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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 *viz.* 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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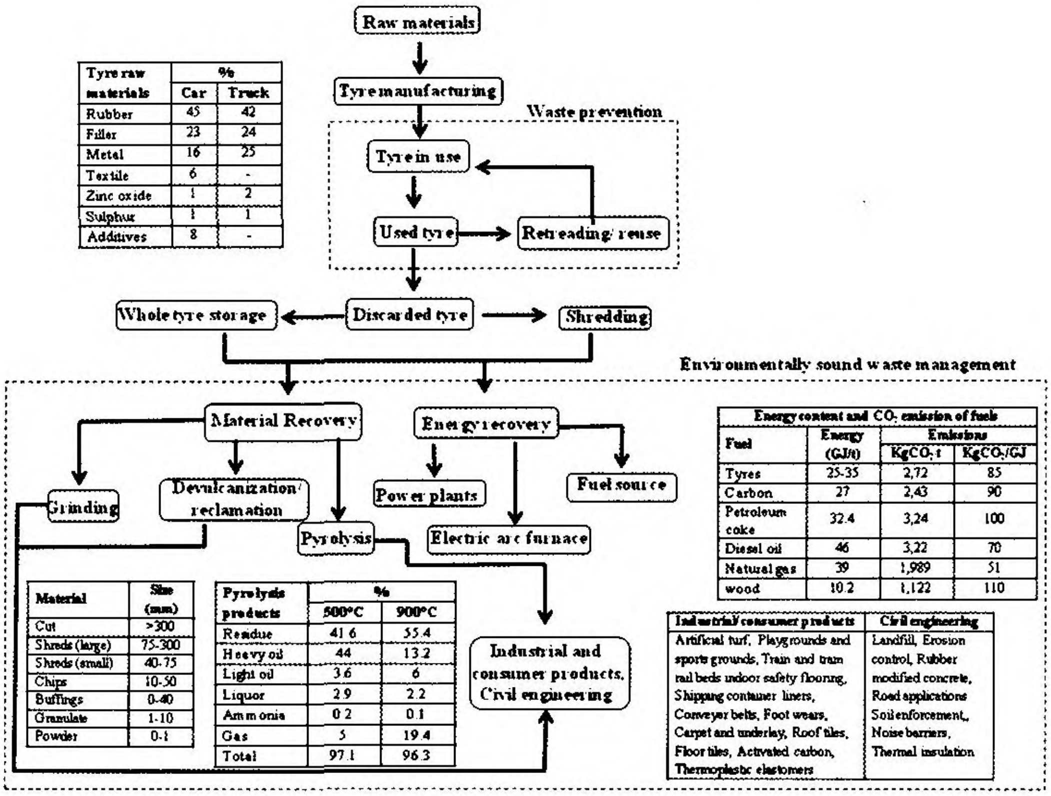


Tyre raw materials	%	
	Car	Truck
Rubber	45	42
Filler	23	24
Metal	16	25
Textile	6	-
Zinc oxide	1	2
Sulphur	1	1
Additives	8	-

Energy content and CO_2 emission of fuels			
Fuel	Energy (GJ/t)	Emissions	
		$KgCO_2$/t	$KgCO_2$/GJ
Tyres	25-35	2,72	85
Carbon	27	2,43	90
Petroleum coke	32.4	3,24	100
Diesel oil	46	3,22	70
Natural gas	39	1,989	51
wood	10.2	1,122	110

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 products	%	
	500°C	900°C
Residue	41.6	55.4
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	97.1	96.3

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

Fig.1. Stages in the life of tyres

radical shift of the reclamation dominated recycling industry to rubber powder based recycling methods focused on material and energy recovery which primarily aims in converting end of life tyres into a useful form for reuse in many applications not in the rubber industry alone as evident from Figure 2 (Abraham *et al.*, 2011; Ayyer *et al.*, 2012; Bandyopadhay *et al.*, 2008; Blumenthal, 1996; Brown, 1997; Burford and Pittolo, 1982; Evans and Anne, 2006; Hammer and Gray, 2004; http://www.kirklandwa.gov/Assets/Planning/Planning+PDFs/TurfTalk.pdf; http://www.cwc.org/tyre_bp/t_bp_pdf/2-03-04.pdf; Jacob and De, 2005; Kim and Burford, 1998; Klingensmith, 1991; Kumar *et al.*, 2013; Myhre and MacKillop, 2002; Rajan *et al.*, 2006; Rouse, 2005). Unfortunately in developing countries, no reliable statistics is available on the fate of discarded tyres.

The concept of devulcanization - selective scission of crosslinks with negligible main chain scission - was coined to plough back more amounts of recycled rubber into the rubber industry itself. Early methods of devulcanization, described as reclamation - since the intention was to reuse the material - significantly reduced the molecular weight of rubber as the processes employed cleaved all bonds indiscriminately, thus limiting the amount

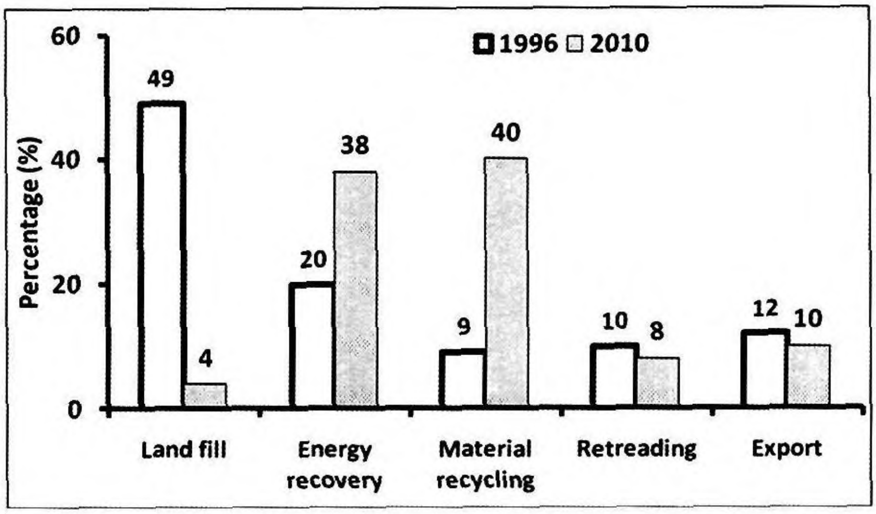


Fig.2. Change in pattern of end-of-life tyre reuse in European Union, (1996-2010)

of reclaim that can be used without deteriorating the physical properties of products (Stevenson, 2007). These methods employed environmentally hazardous production techniques also. In most of the later innovations, devulcanization 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 (Raghavan, 2005; Schnecko, 1994; Warner, 1994). 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 devulcanized rubber using these technologies (http://www.levgum.com; http://www.green-gum-rubber-recycling.com; http://www.recyclatech.com; www. greenrubbergroup.com; www.ecserrubber.com).

The present review focuses on the chemical reactions and the mechanisms involved in various devulcanization processes after providing a bird's eye view of the whole used rubber product management scenario.

Used tyre management strategies

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). As of January 2015, there are 183 Parties to the treaty, which include 180 UN member states plus the Cook Islands, the European Union, and the State of Palestine. 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 (Chem-Risk LLC, 2009; UNEP/CHW.9/18, 2008; UNEP/CHW.10/6/Add.1/Rev.1, 2011).

Table 1. **Recycling strategies of used tyres/rubber products as per Basel Convention regulations**

Recycling strategy	Features	Advantages/disadvantages
Reuse	• Partly worn tyres used for their 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 (http://cement.org/Briefingkit/pdf_files/ TDFBrochure.pdf; http://www.deq.virginia.gov/ Portals/0/DEQ/ Air/StateAdvisory Board/ Tyre_Derived_Fuel.pdf; http://www.epa.gov/epawaste/conserve/ materials/tyres/tdf.htm)
	In electric arc furnace: Carbon from scrap tyres working as reducing agent instead of anthracite in electric arc furnaces making steel. Carbon from scrap tyres 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	• Methods to check air pollution needed
Materials recovery	**Grinding:** Multi stage size reduction of scrap tyres De-beading →Shredding to coarse material →cutting to chips → powdering for industrial and consumer products and civil engineering applications (Tipana and Kale, 1997; Rajalingam and Baker, 1992; Rajalingam *et al.*, 1993; Rajeev and De, 2004; Acetta and Vergnaud, 1981)	• Environment friendly • Activation techniques for compatibilization of blends (Naskar *et al.*, 2001 ; Fuhrmann and Karger, 2003; Kim *et al.*, 2006; Sritragool, 2010; Wellappili *et al.*, 2007; Stevenson, 2007; Dierkes; 2005; Cavalieri *et al.*, 2003)
	• *Ambient grinding* (Feder *et al.*, 1987) • Grinding by cutting, tearing, shearing • Ambient temperature • Spongy and rough particles	• Higher power consumption • High specific surface and wide particle size range
	• *Cryogenic grinding* • Grinding by breaking cryogenically embrittled rubber • Temperature below -80°C • Even and smooth particles (Phadke, 1984)	• 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 (Bebb, 1976; Roy *et al.*, 2005)	• Carbon black: low commercial value as it is a mixture of different types used in tyre manufacture • Steel: Low market value
Reclamation: Un-restricted cleaving of bonds in the crosslinked rubber under the influence of temperature, pressure and chemicals take place.	• Highly degraded product of low properties owing to severe main chain degradation
Devulcanization: Cleaving the sulphidic crosslinks of vulcanized rubber using heat, chemicals and/ or mechanical techniques with no or negligible main chain scission.	• In principle, devulcanization produce a product substituting virgin rubber with minimum main chain scission and maximum crosslink scission

Conventional reclamation processes

Ever since the invention of vulcanization in 1839, efforts have been made to break the crosslinks formed during vulcanization and to retrieve the rubber *chains to obtain a material similar to the* unvulcanized virgin rubber. Almost all such efforts produced a material of increased plasticity which has been identified as reclaim since the intention was to reuse the material. But reclaiming is a procedure in which scrap tyre rubber or vulcanized rubber waste is converted - using mechanical and thermal energy and chemicals - into a state in which it can be mixed, processed, and vulcanized again through cleaving of covalent bonds existing in the vulcanized rubber.

As mentioned in Table 1, reclaiming processes use chemicals - unfortunately toxic -high temperature and pressure, generating environmental problems besides de-polymerization of the crosslinked polymer resulting in poor retention of the virgin rubber properties. It has been confirmed that in reclaiming processes, main chain 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 revulcanizate properties (Myhre, 2005). A general outline of the reclamation processes is given in Figure 3.

Many different reclaiming processes have been used through the years depending on scrap characteristics and economics. As previously mentioned, conventional reclamation processes of any type have been banned in US and whole of Europe and all nations with positive environmental policies. This part is included in this review as these porcesses are still practised in many developing countries. The major reclaiming processes are listed in Table 2.

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.* (Watabe *et al.*, 1980; Anderson, Jr., 1985). Reclamation processes significantly reduce

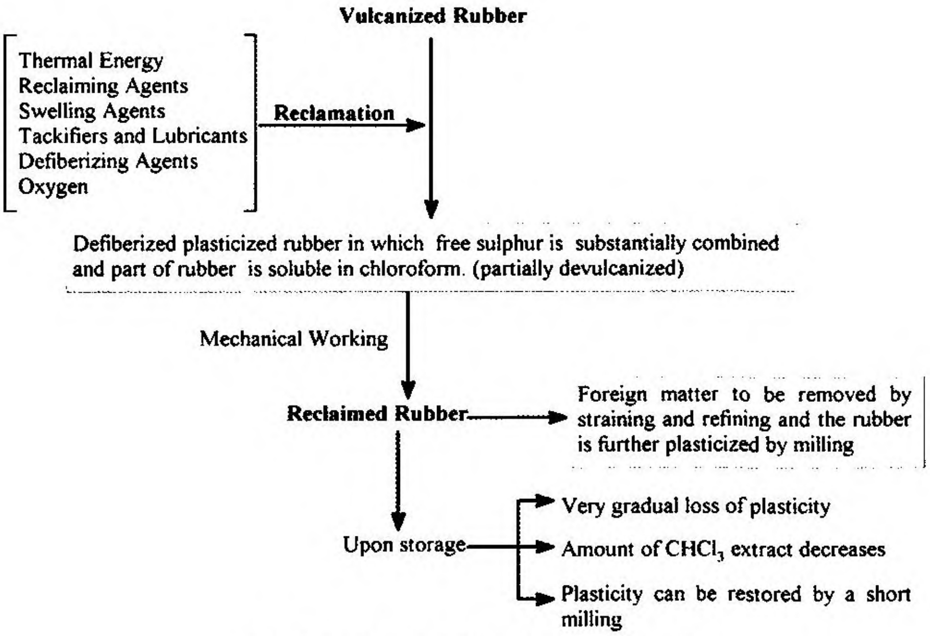


Fig. 3. General outline of reclamation processes

the molecular weight of rubber compared to virgin rubber as the processes employed do not discriminate crosslinks and the main chain. 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 reclaim rubber is highly restricted. The advantages such as lower polymer cost, shorter mixing time, low 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 (Blow, 1998). Several studies have been carried out on the various aspects of reclamation processes, reclaimed rubber properties and incorporation of reclaim in blends with virgin compounds (Albert, 1952; Edirisinghe *et al.*, 2011; Furukawa *et al.*, 1981; Le Beau, 1947; 1967; Rattanasom *et al.*, 2005; Shoaff, 1928; Tewksbury and Howland, 1949; Wheeler, 1947; Winkelmann and Busenburg, 1929).

THE CONCEPT OF DEVULCANIZATION

Rubber products like tyres are high-end engineering products that are designed to last long and hence difficult to devulcanize 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. Ideally, contemporary devulcanization strategies move in this direction and aims at recycling vulcanized rubber through selective cleaving of crosslinks to retrieve the linear polymer chains to reuse the rubber

Table 2. **Conventional reclamation processes**

Thermal process	• Oldest process • Heating crumb using steam in a pan • Pressure: 60psi • Temperature: 260°C • 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 • Initial step removes fabric by boiling in strong acid solution • Second step is devulcanization with 100-300psi high pressure steam • Reclaiming, charring and wetting agents used • 3 hours and 15 minutes • Cooled, dried and massed on two roll mill, strained through 40 mesh screen
Digester process/ alkaline process	• Carried out in double jacked autoclave • Devulcanization 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 • Pressure: 150 psi steam pressure • Not applicable with SBR • 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

hydrocarbon by the rubber industry. (Hammer and Gray, 2004).

The concept of devulcanization – selective scission of crosslinks – with the expected minimum main chain scission will ensure better retention of virgin rubber properties after devulcanization. Another matter of concern is the fact that synthetic rubbers (SRs) are more difficult to recycle, compared with natural rubber (NR). The differences in the reactivity between NR and SRs could be due to the different structures of polymer chain or crosslink sites and the differences in the crosslink type distribution, crosslink densities *etc.* (Verbruggen *et al.*, 1999). The various devulcanization processes make use of any of the typical methods outlined in Figure 4 such as opening by oxidation, opening by heat or shear, opening with nucleophilic reagents, opening by rearrangement and opening by substitution for rupturing the sulphur crosslinks of rubber.

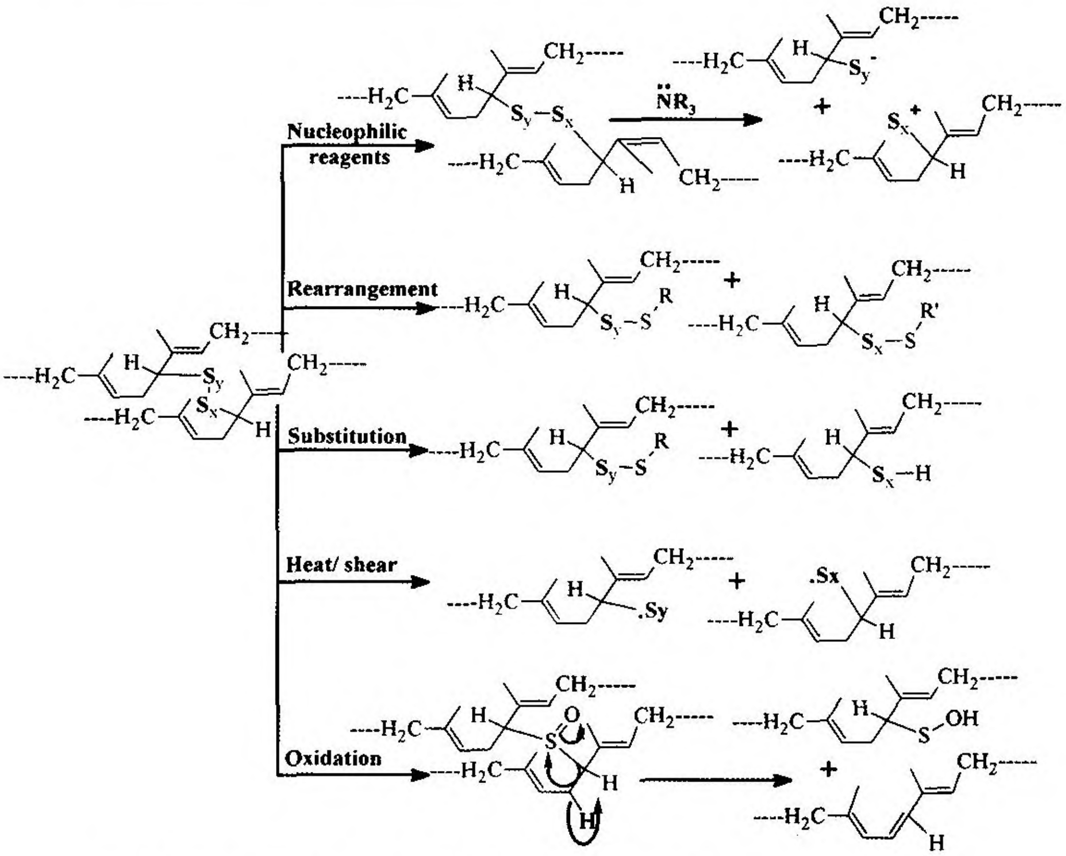


Fig. 4. General principles employed for crosslink scission in devulcanization processes

In the history of devulcanization though several methods are being advocated and developed, only a handful of them succeeded in proving their credibility to be industrially taken up. 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 devulcanization or mechano-chemical devulcanization (Khait, 2005; Myhre, 2005). Irrespective of their industrial viability, several studies have been carried out on the various aspects of devulcanization processes and the revulcanizate properties of devulcanized rubber and its blends with virgin compounds in various ratios (Ishiaku *et al.*, 1999; Lamminmaki *et al.*, 2006; Myhre and MacKillop, 2000). Various devulcanization processes are discussed below emphasizing on the reactions involved and proposed mechanisms.

Chemical/Thermochemical devulcanization

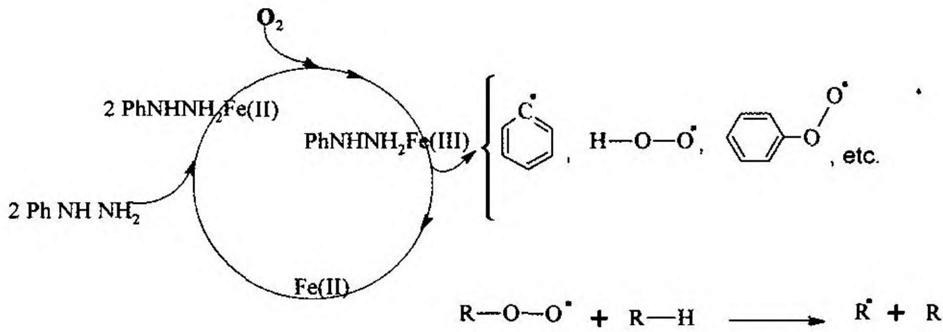
Chemical agents have been used to devulcanize scrap tyres since 1960s. Initially, most chemical devulcanization processes involved mixing of size reduced rubber particles and chemical reagents in a temperature and pressure controlled mixer which resembled the reclamation processes to a greater extent. Generally speaking, rubber is fed into a mixer with a devulcanizing 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 devulcanization carried out under ambient conditions were put forth, some of which are discussed below.

Using ferrous chloride and phenyl hydrazine

A process that regenerates vulcanized rubber by treating the material at room temperature and atmospheric pressure for several hours with ferrous chloride and phenyl hydrazine, in which phenyl hydrazine is the main reagent and $FeCl_2$ acts as catalyst, is reported (Kawabata, 1981; Tamashita *et al.*, 1978) as outlined in Figure 5. Although claimed to be a devulcanization method, this process is essentially a reclamation method in which devulcanization is achieved by the oxidative degradation of rubber chain. If sufficient oxygen is present, various radicals formed by this reaction degrade the rubber molecules through Bolland oxidation mechanism (van Krevelen and te Nijenhuis, 2009).

Using the principles of phase transfer catalysis

The principles of phase transfer catalysis also have been used to devulcanize



$$R\text{—}O\text{—}O^{\bullet} + R\text{—}H \longrightarrow R^{\bullet} + R\text{—}O\text{—}OH$$
$$R\text{—}O\text{—}OH \longrightarrow R\text{—}O^{\bullet} + {}^{\bullet}OH$$
$$R\text{—}O\text{—}OH + R\text{—}H \longrightarrow R\text{—}OH + R^{\bullet} + {}^{\bullet}OH$$
$$R\text{—}O^{\bullet} + R\text{—}H \longrightarrow R\text{—}OH + R^{\bullet}$$
$${}^{\bullet}OH + R\text{—}H \longrightarrow H\text{—}OH + R^{\bullet}$$
$$R\text{—}O\text{—}O^{\bullet} + R \longrightarrow R\text{—}O\text{—}O\text{—}R$$
$$R\text{—}O^{\bullet} + R^{\bullet} \longrightarrow R\text{—}O\text{—}R$$
$$R^{\bullet} + R^{\bullet} \longrightarrow R\text{—}R$$

Fig. 5. Oxidative degradation of rubber

cured rubbers with an onium salt dissolved in an organic solvent, which exchanges its anions for a hydroxyl ion when exposed to the alkali (Nicholas, 1979; 1982). 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 6 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. 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 7.

Monosulphidic crosslinks are also expected to be cleaved according to the scheme (a) given in Figure 8 with little, if any main chain scission. But the scission of monosulphidic crosslinks does not happen as the prominent reaction in the case of crosslinked rubber in which, deprotonation is the more feasible reaction as shown in scheme (b) of Figure 8 (Nicholas, 1982). The process is claimed to cleave 70 to 75 per cent of the crosslinks but when blended with new rubber gave only comparable mechanical properties with control blends with untreated samples.

Using solvent swelling methods

A method to devulcanize rubber crumb by desulphurization of solvent swollen crumb using metallic sodium (Myre *et al.*, 1997; Myre and MacLeod, 1998) preferably in an oxygen free environment is also reported. Molecular hydrogen is supplied which caps the radicals which are formed when the sulphur crosslinks are removed by

$$[Q^+Cl^-]_{org} + [X^-]_{aq} \longrightarrow [Q^+X^-]_{org} + [Cl^-]_{aq}$$

Fig. 6. General representation of phase transfer of ions

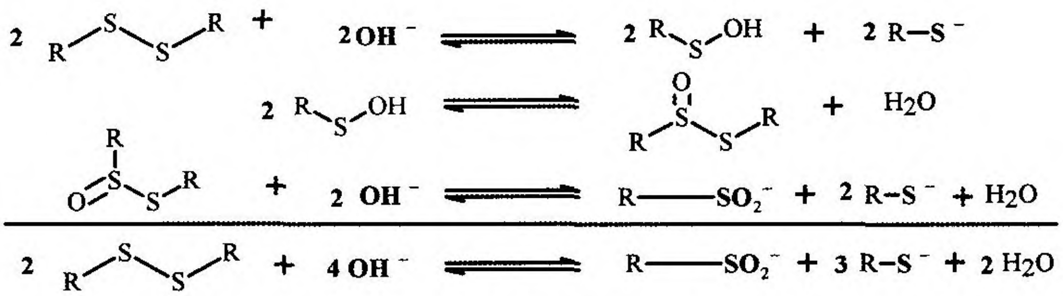


Fig. 7. Selective scission of sulphidic crosslinks by hydroxyl ions

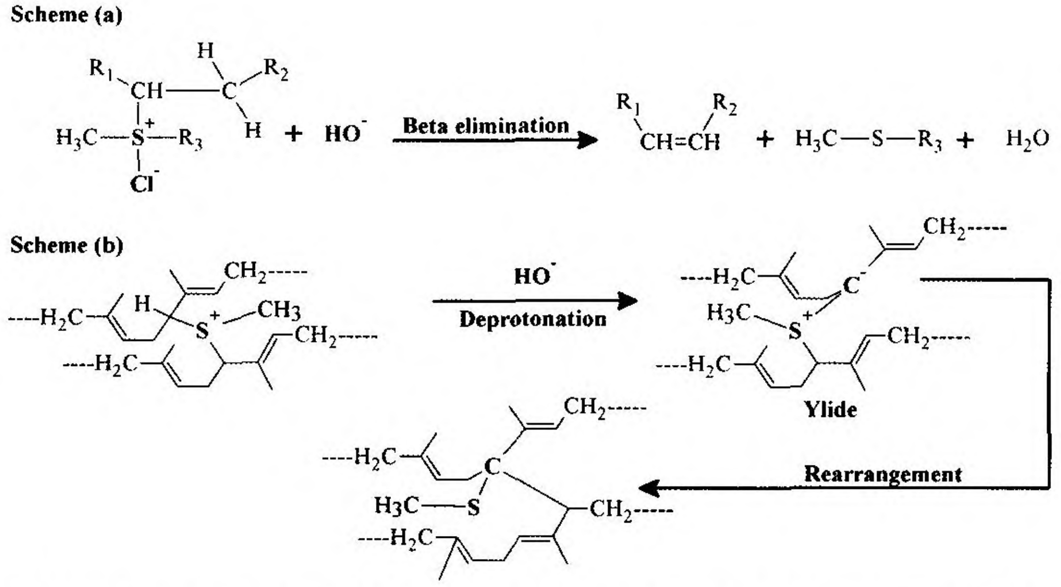


Fig. 8. Expected pattern of monosulphidic crosslink scission [scheme (a)] and the observed prominent deprotonation product [scheme (b)] during phase transfer catalysis of sulphur vulcanized natural rubber

$$\left[R^1_n-S_x-R^2_m\right]_y + 2xy\,Na + yH_2 \longrightarrow \left[R^1_n-H\right]_y + \left[R^2_m-H\right]_y + xy\,Na_2S$$

Fig. 9. Proposed mechanism of desulphurization using metallic sodium

metal as illustrated in Figure 9. This method is not practically viable as it is not advisable or practical to swell the scrap tyres in solvent containing metallic sodium.

Similar approaches involving swelling of crumb in solvents is reported elsewhere (Benko *et al.*, 2004; 2006; Hunt and Kovalak, 1999; 2003; Kwabata and Yamashita, 1980; Watabe *et al.*, 1984).

Hydro-devulcanization involves a process in which a solvent soluble hydrogenation catalyst precursor is imbibed into the core of the crumb along with the swelling solvent which upon heating is converted into an active catalyst and reacts with any of the forms of the sulphur normally present in vulcanized rubber (Mc Farlane, *et al.*, 2008). The outline of the plausible mechanism is as represented in Figure 10.

Though these references are found in literature, none of them had successfully emerged as a viable route for devulcanization probably due to their inherent impracticality and inefficiency associated with large scale trials.

Using chemical probes

Chemical probes used in the structural study of rubber vulcanizates (Moore and Porter, 1963) can be used for devulcanization as they can selectively cleave the crosslinks

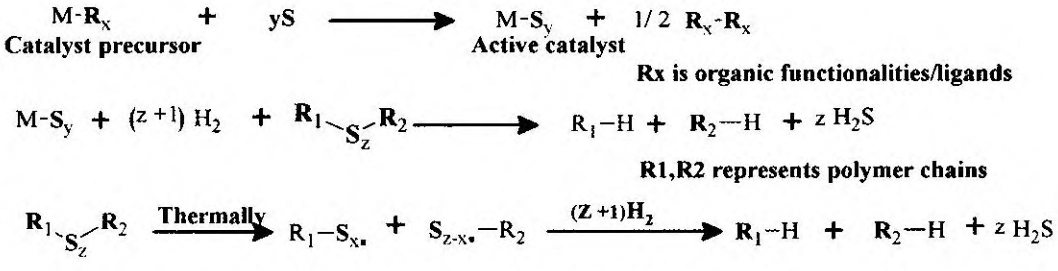


Fig.10. Proposed mechanism of hydro-devulcanization

in the vulcanized rubber network and can thereby cause partial or selective devulcanization. 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 too is impractical for large scale devulcanization 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 primarily used for structural characterization of vulcanizates.

Triphenyl phosphine (Moore and Trego, 1961) is known to open the sulphur crosslinks and convert the polysulphide links into disulphide links and in most cases further to monosulphides according to reaction time, temperature and detailed structure *via* the reaction (Saville and Watson, 1967) shown in Figure 11.

Sodium di-n-butylphosphite cleave di- and polysulphide crosslinks but leaves monosulphide and carbon-carbon crosslinks intact. The process of crosslink cleavage proceeds until monosulphidic crosslinks alone remain as shown in Figure 12.

Thiols in combination with organic bases can selectively cleave sulphur crosslinks (Campbell, 1970). Hexane thiol was found to cleave di- and polysulphidic crosslinks, while 2-propane thiol selectively cleaves polysulphidic crosslinks in a nucleophilic displacement reaction with

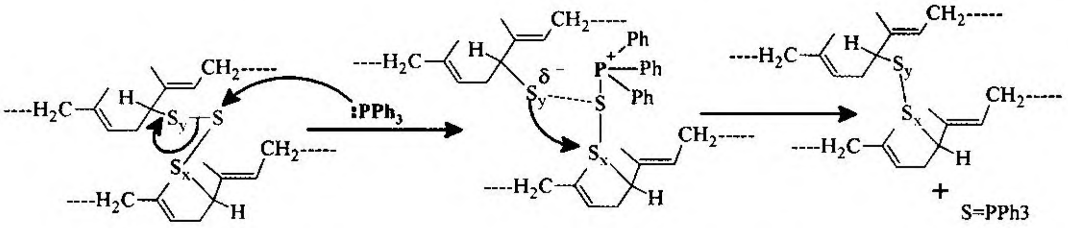


Fig. 11. Desulphuration of crosslinks by triphenyl phosphine

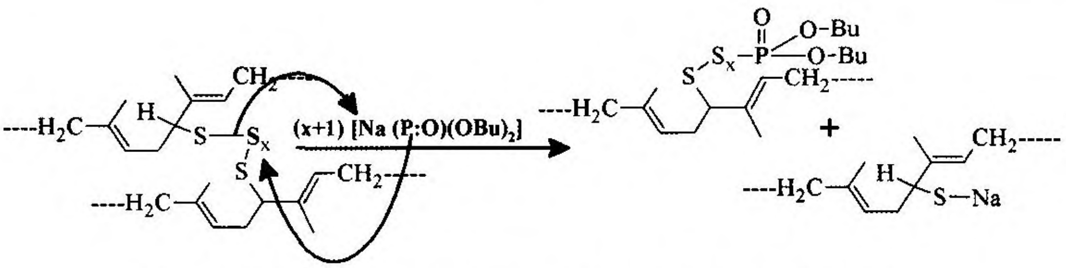


Fig. 12. Cleavage of polysulphidic crosslinks by sodium di-n-butylphosphite

piperidine as base. The thiol-amine combination gives a complex in which sulphur atom has enhanced nucleophilic properties, and is capable of cleaving organic trisulphides and polysulphides as shown in Figure 13.

Methyl iodide reacts with organic sulphides (Fig. 14) to form trimethylsulphonium iodide. The removal of combined sulphur from vulcanized rubber as trimethylsulphonium iodide was regarded as a persuasive evidence of the presence of sulphide sulphur linked to allylic type residues. However, in the presence of methyl iodide over very long periods of time, even alkyl sulphides are unstable (Selker, 1948; Minoura, 1958).

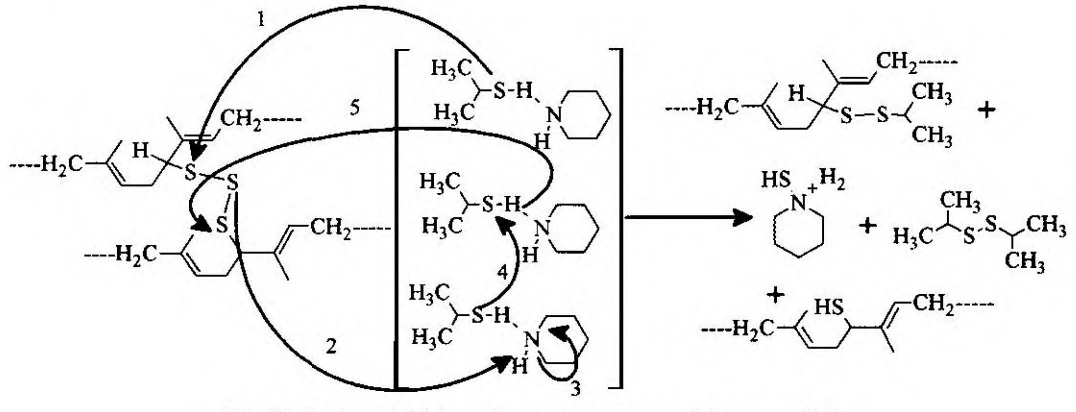


Fig. 13. Action of thiol- amine reagent upon sulphur crosslinks

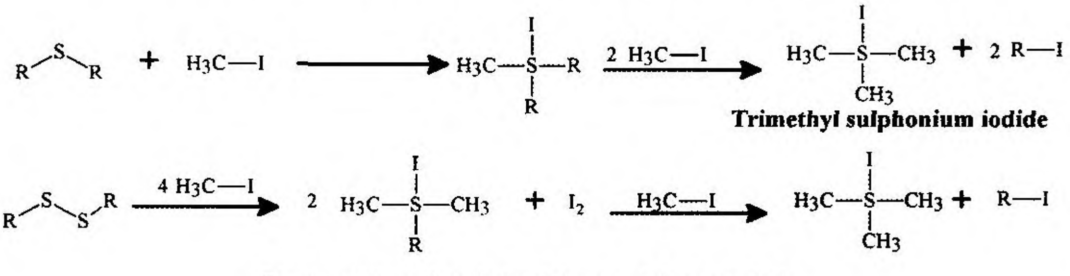


Fig. 14. Action of methyl iodide on sulphur crosslinks

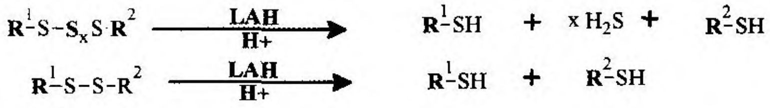
Lithium aluminium hydride (LAH) has been used for qualitative and quantitative analysis of the polysulphide content of various types of rubber vulcanizates (Studebaker, 1970; Studebaker and Nabors, 1959). When organic polysulphides are treated with lithium aluminium hydride in an ethereal solvent at moderate temperatures followed by a weak acid, the terminal groups are liberated as thiols and the interior sulphur atoms are converted into hydrogen sulphide as illustrated in Figure 15.

The reactions of polysulphidic crosslinks with phenyl lithium occurs rapidly at room temperature. Reaction of phenyl lithium with a vulcanizate cleaves disulphide and polysulphide crosslinks only and the monosulphidic crosslinks remain intact. The reactions of phenyl lithium with model compound are given in Figure 16 (Gregg Jr. and Katrenick, 1970).

Thermo-mechanical / Mechanical devulcanization

Thermo-mechanical devulcanization employs just heat and/or shear in the absence of chemical agents to devulcanize rubber. The negative aspect of thermo-mechanical regeneration of scrap rubber is that, with the entire shear that is used and the temperature attained, there is much main chain scission leading to considerable loss of physical properties. Meanwhile, mechanical devulcanization envisages devulcanization of vulcanized 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.

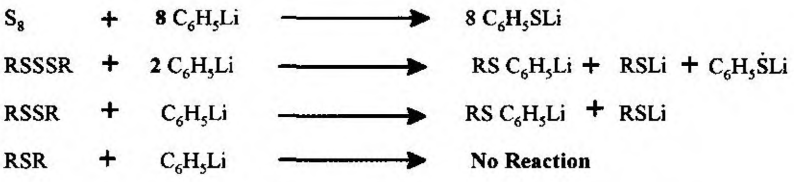
High Pressure High Temperature Sintering (HPHTS) represented in Figure 17 is a novel recycling technique that makes it possible to recycle vulcanized rubber powder made from waste rubber through the application of heat and pressure alone



$$R^1\text{-}S\text{-}S_xS\text{-}R^2 \xrightarrow[H+]{LAH} R^1\text{-}SH + xH_2S + R^2\text{-}SH$$

$$R^1\text{-}S\text{-}S\text{-}R^2 \xrightarrow[H+]{LAH} R^1\text{-}SH + R^2\text{-}SH$$

Fig. 15. Action of lithium aluminium hydride on sulphur crosslinks



$$S_8 + 8\,C_6H_5Li \longrightarrow 8\,C_6H_5SLi$$

$$RSSSR + 2\,C_6H_5Li \longrightarrow RS\,C_6H_5Li + RSLi + C_6H_5\dot{S}Li$$

$$RSSR + C_6H_5Li \longrightarrow RS\,C_6H_5Li + RSLi$$

$$RSR + C_6H_5Li \longrightarrow \textbf{No Reaction}$$

Fig. 16. Action of phenyl lithium on sulphur crosslinks

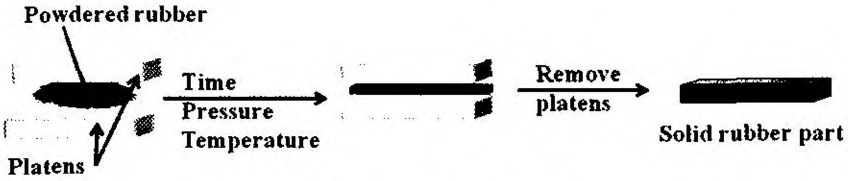


Fig. 17. General representation of the process of high pressure high temperature sintering

(Hrdlicka *et al.*, 2011; Morin *et al.*, 2002). The authors claim that recycled rubbers produced *via* HPHTS have the potential to replace virgin rubber in numerous applications based on the observed mechanical properties of sintered rubber that are comparable with those of conventionally manufactured rubbers. According to the suggested mechanism of particle adhesion, the applied pressure (0.5 MPa to 26 MPa) compress the particles to intimate contact while the temperature (80 ºC to 240 ºC) 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 (Gugliemotti *et al.*, 2012; Acetta and Vergnaud, 1981).

Solid state milling (Cavalieri *et al.*, 2003; Yap, 2000; Zhang *et al.*, 2007; Zhang *et al.*, 2012) and mechanical grinding in a two roll mill (Madhusoodanan *et al.*, 1998) appear to be a simple, low cost method for the devulcanization of crosslinked rubber vulcanizates at ambient temperature without the use of any chemicals. The mechanical properties of revulcanized samples after mechanical devulcanization of a tread formulation (Madhusoodanan *et al.*, 1998) are given in Table 3.

Several studies on mechanical devulcanization by breaking the crosslinking points in the rubber matrix selectively in a twin screw extruder (Bilgili *et al.*, 2000; Matsushita *et al.*, 2003; Shaw, 2010; Sutanto *et al.*, 2006; Tzoganakis and Zhang, 2004; Wiebner *et al.*, 2012; Zhang *et al.*, 2009) are also reported. 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 (Fukumori and Matsushita, 2003). The reactor consists of three zones *viz.* pulverizing zone, devulcanizing zone and cooling zone. In the pulverizing zone the crushed rubber material is converted into fine particles by shear stress and heated to devulcanization reaction temperature quickly. The residence time assured is to be

Table 3. **Revulcanizate properties of retread compound after mechanical devulcanization in a two roll mixing mill**

Properties	Virgin	Devulcanized
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

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

long enough to complete the devulcanization reaction under shear flow in the next devulcanization 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 vulcanized 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 18 (Fukumori and Matsushita, 2003).

Revulcanizate properties of waste ground rubber tyre (GRT) powder devulcanized using a twin screw extruder with and without devulcanizing chemicals in a counter rotating twin screw extruder in comparison with the mechanical properties of a commercial devulcanized GRT (reclaim) reproduced from literature, (Maridas and Gupta, 2013) is given in Table 4. The data gives comparable results for all the vulcanizates except for the higher elongation and the associated lower modulus of revulcanized commercial reclaim

The objective of patented HSM devulcanization technology (Fisher, 2013) is to devulcanize rubber production scraps and reintroduce them into the production chain through a 100% mechanical process. 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. A new class of machine has been developed to apply the stresses required to rupture the crosslink

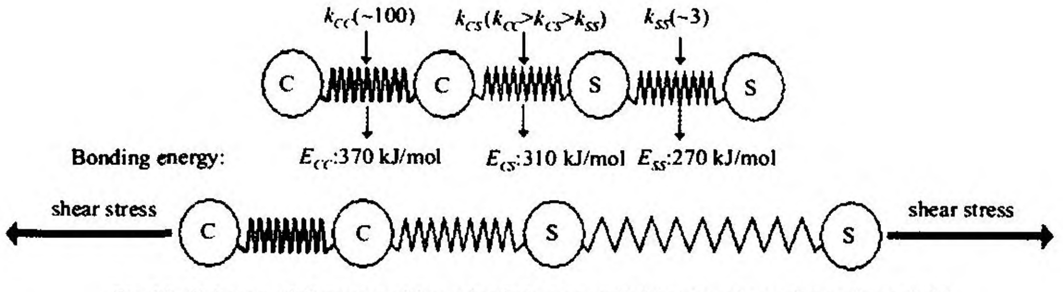


Fig.18. Scheme of decomposition of sulphur crosslinking bonds under a shear field

Table 4. **Comparison of revulcanizate properties of GRT powder devulcanized using a twin screw extruder with commercial reclaimed 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: Devulcanized rubber - 100; ZnO - 5; stearic acid - 3; Accinox-TQ - 0.8; CBS - 0.8; Sulphur – 1.5

bonds. This process is claimed to be applicable to any kind of rubber production waste in which devulcanization 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.

Some other methods like straining of solvent swollen rubber through the tiny pores of a metallic plate (Lima and Carlos, 1997), and impinging vulcanized rubber by ultra high speed fluid jet (Cheng and Lin, 2012) are also reported. Some of these methods, especially the mechanical grinding at ambient temperatures point to the possibility of devulcanization of in-house waste of any manufacturing unit with the existing facilities and capabilities.

Mechano-chemical devulcanization

Most of the mechanochemical devulcanization processes like the De Link process (Sekhar *et al.*, 1998) and the Lev Gum process (Goldshtein and Kopylov, 2002) uses mechanical shear along with chemical modifiers for devulcanization. The process is mostly carried out in a two roll mill at ambient temperature conditions. 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 devulcanized sample along with the plasticity increase brought in by the crosslink scission. This point to the fact that the initial viscosity of the mechano-chemically devulcanized samples may some times be misleading as far as the efficiency of devulcanization is concerned. In earlier studies of mechanochemical devulcanization, combinations of accelerator, ZnO, softening agents and peptizing agents were used as devulcanization agents. Later, processes employing various other devulcanizing agents also came to picture.

Devulcanization using disulphides

Disulphides are widely employed class of devulcanization agent. Several reports of the use of various disulphides for devulcanization studies (De *et al.*, 1999; Jana and Das, 2005a, b) are found in literature. The proposed mechanism through a four step sequence is demonstrated in Figure 19.

Step I. Thermal degradation of diphenyl disulphide into reactive radicals which would then attack the crosslinks to bring about the actual devulcanization

Step II. Breaking of sulphur crosslinking bond under the action of the reactive radicals

Step III. Formation of new active cross-linking site to ensure good

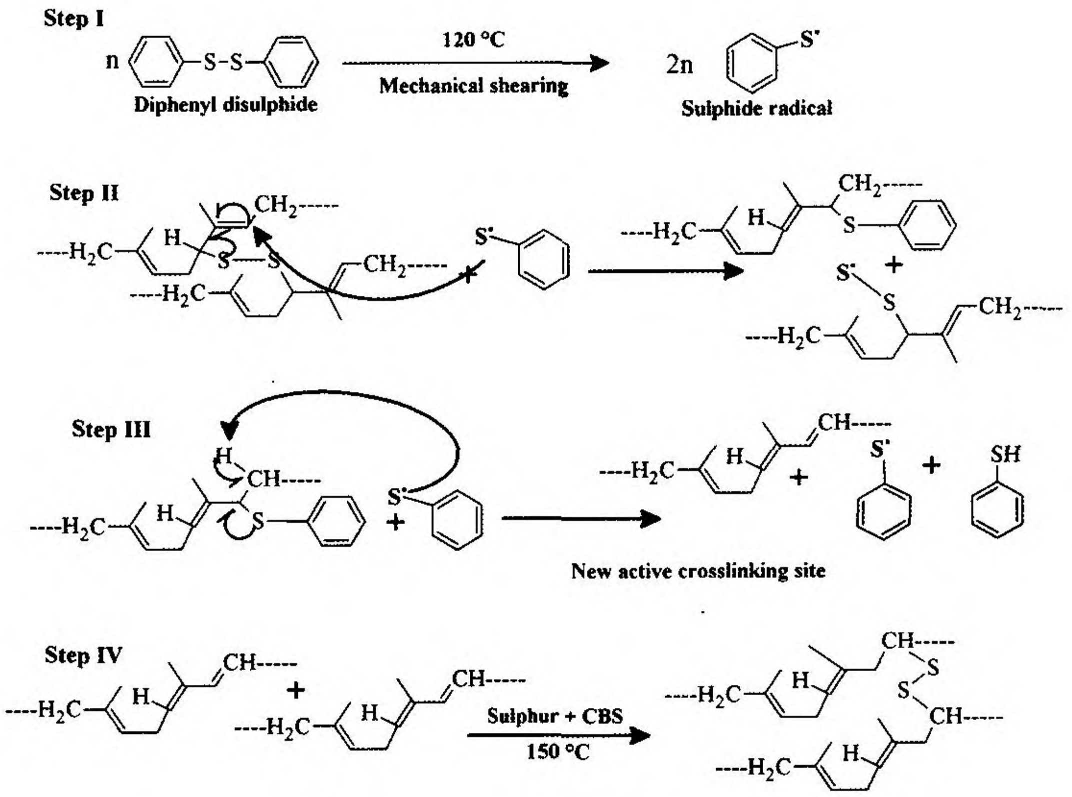


Fig. 19. Mechanism of action of devulcanization using disulphides

revulcanization of the devulcanized sample.

Step IV. Revulcanization process in which the regenerated rubber can be revulcanized alone or mixed with fresh rubber as per the product requirements

The results of mechano-chemical devulcanization studies of unfilled natural rubber cured with high, medium and low sulphur formulations on a two roll mill with the incorporation of 1 phr diaryl disulphide (Jana and Das, 2005) are given in Table 5. The observations reveal that the per cent retention of tensile strength is higher for the revulcanizates whose initial vulcanizates are cured with medium and low sulphur formulations while the high sulphur cured vulcanizates have low per cent retention of tensile strength upon revulcanization. Also the per cent retention of tear strength of revulcanizates from low sulphur cured original sample is the highest where as the other two have comparable tear strength retention upon revulcanization. As the results are in contradiction with the existing understanding that, high sulphur cures lead to predominantly polysulphidic linkages which are easier to break, it might be an indication of the role of the cure system

Table 5. **Vulcanizate properties of fresh natural rubber and its revulcanizates after devulcanization using diaryl disulphide**

Properties	*High Sulphur*		*Medium sulphur*		*Low sulphur*	
	Original	Revulc	Original	Revulc	Original	Revulc
Tensile strength (MPa)	16.82	9.4	15.34	12.11	16.87	14.44
Elongation at break (%)	1048	1006	1333	1065	1300	1011
Modulus at 100 % (MPa)	0.51	0.64	0.62	0.62	0.53	0.56
Modulus at 300 % (MPa)	0.81	0.96	0.93	0.95	0.85	0.85
Tear strength (N/mm)	23.23	18.1	22.5	17.1	18.26	16.57
Shore A hardness	40	38	36	37	32	36
Crosslink density (moles/g x 10^4)	0.7	0.42	0.63	0.44	0.58	0.4

Vulcanization/revulcanization 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)

employed for the vulcanization of original compound as well as the revulcanizate, and the crosslink densities of these samples on the revulcanizate properties.

The De Link process

De Link process (Newell, 1996; Sekhar *et al.*, 1998; Sekhar, 2014) envisages a mechano-chemical devulcanization 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 vulcanized 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 vulcanized rubber in Step I of the process, providing a final compound which is ready

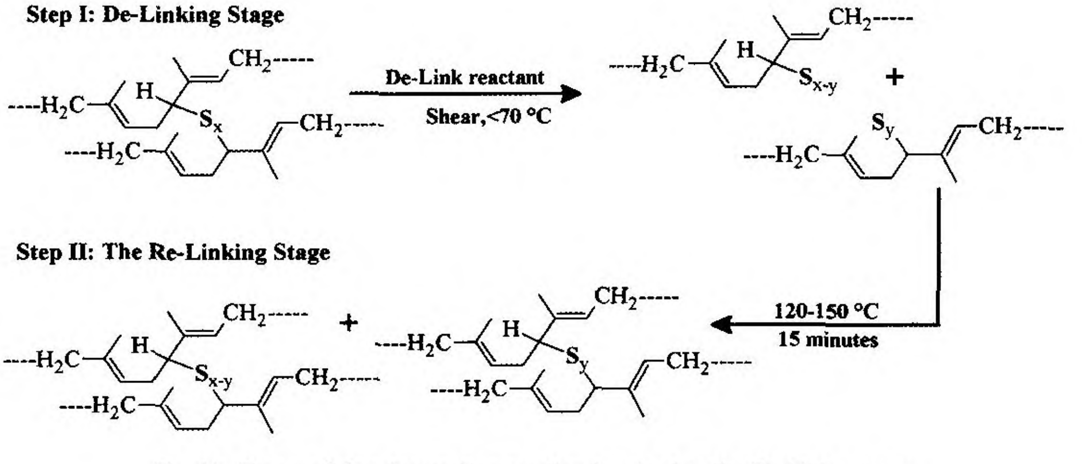


Fig. 20. Proposed devulcanization reaction involved in the De Link process

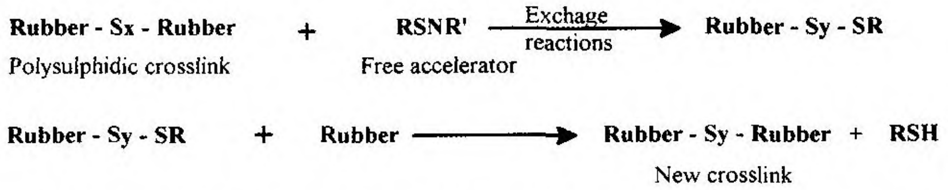


Fig. 21. Exchange reactions between the polysulphidic crosslinks of the vulcanizate and the free accelerator

to be moulded and vulcanized without further addition of any vulcanizing agents (Step II) as illustrated in Figure 20.

Though the mechanism of SKS reaction is shear mediated, the concept of inducing changes in degree of crosslinking of vulcanizates containing polysulphidic crosslinks in the presence of free accelerators were previously reported (Shumanov *et al.*, 1976). According to this study, exchange reactions take place between the polysulphidic crosslinks of the vulcanizate and the free accelerator containing S-S or S-N bonds under the influence of heat as outlined in Figure 21.

Vulcanizate properties obtained for blends of virgin rubber and different types of vulcanized scrap devulcanized using De Link masterbatch, reproduced from literature (Sekhar, 2014) is listed in Table 6. The results show that the nature of scrap used for devulcanization plays an important role in determining the vulcanizates properties of the end product along with the quantity of incorporation of devulcanized rubber in the new compound.

Table 6. **Vulcanizate properties obtained by devulcanization using De Link masterbatches**

Type of vulcanized 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

Counter cure process

Counter Cure is a mechanochemical devulcanization process developed by ESCER Holding Corp, New York, (www.escerrubber.com) in which a counter cure reagent attack the crosslinks at their weakest point - which is found to be the carbon to sulphur bond as per valence bond analysis- without damaging the carbon polymer chain. The process involving three steps is advocated to enable manufacturers to devulcanize waste rubber in-house on existing machinery resulting in a material that can be used as a primary replacement for virgin rubber. The steps involved are shown in Figure 22.

Step I: A mix of a quinone group and benzoic acid creates a benzoyl radical which get converted into phenyl radical

Step II: The phenyl radical under ambient temperature, selectively attacks a transverse sulphur bond and severs it at its weakest point

Step III: The reagent further inhibits C-S bond from reconnecting by blocking the macro radical. Free sulphur is separated from the macro radical and remains in the mixture.

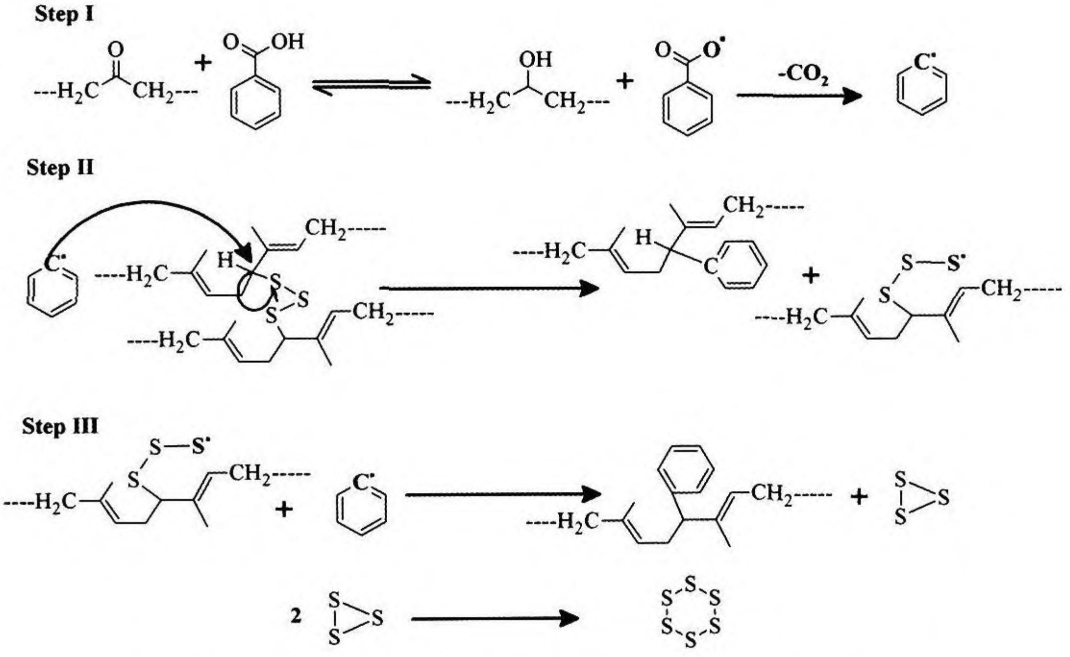


Fig. 22. Proposed mechanism of devulcanization in the Counter Cure process

Devulcanization using benzoyl peroxide

Devulcanization of natural rubber compounds by means of benzoyl peroxide (BPO) as a devulcanizing agent have also been investigated (Rooj *et al.*, 2011) and a plausible reaction mechanism involving three steps for the action of benzoyl peroxide in devulcanization was suggested. The cured rubber is devulcanized in a sigma mixer with the addition of different amounts of benzoyl peroxide at temperature of 80°C at a rotor speed of 60 rpm. The proposed reaction mechanism involving the following three steps is illustrated in Figure 23.

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 revulcanized gum samples after chemical and mechanochemical devulcanization using benzoyl peroxide as devulcanization aid is given in Table 7.

Table 7. **Mechanical properties of chemically and mechanochemically devulcanized natural rubber using benzoyl peroxide**

Properties	Original	Chemical*	Mechano chemical
Tensile strength (MPa)	15.01	13.72	11.15
Elongation at break (%)	1200	1151	1101
Modulus at 100 % (MPa)	1.01	0.92	1.04
Modulus at 300 % (MPa)	1.5	1.23	1.43

*Devulcanization in xylene at 80°C using BPO as devulcanizing agentRevulcanization formulation (phr): ZnO - 5; stearic acid – 2; Anti oxidant - 1; sulphur – 2; CBS - 1

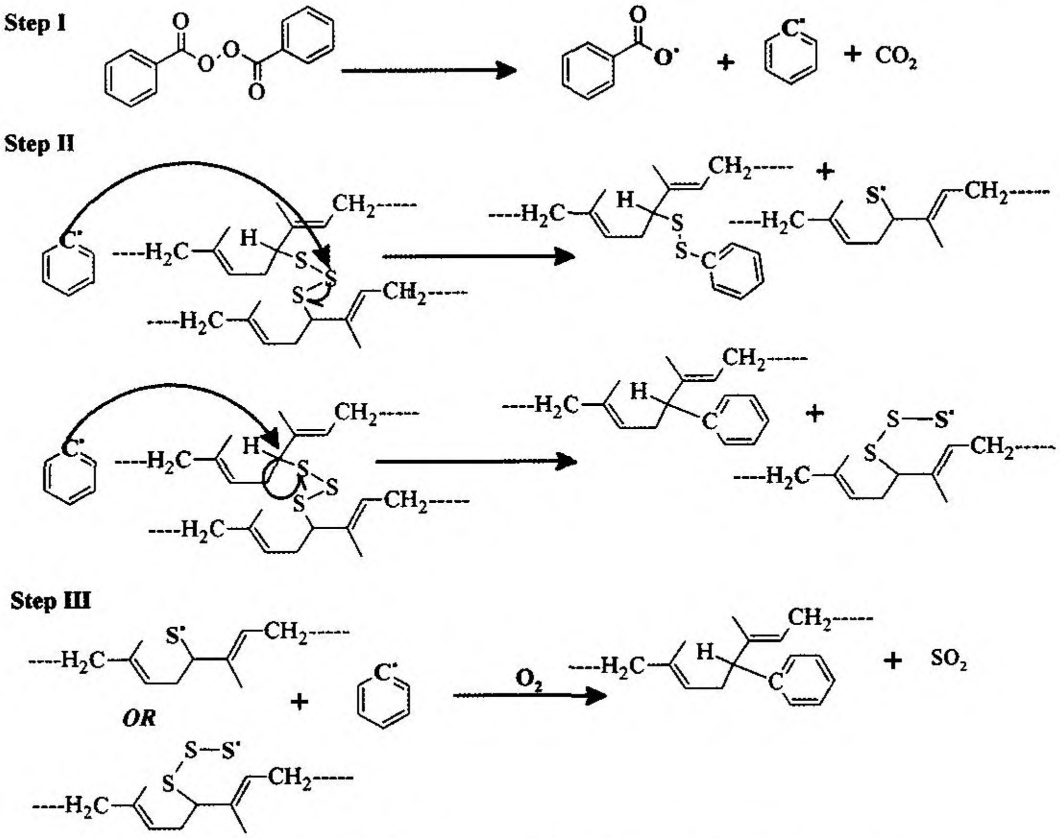


Fig. 23. Mechanism of devulcanization by the action of benzoyl peroxide

Lev Gum process

Lev Gum process is an industrially practised mechanochemical devulcanization method (Beirakh *et al.*, 2004) carried out at room temperature and involves pouring the shredded rubber and a modifying composition in between two rollers that further crush the particles. 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 (Zamir, 2011).

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 or 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

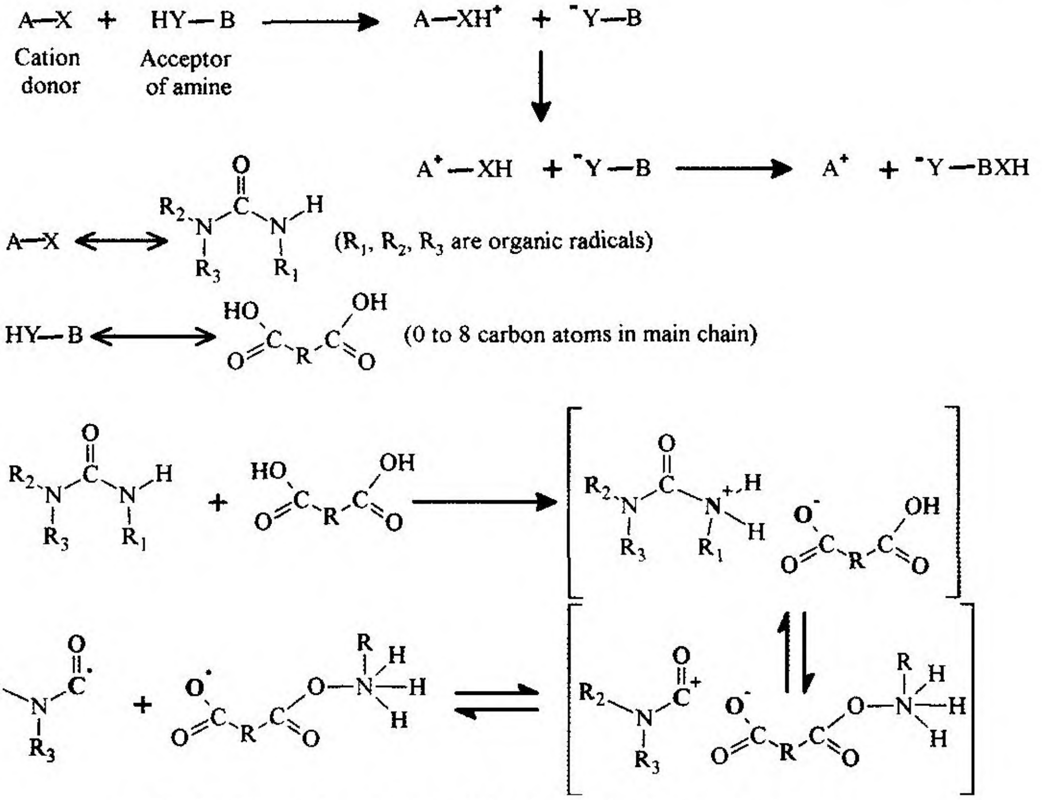


Fig. 24. Proposed mechanism of devulcanization by Lev Gum process

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 24.

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.

The 300 per cent modulus, elongation at break and tensile strength of car tyre buffings devulcanized using 4 per cent of the Lev Gum modifier (urea and adipic acid) followed by blending with 23% virgin natural rubber cured using the formulation, sulphur-0.9 per cent; ZnO-1.0 per cent; Stearic acid-0.5 per cent; CBS-0.2 per cent was reported as 13.8 MPa, 350 per cent and 18.5 MPa respectively (Beirakh *et al.*, 2004). As the corresponding results for a control vulcanizate was not provided, the efficiency of the process cannot be ascertained.

Thiuram disulphides as devulcanization aid

A method of mechano-chemical devulcanization of waste natural rubber using thiuram disulphides [tetramethyl thiuram disulphide (TMTD) and tetra benzyl thiuram disulphide (TBzTD)] on a two roll mixing mill in which, the thiuram compound acts as the devulcanizing agent during the devulcanizing process and as a curing agent during revulcanization, are found in literature (Mandal *et al.*, 2012, Namsri and Thanawan, 2009). The proposed mode of action of the devulcanization agent involves three steps *viz,*

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 as outlined in Figure 25.

The mechanical properties of revulcanized GRT samples after mechanochemical devulcanization on a two roll mill in the presence of varying concentrations of TBzTD (Mandal *et al.*, 2012) is given in Table 8. Results indicate that the tensile strength of the revulcanized samples are not influenced by the concentration of thiuram disulphide. The changes in elongation percentage and modulus seem to be related to the general response of the variation of these properties to curative dosage during vulcanization rather than any effect of devulcanization.

Table 8. **Revulcanizate properties of GRT devulcanized 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

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

High pressure high temperature sintering (HPHTS) with incorporated additives

A mechanochemical devulcanization 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 (Tripathy *et al.*, 2002). 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 devulcanized samples after revulcanization. The action of maleic anhydride on rubber was previously reported (Bacon and Farmer, 1939) and the reaction is proposed by the formation of links between double bonds either in the same chain or in adjacent molecules, the double bonds thus becoming saturated and the possible loss of crosslinks owing to conjugation is taken care of. Figure 26

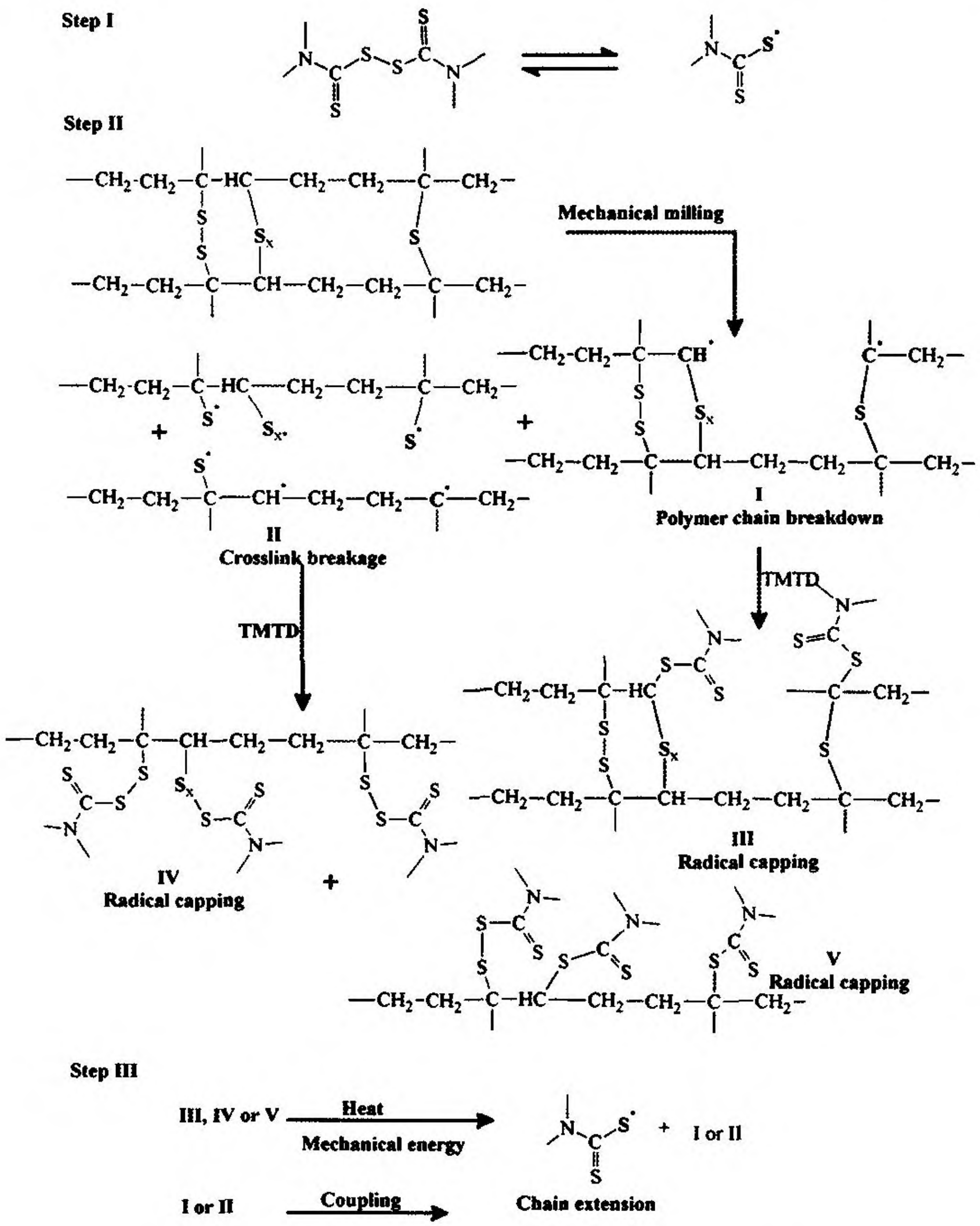


Fig. 25. Mechanism of devulcanization assisted by thiuram disulphides

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

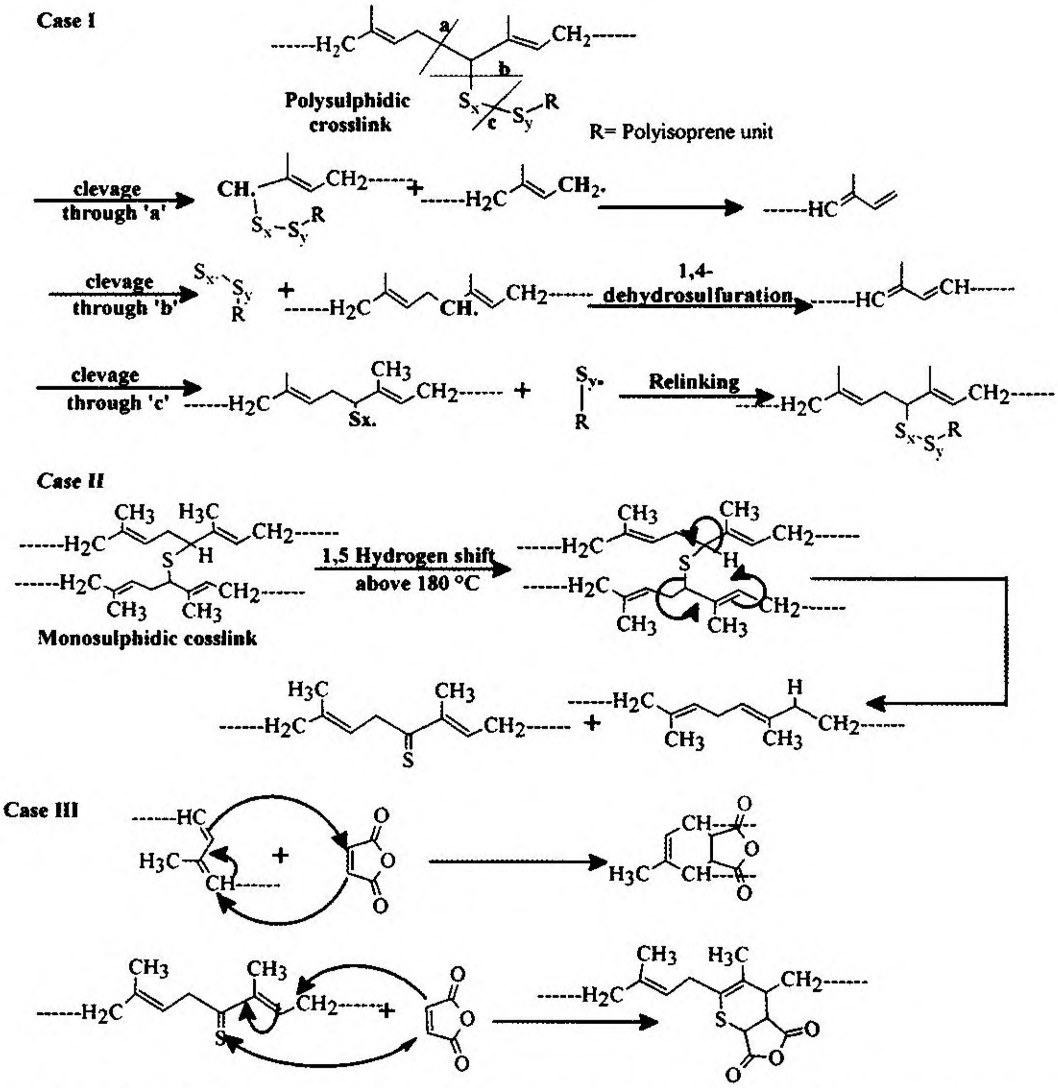


Fig. 26. Breaking of crosslinks during sintering (case I and case II) and Diels Alder reaction and thionylcycloaddition of the derived products with additives

Table 9. **Effect of additives on sintered natural rubber**

Properties	NR original	NR sintered	NR sintered with 2% phthalic anhydride	NR sintered with 4% phthalimide
Tensile strength, MPa	12.9	5.3	8.9	9.6
Elongation at break,%	417	516	499	534
Modulus at 100%, MPa	1.8	0.9	1.1	1.4

and thionyl cycloaddition of these structures with the additives.

The influence of various additives on the tensile properties of sintered gum natural rubber as given in Table 9, claim that the mechanical properties of sintered materials can be improved by incorporating small amounts of dienophiles or dipolar organic additives.

Other processes

The mechanism of devulcanization of sulphur vulcanized natural rubber with aromatic disulphides and aliphatic amines under various temperature conditions (Dierkes *et al.*, 2005) through model compound studies showed that higher ranks of the sulphide crosslinks are devulcanized quite easily whereas the lower trisulphidic and disulphidic crosslinks reacted slowly. The monosulphidic crosslinks did not devulcanize at all in the temperature range used for the study.

Another patented process of mechanochemical devulcanization in a two roll mill at ambient conditions employing a novel devulcanizing 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 ashless solid, preferably inorganic crystalline filler whose role is to promote deformational tension between rubber polymers during the mechanical action in devulcanization and coat the fragmented rubber particles in order to inhibit their sticking (Asasdauskas and Jukna, 2014). 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 vulcanizate properties obtained by incorporation of buffing dust devulcanized by this method to those cases where untreated buffing dust is incorporated as such, reproduced from literature (Asasdauskas and Jukna, 2014), are listed in Table 10. It is observed that the devulcanization of the buffing dust by the said process allows incorporation of higher

Table 10. **Comparison of vulcanizate properties of blends of virgin rubber/ devulcanised buffing dust and virgin rubber/ untreated buffing dust**

Properties	Control	Untreated buffing dust		Devulvanized buffing dust	
		10%	20%	10%	20%
Tensile strength, MPa	19.6	15.6	12.8	18	15.9
Elongation at break,%	453	383	343	410	378
Hardness, Shore A	67	67	66	69	65

loadings of the same into new products with better retention of vulcanizate properties.

The results of comparison of four different devulcanization techniques for the mechanochemical devulcanization 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 (SCO$_2$R, 180°C), is reproduced in Table 11 (Shi *et al.*, 2013). It is clearly evident from the data that low temperature shear devulcanization is superior to other processes with regard to revulcanizate properties.

Many similar process making use of different devulcanization agents, and devulcanization equipments are also found in literature (De *et al.*, 2000; Duin *et al.*, 2005; Goldshtein and kopylov, 2002; Hess, 2009; Jana and Das, 2005; Joseph *et al.* 2014; 2015; Kojima *et al.*, 2004; Premachandra *et al.*, 2011; Saiwari *et al.*, 2013; Tang, 2007; Thaicharoen *et al.*, 2010; 2015).

Table 11. **Comparison of revulcanizate properties of GTR devulcanized by different methods**

Properties	LTSR	HTSR	TSER	SCO$_2$R
Tensile strength (MPa)	11.4	6.4	6	3.2
Elongation at break (%)	324	226	221	238
Modulus at 100% (MPa)	2.82	2.51	2	1.2
Shore A hardness	65	57	57	44

Revulcanization formulation (phr):Devulcanized rubber – 100; ZnO- 2.5; stearic acid – 0.34; sulphur – 1.5, TBBS – 0.8

Ultrasonic devulcanization

One continuous process for devulcanization of rubbers is based on the use of high power ultrasound electromagnetic radiation (Dinzburg and Berdichevsky, 1999; 2002; Isayev *et al.*, 1995; Roberson and Boron, 1998) and was most extensively studied by Isayev and coworkers (Hong and Isayev, 2001; 2002a, b, c; Isayev *et al.*,1996; Levin *et al.*, 1997; Levin *et al.*, 1996; Oh and Isayev, 2002; Shim and Isayev, 2001; Tukachinsky *et al.*,1996; Un *et al.*, 2003; Yashin and Isayev, 2000; Yun, *et al.*, 2001; Yun and Isayev, 2003).

The ultrasonic waves at certain levels, in the presence of pressure and heat can quickly break up three dimensional networks in vulcanized 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. Isayev and coworkers have carried out extensive studies attempting to develop polymer processing technology with the aid of high power ultrasonics. 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 devulcani-

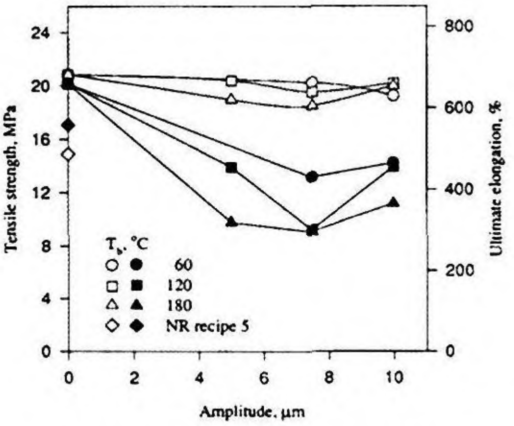


Fig. 27. Physical properties of revulcanized unfilled NR vulcanizates after ultrasound devulcanization

zation process since the bonds at crosslink sites have lower bond energy than the carbon - carbon (C-C) bonds of the main chain.

The mechanical properties of the ultrasonically devulcanized (varying barrel temperatures and amplitude) unfilled NR vulcanizates after revulcanization is demonstrated in Figure 27 (Tapale and Isayev, 1998). It is observed that the tensile strength of the revulcanizates is lowered with increasing ultrasound amplitude to a minimum at 7.5 μm whereas the elongation at break of the revulcanized samples is comparable with that of the original sample.

The process of ultrasonic devulcanization appears to be very fast, simple, efficient and free of solvents and chemicals. Experiments have been carried out on ultrasound devulcanization 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 devulcanization also alters the revulcanization kinetics of rubbers. The specialized technological applications required for the conduct of the process challenges large scale application of ultrasonic devulcanization

Microwave devulcanization

Microwave technology (Bani *et al.*, 2010; Hunt and Hall, 1994; Novotony *et al.*, 1978; Seghar *et al.*, 2015) has also been proposed to devulcanize waste rubber employing microwave electromagnetic energy to break the S-S or C-S bonds. 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 260-350ºC. 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. While the dipolar polarization mechanism (dielectric heating) explains the heating phenomena of dipoles, the ionic conduction mechanism explains the heating in samples with free ions or ionic species. The interfacial polarization (also called the Maxwell Wagner effect) mechanism describes the heating in non-homogeneous systems created by the suspension of conducting particles in a non-conducting medium.

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 devulcanization. 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, devulcanization efficiency can be improved at reduced processing time and cost savings. Study on the chemical modifications in SBR by microwave devulcanization (Hirayama and Saron, 2012) points that the high temperature applied during the process causes degradation of polymer backbone and induce chemical modifications generating devulcanized rubber with inferior properties. To improve devulcanization efficiency and reduce treatment energy, promising new approaches consisting of combined microwave irradiation with the effect of diphenyl sulphide (Vega *et al.*, 2008), impregnation of the waste rubber with ionic solvent and then heat treating the impregnated material with microwave radiation (Seghar *et al.*, 2015), are also found in literature.

Biological/Biotechnological devulcanization

Biological devulcanization of vulcanized rubber has been used in some cases, although vulcanized materials are resistant to normal microbial attack. Several researchers (Berekaa *et al.*, 2005; Bohm and Stephanopoulos, 2011; Christofi *et al.*, 2010; Straube *et al.*, 1994; Yusof and Ahmad, 2010) have reported the use of different types of micro organisms to attack the sulphur bonds in vulcanized elastomers.

The unvulcanizing process of crumb rubber by both chemical treatment with di-(cobenzanidophenyl) disulfide, and microbial treatment with *Thiobacillus peromatabolis* is reported (Kim and Park, 1999). The sulfur content in the crumb rubber was decreased up to 8 per cent by chemical treatment and 30% by a 30-day microbial treatment. The mechanical performance of the natural rubber compounds blended with the treated crumb rubber were better than that of the blend with the untreated crumb. The best results showed up in the 30-day microbial-treated rubber blend according to the report. A white rot basidiomycete, *Ceriporiopsis subvermispora*, degraded vulcanized natural rubber sheets on a wood medium (Sato *et al.*, 2004). The fungus decreased the total sulphur content of the rubber by 29 per cent in 200 days, accompanied by the cleavage of sulphide bonds between polyisoprene chains.The oxidative cleavage of sulphide bonds by *C.subvermispora* demonstrates that ligninolytic basidiomycetes are potential microbes for the biological devulcanization of rubber products.

A bacterium isolated from old tire sample in Alexandria, Egypt, was shown to be able to utilize natural rubber and other isoprenoid compounds as a sole source for carbon and energy (Berekaa, 2006). Devulcanization studies using a strain of *Nocardia* pointed that, the effectiveness of the biological treatments are highly dependent on the composition of the sample to be devulcanized and is affected by the polymer type, presence of filler, cure system employed, etc (Tsuchii *et al.*, (1997). Enzymatic devulcanization (Yusof and Ahmad, 2010) is a new technique which uses enzyme secreted by bacteria to break the sulphur bonds in the vulcanized rubber structure.

Irrespective of all these innovations large space and time requirements challenge the industrial expansion of biotechnological devulcanization processes among which the innovations by Recyclatech (Christoffee, *et al.*, 2010; 2011; http://www.recyclatech.com; Oldfield, 2005) is an exception. The

Recyclatech Technology is claimed to be the only proven biotechnology, using novel microorganisms that can desulphurise the specific sulphur vulcanization bonds in natural and synthetic rubber products demonstrated in model compounds containing $C\text{-}S_n\text{-}C$ bonding found in vulcanized rubber through a process involving mechanical grinding and microbial treatment. The green microbial process facilitates surface modification of rubber crumb enabling the rubber particles to chemically bond with other materials in compounds, thereby becoming an integral part of the material structure rather than just filler. The process envisages the reprocessing of used tyres into reusable rubber, economically, profitably and without any environmental impact.

CONCLUSION

Considerable scientific attention has been given to study and understand the sulphur vulcanization process and the reaction mechanisms involved. It is doubtful if such an earnest attempt to understand the chemical reactions and mechanisms related to devulcanization have ever been made. The review presents the various practices used for environmentally sound management of end of life tyres and other rubber products giving emphasis to the proposed chemical reactions and mechanisms involved in those practices. The initial attempt at reusing rubber was through reclaiming followed by the use of finely ground rubber. Later there have been numerous attempts to produce reusable rubber through devulcanization by using some of the following methods and techniques *viz.* ultrasonic, microwave, bacterial degradation, chemical/ mechano-chemical, swelling in active solvents *etc.* Neither of these methods led to products that could be used in the same manner as original unvulcanized rubber polymers. Most of the processes have drawbacks, limiting their use on a large scale. Some chemical and bio-chemical processes appear to be capable of devulcanizing rubber but they either devulcanize a superficial layer on the rubber crumb or are inefficient. An additional concern about some of these processes is that they require relatively high temperatures, which lead to greater chance for thermal degradation reactions which can shorten the length of polymer chains or otherwise change their chemical structures such that their mechanical properties are adversely affected, thus limiting their usage in new rubber products.

A recent study (Shi *et al.*, 2013) involving comparison of GTR devulcanized by different methods adopting different devulcanization conditions pointed that a combination of several important factors such as temperature, shear force, reaction time, devulcanization atmosphere and reclaiming agent plays a vital role in controlling the devulcanization efficiency. Based on the study it is suggested that devulcanization carried out without higher shear force at low temperatures in an oxygen free environment would generate the best quality devulcanized rubber. The idea behind coupling some of these methods (Filermans and Wicks, 2002) with an objective to improve the devulcanization efficiencies might be based on the former concept and is worth mentioning though the outcome was not as desired.

The current recycling methods centered on energy and material recovery renders a minute fraction of the total annual output of used rubber brought back to the rubber industry, as the reclamation/ devulcanization processes for material recovery delivers either partly devulcanized or highly degraded products whereas products of other recycling strategies are favoured consumables for industries like civil engineering or power generation rather than the rubber industry. Thus, further efforts should be directed to improve the selectivity in bond scission of these devulcanization processes. Optimal conditions have to be established which will yield revulcanized rubber with best performance characteristics. The world scene therefore is in need of a feasible innovative technology that could effectively and efficiently devulcanize used rubber, enabling its significant reuse in the rubber industry.

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