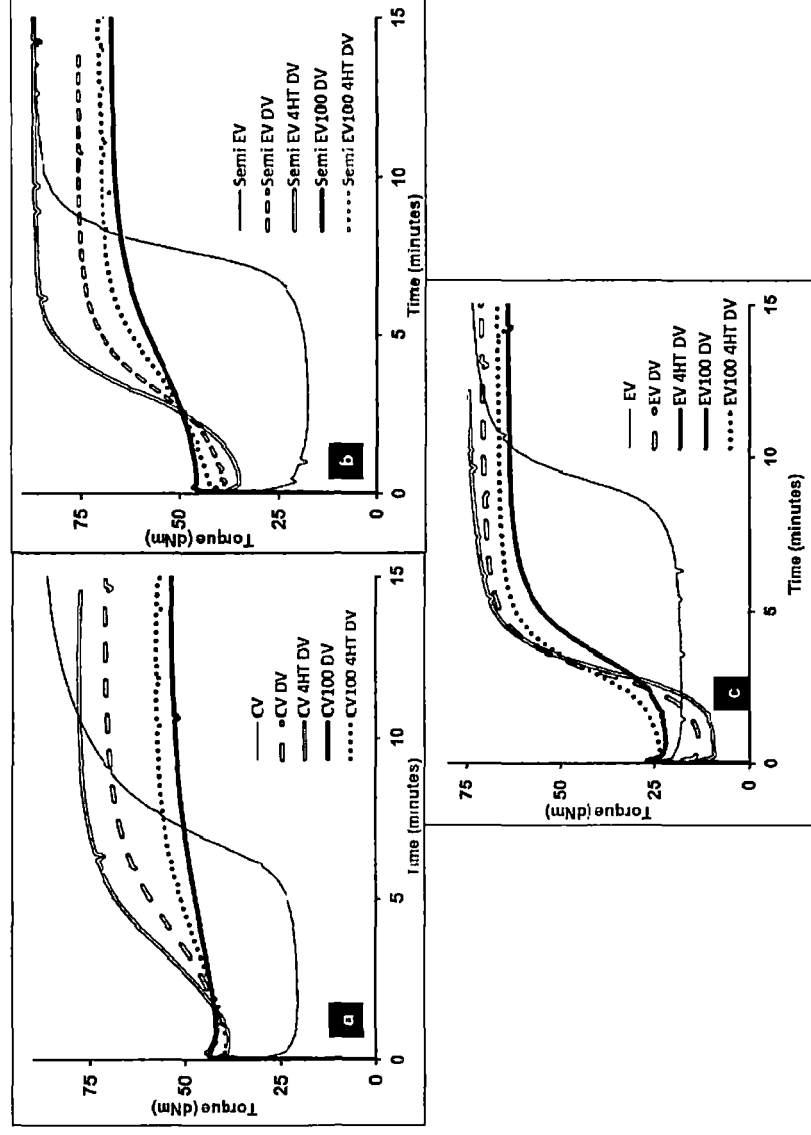
Figure 5.8 Cure curves of **a**: CV; **b**: Semi EV and **c**: EV cured NR samples devulcanised after ageing at 100°C

Table 5.10 Comparison of cure characteristics of samples devulcanised with and without ageing 100^0 C

Sample		Torque (dNm)					
		Un-aged			Aged at 100°C for three days		
		Minimum, M_L	Maximum, M_H	M_H-M_L	Minimum, M_L	Maximum, M_H	M_H-M_L
CV	DV	48.6	78	29.4	41.9	53.5	11.6
	4HT DV	34	78.3	44.3	40.6	57.8	17.2
Semi	DV	47.9	83.6	35.7	43.3	67.2	23.9
EV	4HT DV	33.9	79.1	45.2	42.6	71.1	28.5
EV	DV	18.6	79	60.4	22.1	64.4	42.3
	4HT DV	9.5	75.5	66	25.5	67	41.5

The minimum torque of the mechanically devulcanised CV and semi EV samples devulcanised after ageing at 100°C for three days were lower than that of the corresponding values for un-aged samples. For 4HT assisted devulcanised CV and semi EV samples prepared from 100°C aged NR vulcanisates, the minimum torque was higher in comparison with the corresponding devulcanised samle prepared from un-aged NR vulcanisates. In the case of EV cured vulcanisates, the minimum torque after devulcanisation of samples aged at 100°C was significantly higher than the corresponding values of vulcanisates devulcanised without ageing.

Revulcanisate properties

Table 5.11 gives the revulcanisate properties of the CV, semi EV and EV samples prepared from devulcanisation of NR vulcanisates aged at 100°C for three days and the stress-strain curves are given in Figure 5.9.

Table 5.11 Revulcanisate properties of samples devulcanised after ageing at 100°C

Sample	Tensile Strength, MPa	Elongation at Break, %	M100, MPa	M200, MPa	M300, MPa	Tear strength, N/mm
CV	26	689	2.3	5.1	8.8	96
CV100	14.6	340	3.2	7.6	12.6	31.4
CV100 DV	6.9	339	1.6	3.4	5.8	16.3
CV100 4HTDV	8.9	393	1.7	3.6	6.1	19.9
SEV	28.3	697	2.4	5.5	9.6	102.9
SEV100	14.8	393	3.8	9.1	15	36
SEV100 DV	11.2	407	1.9	4.1	7.2	22.1
SEV100 4HTDV	15.5	531	1.9	4	6.8	28
EV	24.7	690	1.8	4.2	7.6	101
EV100	21	512	2.5	6	10.7	43.4
EV100 DV	15.5	564	1.7	3.6	6.2	38.5
EV100 4HTDV	18	635	1.7	3.5	6	43.3

Severe reduction in vulcanisate properties was observed after ageing at 100°C for three days especially for CV and semi EV samples. The modulus values of the aged vulcanisates are significantly higher than the original vulcanisates after ageing. As modulus at 100per cent is a direct indication of crosslink density of the vulcanisate, the increase in crosslink density of the vulcanisate has to be acknowledged[21].Comparison of tensile strength and tear strength of the virgin, aged and revulcanised samples are given in Figure 5.10.
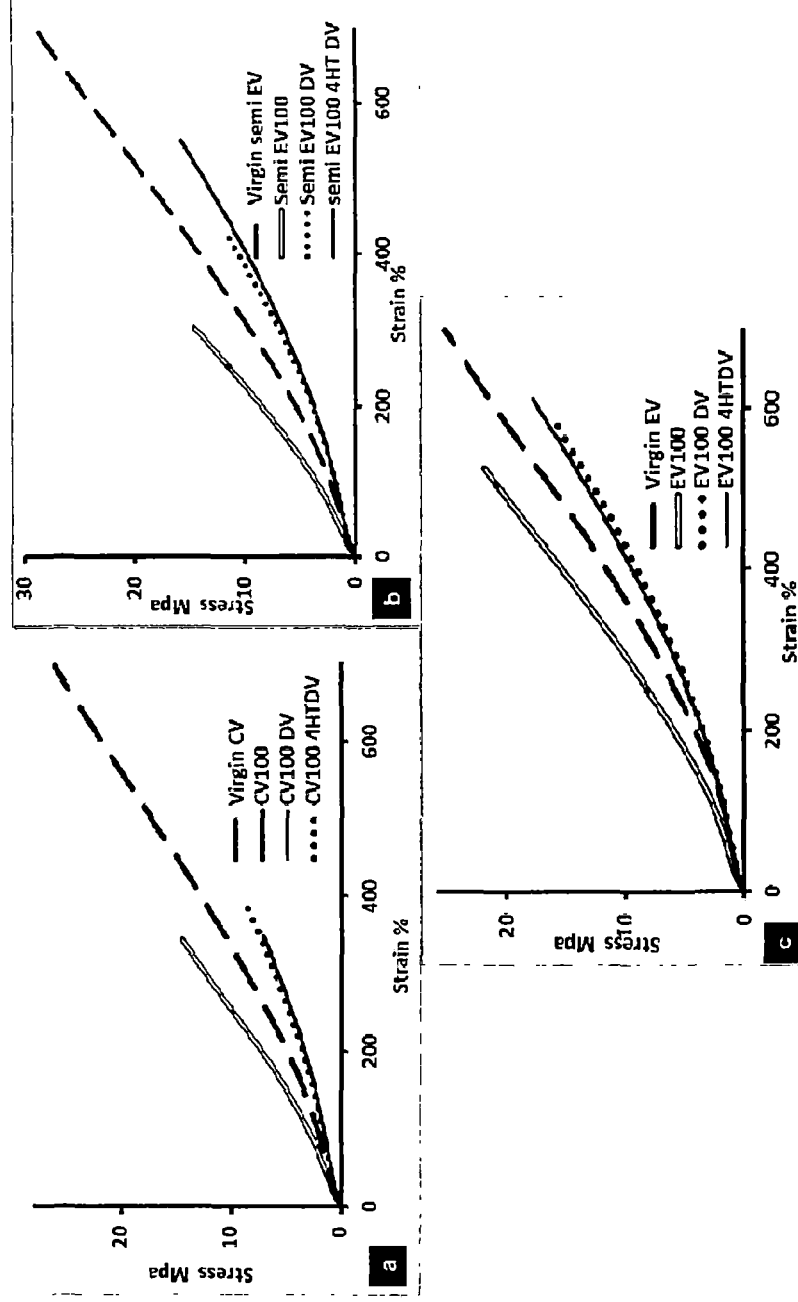
Figure 5.9 Stress strain curves of **a**: CV; **b**: Semi EV and **c**: EV cured NR vulcanisates devulcanised after ageing at 100°C
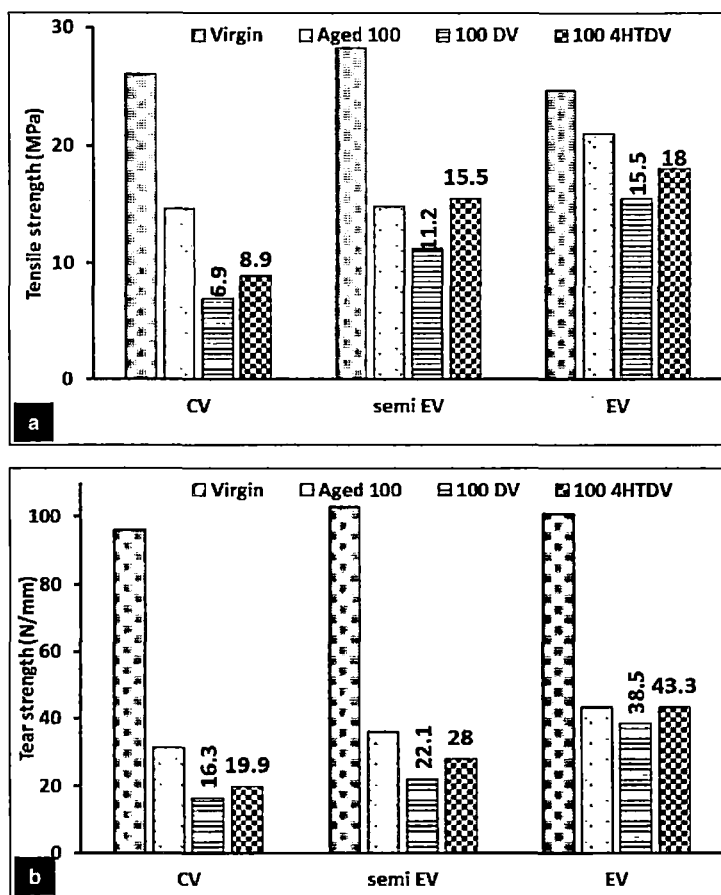
Figure 5.10 Comparison of **a:** tensile strength and **b:** tear strength of the revulcanisates (devulcanised after aging at 100^0C) with corresponding original samples

A comparative diagram of the revulcanisate tensile strength and tear strength of the devulcanised samples (both un-aged and aged) along with the corresponding original properties are outlined in Figure 5.11 and 5.12.
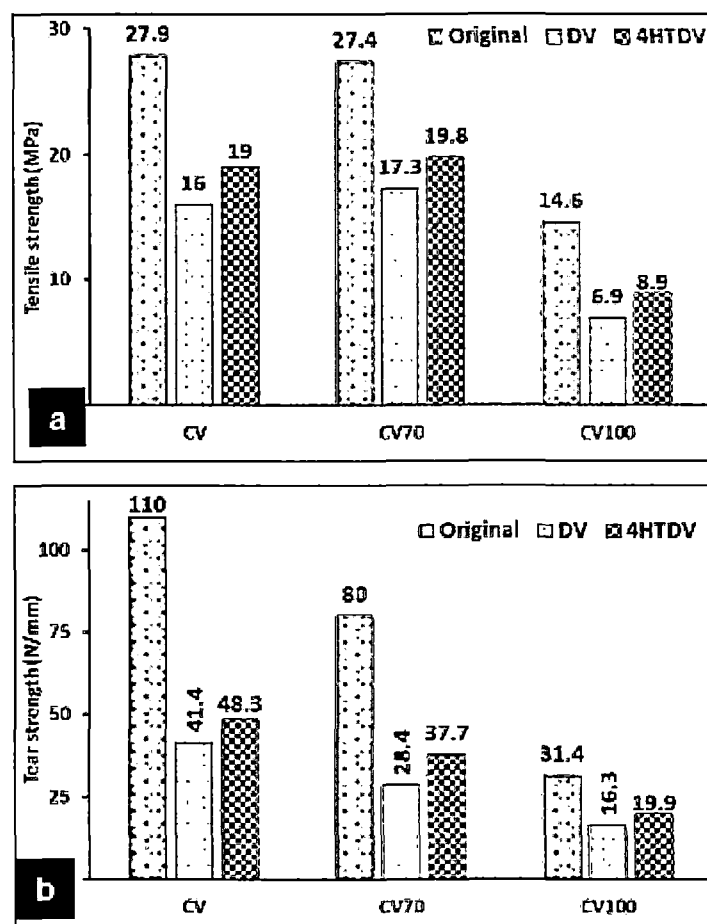
Figure 5.11 Tensile strength **(a)** and tear strength **(b)** of original and revulcanised CV samples (unaged and aged)
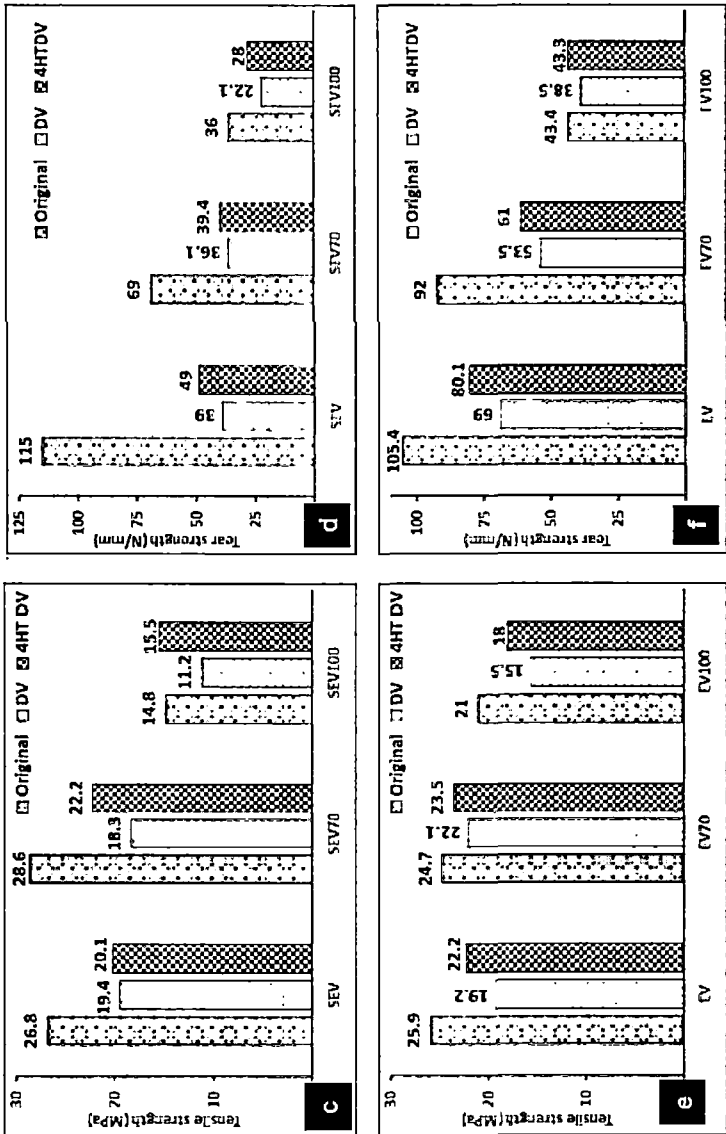
Figure 5.12 Tensile strength and tear strength of original and revulcanised **c** & **d**: semi EV; **e** & **f**: EV samples (unaged and aged)

From the results of the comparative evaluation of the devulcanised samples before and after ageing, it might be assumed that the decisive factor in the revulcanisate properties of devulcanised rubbers are the state of the material to be devulcanised. Being the per cent recovery of vulcanisate properties remaining comparable for different rubbers for a particular devulcanisation process, higher revulcanisate properties can be achieved if the material to be devulcanised is of good quality. The present study reveals that, the per cent retention of properties after devulcanisation or ageing is highly dependent on the cure system used for initial curing of the sample. In other words, the level of degradation suffered by the rubber to be devulcanised determines the revulcanisate properties of the devulcanised rubber which is highly determined by the initial vulcanisation formulation of the sample. In all the cases stable free radical assisted devulcanised samples gave better revulcanisate properties. Therefore stable free radical assisted devulcanisation is a promising method for efficient devulcanisation of used rubber vulcanisates.

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Chapter 6

Optimization of 4-Hydroxy Tempo assisted Devulcanisation of Carbon Black Filled NR Vulcanisates

6.1 INTRODUCTION

Devulcanisation aims in converting used rubber into a processable and vulcanisable product through cleaving of C-S, S-S and C-C crosslinks existing in the vulcanised rubber. Stable free radical, 4-hydroxy TEMPO (4HT) is found to be an effective aid for the mechanical devulcanisation of rubber vulcanisates. The effect of concentration of 4HT (0-6phr) on the efficiency of devulcanisation of carbon black filled NR vulcanisates was studied and the possible mode of action of this devulcanisation aid is investigated in this chapter. In order to study the effect of the crosslink distribution of the original sample[1, 2] on the devulcanisation efficiency, original samples were prepared using CV, semi EV and EV cure systems. The crosslink distribution pattern of the original sample, and the extent to which the different types of crosslinks which have been de-bonded or broken during the shearing process, in the presence and absence of 4HT was determined by chemical probe analysis[3]. A comparative study between stable free radical and other devulcanisation methods is also discussed.

Based on the hypothesis developed from the observations of previous chapters, 4HT is expected to stabilize the free radicals generated by crosslink scission under the influence of shear. This stabilization will prevent the possible recombination of once cleaved crosslinks, thereby increase the net effective number of cleaved crosslinks in comparison with simple mechanical devulcanisation.

6.2 EXPERIMENTAL

6.2.1 Effect of 4HT concentration on devulcanisation of NR vulcanisates

Vulcanisates with known formulations and properties were prepared as per formulations given in Table 2.3. Devulcanisation was done in a laboratory two roll mixing mill as described in chapter 2 using chips of $1 cm^2$ size cut from tensile sheets moulded from the original vulcanisate and revulcanised using the formulation given in Table 2.5. Rubber Process Analyser RPA 2000 was used to monitor the cure characteristics at $150^{\circ}C$ and strain sweep studies of the devulcanised raw samples at $(60^{\circ}C)^{4, 5}$. Test samples were moulded in an electrically heated hydraulic press for their respective cure times (t_{c90}). Tensile strength and tear strength measurements of the revulcanised samples were performed with a Zwick UTM. The crosslink density, per cent devulcanisation, Horikx analysis, crosslink distribution pattern, SEM analysis of the tear fracture surface and TG analysis of the samples were carried out by respective methods described in chapter 2.

6.2.2. Comparison of 4HT assisted devulcanisation with industrially practiced mechano-chemical devulcanisation processes

The results of the studies with stable free radical assisted devulcanisation showed that 4HT is an efficient devulcanisation aid probably owing to its ability to block the re-crosslinking of once cleaved crosslinks. The comparison studies described in chapter 4 showed that, industrially practiced mechano-chemical devulcanisation processes were in no way different from mechanical devulcanisation. Hence, the comparative study with industrially practiced mechano-chemical devulcanisation processes like De Link process and Lev Gum process was extended to include stable free radical assisted devulcanisation following the same experimental procedures described in Chapter 4.

6.2.3. Effect of 4HT on commercial devulcanised rubber

The effect of stable free radical on a commercial devulcanised rubber on a second round devulcanisation in a two roll mill was investigated using a commercially available devulcanised rubber (DRC) supplied by Sundaram Industries Limited, Chennai, India. The DRC was initially characterized by thermogravimetric analysis (Table 6.1) and three experimental cases were analyzed.

Table 6.1 Composition of DRC determined by TGA

Components	Quantity (%)
Acetone extractable	11.84
Rubber hydrocarbon	53.4
Carbon black	28.9
Ash	5.8

Case i: 100g DRC was blended with 10g virgin rubber and revulcanised

Case ii: DRC was subjected to mechanical devulcanisation in the tight nip of two roll mill (55passes), blended with 10g virgin rubber per 100g DRC and revulcanised

Case iii: DRC was subjected to mechanical devulcanisation with the aid of 2phr 4-Hydroxy TEMPO in the tight nip of two roll mill (30passes), blended with 10g virgin rubber per 100g DRC and revulcanised

The residual crosslink densities of the devulcanised samples were determined and the devulcanised samples were revulcanised using the revulcanisation formulation given in Table 2.5.

6.2.4. Comparison of ultrasound devulcanisation processes with stable free radical assisted devulcanisation

Similarly, a comparative study of the stable free radical assisted mechanical devulcanisation and ultrasound devulcanisation was also conducted. In this case, the revulcanisate properties of the ultrasonically devulcanised carbon black filled NR vulcanisates were compared with the revulcanisate properties of the stable free radical assisted mechanical devulcanisation of identical vulcanisates. As the facility for ultrasound devulcanisation was not available in the laboratory, the comparison was made with the results available in the literature. Formulation for the preparation of NR vulcanisates employed for ultrasound devulcanisation and its subsequent revulcanisation obtained from the literature[6] is given in Table 6.2.

Table 6.2 Formulation for original vulcanisate and revulcanisate preparation for comparison with ultrasound devulcanisation

	Original (phr)	Revulcanisation (phr)
Devulcanised rubber	-	100*
Natural Rubber	100	-
HAF black	35	-
Naphthenic oil	3.5	-
ZnO	5	2.5
Stearic acid	1	0.5
TDQ**	1.5	-
CBS	1	0.5
Insoluble sulphur	2	2

* Rubber hydrocarbon (RH) =50

**2,2,4 trimethyl-1,2 dihydroquinoline

NR vulcanisates were prepared in the laboratory using the formulation given in Table 6.2. These vulcanisates were devulcanised mechanically and with the assistance of 4HT and revulcanised with the formulation given in Table 6.2. The revulcanisate properties were compared with the corresponding results of the ultrasound devulcanised samples from literature.

6.3. RESULTS AND DISCUSSION

6.3.1. 4-Hydroxy TEMPO assisted mechanical devulcanisation

6.3.1.1 Number of passes for devulcanisation

The observed variation in the required number of passes for devulcanisation of CV, semi EV and EV vulcanisates with varying amounts of 4HT is listed in Table 6.3. It has been observed that, the required number of passes through the tight nip of the two roll mill for effective devulcanisation lowered significantly with the incorporation of stable free radical.

Table 6.3 Number of passes required for devulcanisation with varying amounts of 4-Hydroxy TEMPO

4HT, phr	No. of passes		
	CV	Semi EV	EV
0	52	46	35
1	49	45	33
2	40	45	30
3	35	40	26
4	35	35	24
5	30	30	24
6	30	30	-

This lowering in number of passes for devulcanisation implies a net lowering in the time of devulcanisation which will be reflected as lower energy consumption for stable free radical assisted devulcanisation in comparison with mechanical devulcanisation. Though, the required number of passes for devulcanisation of CV vulcanisates were higher than the semi-EV vulcanisates for mechanical devulcanisation, it lowered with the increase in 4HT dosage and became the same since the incorporation of 4phr stable free radical during devulcanisation. The EV samples got devulcanised with the least numbers of passes both for mechanical and 4HT assisted devulcanisation. This observed lowering of devulcanisation time with the incorporation of 4HT as a devulcanisation aid in the mechanical devulcanisation might be an indication of the ability of stable free radical in improving the mechanical devulcanisation of vulcanisates.

6.3.1.2. *Characterization of devulcanised samples*
Processability analysis

The strain sweep test can assess the relative contribution of the viscous and elastic components in the polymer. The plot of strain versus corresponding tan delta values of the devulcanised samples (before adding virgin NR) carried out at 60°C (uncured state) is given in Figure 6.1. As the process of devulcanisation aims to cleave the sulphur crosslinks and thereby release the polymer chains, the devulcanised rubber can be regarded as an uncured rubber compound. As the efficiency of devulcanisation increases, the effective number of crosslink cleavage increases thereby the rubber tends to be increasingly viscous with improved processability. This lowering of elastic modulus/torque and the corresponding increase in viscous torque will hence vary based on the percent devulcanisation of the rubber.
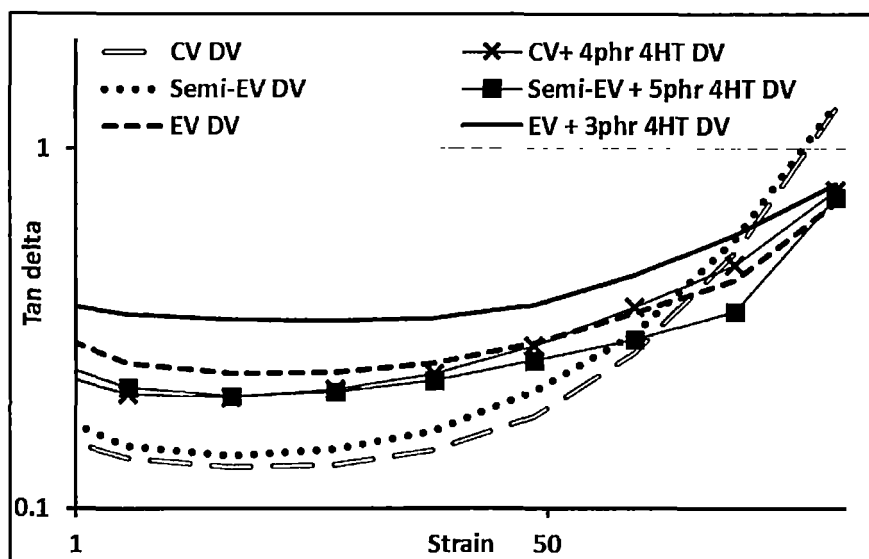
Figure 6.1 Processability of devulcanised samples

Devulcanised samples with higher per cent devulcanisation will have higher tan delta value and therefore better processability compared with the samples having lower per cent devulcanisation and consequent lower processability. The lower value of tan delta associated with the vulcanisates with low per cent devulcanisation is due to the presence of high gel content, which causes the elastic response to be significantly higher due to the formation of a loose network[7]. This variation in tan delta values due to variation in viscosity/processability is clearly visible at lower strains as under the influence of higher strains untangling of the chains will occur and the tan delta values of all samples might be similar.

IT can be observed Figure 6.1 that, the tan delta values of the vulcanisates devulcanised with the assistance of stable free radical were significantly higher than that of the corresponding vulcanisates devulcanised by mechanical devulcanisation. EV vulcanisates devulcanised by 4HT assisted method was associated with the highest tan delta value in

comparison with other devulcanised samples. The tan delta value of mechanically devulcanised EV samples were observed to be marginally higher than the tan delta value of CV and semi EV vulcanisates devulcanised with the aid of optimum dosage of 4HT. It might be inferred that, the higher tan delta at lower strains of the EV vulcanisates indicate the better processability and/or lower viscosity[8] of the devulcanised EV vulcanisate than the CV and semi-EV samples.

Residual crosslink density and percent devulcanisation

The efficiency of devulcanisation was estimated by determining the residual crosslink density of the devulcanised samples at various concentrations of 4HT. The residual crosslink densities and corresponding per cent devulcanisation[9-12] are given in Table 6.4 and the graphical representation of lowering of crosslink density with 4HT concentration is illustrated in Figure 6.2. It can be observed that the variation in residual crosslink density and percent devulcanisation of all vulcanisates are not alike. The highest percent devulcanisation of 40.5 per cent and 80.6 per cent for mechanical and 4HT assisted devulcanisation respectively was achieved by EV samples. The optimum loading of 4HT was the lowest of 3phr for EV samples whereas in the case of CV and semi EV cured samples, the optimum dosage was about 4-5phr. Also, earlier reports justifies this observation with the evidence that degree of devulcanisation is higher for systems with smaller amounts of polysulphidic crosslinks[13]. The better response of EV cured samples towards devulcanisation might also be due to the low initial crosslink density of the original sample as mentioned in chapter 5.
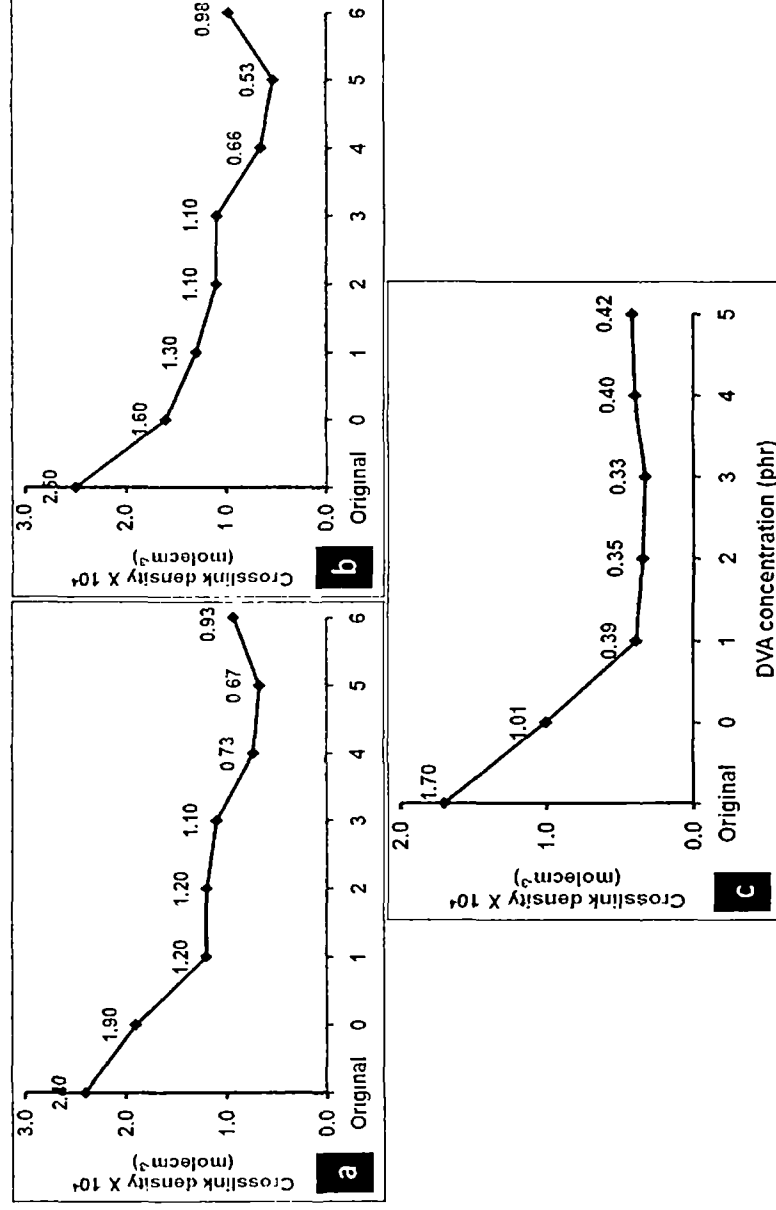
Figure 6.2 Effect of 4HT concentration on residual crosslink density of **a:** CV; **b:** semi EV and **c:** EV cured samples

Table 6.4 Effect of 4HT concentration on residual crosslink density and percent devulcanisation

Sample	Crosslink density x 10^4, mole/cm^3			Percent devulcanisation, %		
	CV	Semi EV	EV	CV	Semi EV	EV
Virgin	2.4	2.5	1.7	-	-	-
0phr 4HT	1.9	1.6	1.01	20.8	36	40.5
1phr 4HT	1.2	1.3	0.39	50	48	77.1
2phr 4HT	1.2	1.1	0.35	50	56	79.4
3phr 4HT	1.1	1.1	0.33	54.2	56	80.6
4phr 4HT	0.73	0.66	0.4	69.6	73.6	76.5
5phr 4HT	0.67	0.53	0.45	72.1	78.8	73.5
6phr 4HT	0.93	0.98	-	61.3	60.8	-

The considerable difference in the crosslink density reduction of devulcanised samples in the presence and absence of 4HT clearly establish the role of 4HT in increasing the efficiency of devulcanisation process. It is observed that, the crosslink density of the vulcanisates decrease gradually with increasing concentration of 4HT to a minimum and then increases. This particular 4HT concentration associated with maximum devulcanisation efficiency might be regarded as the optimum 4HT concentration for that particular sample and is expected to be reflected in the revulcanisate properties also.

Horikx analysis

A plot of sol fraction of CV, semi EV and EV cured vulcanisates devulcanised mechanically and with the assistance of 4HT against the relative decrease in crosslink density plotted along with the standard Horikx curves is given in Figure 6.3, Figure 6.4 and Figure 6.5 respectively.

According to Horikx theory, the data below the chain scission curve means that devulcanisation process has occurred by selective breakage of crosslinks whereas, data above and very close to the chain scission curve relate to degraded samples owing to higher degree of main chain scission[14].
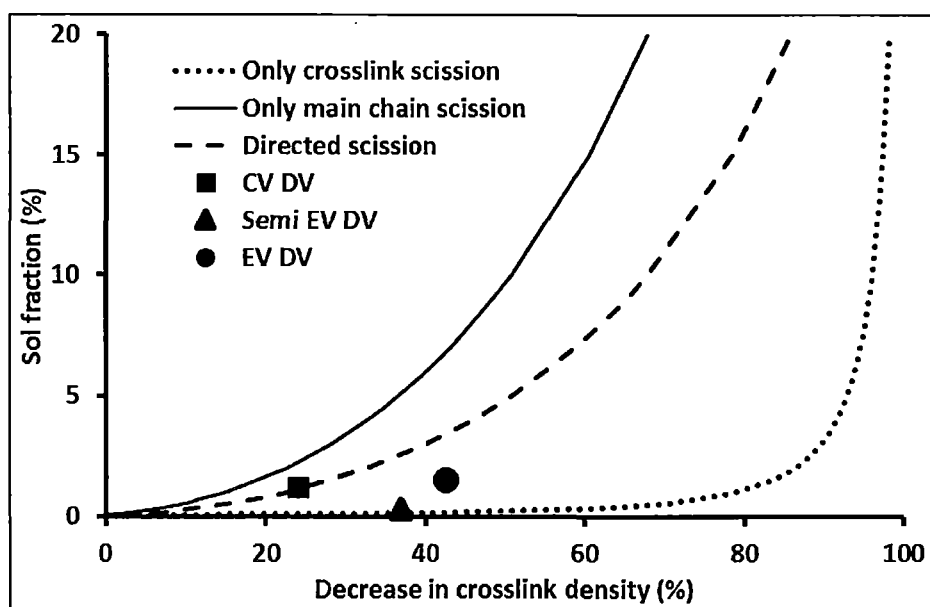
Figure 6.3 Horikx plot of mechanically devulcanised NR samples

The data of the devulcanised CV samples lies in the area between the standard crosslink scission curve and the directed scission curve but closer to the latter, indicating main chain scission dominated devulcanisation process. In the case of devulcanised semi EV samples, the data lies closer to the standard crosslink scission curve indicating that mechanical devulcanisation of semi EV samples predominantly involves crosslink scission. For EV samples, the data lies midway between the standard directed scission curve and crosslink scission curve indicating that the mechanical devulcanisation of EV samples proceeds via a combination of

crosslink scission and random scission in which main chain scission occurs in the neighbourhood of the crosslink sites[15].

Generally for the best devulcanisation results, it is necessary to keep the devulcanisation temperature as low as possible to obtain a high ratio of crosslink to main chain scission, and a homogenous breakdown of the vulcanised network[16,17] which is observed to be accomplished in the mechanical devulcanisation process of EV samples as per the Horikx analysis results. This is reflected as such in the percent devulcanisation calculated from the crosslink density data obtained from the swelling studies also. CV samples whose devulcanisation involves predominant main chain scission, is associated with the least percent devulcanisation whereas EV samples with an equilibrium between crosslink and main chain scission has the highest percent devulcanisation. The devulcanised semi EV samples with predominant crosslink scission and lesser main chain scission have a percent devulcanisation in between the other two systems.

Figure 6.4 shows the Horikx plot of vulcanisates devulcanised with the assistance of 4HT. Here, the amount of 4HT used as a devulcanisation aid was lower than the optimum dosage needed for highest per cent devulcanisation in all cases. It can be observed from the figure that, the Horikx data for the CV vulcanisates devulcanised with 3phr 4HT have moved closer towards the crosslink scission curve in comparison with the corresponding data for the mechanical devulcanisation. Also in this case, a higher per cent devulcanisation was observed.

The Horikx data for the semi EV samples devulcanised with the assistance of 3phr 4HT lies in between the directed scission curve and crosslink scission curve denoting that crosslink scission is the predominant chain scission happened during 4HT assisted devulcanisation. The data also reveals that, more number of main chains are cleaved thereby increasing the

sol fraction of the devulcanised sample in comparison with the mechanical devulcanisation of semi EV vulcanisates. While the Horikx data of 4HT assisted devulcanised CV and semi EV samples were comparable, the Horikx data of EV sample devulcanised with the aid of 1phr 4HT lies distinctly different. The comparatively higher sol fraction associated with higher per cent devulcanisation make the Horikx data of devulcanised EV sample indicates predominant crosslink scission along with directed scission of main chain.
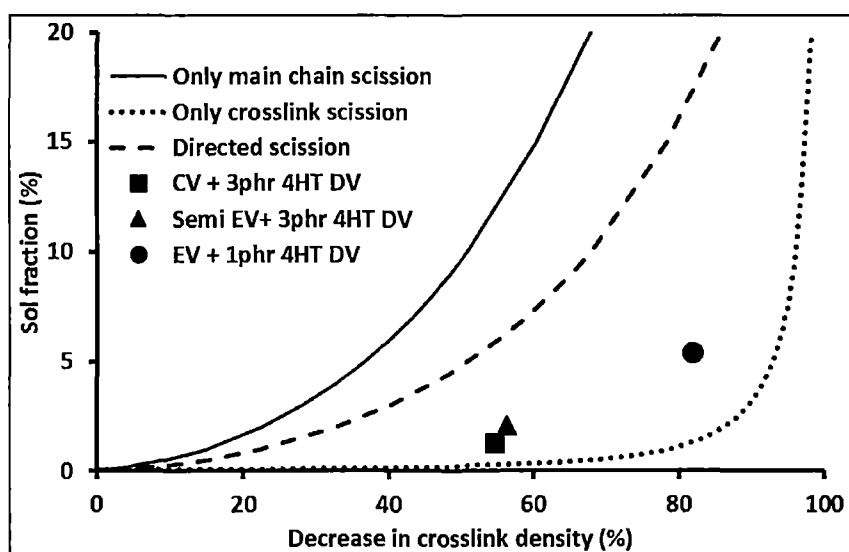
Figure 6.4 Horikx plot of NR samples devulcanised with 4HT(less than optimum amount

The Horikx plot of the samples devulcanised with optimum dose of 4HT given in Figure 6.5 shows the significant increase in sol fraction and decrease in crosslink density of CV and semi EV samples. The Horikx data for CV vulcanisate lies in between the directed scission and crosslink scission curve. Also, it can be observed that the highest sol fraction for devulcanised rubber was associated with the CV vulcanisate although the per cent devulcanisation was the lowest in the group. The Horikx data of the

devulcanised CV sample lies closer towards the directed scission curve than towards the crosslink scission curve. Hence it might be assumed that comparatively higher amount of main chain scission via directed scission have taken place during the devulcanisation of CV vulcanisates in this case, producing more sol fraction even with lower per cent devulcanisation.
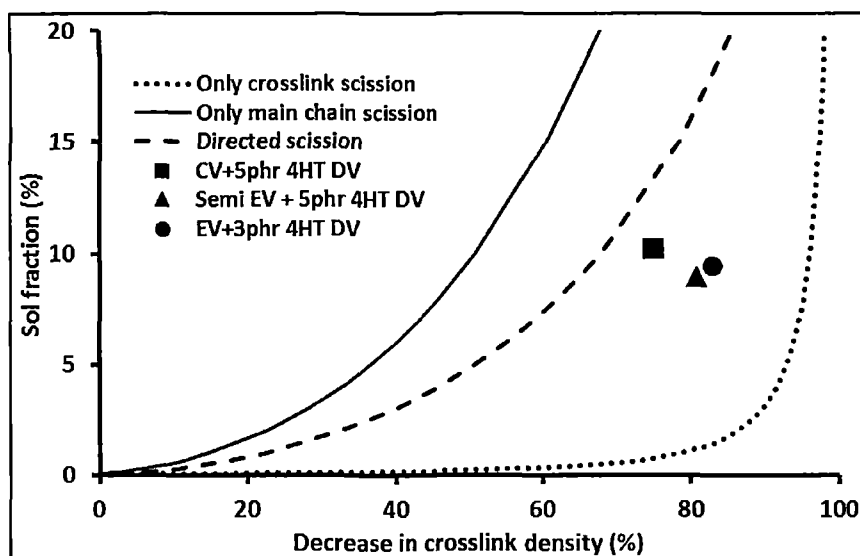
Figure 6.5 Horikx plots of NR samples devulcanised with optimum 4HT concentration

In the case of semi EV sample, both the sol fraction and per cent devulcanisation increased considerably in comparison with 3phr stable free radical assisted devulcanisation. It can be observed from the figure that the data lies in between crosslink scission and directed scission curve, with a little more inclination towards the crosslink scission curve. This indicates that, devulcanisation of semi EV sample with optimum dose of 4HT proceeds via combination of main chain scission and crosslink scission, in which crosslink scission can assumed to be prominent. Hence, it can be observed that the per cent devulcanisation of both CV and semi EV samples devulcanised with optimum 4HT was comparable while the sol fraction

associated with these devulcanised samples differ considerably owing to difference in the nature of bond scission involved. If this observation is correct, it is expected that the per cent retention of properties of the revulcanised CV samples might be lower than that of the corresponding semi EV samples.

The percent devulcanisation of EV samples is the highest and the data lies almost in the middle of crosslink scission curve and directed scission curves. This might be an indication that the devulcanisation of EV cured samples with the aid of optimum 4HT dose proceeds by almost equivalent contribution of main chain scission (via directed scission) and crosslink scission.

Crosslink distribution pattern

Chemical probe analysis of the samples revealed the absolute nature of bond scission involved in the devulcanisation process. The sulphur vulcanised rubber contains three types of crosslinks namely, polysulphidic, disulphidic and monosulphidic crosslinks[18,19]. The ratio of these three types of crosslinks present in a vulcanisate is determined by the cure system employed such as conventional, semi efficient and efficient systems as mentioned in chapter 1.

The increasing order of bond dissociation energy is sulphur - sulphur bond (S-S: $271.7 KJmol^{-1}$), followed by carbon – sulphur bond (C-S: $301 KJmol^{-1}$) and the carbon - carbon bond (C-C: $347 KJmol^{-1}$)[13,20]. Since the shear force exerted during devulcanisation applied on the sample is the same, the crosslink distribution pattern of the devulcanised samples are to be expected to vary from each other corresponding to the crosslink distribution pattern of the original vulcanisates. The crosslink distribution pattern of these three NR vulcanisates considered in this study, determined by chemical probe analysis, is given in Figure 6.6.
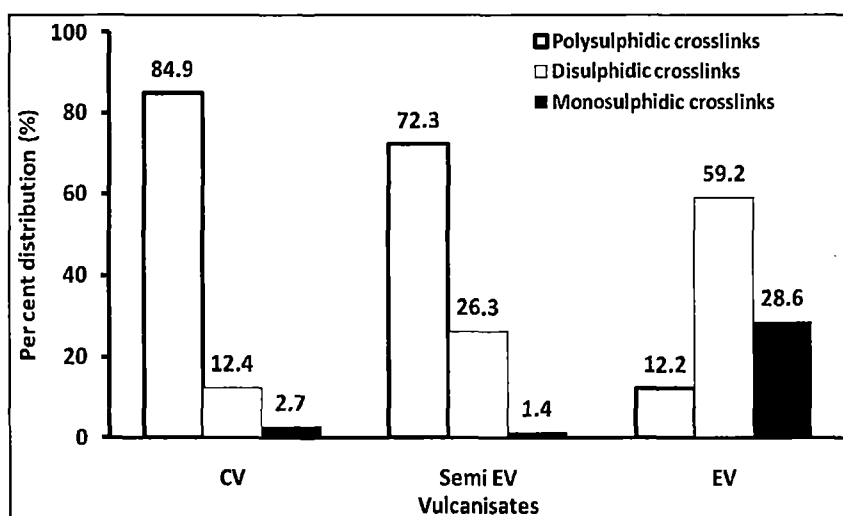
Figure 6. 6 Crosslink distribution pattern of original CV, semi EV and EV vulcanisates

The majority crosslink type of CV vulcanisates was polysulphidic crosslinks (84.9 per cent) followed by disulphidic crosslinks (12.4 per cent) and the least fraction of 2.7 per cent by monosulphidic crosslinks. In the case of semi EV cured vulcanisates, the crosslink distribution pattern was similar to that of the former but with a different percent distribution of crosslinks. The share of polysulphidic crosslinks in semi EV vulcanisates lowered while that of the disulphidic crosslinks increased in comparison with the CV vulcanisates. For EV vulcanisates, disulphidic crosslinks were the majority crosslink type (59.2 per cent) followed by a contribution of 28.6 per cent by monosulphidic crosslinks and the remaining 12.2per cent crosslinks belonged to polysulphidic type.

A comparison of the crosslink distribution pattern of the original and devulcanised CV samples is given in Figure 6.7.
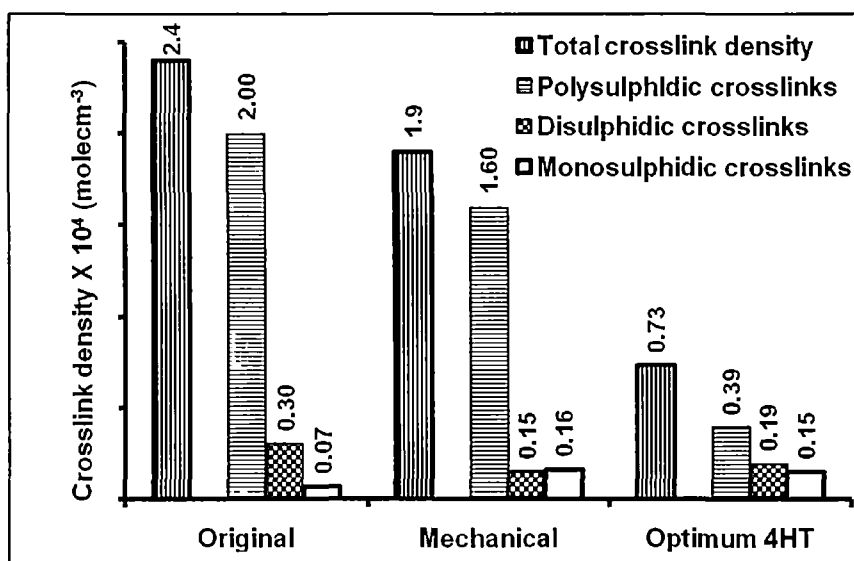
Figure 6. 7 Crosslink density and crosslink distribution of original and devulcanised CV samples

The profound reduction in residual crosslink density of the 4HT assisted devulcanised sample is obvious from the figure. The total crosslink density of 2.4×10^{-4} mole/cm^3 of the original CV cured sample was reduced to 1.9×10^{-4} mole/cm^3 after mechanical devulcanisation while the same was reduced to 0.73×10^{-4} mole/cm^3 after 4HT assisted devulcanisation. The significant difference in residual crosslink density between these two devulcanised samples is propelled by the considerably larger number of polysulphidic bond scission in 4HT assisted devulcanisation. However, the disulphidic crosslink densities of both the devulcanisates were comparable, while the absolute number of monosulphidic crosslinks increased after devulcanisation. Hence, it might be assumed that the higher level of reduction in the absolute number of polysulphidic crosslinks (ie.majority crosslink type) is the reason behind the high per cent devulcanisation in the presence of stable free radical.

Figure 6.8 shows the crosslink density and distribution of the original and devulcanised semi EV vulcanisates which shows similar trends as in the devulcanisation of CV samples.
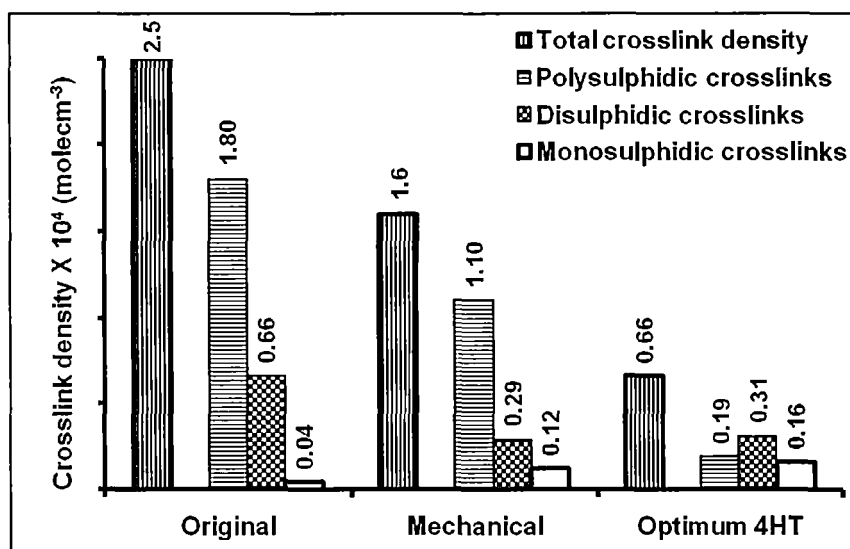
Figure 6. 8 Crosslink density and crosslink distribution of original and devulcanised semi- CV samples

This might be attributed to the similar crosslink distribution pattern of the original CV and semi EV vulcanisates except for the absolute per cent of various crosslinks. The residual crosslink density of the 4HT assisted devulcanised samples was considerably lower than the corresponding mechanically devulcanised samples. Also, the disulphidic crosslink densities in both the devulcanised samples were comparable and the residual monosulphidic crosslink densities of the devulcanised samples were higher than that of the original vulcanisate. This increase in the absolute number of monosulphidic crosslinks might be due to the chain shortening reactions taking place in the vulcanisates during devulcanisation under the influence of shear at ambient conditions, which is quite similar to the crosslink

desulphuration reactions occurring during post crosslinking at vulcanisation temperatures.

Since the crosslink distribution pattern of the original EV vulcanisate differed from that of the CV and semi EV vulcanisates, the crosslink distribution pattern of the devulcanised EV samples also differed from the CV and semi EV samples (Figure 6.9).
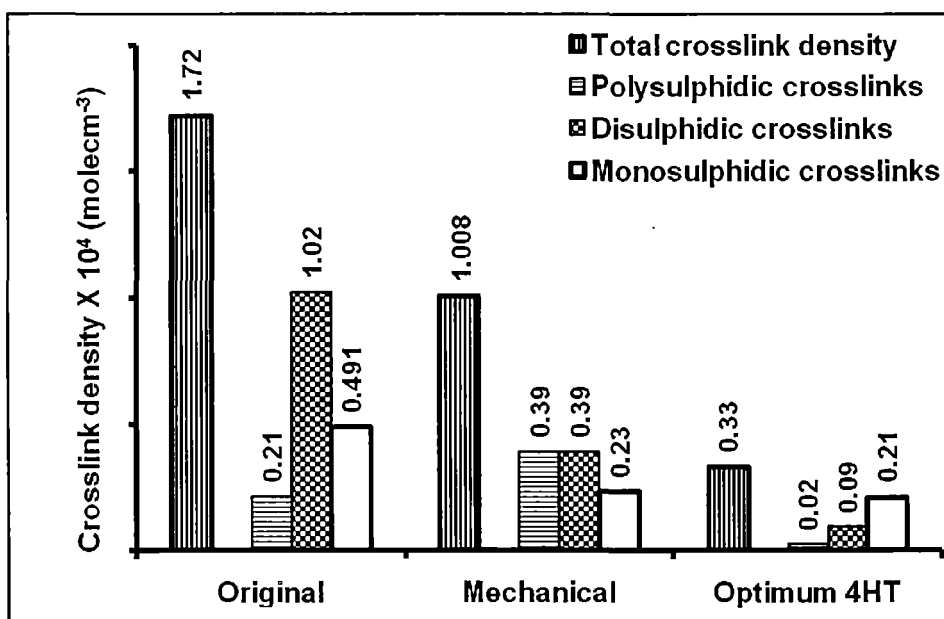
Figure 6. 9 Crosslink density and crosslink distribution of original and devulcanised EV samples

The crosslink density of the original EV vulcanisate was 1.72x10⁻⁴mole/cm³ which lowered to 1.008x10⁻⁴mole/cm³ after mechanical devulcanisation. Assistance of optimum dosage of stable free radical in mechanical devulcanisation further lowered the residual crosslink density to 0.33x10⁻⁴mole/cm³. The polysulphidic crosslink density of the mechanically devulcanised EV sample was higher than the original EV vulcanisate, while the same for 4HT assisted devulcanised sample was significantly lower.

The increase in the polysulphidic crosslink density upon mechanical devulcanisation of EV sample might also be due to the re-crosslinking of cleaved crosslinks (both disulphidic and polysulphidic) during devulcanisation[21]. When stable free radical is used as a devulcanisation aid, these cleaved crosslink fragments might be stabilised instantaneously, thereby limiting the chance of their re-crosslinking and hence the residual polysulphidic crosslink density dropped. Significant lowering of disulphidic crosslink density (majority crosslink type) was observed upon 4HT assisted devulcanisation in comparison with the corresponding mechanically devulcanised sample which attributes to the higher per cent devulcanisation of 4HT assisted devulcanisation of EV sample.

The absence of increase in the monosulphidic crosslink density in this case might be attributed to the (i) lesser number of polysulphidic crosslinks of the original EV vulcanisates that can undergo crosslink desulphuration reactions during devulcanisation and (ii) the higher proportion of monosulphidic crosslinks in the original EV vulcanisate leading to increased number of monosulphidic bond scission than the number of monosulphidic crosslinks formed from crosslink desulphuration.

Comparison of per cent variation of crosslinks during devulcanisation

Even though, the major share of the cleaved bonds belongs to the majority crosslink type in each case, the percent cleavage of bond types presents a different picture as shown in Table 6.5. Mechanical devulcanisation of CV and semi EV samples result in a lower percent reduction of polysulphidic crosslinks (majority crosslink type) in comparison with that of the reduction of disulphidic bonds. But, when 4HT was used as devulcanisation aid, the per cent of polysulphidic bond cleaved increased substantially and was well above the percent cleavage of disulphidic bonds in both the cases.

Table 6.5 Percent change in crosslink density after devulcanisation

Crosslinks	CV		Semi - EV		EV	
	Mech anical	Optimum 4HT	Mecha nical	Optimum 4HT	Mecha nical	Optimum 4HT
Total	-21	-70	-36	-74	-41.6	-80.8
Polysulphidic	-20	-80.5	-38.9	-89.4	+85.7	-90.1
Disulphidic	-50	-37	-56	-53	-61	-91
Monosulphidic	+128	+114	+200	+300	-53	-57

+ denotes an increment and – denotes a decrement

Since, polysulphidic crosslinks with the least bond dissociation energy were the majority crosslink type of the CV vulcanisates, the majority of the crosslinks cleaved during devulcanisation would be polysulphidic crosslinks. But these cleaved crosslinks might have recombined, resisting the net crosslink density reduction, and might have undergone desulphuration into shorter crosslinks thereby increasing the net number of monosulphidic crosslinks. The disulphidic crosslinks cleaved under shear might also have recombined to form polysulphidic crosslinks thereby lowering the net effective number of disulphidic crosslinks in the devulcanised rubber and a higher per cent of polysulphidic crosslinks.

In the presence of 4HT, the higher number of polysulphidic crosslinks cleaved in CV vulcanisates might get stabilized thereby lowering the possibility of re-crosslinking and crosslink desulphuration. Since the initial polysulphidic crosslink scission reduces the viscosity of the vulcanisate, the shear experienced by the vulcanisate will get lowered and correspondingly the net number of disulphidic bonds cleaved will be lowered. Hence, the per cent of polysulphidic crosslinks in the devulcanised samples get reduced along with the reduction in total crosslink density, while that of the disulphidic crosslinks increased compared with the mechanical devulcanisation.

In the case of semi EV samples, similar trend was followed with the exception that, since considerable disulphidic crosslinks are also present in the vulcanisate, both polysulphidic and disulphidic crosslinks would have cleaved under the influence of shear during mechanical devulcanisation. The very low absolute number of monosulphidic crosslinks in original semi EV sample manifested as a significant increase in the per cent increase of monosulphidic crosslinks after devulcanisation in comparison with that in the case of devulcanisation of CV vulcanisates.

For EV vulcanisates with disulphidic crosslinks as the majority crosslink type, an increase in the absolute number of polysulphidic crosslinks was observed in the mechanically devulcanised samples in comparison with the original vulcanisate. On the contrary, 90.1per cent reduction in the absolute number of polysulphidic crosslinks took place in 4HT assisted devulcanisation. At the same time, both the disulphidic and monosulphidic crosslink densities lowered after mechanical and 4HT assisted devulcanisation of EV samples.

The increase in absolute number of polysulphidic crosslinks after mechanical devulcanisation might be due to the re-crosslinking of cleaved bonds (both the majority disulphidic crosslinks and polysulphidic crosslinks). As the number of polysulphidic crosslinks in the original EV vulcanisate were low, the effect of recombination of crosslink fragments were observed as an increase in the absolute number of polysulphidic crosslinks. The absence of such an increase in other cases, where polysulphidic crosslinks forms the major share, might be because the number of cleaved polysulphidic bonds is much more than those formed by recombination and the effect of re-crosslinking was observed as the low percent reduction in the number of polysulphidic crosslinks of mechanically devulcanised CV and semi EV samples.

Since disulphidic crosslinks were the majority crosslink type, the reduction in absolute number of disulphidic crosslinks specifically determined the residual crosslink density of the devulcanised EV sample. The low absolute number of polysulphidic crosslinks in the original EV sample limited the possibility of desulphuration reactions and correspondingly, no increase in the absolute number of monosulphidic crosslinks were observed after devulcanisation.

Proposed mechanism for stable free radical assisted mechanical devulcanisation

Examining the crosslink distribution pattern of the original and the corresponding devulcanised samples three observations could be made;

(i) The reduction in the absolute number of majority crosslink type, *i.e.* polysulphidic crosslinks in CV and semi-EV systems whereas disulphidic crosslinks in EV system is the reason behind better devulcanisation.

(ii) Under shear in a two roll mill, polysulphidic crosslinks in vulcanisates undergo chain shortening reactions at ambient conditions similar to the post-crosslinking chemical reactions during curing temperatures.

(iii) The assistance of 4HT during devulcanisation considerably increased the devulcanisation efficiency probably by blocking the re-crosslinking of cleaved crosslinks.

On account of the observations from Horikx analysis and chemical probe studies, a mechanism is proposed for the stable free radical assisted mechanical devulcanisation of NR vulcanisates as illustrated in Figure 6.10
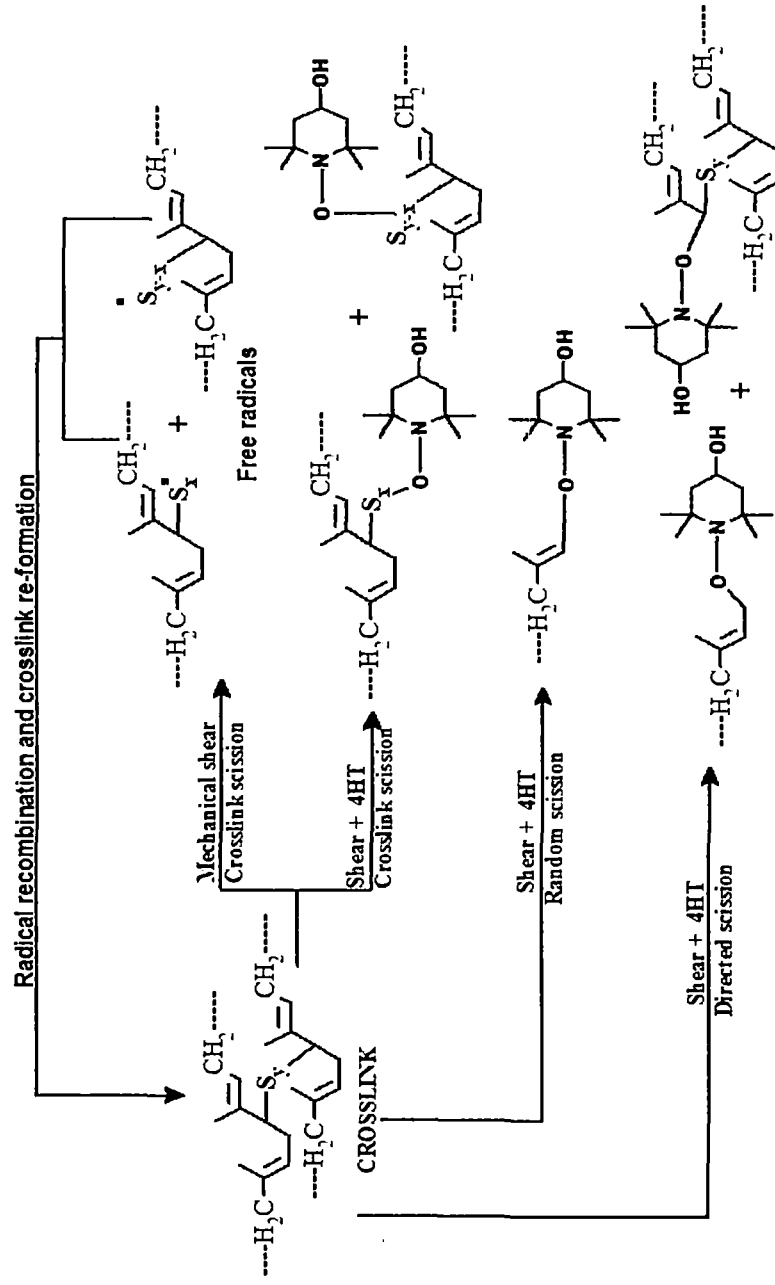
Figure 6.10. Proposed mechanism for stable free radical assisted mechanical devulcanisation of sulphur cured NR vulcanisates

The devulcanisation of rubber vulcanisates under the influence of shear generates crosslink fragments which are free radicals as a result of bond scission. These free radicals can recombine to reform the once cleaved crosslinks, unless stabilized by some species. Stable free radicals can instentaneously combine with the free radicals generated from crosslink scission there by stabilizing those radicals and hence preventing their recombination. Hence, the effective number of crosslinks cleaved will be higher for stable free radical assisted devulcanisation in comparison with the pure mechanical devulcanisation of the corresponding vulcanisate. It is reported that the reaction between the thyl radical (RS$^\bullet$) and the nitroxide radical (>NO$^\bullet$) yields an unstable adduct (>NO-SR) which can decompose via heterolysis/ hemolysis of N-O bond into various products[22-24]. However the fate of adduct formed during 4HT assisted devulcanisation of NR vulcanisates is not clear.

It is worth mentioning that, stable free radical is not a devulcanisation agent as it has no influence over the crosslink scission of the rubber vulcanisate but, it is an efficient devulcanisation aid which can considerably increase the effectiveness of shear induced devulcanisation process. The significant lowering of residual polysulphidic crosslink density of CV and semi EV vulcanisates after 4HT assisted devulcanisation in comparison with the corresponding mechanically devulcanised samples, and the increase in absolute number of polysulphidic crosslinks of the mechanically devulcanised EV vulcanisate and absence of such an increase for the 4HT assisted devulcanisation supports the proposed mechanism.

Thermo gravimetric analysis

Thermogravimetry was employed to study the changes occurring in rubber vulcanisates during devulcanisation by analyzing the variation in decomposition pattern of original vulcanisate and the devulcanised

samples[20]. The analysis allowed the estimation of degree of destruction of polymer chains in response to devulcanisation process through determination of formation of intermediates with lower molecular masses than those of the original vulcanisate. Figure 6.11, 6.12 and 6.13 represents the TGA curves of original and devulcanised CV, semi EV and EV vulcanisates respectively.

Table 6.6 tabulates the various thermo-analytical data obtained from the TG analysis of CV, semi EV and EV vulcanisates which depicts the variation of initial decomposition temperature (Ti), thermal stability index at 5per cent mass loss (T5) and temperature of peak dissociation (Tp) of the devulcanised samples observed from the DTG curves. The low Ti of devulcanised samples in comparison with the corresponding virgin vulcanisates might be attributed to the degradation products of lower thermal stability formed during devulcanisation process.

Table 6.6 Thermogravimetric data of v original and devulcanised NR samples

Vulcanisate	Initial decomposition temperature, Ti (°C)	Thermal stability index, T5 (°C)	Peak dissociation temperature, Tp (°C)
Virgin CV	200	298	392
CV DV	138	259	380
CV 4HT DV	147	261	387
Virgin semi EV	200	293	388
Semi EV DV	149	260	384
Semi EV 4HT DV	157	259	386
Virgin EV	200	287	396
EV DV	167	266	380
EV 4HT DV	155	263	389
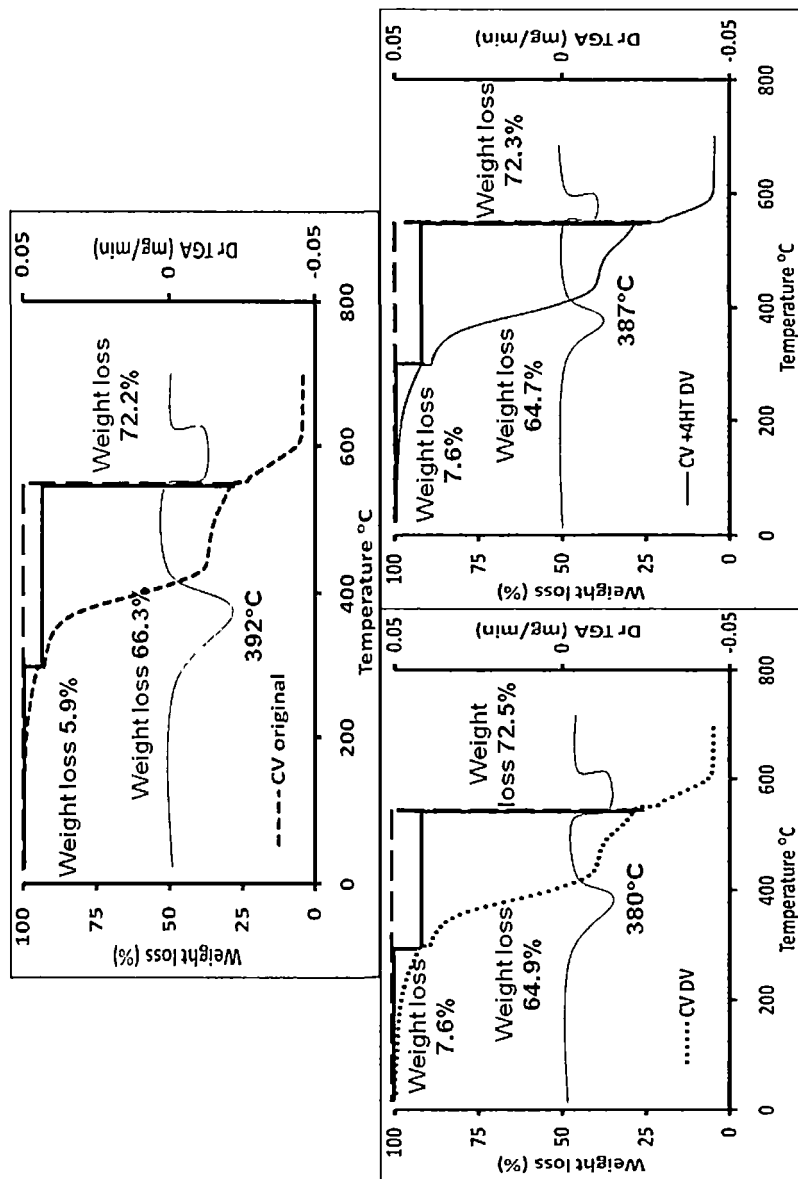
Figure 6.11 TG analysis of original and devulcanised CV vulcanisate

Though, the initial decomposition temperatures of devulcanised samples varied considerably, the thermal stability index at 5per cent decomposition were comparable. This might be indicating that, though the devulcanisation process might be generating low amounts of degraded products with different levels of thermal stability to give varying values for Ti, the extend of degradation suffered by the devulcanised network is almost comparable to give comparable T5 values. The lowering of Tp values after devulcanisation might be an indication of the degradation of the vulcanisates brought in by the devulcanisation process, which have lowered the thermal stability of the vulcanisate thereby reducing the peak dissociation temperature. Based on this assumption, it can be inferred that 4HT assisted devulcanisation imparts less degradation to the devulcanised rubber in comparison with the mechanical devulcanisation of corresponding vulcanisate. The thermogravimetric data given in Table 6.7 shows that, the experimental values of total organic matter were higher than the theoretical value in all cases including original samples.

Table 6.7 Composition of original and devulcanised samples determined by TGA

Vulcanisates	Total organic ingredients, %		Rubber, %		Organic non-polymeric ingredients, %	
	Theor.	Exper.	Theor.	Exper.	Theor	Exper.
Virgin CV	71.1	72.1	64.3	66.2	6.8	5.9
CV DV		72.5		64.9		7.6
CV 4HT DV	71.6	72.3	63	64.7	8.6	7.6
Virgin semi EV	71.1	72.6	64.3	66.8	6.8	5.8
Semi EV DV		73.3		65.5		7.8
Semi EV 4HT DV	71.5	72.5	63	64.9	8.5	7.6
Virgin EV	70.8	72.3	65	66	5.8	6.3
EV DV		73		65		8
EV 4HT DV	71.3	72.5	63.7	65	7.6	7.5
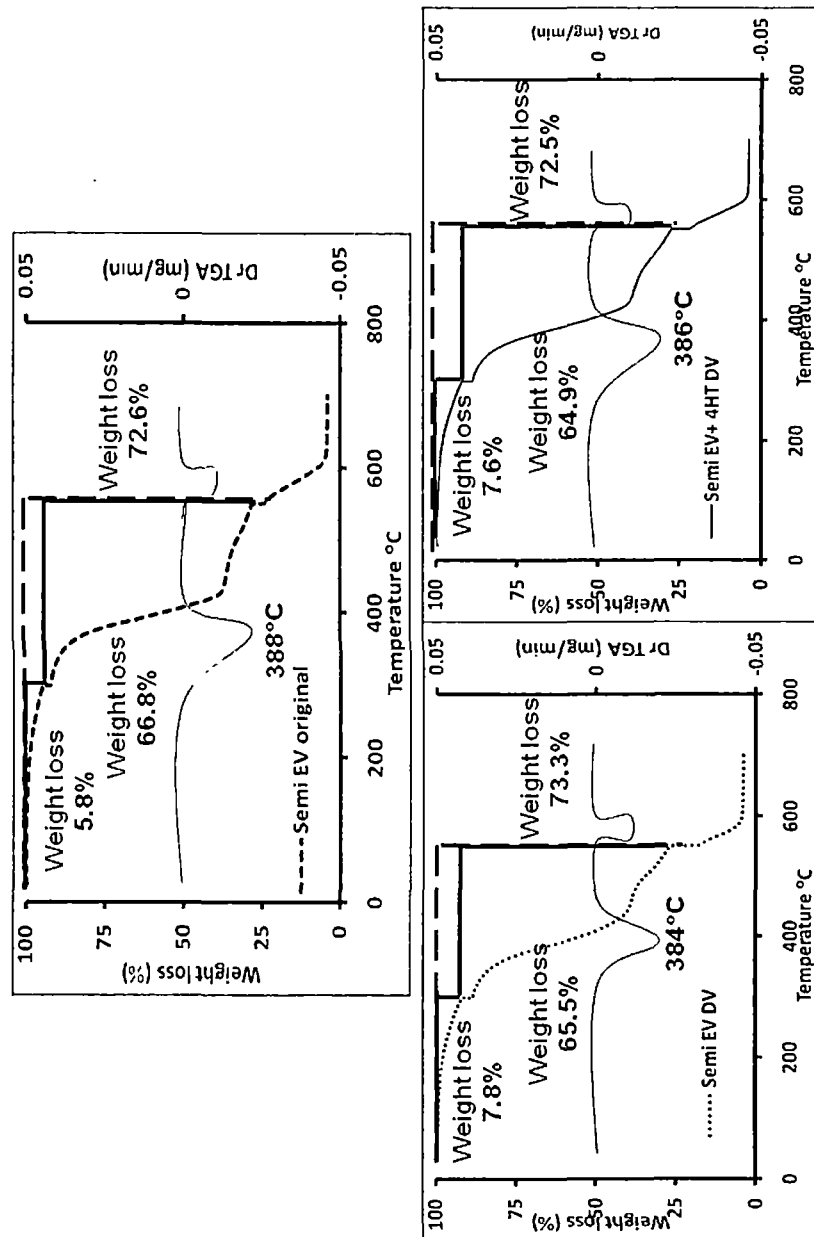
Figure 6.12 TG analyses of original and devulcanised semi-EV vulcanisates
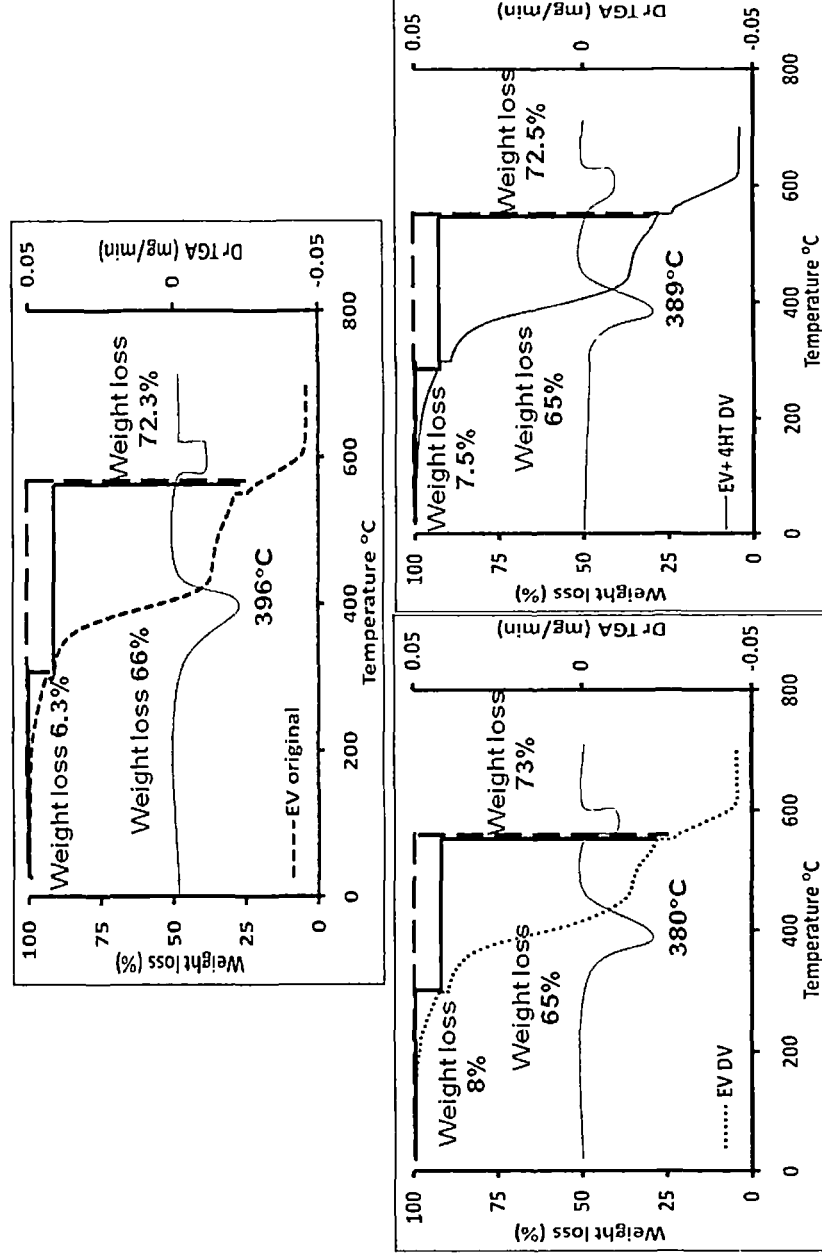
Figure 6.13 TG analyses of original and devulcanised EV vulcanisates

However, the extent of increase from the theoretical value is comparatively higher for the mechanically devulcanised vulcanisates in comparison with the original and the 4HT assisted devulcanised samples. Considering the response of the original vulcanisates as ideal, it might be assumed that 4HT assisted devulcanisation yield devulcanised rubber that resemble the original vulcanisate more closely than that of the corresponding devulcanisate from mechanical devulcanisation.

The theoretical value of organic non-polymeric substances were higher than the experimental value in the case of original vulcanisates (except EV vulcanisate) and vulcanisates devulcanised with the aid of stable free radical. The comparative increase in the organic non-polymeric substances and the corresponding reduction in the rubber hydrocarbon content of the mechanically devulcanised samples might be due to the polymer degradation products from the devulcanisation process which decomposed at lower temperatures thereby increasing the organic non-polymeric contents of the devulcanised samples over the virgin vulcanisates. Besides, the earlier decomposition of these polymer degradation products will lead to net effective lowering of rubber hydrocarbon content. It can be assumed from the observations that, availing the assistance of stable free radical during mechanical devulcanisation minimizes the extent of polymer degradation under the influence of shear.

6.3.2 Revulcanisation of devulcanised rubber

6.3.2.1 Characterization of revulcanised samples

Cure characteristics

All the devulcanised samples, irrespective of the cure system used for the preparation of the original samples were revulcanised using the revulcanisation formulation given in Table 2.5 with 1.5phr sulphur and

0.8phr MOR. The cure curves of the virgin compounds and devulcanised samples are illustrated in Figure 6.14 and the cure characteristics are are given in Table 6.8.

Table 6.8 Cure characteristics of virgin and devulcanised samples

Sample/ 4HT loading		Torque (dNm)			Scorch Time, min	Cure time (min)
		Minimum, M_L	Maximum, M_H	M_H-M_L		
CV	Original	1.3	14.6	13.3	3.8	10.6
	0 phr	4.6	10.1	5.5	2.1	6
	1 phr	3.5	10.8	7.3	1.3	4.9
	2 phr	2.6	11	8.4	1.1	4.7
	3 phr	2.4	11.3	8.9	1	4.6
	4 phr	2.1	11.3	9.2	0.9	4.8
	5 phr	2	11.6	9.6	1	4.7
	6 phr	1.8	11.1	9.3	1	4.8
Semi EV	Original	0.9	14.4	13.5	3.4	5.9
	0 phr	4.1	11.4	7.3	1.2	3.4
	1 phr	2.5	11	8.5	1.1	3.5
	2 phr	2	10.6	8.6	1.1	3.3
	3 phr	1.4	10.4	9	1	3.5
	4 phr	1.8	11	9.2	1.1	3.3
	5 phr	1.8	11	9.2	1.1	3.3
	6 phr	1.5	10.6	9.1	1.2	3.7
EV	Original	0.9	11.4	10.8	4.9	11
	0 phr	1.5	10.5	9	0.9	3.4
	1 phr	1	10.9	9.9	0.7	3
	2 phr	0.8	10.7	9.9	0.7	3.8
	3 phr	0.8	10.5	9.7	0.8	4
	4 phr	0.8	10.6	9.8	0.9	3.9
	5 phr	0.9	10.4	9.5	0.8	3.9
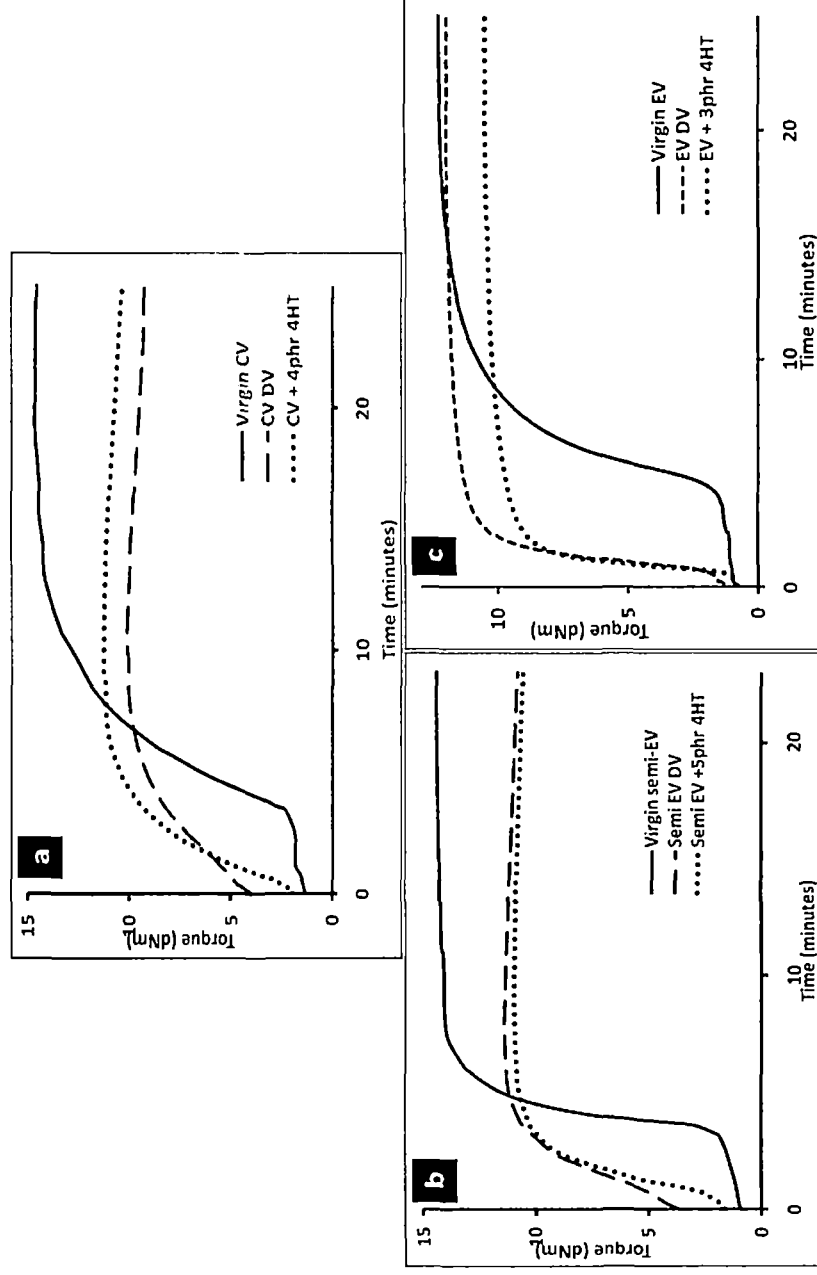
Figure 6.14 Cure curves of virgin, mechanically devulcanised and 4HT assisted devulcanised a: CV; b: semi-EV and c: EV vulcanisates.

Crosslink density of revulcanised samples

Crosslink densities of the revulcanised samples are given in Table 6.9 and the corresponding values were graphically plotted in Figure 6.15. It can be observed that, the crosslink densities of the revulcanised samples were comparable with the crosslink density of the corresponding virgin vulcanisates.The crosslink density of the revulcanised samples might be contributed from two factors viz. (i) contribution from the newer crosslinks formed during revulcanisation of devulcanised sample and (ii) contribution from the residual crosslink density of the devulcanised sample. In this regard, the crosslink density contribution from the residual crosslinks in the devulcanised rubber is higher for mechanically devulcanised samples which lowers with increasing dose of 4HT during devulcanisation. But, with regard to the formation of newer crosslinks, it has to be assumed that, a devulcanised sample with high per cent devulcanisation (low residual CLD) might be a better candidate for revulcanisation as it can provide more number of sites available for crosslinking compared with a poorly devulcanised sample.

Table 6.9 Revulcanisate crosslink densities of samples devulcanised with varying amounts of 4HT

4HT loading	Crosslink density x 10^4, mole/ cm^3		
	CV	Semi EV	EV
Virgin	2.4	2.5	1.7
0phr 4HT	2.2	2.6	2.2
1phr 4HT	2.4	2.5	2
2phr 4HT	2.5	2.2	1.9
3phr 4HT	2.5	2.2	1.9
4phr 4HT	2.5	2.2	1.9
5phr 4HT	2.6	2.2	1.9
6phr 4HT	2.5	2.3	-

Optimization of 4HT assisted devulcanisation of NR
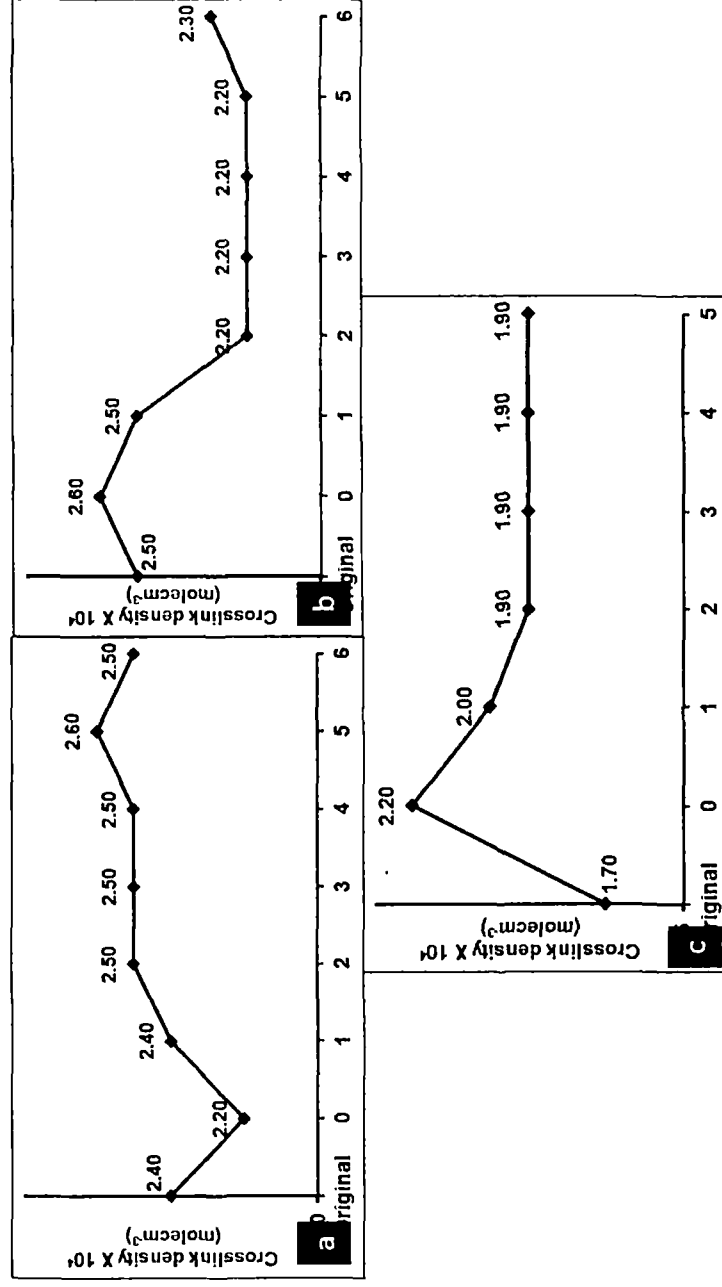
Figure 6.15 Revulcanisate crosslink density of devulcanised a: CV; b: semi-EV and c: EV vulcanisates in comparison with the crosslink density of corresponding original samples

Crosslink distribution of revulcanised samples

The revulcanisation of all the devulcanised samples were carried out using the revulcanisation formulation given in Table 2.5 (CV cure). The per cent distribution of crosslinks in virgin vulcanisates and the corresponding revulcanisates after mechanical devulcanisation and that devulcanised with optimum concentration of 4HT is represented in Figure 6.16.

The percent distribution of crosslinks in revulcanised samples varied from the corresponding original vulcanisates. Upon revulcanisation of mechanically devulcanised CV sample (CV DV/RV), the per cent contribution from disulphidic and monosulphidic crosslinks increased whereas, that from the polysulphidic crosslinks reduced in comparison with the virgin CV sample. For revulcanised CV vulcanisate after 4HT assisted devulcanisation (CV 4HTDV/RV), the per cent contribution from polysulphidic crosslinks further reduced with a corresponding increase in the per cent contribution from disulphidic crosslinks in comparison with the revulcanisate of mechanically devulcanised CV sample. But, the contribution from monosulphidic crosslinks was comparable with the per cent contribution of virgin CV vulcanisate.

Just as in the case of CV vulcanisates, the per cent contribution of polysulphidic crosslinks lowered after revulcanisation in comparison with the virgin vulcanisate for semi EV samples also. The per cent contribution of disulphidic crosslinks in revulcanised mechanically devulcanised samples (semi-EV DV/RV) was lower than that in the virgin sample, while that of the 4HT assisted devulcanised semi EV sample after revulcanisation (semi-EV 4HTDV/RV) was significantly higher. The per cent contribution from monosulphidic crosslinks was higher in the revulcanisates than in the virgin vulcanisate.

Optimization of 4HT assisted devulcanisation of NR
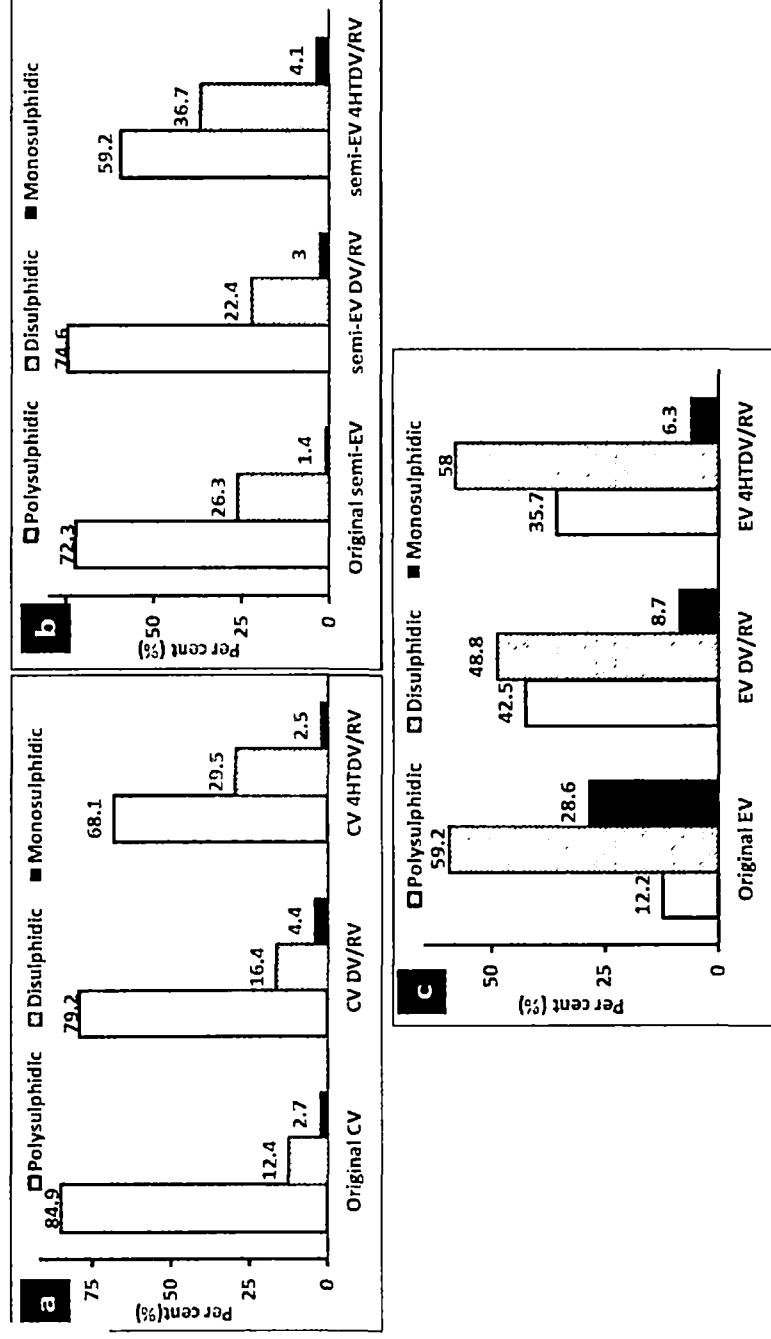
Figure 6.16. Percent distribution of crosslinks in original and revulcanised **a:** CV **b:** semi EV and **c:** EV samples.

Revulcanised EV samples (both EV DV/RV and EV 4HTDV/RV) showed maximum deviation in the distribution pattern of crosslinks from the virgin vulcanisate. This might due to the CV system used for the revulcanisation of these samples. Hence, the percent distribution of crosslinks in the revulcanised EV samples had the features of both CV and EV cured vulcanisates. The increase in the per cent of polysulphidic crosslinks in the revulcanisates followed the same trend as in the case of revulcanised CV and semi EV vulcanisates with a higher per cent of polysulphidic crosslinks in the revulcanised mechanically devulcanised samples. Here, the per cent contribution from disulphidic crosslinks in 4HT assisted devulcanised sample after revulcanisation was comparable with virgin vulcanisate while the mechanically devulcanised sample had a lower per cent of disulphidic crosslinks compared with the virgin vulcanisate. The per cent of monosulphidic crosslinks present in the revulcanisates were significantly lower than that in the virgin vulcanisate and is the lowest for the revulcanisate of 4HT assisted devulcanised sample.

The crosslink distribution pattern of revulcanised CV samples (CV DV/RV and CV+4HTDV/RV) in comparison with the corresponding devulcanised samples (CV DV) is given in Figure 6.17. It shows that, though the net number of newly formed polysulphidic crosslinks were higher in the case of revulcanisation of 4HT assisted devulcanised samples, the higher residual polysulphidic crosslink density of the mechanically devulcanised CV samples (CV DV) ensured higher per cent of polysulphidic crosslinks in the revulcanised CV sample (CV DV/RV) after mechanical devulcanisation. Higher numbers of disulphidic crosslinks are formed during the revulcanisation of CV vulcanisates devulcanised with the aid of 4HT (CV+4HT DV/RV), probably due to the availability of more number of sites available for crosslinking. Interestingly, it is observed that, the absolute number of monosulphidic crosslinks in the revulcanisates were less than the

number of monosulphidic crosslinks present in the corresponding devulcanised samples. This might be due to the resulphuration of monosulphidic crosslinks present in the devulcanised sample during revulcanisation.
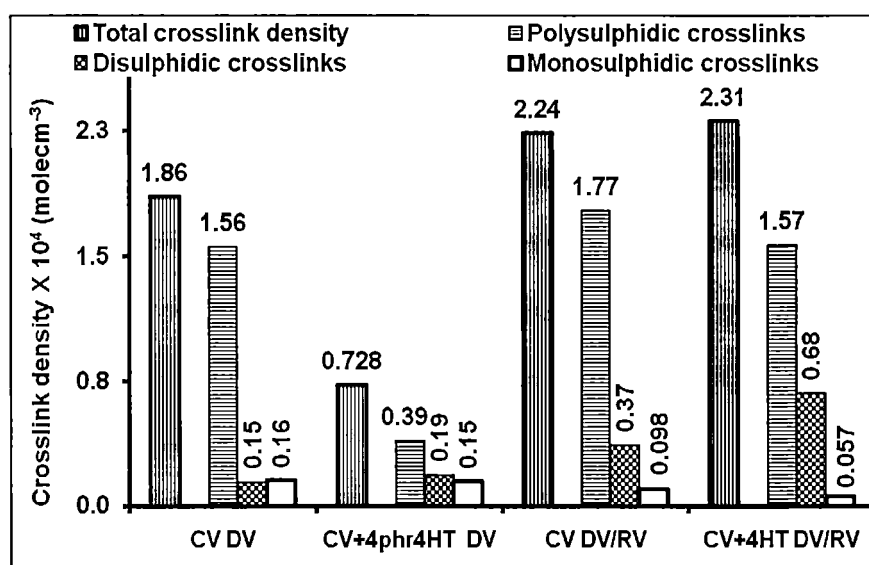
Figure 6.17 Crosslink distribution of devulcanised and revulcanised CV samples

Figure 6.18 illustrates the crosslink distribution pattern of the revulcanised semi EV samples after mechanical devulcanisation (semi-EV DV/RV) and stable free radical assisted devulcanisation (semi-EV+4HT DV/RV) in comparison with the residual crosslink distribution of the corresponding devulcanised samples (semi-EV DV and semi-EV+4HT DV). The high residual polysulphidic crosslink density of the mechanically devulcanised samples (semi-EV DV) might have resulted in the revulcanisate (semi-EV DV/RV) polysulphidic crosslink density higher than the corresponding revulcanisate of 4HT assisted devulcanised (semi-EV+4HT DV/RV) sample. Since the residual disulphidic crosslink densities

of both devulcanised samples were comparable, the disulphidic crosslink densities of the revulcanisates were also comparable. As observed in the case of CV vulcanisates, the monosulphidic crosslink densities of the revulcanisates were lower than the residual monosulphidic crosslink densities of corresponding devulcanised samples.
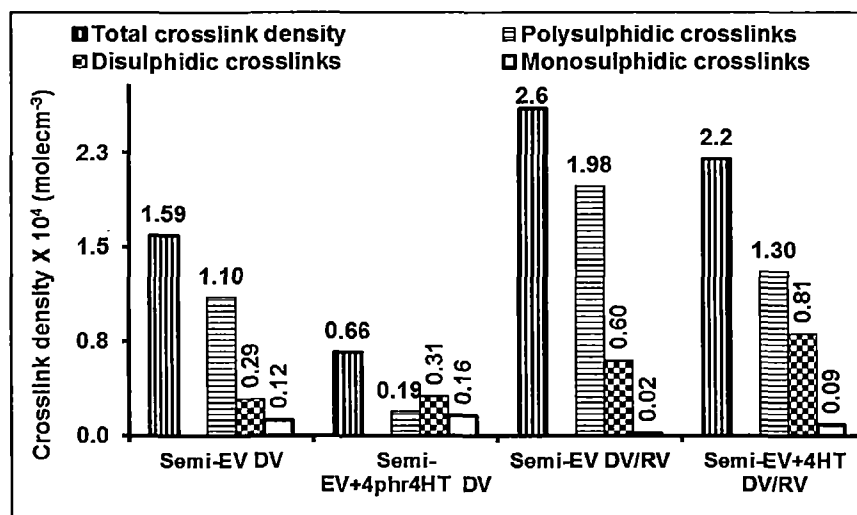
Figure 6.18 Crosslink distribution of devulcanised and revulcanised semi-CV samples

Just as in the case of virgin EV vulcanisate, the majority crosslink type in the revulcanisates (EV DV/RV and EV+4HTDV/RV) also was disulphidic crosslinks (Figure 6.19). But, in the revulcanisates of EV samples, the per cent of polysulphidic crosslinks were significantly higher and the monosulphidic crosslink density was lower than that in the virgin vulcanisate. As in the case of CV and semi-EV vulcanisates, the polysulphidic crosslink density of the revulcanised EV vulcanisate after mechanical devulcanisation (EV DV/RV) was higher than the corresponding revulcanisate after 4HT assisted devulcanisation (EV+4HT DV/RV)

probably due to the higher number of residual polysulphidic crosslinks present in the mechanically devulcanised EV sample.
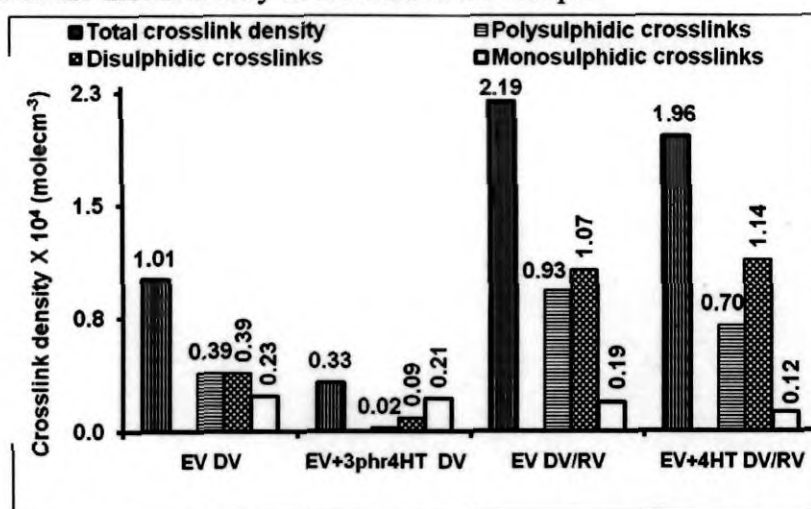
Figure 6.19 Crosslink distribution of devulcanised and revulcanised EV samples

The disulphidic crosslink density of the revulcanised EV vulcanisates were greater than that of the polysulphidic crosslinks, and the disulphidic crosslink density was marginally higher in the case of 4HT assisted devulcanised sample after revulcanisation (EV+4HT DV/RV) irrespective of the fact that, the residual disulphidic crosslink density of the mechanically devulcanised samples (EV DV) was higher. The monosulphidic crosslink densities of the revulcanised samples were lower than the corresponding devulcanised samples indicating the sulphuration of monosulphidic crosslinks to sulphidic crosslinks of higher rank during revulcanisation.

SEM analysis

Scanning electron microscopy (SEM) is utilized to record the images of a surfaces of materials at a desired position to obtain topographic/ morphological picture with better resolution. In the case of polymers and

rubbers, SEM study commonly aims at visualization of phase morphology, surface and cross-sectional topography, surface molecular order and elucidation of failure mechanism. The fracture surface of the test specimens, gives characteristic topographical features which is recorded as an SEM image and can be related to strength properties[26]. SEM photomicrographs of the tear fractured surface of the original and revulcanised semi EV samples are shown in Figure 6.20 (a) and 6.20 (b) & (c) respectively.
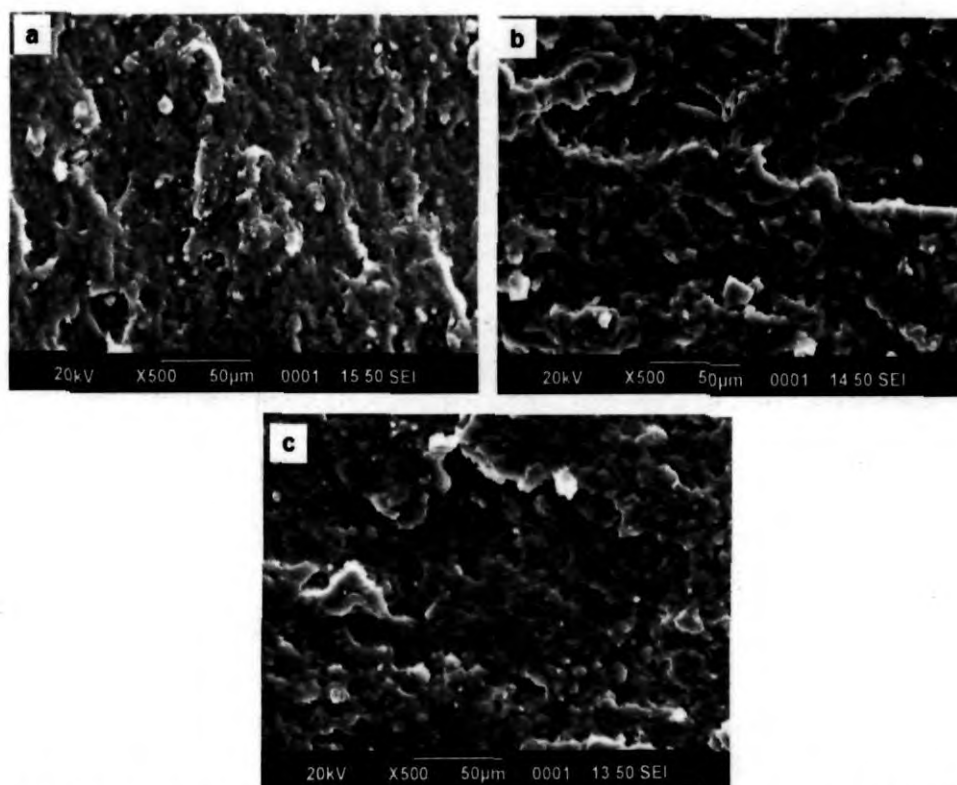
Figure 6.20 SEM of tear fractured surfaces of **a:** virgin; **b:** mechanically devulcanised and **c:** 4HT assisted semi-EV vulcanisates

The SEM micrograph of the original vulcanisate 6.20 (a) show smooth fractured surfaces with good homogeneity. Although Fig. 6.20 (b)

and (c) shows smooth fractured surface, but have irregular crack paths making the vulcanisate vulnerable under mechanical stress.

6.3.2.2. Revulcanisate properties

The mechanical properties of the revulcanised samples positively correlated with the percent devulcanisation of the corresponding devulcanised samples. The variation of tensile tear strengths of the revulcanised samples with increasing concentration of 4HT in comparison with the virgin vulcanisate properties are illustrated in Figure 6.21.
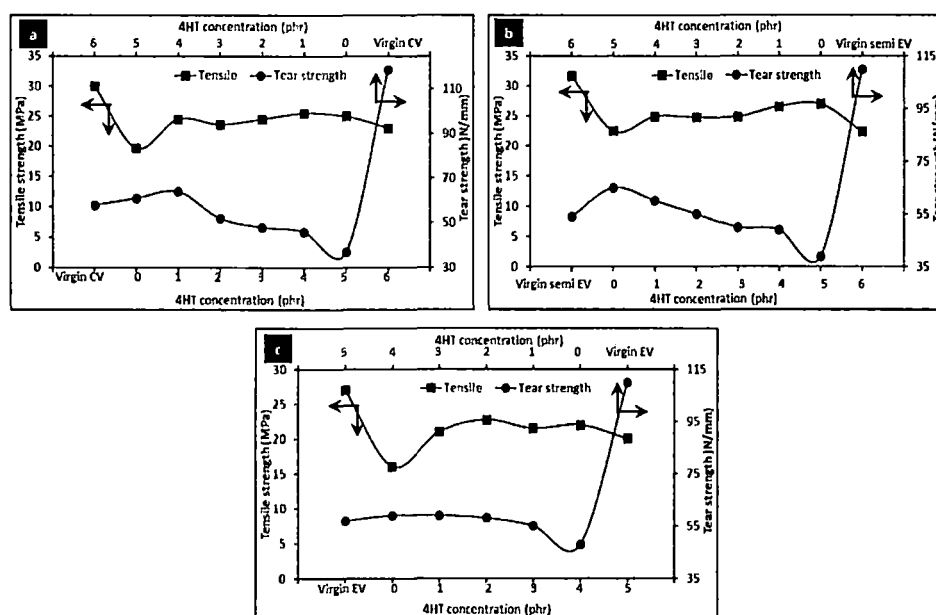
Figure 6.21 Comparison of revulcanisate tensile strength and tear strength of a: CV, b: semi-EV and c: EV samples devulcanised with varying 4HT concentrations (corresponding axes denoted by arrows)

The revulcanisate properties of devulcanised samples with the varying amounts of 4-Hydroxy TEMPO used for devulcanisation are given in Table 6.10. The corresponding stress strain curves of the original and

revulcanised CV, semi EV and EV samples devulcanised mechanically and with optimum dosage of 4HT are given in Figure 6.22.

Table 6.10 Revulcanisate properties of samples devulcanised with varying amounts of 4HT

Vulcanisate/ 4HT dosage		Tensile strength (MPa)	Elongation at Break (%)	M100 (MPa)	M200 (MPa)	M300 (MPa)	Tear strength (N/mm)
	Virgin	30	671	2.2	5.1	9.4	119
	0phr	19.7	533	1.9	4.3	7.8	37
	1phr	24.5	617	2	4.4	8	46
	2phr	23.6	613	2	4.5	8	48
CV	3phr	24.5	616	2.1	4.7	8.2	52
	4phr	25.5	668	2.1	4.6	8.3	64
	5phr	25	683	2	4.4	7.9	61
	6phr	23	618	2	4.3	7.7	58
	Virgin	31.6	634	2.6	6.2	11	110
	0phr	22.5	579	2	4.3	7.7	39
	1phr	24.9	627	2	4.4	7.8	49
Semi EV	2phr	24.8	637	2	4.4	7.7	50
	3phr	24.9	637	2	4.4	7.8	55
	4phr	26.6	634	2.1	4.5	8.2	60
	5phr	27	662	2	4.4	7.9	65
	6phr	22.4	634	1.7	3.8	6.7	54
	Virgin	27	699	2	4.6	8	110
	0phr	16	457	2.2	4.8	8.5	48
	1phr	21	565	2	4.8	8	55
EV	2phr	22.7	604	2	4.5	8	58
	3phr	21.5	587	2	4.5	7.8	59
	4phr	22	591	2	4.6	8	59
	5phr	20	566	2	4.6	7.8	57
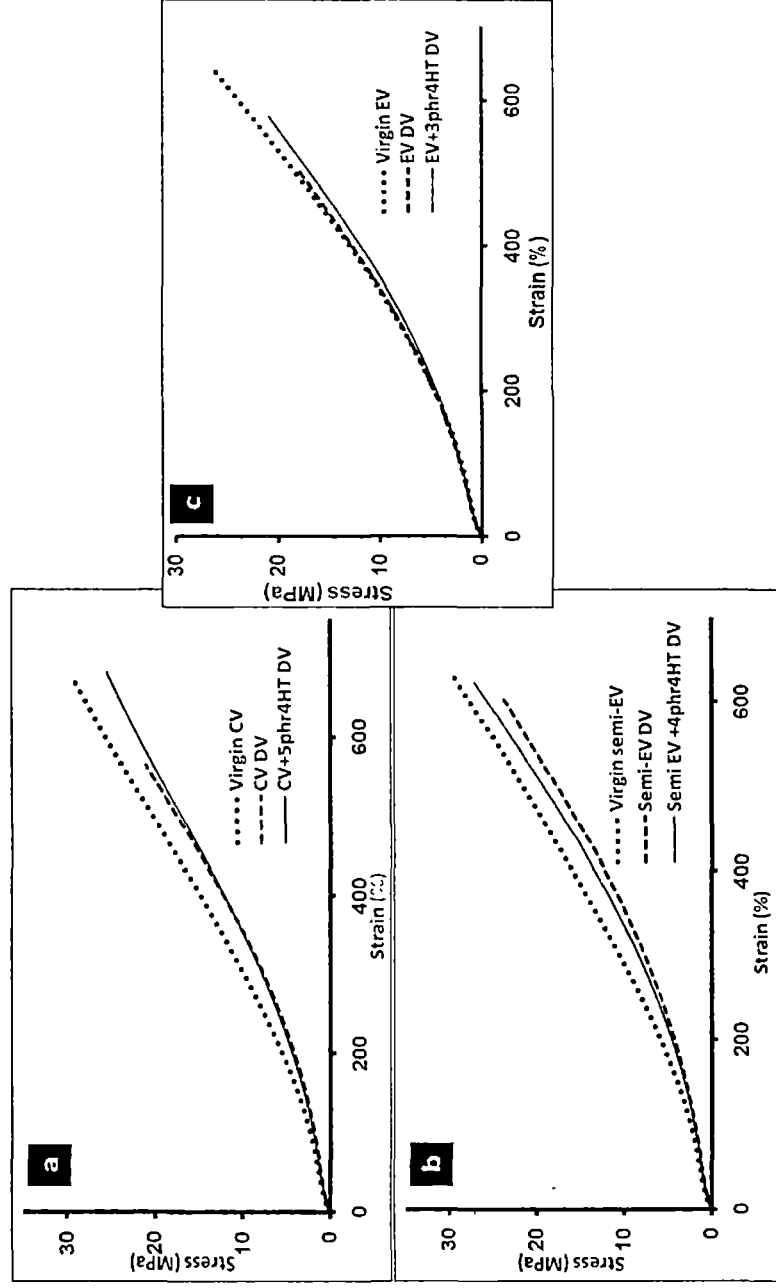
Figure 6.22 Stress strain curves of the original and revulcanised **a:** CV, **b:** semi-EV and **c:** EV samples devulcanised mechanically and with optimum concentration of 4HT

The revulcanisate properties of the devulcanised samples indicate that, the incorporation of stable free radical as a devulcanisation aid has led to increment in vulcanisate properties corresponding to the higher per cent devulcanisation associated with those samples. It is observed that, the mechanical properties of the revulcanisate after mechanical devulcanisation were significantly lower than that of the corresponding virgin rubber property which improved significantly when 1phr stable free radical is used as devulcanisation aid. Further increase in 4HT concentration resulted in only marginal increase in these properties (except tear strength). How ever tear strength showed a systematic increase with 4HT concentration and reached a maximum at optimum 4HT concentration.

The stress-strain curves of the original and the revulcanised EV samples were almost identical indicating the higher positive response of EV samples to devulcanisation. In the case of CV vulcanisates, the revulcanisation stress-strain curves of both mechanically and 4HT assisted devulcanised samples were comparable. The stress-strain curve of the revulcanised 4HT assisted devulcanised semi EV samples tends closer to the stress-strain curve of the virgin vulcanisate showing higher resemblance of the 4HT assisted devulcanised sample to the virgin vulcanisate compared with the mechanically devulcanised sample.

6.3.3. Comparison of industrially practiced mechano-chemical devulcanisation processes with 4HT assisted devulcanisation

The investigations in Chapter 4 revealed that the industrial mechano-chemical devulcanisation processes are in no way different from mechanical devulcanisation. Also, the superior nature of devulcanisation attained with 4HT assisted devulcanisation over mechanical devulcanisation was established by the studies described in Chapter 5 and Chapter 6. Hence, 4HT assisted devulcanisation is certainly expected to give better results in comparison with industrial processes like De Link process and Lev Gum

process of devulcanisation. The following section presents comparison of 4HT assisted devulcanisation (of semi EV cured NR vulcanisates) with industrially practiced processes.

The residual crosslink density of the 4HT assisted devulcanised sample (Figure 6.23 a) was significantly lower than the other devulcanised samples. Correspondingly, a significantly higher per cent devulcanisation was obtained for the 4HT assisted devulcanised sample (79per cent) in comparison with that of the devulcanised samples from other methods (≈35per cent).

This was also reflected in higher tan delta value of the 4HT assisted devulcanised sample during processability analysis (Figure 6.23 c) and low minimum torque during revulcanisation (Figure 6.24 a). The Horikx plot (Figure 6.23 b) shows that, the data of 4HT assisted devulcanised sample lies in between the crosslink scission curve and main chain scission via directed scission curve. This indicates that, the higher per cent devulcanisation of the 4HT assisted devulcanised vulcanisate is taking place predominantly through crosslink scission without considerable deterioration of main chain.

The crosslink distribution pattern of the devulcanised samples (Figure 6.23 d) shows that, the polysulphidic crosslink density of the 4HT assisted devulcanised sample was significantly lower than other corresponding samples. Also, the residual crosslink density contribution from disulphidic and monosulphidic crosslinks together was comparable for all the devulcanised samples which is about 0.5×10^{-4}mole cm^{-3}. These observations and results in chapter 4 points to the fact that, the devulcanising agents used in both De link and Lev Gum processes are not capable of preventingbthe recombination of the free radicals formed from shear induced crosslink scission.
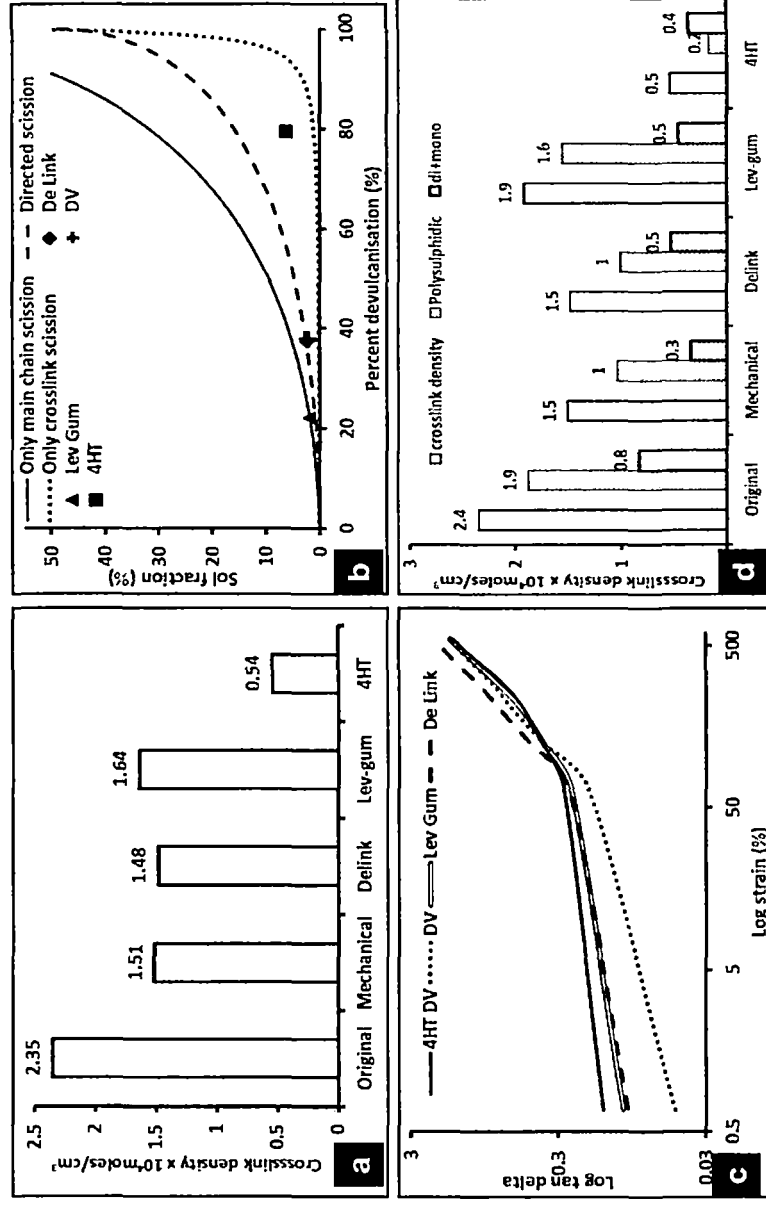
Figure 6.23 Comparison of **a:** Residual crosslink density; **b:** Horikx data; **c:** processability and **d:** crosslink distribution pattern of the NR samples devulcanised by different methods
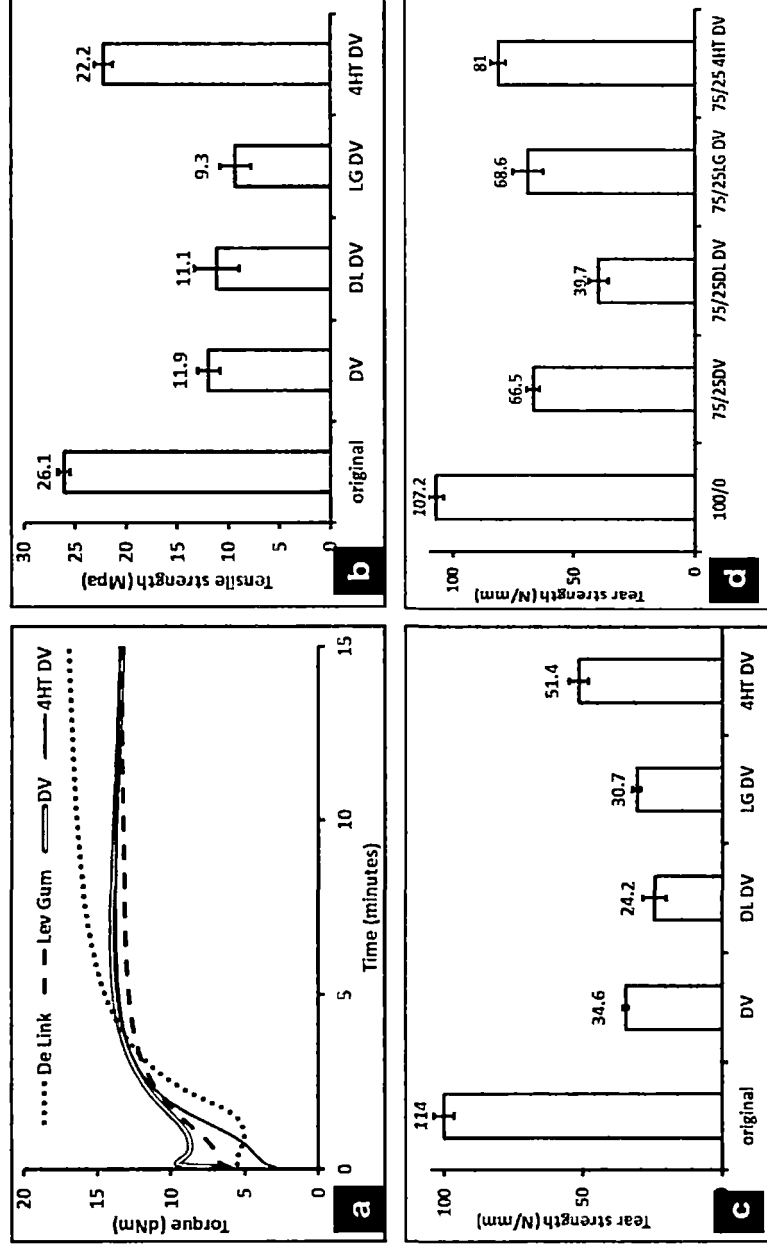
Figure 6.24 a: Revulcanisation cure curves; **b:** revulcanisate tensile strength and **c:** revulcanisate tear strength and **d:** tear strength of NR/DVR 75/25 blends of the NR samples devulcanised by different methods

The revulcanisate properties (Figure 6.24 b and c) of the 4HT assisted devulcanised samples were significantly higher than the corresponding properties of revulcanisates from other devulcanisation methods. The revulcanisate tensile strength of the 4HT assisted devulcanised samples was 22MPa while that of the revulcanisates from other devulcanisation strategies was about 10MPa to 12MPa. Similar trend was observed for other properties also. In the case of 75/25 blends of NR and devulcanised rubber, all the vulcanisate properties except tear strength were comparable for all the blends. The blend with 4HT assisted devulcanised rubber had significantly higher tear strength than other blends as observed from Figure 6.24 d.

6.3.4. 4HT assisted devulcanisation of commercial devulcanised rubber

The effect of stable free radical upon a commercially available devulcanised rubber compound (DRC) was evaluated by comparing the characteristics of devulcanised rubber and its revulcanisate properties.

6.3.4.1. Residual crosslink density and per cent devulcanisation

The commercial devulcanised rubber (DRC) was subjected to a second round devulcanisation with (DRC+4HT DV) and without (DRC DV) the assistance of 2phr stable free radical (as stated in section 6.2.3). During second round devulcanisation, DRC was subjected to 40 numbers of passes through the tight nip of two roll mill when devulcanised without 4HT while the required numbers of passes reduced to 25 when devulcanised with the assistance of 4HT.

The variation in residual crosslink density and per cent devulcanisation of the DRC under different cases considered in the present study is represented in in Figure 6.25. It can be observed that, the residual crosslink density of DRC ($\approx 2 \times 10^{-4}$mole/cm^3) reduced significantly by

mechanical devulcanisation (1.2×10^{-4} mole/cm^3) which further reduced to a still lower value upon 4HT assisted devulcanisation (0.85×10^{-4} mole/cm^3). Correspondingly, the per cent devulcanisation increased from 40per cent after mechanical devulcanisation to 57.5per cent after 4HT assisted devulcanisation. This indicates that, 4HT could increase the extent of devulcanisation of commercial devulcanised rubber which is expected to increase the revulcanisate properties also.
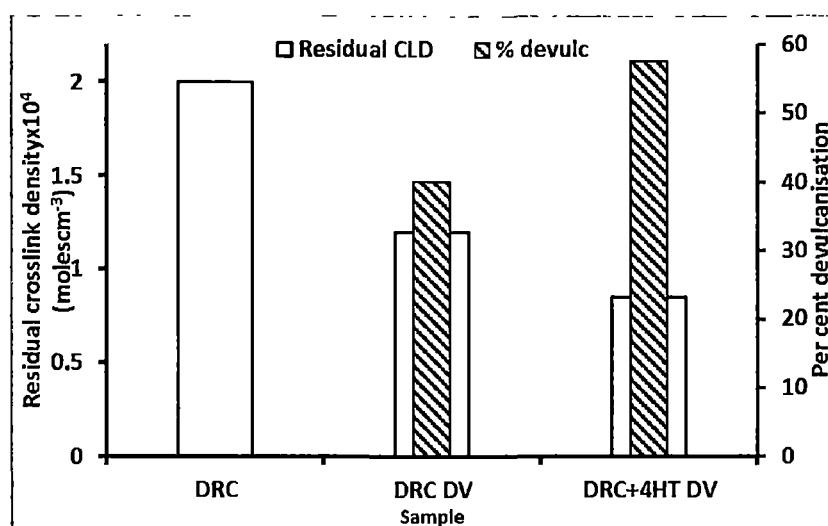
Figure 6.25 Residual crosslink density and per cent devulcanisation of DRC after second round devulcanisation

6.3.4.2. Revulcanisation of DRC

The commercial DRC and DRC subjected to second round devulcanisation were revulcanised following the revulcanisation formulation given in Table 6.1. The revulcanisation cure characteristics of DRC represented in Table 6.11 shows that, the minimum torque of the 4HT assisted devulcanised DRC was the lowest, while the maximum torque was comparable in all cases. Correspondingly, the highest total torque was

attained by 4HT assisted devulcanised DRC. The scorch time and cure time of all the devulcanised samples were comparable.

Table 6.11 Cure characteristics on revulcanisation of DRC

Devulcanisation process		Torque (dNm)			Scorch Time, min	Cure time (min)
		Minimum M_L	Maximum M_H	M_H- M_L		
Case i	DRC	5	11.3	6.3	1.9	5.4
Case ii	DRC DV	3.8	10.3	6.5	2.2	6.1
Case iii	DRC+ 4HT DV	1.5	10.5	9	1.4	5.9

The revulcanisate properties of DRC listed in Table 6.12 illustrates the significant improvement brought into the revulcanisate properties of commercial DRC upon second round devulcanisation with the assistance of stable free radical.

Table 6. 12 Revulcanisate properties of DRC

Sample		Tensile Strength (MPa)	Elongatio n at break (%)	M100 (MPa)	M200 (MPa)	M300 (MPa)	Tear strength (N/mm)
Case i	DRC	12.1	376	2.3	4.9	8.8	27.7
Case ii	DRC DV	14.7	428	2.3	5	8.8	27.7
Case iii	DRC+ 4HT DV	17	495	2.3	4.9	8.5	55.7

The tensile strength of revulcanised DRC was 12.1MPa while that increased to 14.7MPa after second round mechanical devulcanisation. When second round devulcanisation was carried out with the aid of 4-Hydroxy TEMPO, the revulcanised tensile strength of DRC increased to 17MPa. Corresponding variations were observed in elongation at break also. The

modulus values of all the revulcanisates were comparable. The most significant change was observed with the tear strength of revulcanised samples. The tear strength of DRC when revulcanised as such was 27.7N/mm which remained unchanged after second round mechanical devulcanisation irrespective of the improvements in the revulcanisate tensile strength and elongation at break. But, when second round devulcanisation was carried out with the assistance of 4-Hydroxy TEMPO, the revulcanisate tear strength almost doubled in comparison with the other two cases. This further support the concept that, tear strength is more sensitive towards the efficiency of devulcanisation rather than tensile strength.

6.3.5. Comparison of 4HT assisted devulcanisation with ultrasound devulcanisation process

In order to further validate the efficiency of the novel 4HT assisted devulcanisation process, a comparative study with ultrasound devulcanisation was also carried out. The respective revulcanisate properties are listed in Table 6.13.

Table 6.13. Comparison of revulcanisate properties of ultrasound, mechanical and 4HT assisted devulcanised samples

Properties	Virgin compound	Type of devulcanisation		
		Ultrasound	Mechanical	With 4HT
Tensile Strength (MPa)	32	16	14	21.9
EB (%)	718	430	400	539
M100 (MPa)	2.2	-	2.11	2.3
M200 (MPa)	5.1	-	4.8	5.1
M300 (MPa)	9.1	-	8.8	9.2
Tear strength (N/mm)	95.3	-	31.2	52.3

Since practical ultrasound devulcanisation facility was not available, the comparison was carried out by the 4HT assisted devulcanisation of an

identical compound prepared using the formulation described in literature and comparing the revulcanisate properties[6]. The percent retention of vulcanisate properties after mechanical devulcanisation of NR vulcanisate prepared according to the formulation obtained from literature without and with the assistance of 4HT in comparison with the corresponding values obtained for ultrasound devulcanisation is given in Figure 6.26.
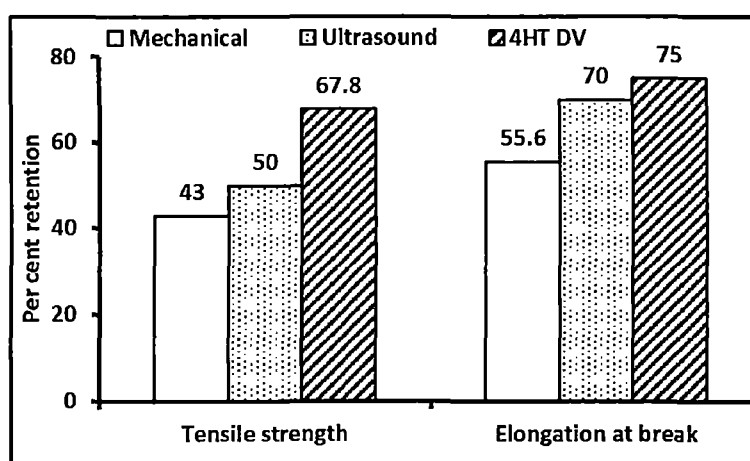
Figure 6.26 Percent retention of revulcanisate properties of ultrasound, mechanical and 4HT assisted devulcanised samples

The per cent retention of tensile strength and elongation at break after revulcanisation of 4HT assisted devulcanised sample was higher than the corresponding values for ultrasound devulcanisation. The moduli values and tear strength of the ultra sound devulcanisation were not provided in the literature hence, comparison could not be made.

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Chapter 7
Role of Carbon Black Filler on the Devulcanisation
of NR Vulcanisates

7.1 INTRODUCTION

Carbon black is mainly used in rubber industry to reinforce rubber—that is, to increase the resistance of rubber to abrasion, tear, fatigue and flexing. Carbon black also influences the electrical and thermal properties, chemical and thermal resistance, processing characteristics, flow behaviour, vulcanisation kinetics, and many other vulcanisate properties of the elastomers[1,2]. The level of reinforcement varies with the particle size of carbon black filler[3]. The reinforcement of elastomers and the improvement of other properties by the incorporation of carbon blacks are associated with the chemical and physical interactions between the polymer matrix and carbon blacks and were extensively studied[4-13]. Since carbon black plays a vital role in the vulcanisate properties and processing characteristics of rubber vulcanisates, it seems relevant to investigate the role of carbon black filler in the devulcanisation of rubbers.

The effects of carbon black on the ultrasonic devulcanisation of NR vulcanisates were studied by Hong and Isayev[14]. Studies on the effect of carbon black amount on devulcanisation of natural rubber by microwaves was previously carried out[15]. The results of the study indicates that, the increase of the temperature is responsible for the occurrence of devulcanisation, which is dependent on both the amount of carbon black present in the rubber and the time of exposure to microwaves. The effects of ultrasound on devulcanisation of unfilled and carbon black (CB) filled isoprene rubber (IR) were studied by Sun[16]. It was being observed that, devulcanisation of filled IR resulted in more main chain scission than in

unfilled IR due to the immobility of bound rubber at the filler surface which leads to lower properties in revulcanised rubbers than in virgin rubber.

This chapter describes the investigation on the effect of type and amount of carbon black present in the original vulcanisate upon the devulcanisation efficiency and revulcanisate properties of the devulcanised samples.

7.2. EXPERIMENTAL

Carbon black filled NR vulcanisates of known composition and properties were prepared with 40phr carbon black fillers (Table 7.1) to study the role of filler type and with varying the HAF concentration (20 to 60phr) to study the effect of filler concentration upon devulcanisation following the respective formulations given in Table 7.2.

Table 7.1 Fillers used to study the effect of filler type on devulcanisation

Type of filler	Particle size, nm	Reinforcement type
ISAF (N220)	24-33	High reinforcement
HAF (N330)	28-36	Medium to high reinforcement
FEF (N550)	39-55	Medium reinforcement
GPF (N660)	49-73	Medium reinforcement

Devulcanisation of the CB filled vulcanisates were carried out as described in chapter 2 with and without the assistance of stable free radical and revulcanised using the formulation given in Table 7.1. The devulcanisation of NR vulcanisates with lower amounts of filler (20phr and 30phr) were difficult especially in the case of mechanical devulcanisation. This might be due to the high accumulation static current induced in the sample to be devulcanised due to the shearing force exerted during devulcanisation at tight nip. As the amount of filler present in the system

was low compared with the rubber hydrocarbon content of the vulcanisate, the dispersal of generated static current was not effective and hence the vulcanisate tend to stick on to the rolls of the two roll mill.

Table 7.2 Formulations of original samples with varying filler type and filler amount

Ingredients	Original compound (phr)		Revulcanisation (phr)
	Filler type	Filler amount	
Natural Rubber	100	100	10
Devulcanised rubber	-	-	100*
Carbon black	40$^@$	20$^{@@}$	-
Naphthenic oil	4	2$^\#$	-
ZnO	5	5	3
Stearic acid	2	2	2
TDQ	1.5	1.5	1.5
CBS	0.6	0.6	1.5
Insoluble sulphur	2.5	2.5	0.8

*Rubber hydrocarbon (RH) =50
$^@$ Filler type was varied as 40phr of ISAF, HAF, FEF and GPF blacks
$^{@@}$ HAF amount was varied as 20phr, 30phr, 40phr, 50phr and 60phr
$^\#$Oil was varied as 2phr,3phr, 4phr, 5phr and 6phr respectively for increasing filler content from 20phr to 60phr

The effect of filler types and filer amount along with the role of stable free radical in such cases of devulcanisation were investigated by characterizing the devulcanised samples by assessing the percent devulcanisation associated with each case and through monitoring the corresponding revulcanisate properties of the devulcanised samples. The effect of filler concentration upon devulcanisation was characterized by processability analysis by strain sweep measurements.

7.3 RESULTS AND DISCUSSION

7.3.1 Effect of type of carbon black

The influence of type of carbon black present in the original sample to be devulcanised on devulcanisation and revulcanisate properties of the devulcanised samples were studied by the devulcanisation of NR vulcanisates filled with ISAF, HAF, FEF and GPF blacks. The effect of stable free radical on the devulcanisation of these samples were also analyzed.

7.3.1.1 Number of passes through the tight nip

As already observed in previous chapters, the time or the number of passes through the tight nip of the two roll mill required for devulcanisation varies with several factors related to the physical and chemical state of the vulcanisates to be devulcanised and devulcanisation conditions. It is being observed by this study that, the type of filler present in the vulcanisate also affects the time required for devulcanisation. The number of passes required for devulcanisation of NR vulcanisates filled with different carbon black fillers are given in Table 7.3.

Table 7.3 Number of passes required for devulcanisation of NR samples with different carbon blacks

Carbon black	Number of passes through tight nip	
	Mechanical	4HT assisted
ISAF	60	39
HAF	50	40
FEF	50	42
GPF	60	36

The required number of passes through the tight nip for devulcanisation is lowered significantly by the use of 4HT as a devulcanisation aid. The observations indicate that, filler size does not significantly influence the number of passes required for devulcanisation.

7.3.1.2 Residual crosslink density and per cent devulcanisation

The crosslink densities of the devulcanised samples and the corresponding virgin vulcanisates along with their respective per cent devulcanisation are listed in Table 7.4.

Table 7.4 Crosslink densities of original and devulcanised samples with corresponding per cent devulcanisation

Vulcanisate/ Filler type		Crosslink density x10^4, mole/ cm^3	Per cent devulcanisation (%)
ISAF	Virgin	1.26	-
	DV	0.98	22
	4HT DV	0.77	39
HAF	Virgin	1.4	-
	DV	1.1	21
	4HT DV	0.8	43
FEF	Virgin	1.48	-
	DV	1.13	24
	4HT DV	0.85	43
GPF	Virgin	1.33	-
	DV	1	25
	4HT DV	0.8	40

The residual crosslink densities of the vulcanisates devulcanised with the assistance of stable free radical are significantly lower than the corresponding values of mechanically devulcanised samples. Correspondingly, the per cent devulcanisation of 4HT assisted devulcanised

samples were significantly higher than that of the mechanically devulcanised samples. Within the group both mechanically devulcanised samples and 4HT assisted devulcanised samples have comparable percent devulcanisation. This indicates that, the particle size of the carbon black filler present in the samples to be devulcanised does not have significant role in efficiency of devulcanisation.

7.3.1.3 Cure characteristics

The cure curves of the original and devulcanised NR vulcanisates containing different types of filler is given in Figure 7.1 and the cure characteristics are listed in Table 7.5.

Table 7.5 Cure characteristics of original and corresponding devulcanised samples with different carbon black fillers

| Vulcanisate | Torque (dNm) | | M_H-M_L | Scorch Time, min | Cure time (min) |
	Minimum, M_L	Maximum, M_H			
Virgin ISAF	1.7	15.5	13.8	4.1	11.4
ISAF DV	6.4	15	8.6	1.2	5
ISAF 4HT DV	2.7	13.3	10.6	1	4.7
Virgin HAF	1.4	15.1	13.7	3.9	10.9
HAF DV	5.9	13.3	7.4	1.3	4.9
HAF 4HT DV	2.7	12.7	10	1	4.4
Virgin FEF	1	14.7	13.7	3.7	10
FEF DV	6.2	13.5	7.3	1.4	4.8
FEF 4HT DV	2.5	12.7	10.2	1	4.4
Virgin GPF	1	13.9	12.9	4.2	10.5
GPF DV	5.7	13.1	7.4	1.4	4.8
GPF 4HT DV	2.6	12.3	9.7	1	4.3
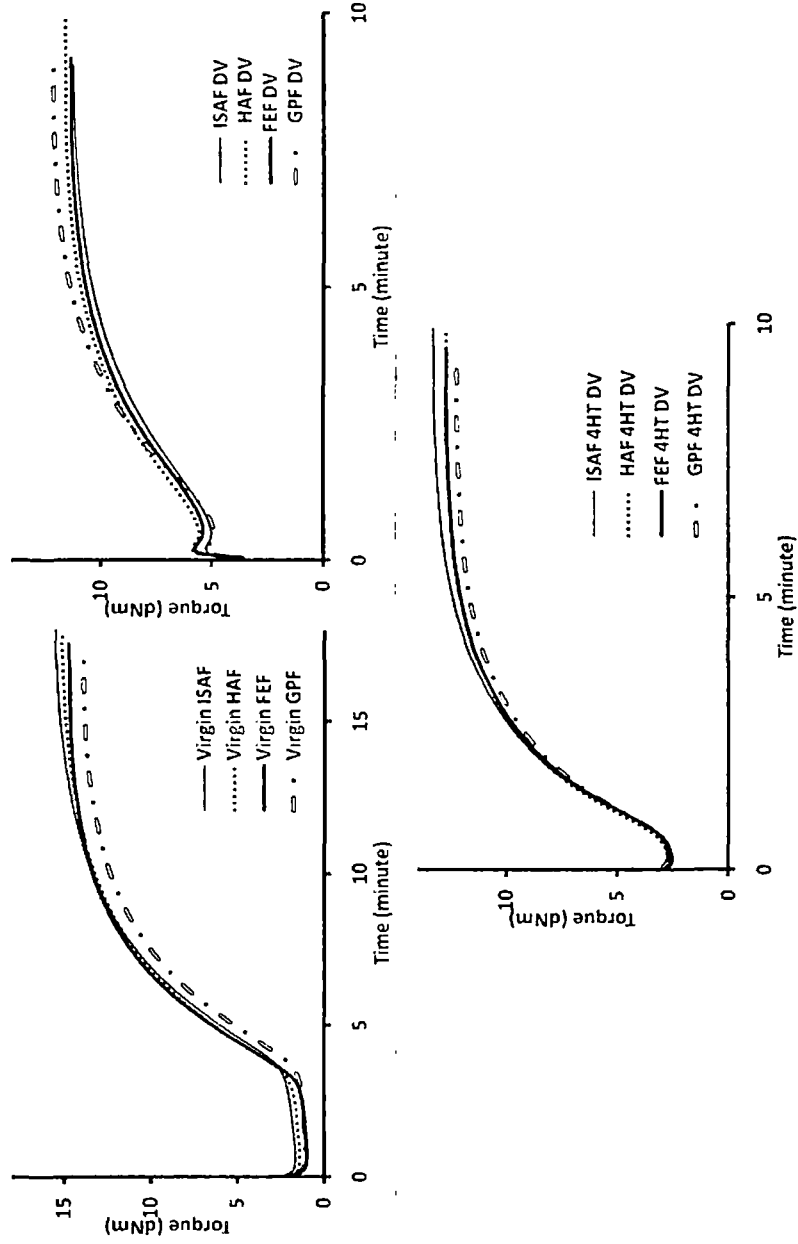
Figure 7.1 Cure curves of the original and devulcanised NR samples filled with different carbon blacks

It can be observed that, there is only marginal difference in the cure characteristics of the virgin vulcanisates corresponding to the change in filler type. The minimum torque of the virgin vulcanisates decreased in the order ISAF> HAF>FEF≥GPF while the maximum torque increased in the reverse order as GPF<FEF<HAF<ISAF making the total torque comparable.

In the case of devulcanised samples, higher minimum torque, lower maximum torque, lower total torque, low scorch time and cure time were observed in comparison with the corresponding virgin vulcanisates. The minimum torque were comparable for all devulcanised samples within the group while the maximum torque decreased with increase in particle size of filler. Lower minimum torque and a corresponding higher total torque were associated with the 4HT assisted devulcanised samples in comparison with the corresponding mechanically devulcanised samples.

7.3.1.4 Crosslink density of revulcanised samples

The revulcanisate crosslink densities of the devulcanised samples in comparison with the corresponding virgin vulcanisates are given in Table 7.6.

Table 7.6 Crosslink densities of original and revulcanised samples

Filler present in vulcanisate	Crosslink density x10^4, mole/ cm^3		
	Virgin	Revulcanised	
		DV	4HT DV
ISAF	1.26	1.74	1.71
HAF	1.4	1.84	1.77
FEF	1.48	1.57	1.8
GPF	1.33	1.63	1.82

The crosslink densities of the revulcanised samples were higher than the corresponding virgin vulcanisate. In the case of ISAF and HAF filled samples, the revulcanisate after mechanical devulcanisation had higher crosslink density than the corresponding 4HT assisted devulcanised sample whereas for FEF and GPF filled vulcanisates, 4HT assisted devulcanisation gave higher crosslink density to the revulcanisate than the corresponding mechanically devulcanised sample.

7.3.1.5 Revulcanisate properties

Comparison with vulcanisate properties of original sample

The revulcanisate properties of the devulcanised samples in comparison with that of the original samples are given in Table 7.7.

Table 7.7 Revulcanisate properties of NR vulcanisates filled with different carbon blacks

Vulcanisate	Hard-ness (shore A)	Tensile Strength (MPa)	Elongation at break (%)	M100 (MPa)	M200 (MPa)	M300 (MPa)	Tear strength (N/mm)
Virgin ISAF	67	26.5	629	2.0	4.6	8.4	111.9
ISAF DV	63	12.8	382	1.8	4	8.1	39.4
ISAF 4HTDV	65	20.1	478	2.0	4.2	8	63.2
Virgin HAF	68	25.3	584	2.1	5.2	9.5	116.4
HAF DV	63	13.4	361	1.9	4.5	9.2	36.8
HAF 4HTDV	66	18.7	506	1.8	4	7.5	59.6
Virgin FEF	66	22	533	2.2	5.6	10	67.9
FEF DV	64	11.8	333	2	4.9	9.7	32.4
FEF 4HTDV	66	17.5	441	2	4.5	8.9	50.7
Virgin GPF	65	23	556	2.0	5.1	9.3	62.5
GPF DV	64	7.6	246	2.1	5.0	-	35.8
GPF 4HTDV	64	18.0	473	1.9	4.4	8.1	61.0
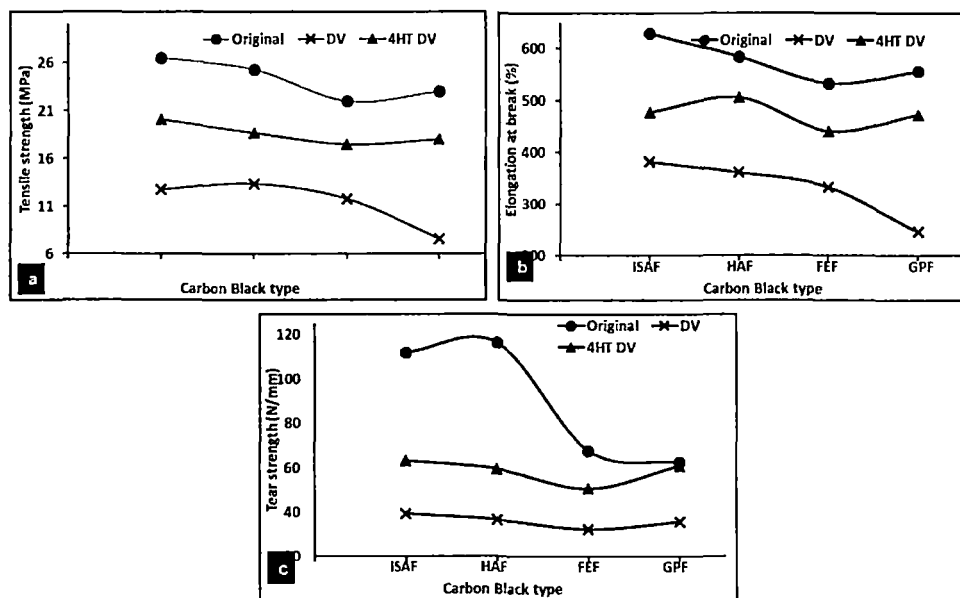
Figure 7. 2 Revulcanisate **a:** tensile strength; **b:** elongation at break; **c:** tear strength of NR samples filled with different carbon blacks in comparison with corresponding original properties

The shoreA hardness of the virgin vulcanisates were almost comparable with higher hardness for vulcanisates with lower particle sized filler. The hardness of all mechanically devulcanised samples were comparable but lower than the corresponding virgin vulcanisate especially in the case of vulcanisates with lower particle sized carbon blacks. The hardness of 4HT assisted devulcanised samples were higher than the corresponding mechanically devulcanised sample except for vulcanisates

with GPF black as filler. The variations observed in the tensile strength, elongation at break and tear strengths are illustrated in Figure 7.2.

The tensile strength of the original vulcanisates decreased as the size of the filler increased from ISAF to GPF. The trend is more obvious with tear strength. The elongation at break followed the former trend except virgin GPF vulcanisate with a higher elongation than the virgin FEF vulcanisate. The 100per cent modulus were comparable for all virgin vulcanisates while the 200 per cent and 300per cent modulus values increased with the increase in particle size of the filler except for virgin GPF filled sample. The low tensile and tear strengths of the FEF and GPF filled vulcanisates were due to the low reinforcing effect of these fillers owing to their larger size compared with ISAF and HAF blacks. When filler loading is the same, fillers with lower particle size has more irregularity and hence more bound rubber which transforms the compound from soft to stiff, owing to the loss of segmental mobility of polymer chains and consequently decreased flexibility of the rubber matrix leading to lower elongation at break[13].

Irrespective of the particle size of the filler used for the preparation of original sample, tensile strength of the mechanically devulcanised vulcanisates were comparable except for mechanically devulcanised GPF vulcanisate. Significantly higher revulcanisate tensile strengths were obtained when 4HT was used as a devulcanisation aid.

The elongation at break of the mechanically devulcanised samples decreased as the particle size of the filler increased from ISAF to GPF while that of the 4HT assisted devulcanised samples had comparatively higher elongation values. Correspondingly, the modulus values of the mechanically devulcanised samples increased with increasing particle size of the filler in the vulcanisate while that of the 4HT assisted devulcanised samples have comparable modulus values irrespective of the variation in the carbon black

filler present in the vulcanisate. As observed with previous studies on the effect of stable free radical on the devulcanisation of NR vulcanisates, the tear strength of the revulcanisates were considerably improved when devulcanisation was carried out with the aid of stable free radical.

Per cent retention of properties

The percent retention of tensile strength and tear strength associated with the revulcanised samples given in Figure 7.3a and 7.3b again confirms the advantage of 4HT as sisted devulcanisation.

Table 7.8 Per cent retention of mechanical properties of revulcanised NR samples filled with different carbon blacks

Vulcanisate	Per cent retention (%)					
	Tensile Strength	Elongation at break	M100	M200	M300	Tear strength
ISAF DV	48.5	60.6	90	88.5	95.5	35.2
ISAF 4HT DV	75.8	76	101.9	100.6	103.5	56.5
HAF DV	53.2	61.8	87.5	85.6	96.4	31.6
HAF 4HT DV	73.9	86.7	84.1	77.2	78.5	51.2
FEF DV	53.7	62.4	91.6	86.4	96.5	47.7
FEF 4HT DV	79.6	82.6	89.9	82.6	88.3	74.7
GPF DV	33.1	44.2	104.5	99.2	-	57.3
GPF 4HT DV	78.6	85.1	95.1	86	86.7	97.6

It can be observed that, the per cent retention (Table 7.8) values might mislead if not evaluated along with the absolute values. The percent retention of tear strength increased significantly as the particle size of filler increased. But, the per cent retention of tensile strength does not show such a trend. The higher per cent retention of tear strength associated with the revulcanisates of carbon blacks of higher particle size were due to the

significantly lower initial tear strength of these samples in comparison with those vulcanisates with low particle sized fillers. The percent retention of revulcanisate properties could vary significantly between samples with comparable revulcanisate properties based on the variation in absolute value of corresponding vulcanisate properties for original vulcanisates.
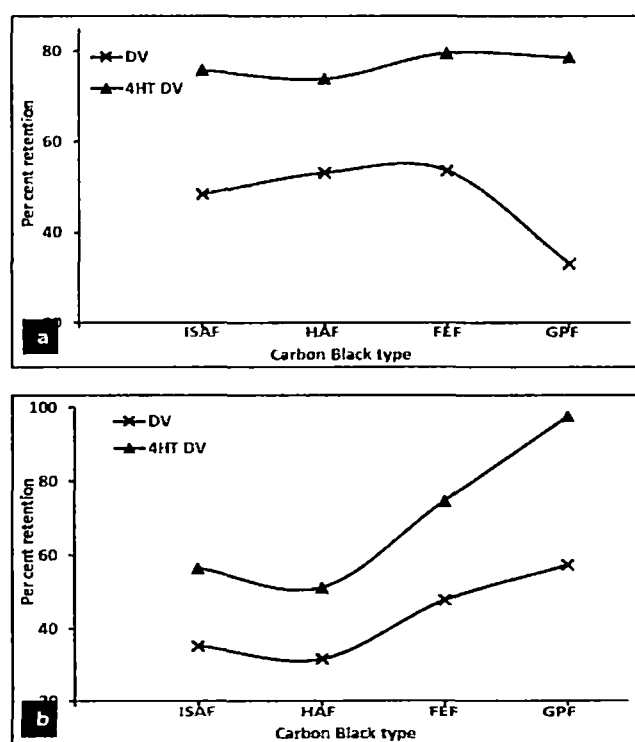
Figure 7.3 Per cent retention of revulcanisate **a:** tensile strength and **b:** tear strength of NR samples filled with different carbon blacks

Comparison with the vulcanisate properties of original NR-GPF sample

Comparison of mechanical properties of original NR/GPF vulcanisates with the revulcanisate properties of devulcanised samples indicates that (Figure 7.4) irrespective of the type of filler system used for

the preparation of original sample, the 4HT assisted devulcanised rubber can provide revulcanisate properties almost comparable with the original GPF vulcanisate. This observation indicates the possibility of un-devulcanised parts present in the devulcanised rubber matrix acting as a filler during revulcanisation with a particle size comparable with the particle size of GPF black thereby attaining the reinforcement level associated with GPF black in a rubber vulcanisate. Thus, the revulcanisate properties of the devulcanised samples could not rise above the vulcanisate properties attainable by GPF filled NR vulcanisate irrespective of the particle size of the filler used in original sample preparation.

In mechanically devulcanised samples, these vulcanised moieties present in the devulcanised rubber might be still of higher particle size or the number of such moieties would be so large that, they could not be properly dispersed in the matrix to exert any reinforcing effect. They might be acting as points of weakness and result in still lower revulcanisate properties. The higher per cent devulcanisation associated with 4HT assisted devulcanisation might be ensuring these moieties to disperse within the devulcanised rubber just like a filler and influence the revulcanisate properties of the devulcanised rubber based on the particle size of these structures.
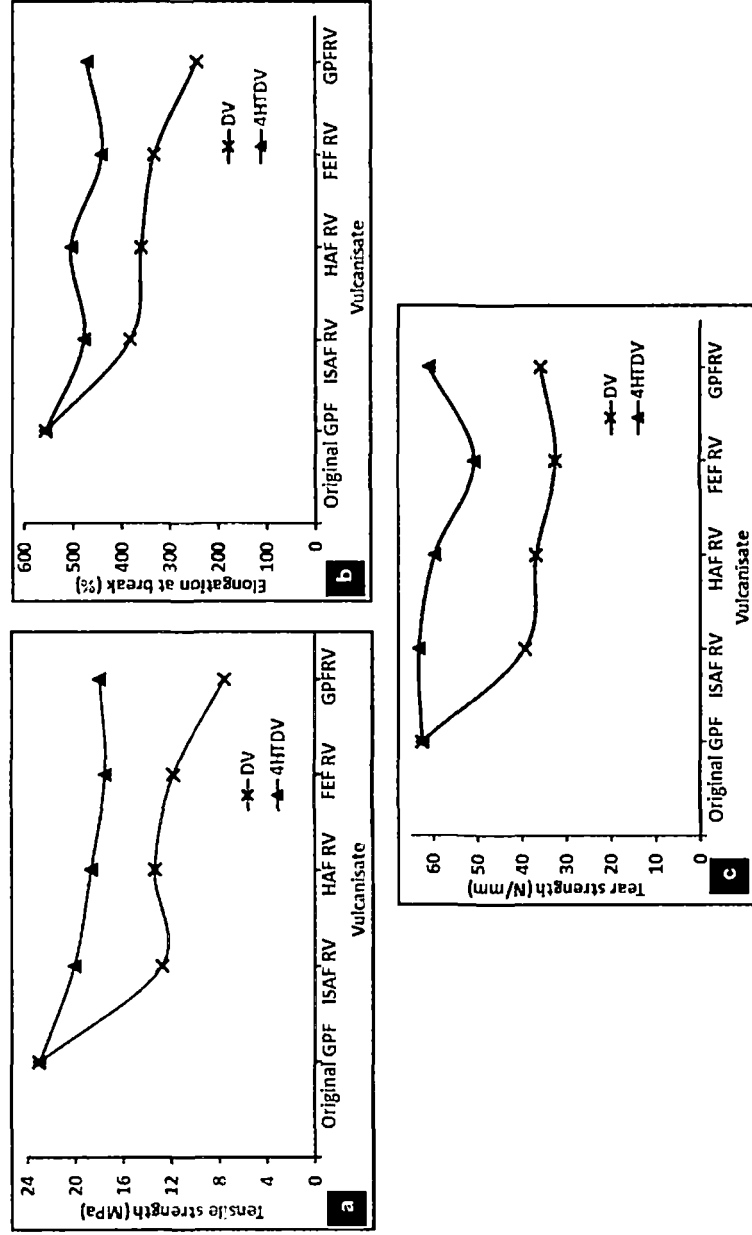
Figure 7.4 Comparison of revulcanisate **a:** tensile strength; **b:** elongation at break and **c:** tear strength of the 4HT assisted devulcanised NR samples with original properties of NR/GPF vulcanisate

In the case of devulcanised samples prepared by the devulcanisation of original NR vulcanisate filled with GPF black, the revulcanisate properties shows a tendency to improve over that of corresponding sample with HAF. This might be due to the uniformity in the size of fillers — both GPF and vulcanised moieties- present in the revulcanisate rendering more effective reinforcement to attain higher revulcanisate properties.The revulcanisate properties of the samples devulcanised with the assistance of 4HT along with the corresponding vulcanisate properties of the original GPF filled NR vulcanisate is given in Table 7.9

Table 7.9 Revulcanisate properties of 4HT assisted devulcanised samples and corresponding properties of original GPF filled sample

Vulcanisate	Hard-ness (shore A)	Tensile Strength (MPa)	Elongation at break,%	M100, MPa	M200, MPa	M300, MPa	Tear strength, N/mm
Virgin GPF	65	23	556	2.0	5.1	9.3	62.5
ISAF 4HT DV	65	20.1	478	2.0	4.2	8	63.2
HAF 4HT DV	66	18.7	506	1.8	4	7.5	59.6
FEF 4HT DV	66	17.5	441	2	4.5	8.9	50.7
GPF 4HT DV	64	18.0	473	1.9	4.4	8.1	61.0

7.3.2 Effect of amount of carbon black present in original vulcanisate

The role of carbon black content present in the samples to be devulcanised on devulcanisation efficiency and the resultant revulcanisate properties were studied using HAF filled NR vulcanisates. The HAF content in the vulcanisates were varied from 20phr to 60phr. The original samples were devulcanised, characterized by determining the percent devulcanisation, sol fraction and processability and was correlated with the revulcanisate properties.

7.3.2.1 Required number of passes for devulcanisation

The amount of filler present in the vulcanisate to be devulcanised is also found to be influencing the number of passes required for devulcanisation. The number of passes required for devulcanisation of NR vulcanisates filled with varying amounts of HAF black is given in Table 7.10. It can be observed that, the required number of passes through the tight nip for devulcanisation is lowered significantly when stable free radical was used as a devulcanisation aid.

Table 7.10 Number of passes required for devulcanisation of NR samples with varying HAF loading

HAF loading	Number of passes through tight nip	
(phr)	Mechanical	4HT assisted
20	Stopped after	25
30	30passes	40
40	50	35
50	45	35
60	40	30

As previously mentioned, the devulcanisation time of 20phr and 30phr HAF filled vulcanisates were limited to 30passes through the tight nip as it become increasingly difficult to devulcanise the sample further. In the case of 4HT assisted devulcanisation, the vulcanisate had a better response towards devulcanisation and roll sticking was minimized. The 4HT assisted devulcanisation of 20phr HAF filled samples were limited to 25passes through tight nip owing to static current, but the devulcanised sample appeared to have attained a better level of devulcanisation compared with the corresponding mechanically devulcanised sample. The problem of static current was further reduced for devulcanisation of HAF filled vulcanisates with higher loadings of HAF and the required number of passes was decided

based on the devulcanisation state assessed by the visual appearance of the samples. It can also be observed that, the number of passes through the tight nip required for devulcanisation reduced as the filler loading of the vulcanisate increased.

7.3.2.2 Processability analysis

The processability of devulcanised samples was ascertained based on the tan delta values of the devulcanised samples in the uncured state at 60°C. The plot of tan delta values against strain of the devulcanised samples along with the corresponding original compounds were plotted in Figure 7.5.

Since tan delta value represents the ratio of viscous modulus of the rubber to the elastic modulus, a higher tan delta value is associated with a higher viscous behavior and lower elastic behavior. As the elastic part of the vulcanisate increases upon crosslinking with a corresponding reduction in the viscous content, the reverse condition is expected after devulcanisation. That is, upon devulcanisation the crosslinks which imparts the elastic nature to the vulcanisates are cleaved thereby bringing back the viscous nature of the raw rubber as the prominent nature. As the efficiency of devulcanisation increases, the viscous content is expected to increase with a corresponding increase in the tan delta values.

The tan delta values of the 4HT assisted devulcanised samples were significantly higher than that of the corresponding mechanically devulcanised samples indicating higher viscous part of the former in comparison with the latter. The variation of tan delta values under the influence of varying filler content is also observed from the Figure. Figure 7.5a demonstrates the lowering of uncured tan delta response with increasing concentrations of carbon black due to the increase in the density of carbon black aggregate-aggregate network leading to a higher uncured elastic modulus response[17].
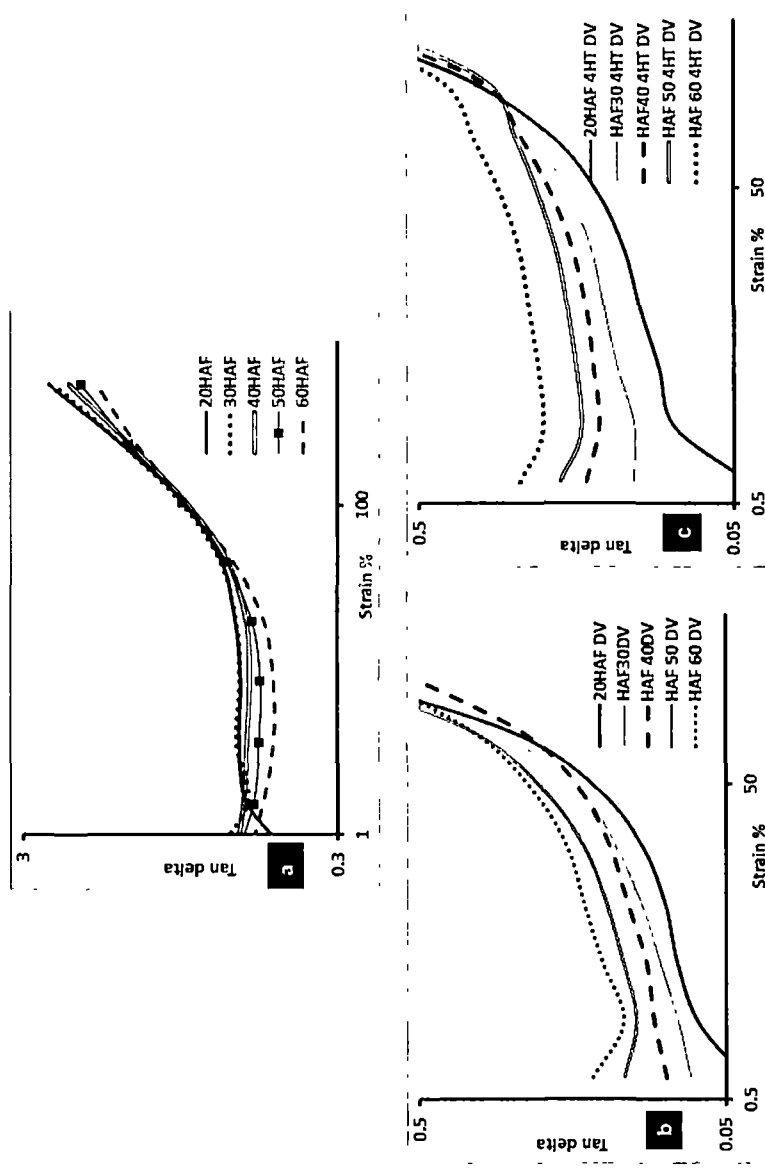
Figure 7.5 Effect of HAF concentration on the processability of **a**:original, **b**: mechanically devulcanised and **c**: 4HT assisted devulcanisation samples

Although devulcanisation ideally envisages crosslink scission to ensure retrieval of un-crosslinked elastomer, it practically could render a sample with significant number of crosslinks still present. Hence devulcanised rubber with varying per cent devulcanisation shows corresponding variations in the tan delta response based on the variation in its elastic and viscous components but still remain as partially cured elastomer. Thus, the uncured tan delta response of the devulcanised samples followed the trend corresponding to the cured rubber with varying filler content. Here, increased carbon black loadings reduce the amount of rubber available for crosslinking and increase the interface area between rubber and carbon black which results in an increase in tan delta value with filler loading (Figure 7.5b and Figure 7.5c)[18,19].

7.3.2.3 Residual crosslink density and per cent devulcanisation

The crosslink densities of the virgin vulcanisates and the residual crosslink densities of the corresponding 4HT assisted devulcanised samples along with their respective per cent devulcanisation is given in Table 7.11. It can be observed that, the crosslink density of the virgin vulcanisate increased with increase in filler content in the vulcanisate with same cure formulation which is a common observation This is due to the strong interaction between rubber molecules and the surface of the carbon black particles as CB had little influence on chemical crosslink density introduced by chemical vulcanisation[20]. Correspondingly, the residual crosslink density of the 4HT assisted devulcanised samples increased from 20phr HAF loaded vulcanisate to 60phr HAF loaded vulcanisate.

At lower filler content and lower crosslink density of the virgin vulcanisate, the per cent devulcanisation was higher and vice versa. But as the filler content present in the virgin vulcanisate increased with corresponding increase in crosslink density, reduction in per cent

devulcanisation was observed. The reduction in per cent devulcanisation became marginal when the filler content increased from 50phr to 60phr.

Table 7.11 Crosslink densities of original and devulcanised samples with corresponding per cent devulcanisation

Vulcanisate/ HAF loading		Crosslink density x10^4, mole/ cm^3	Per cent devulcanisation (%)
20phr	Virgin	1.24	-
	4HT DV	0.54	56
30phr	Virgin	1.3	-
	4HT DV	0.61	53
40phr	Virgin	1.34	-
	4HT DV	0.67	50
50phr	Virgin	1.41	-
	4HT DV	0.75	47
60phr	Virgin	1.52	-
	4HT DV	0.82	46

7.3.2.4 Horikx analysis

The Horikx plot of the 4HT assisted devulcanised NR with varying HAF loading is given in Figure7.6. The Figure indicates that, the sol fraction of the devulcanised rubber increased marginally with increase in the filler loading of the original vulcanisate. The data moved closer to the directed scission curve. This indicates that, the increase in the sol fraction of the devulcanised samples with increase in the filler content of the original vulcanisate might be attributed to the increase in the main chain scission associated with these samples upon devulcanisation. However, the Figure also indicates that the 4HT assisted devulcanisation of these samples did not cause significant main chain degradation of rubber and hence good revulcanisate properties could be expected.
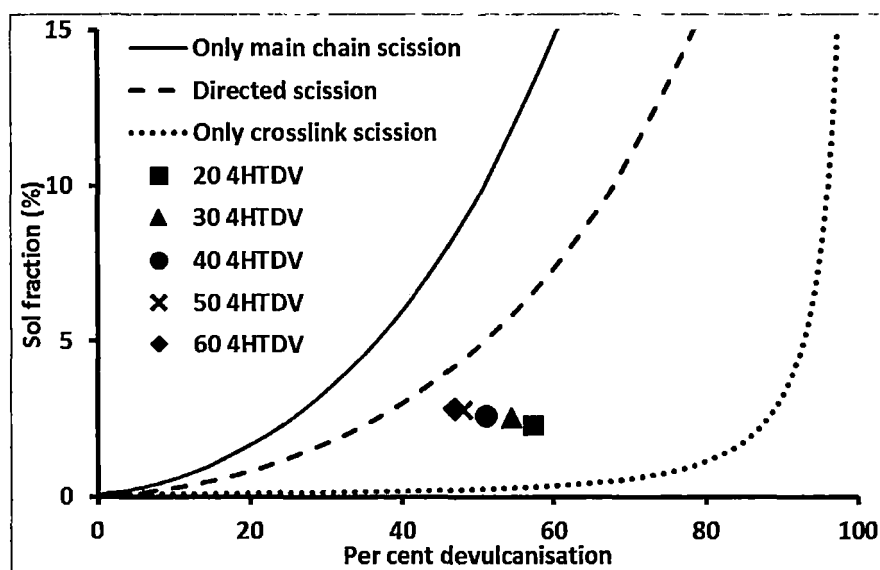
Figure 7.6. Horikx plot of 4HT assisted devulcanised NR samples with varying HAF loading

Variation in sol fraction of both mechanically and 4HT assisted devulcanised NR vulcanisates with varying HAF content illustrated in Figure7.7 reveals that, the sol fraction of the 4HT assisted devulcanised samples were significantly higher than the corresponding mechanically devulcanised sample. In the case of devulcanised NR containing 60phr HAF in the original vulcanisate, the sol fraction was comparable for both mechanical and 4HT assisted devulcanisation. Since, it was observed from Figure 7.6 that the sol fraction of the devulcanised samples prepared from original vulcanisates with higher filler loading tend to increase due to higher per cent of main chain scission, the former observation can conclusively correlated to per cent devulcanisation only after evaluating the revulcanisate properties.
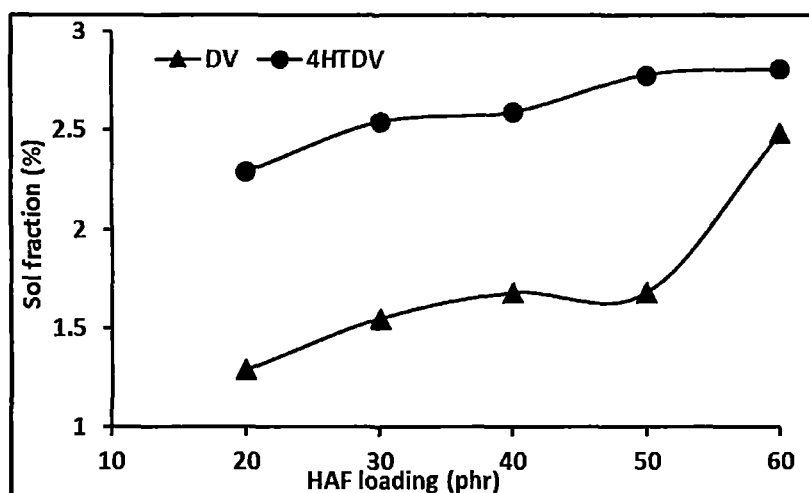
Figure 7.7 Sol fraction of mechanically and 4HT assisted devulcanised NR samples with varying HAF loading

7.3.2.5 Cure characteristics

The cure characteristics of the original and the corresponding devulcanised samples are given in Table 7.12 and the respective cure curves are out lined in Figure 7.8. It can be observed from the cure curves that both the minimum torque and maximum torque of the virgin NR vulcanisates increased with the increase in HAF loading. In the case of mechanically devulcanised samples, the magnitude of hike in minimum torque with increasing filler concentration is more prominent and the increase in maximum torque with increasing filler loading is reduced. The cure curves of 4HT assisted devulcanised samples were also like the mechanically devulcanised samples except that the minimum torque of devulcanised samples are comparable. The general observations associated with the cure curves of devulcanised samples such as low scorch time and cure time can also be observed.

Table 7.12 Cure characteristics of original and corresponding devulcanised samples containing different amount of HAF

HAF (phr)	Vulcanisate	Torque (dNm)		M_H- M_L	Scorch Time, min	Cure time (min)
		Minimum, M_L	Maximum, M_H			
	Virgin	0.8	10.2	9.4	4.3	10.2
20	DV	4.4	10.3	5.9	1.8	5.1
	4HT DV	2.2	10	7.8	1.3	4.6
	Virgin	1.1	12.7	11.6	4.1	10.4
30	DV	5.3	10.1	4.8	1.7	5
	4HT DV	2.2	11.3	9.1	1.1	4.5
	Virgin	1.4	15.2	13.8	3.8	10.4
40	DV	5.5	12.7	7.2	1.6	5
	4HT DV	2.3	13.2	10.9	0.97	4.5
	Virgin	1.9	19.1	17.2	3.5	10.4
50	DV	6.4	14.4	8	1.4	4.9
	4HT DV	2.6	14.2	11.6	0.95	4.5
	Virgin	2.3	21.8	19.5	3.1	10.9
60	DV	7.2	15.5	8.3	1.4	5
	4HT DV	2.9	13.1	10.2	1	3.5

The increase in minimum torque with HAF loading in virgin compound might be because the HAF particles with larger surface area had a greater adhesion between the filler and the rubber and cause the immobilization of more number of rubber molecules on surface of blacks thereby stiffening the composite owing to the loss of segmental mobility of polymer chains and consequently, decrease the flexibility of rubber matrix. As the crosslink densities of the samples are increased by the higher filler loading which will also contribute to an increase in total torque with filler loading.
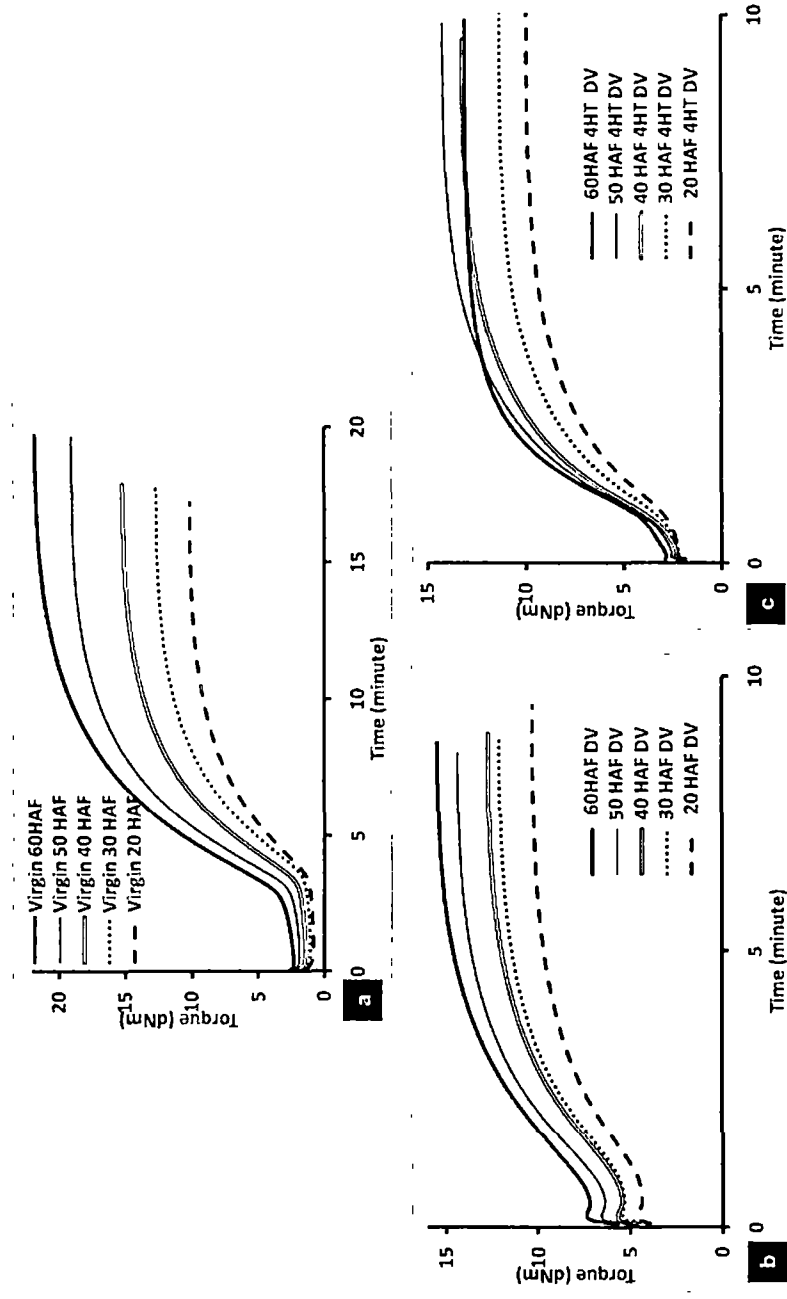
Figure 7.8 Cure curves of **a:** virgin compounds and corresponding **b:** mechanically devulcanised and **c:** 4HT assisted devulcanised samples

With respect to the devulcanised samples, the minimum torque was increased and maximum torque decreased bringing a net reduction in the total torque of the devulcanised samples in comparison with the corresponding virgin vulcanisates. Though higher than the minimum torque of virgin vulcanisate, the minimum torque of 4HT assisted devulcanised rubber were lower. Hence, the total torque of the 4HT assisted devulcanised samples are higher than the corresponding mechanically devulcanised samples.

7.3.2.6 Crosslink density of the revulcanised samples

The devulcanised samples were revulcanised using the formulation given in Table 7.1 and the corresponding revulcanisate crosslink densities attained by these samples are given in Table 7.13 in comparison with the respective crosslink density of the virgin vulcanisates.

Table 7.13 Revulcanisate crosslink densities in comparison with the crosslink densities of the corresponding original samples

HAF loading, phr	Crosslink density x 10^4, mole/ cm^3		
	Virgin	DV/RV	4HT DV/RV
20	1.24	1.58	1.43
30	1.3	1.67	1.56
40	1.34	1.81	1.65
50	1.41	1.83	1.69
60	1.52	1.86	1.72

The revulcanisate crosslink densities of all the devulcanised samples were significantly higher than the corresponding virgin vulcanisates. The per cent increase of crosslink densities of the revulcanised samples in comparison with the corresponding virgin vulcanisates plotted in Figure 7.9

shows that the per cent increase in revulcanisate crosslink densities were higher for the mechanically devulcanised samples than the corresponding samples devulcanised with the assistance of 4-Hydroxy Tempo. The low revulcanisate crosslink densities of the 4HT assisted devulcanised samples might be due to the low residual crosslink densities of these samples in the devulcanised state in comparison with the respective mechanically devulcanised samples as seen in previous cases.
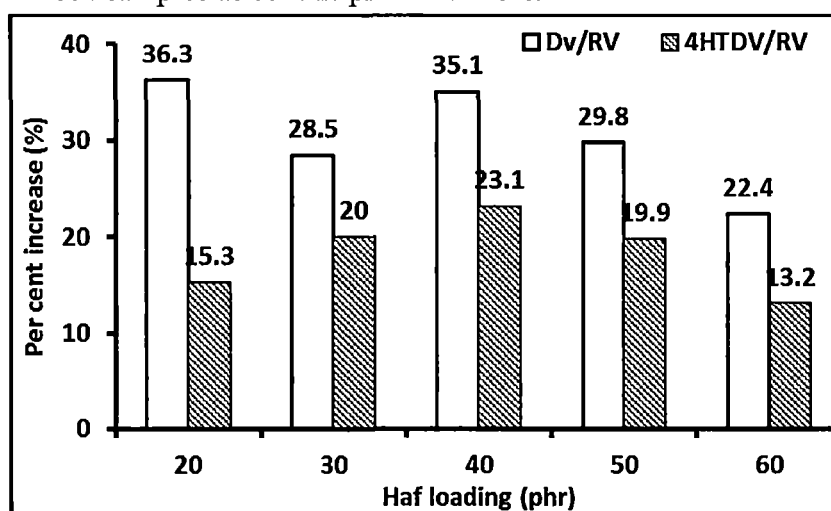
Figure 7.9 Per cent increase in revulcanisate crosslink densities with respect to corresponding virgin vulcanisates.

7.3.2.7 Revulcanisate properties

Comparison of the tensile strength, elongation at break and tear strength of the virgin vulcanisates with varying filler loading and the corresponding revulcanisates are shown in Figure 7.10.
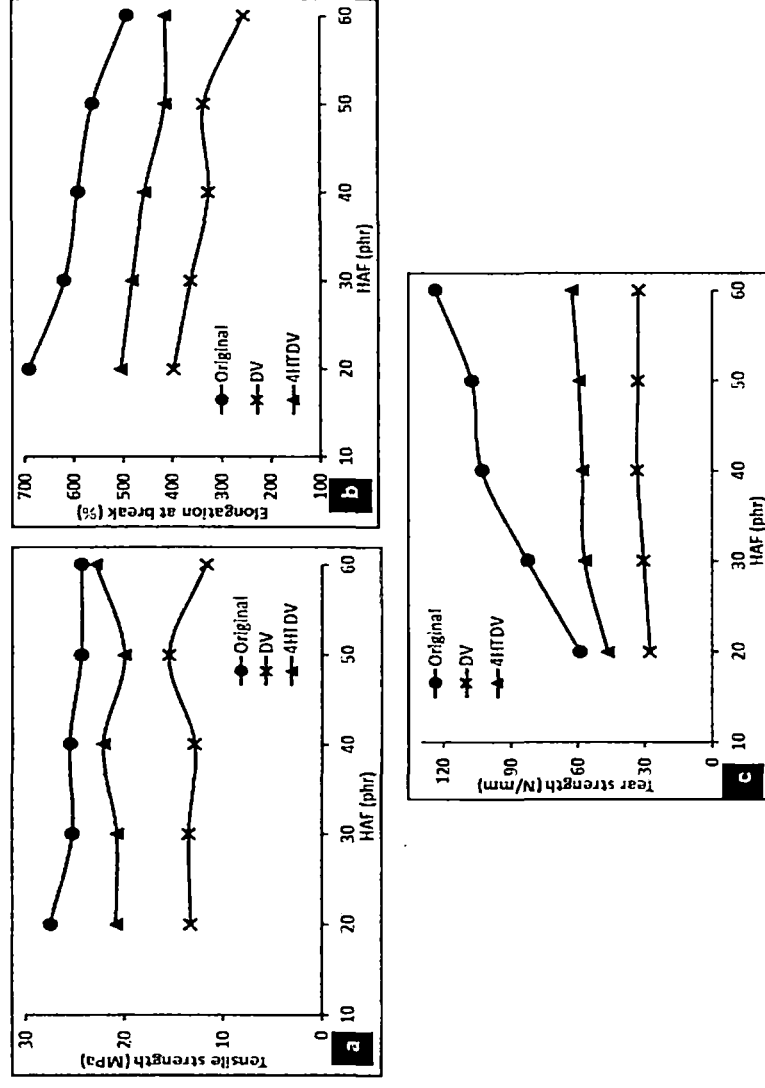
Figure 7.10 Revulcanisate **a:** tensile strength **b:** elongation at break and **c:** tear strength of devulcanised samples with varying HAF loading in comparison with corresponding properties of original sample.

The revulcanisate properties of the devulcanised samples were listed in Table 7.14 and the stress-strain curves are given in Figure 7.11 while the per cent retention of properties is given in Table 7.15.

Table 7.14 Revulcanisate properties of devulcanised NR samples filled with different amounts of HAF black

HAF (phr)	Vulcanisate	Tensile Strength (MPa)	Elongation at break (%)	M100 (MPa)	M200 (MPa)	M300 (MPa)	Tear strength (N/mm)
	Virgin	27.6	692	1.2	2.6	5	58.9
20	DV	13.3	398	1.7	3.5	6.9	27.7
	4HTDV	20.9	505	1.6	3.4	6.6	46.5
	Virgin	25.3	620	1.7	3.9	7.3	82.4
30	DV	13.5	364	2.0	4.4	8.9	30.6
	4HTDV	20.8	482	2.1	4.7	8.7	57
	Virgin	25.6	592	2.3	5.4	7.4	103
40	DV	12.9	326	2.3	5.5	11.1	33.5
	4HTDV	22.2	457	2.5	5.5	10.1	57.9
	Virgin	24.4	562	2.7	6.6	11.5	107.6
50	DV	15.5	336	2.7	6.5	12.7	33.2
	4HTDV	20	415	2.6	6	11.4	59.5
	Virgin	24.4	493	4.3	9.7	15.4	123.8
60	DV	11.7	256	3.1	7.8	-	33
	4HTDV	22.9	414	3.1	7.6	14.4	62.5

The general observations that can be made from the revulcanisate properties are

(I) The tensile strength and elongation at break of the original samples decreased and the modulus values and tear strength increased with increasing HAF loading.
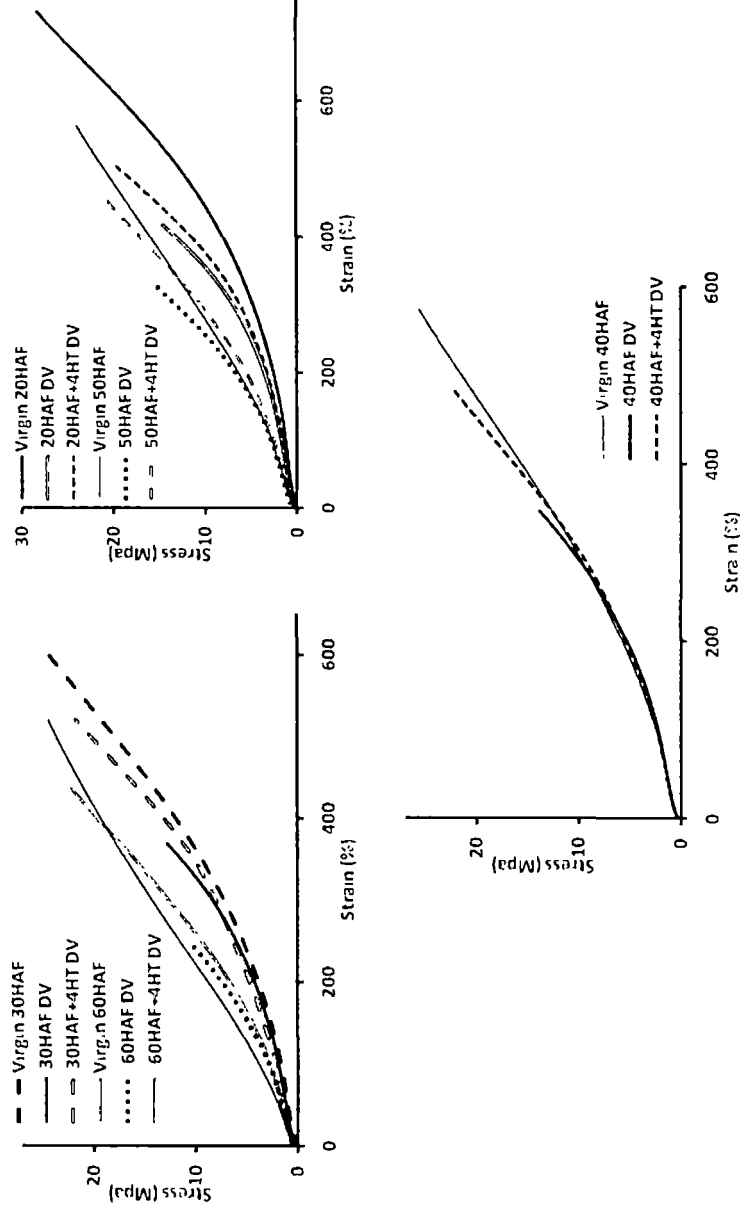
Figure 7.11 Stress-strain curves of virgin and devulcanised NR samples with varying HAF loading

(II) The revulcanisate properties of the 4HT assisted devulcanised samples were significantly higher than that of the mechanically devulcanised samples.

Table 7.15 Per cent retention of vulcanisate properties of NR samples filled with different amounts of HAF black

Vulcanisate	Per cent retention (%)					
	Tensile Strength	Elongation at break	M100	M200	M300	Tear strength
20DV	48.1	57.5	140.5	136.3	139.9	47.1
204HT DV	75.8	73	134.2	131.6	133.7	79
30DV	53.4	58.7	118	112.8	122.5	37.2
304HT DV	82	77.7	126.2	119.5	119.2	69.2
40DV	50.3	55.2	100.1	102.8	149.2	32.5
404HT DV	86.8	77.2	108.4	103.6	135.9	56.2
50DV	63.3	59.9	102.9	98.9	110.2	30.8
504HT DV	82	73.9	96.8	91.4	98.5	55.3
60DV	47.8	52.1	70.7	79.7	-	26.7
604HT DV	94	84	71.2	78.6	93.5	50.5

The maximum retention of tensile strength and elongation at break for mechanical devulcanisation were obtained for revulcanisate with 50phr HAF incorporated and the minimum retention was obtained for revulcanised sample from virgin vulcanisate with 60phr HAF incorporated. For 4HTassisted devulcanisation, maximum retention was observed with 60phr HAF incorporated samples while the minimum retention was obtained with the revulcanisation of 20phr HAF incorporated sample.

Although the absolute value of tear strengths of the devulcanised samples increased with the increase in HAF loading from 20phr to 60phr, the per cent retention of tear strengths of the revulcanisates decreased with

increasing HAF loading. At forces somewhat below those causing main-chain fracture, detachment of polymer molecules from carbon black particles occur. Thus the initial short network strand become longer at high stresses giving more strength and tear resistance with increase in filler loading[21] in the case of original samples. In the case of revulcanisates, the amount of gel particles might be the most influencing factor determining the tear strength.

As observed from previous chapters, higher retention of revulcanisate tensile properties can be achived by moderate levels of devulcanisation and the tear properties are the most sensitive markers for efficiency of devulcanisation. In the case of NR vulcanisates with constant filler loading, revulcanisate tear strength increased with increase in per cent devulcanisation. However, when filler loading in original sample is varied from 20 to 60phr, though the per cent devulcanisation decreased revulcanisate tear strength increased. In this case it has to be assumed that, the effect of per cent devulcanisation upon tear properties were masked by the increase in the amount of filler present in the vulcanisate which was found to improve the tear properties specifically as observed in chapter three.

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Chapter 8

Devulcanisation of NR/BR Blends

8.1 INTRODUCTION

Blending of elastomers usually aim at improvement in the performance chatacteristics of rubber products. Blending of butadiene rubber (BR) with natural rubber (NR) improves its processing characteristics and abrasion resistance[1]. Blending with BR allows NR to have higher curing temperature and improved heat stability[2,3]. Blends of NR and BR contributes to cost reduction and improved performance for tyres[4].

Stefan tested several conditions for the devulcanisation of BR with the use of DPDS in order to elaborate the best conditions for an efficient process[5]. It was observed that addition of DPDS leads to effective devulcanisation of BR and prolonged devulcanisation time reduces the degree of devulcanisation by recombination of the broken crosslinks. Hong and Isayev studied the ultrasonic devulcanisation of sulphur cured natural rubber (NR)/styrene butadiene rubber (SBR) blends with the goal of understanding the devulcanisation of rubber vulcanisates in which two networks of different natures were present[6]. Microwave devulcanisation of ground tyre rubber (GRT) - which contains natural rubber (NR) and styrene-butadiene rubber (SBR) as polymeric material - was carried out to understand the physical and chemical changes that occur in the ground tire rubber after different microwave exposure periods[7]. It was observed that, substantial amounts of the NR chain were decomposed and broken during the treatment and efficient compatibilization of the elastomeric phases has taken place.

Cured NR is rather easy to be re-plasticized, though it is not yet conclusive whether the predominant mechanism is devulcanisation or

polymer scission. SBR and BR vulcanisates are more difficult to devulcanise, as the network fragments tend to re-combine, resulting in an uncontrolled re-crosslinking of the polymer[5, 8]. Hence, NR might be regarded as a non-critical component in the blends of NR with other rubbers and will be devulcanised sufficiently under the devulcanisation circumstances chosen for other components in the blends[8].

Present chapter intends to investigate the effect of polybutadiene rubber content on the devulcanisation efficiency of NR/BR blends by varying the BR content in the blend from zero to 50per cent. The effect of cure system employed for the preparation of the original blend and the dosage of curatives used for vulcanisation of original blend (varying crosslink densities) was also studied. Since tyres use various ratios of NR/BR blends for different parts based on performance requirements, the maximum share of waste rubber (GRT) would be an NR/BR blend. Hence, the present study focusing on the various aspects of devulcanisation of NR/BR blends seems much relevant both in the academic level and on practical grounds.

8.2 EXPERIMENTAL

Devulcanisation of blends of natural rubber and polybutadiene rubber cured with both CV and semi EV cure systems were carried out in comparison with the devulcanisation of NR vulcanisate. The polymer compositions of the vulcanisates are given in Table 8.1.

Table 8.1 Polymer composition of CV and semi EV cured original NR/BR blends

Polymer	Blend ratio				
Natural Rubber	100	80	70	60	50
Butadiene Rubber	0	20	30	40	50

The original samples are prepared using the formulation given in Table 8.2 and revulcanised after blending with 10g NR per 100g devulcanised rubber using the revulcanisation formulation given in Table 8.2.

Table 8.2 Formulation of CV and semi EV cured original NR/BR blends and their revulcanisates

Ingredients	Original compound (phr)		Revulcanisation (phr)
	CV cure	Semi EV cure	
Rubber hydrocarbon@	100	100	100
HAF	50	50	-
Naphthenic oil	6	6	-
Zinc oxide	5	5	3
Stearic acid	2	2	2
Antioxidants*	2.5	2.5	-
CBS	1	1.2	2
Insoluble sulphur	2.5	1.3	0.5

@NR/BR ratio was varied as 100/0, 80/20, 70/30, 60/40 and 50/50
*1phr TDQ and 1.5phr Memox 6C

Comparative study of the effect of crosslink density of the original vulcanisate upon the devulcanisation efficiency was carried out using semi EV cured 50/50 blends of NR and BR. The accelerator sulphur ratio was kept constant at 0.92 while the amount of curatives was varied to obtain varying crosslink densities. The logic behind choosing the blend ratio as 50/50 was, to investigate the possibility of improving the devulcanisation efficiency of 50/50 blend, which is the most probable composition of GTR through adjusting the crosslink density of the vulcanisate. The formulation adopted for preparation of virgin 50/50 blend vulcanisates was similar to the one adopted for the preparation of original semi EV samples given in Table

8.1 with varying curative dosage as given in Table 8.3. The revulcanisation formulation employed was same as given in Table 8.2.

Table 8.3 Formulation of semi EV curedoriginal 50/50 blends of NR/ BR blends with different crosslink densities

Ingredients	Virgin vulcanisate (phr)			
	I	II	III	IV
CBS	0.65	0.92	1.2	1.38
Insoluble sulphur	0.7	1	1.3	1.5

The variation in devulcanisation efficiency was assessed based on the percent devulcanisation of devulcanised samples and the corresponding revulcanisate properties.

8.3 RESULTS AND DISCUSSION

8.3.1 Effect of BR content on the devulcanisation of CV cured NR/BR blends

The role of BR content in the devulcanisation of NR/BR blends was investigated by devulcanisation of CV cured vulcanisates containing varying amounts of polybutadiene and NR. The BR content in the blends was varied from zero to 50 parts. The samples were devulcanised and the effect of increasing amounts of BR in the NR/BR blends upon the revulcanisate properties was compared.

8.3.1.1 Number of passes for devulcanisation

The required number of passes through the tight nip of the two roll mill for devulcanisation of 200g of virgin vulcanisates with and without the assistance of 4phr 4-Hydroxy TEMPO varied for different vulcanisates and the variations are represented in Figure 8.1
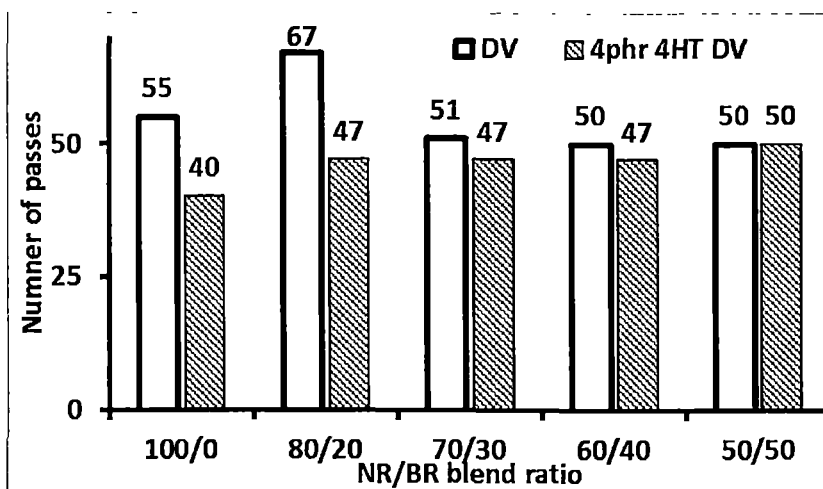
Figure 8.1 Number of passes required for devulcanisation of CV cured NR/BR blends

It can be observed form the figure that, the required number of passes through the tight nip for devulcanisation considerably reduced in the presence of 4HT for NR vulcanisate and 80/20 blends of NR and BR. On the other hand, the required number of passes for devulcanisation increased when 20parts BR was incorporated to NR to form 80/20 blends in comparison with virgin NR vulcanisate. In the case of other blends, the numbers of passes for mechanical devulcanisation were limited to 50, on the grounds that the devulcanised rubber was not forming a sheet even after 50passes through tight nip. But, in the case of blend vulcanisates devulcanised with the assistance of 4phr 4HT, the devulcanised samples turned into sheet structure and the state of devulcanisation resembled almost that of the NR vulcanisate at about 47 to 50 passes through the tight nip.

8.3.1.2 Residual crosslink density and per cent devulcanisation

Residual crosslink densities of the devulcanised samples were compared with the crosslink density of the corresponding virgin vulcanisates and the per cent devulcanisation were determined. The residual crosslink

densities after mechanical devulcanisation of the blends could not be determined as they remained as powder after devulcanisation whose crosslink density determination by swelling will give erroneous results due to the accumulation of solvent in between the particles. The crosslink density of the CV cured virgin vulcanisates and the residual crosslink densities of the 4HT assisted devulcanised samples along with corresponding per cent devulcanisation were given in Table 8.4.

Table 8.4 Crosslink densities of the CV cured original and 4HT assisted devulcanised NR/BR blends

NR/BR blend ratio	Crosslink density $\times 10^4$, mole/cm^3		Per cent devulcanisation, %
	Virgin	4HT DV	
100/0	1.72	0.56	67.4
80/20	1.72	0.67	61
70/30	1.84	0.69	62.5
60/40	1.88	0.59	68.6
50/50	1.85	0.55	70.3

The crosslink density of the virgin NR vulcanisate and the 80/20 blends of NR and BR were the same, while that of the other blends were marginally higher. The residual crosslink densities of the 4phr 4HT assisted devulcanised NR vulcanisate and 50/50 blend were comparable and were the lowest. The residual crosslink density of the devulcanised samples increased when BR was incorporated till 70/30 blend where after it decreased for 60/40 blend and further reduced for 50/50 blend with corresponding variation in the per cent devulcanisation.

8.3.1.3 Cure characteristics

The cure characteristics of the virgin vulcanisates cured with CV cure system and the corresponding devulcanised samples during

revulcanisation were given in Table 8.5. The respective cure curves are represented in Figure 8.2.

Table 8.5 Cure characteristics of original and corresponding devulcanised samples of CV cured NR/BR blends

Vulcanisate/ NR/BR Blend Ratio	Torque (dNm)			Scorch Time, min	Cure time (min)
	Minimum, M_L	Maximum, M_H	M_H-M_L		
Virgin 100/0	1.8	20.1	18.3	2.9	7.6
100/0 DV	8.4	17.4	9	1.4	6.1
100/0 4HTDV	3.8	15	11.2	0.9	5.2
Virgin 80/20	1.6	19.4	17.8	3.4	7.9
80/20 DV	8	16.3	8.3	1.5	6.5
80/20 4HTDV	5.1	15.7	10.6	0.9	5.6
Virgin 70/30	1.8	20.6	18.8	3.6	8.8
70/30 DV	8.7	17	8.3	1.7	6.6
70/30 4HTDV	5	16.3	11.3	1	6
Virgin 60/40	2	20.4	18.4	3.9	8.4
60/40 DV	8.1	17.5	9.4	1.6	7.1
60/40 4HTDV	5.2	16.8	11.6	1	6.2
Virgin 50/50	2	19.8	17.8	4.1	8.9
50/50 DV	8	17.4	9.4	1.7	7.6
50/50 4HTDV	5.6	16.9	11.3	1	6.3
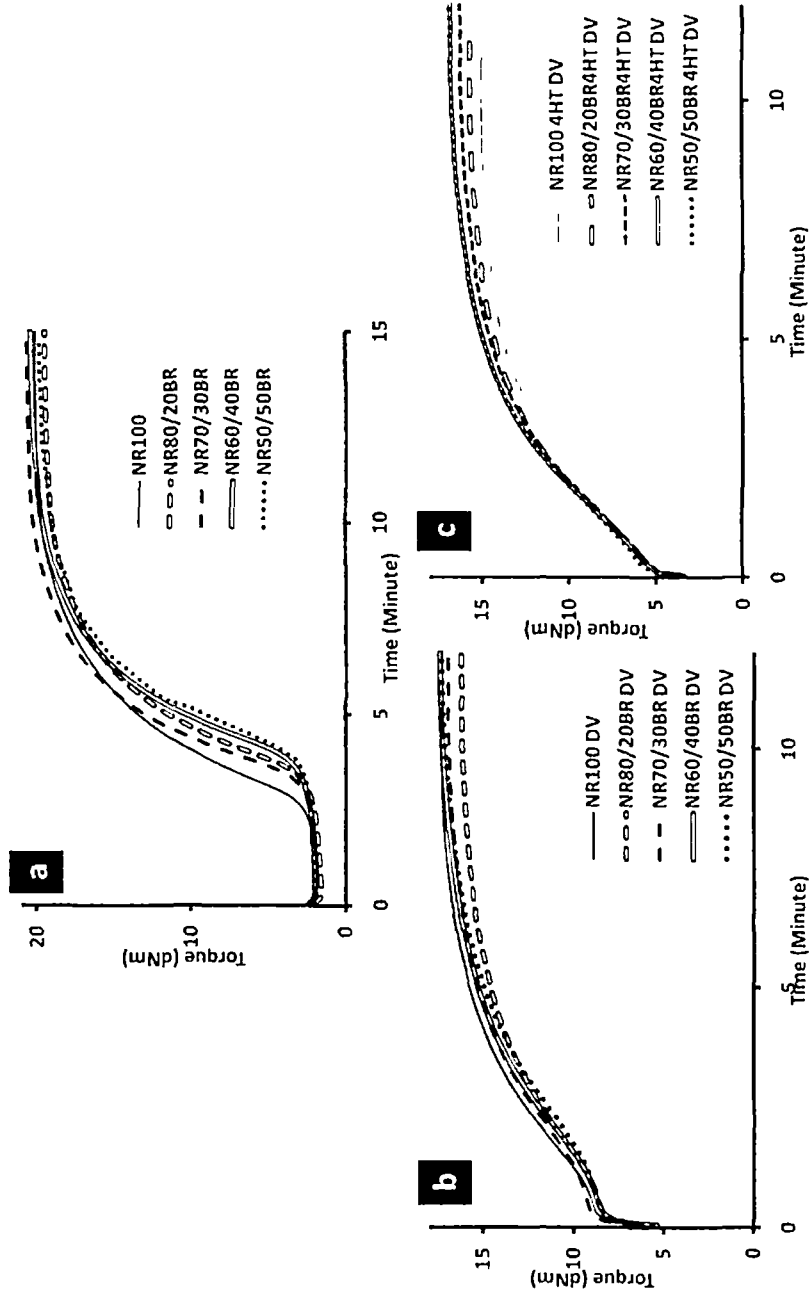
Figure 8.2 Cure curves of **a:** CV cured virgin NR/BR blends and the corresponding **b:** mechanically and **c:** 4HT assisted devulcanised samples

The cure characteristics of the virgin NR and the NR/BR blend vulcanisates were similar except for the increase in pre vulcanisation scorch time of the blends with the increase in the BR content in the blend probably due to the higher reactivity of NR than BR resulting in shorter cure times and higher cure rate index (CRI)[9]. Irrespective of the blend ratio, the total torque of all the virgin vulcanisates remained comparable. The devulcanised samples had shorter scorch times, higher minimum torque, and lower maximum torques in comparison with the corresponding virgin vulcanisates. The minimum torque of the 4HT assisted devulcanised samples were lower than that of the mechanically devulcanised samples resulting in an increase in the total torque of these samples.

The comparable minimum torques of the virgin vulcanisates indicates that the BR content in the vulcanisate did not influence the minimum torque. In addition, since the minimum torque indirectly relate to the viscosity of the sample, the comparable values for minimum torque of mechanically devulcanised samples point to the similar viscosity of the devulcanised samples corresponding to their similar level of devulcanisation. On the other hand, the lower minimum torque of the 4HT assisted devulcanised samples might be indicating the higher percent devulcanisation of these samples[10].The increase in minimum torque of the devulcanised blends in comparison with devulcanised NR sample might be indicating that, the presence of BR tend to decrease the devulcanisation efficiency.

8.3.1.4 Revulcanisate properties

The revulcanisate properties of the devulcanised samples in comparison with the corresponding properties of the virgin vulcanisates are illustrated in Figure8.3 and are listed in Table 8.6.
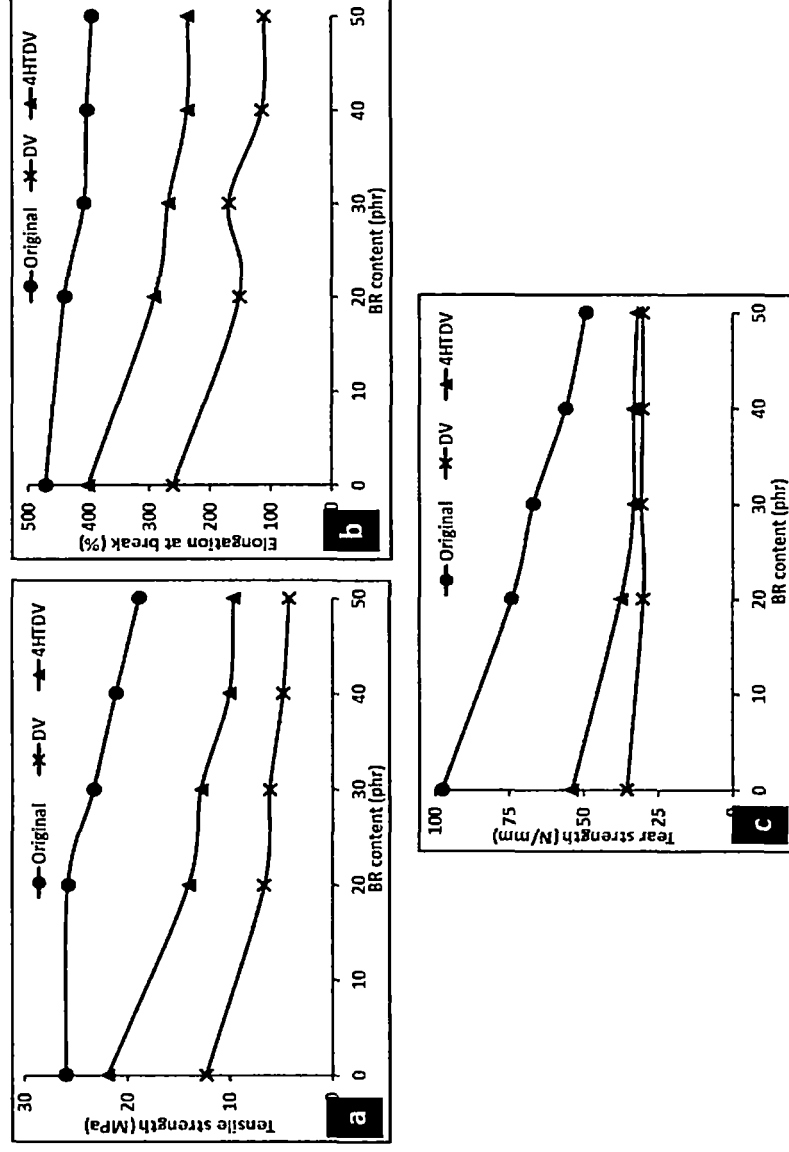
Figure 8.3 a: Tensile strength; **b:** elongation at break and **c:** tear strength of original and corresponding revulcanised samples

Table 8.6 Vulcanisate properties of CV cured original and revulcanised NR/BR blends

Vulcanisate	Tensile Strength (MPa)	Elongation at break (%)	M100 (MPa)	M200 (MPa)	M300 (MPa)	Tear strength (N/mm)
Virgin 100/0	26	472	4.8	9.8	15.7	97.8
100/0 DV	12.3	261	4.3	8.6	-	35.5
100/0 4HT DV	21.9	402	4	8	13.9	53.9
Virgin 80/20	25.8	441	5.3	10.7	17	74.3
80/20 DV	6.6	152	4.3	-	-	30
80/20 4HT DV	14	292	4.3	8.3	-	37.6
Virgin 70/30	23.3	409	5.1	10.6	16.7	66.9
70/30 DV	6.1	170	3.8	-	-	30.6
70/30 4HT DV	12.8	270	4.1	8.1	-	33.2
Virgin 60/40	21.1	404	4.7	9.5	15.2	56
60/40 DV	4.8	115	4.4	-	-	30
60/40 4HT DV	10	238	4	8	-	33.2
Virgin 50/50	18.8	395	4.4	8.7	13.8	49.2
50/50 DV	4.2	110	4	-	-	30.2
50/50 4HT DV	9.6	236	4.1	7.7	-	31.9

Generally, the mechanical performance of NR vulcanisate is much superior to BR vulcanisates and hence intermediate values were expected for the blends based on the blend ratio[9]. The tensile strength, elongation at break and tear strength of the virgin vulcanisates decreased with increase in BR content in the blend[11]. The reduction in tear strength with BR content was more prominent than the reduction of tensile strength and elongation at break.

Revulcanisate properties of the mechanically devulcanised samples were significantly inferior to the corresponding virgin vulcanisates. The

revulcanised tear strength of all the mechanically devulcanised samples was comparable while the tensile properties of the mechanically devulcanised virgin NR vulcanisate were significantly higher than the NR/BR blends.

In the case of mechanical devulcanisation, the revulcanisate of NR alone (100/0 DV) crossed the 200per cent modulus. On the other hand, 4HT assisted devulcanisation enabled all the devulcanised samples to attain 200per cent modulus. The tensile strength of the 4HT assisted devulcanised samples improved significantly compared with the corresponding mechanically devulcanised samples. The revulcanisate tensile strength of the 4HT assisted devulcanised samples were more than double the tensile strength of corresponding mechanically devulcanised sample. But, it can be observed that the absolute value of tensile strength dropped with the increase in BR content in the blend and the hike in tensile strength brought in by the action of 4HT became less relevant as the BR content increased. The elongation at break also followed similar trend. The positive influence of 4HT upon the tear strength of revulcanised NR vulcanisates significantly reduced even when 20 parts BR was incorporated and became marginal as the BR content increased.

Since the vulcanisate properties of the virgin vulcanisates are different, the analysis of the revulcanisate properties along with corresponding of per cent retention values might be more informative. The per cent retention of tensile strength, elongation at break and tear strength of the revulcanised samples are given in Table 8.7 and are graphically illustrated in Figure 8.4. Significant improvement in the percent retention of tensile strength and elongation at break were obtained when 4HT was used as a devulcanisation aid. The percent retention of tensile strength and elongation at break almost doubled in most of the cases upon 4HT assisted devulcanisation in comparison with mechanical devulcanisation. In the case

of tear strength, considerable improvement in per cent retention upon 4HT assisted devulcanisation occurred with NR vulcanisate alone. However for 80/20 NR/BR blend the increment observed was only 10per cent which minimized to almost 5 to 8 per cent for other blends. This is in contrary to the previous observations regarding the devulcanisation of NR vulcanisates that, the positive influence of 4HT assisted devulcanisation were prominently observed with the tear strength of the revulcanisates rather than on the tensile strength.

Table 8.7 Per cent retention of vulcanisate properties of CV cured NR/BR
blends after revulcanisation

Vulcanisate	Per cent retention (%)		
	Tensile Strength	EB	Tear strength
100/0DV	47.5	55.3	36.3
100/0 4HT DV	84.5	85.1	55.2
80/20 DV	25.4	34.5	40.4
80/20 4HT DV	54.5	66.2	50.6
70/30 DV	26.2	41.6	45.8
70/30 4HT DV	55.1	66.1	55.4
60/40 DV	22.9	28.5	53.5
60/40 4HT DV	47.6	59.0	59.2
50/50 DV	22.5	27.8	61.3
50/50 4HT DV	51.2	59.8	64.8

Figure 8.4 Per cent retention of **a**: tensile strength; **b**: elongation at break and **c**: tear strength of CV cured NR/BR blends after revulcanisation

8.3.2 Effect of BR content on devulcanisation of semi EV cured NR/BR blends

The results obtained from the devulcanisation studies on CV cured NR/BR blends indicates that, increasing amounts of BR content in an NR/BR blend significantly lowered the percent retention of vulcanisate properties. Hence, based on the observations with the devulcanisation of NR vulcanisates (chapter 5 and 6) that CV cured NR vulcanisates was associated with lower per cent devulcanisation than the corresponding semi EV and EV cured samples, the previous study was replicated with semi EV cured NR/BR blends.

8.3.2.1 Number of passes for devulcanisation

From the earlier observations, it is evident that the number of passes required for the devulcanisation of a vulcanisate varied with a number of factors. Also, the required number of passes through the tight nip to achieve the necessary level of devulcanisation is considerably lowered by the incorporation of stable free radical as a devulcanisation aid. The number of passes required for the devulcanisation of semi-EV cured NR/BR blends in the presence and absence of stable free radical is represented in Figure 8.5.

The required number of passes through the tight nip of the two roll mill for effective devulcanisation has dropped for semi EV cured NR vulcanisate in comparison with CV cured vulcanisate. Such a decrease is observed in the case of blends especially for blends with lower amounts of BR content when devulcanised with the assistance of 4HT. Though the number of passes was limited at 50numbers as in the previous case, the appearance of the devulcanised sample was improved in comparison with the devulcanisation of CV cured blends especially in the case of 80/20 and 70/30 blends. The lower number of passes required for the devulcanisation of semi-EV cured vulcanisates in comparison with corresponding CV cured

vulcanisates indicates the ease and/or effectiveness of devulcanisation of th
semi–EV cured vulcanisates over the corresponding CV cured vulcanisates.
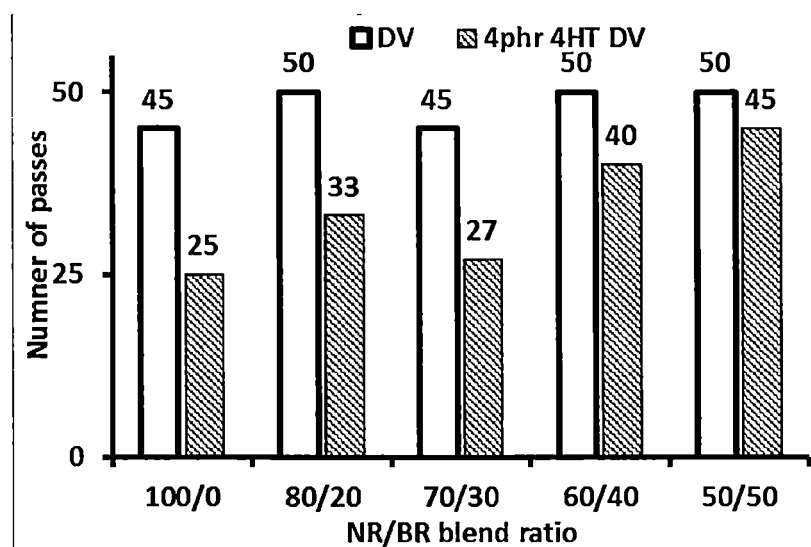
Figure 8.5 Required number of passes for the devulcanisation of semi-E
cured NR/BR blends

8.3.2.2 Residual crosslink density and per cent devulcanisation

The residual crosslink densities and per cent devulcanisation of th
devulcanised samples aregiven on Table 8.8. As mentioned previously, tl
mechanically devulcanised samples of semi-EV cured vulcanisates at low
BR contents formed sheets after 50passes which enabled the crosslir
density determination of those samples also. The crosslink density of tl
semi-EV cured virgin NR vulcanisate was lower than that of the blends as ;
the case of CV curing except that of the 70/30 blend of NR and BR. Tl
abnormally low crosslink density of virgin 70/30 blend might be due i
variation in curative dosage owing to some sort of experimental error. But,
can be observed that, the lowest residual crosslink density of tl
devulcanised samples was also associated with 70/30 blend both aft
mechanical and 4HT assisted devulcanisation. If these observations correla

with the revulcanisate properties also, the effect of crosslink density of the virgin vulcanisate would be an important topic for further investigation.

Table 8.8 Crosslink densities of the semi-EV cured original and devulcanised NR/BR blends with corresponding per cent devulcanisation

NR/BR blend ratio	Crosslink density x 10^4, mole/ cm^3			Per cent devulcanisation, %	
	Virgin	DV	4HT DV	DV	4HT DV
100/0	0.97	0.77	0.45	20.2	53.5
80/20	1.1	0.69	0.43	37.8	61.6
70/30	0.84	0.58	0.32	30.9	62
60/40	1.2	-	0.46	-	62
50/50	1.2	-	0.49	-	59.4

8.3.2.3 Cure characteristics

The cure characteristics of the virgin and devulcanised samples are given in Table 8.9 and the cure curves are given in Figure 8.6. The minimum torque of all the virgin vulcanisates was comparable while the maximum torque varied. The NR vulcanisate had the highest maximum torque and the 70/30 blend had the lowest maximum torque as expected from the crosslink density measurements while the other blends had intermediate maximum torques. The virgin NR vulcanisate had the lowest scorch safety while the blends had comparably higher scorch times.

The mechanically devulcanised samples followed similar trend as that of the virgin vulcanisate, except for the lower scorch time and higher minimum torque of devulcanised samples than the corresponding virgin vulcanisates. The minimum torque of the virgin blends increased marginally as the BR content in the blend increased with a corresponding increase in the maximum torque and total torque except for the 70/30 blend with a low maximum torque owing to its low crosslink density.

Table 8.9 Cure characteristics of original and corresponding devulcanised of semi-EV cured NR/BR blends

Vulcanisate/ NR/BR Blend Ratio	Torque (dNm)			Scorch Time, min	Cure time (min)
	Minimum, M_L	Maximum, M_H	M_H-M_L		
Virgin 100/0	1.5	18.9	17.4	2.1	5.3
100/0 DV	4.5	14.8	10.3	0.8	5.1
100/0 4HTDV	2.2	14.1	11.9	1.1	4.3
Virgin 80/20	1.4	14.5	13.1	2.8	5.8
80/20 DV	5	15.1	10.1	1.4	5.9
80/20 4HTDV	2.5	12.7	10.2	1.4	4.8
Virgin 70/30	1.6	11.7	10.1	3.5	6.8
70/30 DV	3.4	13.6	10.2	1.4	6.1
70/30 4HTDV	1.9	13	11.1	1.5	5.8
Virgin 60/40	1.9	15	13.1	3.3	6.5
60/40 DV	5.5	15.5	10	1.6	6.2
60/40 4HTDV	3.2	14.7	11.5	1.4	5.4
Virgin 50/50	2.1	16	13.9	3.4	6.6
50/50 DV	5.9	16.7	10.8	1.7	6.6
50/50 4HTDV	3.6	15.5	11.9	1.4	5.5

The minimum torque lowered when devulcanisation was carried out with the assistance of 4HT especially for blends with low BR content. The maximum torque of the 4HT assisted devulcanised samples were lower than the corresponding mechanically devulcanised samples thereby imparting comparable total torque to all the devulcanised samples. The scorch time and cure time of the devulcanised samples were lower than the corresponding virgin vulcanisates and the value increased with increase in BR content in the blend.
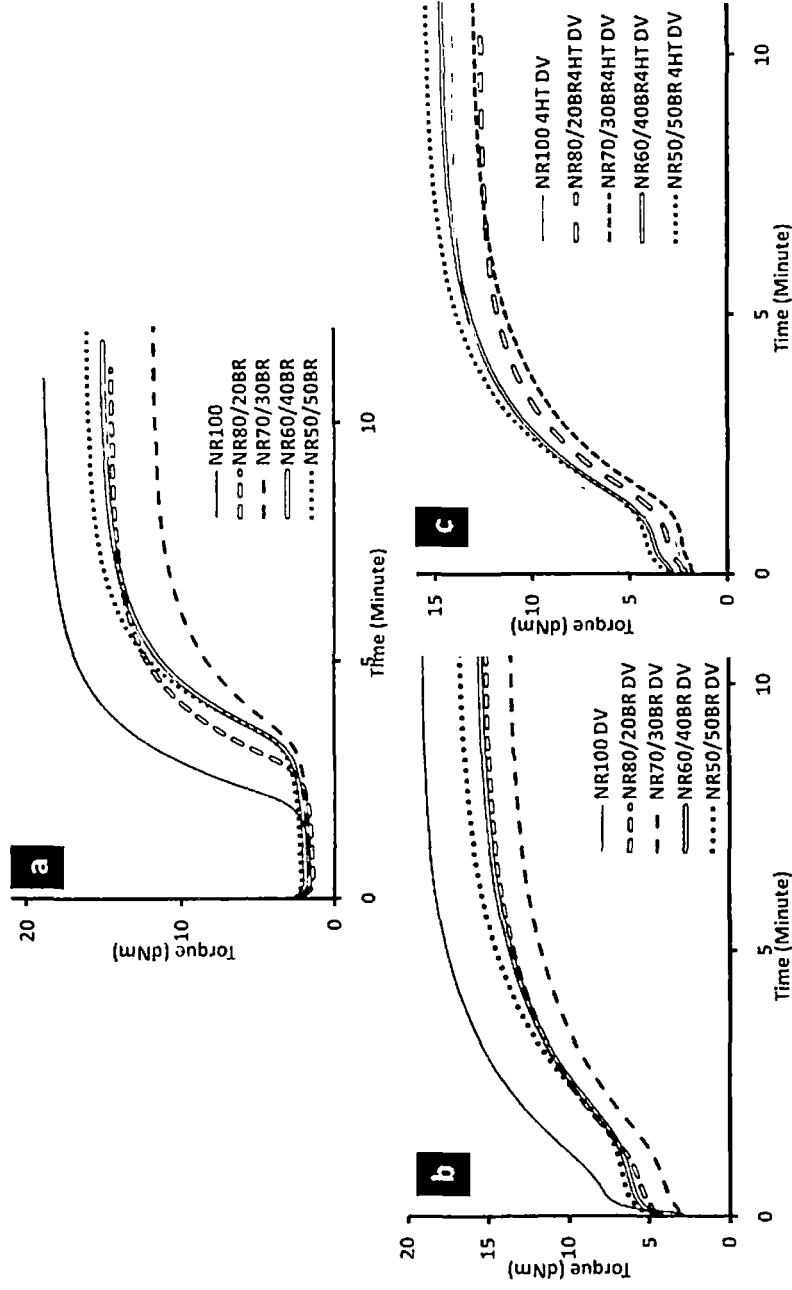
Figure 8.6 Cure curves of **a**: semi-EV cured original and the corresponding **b**: mechanically and **c**: 4HT assisted devulcanised NR/BR blends

8.3.2.4 Revulcanisate properties

The revulcanisate properties of the devulcanised samples in comparison with the corresponding semi-EV cured virgin rubber properties are given in Table 8.10 while the graphical illustration is given in Figure 8.7. The tensile strength of the virgin NR vulcanisate is the highest whereas the 70/30 blend of NR and BR had the highest values of elongation at break and tear strength.

Table 8.10 Mechanical properties of semi-EV cured original and revulcanised NR/BR blends

Vulcanisate	Tensile Strength (MPa)	Elongation at break (%)	M100 (MPa)	M200 (MPa)	M300 (MPa)	Tear strength (N/mm)
Virgin 100/0	25.4	547	2.9	6.2	11.1	108.5
100/0 DV	11	310	2.5	5.4	9.7	47.7
100/0 4HTDV	19.4	454	3	5.4	9.7	67.2
Virgin 80/20	23.5	556	3.0	6.4	10.8	117.8
80/20 DV	12.7	311	3.5	6.8	11.9	41.2
80/20 4HTDV	20.2	486	2.7	5	9	51.9
Virgin 70/30	21.7	574	2.4	5	8.7	124.6
70/30 DV	15.7	385	3.0	5.7	10.4	38
70/30 4HTDV	22.5	495	2.9	5.4	9.8	54.7
Virgin 60/40	21.6	524	2.9	6.2	10.6	77.2
60/40 DV	9.8	260	2.8	5.6	-	35.7
60/40 4HTDV	13.4	361	2.9	5.4	9.9	39.3
Virgin 50/50	21.3	546	2.8	6	10.2	62.7
50/50 DV	10.4	276	2.6	6	-	31
50/50 4HTDV	13.6	341	3.1	5.9	11	34.2
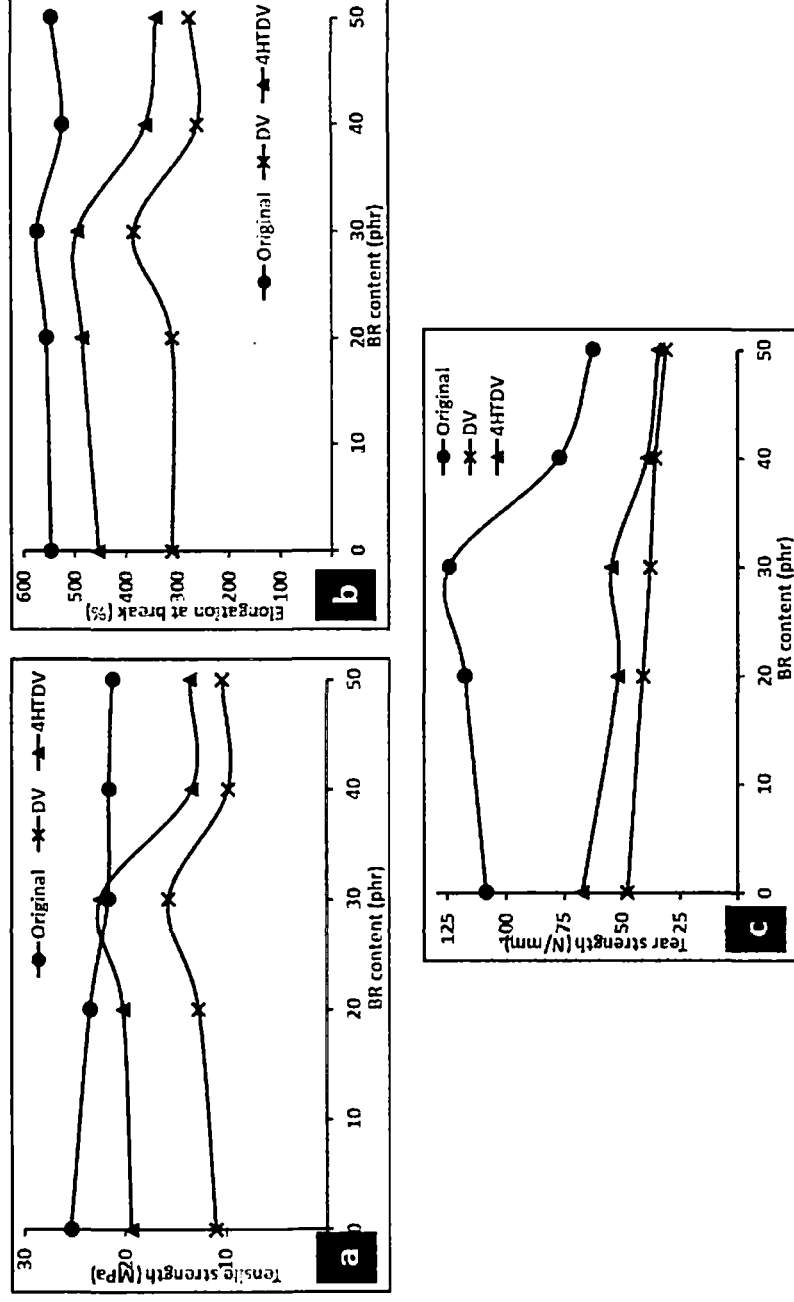
Figure 8.7 a: Tensile strength; **b:** elongation at break and **c:** tear strength of semi EV cured NR/BR blends and corresponding revulcanisates

The revulcanisate tensile properties of the 70/30 blends are the highest owing to the highest percent devulcanisation associated with it. But, the associated tear strengths were lower than that of the revulcanised NR vulcanisate. At the same time, 70/30 blends of NR and BR had the highest revulcanisate tear strength along with 80/20 blend.

The per cent retention of properties after revulcanisation is given in Table 8.11 and is represented in Figure 8.8. The lowest percent retention was associated with tear strength for all revulcanised samples. 80/20 blend of NR and BR had higher per cent retention of tensile properties than devulcanised NR vulcanisate corresponding to its higher percent devulcanisation. The 70/30 blend also had higher percent retention of tensile properties with respect to the highest percent devulcanisation attained due to the low crosslink density of the original sample.

Table 8.11 Per cent retention of vulcanisate properties of semi-EV cured NR/BR blends after revulcanisation

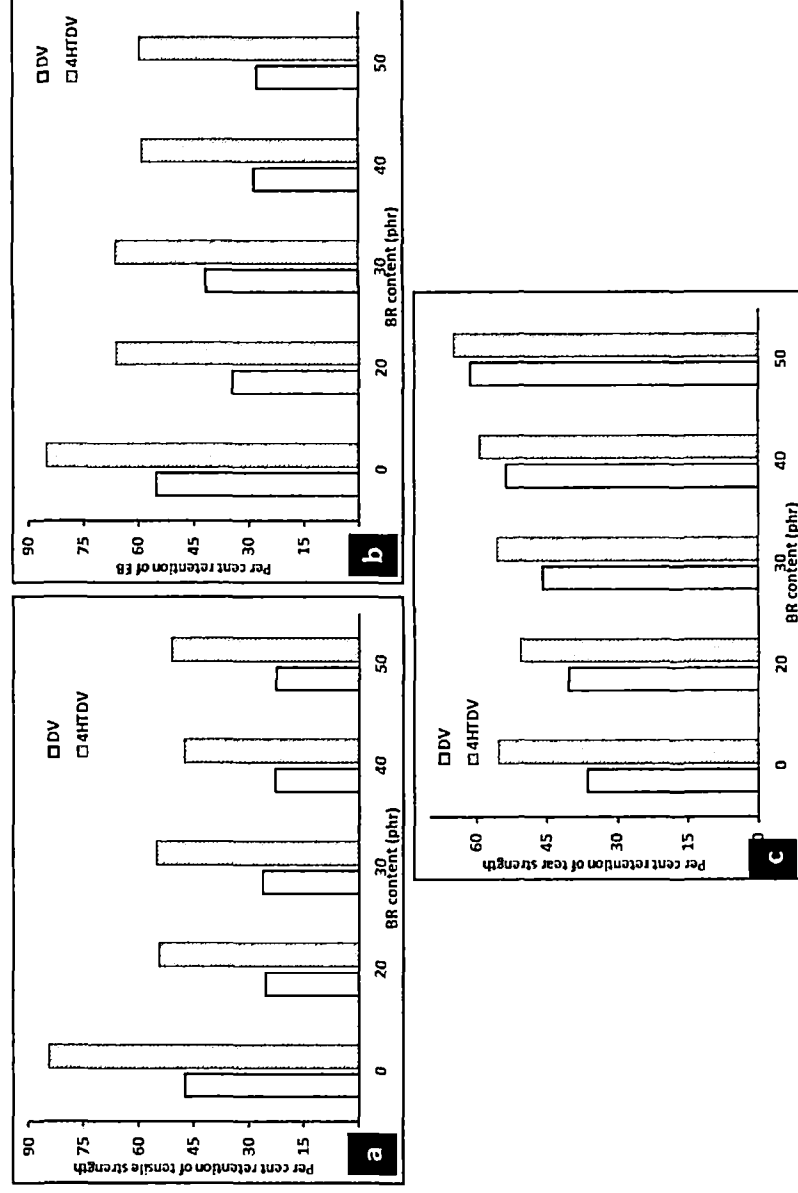| Vulcanisate	Per cent retention (%)		
	Tensile Strength	Elongation at break	Tear strength
100/0DV	43.1	56.7	44
100/0 4HT DV	76.1	82.9	61.9
80/20 DV	54	55.9	35
80/20 4HT DV	85.9	87.3	44
70/30 DV	72.5	67	30.5
70/30 4HT DV	103.9	86.2	43.9
60/40 DV	40.2	46.1	46.2
60/40 4HT DV	62	68.8	50.8
50/50 DV	48.9	50.6	49.5
50/50 4HT DV	63.6	62.5	54.6
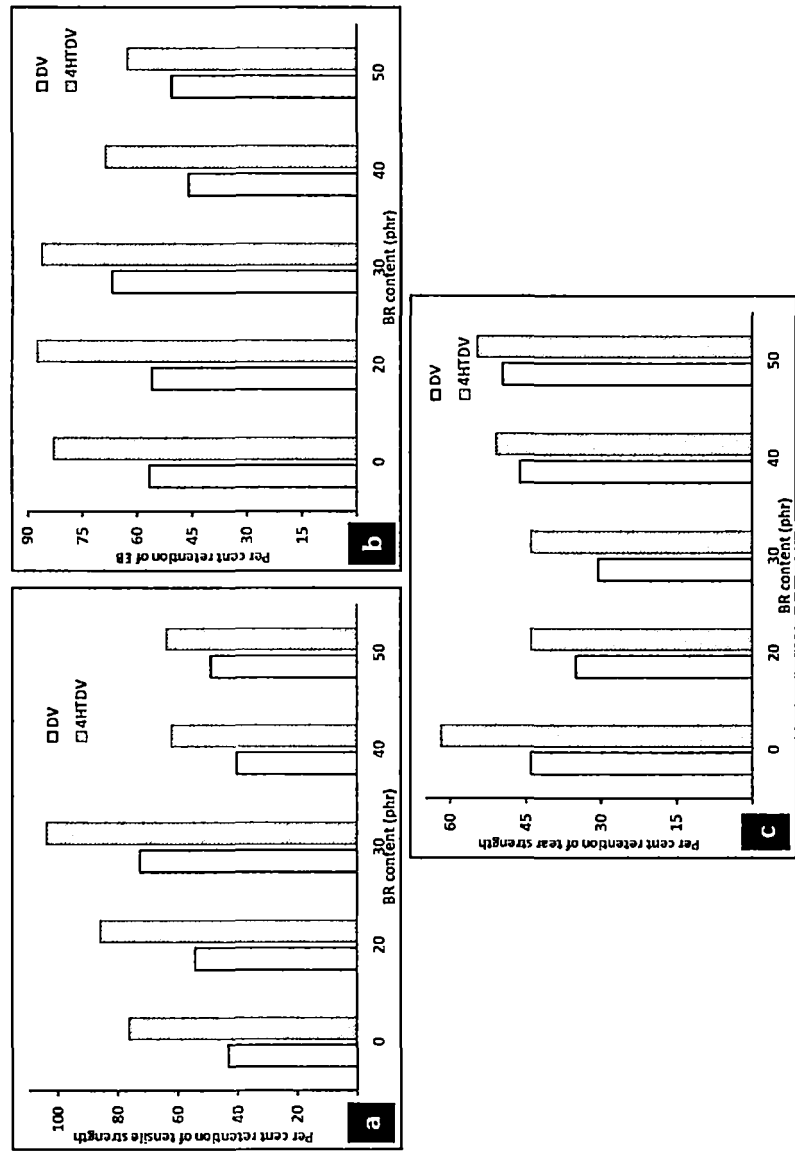
Figure 8.8 Per cent retention of **a:** tensile strength; **b:** elongation at break and **c:** tear strength of semi-EV cured NR/BR blends after revulcanisation

Per cent retention of tear strength after mechanical devulcanisation were the highest for 50/50 blend (49.5per cent) and that after 4HT assisted devulcanisation was the highest for NR vulcanisate (61.9per cent). But, this higher per cent retention of tear strength associated with the 50/50 blend is due to the lowest tear strength of the virgin 50/50 blend vulcanisate. Hence, irrespective of the high per cent retention, the absolute value of revulcanisate tear strength after mechanical devulcanisation of 50/50 blend was significantly lower than revulcanised NR vulcanisate. In all cases, the percent retention of revulcanisate properties increased significantly by incorporating stable free radical as a devulcanisation aid.

8.3.3 Effect of cure system used for preparation of original sample on revulcanisate properties of NR/BR blends

The revulcanisate tensile strengths, elongation at break and tear strength of the NR/BR blends prepared from the devulcanisation of CV and semi EV cured original samples in comparison with the corresponding original properties are listed in Table 8.12, 8.13 and 8.14 respectively.

Table 8.12. Comparison of tensile strength of original and corresponding revulcanisates prepared from CV and semi EV cured NR/BR blends

NR/BR blend ratio	Original, MPa		DV, MPa		4HTDV, MPa	
	CV	Semi EV	CV	Semi EV	CV	Semi EV
100/0	26	25.4	12.3	11	21.9	19.4
80/20	25.8	23.5	6.6	12.7	14	20.2
70/30	23.3	21.7	6.1	15.7	12.8	22.5
60/40	21.1	21.6	4.8	9.8	10	13.4
50/50	18.8	21.3	4.2	10.4	9.6	13.6

It can be observed that, the tensile strengths of the virgin vulcanisates were comparable at same blend ratio, irrespective of the cure

system used. Also, the tensile strength of the original samples reduced with increase of BR content in the blend. The revulcanisate tensile strengths after 4HT assisted devulcanisation was higher than the corresponding mechanically devulcanised sample. For revulcanisate prepared from devulcanisation of NR vulcanisate, type of cure system had marginal influence while in the case of blends, the semi EV cured blends gave higher revulcanisate properties. The revulcanisate tensile strength of the mechanically devulcanised semi EV samples were comparable with that of the corresponding 4HT assisted devulcanised CV samples.

Table 8.13. Comparison of elongation at break of original and corresponding revulcanisates prepared from CV and semi EV cured NR/BR blends

NR/BR	Original, %		DV, %		4HTDV, %	
blend ratio	CV	Semi EV	CV	Semi EV	CV	Semi EV
100/0	472	547	261	310	402	454
80/20	441	556	152	311	292	486
70/30	409	574	170	385	270	495
60/40	404	524	115	260	238	361
50/50	395	546	110	276	236	341

The elongation at break of the semi EV cured original samples was significantly higher than the corresponding vulcanisate prepared by CV curing. The elongation at break marginally increased for semi EV samples (provided the higher EB of semi EV cured 70/30 blend accounts for its lower crosslink density as discussed) while that marginally decreased in the case of CV cured vulcanisates with increase in BR content. The revulcanisate EB of the 4HT assisted devulcanised CV cured blends were comparable with that of the mechanically devulcanised semi EV samples with the exception that the revulcanisate EB of mechanically devulcanised

semi EV cured 70/30 blend was significantly higher than the corresponding revulcanisate from 4HT assisted devulcanisation of CV cured 70/30 blend.

Table 8.14. Comparison of tear strength of original and corresponding revulcanisates prepared from CV and semi EV cured NR/BR blends

NR/BR blend ratio	Original, N/mm		DV, N/mm		4HTDV, N/mm	
	CV	Semi EV	CV	Semi EV	CV	Semi EV
100/0	97.8	108.5	35.5	47.7	53.9	67.2
80/20	74.3	117.8	30	41.2	37.6	51.9
70/30	66.9	124.6	30.6	38	33.2	54.7
60/40	56	77.2	30	35.7	33.2	39.3
50/50	49.2	62.7	30.2	31	31.9	34.2

Tear strength of the semi EV cured original vulcanisates increased with increase in BR content upto 70/30 and then decreased, while that of the CV cured samples continuously decreased with increase in BR content. The improvement in revulcanisate tear strength brought in by the incorporation of 4HT during devulcanisation was comparable for both CV and semi EV cured samples and was significantly lower than that observed in the case of tensile strength and elongation at break. The revulcanisate tear strength of the mechanically devulcanised blends prepared from semi EV samples were comparable with the revulcanisates of 4HT assisted devulcanised corresponding samples prepared from CV cured blends. The revulcanisate tear strengths of all the devulcanised samples were comparable at higher NR/BR blend ratios of 60/40 and 50/50. All these observations suggest the role of cure system used for the vulcanisation of original blends upon their revulcanisate properties similar to that observed in the case of NR vulcanisates in chapter 5 and chapter6.

8.3.4 Effect of crosslink density of original sample on the devulcanisation of NR/BR (50/50) blends

The higher per cent retention of vulcanisate properties obtained for 70/30 blend described in the previous section might be attributed to the low crosslink density of the original blend. Hence, the role ofcrosslink density of the original sample upon the revulcanisate properties of NR/BR blends was investigated using 50/50 blends. Here, the accelerator sulphur ratio was kept constant at 0.93 (semi EV) while the dosage of curatives was varied to obtain blends with different crosslink densities.

8.3.4.1 Number of passes for devulcanisation

The behavior of the vulcanisates during mechanical shearing in the tight nip of the two roll mill varied considerably between the various vulcanisates corresponding to the changes in their respective crosslink densities. As already observed in the previous section, the devulcanisation of 50/50 blends of NR and BR were difficult especially when the process was mechanical shearing alone. Incorporation of 4phr 4Hydroxy TEMPO as devulcanisation aid significantly improved the devulcanisation behavior of the vulcanisates. The variation in required number of passes through the tight nip for the devulcanisation for devulcanisation of 50/50 blends of NR and BR with different CLDs are illustrated in Figure 8.9

The mechanical devulcanisation of all samples required 50 numbers of passes in the two roll mill while the use of 4HT as devulcanisation aid lowered the number of passes. The mechanical devulcanisation time of vulcanisate I (Table 8.3) was halved and a smooth sheet was obtained when devulcanised with the addition of 4HT. For samples II, III and IV the number of passes reduced and the quality of devulcanised sheet improved with the incorporation of 4HT. However, the required number of passes increased with increase in crosslink density of the original sample.
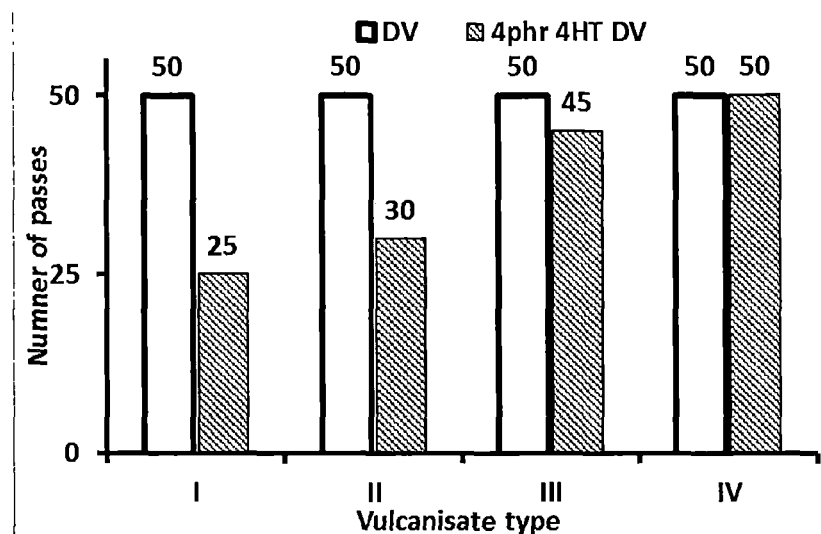
Figure 8.9 Number of passes required devulcanisation of 50/50 NR/BR blends with different CLD

8.3.4.2 Residual crosslink density of devulcanised rubber

The crosslink densities of the virgin 50/50 blend vulcanisates with corresponding residual crosslink densities after 4HT assisted devulcanisation and respective per cent devulcanisation are given in Table 8.15.

Table 8.15 Crosslink densities of the original and 4HT assisted devulcanised 50/50 NR/BR blends with corresponding per cent devulcanisation

Vulcanisate	CBS	Sulphur	Crosslink density x 10^4 (mole/cm^3)		Per cent devulcanisation (%)
			Virgin	4HT DV	
I	0.65	0.7	0.5	0.21	59
II	0.92	1	0.98	0.35	63.7
III	1.2	1.3	1.2	0.44	63.6
IV	1.38	1.5	1.5	0.62	58.9

NR/BR = 50/50 ; (CBS/S = 0.92)

The table shows the increase in crosslink density of original samples with the increase in curative amount. The residual crosslink densities of the devulcanised samples followed similar trend as that of the crosslink density variation observed with the original samples. Thus, comparable per cent devulcanisation for all the devulcanised samples was preserved on devulcanisation. The residual crosslink density of the devulcanised vulcanisate I was the lowest and that of the vulcanisate IV was the highest while that of the others lied in between. The per cent devulcanisation of all the devulcanised samples was about 60per cent. The comparable per cent devulcanisation of the vulcanisates with different initial crosslink densities but common curative ratio might be due to the common per cent distribution of crosslinks present in these samples irrespective of the variations in their absolute numbers. In such vulcanisates with a common crosslink distribution pattern, the distribution of shear stress during mechanical devulcanisation would be similar rendering similar pattern of bond scission. Such a uniformity of bond scission in these vulcanisates might be contributing towards the common per cent devulcanisation of these samples irrespective of the variations in their initial crosslink density and the residual crosslink density of the devulcanised samples. Similar observation was made in another study on the mechanical devulcanisation of NR vulcanisates also[11].

8.3.4.3 Cure characteristics

The cure characteristics of the virgin and the corresponding devulcanised samples are given in Table 8.16. The corresponding cure curves outlined in Figure 8.10 clearly indicates the increase in the torque of the samples with increase in the curative dose. The minimum torque of all the vulcanisates remained the same while the maximum torque increased

from vulcanisate I to vulcanisate IV with correspondin increase in total torque. For devulcanised samples, both the minimum torque and the maximum torque increased with increasing curative dosage resulting in comparable total torque.

Table 8.16 Cure characteristics of original and corresponding devulcanised samples of semi-EV cured 50/50 NR/BR blends

| Vulcanisate | Torque (dNm) | | M_H-M_L | Scorch Time, min | Cure time (min) |
	Minimum, M_L	Maximum, M_H			
I	2.1	8.5	6.4	5.5	11.8
I DV	2.4	13.9	11.5	1.7	7.3
I 4HTDV	1.7	13.8	12.1	2	6.5
II	2.1	12.9	10.8	4	8.1
II DV	4.3	15.8	11.5	1.5	6.8
II 4HTDV	2.8	14.5	11.7	1.4	5.4
III	2	16.2	14.2	3.3	6.5
III DV	5.6	16.6	11	1.5	6.6
III 4HTDV	3.9	15.5	11.6	1.2	5.1
IV	2.2	19.1	16.1	3	6.4
IV DV	6.9	18	11.1	1.4	6
IV 4HTDV	5	16.9	11.9	1.1	5.3

The variation in the minimum torque of the 4HT assisted devulcanised samples corresponded to the residual crosslink densities of the devulcanised samples. Just like in the previous cases, the minimum torque of the 4HT assisted devulcanised samples were lower than the corresponding values for mechanically devulcanised samples. The cure time and scorch time of the virgin vulcanisate decreased with the increase in curative amount. A similar trend is observed for the devulcanisates also but the decrease is marginal compared with that of the original vulcanisates.
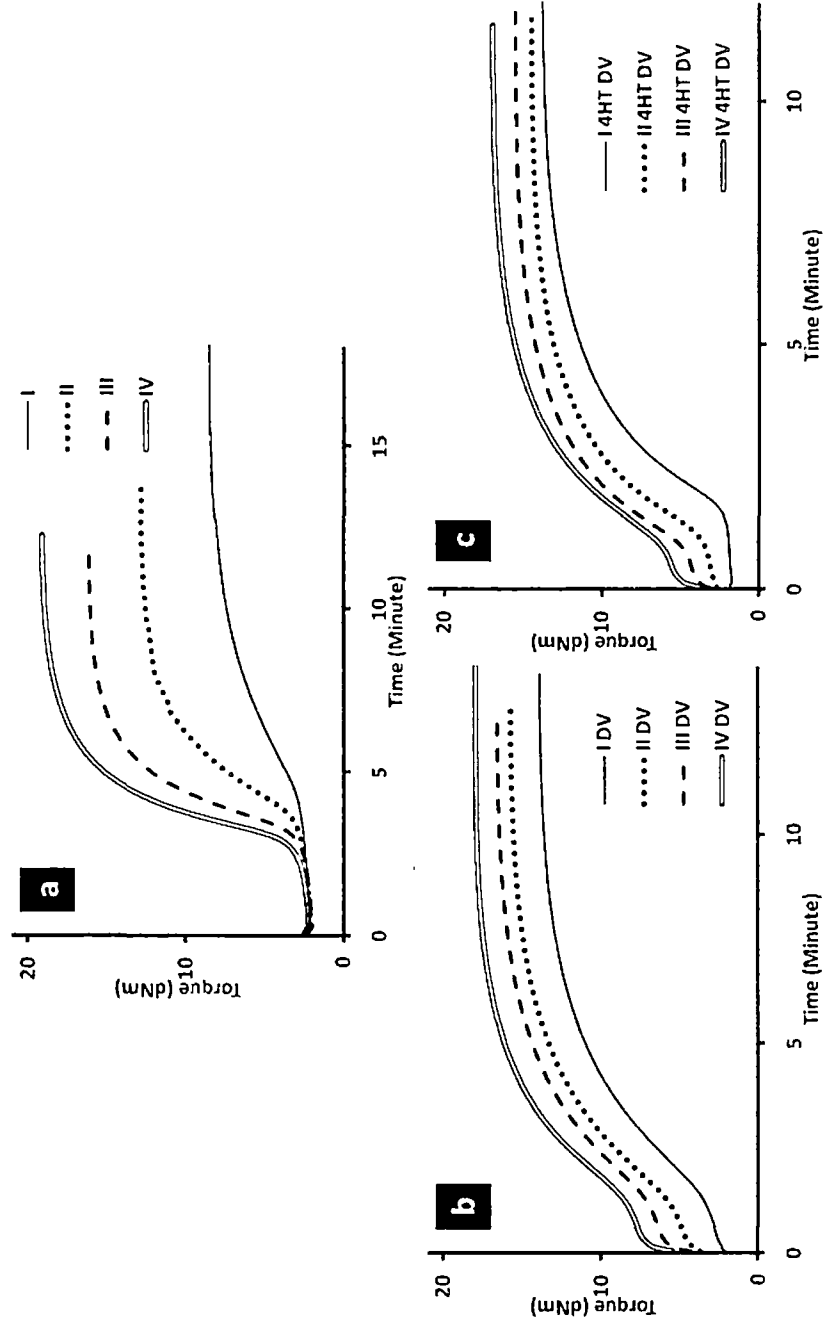
Figure 8.10 Cure curves of the **a:** original; **b:** mechanically and **c:** 4HT assisted devulcanised 50/50 NR/BR blends with different crosslink densities

8.3.4.4 Revulcanisate properties

The purpose of varying the crosslink density of the original sample was to study the effect of the same on devulcanisation efficiency and the resultant revulcanisate properties. The effect of crosslink density (or amount of CBS/sulphur) on the vulcanisate properties of the original sample and that of the corresponding devulcanisate is given in Table 8.17 and in Figure 8.11

Table 8.17 Vulcanisate properties of virgin and revulcanised 50/50 NR/BRblends

Vulcanisate	Tensile Strength (MPa)	Elongation at break (%)	M100 (MPa)	M200 (MPa)	M300 (MPa)	Tear strength (N/mm)
I	13.8	605	1.3	3	5.5	70.3
I DV	12.1	305	2.4	5.9	11	40.4
I 4HTDV	16.3	415	2.1	4.9	9.6	45.1
II	17.3	523	2.1	4.9	8.6	74.1
II DV	6.7	225	2.2	5.4	--	27.4
II 4HTDV	13.2	380	2	4.5	8.7	37.6
III	20.6	546	2.6	5.8	9.7	65.2
III DV	6.3	228	2.2	5	--	28.8
III 4HTDV	9	264	2.4	5.6	--	35.1
IV	16.9	429	3.2	6.9	11.2	52.9
IV DV	5.7	202	2.4	5.3	--	25.7
IV 4HTDV	5.8	209	2.4	5.1	--	28.4

The tensile strength and tear strength of the virgin vulcanisates follow a pattern in which the properties are low at very low and very high curative loadings and approaches the maximum value at intermediate curative loadings. The modulus values increased linearly with increasing curative dosage and elongation at break decreased.
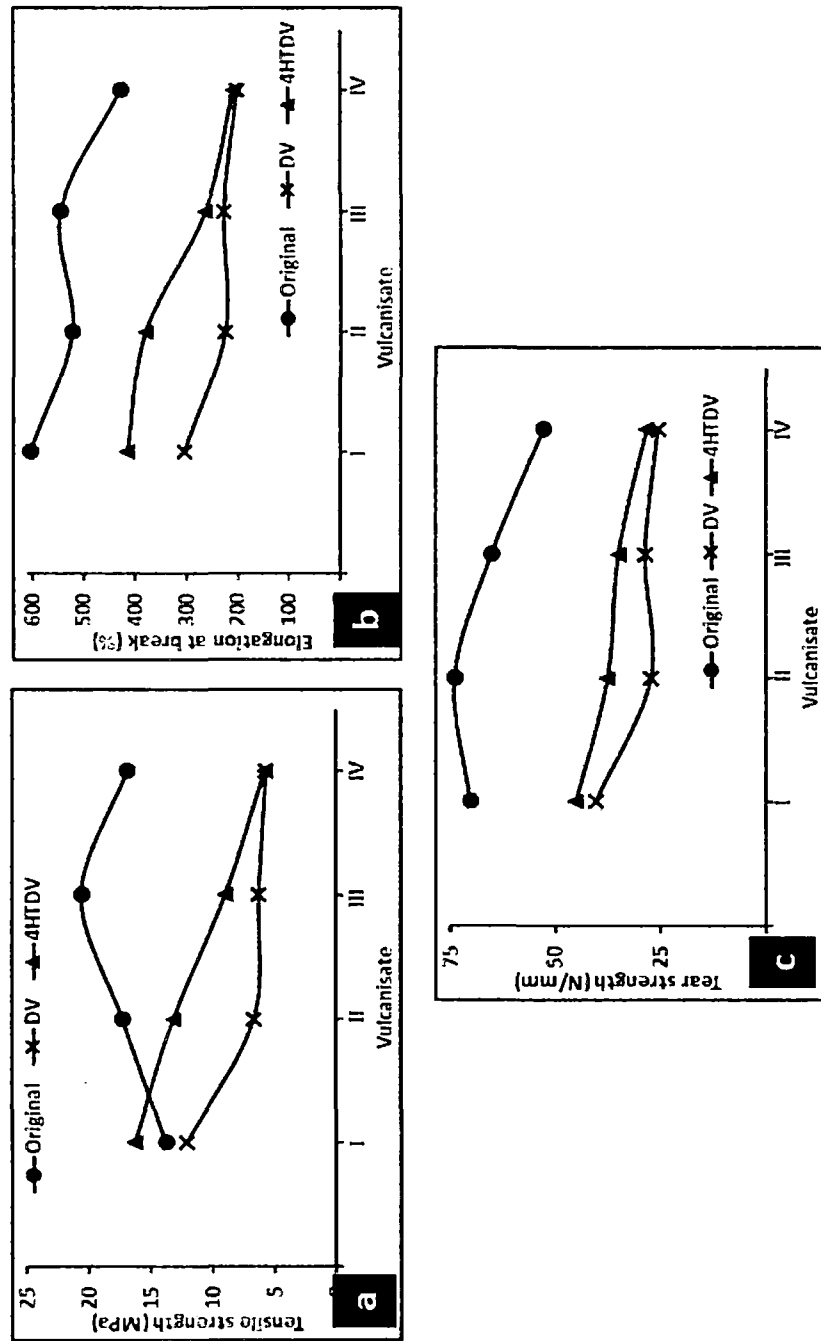
Figure 8.11 Effect of crosslink density of original sample on revulcanisate properties of 50/50 NR/BR blends

In the case of revulcanised samples, the modulus values remained comparable, while all other properties decreased as the crosslink density/curative dosage of corresponding original vulcanisates increased. On revulcanisation, the 4HT assisted devulcanised samples gave higher values of revulcanisate properties in all cases. But, as the crosslink density of the original vulcanisate increased with increase in curative dosage, the positive impact of stable free radical upon the revulcanisate properties were detrimentally affected and become marginal. This can be observed as the comparable and very low revulcanisate properties of both mechanically and 4HT assisted devulcanised samples prepared from vulcanisate IV.

The observations made from the vulcanisate properties are further illustrated in the per cent retention of vulcanisate properties (Figure 8.12 and Table 8.18).

Table 8.18 Per cent retention of vulcanisate properties 50/50 NR/BR blends after revulcanisation

Vulcanisate	Per cent retention (%)		
	Tensile Strength	Elongation at break	Tear strength
I DV	87.7	50.5	57.5
I 4HT DV	118.3	68.7	64.2
II DV	47.9	46.1	36.9
II 4HT DV	79.6	70.3	50.8
III DV	38.9	44	41.5
III 4HT DV	60.8	66	50.6
IV DV	32	47	48.5
IV 4HT DV	34.4	53.6	53.6
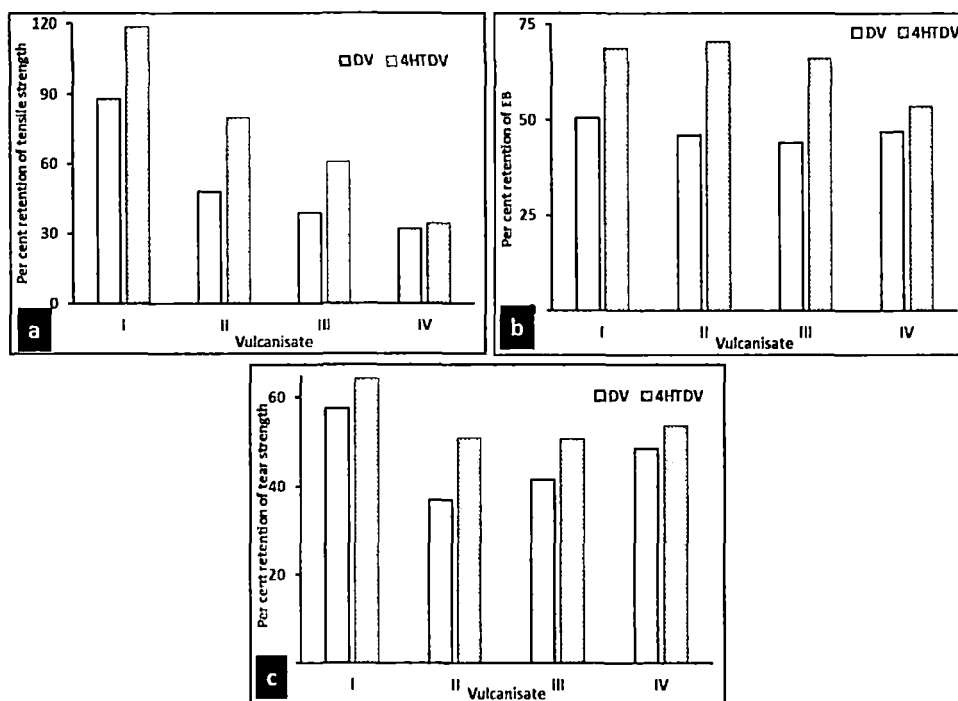
Figure 8.12 Per cent retention of **a:** tensile strength **b:** elongation at break and **c:** tear strength of 50/50 NR/BR blends

In the case of revulcanisate tensile strength of vulcanisate I, the per cent retention of tensile strength is higher than that of the elongation at break and tear strength. The low per cent retention of elongation at break might be due to the higher elongation at break of the virgin vulcanisate I owing to its very low crosslink density. But, after revulcanisation, the crosslink density increased thereby restraining the per cent retention of elongation at break though the tensile strengths were comparable.

The per cent retention of tensile strength and elongation at break of the rvulcanisates reduces as the crosslink density of the virgin sample increases. The low per cent retention of tear strength of the revulcanised

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samples in comparison with that of the tensile strength is a common observation as seen in previous cases also. The higher per cent retention of tear strength associated with revulcanisates of virgin vulcanisate III and IV could be attributed to the low of absolute value of tear strength associated with these virgin vulcanisates.

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Chapter 9

Devulcanisation of Commercial Tyre Tread Buffings

9.1 INTRODUCTION

The various aspects of mechanical, thermo-mechanical and mechano-chemical devulcanisation of ground tyre rubber (GTR) produced from used rubbers and tyre tread buffings were extensively carried out by many researchers. Formela *et al* investigated the possibility of devulcanisation of GTR by a continuous thermo-mechanical process in a twin screw extruder[1] and obtained comparable results with commercial reclaim. Devulcanisation of GTR under the application of high-energy ball milling was also reported[2,3]. Mechano-chemical devulcanisation of old tyre powder at high temperatures using a Banbury mixer and a Brabender[4], devulcanisation of GTR from passenger car tyres swelled in oil containing devulcanisation aids using an internal mixer[5], mechano-chemical devulcanisation of GRT using a laboratory two roll mill[6,7,8], devulcanisation of rubber crumb from recycled tyres employing super critical carbon-di-oxide in a twin screw extruder[9], incorporation of devulcanised rubber waste from end-of–life tyres produced by continuous shear reaction technology[10] *etc.* are reported. Incorporation of chemically treated buffing dust in new compounds[11], devulcanisation of GRT by ultrasound were also found in literature[12, 13, 14].

The previous chapters have been dealing with the devulcanisation of samples with known composition and properties in a laboratory two roll mill and the effect of stable free radical upon the devulcanisation efficiency of the same. This chapter deals with the devulcanisation of commercially available tyre tread buffing with and without the assistance of stable free radical 4-Hydroxy TEMPO. This chapter addresses the practical viability of

the novel devulcanisation process assisted by stable free radical in real world scenario. The optimization of devulcanisation parameters followed by results of devulcanisation of commercial tyre buffing with and without the assistance of stable free radical and the incorporation of the same in a tread formulation were presented in this chapter. The chapter also presents the factory scale devulcanisation trials of the buffing dust.

9.2 EXPERIMENTAL

The commercial buffing dust supplied by M/s MIDAS Mileage Pvt. LTD, Kerala, India and locally available ground tyre rubber (GTR) were characterized by thermogravimetric analysis. The composition of the buffing dust sample and GTR are given in Table 2.1.

9.2.1 Optimization of parameters

The initial optimization of required number of passes through the tight nip for devulcanisation, minimum amount of virgin NR to be blended with 100g of devulcanised rubber for ease of handling during further processing and the curative dosage during revulcanisation were conducted as described in chapter 2.

9.2.2 Effect of 4HT assisted devulcanisation

Further, the effect of 2phr 4HT used as a devulcanisation aid was analyzed by comparative study of required number of passes through the tight nip for devulcanisation, revulcanisate properties and residual crosslink densities of the devulcanised buffing dust. The revulcanisation of devulcanised samples were carried out using the previously optimized revulcanisation formulation after blending 100g devulcanised rubber with 10g virgin NR.

9.2.3 Blends of NR and devulcanised buffing dust

The buffing dust devulcanised mechanically and with the assistance of 4HT was blended with virgin rubber in different ratios and the vulcanisate properties of the blends were evaluated. The 95/5, 90/10, 85/15, 80/20 and 75/25 blends of virgin rubber and devulcanised rubber (DVR) were prepared with a formulation similar to the original formulation used for the preparation of pre-cured tread from which the buffing dust is prepared.

Table 9.1 Formulation used for incorporation of devulcanised buffing dust in tread compound

Ingre-dients (g)	Blend ratio									
	95/5		90/10		85/15		80/20		75/25	
	DV	4HT DV	DV	4HT DV	DV	4HT DV	DV	4HT DV	DV	4HT DV
DVR	9	9.1	17.9	18.3	26.9	27.4	35.8	36.5	44.8	45.7
NR	66.5		63		59.5		56		52.5	
BR	28.5		27		25.5		24		22.5	
HAF	52.3		49.5		46.8		44		41.3	

Common ingredients (phr): Oil – 12; Antioxidant - 3; Zinc oxide – 4; Stearic acid – 2; Sulphur – 2; TBBS - 1

The blending procedure described in chapter 2 was followed. The amount of devulcanised rubber in the blend was determined in such a way that, for the 95/5 blend, 95g virgin rubber and that amount of devulcanised rubber to provide a rubber hydrocarbon content (54.8per cent) of 5g were blended. The amount of carbon black in the blend were adjusted in such a way that, the amount of carbon black present in the devulcanised rubber (30.13per cent) plus that added during the compounding satisfied the amount of carbon black required according to the formulation (*i.e.* Filler correction was made).

9.2.4 Factory scale trial of 4HT assisted devulcanisation

Based on the positive results of 4HT assisted devulcanisation observed from several lab sacle trials, factory scale trial of 4HT assisted devulcanisation of rubber was conducted using buffing dust samples with two different composition supplied by Midas Mileage Private Limited, Kottayam, Kerala, India. The composition of buffing dust samples used for factory scale trials determined by TG analysis is given in Table 9.2.

Table 9.2 Composition of buffing dust used for factory scale evaluation of 4HT assisted devulcanisation determined by TGA

Buffing dust	Components		Per cent	Phr
Composition I	Polymer	NR	42	70
		BR	18	30
	Carbon black		30	50
	Acetone extractable		4	6.7
	Ash		6	10
Composition II	Polymer	NR	36	60
		BR	24	40
	Carbon black		30	50
	Acetone extractable		4	6
	Ash		6	10

Devulcanisation of the larger volumes of two buffing dust samples were carried out both mechanically and with the assistance of 4HT (1phr, 2phr and 4phr) using a two-roll mixing mill of size 105cm x 40cm and friction ration 1:1.25. The devulcanised samples are revulcanised using the optimized revulcanisation formulation (Table 2.4) after blending with10g virgin NR per100g devulcanised rubber. The revulcanisate properties were then compared with the revulcanisate properties obtained by the lab-scale devulcanisation of the corresponding samples.

9.3 RESULTS AND DISCUSSION

9.3.1 Optimization of parameters

9.3.1.1 Curative dosage for revulcanisation

The dosage of curatives required for the revulcanisation of devulcanised buffing dust was optimized based on the cure characteristics and tensile properties of the revulcanised samples. The cure characteristics of the revulcanised samples obtained from Monsanto rheometer are given in Table 9.3 and the corresponding cure curves in Figure 9.1. It can be observed that, the maximum torque of the revulcanisate varied considerably with the variation in curative dosage. The minimum torque of all the vulcanisates were comparable owing to the same level of devulcanisation attained by them. Hence, the total torque increased with increase in curative dosage.
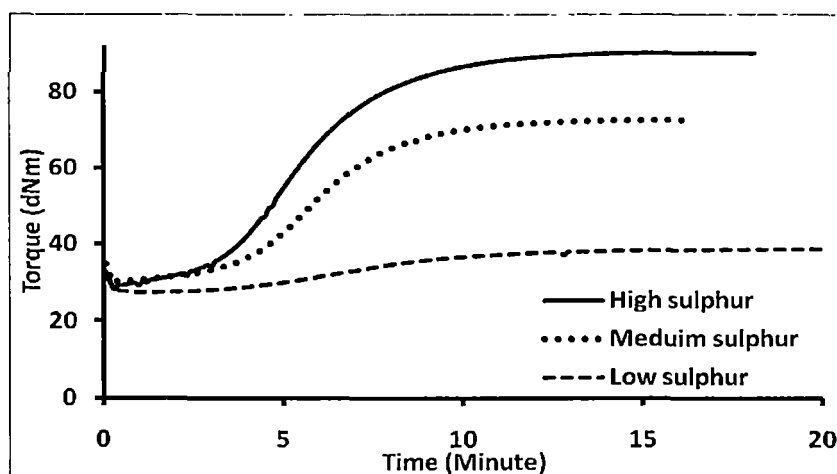
Figure 9.1 Cure curves during revulcanisation of buffing dust with varying sulphur concentration

Table 9.3 Cure characteristics of devulcanised buffing dust revulcanised by different sulphur concentration (MOR- 0.8phr)

Sulphur dosage (phr)	Torque (dNm)			Scorch Time, min	Cure time (min)
	Minimum, M_L	Maximum, M_H	M_H-M_L		
2.5 (High)	28.2	90.2	62	1.1	8.9
1.5 (Medium)	29.7	72.5	42.8	2.1	9
0.8 (Low)	27.3	39.3	12	4.2	12

The tensile strengths of both high sulphur and medium sulphur cured revulcanisates were the higher than the low sulphur cured revulcanisate. But, the revulcanisate elongation at break increased in the order high sulphur cured < medium sulphur cured < low sulphur cured revulcanisate. The highest elongation at break associated with the low sulphur cured vulcanisates was due to the under cured state of the revulcanisate rather than an indication of good vulcanisate property. The modulus values of the high sulphur and medium sulphur cured revulcanisates were comparable while that of the low sulphur cured revulcanisate were significantly low (Table 9.4). Hence medium sulphur formulation was chosen for the revulcanisation of devulcanised buffing dust.

Table 9.4 Revulcanisate properties of devulcanised buffing dust cured using different sulphur concentration

Properties	High sulphur	Medium sulphur	Low sulphur
Tensile Strength (MPa)	13	13	10.1
Elongation at Break (%)	312	404	553
M100 (MPa)	2.8	2.7	2
M200 (MPa)	6	5.8	4
M300 (MPa)	11	10	7

9.3.1.2 Number of passes for devulcanisation

In order to correlate the devulcanisation level of a sample after passing through the tight nip of two-roll mill and its visual appearance and/ or behavior, the cure characteristics and revulcanisate properties of the buffing dust after specified numbers of passes through the tight nip were monitored.

Table 9.5 Cure characteristics of buffing dust devulcanised   by different number of passes

Number of passes	Torque (dNm)		M_H- M_L	Scorch Time, min	Cure time (min)
	Minimum, M_L	Maximum, M_H			
20	33.2	87.1	53.9	2.2	9.4
25	32.4	83.2	50.8	2.5	9.5
30	31.3	86	54.7	2.2	9.4
35	31.9	83.6	51.7	2.3	9.1
40	32.1	82.2	50.1	2.3	8.8
45	34.7	84.7	50	2.5	8.8
50	34	86.1	52.1	2.5	8.6
55	33.8	86.5	52.7	2.5	9.3
60	33.7	88.6	54.9	2.8	9.5

The cure characteristics are listed in Table 9.5 and the corresponding cure curves are outlined in Figure 9.2. The minimum torque, maximum torque, scorch time and cure time of the devulcanised samples are comparable irrespective of the number of passes. This implies that the revulcanisation cure characteristics of the devulcanised samples are marginally influenced by increasing numbers of passes through the tight nip of a two roll mill during mechanical devulcanisation.
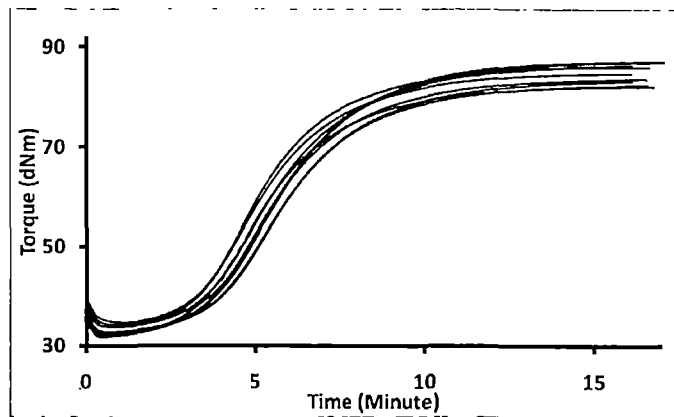
Figure 9.2 Cure curves of buffing dust devulcanised by varying number of passes

The revulcanisate properties of buffing dust devulcanised by different numbers of passes through the tight nip of two roll mill are listed in Table 9.6.

Table 9.6 Revulcanisate properties of buffing dust devulcanised by varying number of passes

No. of passes	Tensile strength (MPa)	Elongation at Break (%)	M100 (MPa)	M200 (MPa)	M300 (MPa)	Tear strength (N/mm)
20	10.8	307	2.7	6.2	11.2	27.1
25	12.4	328	2.6	6	10.8	25.8
30	14.2	416	2.3	5	8.9	26.1
35	14.1	377	2.5	5.7	10.2	26.7
40	11.2	313	2.6	5.9	10.4	27.0
45	11.2	318	2.4	5.5	9.6	26.1
50	11.1	320	2.5	5.6	10.2	27.0
55	11.1	317	2.6	5.9	10.4	25.4
60	9.0	285	2.4	5.4	9.7	27.0

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Highest revulcanisate properties might be obtained with the most effective devulcanisation and minimum main chain degradation of the vulcanisate. Besides, it is worth noticing that the tear strength of the revulcanisates was totally unaffected by the number of passes through the tight nip further pointing that mechanical devulcanisation in a two roll mill cannot significantly improve the tear strength of the devulcanised sample after revulcanisation.

9.3.1.3 Amount of Virgin rubber added per 100g of devulcanised crumb

Handling of devulcanised rubber during further revulcanisation would be much easier if some minimum amount of virgin rubber is added to it as a binding agent as no process oil is used during revulcanisation. The optimum minimum amount of virgin rubber that has to be added per 100g of the devulcanised buffing dust was investigated by adding varying amounts of virgin NR to mechanically devulcanised buffing dust (30passes through tight nip of two roll mill) followed by revulcanisation using the optimized formulation.
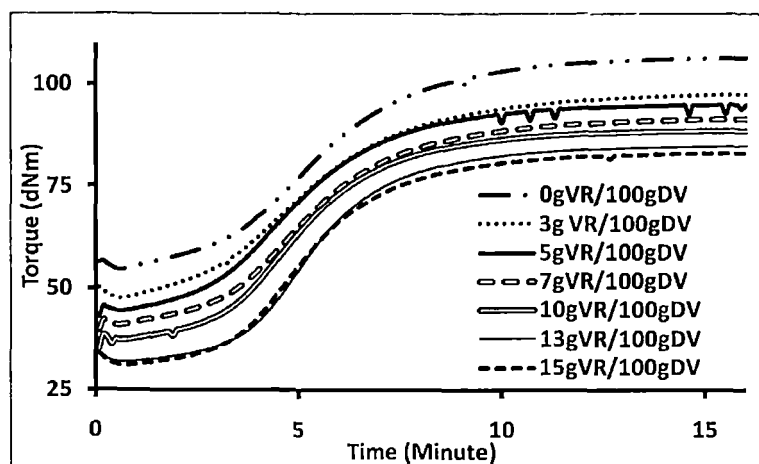
Figure 9.3 Cure curves of the devulcanised buffing dust blended with different amounts of virgin NR

The cure characteristics during revulcanisation of these devulcanised samples are listed in Table 9.7 along with the respective cure curves in Figure 9.3. The minimum torque of the devulcanised samples lowered with increase in the amount of virgin NR added with corresponding lowering of maximum torque. Tthe scorch time of the devulcanised rubber increased marginally with increase in the amount of virgin NR added.

Table 9.7 Cure characteristics of mechanically devulcanised buffing dust blended with varying amounts of virgin NR

Amount of virgin NR (g)	Torque (dNm)			Scorch Time, min	Cure time (min)
	Minimum, M_L	Maximum, M_H	M_H-M_L		
0	54.6	106.4	51.8	1.5	9.2
3	47.7	97.4	49.7	1.5	9.2
5	47.4	94.9	47.5	1.6	8.3
7	41.2	91.6	50.4	1.6	8.7
10	37.5	88.6	51.1	1.9	8.2
13	32	84.8	52.8	2.3	8.4
15	31.4	83.4	52	2.4	8.9

The revulcanisate properties of the devulcanised buffing dust with varying amounts of virgin NR incorporated as binder are given in Table 9.8. The incorporation of low amounts of virgin rubber to the devulcanised rubber as a binder improves the revulcanisate properties of the devulcanised rubber besides the processing advantages during revulcanisation. The tensile strength and elongation at break of the revulcanised sample is improved by the incorporation of virgin rubber. While, the elongation at break increased linearly with increase in the amount of virgin NR added as a binder, the tensile strength increased to a maximum and then decreased. Correspondingly, the modulus values decreased with increase in virgin

rubber addition. The tear strength of the revulcanisate also showed marginal improvement with the increase in the amount of virgin NR added to the devulcanised buffing dust as a binder.

Table 9.8 Revulcanisate properties of devulcanised buffing dust blended with varying amounts of virgin NR

Amount of NR (g)	Tensile strength (MPa)	Elongation at Break (%)	M100 (MPa)	M200 (MPa)	M300 (MPa)	Tear strength (N/mm)
0	8.7	237	3	6.9	-	27
3	11.1	346	2.6	5.9	10.6	26.1
5	13.2	362	2.5	5.7	10.1	27.1
7	14.5	404	2.4	5.3	9.5	30.1
10	15	416	2.4	5.2	9.4	30.3
13	11.6	445	2.1	4.4	7.9	28.5
15	13.3	471	2	4.1	7.2	31.3

Hence, it might be concluded that the optimum conditions for the best revulcanisate properties of mechanically devulcanised buffing dust are 30 to 40 numbers of passes through the tight nip of two-roll mill for devulcanisation, blending of the devulcanised buffing dust with 7g to 10g virgin NR followed by revulcanisation using medium sulphur formulation. The experimental observations gathered from the optimization of various devulcanisation parameters were applied during the devulcanisation and subsequent revulcanisation of all samples considered in this thesis. The revulcanisation formulation and amount of virgin rubber was adopted as such in most cases while the number of passes required for devulcanisation was decided based on the appearance of the devulcanised sample.

9.3.2 Stable free radical assisted devulcanisation of buffing dust and GTR

9.3.2.1 Number of passes for devulcanisation

Devulcanisation was carried out both in the presence and absence of 4HT (4phr). As clearly evident from Figure 9.4, the required number of passes through the tight nip significantly reduced when 4HT was used as a devulcanisation aid. This implies that, stable free radical assisted devulcanisation can be a potential method of devulcanisation of commercial sources of waste rubber also.
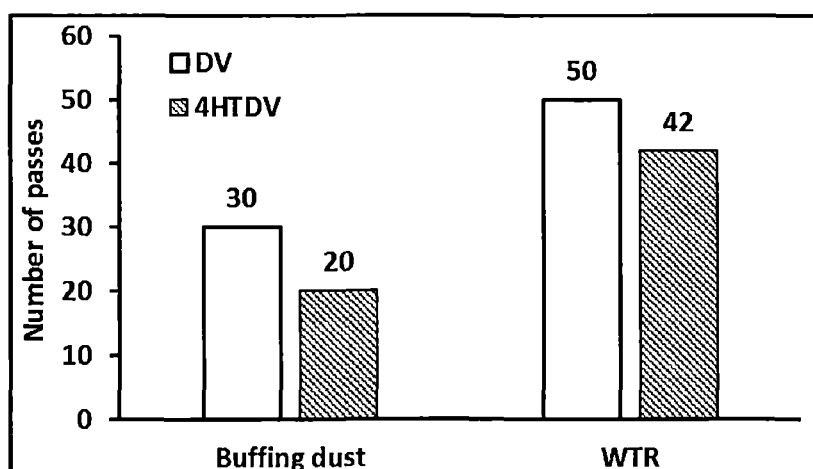
Figure 9.4 Comparison of required number of passes for devulcanisation of buffing dust and GTR

9.3.2.2 Residual crosslink density of devulcanised samples

The residual crosslink densities of devulcanised buffing dust are given in Table 9.9 (that of the mechanically devulcanised GTR could not be determined and hence no comparison could be made). It can be observed that, 53.7per cent reduction in residual crosslink density was obtained when buffing dust was devulcanised with the assistance of 4HT. This straight away point to the higher devulcanisation efficiency associated with 4HT

assisted devulcanisation of buffing dust in comparison with mechanical devulcanisation.

Table 9.9 Residual crosslink densities of mechanically and 4HT assisted devulcanised buffing dust

Devulcanisation	Crosslink density x 10^4, mole/cm^3	Per cent reduction, %
Mechanical	0.54	53.7
4HT assisted	0.25	

9.3.2.3 Revulcanisation

The revulcanisation of devulcanised buffing dust and GTR were carried out by the revulcanisation formulation given in Table 2.5 and the cure characteristics and revulcanisate properties are compared (Table 9.10).

Table 9.10 Cure characteristics and revulcanisate properties of mechanically and 4HT assisted devulcanised buffing dust and GTR

Sample		M_L	M_{H^-} M_L	ts_2, min	Tensile Strength, MPa	EB, %	M100, MPa	M300, MPa	Tear strength, N/mm
		dNm							
Buffing dust	DV	5.1	7.5	2.9	13.8	318	4.7	8.9	25.2
	4HT DV	3.5	9.6	2.9	16.6	451	4.8	8.8	35.4
GTR	DV	6	5.7	2.5	7.74	244	2.9	-	20.6
	4HT DV	4.3	8.1	2	10.8	300	3.1	11	30

The comparative representation of the revulcanisate tensile strength, elongation at break and tear strength of the buffing dust and GTR devulcanised with and without the assistance of 4HT is given in Figure 9.5.
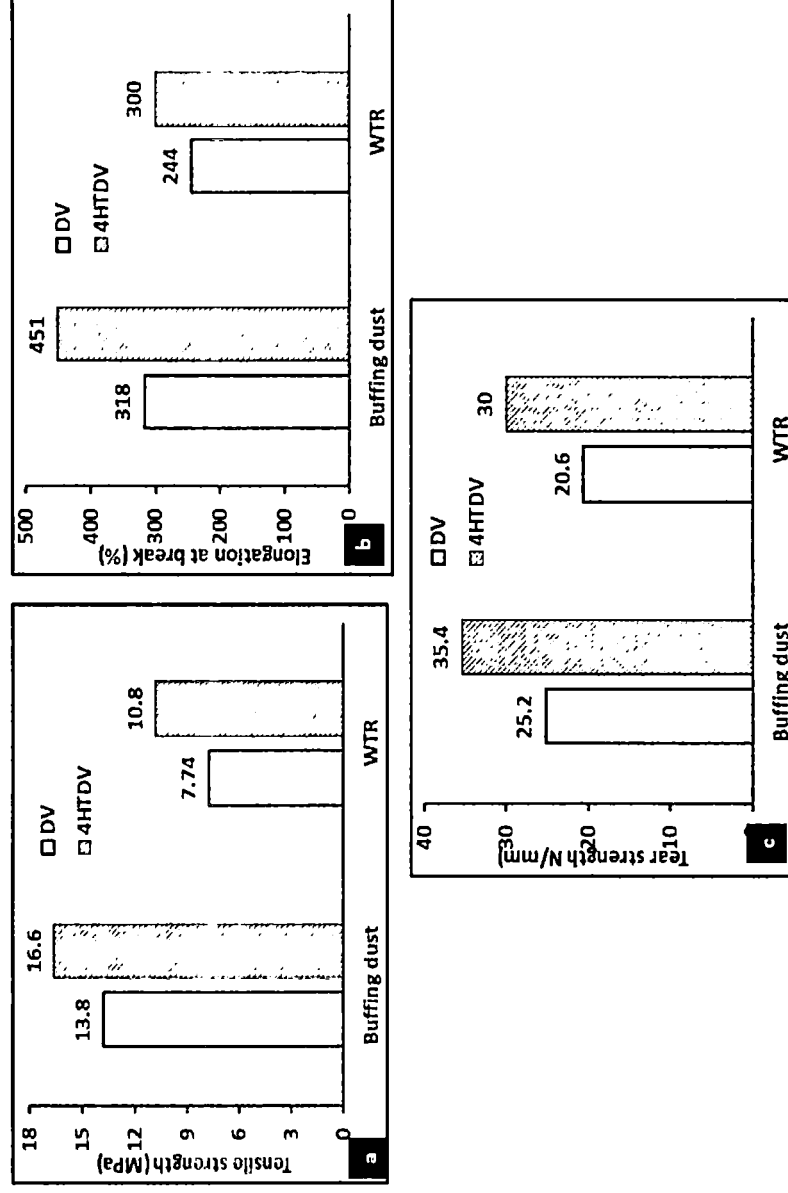
Figure 9.5 Revulcanisate **a:** tensile strength; **b:** elongation at break and **c:** tear strength of devulcanised buffing dust and GTR

The minimum torque of 4HT assisted devulcanised samples were lower than that of the corresponding mechanically devulcanised samples and the maximum torques were comparable. Hence, the total torque of the 4HT assisted devulcanised samples were higher than the corresponding mechanically devulcanised samples. The revulcanisate properties of the buffing dust and GTR devulcanised with the assistance of 4HT were significantly higher than that obtained for the corresponding mechanically devulcanised sample. The revulcanisate properties of GTR were lower than that of buffing dust indicating the role of quality of sample used for devulcanisation upon the revulcanisate properties.

9.3.3 Blends of virgin rubber (NR/BR) and devulcanised buffing dust

Commercial buffing dust devulcanised with and without the assistance of 4HT was blended with virgin rubber (NR/BR blend) in different ratios to prepare a compound resembling the tread from which the buffing dust is prepared. The vulcanisate properties of the blends were compared with that of the control compound in which no devulcanised rubber is added. The ageing characteristics of the blends were also evaluated.

9.3.3.1 Cure characteristics

The cure characteristics of the control compound and the blends of natural rubber and devulcanised rubber are given in Table 9.11 and the respective cure curves are given in Figure 9.6.

The minimum torque of all the vulcanisates were comparable while the maximum torque of the control compound was the least. A marginal increase in minimum torque of the blends were observed with increase in the amount of devulcanised rubber in blends with mechanically devulcanised buffing dust. Such an increase of minimum torque is not observed with the blends with 4HT assisted devulcanised buffing dust.

Table 9.11 Cure characteristics of blends of virgin rubber and devulcanised buffing dust

Blend ratio/ Devulcanisation method		Torque (dNm)			Scorch Time, min	Cure time (min)
		Minimum, M_L	Maximum, M_H	M_H-M_L		
100/0	Control	2	14.9	12.9	3.5	8.8
95/5	Mechanical	1.6	15.6	14	3.4	8
	4HT assisted	1.9	16.1	14.2	3.6	8
90/10	Mechanical	1.7	15.1	13.4	3.4	7.8
	4HT assisted	2	15.9	13.9	3.4	7.8
85/15	Mechanical	2	15.3	13.3	3.1	7.2
	4HT assisted	2.1	15.4	13.3	2.8	7
80/20	Mechanical	2.2	15.4	13.2	2.8	6.9
	4HT assisted	1.9	16	14.1	3.1	7.3
75/25	Mechanical	2.3	15	12.7	2.7	6.7
	4HT assisted	2.2	15.7	13.5	3	7.1
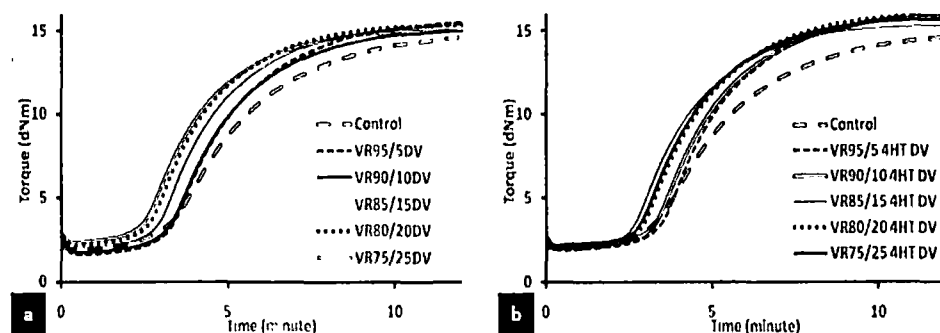
Figure 9.6 Cure curves of blends of virgin rubber and a: mechanically
b: 4HT assisted devulcanised buffing dust

The Scorch time of the 95/5 and 90/10 blends were comparable with that of the control where after it decreased with increase in the amount of devulcanised rubber present in the blend. The cure times of all the the

blends were lower than the control and decreased with increase in devulcanised rubber content in the blend.

9.3.3.2 Vulcanisate properties

The vulcanisate properties of blends of virgin rubber and devulcanised buffing dust in comparison with the corresponding properties of the control are given in Table 9.12. The trends observed in the vulcanisate properties of the blends in comparison with the corresponding property of the control are illustrated in Figure 9.7 and 9.8.

Table 9.12 Vulcanisate properties of blends of virgin rubber and devulcanised buffing dust

Vulcanisate		Hardness (Shore A)	Tensile strength (MPa)	EB (%)	M300, MPa	Tear strength (N/mm)	Abrasion loss (mm^3)	Heat build-up (°C)
Control, 100/0		63	20.6	512	10.7	92.7	57	17
95/5	NR/DV	63	21.3	580	9.9	87.8	54	18
	NR/4HT DV	63	21.8	582	9.7	90	54	19
90/10	NR/DV	62	22.2	594	9.3	68	72	18
	NR/4HT DV	63	21.4	580	9.3	82.3	72	19
85/15	NR/DV	62	22	581	9.4	63.8	72	18
	NR/4HT DV	62	21.3	522	9.2	79.8	72	19
80/20	NR/DV	61	20.5	557	9.2	60	72	19
	NR/4HT DV	62	19.3	527	9.3	73.5	72	19
75/25	NR/DV	61	20.1	563	8.9	49.6	90	17
	NR/4HT DV	61	19.9	545	9.2	54	81	18
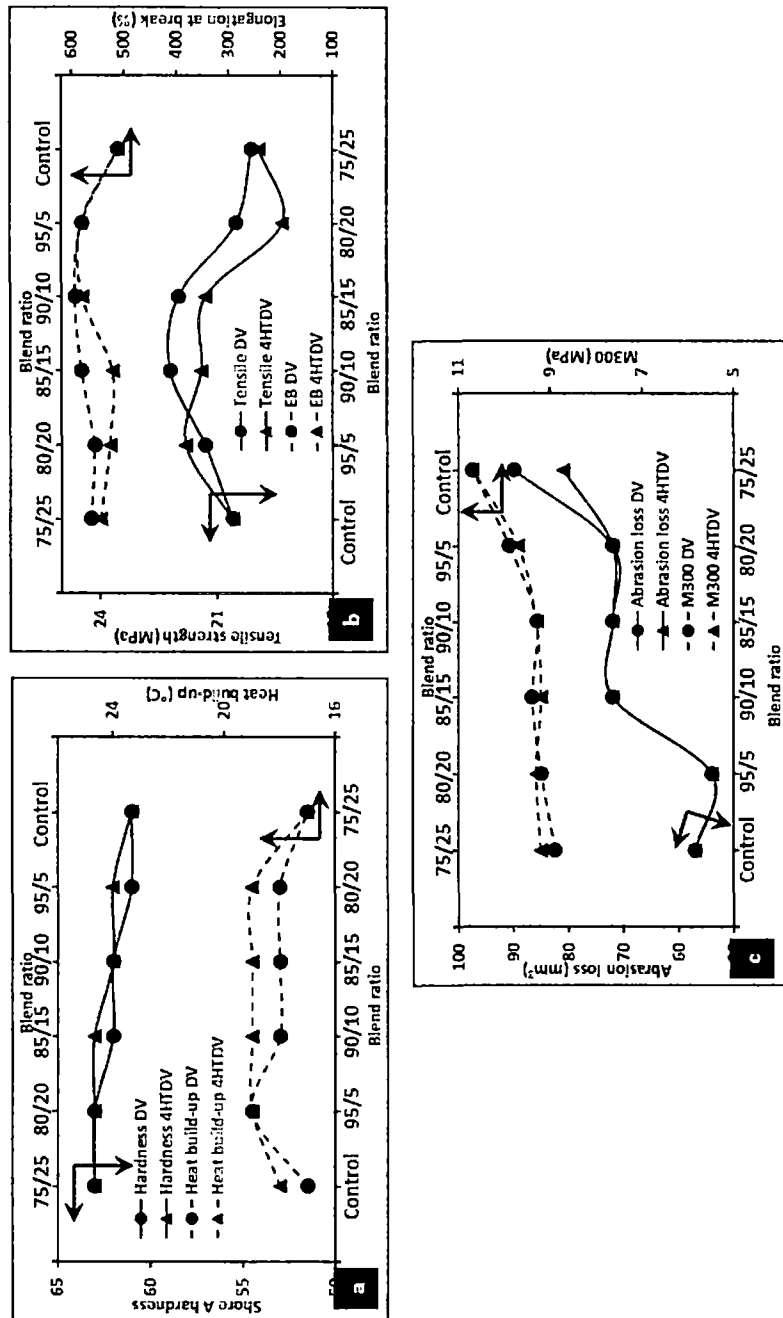
Figure 9.7 Variation in **a:** Shore A hardness & heat build-up; **b:** tensile strength & elongation at break and **c:** M300 & abrasion loss of blends of virgin rubber and devulcanised buffing dust

The hardness of the blends were comparable with the control but decreased marginally with increasing amounts of devulcanised rubber in the blend. The tensile strength of the blends was affected by the incorporation of devulcanised rubber marginally. The detrimental effect of incorporation of devulcanised rubber was not perceived with the tensile strengths of blends even up to a blend ratio of 80/20. The elongation at break of all the blends were higher than the control vulcanisate. Correspondingly, the 300 per cent modulus of the blends were marginally lower than that of the control vulcanisate. The abrasion loss of the 95/5 blends were lower than the control vulcanisate, while that of the other blends were significantly higher than the control. The heat build-up of the blends were comparable with that of the control.

With regard to the afore mentioned vulcanisate properties, the blends of virgin rubber with both mechanically and 4HT assisted devulcanised buffing dust showed similar response irrespective of the fact that, when these devulcanised samples were revulcanised as such, 4HT assisted devulcanisation gave significantly higher values for revulcanisate properties. This observation was similar to incorporation of devulcanised NR vulcanisates in fresh compound as described in Chapter 4 and 6. The profound positive effect of 4HT assisted devulcanisation is clearly reflected in the tear strengths of the blends as depicted in Figure 9.9.

The tear strength of the blends were significantly lower than the control vulcanisate especially for those blends prepared with the incorporation of mechanically devulcanised buffing dust. The lowering of tear strength of the blends were substantial with the increase in the amount of devulcanised rubber in the blend. These observations might be indicating that, the tear strength of the devulcanised rubbers after revulcanisation or that of the blends in which they are incorporated are remarkably influenced by the level of devulcanisation attained by the devulcanised rubber.
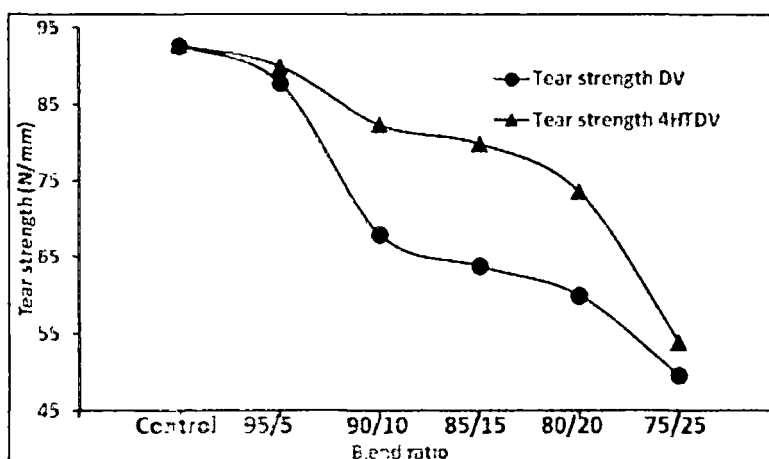
Figure 9.8 Variation in tear strength of the blends of virgin rubber and devulcanised buffing dust

Also, most of the vulcanisate properties except tear strength and abrasion resistance of the blends in which devulcanised rubber is incorporated are comparable with the control. It might be noted that, in all the cases filler correction was applied. Some of the properties might also improve if filler correction is omitted during the preparation of blends as seen in Chapter 3. Hence, it might be accorded that, judicious decisions taken by the compounder based on the product requirements would allow the incorporation of devulcanised rubber in newer compounds in larger volumes.

9.3.3.3 Effect of ageing on vulcanisate properties

The effect of ageing at 70°C for seven days upon the vulcanisate properties of the blends of virgin rubber and devulcanised rubber were evaluated by ageing in an air oven.

Ageing at 70°C for seven days

The vulcanisate properties of the control vulcanisate and the blends of virgin rubber and devulcanised buffing dust after ageing at 70°C for seven days are given in Table 9.13. The trends observed with the vulcanisate properties after ageing are different from that of the original vulcanisate. The tensile strength of the blends were lower than the control after ageing and it decreased with increase in the amount of devulcanised buffing dust in the blend. Here, the blend with 4HT assisted devulcanised buffing dust had marginally higher tensile strength than that of the corresponding blend with mechanically devulcanised buffing dust in most cases. The elongation at break also followed the same trend.

Table 9.13 Comparison of ageing properties of blends of virgin rubber and devulcanised buffing dust with the control tread formulation

Vulcanisate	Tensile strength (MPa)	Elongation at Break (%)	M100 (MPa)	M200 (MPa)	M300 (MPa)	Tear strength (N/mm)
Control, 100/0	21	470	3.2	7.5	12.6	59.4
NR95/5DV	19.1	447	3.5	7.6	12.3	63.8
NR95/5 4HTDV	17.4	397	3.6	7.8	12.5	65.3
NR90/10DV	16.7	412	3.2	7.1	11.6	52.1
NR90/10 4HTDV	17.8	406	3.5	7.7	12.6	58.1
NR85/15DV	17.2	407	3.3	7.3	12	54.7
NR85/15 4HTDV	17.5	405	3.4	7.5	12.3	64.4
NR80/20DV	16.5	398	3.2	7.1	11.8	51
NR80/20 4HTDV	17	391	3.5	7.5	12.4	56.3
NR75/25DV	15.8	374	3.3	7.3	12.1	49.3
NR75/25 4HTDV	16.3	385	3.4	7.4	12.1	56.2

The 100per cent, 200per cent and 300per cent modulus values of the blends were comparable with that of the control vulcanisate after ageing. The tear strength of the blends with 4HT assisted devulcanised buffing dust were higher than that of the corresponding blend with mechanically devulcanised buffing dust and even higher than that of the control vulcanisate in some cases. The influence of ageing at 70°C for seven days can be more clearly understood from the per cent retention of vulcanisate properties given in Table 9.14.

Table 9.14 Per cent retention of vulcanisate properties of blends of virgin rubber and devulcanised buffing dust after ageing at 70°C for seven days

Vulcanisate	Per cent retention (%)			
	Tensile strength	Elongation at Break	M300	Tear strength
Control, 100/0	101.9	91.8	117.8	64.1
NR95/5DV	89.7	77.1	124.2	72.7
NR95/5 4HTDV	79.8	68.2	128.9	72.6
NR90/10DV	75.2	69.4	124.7	76.6
NR90/10 4HTDV	83.2	70.0	135.5	70.6
NR85/15DV	78.2	70.1	127.7	85.7
NR85/15 4HTDV	82.2	77.6	133.7	80.7
NR80/20DV	80.5	71.5	128.3	85.0
NR80/20 4HTDV	88.1	74.2	133.3	76.6
NR75/25DV	78.6	66.4	136.0	99.4
NR75/25 4HTDV	81.9	70.6	131.5	104.1

The tensile strength of the control vulcanisate resisted the deteriorating influence of ageing to a higher extent while that of the blends

were badly affected. On the other hand, the tear strength of the control vulcanisate was the most detrimentally affected upon ageing at 70°C. The blends with 4HT assisted devulcanised buffing dust showed higher retention of tensile strength after ageing compared with the corresponding blend with mechanically devulcanised buffing dust and the per cent retention of vulcanisate properties decreased with increasing amounts of devulcanised buffing dust present in the blend.

9.3.4 Factory scale trials of 4HT assisted devulcanisation

Based on better results obtained for the laboratory scale devulcanisation studies of 4HT assisted devulcanisation of rubbers in comparison with many other devulcanisation methods, the practical feasibility of the proposed novel devulcanisation method is experimented on a factory scale. Two types of commercial buffing dust (Table 9.2) were used for the devulcanisation studies.

9.3.4.1 Cure characteristics

Similar revulcanisation cure characteristics obtained for buffing dust devulcanised in factory scale trials and lab-scale devulcanisation are listed in Table 9.15. Incorporation of 4HT lowered the minimum torque of the sample in both cases. Closer examination of cure characteristics Indicates that, the minimum torque of the factory scale devulcanised samples were marginally higher than the corresponding sample devulcanised in the laboratory in most cases. On the other hand, the maximum torque of the factory scale devulcanised sample were higher than the corresponding sample devulcanised through the lab-scale process. Correspondingly, the total torque during revulcanisation was higher for the samples after factory scale devulcanisation. The scorch time of the samples after both types of devulcanisation were comparable.

Table 9.15 Revulcanisation cure characteristics of buffing dust after factory scale and lab-scale devulcanisation

Amount of 4HT, phr	Devulcanis-ation	Torque (dNm)			Scorch Time, min	Cure time (min)
		Minimum, M_L	Maximum, M_H	M_H-M_L		
Buffing dust sample I						
0	Lab-scale	3.9	11.6	7.7	2.5	5.9
	Factory-scale	4.2	13	8.8	2.5	6.2
1	Lab-scale	2.8	12.6	9.8	2.2	5.7
	Factory-scale	3	13.2	10.2	2.2	5.9
2	Lab-scale	2.4	13.3	10.9	2.5	5.8
	Factory-scale	2.4	12	9.6	2.5	6
4	Lab-scale	2.3	12.6	10.3	2.4	5.4
	Factory-scale	2.6	13	10.4	2.9	6
Buffing dust sample II						
0	Lab-scale	4.6	13.4	8.8	2.4	6
	Factory-scale	4.6	13.8	9.2	2.9	6.7
1	Lab-scale	3.4	13.3	9.9	2.4	5.9
	Factory-scale	3.9	13.9	10	2.5	6.3
2	Lab-scale	2.9	12	9.1	2.7	6
	Factory-scale	3.4	13.3	9.9	2.6	6.1
4	Lab-scale	3.4	13.9	10.5	2.9	6
	Factory-scale	3.3	14.2	10.9	2.7	5.8

9.3.4.2 Revulcanisate properties

The revulcanisate properties of the devulcanised buffing dust are given in Table 9.16 and are illustrated in Figure 9.8.
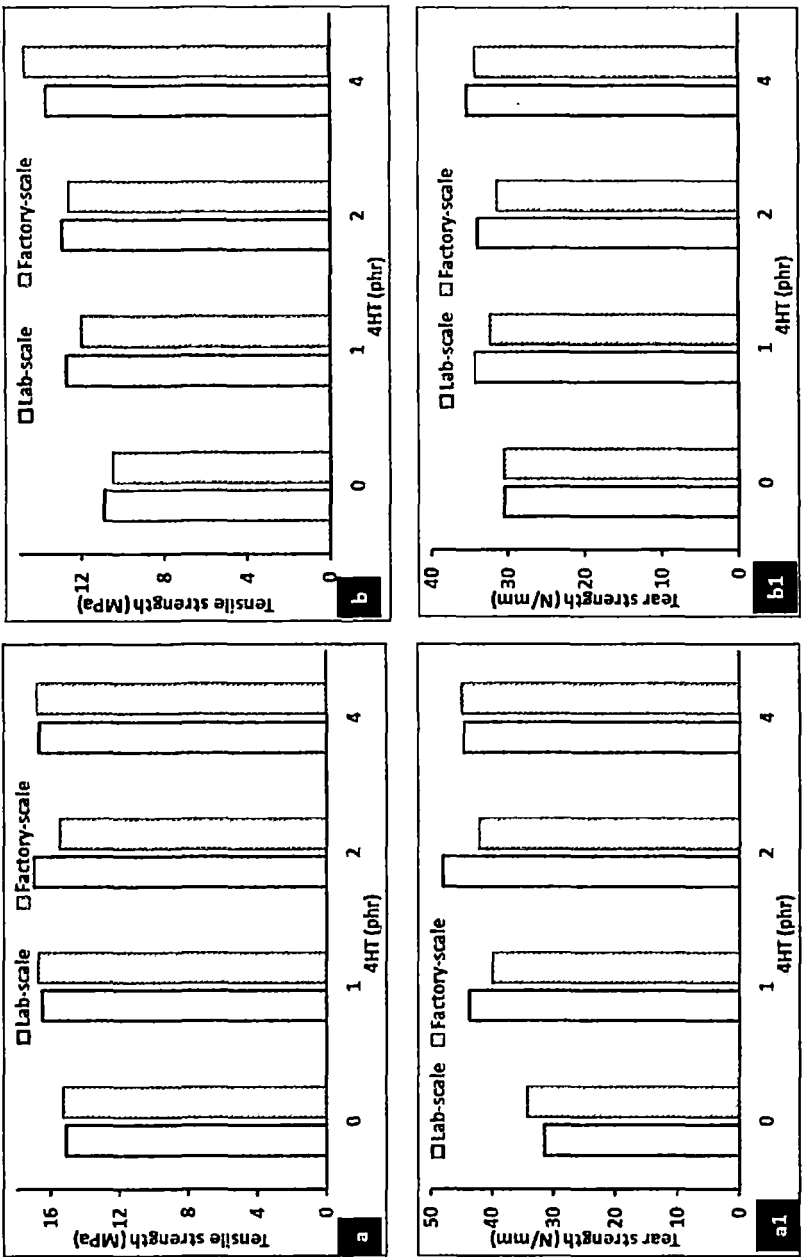
Figure 9.9 Revulcanisate **a** & **b**: tensile strength; **a1** & **b1**: tear strength after factory scale devulcanisation of buffing dust sample I (a & a1) and sample II (b & b1) in comparison with lab scale devulcanisation

Table 9.16 Revulcanisate properties of buffing dust after factory scale and lab-scale devulcanisation

Sample/ 4HT dose	Devulcanisation type	Tensile strength, MPa	Elongation at Break, %	M100, MPa	M200, MPa	M300, MPa	Tear strength (N/mm)
Buffing dust I							
0phr	Lab-scale	15.1	405	1.8	4.4	9	31.6
	Factory-scale	15.3	400	2.4	5.2	9.7	34.2
1phr	Lab-scale	16.5	443	1.8	4.4	8.9	43.6
	Factory-scale	16.7	414	2.2	5.3	10.2	39.9
2phr	Lab-scale	17	441	2	4.9	9.4	48.1
	Factory-scale	15.5	409	2.1	4.9	9.5	42.1
4phr	Lab-scale	16.7	411	2.1	5.3	10.1	44.6
	Factory-scale	16.8	431	2.2	5.3	9.8	45
Buffing dust II							
0phr	Lab-scale	10.9	356	1.9	4.8	10.2	30.4
	Factory-scale	10.5	312	1.9	4.7	9.3	30.5
1phr	Lab-scale	12.7	381	1.7	4.0	8.2	34.3
	Factory-scale	12	372	1.8	4.2	8.2	32.2
2phr	Lab-scale	12.9	365	1.7	4.0	8.1	33.9
	Factory-scale	12.6	368	1.9	4.4	8.8	31.4
4phr	Lab-scale	13.7	343	2.1	5.1	10.5	35.4
	Factory-scale	14.7	363	2.2	5.2	10.9	34.2

Stable free radical assisted devulcanisation

The results obtained in the lab-scale trials were reproduced in the factory scale trials indicating that, 4HT assisted mechanical devulcanisation process is a promising method for maximum property retention through efficient devulcanisation. Another observation is the variation in the amount of stable free radical required to achieve the highest revulcanisate property after devulcanisation. The highest revulcanisate properties were associated with devulcanisation of buffing dust with the assistance of 2phr stable free radical in the case of lab-scale devulcanisation while with the aid of 4phr stable free radical in the case of factory trials. This might be due to the absence of proper mechanical assistance like conveyer belts to ensure efficient and uniform utilization of 4HT during devulcanisation while handling larger volumes of samples.

The results further points to the already discussed concept of effect of poly butadiene content upon the devulcanisation of NR/BR blends. The buffing dust samples with different NR/BR composition behaved in different manners towards devulcanisation. The revulcanisate properties of the buffing dust sample II (NR/BR=60/40) were not significantly improved by 4HT assisted devulcanisation in comparison with the 4HT assisted devulcanisation of sample I (NR/BR=70/30). The revulcanised tensile strength after lab-scale devulcanisation process were marginally higher except for the sample devulcanised with the assistance of 4phrHT in which the factory scale devulcanisation gave comparatively higher revulcanisate tensile strength than the corresponding lab-scale devulcanised sample.

The variation in revulcanisate properties and the optimum amount of 4HT required for the best revulcanisate properties for different samples further points that the quality and composition of the sample to be devulcanised plays the decisive role in determining the revulcanisate properties.

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Chapter 10

The Issue of Low Scorch During Revulcanisation of Devulcanised Rubber

10.1 INTRODUCTION

In the earlier stages of rubber recycling, the entire process was defined as reclamation since the intention was to reuse the material. Besides the environmentally hazardous production techniques, the very low molecular weight of reclaimed rubber limited the amount of reclaim that can be used in new products without deteriorating the physical properties[1,2]. Hence, most developed countries adopted a radical shift from the reclamation process of rubber recycling to recycling methods focused on material and energy recovery. These newer strategies primarily aim to convert end-of-life tyres into a useful form for reuse in variety of applications not in the rubber industry alone.

But, the intention to reuse the recycled rubber in the rubber industry itself resulted in further advancements in the rubber devulcanisation industry in which devulcanisation was achieved by applying high temperature and pressure, mechanical, mechano-chemical, microwave or ultrasonic energies, using biotechnological interventions, etc[3]. Though these innovations produced devulcanised rubber with less main chain degradation and better revulcanisate properties than the reclaimed rubber, the inherent problem of low scorch during revulcanisation associated with reclaimed rubber lingered with the devulcanised rubber also[4,5]. Thus, low scorch during revulcanisation continued to be an unsolved issue associated with devulcanisation.

The considerable reduction in scorch time of the devulcanised samples during revulcanisation was attributed to reasons such as crosslink

precursors[6] or residual accelerator derivatives present in the devulcanised samples[7], unreacted curatives[6],[8] or structural modifications like cyclic sulphide structures[9] etc. Gibala et al studied the cure characteristics of devulcanised rubber as such or during its incorporation in virgin compound[8],[10],[11]. These researchers demonstrated that, vulcanisation accelerator's residues present in ground rubber may affect curing characteristics and mechanical properties of rubber compounds filled with ground rubber. Also, it was suggested that accelerator residue migration occurred from ground rubber to elastomer matrix while the migration of sulfur occurred in opposite direction. In the ultrasound devulcanisation studies of unfiled and carbon black filled isoprene rubber by Sun et al., the complete absence of pre-vulcanisation induction period was observed during revulcanisation which was attributed to the existence of accelerator residue in the system[12],[13]. It was also observed that the revulcanisation reaction starts instantaneously once the compounds were heated to the desired temperature. Various devulcanisation experiments using ultrasound were carried out with model styrenebutadiene rubber (SBR) and with ground rubber tire (GRT) by Isayev et al. and the curing behavior, technological properties, and structural characteristics were studied[12],[14],[15].

This chapter intends to investigate further on the reasons behind the observed low scorch safety during revulcanisation of devulcanised rubber, using the results of previous research on this topic as guide lines. The revulcanisation of commercially available samples such as tyre tread buffings, and carbon black filled natural and synthetic rubbers prepared in the laboratory were studied after devulcanisation by various mechanical and mechano-chemical methods.

10.2 EXPERIMENTAL

Carbon black filled vulcanisates of natural and synthetic rubbers of known composition were prepared in the laboratory following the formulation described in Table 2.3. The composition of tyre tread buffings procured from a pre-cured tread manufacturer is given in Table 2.1. Natural rubber vulcanisates are prepared and revulcanised after devulcanisation following the formulation given in Table 2.5. The formulations for preparation and revulcanisation of blends of different rubbers are given in Table 10.1 whereas those for the peroxide vulcanised samples and synthetic rubber vulcanisates, are given in Table 10.2 respectively.

Table 10.1 Formulation for NR/BR and SBR/BR blends

Ingredients	NR/BR phr	SBR/BR phr	Tread phr
NR	50	-	70
SBR	-	60	-
BR	50	40	30
Carbon black	50*	50**	55**
Naphthenic oil	6	10	12
ZnO	4	3	4
Stearic acid	1	2	2
6ppd	2.5	2	2
TDQ	1.5	1	1
Accelerator	1[#]	1[#]	1[##]
Sulphur	1.2	2	2

*GPF; **HAF; [#]CBS; [##]TBBS

During revulcanisation of these samples, the sulphur cure system used for the preparation of original sample was employed. The polymer content during revulcanisation is contributed from the rubber hydrocarbon

part of the devulcanised rubber (50% of weight) and the 10g virgin rubber added per 100g of the devulcanised rubber.

Table 10.2 Formulations used for sulphur curing of synthetic rubbers and vulcanisates and peroxide curing of SR and NR

	Sulphur curing			DCP curing	
Ingredients	EPDM	NBR	SBR	EPDM	NR
	Quantity (phr)				
Polymer	100	100	100	100	100
Carbon black	75*	50**	50**	75*	40**
Process oil	15$^{\#}$	-	10$^{\#\#}$	15$^{\#}$	4$^{\#\#}$
DOP	-	15	-	-	-
ZnO	3	5	3	-	-
Stearic acid	1	2	2	-	-
Anti oxidant	-	2$^{\$}$	3$^{\$\$}$	-	2$^{\$}$
MBTS	1.6	1	-	-	-
TBzTD	2.8	0.1	-	-	-
DTDM	1.6	-	-	-	-
CBS	-	-	1	-	-
Sulphur	0.4	1.5	2	-	-
DCP (100%)	-	-	-	2	2

*GPF; **HAF; $^{\#}$Paraffinic oil; $^{\#\#}$Naphthenic oil; $^{\$}$TDQ; $^{\$\$}$1phr TDQ + 2 phr Mernox 6C

The effect of devulcanisation protocols upon revulcanisation cure characteristics was investigated using carbon black filled NR vulcanisates prepared using semi EV cure system based on formulation given in Table 2.3 and commercial buffing dust (Table 2.1). In these devulcanisation trials no virgin rubber was added to the devulcanised rubber before revulcanisation. The revulcanisation formulation described in Table 2.5 was employed.

The scorch characteristics of commercial tyre tread buffings (buffing dust) devulcanised by different methods and that of commercial devulcanised rubber (CDR) prepared by the devulcanisation of buffing dust in comparison with the vulcanisation characteristics of a similsr tread compound was studied. These devulcanised samples were revulcanised using the formulation given in Table 2.5 afer adding 10g virgin NR per 100g devulcanised rubber.

In order to further substantiate and confirm the proposed mechanism and/or reason behind observed low scorch during revulcanisation of devulcanised rubber, revulcanisation of TMTD cured NR vulcanisates were also carried out under different conditions. The formulation used for the preparation of carbon black filled NR vulcanisates for TMTD cure is given in Table 10.3. The revulcanisation was carried out as in the case of semi EV cured NR vulcanisates using the formulation given in Table 2.5 without adding any virgin NR.

Table 10.3 Formulation for TMTD curing of NR

Ingredients	NR/BR phr
NR	100
Carbon black	50
Naphthenic oil	6
ZnO	5
Stearic acid	2
6ppd	2.5
TDQ	1.5
TMTD	3

Devulcanisation of samples were carried out as described in chapter 2 and the cure characteristics during revulcanisation were monitored using a Rubber Process Analyser.

10.3 RESULTS AND DISCUSSION

10.3.1 Cure behaviour of devulcanised rubbers on revulcanisation

10.3.1.1 Revulcanisation of devulcanised NR prepared from sulphur cured vulcanisates

Revulcanisation of devulcanised carbon black filled NR vulcanisates prepared in the laboratory with three different cure systems *viz*, conventional curing (CV), semi efficient curing (Semi EV) and efficient curing (EV) were carried out. The cure curves of original compounds along with their respective revulcanisation cure curves after mechanical devulcanisation (CV DV; Semi EV DV and EV DV) are represented in Figure 10.1.
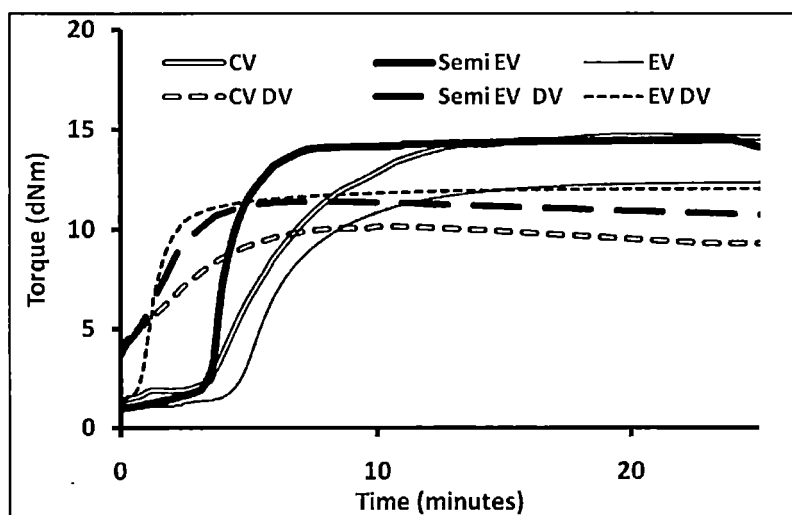
Figure 10.1 Cure curves of original and devulcanised sulphur cured NR vulcanisates

Though the original samples were cured with three different cure systems, same formulation was employed for the revulcanisation of three samples (Table 2.5). The slight variation in scorch time of the samples based on the cure system employed is an established fact, and evident from the cure curves of original vulcanisates. But the revulcanisation cure curves in the Figure 10.1 clearly demonstrate that, the three devulcanised samples cures without any pre-vulcanisation induction time/ scorch time. Hence it is clear that mechanically devulcanised NR vulcanisates cures with low scorch time during revulcanisation irrespective of the type of sulphenamide-sulphur cure system employed during vulcanisation of original sample.

10.3.1.2 Revulcanisation of devulcanised SR prepared from sulphur cured vulcanisates

In order to check whether the low scorch associated with the revulcanisation of devulcanised rubber sample is specific to NR or not, revulcanisation of sulphur vulcanised synthetic rubbers like acrylonitrile butadiene rubber (NBR), ethylene propylene diene rubber (EPDM) and styrene butadiene rubber (SBR) were carried out (Figure 10.2).
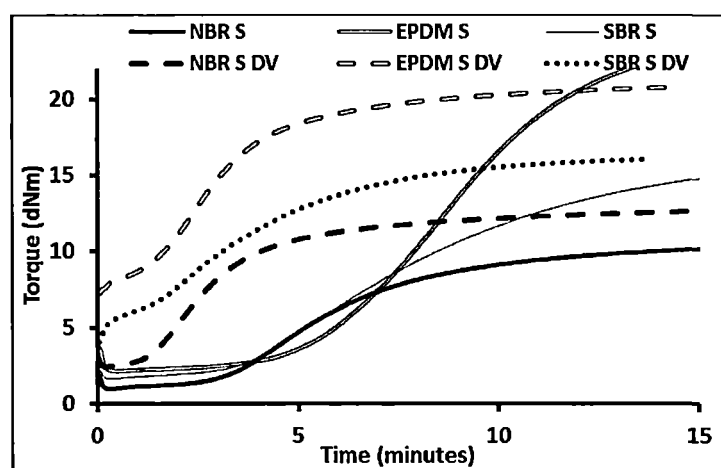
Figure 10.2 Cure curves of sulphur cured synthetic rubbers and their corresponding revulcanisates

The cure curves of mechanically devulcanised sulphur cured synthetic rubbers (NBR S DV; EPDM S DV and SBR S DV) also showed low scorch during revulcanisation similar to revulcanisation of devulcanised natural rubber. The scorch time of the devulcanised rubbers is considerably reduced in comparison with the vulcanisation of original compounds. It can be thus inferred that, devulcanised synthetic rubbers obtained from sulphur cured original samples also suffer from the problem of low scorch time during revulcanisation.

10.3.1.3 Revulcanisation of devulcanised NR/BR and NR/SBR blends prepared from sulphur cured samples

Revulcanisation of blends of BR with NR and SBR were carried out after mechanical devulcanisation and the corresponding cure curves are given in Figure 10.3.
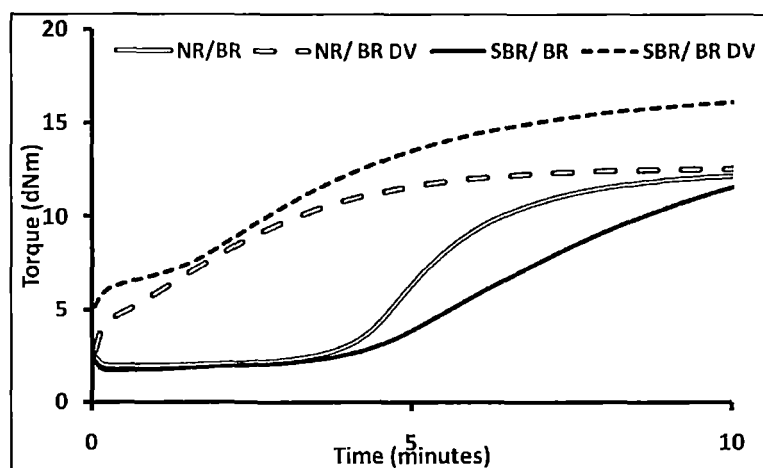
Figure 10.3 Cure curves of original NR/BR and SBR/ BR blends and the corresponding devulcanised samples

The revulcanisation cure curves illustrated in Figure 10.3 in comparison with the vulcanisation cure curves of the respective original

samples (NR/BR & NR/SBR) clearly indicates that the mechanically devulcanised sulphur cured blends of BR with both NR and SBR (NR/BR DV and NR/SBR DV) also encounter low scorch during revulcanisation.

10.3.1.4 Revulcanisation of NR and NR-BR blends (buffing dust) devulcanised by different mechano-chemical methods

Since, the issue of low scorch during revulcanisation is found to be associated with both natural and synthetic rubbers and their blends devulcanised by mechanical devulcanisation process, the effect of different industrially practiced mechano-chemical devulcanisation protocols were also investigated.

The revulcanisation cure curves of carbon black filled NR vulcanisates devulcanised by different devulcanisation methods namely, De Link process (De Link) Lev Gum process (Lev Gum), mechanical devulcanisation (DV) and stable free radical assisted devulcanisation (4HT DV) in comparison with the vulcanisation curves of corresponding original compound is given in Figure 10.4a. Similar devulcanisation trials were carried out using commercial buffing dust (Table 2.1) and the revulcanisation cure characteristics was compared with the vulcanisation curve obtained for a tread compound prepared with the formulation of the tread from which buffing dust is obtained   (Figure 10.4b). The revulcanisation cure cuves of a commercial devulcanised rubber prepared using buffing dust was also included in this comparison. The low scorch associated with revulcanisation of the samples devulcanised by different industrial devulcanisation methods such as De Link process and Lev Gum process and that of the commercial devulcanised rubber establish the fact that issue of low scorch is associated with industrial devulcanisation processes also.
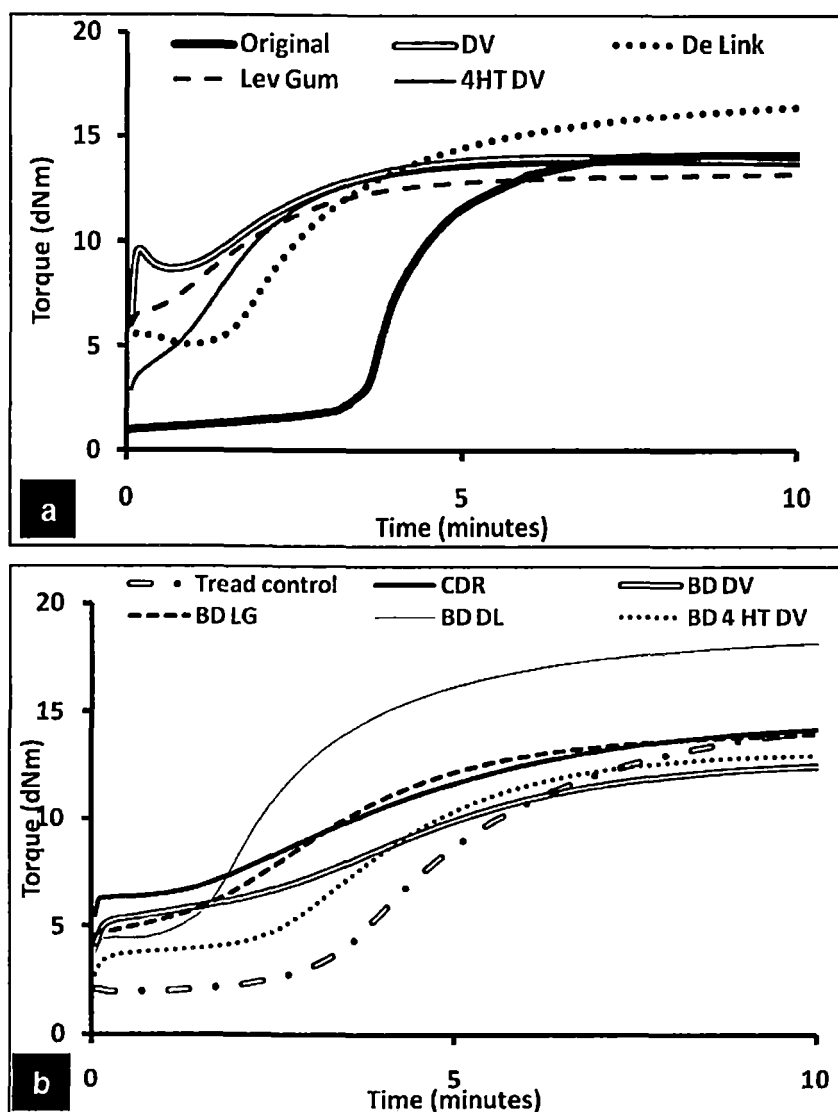
Figure 10.4 Revulcanisation cure curves of **a:** sulphur cured NR vulcanisates devulcanised by different methods in comparison with the original compound; **b:** buffing dust devulcanised by different methods in comparison with CDR and original tread compound

10.3.1.5 *Effect of incorporation of devulcanised rubber in virgin compound*

The effect of incorporation of devulcanised rubber on the scorch characteristics of original compound (Control) is shown in Figure 10.5. CV cured carbon black filled NR vulcanisates (Table 2.3) was mechanically devulcanised and was incorporated into a new compound of similar formulation to form blends of virgin NR and devulcanised rubber in different ratios (85/15; 75/25 and 60/40) and the respective cure curves are plotted.
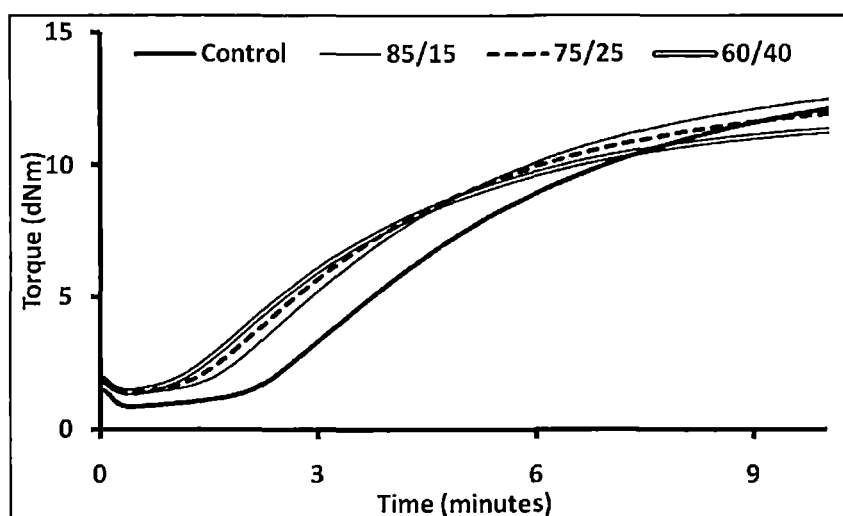
Figure 10.5 Effect of incorporation of devulcanised rubber on scorch time of virgin compound

The figure shows that, the compound in which devulcanised rubber is incorporated is having visibly lower scorch safety than that of the control compound. As the amount of devulcanised rubber in the virgin compound increases, the scorch time reduces proportionately. This indicates that, as the amount of devulcanised rubber in the compound increases, the low scorch effect of the devulcanised rubber influences the cure characteristics of the blend to a greater extend.

10.3.1.6 *Revulcanisation of devulcanised rubbers prepared from peroxide cured samples*

Peroxide cured carbon black filled vulcanisates of NR and EPDM were mechanically devulcanised in a two roll mill and revulcanised. The respective revulcanisation cure curves (NR DCP DV and EPDM DCP DV) in comparison with the revulcanisation cure curves of the mechanically devulcanised corresponding sulphur vulcanised samples (NR S DV and EPDM S DV) are depicted in Figure 10.6. The cue curves of the sulphur cured original samples were also illustrated (NR S and EPDM S).
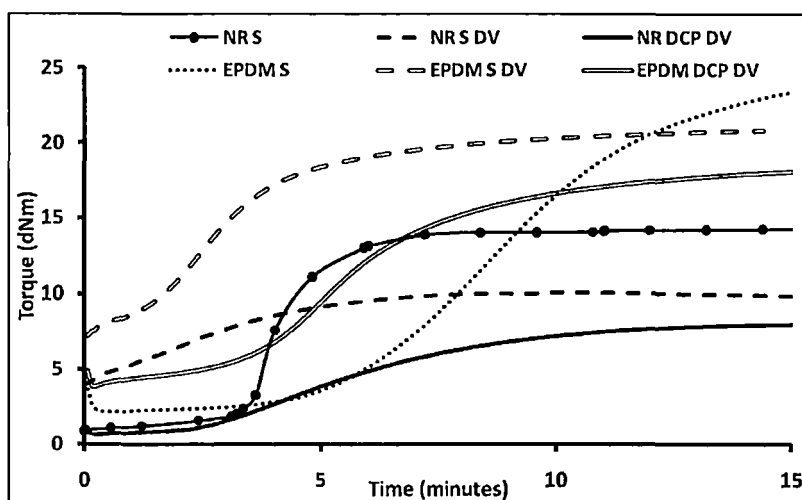
Figure 10.6 Revulcanisation cure curves of DCP cured rubbers in comparison with corresponding sulphur cured samples

Figure 10.6 reveals that, revulcanisation of devulcanised NR and EPDM prepared from peroxide cured samples, using delayed action accelerators preserve the inherent scorch safety of the accelerator system. In other words, the issue of low scorch associated with the revulcanisation of devulcanised rubber is limited to the devulcanised samples which are sulphur vulcanised initially. This observation is similar the previous work reported by Gibala et al[8].

Absence of pre-vulcanisation scorch time associated with peroxide vulcanisation is a universal fact[16,17]. Also, the scorch safety assurance of sulphenamide accelerators is proven[18-21]. Hence, based on these observations and the previous studies on low scorch of devulcanised rubbers, it can be assumed that, the low scorch associated with revulcanisation of devulcanised rubbers is directly related to the sulphur vulcanisation undergone by these rubbers for their initial product life. As already mentioned, several reasons are proposed for the observed low scorch based on previous research[2-8, 22-26] but the issue still remain unsolved and hence revisited.

10.3.2 Analysis of possible causes for low scorch

The various proposed reasons for the low scorch safety associated with the revulcanisation of devulcanised rubbers is systematically analysed in the following sections.

10.3.2.1 Role of residual accelerator derivatives

Residual accelerator derivatives or curatives have been advocated as the reason behind the observed low scorch during revulcanisation of devulcanised rubbers. In agreement with the previous reports[25], it can be observed from the cure curves that, there is no torque reduction associated with the revulcanisation of devulcanised rubbers and the curing starts instantly upon heating. These observations are assigned to be attributed to the presence of crosslink precursors and/ or unreacted curatives in the devulcanised rubber[7]. Another probable reason is cyclic sulphide links formed during the devulcanisation process that can reform into intermolecular crosslinks at revulcanisation temperature[26].

But, the revulcanisation studies of solvent extracted devulcanised rubber by Gibala and Hamed, showed no improvements in the scorch safety during revulcanisation in comparison with the corresponding un-extracted

samples and hence concluded that, active accelerator fragments (which are expected to cause low scorch) in the devulcanised rubber cannot be removed by solvent extraction[8]. This was against the previous suggestion made by Layer that accelerator fragments are not irreversibly bound to the rubber network[27]. Hence it might be assumed that, residual accelerator derivatives and curatives are not the reason behind low scorch of devulcanised rubber or they should exist as non-extractable moieties by being bound to the devulcanised rubber network or in a modified form.

10.3.2.2 Role of zinc bound residual accelerator derivatives

As the scorch limiting agents are non-extractable, there is a possibility for these species to form zinc bound complexes which enables them to remain non extractable and still remain in the matrix and induce low scorch curing during revulcanisation. The role of zinc species in inducing low scorch during revulcanisation was investigated using activator free (ZnO and stearic acid are not used) carbon black filled CV cured NR vulcanisates (Table 2.3). The corresponding cure curves are given in Figure 10.7.

The cure curves depicted in Figure 10.7 indicates the significantly low torque of the original NR vulcanisate cured in the absence of zinc oxide (NR/no ZnO) in comparison with the corresponding vulcanisate cured in the presence of activators (NR with ZnO) are in agreement with the previous reports[28,29]. The higher fraction of residual curatives, and wastefully combined sulphur in the vulcanisate after activator-free curing[27, 30-36] is indirectly reflected as the higher torque attained during revulcanisation of corresponding devulcanised samples (NR/no ZnO DV/no curative and NR/no ZnO DV + curative). On the other hand, the devulcanised sample from NR vulcanisates cured with activators (NR DV/no curative) gave a straight line cure curve except for the initial steep rise when revulcanised in the absence of revulcanising agents.
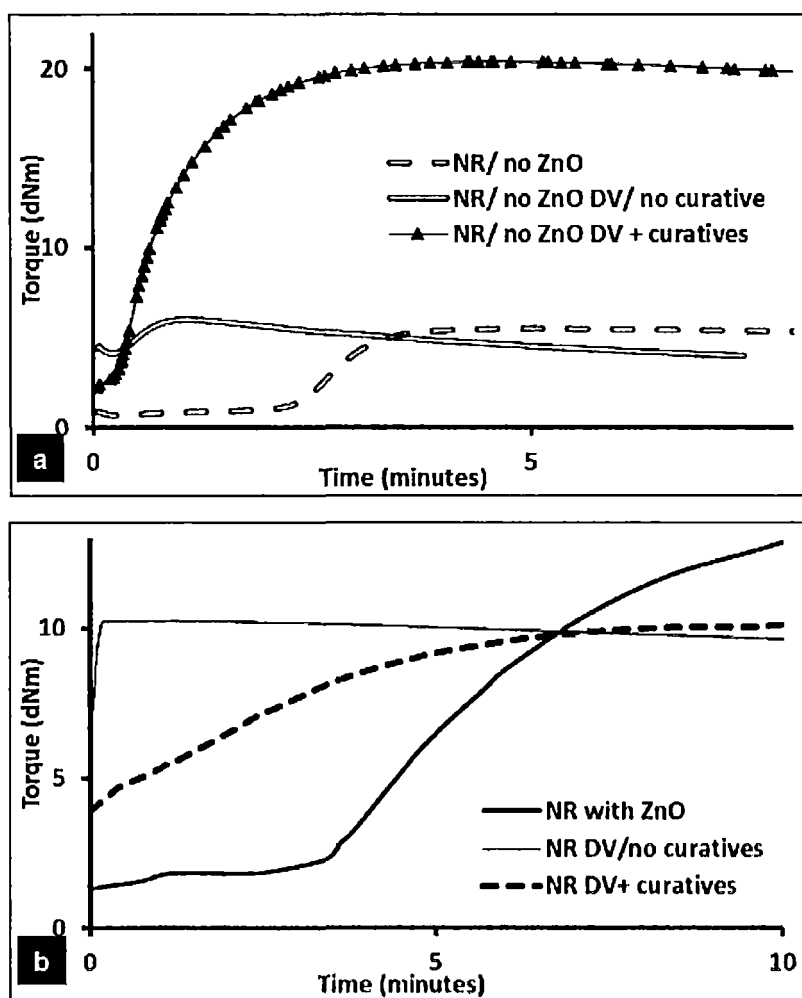
Figure 10.7. Vulcanisation cure curves of NR samples cured **a:** without activators and **b:** with activators and the corresponding revulcanisation cure curves after devulcanisation

The most relevant point to be noted from these cure curves on the context of this chapter is that, all the devulcanised samples in the Figure 9.7 are revulcanised without a pre-vulcanisation scorch period. This suggests that the presence or absence of zinc ions is immaterial in regard with the low

scorch time associated with the revulcanisation of devulcanised rubbers. Hence it might be inferred that the presence or absence of residual accelerators or curatives trapped in the matrix as non-extractable zinc bound moieties are not the reason behind the low scorch times associated with the revulcanisation of devulcanised rubbers.

10.3.2.3 Role of curatives used for revulcanisation

The influence of vulcanisation agents added for the revulcanisation of devulcanised sample upon the scorch time is investigated using devulcanised buffing dust. As already seen, when devulcanised rubber is revulcanised as such, no curing takes place. The effect of different vulcanisation agents and auxiliary chemicals are investigated and it was found that no curing (increase in torque) take place unless accelerator and sulphur is provided.

There are earlier reports supporting this argument that if additional free sulphur is present, cure within the devulcanised sample advances forward, releasing accelerator fragments which will in turn speed up the vulcanisation in matrix[8]. This might be the reason behind the observed increase in torque even when activator-free devulcanised samples with unreacted curatives remaining in the matrix are revulcanised as such. Figure 10.8 illustrates the revulcanisation cure curves of mechanically devulcanised buffing dust in comparison with the vulcanisation curve of similar tread formulation in the presence or absence of various curing agents and auxiliary curing agents.

Figure 10.8 points that the pre-vulcanisation induction time on revulcanisation is significantly shorter than that of the original compound prepared using the tread formulation from which the buffing dust is collected. The cure curves also reveal that, the curatives or auxiliary agents used during revulcanisation do not influence the revulcanisation scorch. This is similar to the observation made by Layer during re-curing of

vulcanisates by swelling in additional curatives into cured networks followed by heating[27]. He observed that added sulphur caused increase in rheometer torque due to further curing of sample without any induction period before cure. Hence, it can be assumed that, low scorch associated with the revulcanisation of devulcanised rubbers is not under the influence of revulcanising agents or due to the devulcanisation process the rubber has undergone.
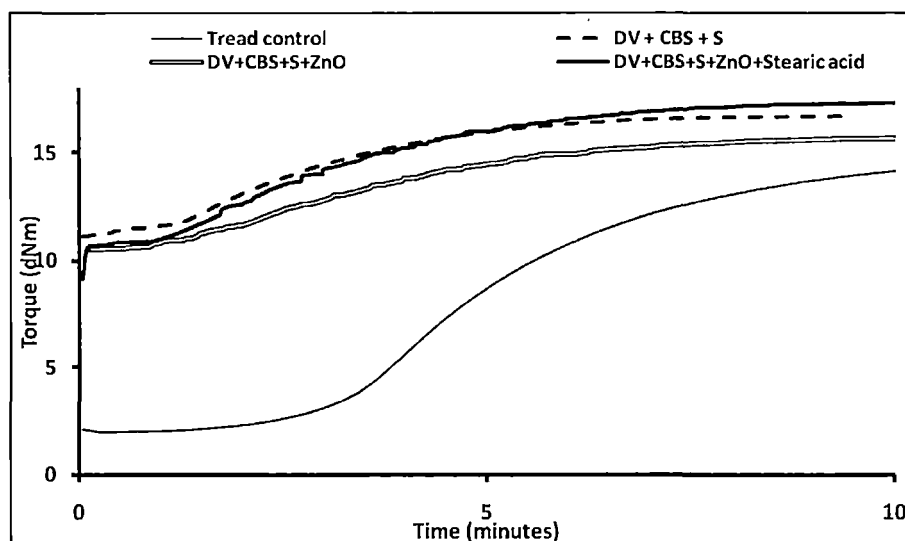
Figure 10.8. Influence of revulcanisation agents on scorch safety of mechanically devulcanised buffing dust

10.3.2.4 Role of crosslink precursors and cyclic sulphide links

Since the chances of residual accelerator moieties, either extractable or non-extractable, influencing the scorch behaviour of devulcanised rubber is ruled out, the role of residual crosslink precursors and cyclic sulphide links have to be investigated. Crosslink precursors are immediate predecessors to crosslinks which get converted to crosslinks once it reach cure temperature[37], while cyclic sulphides will get thermally opened up forming crosslinks[26]. Both these species might be remaining in the

vulcanisate as residual effects of initial vulcanisation attached to the rubber chain[35, 38-40] and the formation of crosslinks from these moieties during revulcanisation is beyond control. The concentration of these species might be supplemented by the devulcanisation process since reactions similar to post crosslinking chemistry are expected to take place during devulcanisation under the influence of shear at ambient conditions[41] but cannot be conclusively stated with the present state of understanding.

10.3.3 Effect of pre-vulcanisation inhibitors during revulcanisation of devulcanised rubber

Provided, the instantaneous crosslink formation from the crosslink precursors (remaining from the initial vulcanisation) is the reason for low scorch time during revulcanisation of devulcanised rubbers,

(i)   Why there is no curing when devulcanised rubber is brought to curing temperatures without adding curatives?

(ii) As crosslink precursors will get converted instantly into crosslinks at curing temperatures, why isn't there a scorch delay corresponding to the accelerator system employed during revulcanisation observed?

(iii) Is there any role for pre-vulcanisation inhibitors (PVI) during the revulcanisation of devulcanised rubbers?

Answers to the first two questions are obtained once the effect of PVI during revulcanisation of devulcanised rubbers was investigated. As we are dealing with the issue of low scorch safety it seems to be judicious to study the effect of pre-vulcanisation inhibitors on revulcanisation. Pre-vulcanisation inhibitors are chemicals that can effectively increase the induction time before actual curing commences, while retaining other aspects of cure such as rate of cure, time to maximum cure, maximum crosslink density etc[42-44]. The effect of incorporation of 0.1phr of N-

(cyclohexylthio) phthalimide (CTP), the most widely used PVI in the revulcanisation formulation of devulcanised buffing dust is illustrated in Figure 10.9.
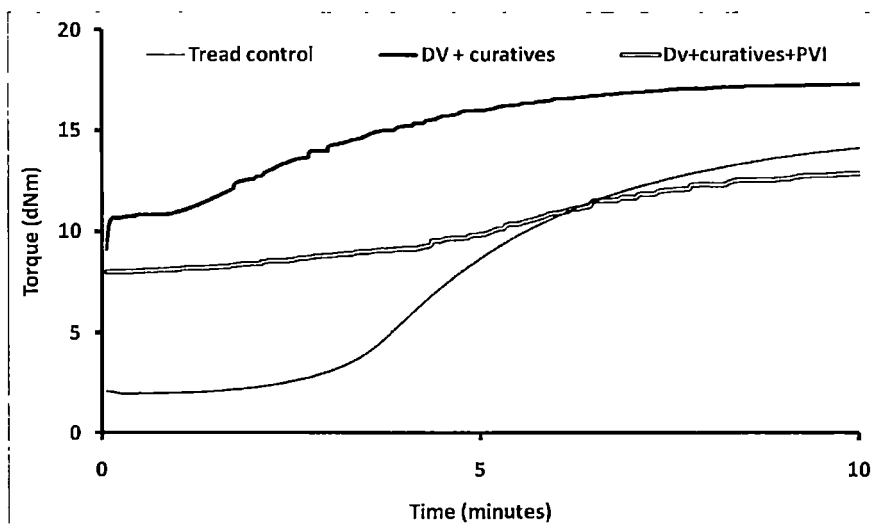
Figure 10.9 Effect of 0.1phr PVI on the revulcanisation of devulcanised buffing dust

The Figure 10.9 shows that, the incorporation of PVI increased the scorch time during revulcanisation of devulcanised buffing dust. After the incorporation of PVI in the revulcanisation formulation, the scorch time characteristic to the sulphenamide cure system is retained.

10.3.4 Probable reason and plausible mechanism for low scorch during revulcanisation of devulcanised rubber

As PVI induced scorch time during the revulcanisation of devulcanised rubber, it can be assumed based on the mechanism of PVI action that, MBT was involved in the low scorch behaviour during revulcanisation. The action of PVI is based on the fact that, MBTS formation is the key step towards crosslinking and hence if its formation can be arrested, the whole crosslinking reaction can be delayed[38]. MBTS

formation is being blocked by CTP by consuming MBT thereby preventing any chance of MBT further reacting with sulphenamides to form MBTS. The presence of MBT during revulcanisation of devulcanised rubber was previously reported[8].

Other questions to be addressed are,

(i)   If MBT is the reason behind low scorch during revulcanisation of devulcanised rubbers, why didn't solvent extraction solve the issue?

(ii)   What is the role of crosslink precursors in regard with the low scorch during revulcanisation of devulcanised rubbers?

The first question suggests the possibility that MBT is not present in the devulcanised rubber system in an extractable free form but is generated *in situ* during revulcanisation process. In such a case, MBT could remain non-extractable and could simultaneously induce low scorch during revulcanisation. The answer to the question regarding the involvement of crosslink precursors lies in the identification of the source for *in situ* generation of MBT during revulcanisation.

The instantaneous steep rise of torque initially during the revulcanisation of devulcanised samples is a general observation during revulcanisation of devulcanised samples. A few researchers have acknowledged this observation[25] while many others have not. The revulcanisation cure curves of devulcanised rubbers in most cases exhibit such an instantaneous steep increase in torque which lies so close to the Y axis of the cure curve so that it almost overlap the torque axis. As the pre vulcanisation scorch period during revulcanisation follows this initial rise in torque, Isayev denoted the induction period during revulcanisation as pseudo induction period[25]. This sudden increase of torque take place instantaneously, once the sample is brought to cure temperatures. As evident from the previous cure curves, this increase is observed even in the

absence of revulcanising curatives. Hence, crosslink precursors and/or cyclic sulphide links present in the devulcanised rubber might be contributing to this instantaneous initial crosslinking and resultant increase in torque.

From the crosslinking chemistry of sulphur vulcanisation, it is observed that MBT is released as a byproduct of crosslink formation[32, 33, 38,45]. The MBT thus released can in turn form MBTS which can lead to further crosslinks in the presence of accelerator and sulphur in the revulcanisation formulation. With each MBT released from each crosslink formed a newer crosslink will be created and thus cure of the vulcanisate will proceed without an induction period as a continuation of the initial increase in torque, provided there is enough curatives in the matrix enabling the conversion of MBT to MBTS. If no free curatives are available in the vulcanisation system MBT generated from the initial crosslink formation from precursors will fail to initiate further crosslinking. This explains the reason behind absence of curing when devulcanised rubber is heated without curatives. In the presence of PVI, the initial instantaneous crosslink formation from precursors still happen, but the MBT released from that reactions will be arrested till whole of the PVI is consumed and thus the rubber get vulcanised with a 'pseudo induction period'. Based on these observations, a probable mechanism for low scorch during revulcanisation of devulcanised rubber is outlined in Figure 10.10.

The crosslink precursors and or cyclic sulphides present in the devulcanised rubber will undergo instantaneous crosslinking at revulcanisation temperatures. This crosslink formation is accompanied by the release of MBT as a byproduct. MBT thus released would catalyze further crosslinking in the presence of curatives provided for revulcanisation, which would eventually result in low scorch during revulcanisation of devulcanised rubber.
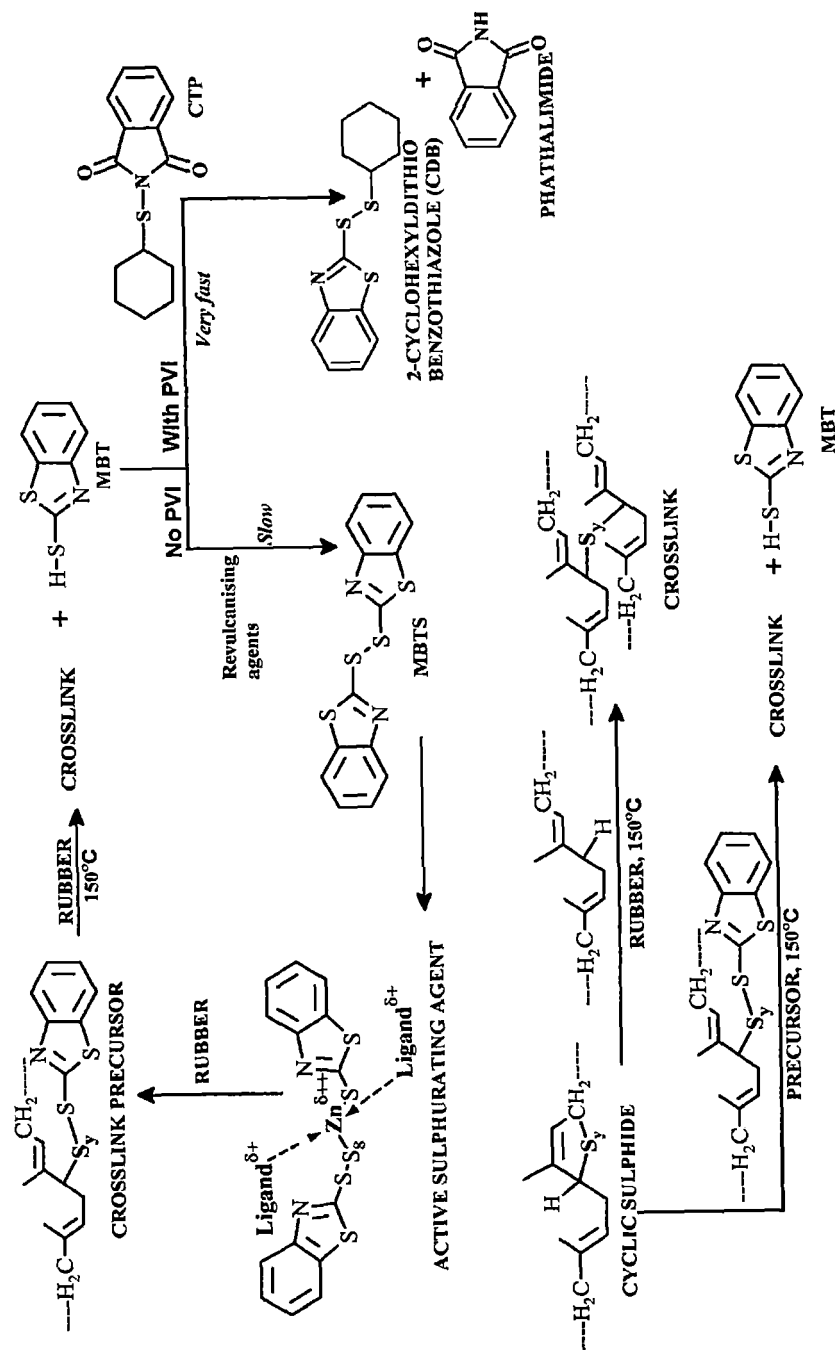
Low scorch during revulcanisation

Figure 10.10 Probable mechanism for low scorch during revulcanisation of devulcanised rubber

Stable free radical assisted devulcanisation

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On the other hand, when PVI is present in the devulcanised rubber during revulcanisation, the MBT released from the initial crosslink formation will be promptly blocked and rendered ineffective towards further crosslinking till whole of the PVI is consumed. Hence, in such cases there could be the instantaneous crosslink formation from crosslink precursors and/or cyclic sulphides present in the devulcanised rubber, but further crosslinking would be under the sole influence of revulcanisation cure system employed. Thus, the revulcanisation of devulcanised rubber could take place with (pseudo)scorch safety corresponding to the accelerator/sulphur system employed for revulcanisation.

10.3.5 Revulcanisation of mechanically devulcanised NR vulcanisate initially cured by TMTD

In order to further substantiate the proposed reason for observed low scorch during revulcanisation of devulcanised rubbers, revulcanisation of TMTD cured mechanically devulcanised NR vulcanisates were carried out under different strategies. As TMTD vulcanisation does not involve the MBT pathway, it is expected that if the proposed mechanism for low scorch holds good, devulcanised NR-TMTD vulcanisates when re-cured using sulphenamide should retain the scorch time characteristic to the sulphur/ sulphenamide system.

Figure 10.11 indicates the revulcanisation cure curves of mechanically devulcanised NR vulcanisates (at 150°C) as such without using any revulcanisation agents. Here two cases were considered (i) the devulcanised rubber was revulcanised as such (NR/TMTD DV) and (ii) the devulcanised rubber was subjected to cold acetone extraction to remove the residual chemicals and the acetone extracted devulcanised rubber was revulcanised (NR/TMTD DV Ace Extd.).

Figure 10.11 Cure curves of mechanically devulcanised TMTD cured NR samples revulcanised without curatives

The revulcanisation cure curves points that, the cure behavior of the devulcanised rubber revulcanised without acetone extraction varied distinctly from that of the acetone extracted sample. The non acetone extracted devulcanised sample showed a scorch less curing with a gradual increase in the torque while, the acetone extracted sample showed marginal increase in torque. This might be accounted to the presence of residual TMTD present in the devulcanised sample in the case of non acetone extracted devulcanised sample. The removal of residual TMTD through acetone extraction possibly eliminated the chance of such crosslinking during revulcanisation which resulted is absence of an initial rising portion in the revulcanisation cure curve of acetone extracted sample.

Since, the non-acetone extracted devulcanised sample revulcanised as such, without any curatives showed low scorch curing similar to cure characteristic of TMTD vulcanisation, it can be assumed that the revulcanisation of such a sample using sulphenamide accelerator will also give low scorch curing owing to the action of residual TMTD and expected

scorch delay cannot be observed. The revulcanisation cure curves of both acetone extracted and non-acetone extracted devulcanised NR-TMTD vulcanisates in the presence of revulcanisation curatives illustrated in Figure 10.12 confirmed this argument.
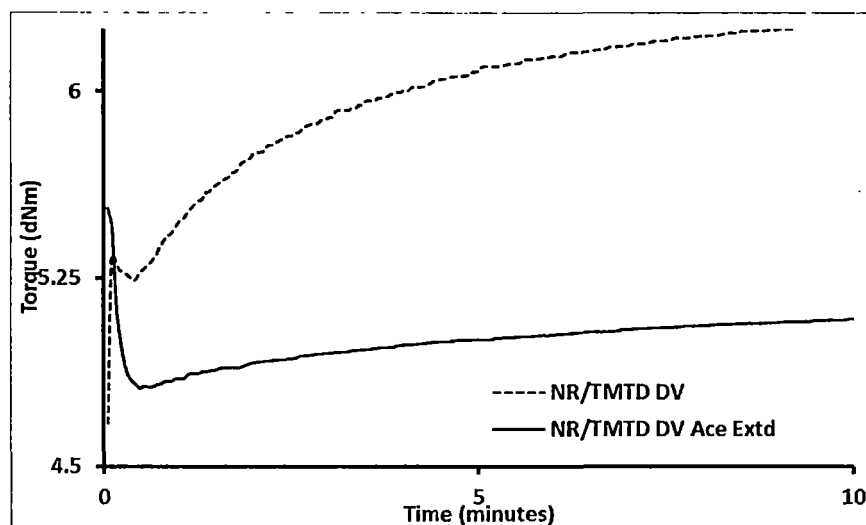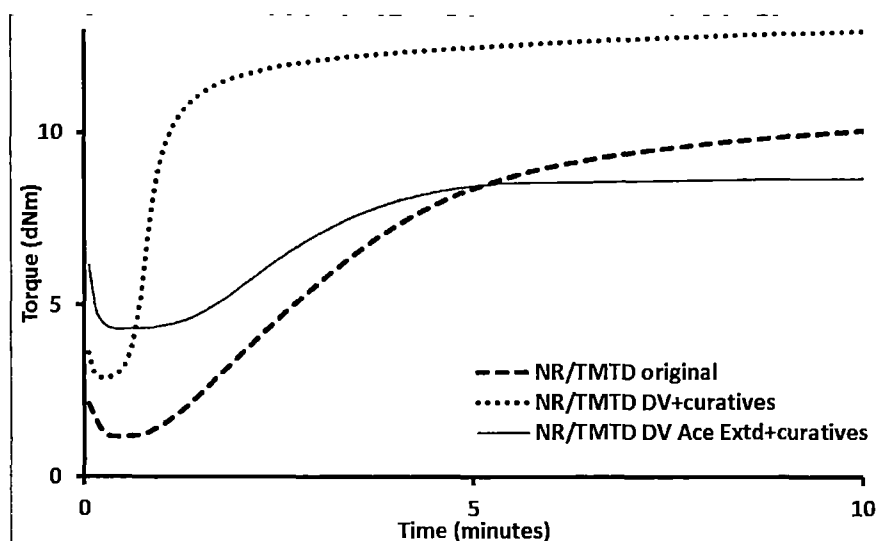

Figure 10.12 Cure curves of mechanically devulcanised TMTD cured NR samples revulcanised with curatives

The revulcanisation cure curve of the non acetone extracted mechanically devulcanised NR-TMTD vulcanisate (NR/TMTD DV + curatives) was steeper than the virgin NR-TMTD vulcanisate (NR/TMTD original) which might be attributed to the combined action of revulcanisation curatives along with the residual TMTD present in the devulcanised rubber. In the case of sample revulcanised after acetone extraction (NR/TMTD DV Ace Extd+curatives), the absence of residual TMTD ensures that, the scorch time characteristic with the sulphenamide accelerator used for revulcanisation was retained.

In this context it might be worth recalling that, the revulcanisation of solvent extracted devulcanised samples from sulphenamide cured vulcanisates did not improved the scorch time. Thus, this observation regarding the devulcanised NR-TMTD vulcanisate upon revulcanisation might be regarded as a confirmation to the proposed mechanism of low scorch during revulcanisation of devulcanised rubbers. As, no MBT is released from the marginal number of crosslinks formed from the crosslink precursors in the devulcanised NR-TMTD vulcanisate, no further crosslinks will be generated on account of the initially formed crosslinks if any and hence the scorch safety of the sulphenamide accelerator used for revulcanisation was preserved.

Figure 10.13 indicates the effect of PVI upon the revulcanisation of devulcanised NR-TMTD vulcanisate. The cure curves indicate that, the scorch time of the non acetone extracted devulcanised sample was not at all affected by the presence of PVI (NR/TMTD DV + curatives +PVI) while, that of the acetone extracted devulcanised sample showed a marginal increase in scorch time owing to the incorporation of PVI(NR/TMTD DV Ace Extd + curatives+ PVI). The absence of improvement in scorch time of non acetone extracted devulcanised sample is due to the fact that, the low scorch associated with this sample during revulcanisation is attributed to the crosslink formation by residual TMTD from the original vulcanisate which cannot be checked by PVI as the process does not involve MBT species. Residual TMTD continue to from crosslinks which will be carried forward by the sulphenamide accelerator in due time. The scorch time characteristic to sulphenamide accelerator could not be observed as residual TMTD ensures crosslink formation at the early stage of revulcanisation.

In the case of devulcanised NR-TMTD vulcanisate revulcanised after acetone extraction, no residual TMTD will be present in the devulcanised sample to drive crosslinking during the initial stages of

revulcanisation, and hence crosslink formation would be under the influence of sulphenamide accelerator provided in the revulcanisation formulation. Hence cure curve characteristic to sulphenamide accelerator with a pre-vulcanisation induction time was observed which was improved by PVI.
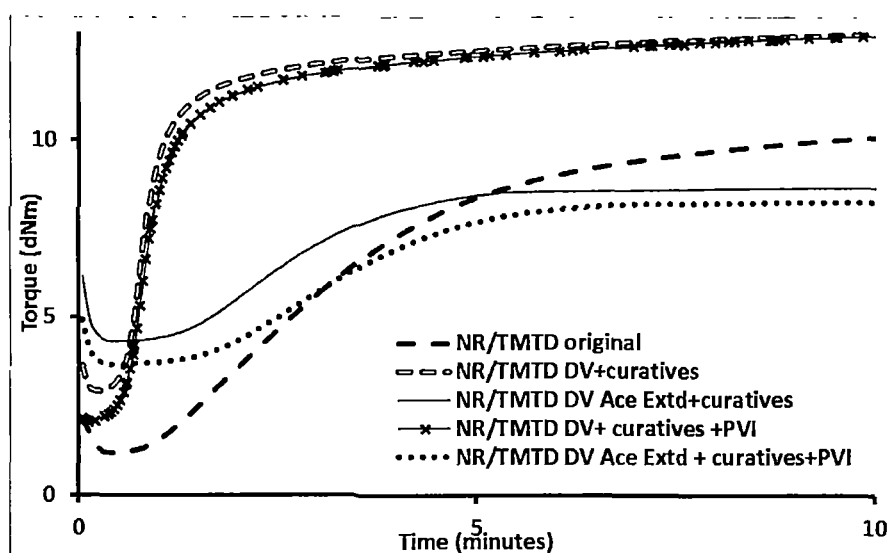
Figure 10.13 Cure curves of mechanically devulcanised TMTD cured NR samples revulcanised with curatives and PVI

However, it is worth remembering that, instantaneous crosslink formation via the existing crosslink precursors from initial TMTD curing, followed by the release of dimethyl dithiocarbamic acid (DMDCA) and/or thiurampersulphenyl anion or related species[35, 38, 46, 47] that can potentially initiate further crosslinks (in the presence of sulphur and/or TMTD) and scavenge the scorch time just like MBT is a possibility in this case also. But it was observed that, the revulcanisation of devulcanised TMTD cured NR vulcanisates after acetone extraction using CBS/sulphur system proceeded with scorch safety while that without acetone extraction cured without a pre-vulcanisation induction time. Correlating both these conditions, it might be

assumed that, the number of residual crosslink precursors remaining in the vulcanisate after initial TMTD curing must be nil or negligibly small, that the byproducts of the crosslink formation from these moieties could not interfere detrimentally with the scorch safety assured by the CBS/sulphur system used for revulcanisation of these devulcanised samples. Hence, scorch safety is assured when TMTD cured devulcanised samples were revulcanised using CBS/sulphur system after acetone extraction, but absent when revulcanised without acetone extraction. On the other hand, since when TMTD is used as an accelerator in the presence of sulphur, the degree of crosslinking would be proportional to the sulphur content and accordingly, the cure system might shift to an inefficient one[49]. In such cases chances are high that, the number of residual crosslink precursors in the devulcanised samples might be high and they might lower scorch safety during the revulcanisation of these samples after devulcanisation as in the case of sulphur cured rubbers.

10.3.6 Incorporation of devulcanised rubber in virgin compound

Thus, the issue of low scorch associated with the revulcanisation of devulcanised rubbers can be tackled by including low amounts of PVI in the revulcanisation formulation. Figure 10.14 represents the revulcanisation cure curves of devulcanised buffing dust under different conditions. As previously observed, the incorporation of PVI improved the scorch time of devulcanised buffing dust during revulcanisation (DV+curatives+PVI) in comparison with the corresponding sample revulcanised without PVI (DV+curatives). On the other hand, scorch time of the similar devulcanised sample blended with 10g NR per 100g devulcanised rubber (DV+NR+curatives+PVI) was less than the former when revulcanised in the presence of same amount of PVI. When excess PVI was incorporated during revulcanisation (DV+NR+curatives+Xs PVI), the scorch time improved significantly.
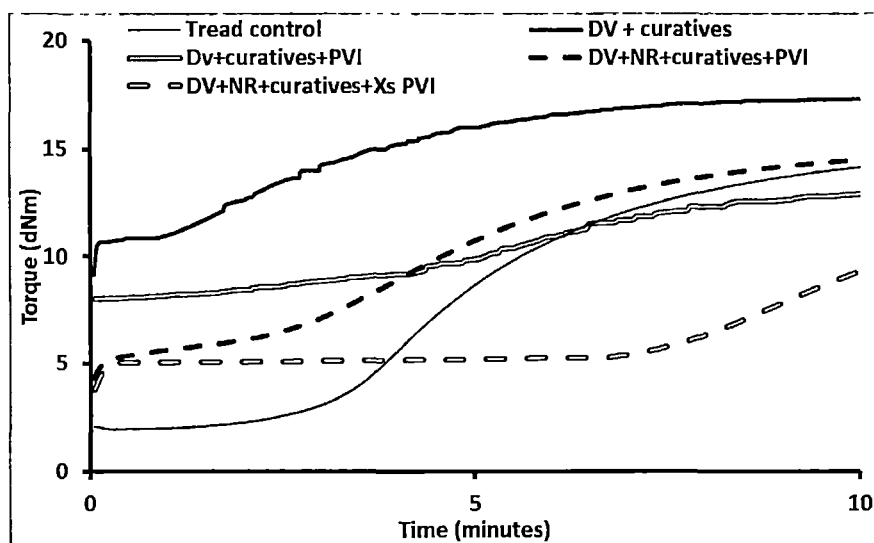
Figure 10.14 Effect of virgin rubber on the action of PVI during revulcanisation of devulcanised buffing dust

In the presence of virgin rubber, the effect of PVI is reduced, but when excess PVI is added the induction time is restored. These observations indicate that, when devulcanised rubber is incorporated into a matrix of virgin rubber, the volume of the compound increased though the amount of devulcanised rubber is the same. Hence, the availability of PVI per unit volume of the compound reduced and the efficiency of inducing scorch delay by blocking MBT reduced. When excess PVI is present in the system, PVI concentration around the proximity of each devulcanised rubber particle will be maintained and hence scorch time returns.

The studies conducted by Layer on a second round curing of NR vulcanisates after swelling in sulphur[27], cure characteristics of SBR/ground rubber vulcanisate blends[8] by Gibala and Hamed and the observations from present study points to the fact that, powdering of rubber vulcanisates and/or devulcanisation processes have no role on the low process safety of these materials, but it is inherent to the accelerated sulphur vulcanisation

chemistry. Thus, the issue of low scorch associated with the revulcanisation of devulcanised rubber (DVR) or the reduced scorch safety when ground rubber vulcanisates is blended with fresh rubber compound are not *per se* associated with these materials but is solely related to the cure system used for the preparation of the original sample from which these materials (DVR & ground rubber vulcanisates) are sourced.

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Chapter 11

Summary and Conclusions

11.1 Introduction

Devulcanisation of carbon black filled rubber vulcanisates through mechanical/ mechano-chemical processes in a two-roll mill is a well-established technique. Though several devulcanisation agents have been used to devulcanise cured rubbers, the similarity in mode of action and the comparable accomplished revulcanisate properties obtained by various mechano-chemical devulcanisation methods were not critically evaluated. Also, the capability of thus claimed devulcanising agents in targeted crosslink cleavage and subsequent radical stabilization under ambient conditions seems doubtful. Comparison of the mechanical devulcanistion with industrially practiced mechanochemical devulcanisation processes gave comparable revulcanisate properties. Hence it was assumed that, any shear induced devulcanisation process should be a dynamic process in which crosslink breaking and reformation are competitive and any chemical/process which can effectively and instantaneously block the recombination of the radicals formed can significantly improve the devulcanisation process. The novelty of this work is that the issue of recombining of the radicals formed by crosslink scission and consequent reformation of once cleaved crosslinks was addressed by the addition of a stable free radical which can instantaneously and effectively block the radical recombination under ambient conditions thereby substantially increasing the per cent devulcanisation.

Though direct experimental evidence to prove the reaction between sulphur radical generated by crosslink scission and the stable free radical, 4-Hydroxy TEMPO, leading to arresting the recombining of broken crosslink

moieties could not be presented, indirect evidence like significant reduction in residual crosslink density, especially the large reduction of residual polysulphidic crosslinks in 4HT assisted devulcanisation, with corresponding substantial improvement in revulcanisate properties point towards the strong possibility of such a reaction. The reaction between sulphur free radicals generated by the scission of thiols and disulphides with stable free radicals are already reported. Various factors like type of rubber, the rubber blend ratios, cure system and crosslink density of the original sample, amount and type of filler used, the extend of ageing undergone by the sample, *etc.* can influence the devulcanisation efficiency and the subsequent revulcanisate properties.

The cure system and hence the crosslink distribution pattern of the sample to be devulcanised is found to play an important role in the per cent devulcanisation. The per cent devulcanisation obtained by mechanical devulcanisation of CV, semi EV and EV samples were about 21per cent, 36per cent and 41per cent respectively which became 72per cent, 79per cent and 81per cent respectively with the incorporation of optimum amount of 4HT during devulcanisation. Incorporation of 4HT, not only increased the per cent devulcanisation substantially but led to comparable per cent devulcanisation of the three types of samples. It is interesting to note that, EV cured NR samples gave significantly higher level of per cent devulcanisation than the CV and semi EV cured samples, irrespective of the fact that, the amount of polysulphide bonds with lower bond energy (easy scission) was lowest for EV samples. On the other hand, the highest increase in per cent devulcanisation upon 4HT incorporation was achieved by CV cured samples having highest number of polysulphidic crosslinks. The crosslink distribution studies also confirmed that, the residual crosslink density of devulcanised samples is predominantly determined by the cleavage of majority crosslink type; *i.e.* polysulphidic crosslinks in CV and

semi EV samples while disulphidic crosslinks in EV sample. These inferences tend us to believe that, not only the bond energy of the crosslink type to be cleaved but the recombining capacity of the broken crosslinks might also play a decisive role in determining the per cent devulcanisation.

Mechanical devulcanisation of NR vulcanisates filled with very small and very large sized carbon black fillers are found to be more difficult than those vulcanisates with intermediate sized carbon black fillers. One notable observation is that, in 4HT assisted devulcanisation of carbon black filled natural rubber, irrespective of the particle size of the carbon black filler used for the reinforcement of NR, the revulcanisate properties of the devulcanised rubber obtained was comparable with the original vulcanisate properties of the GPF filled NR vulcanisate. Studies on the effect of HAF content of the original sample upon devulcanisation efficiency also revealed that the revulcanisate properties of the 4HT assisted devulcanised samples were significantly higher than that of the corresponding mechanically devulcanised samples.

Based on the minimum torque of the devulcanised samples which is indirectly related to the viscosity of the sample, it was observed that similar level of devulcanisation of was attained by the various NR/BR blends upon mechanical devulcanisation irrespective of the BR content in the blend whereas 4HT assisted devulcanised samples attained a higher per cent devulcanisation indicated by a lower minimum torque. The revulcanisate tensile properties of the 4HT assisted devulcanised blends were significantly higher than the corresponding mechanically devulcanised samples whereas the positive influence of 4HT upon the tear strength of revulcanised samples significantly reduced with increase in BR content of the blend. The per cent retention of vulcanisate properties also indicates that, the efficiency of devulcanisation dropped with increase in the BR content in the NR/BR blend. The influence of cross link density and the cure system used for the

preparation of the original blend sample on the efficiency of devulcanisation and the revulcanisate properties point towards the possibility of formulating the rubber compounds not only to attain the property requirements during their service life but the ease of devulcanisation after their use also.

The 4HT assisted devulcanisation of commercial used rubber samples like buffing dust and GTR proposed the feasibility of stable free radical as an effective devulcanisation aid in the real world scenario also. The factory-scale trials carried out using buffing dust further substantiated this point. The revulcanisate properties of the buffing dust and GTR devulcanised with the assistance of 4HT were higher than those obtained for the corresponding mechanically devulcanised sample. The revulcanisate properties of GTR were lower than that of buffing dust indicating the role of quality of sample (effect of ageing) used for devulcanisation upon the revulcanisate properties.

The issue of low scorch during revulcanisation of devulcanised samples were also addressed and the results obtained confirmed that the powdering of rubber vulcanisates and/or devulcanisation processes have no role on the low process safety associated with these materials during revulcanisation, but it is inherent to the accelerated sulphur vulcanisation chemistry and the cure system used for the preparation of the original sample from which these materials are sourced.

11.2 Mechanical devulcanisation of NR vulcanisates

Though, devulcanisation and incorporation of devulcanised rubber in virgin compounds were studied in the past, the effects of incorporation of samples devulcanised by a simple mechanical devulcanisation in a laboratory two-roll mill were not investigated, particularly devulcanised rubber prepared from vulcanisates of known composition and properties. The incorporation of devulcanised samples into fresh natural rubber in three

different ratios *viz.* 85/15, 75/25 and 60/40 was carried out and the effect of blending as well as the influence of amount of filler added on vulcanisate properties was studied. The devulcanisation of samples aged in air oven and incorporation of the same in virgin blends and subsequent evaluation of vulcanisate properties were carried out to simulate real world status.

It was observed that the revulcanisate properties of the devulcanised samples prepared from aged original samples were lower than that obtained for devulcanised sample prepared from un-aged original vulcanisate though the residual crosslink densities of the former was lower (Figure 11.1). This indicates that the higher main chain degradation of the devulcanised samples (imparted by ageing/devulcanisation conditions) led to a calculated lower residual crosslink density which might be misleading while ascertaining the efficiency of devulcanisation.
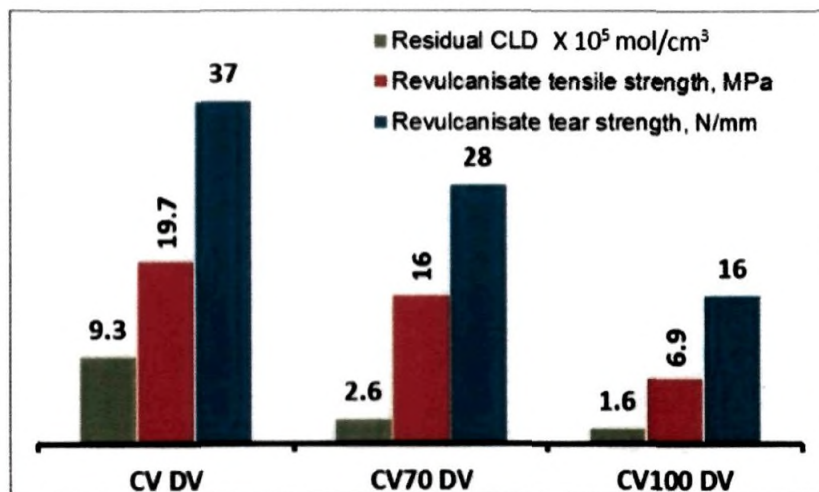

Figure 11.1 Residual crosslink density and revulcanisate properties of mechanically devulcanised samples

Another observation worth noticing is the comparable revulcanisate tensile strength of samples devulcanised from un-aged CV vulcanisate and that aged at 70°C irrespective of significant difference in residual crosslink

densities. On the other hand, the revulcanisate tensile strength of devulcanised samples prepared from CV vulcanisates aged at 100^0C was significantly lower. But, the revulcanisate tear strength tend to follow the pattern corresponding to the level of degradation of original vulcanisate from which they were devulcanised (*i.e.* un-aged>.aged at 70°C> aged at 100°C). Hence, it might be accorded that, the revulcanisate tensile properties of devulcanised samples could be comparable for samples with a large range of per cent devulcanisation and level of degradation while, tear strength of the revulcanisates are highly sensitive towards the changes in level of devulcanisation and/or degradation.

The trends observed while blending mechanically devulcanised rubber with fresh natural rubber in different ratios with and without applying filler correction were evaluated in comparison with a control NR vulcanisate which does not contain devulcanised rubber (Fig 11.2). The hardness and heat build-up of the NR/DVR blends with an applied filler correction is comparable with the control compound whereas it increased with the amount of the devulcanised rubber if filler correction is omitted. The tensile strength showed a systematic reduction as the amount of devulcanised rubber content in the blend was increased and was not significantly influenced by the filler amount at lower blend ratios. Though tear strength also showed a systematic decrease with the increase in devulcanised rubber content in the blend, the tear strengths of the blends without filler correction were significantly higher in comparison with the corresponding blends with an applied filler correction. Abrasion loss was higher at the lower blend ratio (85/15) in the absence of filler correction whereas it remained comparable or lower at higher blend ratios. With the incorporation of highly degraded devulcanised samples (prepared from 100°C aged CV vulcanisates) absence of filler correction was found to be advantageous.
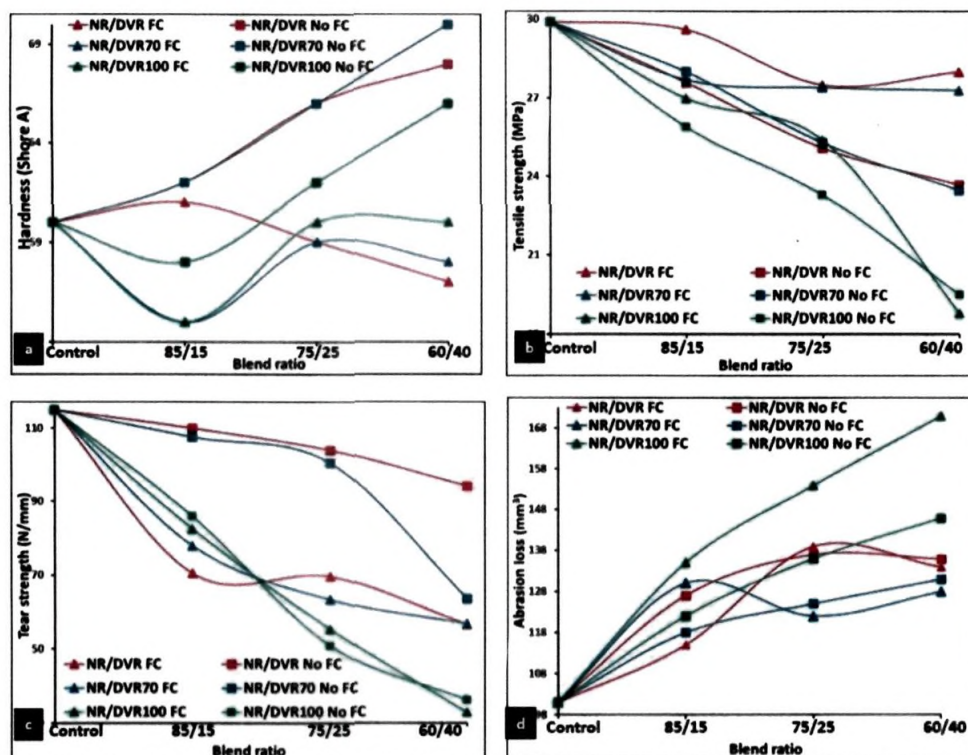
Figure 11.2 a: Hardness **b:** tensile strength **c:** tear strength and **d:** abrasion loss of blends of virgin NR and mechanically devulcanised NR

The vulcanisate properties obtained by the incorporation of mechanically devulcanised rubber in fresh compounds, variation in the properties due to the filler effects and ageing studies of these blends open a promising way of incorporating more amounts of devulcanised rubber in newer products with the in house facilities of any production unit.

11.3 Stable free radical assisted mechanical devulcanisation of NR vulcanisates

Comparison of various mechano-chemical devulcanisation processes with mechanical devulcanisation carried out in the present work led to the assumption that, the actual devulcanising agent in mechano-chemical devulcanisation is the shear force and not the chemical. Since these

chemicals did not play any role in either chemically breaking the cross links or preventing the recombining of broken crosslink moieties, a new concept of adding stable free radical which can prevent the recombining of free radicals generated by crosslink scission was introduced. A plot of change in per cent devulcanisation of NR samples by the incorporation of 1phr 4HT as a devulcanisation aid and the changes in absolute values of revulcanisate properties of corresponding samples are represented in Figure 11.3.
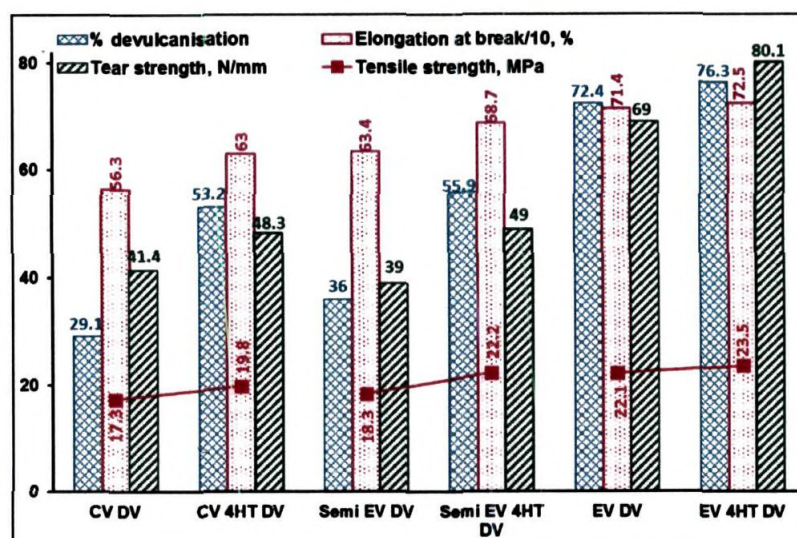

Figure 11.3 Effect of stable free radical (1phr 4HT) on per cen devulcanisation and revulcanisate properties of NF vulcanisates

The incorporation of 4HT as a devulcanisation aid increased the percent devulcanisation which was positively reflected in the revulcanisate properties. The per cent devulcanisation of devulcanised samples varied with the cure system used for vulcanisation of original samples with corresponding variation in revulcanisate properties. The per cen devulcanisation of the samples devulcanised by both methods followed the order CV < semi EV < EV whereas the initial crosslink density of the virgin vulcanisates decreased in the same order. It might be accorded that, the

crosslink density of the sample to be devulcanised might also play decisive role in the per cent devulcanisation and there by the revulcanisate properties of devulcanised samples. The notable observation is that stable free radicals can act as effective devulcanisation aid for mechanical devulcanisation.

11.4 Effect of stable free radical concentration on mechanical devulcanisation

The effect of stable free radical concentration on the required minimum numbers of passes through tight nip for devulcanisation of NR vulcanisates and its correlation with per cent devulcanisation is plotted in Figure 11.4.

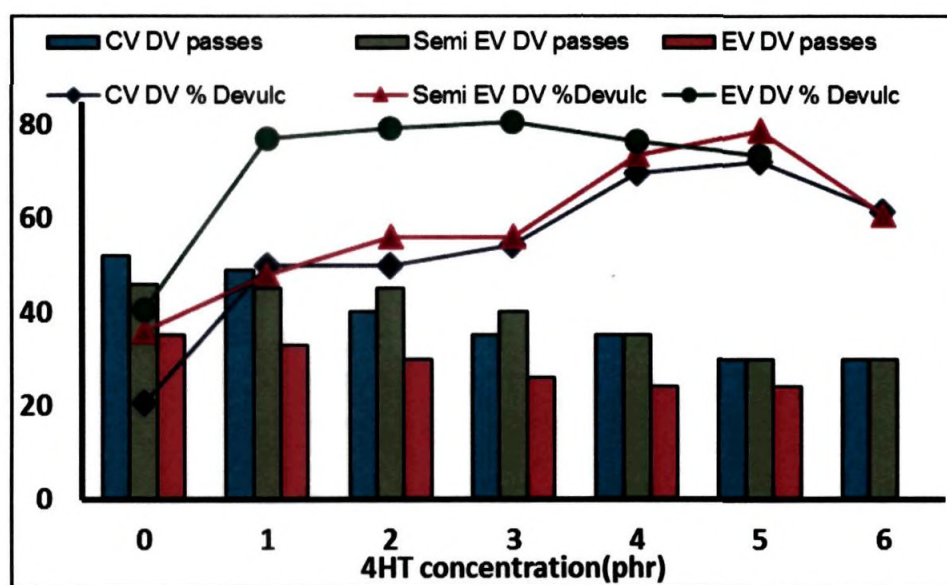**Figure 11.4** Effect of stable free radical concentration on required number of passes for devulcanisation and per cent devulcanisation

The number of passes required for devulcanisation lowered with increase in 4HT concentration up to an optimum concentration. The increase in per cent devulcanisation along with lowering of number of passes with increasing 4HT concentration indicates effective and efficient

devulcanisation which again is reflected as higher revulcanisate properties of the devulcanised samples as observed from Figure 11.5.
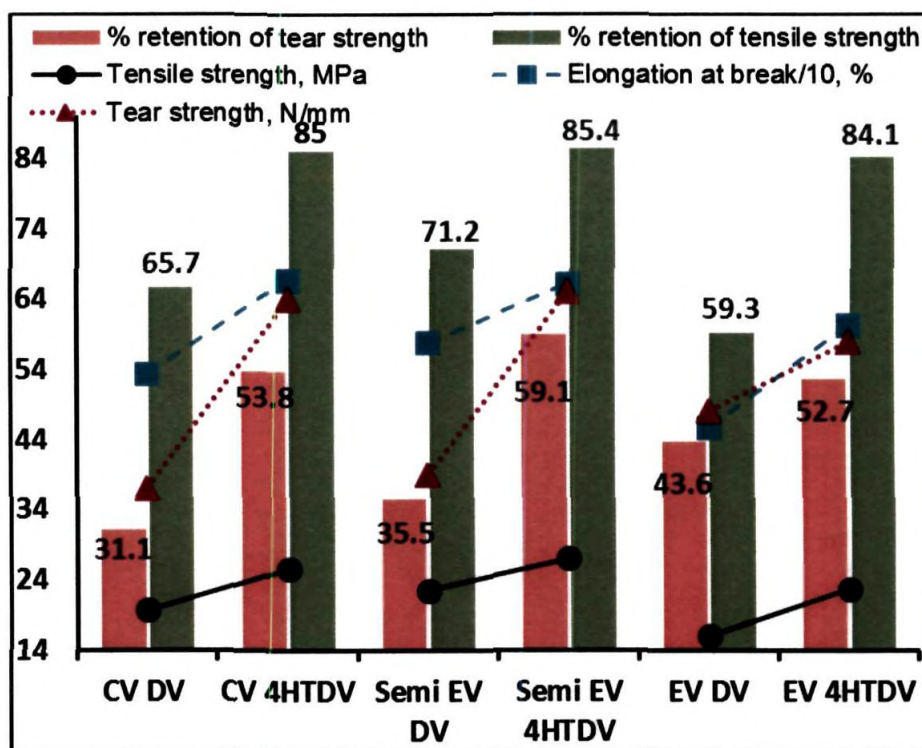

Figure 11.5 Comparison of revulcanisate properties and per cent retention of original properties of mechanically and 4HT assisted (optimum amount) devulcanised NR samples

The figure clearly points to the higher influence of 4HT upon the tear strength over the tensile properties irrespective of the higher per cent retention of tensile strength than tear strength on revulcanisation. The tear strength of the revulcanisate is more influenced by the efficiency of devulcanisation than tensile strength in carbon black filled NR vulcanisates. The results indicates that, mechanical devulcanisation alone can bring about 20-40per cent devulcanisation which is well enough to retain 60-70per cent of the original tensile properties but only with 30-43 per cent retention of original tear properties. With the use of stable free radical as a

devulcanisation aid, the per cent devulcanisation increased up to 70-80 percent with a simultaneous increase in per cent retention of tensile strength to 85per cent and tear strength to 53-59per cent.

11.5 Comparison of stable free radical assisted devulcanisation with contemporary mechano-chemical devulcanisation processes

Based on the above experimental results, a direct comparison of stable free radical assisted devulcanisation and the current industrially practiced mechano-chemical devulcanisation was carried out (Figure 11.6).
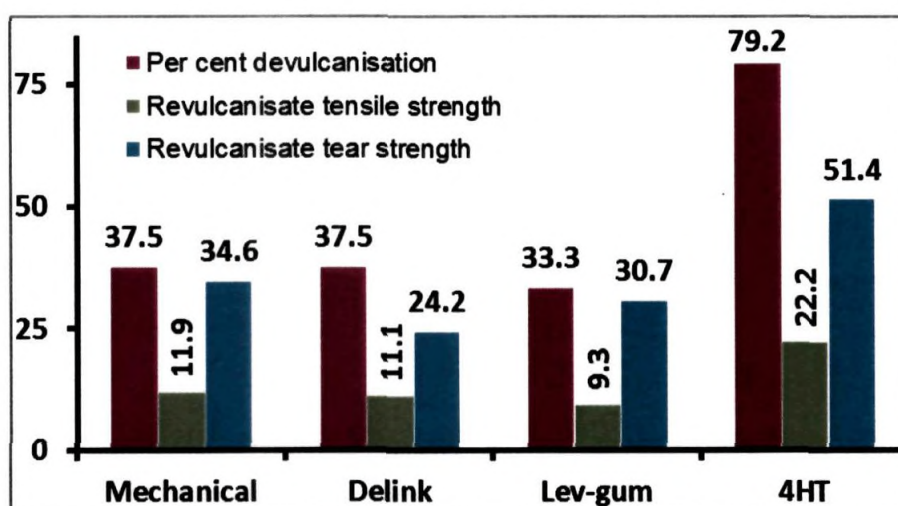

Figure 11.6 Per cent devulcanisation and corresponding revulcanisate properties of NR samples devulcanised by different methods

Figure 11.6 clearly indicates that, the contemporary industrial mechano-chemical devulcanisation processes like De Link process and Lev Gum process gives comparable results with mechanical devulcanisation while 4HT assisted devulcanisation of the same sample gave significantly higher per cent devulcanisation with correspondingly higher revulcanisate properties. These observations suggests that, in currently practiced industrial mechano-chemical processes, targeted crosslink scission and broken crosslink stabilization by the chemicals used as devulcanisation agents are

less likely to happen. The similar crosslink distribution pattern of the samples devulcanised both by mechanical devulcanisation and commercial mechano-chemical devulcanisation processes further confirmed this.

11.6 Plausible mechanism of stable free radical assisted mechanical devulcanisation

The results of the chemical probe analysis of the original and devulcanised CV, semi EV and EV samples devulcanised with and without the assistance of stable free radical provide an understanding of the nature of bond scission involved during devulcanisation to propose the probable mechanism involved. The crosslink distribution pattern after shear induced devulcanisation in a two-roll mill suggested the following behaviour of polysulphidic crosslinks and disulphidic crosslinks as given in Figure 11.7 and Figure 11.8.

The chemical probe analysis of the devulcanised samples showed that mechanical shearing predominantly break the majority crosslink type (polysulphidic crosslinks in CV and semi-EV cure systems while disulphidic crosslinks in EV samples). In addition, polysulphidic crosslinks in vulcanisates undergo chain shortening reactions under shear at ambient conditions similar to the post-crosslinking reactions during curing temperatures. This is indicated by an increase in the absolute value of mono-sulphidic crosslinks of the devulcanised samples over that of the corresponding virgin vulcanisates.

On the other hand, significant reduction in total crosslink density by the breaking of majority crosslinks will give resultant devulcanisation. During mechanical devulcanisation of CV and semi EV samples, the per cent reduction of polysulphidic crosslinks (majority crosslink type) is lesser than that of disulphidic bonds. But in the presence of 4HT, the percent of polysulphidic bond cleavage increased substantially while that of the per cent cleavage of disulphidic bonds remained comparable to the former case

resulting in the higher per cent devulcanisation for 4HT assisted devulcanisation.
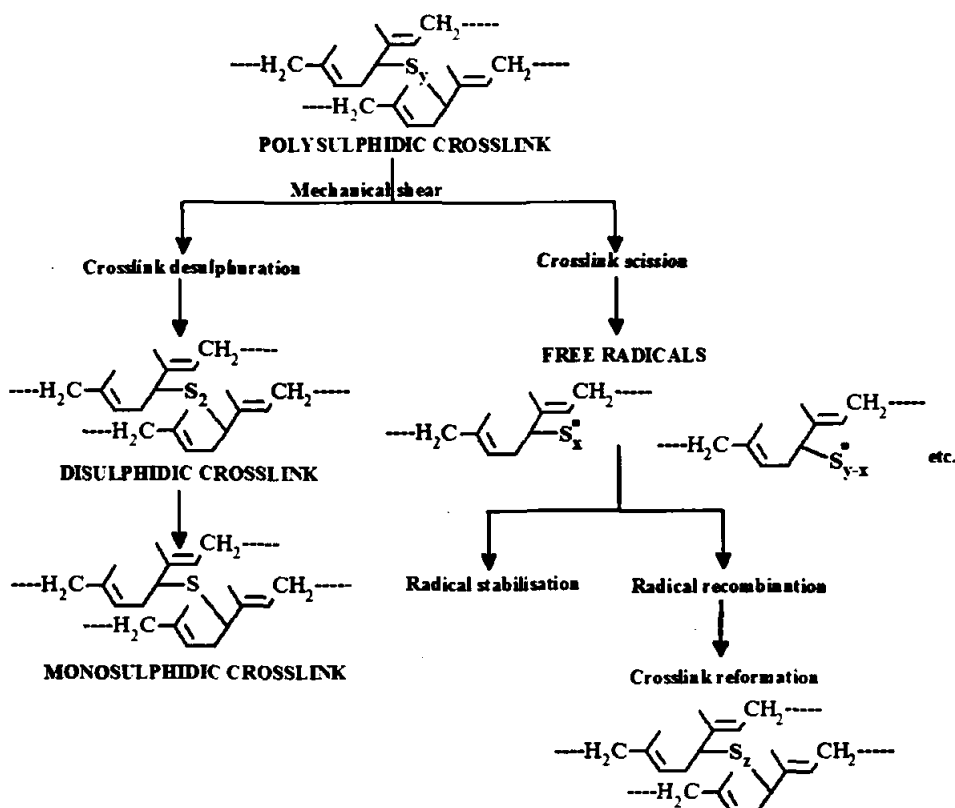
Figure 11.7 Behaviour of polysulphidic crosslinks during devulcanisation in a two-roll mill

Mechanical devulcanisation of EV samples increased the absolute value of polysulphidic links, indicating the possibility of re-crosslinking of cleaved bonds which is not observed with 4HT assisted devulcanisation suggesting the probable stabilization of broken crosslink fragments. No such increment is observed in mechanical devulcanisation of CV and semi EV samples were polysulphidic crosslinks comprises the majority share perhaps

due to the higher number of cleaved polysulphidic bonds than those formed by recombination. In addition, the large difference in the percent cleavage of polysulphidic bonds in the absence and presence of 4HT favours this assumption.
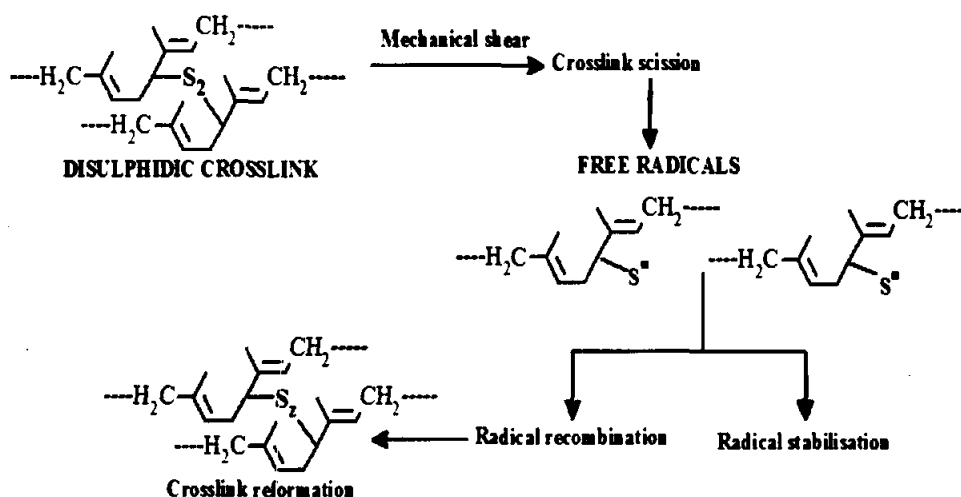

Figure 11.8 Behaviour of disulphidic crosslinks during devulcanisation in a two-roll mill

In short, crosslink cleavage will result in efficient devulcanisation only if the crosslink fragments formed by crosslink scission were stabilized and thus prevented from recombining. Or else, they recombine to form new crosslinks resulting in low net cleavage of crosslinks and hence lower per cent devulcanisation. In all cases under present work, 4HT is found to effectively stabilize broken crosslinks thereby increasing the per cent devulcanisation.

11.7 Influence of filler type and filler content on devulcanisation of NR vulcanisates

The role of carbon black filler type and amount of filler present in the virgin NR vulcanisates on the devulcanisation efficiency and

revulcanisate properties were investigated. The plot of per cent retention of vulcanisate properties of NR vulcanisates containing different types of carbon blacks along with corresponding revulcanisate properties is given in Figure 11.9.

Though the per cent devulcanisation were comparable, the revulcanisate tensile properties tended to decrease with increasing particle size of the filler in the case of mechanically devulcanised samples whereas, it remained comparable for all samples after 4HT assisted devulcanisation. Though the revulcanisate tear strength of the samples were comparable, the per cent retention of tear strength after revulcanisation increased with increase in the size of filler present in the vulcanisate both in the case of mechanical and 4HT assisted devulcanisation. This might be attributed to the fact that, the revulcanisate tear strength attainable after devulcanisation might almost be a constant and lowering of tear strength with increasing size of filler present in the virgin vulcanisate magnified the per cent retention after revulcanisation as the particle size of the filler increased.

The revulcanisate properties of devulcanised NR vulcanisates with HAF loading varying from 20phr to 60phr are given in Figure 11.10. All revulcanisate properties were better with 4HT assisted devulcanised samples. The revulcanisate tensile strengths were comparable both in the case of mechanical and 4HT assisted devulcanisation within the group while elongation at break lowered with increasing filler content.
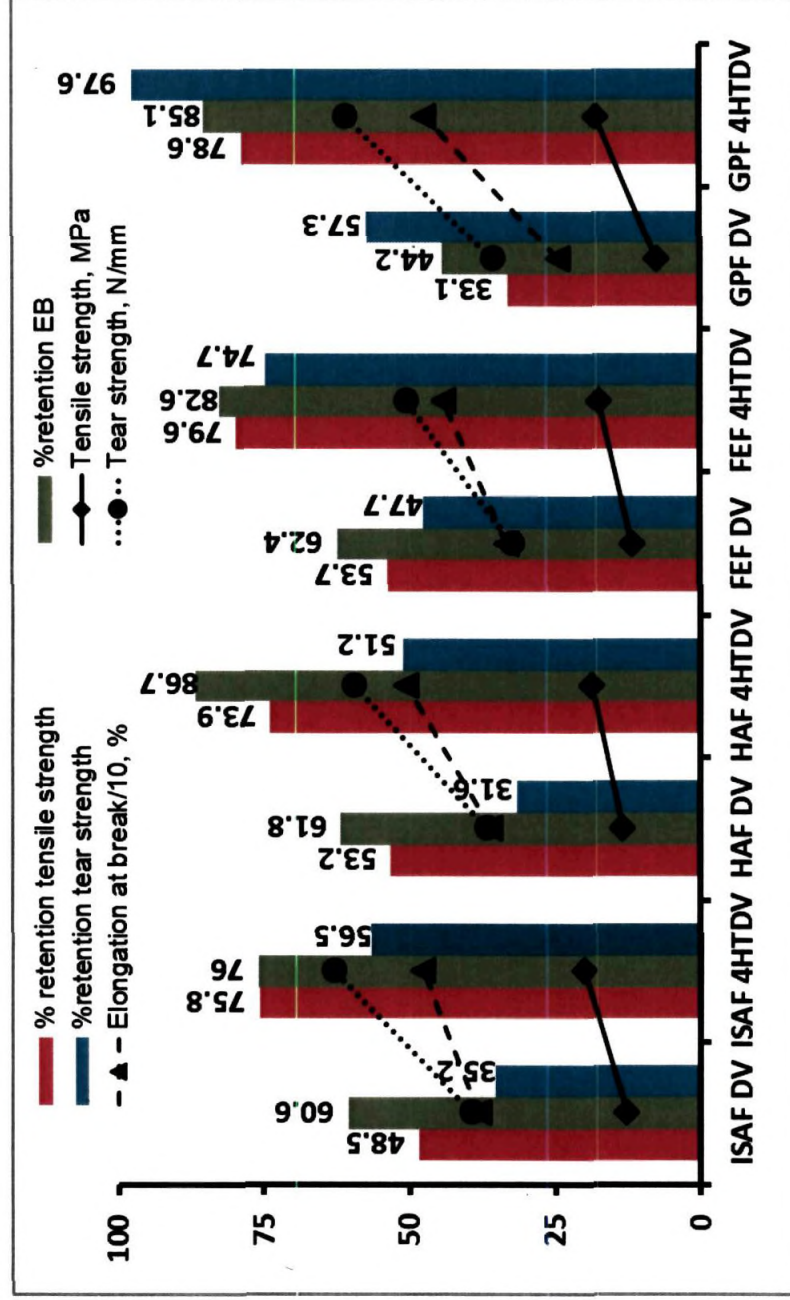
Figure 11.9 Revulcanisate properties and percent retention of original properties of NR samples containing different types of carbon black
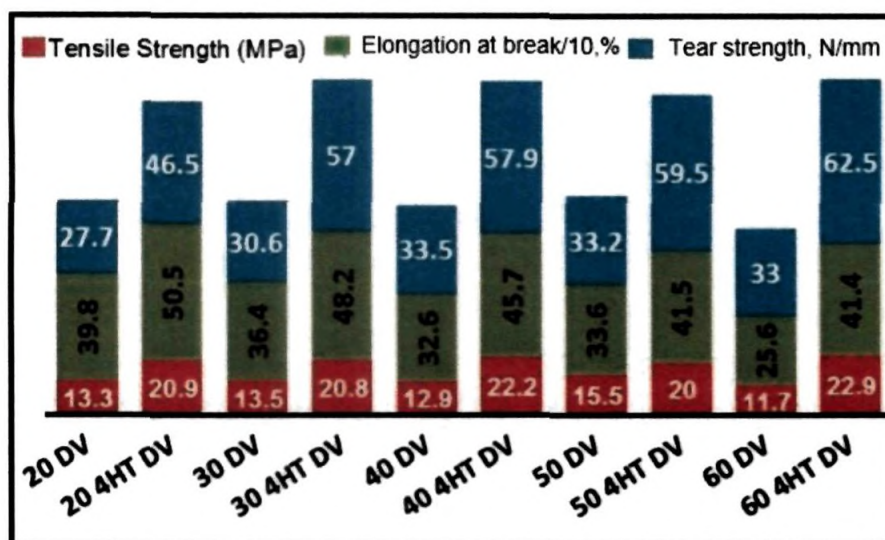
Figure 11.10 Revulcanisate properties of NR samples with varying HAF content

The revulcanisate tear strengths of the mechanically devulcanised samples were comparable in all the cases while that of the 4HT assisted samples increased with filler content (filler effect). Another matter of interest is that, upon revulcanisation, the type of filler present in the vulcanisate does not have a decisive role on the revulcanisate properties especially when stable free radical was used as a devulcanisation aid. It was observed that, irrespective of the type of filler system used for the preparation of original vulcanisate, the 4HT assisted devulcanised rubber can provide revulcanisate properties almost comparable with the original GPF vulcanisate. This indicates that the residual crosslinked parts present in the devulcanised rubber matrix might be acting as filler during revulcanisation with a particle size comparable with the particle size of GPF black thereby attaining the reinforcement level comparable with GPF black filled virgin natural rubber vulcanisate. Hence, it might be accorded that under the present devulcanisation conditions in this study, the revulcanisate

properties could not rise above the vulcanisate properties attainable by GPF filled NR vulcanisate.

11.8 Influence of BR content on the devulcanisation of NR/BR blends

The effect of polybutadiene rubber on the devulcanisation of NR/BR blends was investigated as majority share of the rubber waste comes from used tyres which are blends of NR and BR in different ratios. The investigations on the influence of cure system used for the vulcanisation of original sample showed that the devulcanised samples prepared from semi EV cured NR/BR blends gave significantly better revulcanisate properties than those from CV cured blends. The revulcanisate properties of semi-EV cured NR/BR blends with varying NR and BR content with corresponding virgin vulcanisate properties are plotted in Figure 11.11.
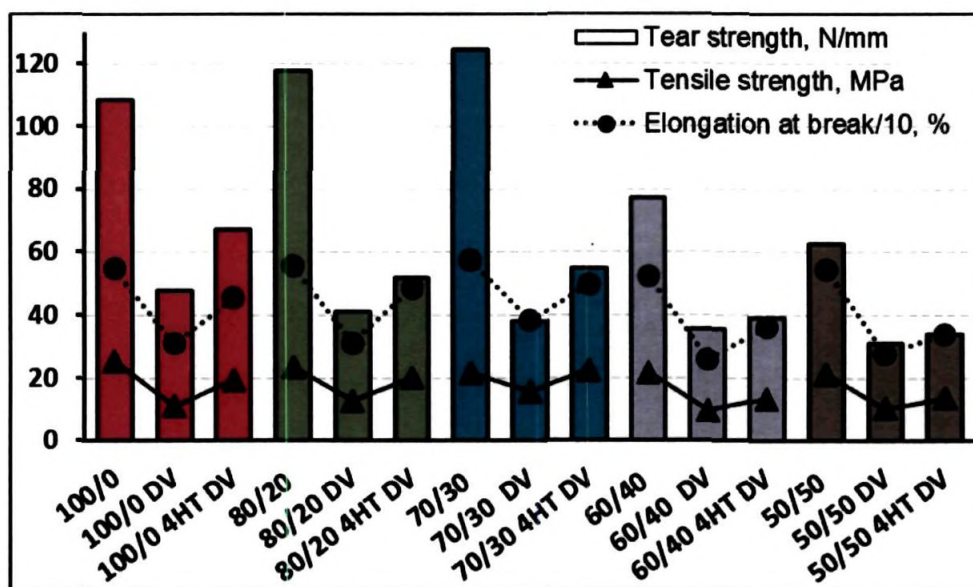

Figure 11.11. Vulcanisate properties of original and revulcanised NR/BR blends

The tensile strength and elongation at break of the virgin vulcanisates were comparable irrespective of the blend ratio whereas the

tear strength of the vulcanisates lowered with increasing BR content in the blend. Similar trend was observed with the revulcanisate properties of samples after devulcanisation but with higher absolute values for 4HT assisted devulcanisation. Hence, the per cent retention of vulcanisate properties were expected to be comparable in both cases of devulcanisation within the group. The positive influence of 4HT upon devulcanisation was more prominent with the revulcanisate tear properties rather than the tensile properties. On the other hand, the positive influence of 4HT upon the NR vulcanisate was significantly higher than that of all blends and it lowered with increasing BR content in the blend.

The effect of crosslink density of the original sample on the devulcanisation of NR/BR (50/50) blends is demonstrated in Figure 11.12.
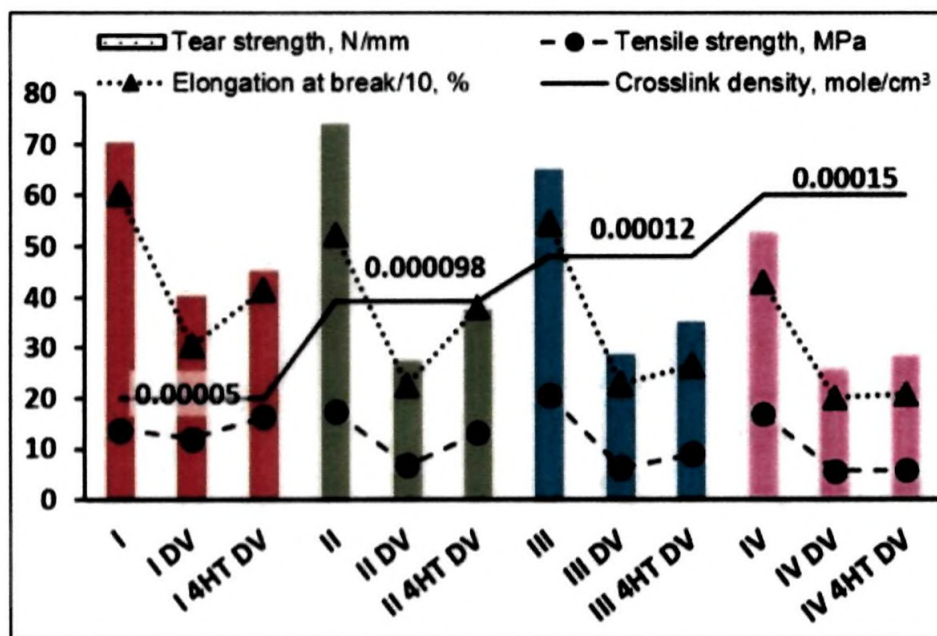

Figure 11.12 Variation of virgin vulcanisate and revulcanisate properties of NR/BR blends with varying initial crosslink density

The figure illustrates that, as the crosslink density of the blends was increased the virgin vulcanisate properties improved to a maximum and thereafter decreased. On the other hand, the maximum revulcanisate properties were associated with the NR/BR blend with the lowest crosslink density for virgin vulcanisate and it decreased with increasing crosslink density of the virgin vulcanisate. Hence it might be assumed that, in order to obtain the best devulcanisation results, the crosslink density of the rubber products might be adjusted in such a way that it should be the minimum possible crosslink density satisfying the product requirements so that the devulcanisation of these products would be much easier and effective.

11.9 Devulcanisation of commercial tyre tread buffings

The ability of stable free radical to improve the devulcanisation efficiency and revulcanisate properties associated with mechanical devulcanisation has been successfully established through the devulcanisation studies carried out using vulcanisates of known composition and properties. The practical viability of the novel stable free radical assisted devulcanisation was counter checked using devulcanisation of commercial tyre tread buffing and GTR. The mechanical devulcanisation of these commercial samples with the assistance of 4HT gave higher revulcanisate properties. Also, the devulcanised buffing dust was incorporated into a tread formulation in various ratios and the vulcanisate properties were examined in comparison with a control tread formulation containing no devulcanised rubber as represented in Figure 11.13.
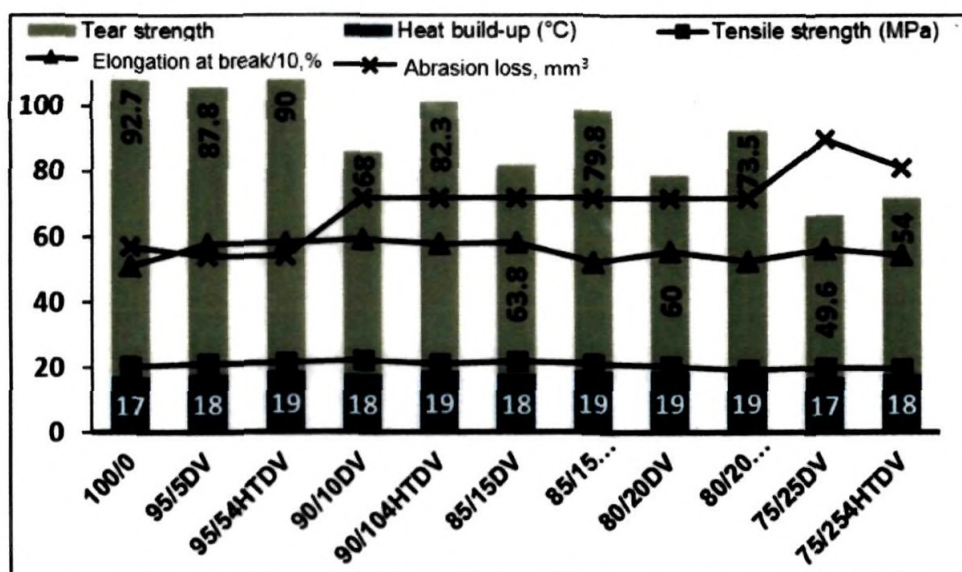
Figure11.13 Vulcanisate properties of virgin rubber/ devulcanised buffing dust blends with control sample

Vulcanisate properties like tensile strength, elongation at break, heat build-up, *etc.* of the blends of virgin rubber with both mechanically devulcanised and 4HT assisted devulcanised buffing dust were comparable with the control even up to a blend ratio of 75/25. The abrasion loss of both set of blends were higher than the control except for 95/5blend. The tear strength of the blends with 4HT assisted devulcanised buffing dust were significantly higher than the corresponding blend with mechanically devulcanised buffing dust. The results also suggest that incorporation of mechanically devulcanised buffing dust up to 5parts without compromising on performance requirements is possible. Further, viability of the novel devulcanisation process on a larger scale was demonstrated by the factory scale devulcanisation of buffing dust which reproduced the results obtained during lab-scale experiments.

11.10 Scorch characteristics during revulcanisation of devulcanised rubber

The issue of low scorch during revulcanisation of devulcanised rubber has been an unsolved issue associated with devulcanisation of rubbers. Though several reasons have been advocated for this, the real cause behind this issue has not been fully established yet. Hence, a critical analysis of the various proposed reasons for observed low scorch during revulcanisation of devulcanised rubber have been made based on the earlier experimental results obtained from literature and experiments conducted during the course of present study.

The studies led to the conclusion that, the MBT moiety released during the formation of newer crosslinks from the crosslink precursors remaining in the devulcanised rubber (from the initial vulcanisation) is the reason behind the low scorch safety associated with revulcanisation of devulcanised rubber.

This issue was tackled by the incorporation of PVI during revulcanisation which further confirmed that MBT species is responsible for the low scorch associated with devulcanised rubber. This argument was further clarified by revulcanisation of devulcanised NR vulcanisates which was initially cured with TMTD alone which eliminated the possibility of MBT release during revulcanisation. The various probable reasons behind low scorch during revulcanisation of devulcanised rubber and their systematic analysis to sort out the cause for observed low scorch during revulcanisation of devulcanised rubber are outlined in the flow chart given in Figure 11.14.
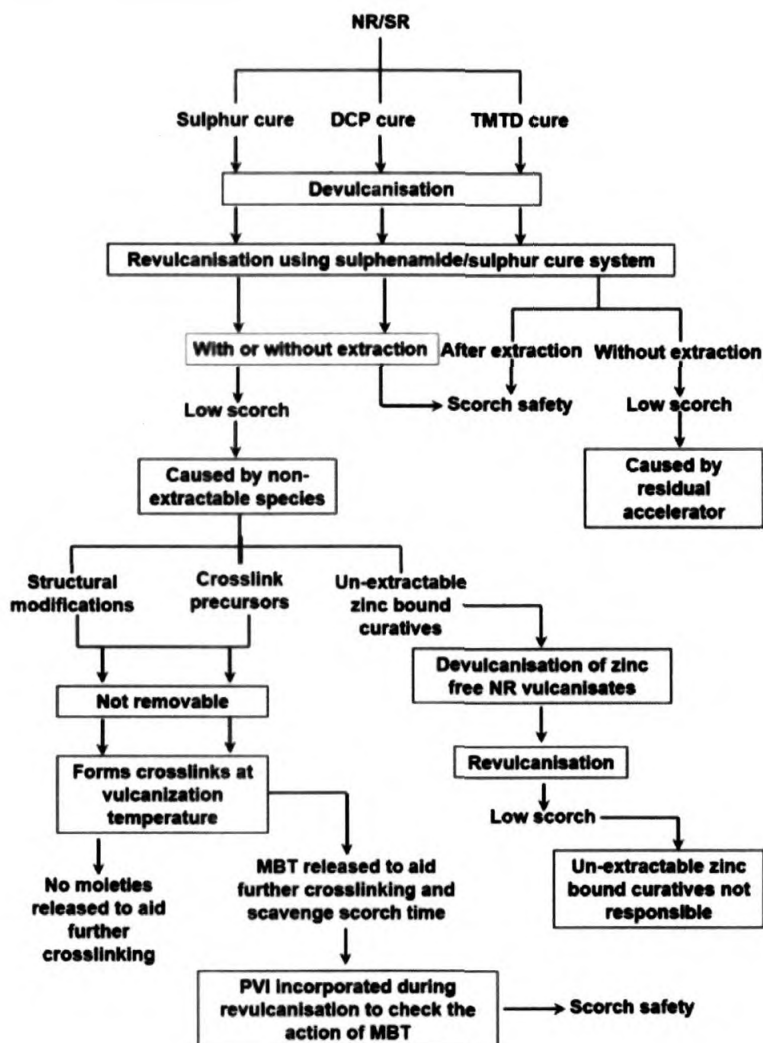
Figure 11.14 Chart describing the reasons behind the issue of low scorch during revulcanisation of devulcanised rubber

Though PVI is found to be effective in introducing pre-vulcanisation scorch time during revulcanisation of devulcanised rubber, it was also found that PVI cannot deal with the scorch safety issue associated with the

incorporation of devulcanised rubber in virgin compounds due to concentration issues.

Futur outlook

Based on the results and observations made from the present work it is expected that the outcomes of the following studies would be relevant and practically useful if carried out

- Effect of storage on the behaviour and revulcanisate properties of samples devulcanised with the assistance of stable free radical
- Role of particle size of rubber crumb to be devulcanised and shear force used for devulcanisation upon revulcanisate properties of devulcanised rubber.
- Investigations on the low impact of stable free radical on BR based on structural studies using chemical probes
- Scope of designing products with an intention of easy and efficient devulcanisation

PUBLICATIONS

George, B., **Joseph, A.M.**, Madhusoodanan, K.N., Alex, R. and Jacob, J. Stable free radical assisted devulcanization: **Patent processing**

Joseph, A.M., George, B., Madhusoodanan, K.N. and Alex, R. (2015). Current status of sulphur vulcanisation and devulcanisation chemistry: Process of vulcanization. *Rubber Science*, **28**(1): 82-121

Joseph, A.M., George, B., Madhusoodanan, K.N. and Alex, R. (2016). The current status of sulphur vulcanization and devulcanization chemistry: Devulcanization. *Rubber Science*, **29**(1): 62-100,

Joseph, A.M., George, B., Madhusoodanan, K.N. and Alex, R. (2016). Effect of devulcanisation on the crosslink density and crosslink distribution of carbon black filled natural rubber vulcanisates. Rubber Chemistry and Technology, doi: 10.5254/ rct.16.84819

Joseph, A.M., George, B., Madhusoodanan, K.N. and Alex, R. The issue of low scorch during revulcanisation of devulcanised rubber. Under review (Rubber Chemistry and Technology)

Impact of Filler Correction on the Vulcanizate Properties while Incorporation of Devulcanised Rubber in Fresh Compounds: Under review (Progress in Rubber Plastics and Polymer Recycling Technology)

PRESENTATIONS

Joseph, A.M., George, B., Madhusoodanan, K.N. and Alex, R. (2014). A novel and efficient mechanochemical devulcanization process. In: *Proceedings of the IRMRA 22nd Rubber Conference,* 21-22 November 2014, New Delhi, India.

Joseph, A.M., George, B., Madhusoodanan, K.N. and Alex, R. (2014). Devulcanisation: mechnochemical approach. *Presented at UGC sponsored National seminar,* St. Paul's College, Kalammassery, Ernakulam, Kerala, December 2014.

Joseph, A.M., George, B., Madhusoodanan, K.N. and Alex, R. (2015). A potential mechanochemical process for efficient devulcanization. In: *Proceedings of the 27th Kerala Science Congress,* 27-29 January 2015, Alappuzha, Kerala, India.

Joseph, A.M., George, B., and Madhusoodanan, K.N. (2015). Comparison of a novel devulcanisation process with contemporary industrial devulcanisation processes. *Presented at IRMRA- CII National conference,* 16-17 December 2015, Mumbai, India.

Joseph, A.M., George, B., Madhusoodanan, K.N. and Alex, R. (2016). Effect of devulcanisation on the crosslink density and crosslink distribution of carbon black filled natural rubber vulcanisates. Presented at *International conference on Advances in Polymer Technology,* 24-25 February 2016, Department of Polymer Science and Rubber Technology, CUSAT, Ernakulam, India.

George, B., **Joseph, A.M.,** Madhusoodanan, K.N. and Alex, R. (2016), Comparison of a novel devulcanisation process with current industrial devulcanisation processes. Presented at *International conference on Advances in Polymer Technology, APT'16,* 24-25 February 2016, Department of Polymer Science and Rubber Technology, CUSAT, Ernakulam, India.

Joseph, A.M., George, B., Madhusoodanan, K.N. and Alex, R. (2016). An efficient mechanochemical process for devulcanisation of carbon black filled natural rubber vulcanisates. *Presented at International Rubber Conference - Rubber Con,* 1-3 March 2016, Chennai, India.

- **Best paper award**

Joseph, A.M., George, B., Madhusoodanan, K.N. and Alex, R. (2014). Devulcanisation: mechano-chemical approach. *Presented at UGC sponsored National seminar,* St. Paul's College, Kalammassery, Ernakulam, Kerala, December 2014.

- **Best Technical paper Award**

Joseph, A.M., George, B., and Madhusoodanan, K.N. (2015). Comparison of a novel devulcanisation process with contemporary industrial devulcanisation processes. *Presented at IRMRA- CII National conference,* 16-17 December 2015, Mumbai, India.

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- **Best paper award**

Joseph, A.M., George, B., Madhusoodanan, K.N. and Alex, R. (2014). Devulcanisation: mechano-chemical approach. *Presented at UGC sponsored National seminar,* St. Paul's College, Kalammassery, Ernakulam, Kerala, December 2014.

- **Best Technical paper Award**

Joseph, A.M., George, B., and Madhusoodanan, K.N. (2015). Comparison of a novel devulcanisation process with contemporary industrial devulcanisation processes. *Presented at IRMRA- CII National conference,* 16-17 December 2015, Mumbai, India.

- Won B-Grade in Kerala School Youth festival for Essay Writing in 2002
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APPENDIX

EFFECT OF DEVULCANIZATION ON CROSSLINK DENSITY AND CROSSLINK DISTRIBUTION OF CARBON BLACK FILLED NATURAL RUBBER VULCANIZATES

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ABSTRACT

Carbon black filled natural rubber (NR) vulcanizates were devulcanized at ambient temperature in a two roll mill. The effect of cure system, that is, conventional vulcanization (CV), semiefficient vulcanization (semi EV), and efficient vulcanization (EV) systems, used for vulcanization of the original sample, on the efficiency of devulcanization was studied. The efficiency of devulcanization expressed as percentage devulcanization of the samples calculated from residual crosslink density measurements was correlated with the sol fraction of the devulcanized samples based on Horikx analysis. Using chemical probe analysis, we determined (i) the crosslink distribution pattern of the original sample, (ii) the extent to which the different types of crosslinks that is, polysulfidic, disulfidic, and monosulfidic crosslinks—have been debonded or broken during the shearing process in the two roll mill, and (iii) the pattern of bond formation during revulcanization. Mechanical shearing predominantly breaks the majority crosslink type (polysulfidic crosslinks in CV and semi EV cure systems and disulfidic crosslinks in EV samples). Irrespective of the significant reduction in total crosslink density in all three sets of samples, chain shortening reactions similar to the post-crosslinking chemical reactions at curing temperatures also occur during mechanical shear at ambient conditions, which increased the absolute value of monosulfidic links in CV and semi EV systems. However, in the devulcanized EV system, the absolute value of polysulfidic crosslinks increased, which might be due to the re-crosslinking of the cleaved bonds. All the devulcanized samples were revulcanized, and the mechanical and morphological properties were analyzed. The percentage retention of the vulcanizate properties after revulcanization of the devulcanized samples correlated very well with efficiency of devulcanization. [doi:10.5254/rct.16.84819]

INTRODUCTION

Environmentally benign methods of disposal of end of life tires and other waste rubber products is a global concern. It is estimated that about one billion waste tires are produced globally per year. Legislations, regulatory measures, and adoption of new technologies for ground rubber production have substantially reduced the landfill of used tires in Europe from 50% in 1996 to 4% in 2010. Currently, material recycling and energy recovery or thermal recycling by using waste tires as fuel constitute about 80% of the recycling process in European Union countries.[1] Other developed countries also follow similar trends. Unfortunately, no reliable statistics are available on the production, recovery rate, and recycling of used tires and other rubber products in emerging economics.

The most essential step of any rubber product manufacture is the process of vulcanization, which introduces crosslinks between rubber polymer chains to form a three-dimensional network. Reuse of the vulcanized rubber as a processable material demands the selective cleaving of crosslinks—which is not an easy task—to retrieve the linear polymer chains. Devulcanization is a recycling strategy aimed at selective scission of crosslinks in a vulcanized network with no or negligible main chain scission, so that larger volumes of the reclaimed material can be ploughed back into the rubber industry itself. Among the prominent methods reported, devulcanization is achieved by applying high temperature and/or pressure,[2-8] microwave,[9-11] or ultrasonic

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THE CURRENT STATUS OF SULPHUR VULCANIZATION AND DEVULCANIZATION CHEMISTRY: PROCESS OF VULCANIZATION

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The article presents the first part of the review on the current status of sulphur vulcanization and devulcanization chemistry. The purpose of presenting a review of the chemistry of sulphur vulcanization and devulcanization was to develop a devulcanization process and also to address the issue of very low scorch during revulcanization

Accelerated sulphur vulcanization is a very complex chemical process. Although consensus on various reaction mechanisms are yet to reach, there is widespread agreement about three basic steps involved. These are: (i) accelerator chemistry in which the reactions of accelerator, activator and sulphur leading to the formation of an active sulphurating agent (ii) crosslinking chemistry which involves the reactions of the active sulphurating agent leading to the formation of crosslink precursors and subsequent reactions of these precursors to form polysulphidic crosslinks and (iii) postcrosslinking chemistry leading to chain shortening and degradation of the polysulphidic crosslinks and other main chain modifications. The current understanding of the chemical reactions and the underlying mechanism involved in these basic steps, both in accelerator, activator and sulphur as well as accelerator- cum- sulphur donor and activator cure systems are reviewed. Reaction mechanisms leading to scorch delay inherent to sulphenamide accelerators and those involved by the addition of prevulcanization inhibitors are also presented

Keywords: Accelerator chemistry, Crosslinking chemistry, Postcrosslinking chemistry, Sulphur vulcanization

INTRODUCTION

The life history of natural rubber (Heideman, 2004; www.britannica.com.; Aprem, et al., 2005) can be dated back to 11 June 1496, the day on which Christopher Columbus returned from his second voyage, bringing back the first rubber balls from the West Indies. The next landmark was the Spanish discovery of the use of latex for the water proofing of leather and fabrics in 1615. The rubber industry in Europe really started with Charles Macintosh in 1818, when he started exploiting the naphtha-based rubber solution as a water proofing layer between

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THE CURRENT STATUS OF SULPHUR VULCANIZATION AND DEVULCANIZATION CHEMISTRY: DEVULCANIZATION

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The article presents the final part of the review on the current status of sulphur vulcanization and devulcanization chemistry Though considerable scientific attention has been given to study and understand the sulphur vulcanization process and the reaction mechanisms involved, it is doubtful whether an equivalent effort has been made to understand the reaction mechanisms involved in reclamation/devulcanization processes The present review focuses on the current understanding of the chemical reactions and the proposed underlying mechanisms of different devulcanization processes after providing a bird's eye view of the whole used rubber products management scenario. The various devulcanization processes are discussed under headings as chemical/ thermo chemical devulcanization, thermo-mechanical/mechanical devulcanization,mechano-chemical devulcanization, microwave devulcanization, ultrasonic devulcanization and biological/ biotechnological devulcanization The revulcanizate properties of the devulcanized samples by various processes are also discussed

Keywords: Devulcanization reclamation, recycling, revulcanizate properties

INTRODUCTION

Utilization and disposal of used tyres represent an enormous challenge to industrialized countries worldwide because of their three dimensional-crosslinked-structure which renders them non-biodegradable, raising serious disposal concerns (Synder, 1998; Dierkes, 1996; Gou *et al.*, 2010; Klingensmith and Rodgers, 1994; Reschner, 2008). It is estimated that about 300 million scrap tyres are generated in US annually, a situation that is mirrored in countries round the world in various proportions. The most obvious hazard associated with the uncontrolled disposal and accumulation of large number of tyres is the potential for large fires which are extremely detrimental to the environment. Even if large outside tyre piles do not catch fire, they still pose a serious problem for human health and the environment by being an ideal breeding ground for mosquitoes.

The various stages in the life cycle of tyres are presented in Figure 1. In response to the environmental problems and health hazards caused by countless illegal scrap tyre piles around the globe, most developed countries have developed legal guidelines addressing this issue. These legislations to ensure environmental safety, resulted in

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