Available online at www.sciencedirect.com
ScienceDirect
Prog. Polym. Sci. 31 (2006) 811–834
PROGRESS IN POLYMER SCIENCE
www.elsevier.com/locate/ppolysci

Science and technology of rubber reclamation with special attention to NR-based waste latex products

V.V. Rajan[a], W.K. Dierkes[a], R. Joseph[b], J.W.M. Noordermeer[a,*]

[a] *University of Twente, Faculty of Science and Technology, Department of Rubber Technology, P.O. Box 217, 7500 AE Enschede, The Netherlands*
[b] *Cochin University of Science and Technology, Dept. of Polymer Science & Rubber Technology, Kochi–22, Kerala, India*

Received 13 February 2006; received in revised form 9 August 2006; accepted 9 August 2006

Abstract

A comprehensive overview of reclamation of cured rubber with special emphasis on latex reclamation is depicted in this paper. The latex industry has expanded over the years to meet the world demands for gloves, condoms, latex thread, etc. Due to the strict specifications for the products and the unstable nature of the latex as high as 15% of the final latex products are rejected. As waste latex rubber (WLR) represents a source of high-quality rubber hydrocarbon, it is a potential candidate for generating reclaimed rubber of superior quality. The role of the different components in the reclamation recipe is explained and the reaction mechanism and chemistry during reclamation are discussed in detail. Different types of reclaiming processes are described with special reference to processes, which selectively cleave the cross links in the vulcanized rubber. The state-of-the-art techniques of reclamation with special attention on latex treatment are reviewed. An overview of the latest development concerning the fundamental studies in the field of rubber recycling by means of low-molecular weight compounds is described. A mathematical model description of main-chain and crosslink scission during devulcanization of a rubber vulcanizate is also given.
© 2006 Elsevier Ltd. All rights reserved.

Keywords: Rubber; Reclamation; Latex products; Main-chain scission; Crosslink scission; Devulcanization

Contents

1. Introduction . . . 812
2. Role of reclaiming agents, oils and catalysts. . . . 814
3. Reaction mechanism during reclamation of vulcanized rubber . . . 815
   3.1. Main-chain scission (phenyl hydrazine-iron chloride) . . . 815
   3.2. Crosslink scission (triphenyl phosphine) . . . 815
   3.3. Main-chain and crosslink scission (thiols and disulfides) . . . 816
4. Opening of sulfur cross links . . . 816
5. Different types of reclaiming processes . . . 816

*Corresponding author. Tel.: +31 53 489 2529; fax: +31 53 489 3823.
E-mail address: J.W.M.Noordermeer@utwente.nl (J.W.M. Noordermeer).

0079-6700/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.progpolymsci.2006.08.003

5.1. Thermal processes . . . 817
5.1.1. Heater or pan process . . . 817
5.1.2. Digester process . . . 817
5.1.3. Alkaline process . . . 817
5.1.4. Neutral process . . . 817
5.1.5. High-pressure steam process . . . 817
5.1.6. Engelke process . . . 817
5.1.7. Continuous steam process . . . 818
5.2. Thermo-mechanical process . . . 818
5.2.1. High-speed mixing . . . 818
5.2.2. Reclaimator process . . . 818
5.3. Mechano-chemical methods . . . 818
5.3.1. Trelleborg cold reclaiming (TCR) process . . . 818
5.3.2. De-Link process . . . 818
5.3.3. Swelling in benzene with a sulfoxide . . . 819
5.4. Microwave recycling . . . 820
5.5. Ultrasound recycling . . . 821
5.6. Selective scission of cross links by chemical probes . . . 821
5.6.1. Comparison of chemical probes and reclaiming . . . 822
5.7. Other chemical methods . . . 822
5.8. Biotechnological processes for reclaiming of rubber . . . 823
5.9. Devulcanization in supercritical carbon dioxide . . . 823
6. Latex products reclaiming . . . 823
7. Model compound studies on the devulcanization of natural rubber using 2,3-dimethyl-2-butene . . . 826
8. Model description of main-chain scission and crosslink scission . . . 829
8.1. Chain scission at random . . . 829
8.2. Crosslink scission . . . 830
8.3. Intermediate stages between crosslink scission and main-chain scission . . . 830
9. Advantages of reclaimed rubber . . . 831
9.1. Easy breakdown and reduced mixing time . . . 831
9.2. Easy calandering and extrusion . . . 831
9.3. Influence on ageing properties . . . 831
10. Uses of reclaimed rubber . . . 831
Acknowledgments . . . 832
References . . . 832

1. Introduction

Charles Goodyear invented the process of sulfur vulcanization in 1839, and as a result of his discovery the rubber industry expanded explosively. The first products manufactured from vulcanized rubber in the 1840s were footwear, but soon many different types of rubber goods, sheet rubber and hard rubber articles were produced. In those days, before the establishment of rubber plantations in India, all raw rubber was collected from the jungles of Brazil [1,2]. The demand for crude rubber soon overtook supply, with prices sky-rocketing. At that time there was a great economic incentive to spur the development of re-using scrap vulcanized rubber.

One method of recycling scrap rubber is to grind it as fine as possible and blend it with new rubber as elastomeric filler. This was the first method of reclaiming and a patent was granted to Charles Goodyear himself for this technique. This was suitable for compounding carriage springs, which were fairly large barrel-shaped molded articles. However, most of the demand and growth in those days were in the footwear business and simply using ground rubber, quality wise these products were not acceptable for this application. Boots and shoes were the most important rubber products in the 19th century. They were formulated with a fairly low level of sulfur in order to prevent unsightly sulfur bloom. As a result, they were lightly vulcanized and could easily be reclaimed. Such a material can be successfully devulcanized or partially replasticized by the action of steam alone at a higher temperature but for a substantially longer

period of time than the original vulcanization cycle. This is known as the heater process, patented by Hiram L. Hall in 1858 [3]. The product of this reclaiming process was revulcanizable and could be blended with the new natural rubber at a higher percentage.

In order to make a high-quality reclaim, reinforcing fibers must be removed from the rubber scrap. In the early years this was done by the cottage industry in which women and children stripped the rubber from the fabric of old boots "by soaking the rubber in water, and then taking a small knife and starting to separate the rubber from the cloth and stripping it off". Eugene H. Clapp [1] used an air-blast method of separating fibers and rubber after the scrap was ground. Clapp did not patent the technique but managed to keep it secret for several years. Although Clapp's method is the early version of present-day de-fibering equipment, it was not developed to the point that it could produce a raw material of more than mediocre quality. Better methods of producing large quantities of higher-quality reclaim were needed.

It had been common knowledge for many years that acid has a degrading effect on fabric and that rubber is resistant to acid. N. Chapman Mitchell [1] was a leader in the development of the acid process, and started the first company to produce reclaimed rubber by that method. Mitchell filed patents on the process in 1881, which were granted, but they were poorly drawn and were later on canceled. In the acid process, the ground scrap was boiled for several hours in a fairly strong solution of either sulfuric or formic acid to destroy the fabric; the rubber was washed and devulcanized with high-pressure steam in the so-called pan process; a two-step operation. Although the acid process was used quite successfully for a longer period of time, it had its shortcomings. One of the problems was the inability to process high-sulfur rubber scrap, such as bicycle tire scrap. If the acid was not thoroughly washed, it could cause poor aging characteristics. The high quantities of free sulfur in such types of rubber scrap tend to cause further vulcanization during the process instead of devulcanization.

A breakthrough was achieved in 1899 with the patent of Arthur H. Marks, which describes an invention that came to be known as the alkali digester process. Ground rubber, fiber and a dilute solution of caustic soda were cooked at high pressure for about 20 h. This process caused de-fibering, desulfuring and devulcanization of the rubber scrap in one step. This technique could be used to reclaim any type of rubber scrap available at that time. A year later, in 1900, Marks obtained another patent on an improvement that involved steam jacketing the vessel and agitation of the mass. This is the method used by most reclaimers for more than 50 years.

Two other important developments occurring at the turn of the 19th century involved the introduction of new machines to greatly improve the quality of reclaimed rubber. One development was the refiner that is a special type of mill used to produce a much smoother and more homogeneous product. The other was the strainer, which is an extruder equipped with a screen for removal of foreign matters from the rubber. With the exception of invention of the Reclaimator in 1953, developments in the reclaiming industry since the time of Marks have been mostly evolutionary rather than revolutionary [4].

The reclaimator process is the only commercially successful continuous technique for devulcanizing rubber scrap; all the other techniques are batch processes. The reclaimator is a special type of screw-extrusion machine. It is jacketed to provide several zones of controlled temperature using either hot oil or cooling water and the clearances between the screw and the chamber wall are close and adjustable. The rubber is subjected to a controlled amount of high shear and pressure in continuously moving equipment.

The latex industry has expanded over the years to meet the world demand for examination gloves, condoms, latex thread, etc. Due to strict specifications for latex products, up to 15% of the products might be rejected. These rejects create a major disposal problem for the rubber industry. Since latex product waste represents a source of high-quality rubber hydrocarbon it is a potential feedstock for reclaimed rubber of superior quality.

Probably the largest numbers of defects encountered in articles produced by latex dipping are pinholes, craters and blisters. These defects are caused by air bubbles entrapped in the latex compound, particles of dirt in the latex compound and on the former, and greasy areas of the former [5]. The former is the positive mold, which is dipped in the latex repeatedly, onto which the rubber remains as a film and is cured in an oven. The rubber article is later manually removed from the former. Problems arising from particles of dirt and dust settling on the former are especially critical in

dry-coagulant dipping processes. This is because the coacervant film usually goes through a tacky stage as it dries.

Over the past 43 years, the world NR latex (NRL) consumption has grown at an average of 4.2% per year, increasing to an estimated 925,000 tons in 2003. However, the growth was not smooth; NRL consumption had a slower growth period from 1960 to 1983, with an average growth rate of 2.1% per year and a faster growing period from 1984 to 2003, averaging 5.6% per year. In terms of actual tonnage the increase was 159,000 and 597,000 tons [6] for the respective periods. The main driving force of the faster growth rate of the latter period was and still is the AIDS-HIV threat and the consequent growing awareness of the need for protection, reflected in the rapid rise of demand for medical gloves, in particular, since the mid-1980s. Gloves were the main reason for the rising NRL uptake over the past 20 years; it was and still is playing the leading role in the latex world [7]. The product range of NRL is wide and varied, ranging from industrial to household over medical applications.

The main area of growth of latex consumption was Asia from 1984 to 2003, the average growth rate for the region was 9.2% a year, increasing its annual consumption from 144,000 to 692,000 tons. This is 5% above the world rate for the same period. As of 2003, the annual consumption levels of the other five regions are: North America 101,000 tons, Latin America 33,000 tons, European Union 78,000 tons, other European countries 14,000 and Africa 4000 tons.

The rubber industry faces a major challenge in finding a satisfactory way to deal with the increasing quantities of rubber goods, which reach the end of a useful life and are rejected from the factories as scrap. The main source of waste rubber is discarded rubber products, such as tires, rubber hoses, belts, shoes and flash. Recycling of waste rubber has important implications, such as [8]:

(i) *Protection of the environment*: The environmental pollution caused by waste rubber is getting more and more serious. Piles of discarded tires are good breeding places for mosquitoes and disease. They spread infections such as encephalitis and malaria. Tire dumps catch fire, they are difficult to extinguish.
(ii) *Conservation of energy*: Raw materials for rubber industry are based on oil to a large extent, especially in countries where natural rubber resources are scarce. More than 70% of the raw materials for the synthetic rubber are made from oil. Moreover, waste rubber is a high-value fuel with a calorific value of approximately 3.3×10^4 kJ/kg, [9]; the highest value in the industrial waste sector similar to that of coal.
(iii) *Use as industrial raw material*: Regenerated rubber and powdered rubber are raw materials not only for the rubber industry.
(iv) Reducing the costs and improving the processing behavior of rubber compounds.

For the reasons mentioned above, recycling of waste rubber has received much attention in recent years worldwide [9]. Important references on disposal problems are Crane et al. [10] as well as Beckman [11]. Klingensmith [12], and recently Myhre[13] did a lot of work on recycling. Excellent overviews are provided by Manuel and Dierkes [14], Dunn [15] and LeBeau [16]. A comprehensive review on the chemistry of reclamation is provided by Warner [17] and Yamashita [18].

2. Role of reclaiming agents, oils and catalysts

The following definition was adopted in 1981 by the Rubber Recycling Division of the National Association of Recycling Industries, Inc.: Reclaimed rubber is the product resulting when waste vulcanized scrap rubber is treated to produce a plastic material which can be easily processed, compounded and vulcanized with or without the addition of either natural or synthetic rubbers [19]. Regeneration can occur either by breaking the existing cross links in the vulcanized polymer or by promoting scission of the main chain of the polymer or a combination of both processes.

A definition of reclaiming agents, catalysts and reclaiming oils depends on their reaction and function within the process. Yamashita [18] published a review on the different reactions that might occur during reclaiming. The auto-oxidation accelerated degradation reactions are described and these reactions occur particularly in reclaiming processes that involve shearing actions. Without the addition of reclaiming agents, auto-oxidation reactions will progress through hydroperoxides formed by the attack of oxygen, which is always present in the rubber. Utilization of reclaiming agents speeds up and introduces new pathways for the reclamation reactions. Reclaiming catalysts are chemical

compounds, which are effective in only small amounts during reclamation.

Reclaiming oil has several roles apart from raising the plasticity of reclaimed rubber, such as an accelerating action on the oxidation of the rubber [18] and a gel preventing action by acting as a radical acceptor. It also facilitates the dispersion of the reclaiming agent into the rubber matrix. Hence reclaiming oil with a high compatibility with the rubber should be used. The reclaiming oils often have active double bonds or methylene groups in the molecules, through which they are more easily oxidized than the rubber molecule. It is assumed that these activated molecules formed by the auto-oxidation reaction, accelerate the oxidation of the rubber.

3. Reaction mechanism during reclamation of vulcanized rubber

The reaction mechanisms in reclaiming are complex and not well investigated. However, the following basic reactions can be formulated: Reclamation can occur by breaking the existing cross links in the vulcanized rubber (crosslink scission) or by promoting scission of the main chain of the polymer (main-chain scission) or by both processes. All three possibilities are considered separately in the following sections.

3.1. Main-chain scission (phenyl hydrazine-iron chloride)

As an example of this mechanism, the phenyl hydrazine–iron (II) chloride system (PH–$FeCl_2$) is very effective for the oxidative degradation of the rubber molecules at low temperatures. In the degradation reaction of polyisoprene rubber with the PH–$FeCl_2$ system in air, the phenyl hydrazine is the main reagent and $FeCl_2$ acts as catalyst: the rate of degradation of the rubber is determined by the phenyl hydrazine concentration. Phenyl hydrazine is itself easily degraded by oxygen and it is known that nitrogen gas is liberated in this reaction [20]. The rate of degradation is very high in the presence of a metal salt. The initial oxidative degradation of rubber molecules with the PH–$FeCl_2$ system is outlined below (Fig. 1).

If sufficient oxygen is present, the various radicals formed by this reaction degrade the rubber molecules as indicated in Fig. 2 [21].

The hydroperoxide is decomposed in the presence of transition metals as shown in Fig. 3.

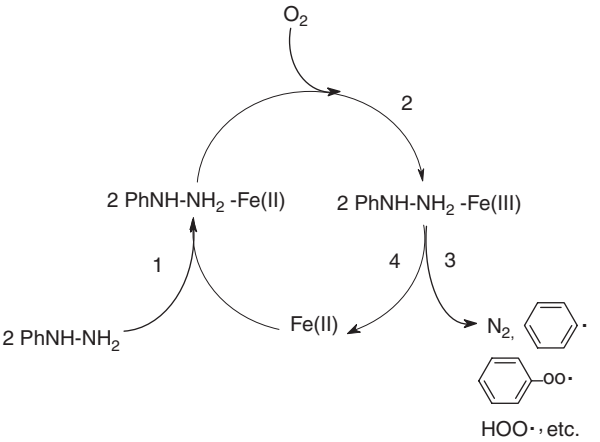


Fig. 1. Oxidation mechanism for the PH–$FeCl_2$ system (adapted from Ref. [20]).

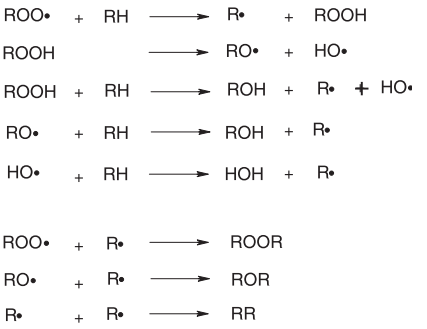


Fig. 2. Bolland oxidation mechanism (RH = rubber hydrocarbon) (adapted from Ref. [21]).

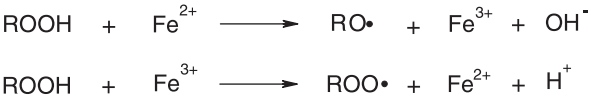


Fig. 3. Decomposition of peroxides by ions of metals (redox mechanism) (adapted from Ref. [21]).

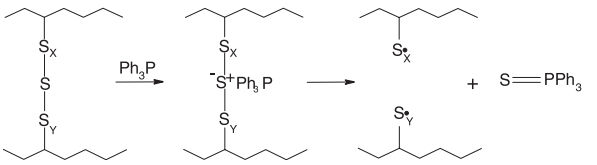


Fig. 4. Opening of sulfur crosslinks by triphenyl phosphine (adapted from Ref. [22]).

3.2. Crosslink scission (triphenyl phosphine)

Triphenyl phosphine is known to open the sulfur cross links by a nucleophilic reaction [22] as shown in Fig. 4.

The radicals can recombine, but a reaction with a double bond is also possible, with the net effect that the crosslink is broken.

3.3. Main-chain and crosslink scission (thiols and disulfides)

Thiols and disulfides interact with radicals formed during the degradation of the rubber network. It is assumed that they initiate an oxidative breakdown of sulfur cross links and a degradation of rubber vulcanized [23] and inhibit gel formation by combination with the radicals. A vulcanizate that is recycled with thiols and disulfides shows a larger degree of network breakdown. In thermo-mechanical processes disulfides and thiols are equally reactive [9]. Aliphatic thiols are found to be less active than aromatic thiols. The efficiency of aromatic compounds seems to increase when alkyl groups or halogens are substituted on the benzene ring. A mechanism that is often proposed for the reaction of disulfides with sulfur vulcanizates is the opening of cross links or the scission of chains by heat and shearing forces and their reaction with disulfides, which prevents recombination. Atmospheric oxygen is also said to prevent recombination by stabilizing the radical sites. Other compounds with a stabilizing effect are antioxidants [24]. The result is a drop in molecular weight of the polymer. During the thermal degradation hydrogen sulfide and thiols are produced.

4. Opening of sulfur cross links

Various chemical probes are already used in crosslink structure analysis for opening the sulfur cross links [25]. The reactions described in Figs. 5–9 have been proposed as typical methods for rupturing the sulfur cross links of rubbers [18].

These reactions take place under the given reaction conditions, but the complete reaction is not as simple as shown. Hydrogen addition and reduction reactions are also possible but these are to be avoided from the point of view of reclaiming.

5. Different types of reclaiming processes

There are basically four different levels of recycling [25]:

(i) material recycling;
(ii) monomer recycling;
(iii) fuel recycling;
(iv) energy recycling.

In this study only material recycling will be taken into consideration.

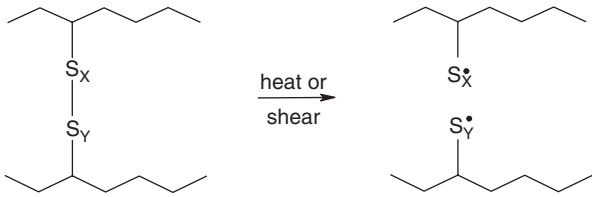


Fig. 6. Opening of sulfur crosslinks by heat or shear (adapted from Ref. [18]).

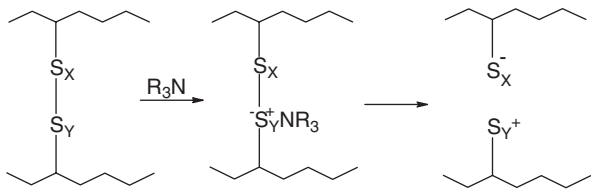


Fig. 7. Opening of sulfur crosslinks by nucleophilic reagents (adapted from Ref. [18]).

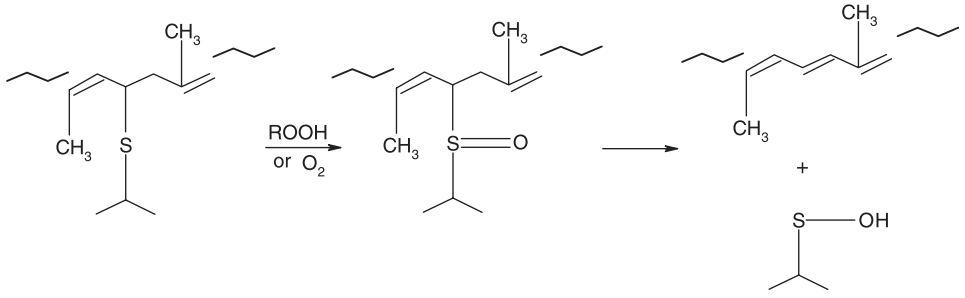


Fig. 5. Opening of sulfur crosslinks by oxidation; ROOH = organic hydroperoxide (adapted from Ref. [18]).

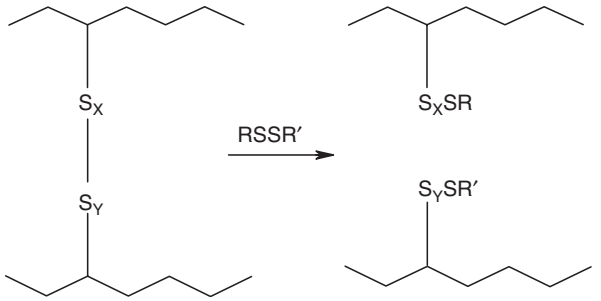


Fig. 8. Opening of sulfur crosslinks by rearrangement (adapted from Ref. [18]).

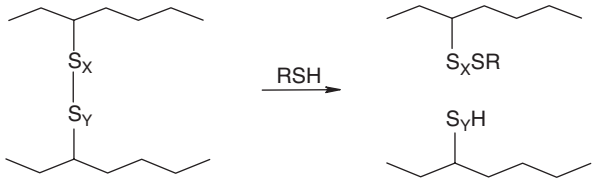


Fig. 9. Opening of sulfur crosslinks by substitution (adapted from Ref. [18]).

The two principle methods to obtain a re-usable recycled rubber material are:

(i) grinding of the rubber and reusing it in the form of a granulate or surface activated powder;
(ii) treating the material in a reclaiming process to generate a visco-elastic reclaim.

Different processes are developed in order to reclaim vulcanized rubber.

5.1. Thermal processes

In this section, reclaiming processes that make use of heat and possibly chemicals to plasticize the rubber scrap are summarized [4].

5.1.1. Heater or pan process

The heater or pan process is one of the oldest and most simple processes used in the rubber reclaim industry. In this process, finely ground, fiber-free rubber powder is mixed with oils and reclaiming agents and put into trays. The trays are designed to help to spread the heat into the powdered mass by means of hollow metal pipes going through the bulk of the material. These trays are heated with steam inside the heater to the desired temperature, typically 180 °C for 5–10 h. Reclaiming chemicals are aromatic thiols, disulfides and aromatic oils. Their use allows lower temperatures and shorter reclaiming times and produces a product with superior mechanical properties.

5.1.2. Digester process

In this method the ground scrap material is mixed with fiber dissolving agents, water, plasticizing oils and, if needed, reclaiming agents. This mix is then transferred to a large jacketed agitator-equipped autoclave. It is heated to 180–210 °C for 5–24 h by using steam. Afterwards the digester is emptied in a blow-down tank, the material is washed, dried and then ready for final refining and straining steps.

5.1.3. Alkaline process

The fiber in the scrap is digested by the use of sodium hydroxide in a high concentration (up to 7%): the cellulose in the fiber-containing scrap is hydrolyzed. After recycling, a washing procedure is required to remove excess de-fiberizing agent. The crumb is then dried and refined. The process is found to be detrimental to SBR containing rubber material, as hardening takes place.

5.1.4. Neutral process

An improvement to overcome the hardening problem was the development of the neutral process. In this process, zinc chloride and pine oil are used [3]. Calcium chloride or zinc chloride is added for the hydrolysis of the textile.

The heater, digester, alkaline and neutral processes use long reaction cycles are characterized by long recycling time.

5.1.5. High-pressure steam process

More recent developments aimed at shorter reaction times. In the high-pressure steam process [3], fiber-free, coarse ground rubber scrap is mixed with reclaiming agents and reclaimed in a high-pressure autoclave at a temperature around 280 °C for 1–10 min.

5.1.6. Engelke process

Another modification is the Engelke process [26], in which coarse ground rubber scrap, mixed with plasticizing oil and peptizers, is lowered in cages into a small autoclave. This mixture is heated to very high temperatures for 15 min, after which refining and straining takes place.

5.1.7. Continuous steam process

A continuous steam process uses temperatures around 260 °C and high pressures in a hydraulic column. The rubber is ground and water is used as a carrying medium and to seal the material from extraneous oxygen, because otherwise heat and pressure would cause combustion. Heat and pressure combined with the injected chemical agents cause a substantial breakdown of the rubber in suspension.

5.2. Thermo-mechanical process

During most mechanical processes a strong rise in temperature occurs that aids in degrading the rubber network. Thermo-mechanical recycling of rubber is assumed to be a combination of breaking of carbon-to-carbon bonds and sulfur cross links. This results in the formation of soluble branched structures and fragments of gel. The modern material recycling processes all use thermo-mechanical regeneration methods. Recycling chemicals and oils are frequently used in addition to the thermal and mechanical breakdown: disulfides, thiols, amines and unsaturated compounds are the most common recycling chemicals. They are added in quantities of around 1 wt% [3]. Softeners lower the thermal degradation resistance of a vulcanizate by weakening the interaction between filler and rubber chains.

5.2.1. High-speed mixing

A fast thermo-mechanical recycling process is the high-speed mixing process. The rubber is stirred at a speed of 500 rpm and the temperature rises to 200 °C [18]. The process takes 15–20 min.

5.2.2. Reclaimator process

The reclaimator process, developed in the 1960s, is a single-screw extrusion process. A flow diagram of the process is given in Fig. 10 [3]. Again, the rubber is quickly heated to 200 °C by shearing forces. As the extrusion time is around 3 min, this process is suitable for synthetic rubbers that show hardening during longer recycling times like SBR.

Another reclaiming process based on extrusion is the Ficker reclaiming method that uses an extruder with co-rotating screws. Temperatures of 240–280 °C are reached.

5.3. Mechano-chemical methods

Plasticization can be improved by using a reclaiming accelerator while applying a mechanical force to the rubber powder in the presence of air at room temperature. In general, at low temperatures a reclaiming catalyst, reclaiming oil and process oil are used jointly with the reclaiming agent. Typical agents are shown in Table 1 [18].

Peroxide in combination with methyl halide (material 1) is a powerful radical initiator for a redox system. Phenyl hydrazine and ferrous chloride as well as tributylamine and cuprous chloride (materials 2 and 3) form a complex with each other. This complex is easily degraded by oxygen, under formation of the oxidation initiators. These systems degrade diene-based rubber in the presence of oxygen at room temperature. Dioxylyldisulfide and 2,2′-dibenzamidodiphenyldisulfide (materials 4 and 5) are used as peptizing agents. *N*-cyclohexylbenzothiazole-2-sulfenamide (material 6) is commonly used as vulcanization accelerator and *N*-isopropyl-*N*′-phenyl-*p*-phenylene diamine (material 7) is used as an antioxidant. Thiophenol and *n*-butylamine (material 8), toluene sulfonic acid and 1, 8-diazabicyclo [5.4.0] undec-7-ene (material 9) as well as the rubber accelerators tetraethylthiuram disulfide and triphenyl phosphine (material 10) were found to increase the plasticity of rubber reclaim. The fact that these reagents behave as reclaiming agents for rubber is explained by their function as a radical acceptor for the rubber radicals that are formed in the mechano-chemical reaction.

5.3.1. Trelleborg cold reclaiming (TCR) process

In the TCR process, small quantities of recycling agents are mixed into cryogenically ground rubber powder. A short treatment is carried out in a powder mixer at room temperature or at a slightly higher temperature. Phenyl hydrazine-methyl halide or diphenyl guanidine is used to react with the vulcanizates [18].

5.3.2. De-Link process

The recycling of rubber crumb with vulcanization accelerators and sulfur on a mill is used in the patented de-link process. The process is not only suitable for NR, but also for EPDM. The rubber is processed on a two-roll mill for approximately 7 min at temperature below 50 °C. The added chemical mixture is prepared from the zinc salt of dimethyldithiocarbamate and mercaptobenzothiazole with stearic acid, sulfur and zinc oxide dispersed in diols [27]. Tetramethyl thiuram disulfide can also be used. It is assumed that the process is based on a proton transfer reaction.

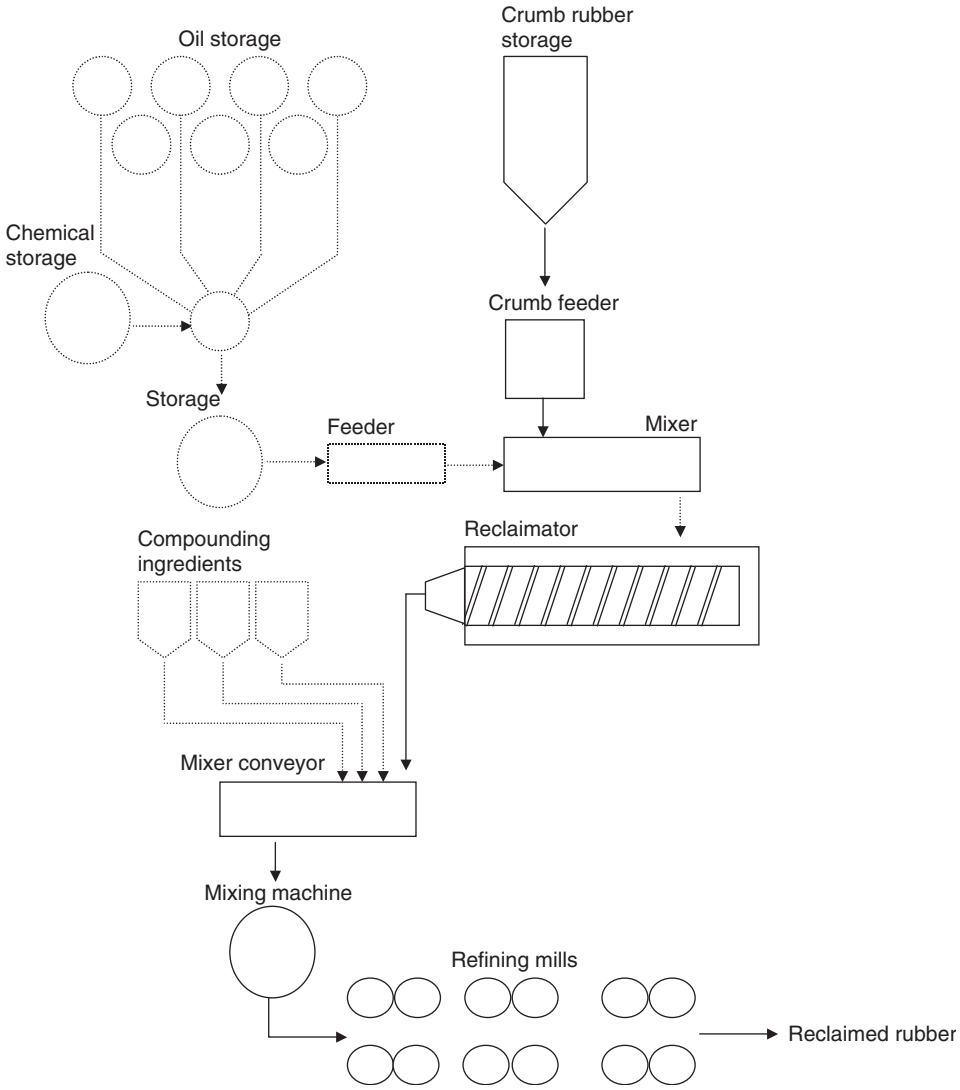


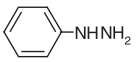
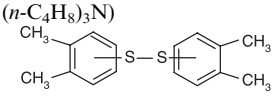
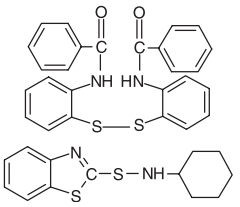
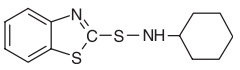
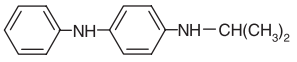
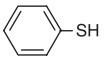
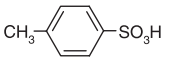
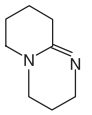
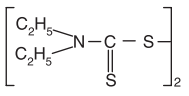
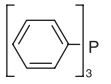
Fig. 10. Flow diagram of the reclaimator process (adapted from Ref. [3]).

The process is more effective for conventional sulfur vulcanizates than semi-efficient and efficient sulfur vulcanizates, the number of cross links is decreased by a factor of 2. As the nip opening of the mill was found to have a significant effect on properties, the vulcanizate breakdown is probably caused by mechanical breakdown.

5.3.3. Swelling in benzene with a sulfoxide

NR vulcanizates are attacked by swelling in benzene with a sulfoxide compound like dimethyl sulfoxide (DMSO) di-*n*-propyl sulfoxide (DPSO) or a mixture of these with thiophenol, methyl iodide or *n*-butyl amine in a mechano-chemical process on a mill [28]. A thiol and DMSO react to form a disulfide and a nucleophilic agent S $(CH_3)_2$. It is reported that these reagents cause selective scission of sulfur bonds. NR is completely degraded by the combination of DMSO and thiophenol, but SBR is much less reactive. Although the degree of swelling in an organic solvent increased, only 2% of sol fraction was formed. The low sol fraction and high swelling ratio is in agreement with the theory of selective crosslink scission [29]. A disadvantage of this process is that solvents like DMSO and methyl iodides are highly toxic.

Table 1
Reclaiming agents used in mechano-chemical methods

No.	Chemical name/abbreviation	Reclaiming accelerator	Reclaiming catalyst
1	Peroxide-methyl halides	ROOR	Me_nX_m
2	Phenyl hydrazine–ferrous chloride (PH–$FeCl_2$)		$FeCl_24H_2O$
3	Tributylamine-cuprous chloride (TBA-CuCl)	$(n\text{-}C_4H_8)_3N$)	Cu_2Cl_2
4	Dixylyldisulfide		
5	2,2′-Dibenzamidodiphenyl disulfide		
6	*N*-cyclohexylbenzothiazole-2-sulfenamide (CBS)		
7	*N*-isopropyl-*N*′-phenyl-*p*-phenylenediamine (IPPD)		
8	Thiophenol-*n*-butylamine (TP–BA)		$n\text{-}BuNH_2$
9	Toluene sulfonic acid-1,8-diazabicyclo 5.4.0]undec-7-ene (TS-DBU)		
10	Tetraethylthiuramdisulfide-triphenyl phosphine (TETD-TPP)		

5.4. Microwave recycling

In this method, microwave electromagnetic energy is used to break the S–S or C–S bonds in the rubber powder [30,31]. By using microwaves, the temperature of the material increases very fast to reach finally 260–350 °C. A pre-condition to reach this temperature level for devulcanization is that the vulcanizates should contain carbon black, making them suitable for this method. Carbon black containing rubber is susceptible to ultra high frequency in a microwave chamber due to interface or ion polarization: accumulation of free electrons at the interface of different phases with a different conductivity and dielectric constant. Microwave energy at 915 or 2450 MHz is sufficient to cleave crosslink bonds but insufficient to cleave polymer chains.

The properties of the reclaim are reported to be better than those of rubber obtained by other reclaiming methods, and EPDM and IIR are particularly suitable for the process. The process is able to convert vulcanized waste such as EPDM (automotive coolant hoses) into a usable compound in just 5 min [32,33]. The process has the disadvantage that it is difficult to control.

5.5. Ultrasound recycling

Next to the microwave radiation, ultrasonic energy is used for the devulcanization of cross linked rubber. The first work with ultrasonic energy was reported by Pelofsky [34] in 1973. In this patented process, solid rubber articles are immersed into a liquid, and then ultrasonic energy is applied whereby the bulk rubber effectively disintegrates and dissolves into the liquid. In this process ultrasonic radiation is in the range of about 20 kHz and at a power intensity of larger than 100 W. Ultrasonic reclaiming of a NR vulcanizate was also reported by Okuda and Hatano in 1987 [35]. They subjected the NR vulcanizate to 50 kHz ultrasonic energy for 20 min to achieve devulcanization. Mangaraj [36] indicated in his patent on vulcanization of rubber by ultrasonic radiation a possibility of rubber degradation and devulcanization by ultrasonic energy. Later Isayev and coworkers reported in a number of publications [37–47] the phenomenon of devulcanization by ultrasonic energy.

The devulcanization process requires a high-energy level to break C–S and S–S bonds [17], which can be provided by an ultrasonic field creating high-frequency extension–contraction stresses. Isayev and his group at the University of Akron, Ohio, designed an ultrasonic reactor of a 38.1 mm rubber extruder with a length to diameter ratio of 11 and a co-axial cone-shaped ultrasonic die attachment equipped with three temperature-controlled zones. The screw is heated electrically or cooled by water. The scrap rubber is fed into the extruder by a conveyor belt with adjustable output. A 3 kW ultrasonic power supply, an acoustic converter and a 76.2 mm cone-tipped horn is used. The horn vibrates longitudinally at a 20 kHz frequency and 5-10 μm amplitude. The scrap rubber particles are transported within the extruder to the chamber with the ultrasound horn, and the recycled rubber can exit this chamber through a die. When SBR is recycled by ultrasound extrusion [48], cleavages of intermolecular bonds such as C–S and S–S as well as C–C bonds in the main chain take place. An increase in ultrasound amplitude is accompanied by significant decrease in molecular weight of the sol fraction and a decrease of the gel content. An increase in the extruder temperature also results in a higher sol fraction. Conventional sulfur vulcanizates are more susceptible to sol production. This process is characterized by substantial main-chain scission.

A continuous ultrasonic devulcanization of unfilled EPDM rubber was also carried out [49], and the mechanical properties of revulcanized EPDM rubber were measured. Gel fraction, crosslink density and dynamic properties were also determined for the virgin vulcanizate, the ultrasonically devulcanized rubber and the revulcanized rubber: The tensile strength of the revulcanized EPDM was much higher than that of the original vulcanizate with elongation at break values being practically unchanged. It is proposed that the improvement in mechanical properties of revulcanized EPDM is mainly due to the extent of non-affine deformation of the bimodal network that possibly appears in the process of revulcanization of ultrasonically devulcanized rubber. For dynamic visco-elastic properties, it is found that devulcanized EPDM is a more elastic material than uncured virgin EPDM and that revulcanized EPDM is less elastic material than the virgin EPDM vulcanizate at the same modulus level.

5.6. Selective scission of cross links by chemical probes

Some chemicals that cause selective scission of sulfur bonds are used as reagents to determine the relative amounts of mono-, di-, and polysulfidic cross links. These reagents are called chemical probes. Thiols in combination with organic bases can selectively cleave sulfur cross links. Hexanethiol was found to cleave di- and polysulfidic cross links, while 2-propane thiol selectively cleaves polysulfidic cross links in a nucleophilic displacement reaction with piperidine as base [50,51].

The thiol–amine combination gives a complex, possibly a piperidinium propane-2-thiolate ion pair, in which the sulfur atom has enhanced nucleophilic properties, and is capable of cleaving organic trisulfides and higher polysulfides within 30 min at 20 °C, according to a mechanism as shown in Fig. 11 [52,53]. Disulfides react at a rate, which is slower by a factor of 1000. The polysulfide cleavage is faster due to p_π–d_π delocalization of the displaced σ-electron pair of RSS^- as outlined in Fig. 12:

A rubber network can easily be swollen by methyl iodide which can be removed afterwards by heating under vacuum. Meyer and Hohenemser [54] introduced the use of methyl iodide to estimate monosulfide linkages in vulcanized natural rubber. The level of network bound iodine reflects the concentration of monosulfide groups since simple saturated monosulfide groups react as shown in Fig. 13:

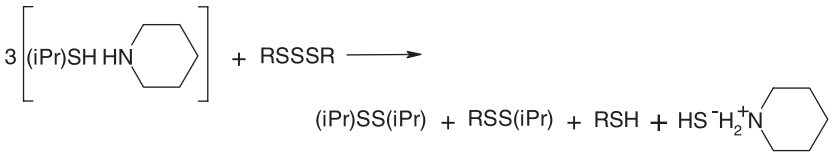


Fig. 11. Cleavage of polysulfide bonds by 2-propane thiol/piperidine probe; iPr = isopropyl and R = rubber polymer (adapted from Refs. [53,54]).

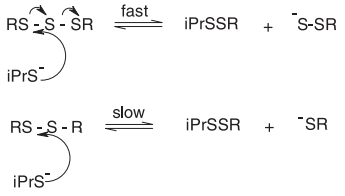


Fig. 12. Cleavage of polysulfide crosslinks and p_π–d_π delocalization; $iPrS^-$ = nucleophilic thiol–amine associate (adapted from Refs. [53,54]).



Fig. 13. Reaction of a monosulfide group with methyl iodide (adapted from Ref. [55]).

Simple disulfides react very slowly with methyl iodide, but their reaction and those of monosulfides can be catalyzed by mercuric iodide [55]. Di-*n*-propyldisulfide reacts as shown in Fig. 14.

Only allylic sulfides breakdown easily to yield extractable trimethyl sulfonium salts, Fig. 15.

It is reported that not only sulfur cross links, but also cyclic monosulfidic structures in vulcanizates react with methyl iodide. Nowadays this reagent is barely used anymore because it is carcinogenic.

Lithium aluminum hydride (LAH) can be used to convert organic poly- and disulfides into thiols. The liberated hydrogen sulfide gives an estimate of the amount of polysulfidic cross links, but again pendant accelerator and cyclic main-chain modifications can also react (Fig. 16).

Triphenyl phosphine [56,57] cleaves di- and polysulfidic bonds in the following manner (Fig. 17).

Sodium dibutyl phosphite [58], cleaves di- and polysulfidic cross links in NR vulcanizates (Fig. 18).

Treatment of a polybutadiene vulcanizate with phenyl lithium in benzene cleaves the polysulfide and disulfide bonds.

5.6.1. Comparison of chemical probes and reclaiming

Some of the chemicals for reclaiming mentioned in the literature are comparable with those used as

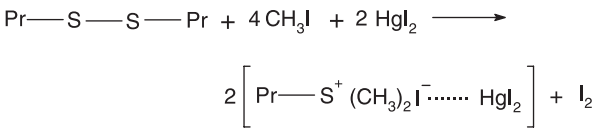


Fig. 14. Reaction of disulfide with methyl iodide catalyzed by mercuric iodide (adapted from Ref. [56]).

probes. Katrenick [59] and Gregg [60] mentioned the use of phenyl lithium, similar to the use of a solution of sodium-aniline as a method for removing combined sulfur described by Miller [61] in 1937. Le Beau [16] mentioned phenol alkyl sulfides and disulfides, aliphatic and aromatic mercaptans, amino compounds and unsaturated compounds as active reclaiming agents. Some of those bear a similarity to the thiol–amine reagents described by Campbell [50].

5.7. Other chemical methods

A phase transfer catalyst has been used for transporting hydroxide ions from water into rubber particles to cleave polysulfide, di- and monosulfide cross links with little main-chain scission [62,63]. The transfer of an anion from water into the organic phase (finely divided rubber) was made possible by means of a quaternary ammonium chloride catalyst having a large hydrocarbon radical attached to the nitrogen. Hydroxide ions transported by onium ions, positively charged higher valence ions of the non-metallic elements, from water rapidly break polysulfide cross links with little or no main-chain scission. The advantage of this method is the possibility of working in an aqueous medium, but the slow rates of diffusion and residual traces of accelerators are disadvantages of this method.

Orthodichlorobenzene (ODCB) dissolves a variety of vulcanizates including hydrocarbon, nitrile and chloroprene rubbers [64]. The procedure involves cutting the vulcanizate into small pieces, refluxing at 180 °C, centrifuging the carbon black, and casting a film. The final film acts like a piece of

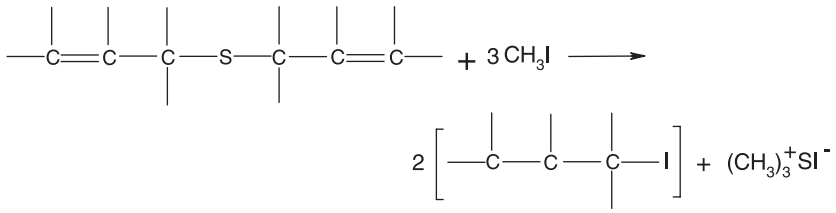


Fig. 15. Reaction of allylic sulfides with methyl iodide (adapted from Ref. [52]).

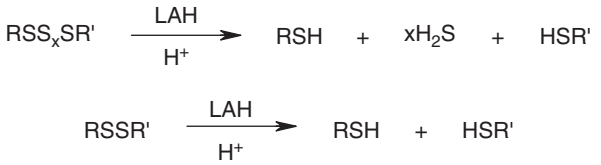


Fig. 16. Reaction of lithium aluminum hydride with polysulfides and disulfides; R = rubber polymer (adapted from Ref. [52]).

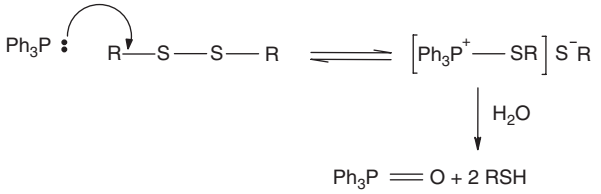


Fig. 17. Cleavage of di- and polysulfidic bonds by triphenyl phosphine (adapted from Refs. [57,58]).

unvulcanized rubber. In the reference it is stated that most or all of the poly-, di- and monosulfidic cross links originally present were cleaved, without excessive degradation.

5.8. Biotechnological processes for reclaiming of rubber

A biotechnological approach of devulcanization of rubberp was reported in a patent by utilizing chemolithiotrope bacteria in an aqueous suspension. The process was developed by Straube et al. [65] for the devulcanization of scrap rubber, by holding the material in a bacterial suspension with a supply of air until elemental sulfur or sulfuric acid is formed.

Biodegradation of the *cis*-1,4-polyisoprene main chain was achieved [66–68] using a bacteria that belongs to the genus Nacardia and led to considerable molecular weight loss of different soft types of NR vulcanizates. In a typical process, rubber powder is treated with different species of Thiobacillus (T. ferrooxidans, T. thiooxidans, and T. thioparus). The total sulfur in the rubber powder was oxidized to sulfate within 40 days. The efficiency of the sulfur oxidation depends to a large extent on the particle size.

5.9. Devulcanization in supercritical carbon dioxide

A new devulcanization process was developed in which supercritical carbon dioxide ($scCO_2$) was used along with devulcanizing reagents [69]. Unfilled polyisoprene rubber vulcanizates with different crosslink distributions were prepared by controlling the cure time and the amount of curatives. Each of the vulcanizates was subjected to Soxhlet extraction using azeotropic acetone/chloroform to remove residual curatives. The devulcanization was performed at various temperatures (140–200 °C) in the presence of $scCO_2$ for 60 min. The product was fractionated into sol and gel components, and the molecular weight of the sol component and the crosslink density of the gel component were determined. The thiol–amine reagent was found to be the most effective one among several devulcanizing reagents; the molecular weight of the resultant sol component was determined and the crosslink density of the gel component decreased substantially from the initial ones. The yield of the sol component increased with increase in CO_2 pressure. In the supercritical fluid state of CO_2, the vulcanizate was more efficiently devulcanized than in an ordinary gaseous state of CO_2. The sol fraction depended considerably on the crosslink distribution in the vulcanizate. These results suggest that the devulcanizing reagents penetrate and diffuse better into the vulcanizate in the presence of $scCO_2$.

6. Latex products reclaiming

The latex industry expanded over the years to meet the world demand for examination gloves, condoms, latex thread, etc. Due to strict specifications for latex products, as much as 15% of the products are sometimes rejected, and these rejects

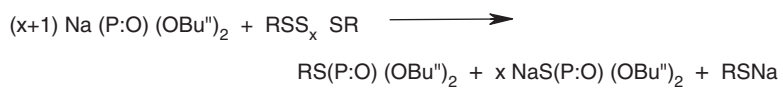


Fig. 18. Cleavage of di- and polysulfides by sodium dibutyl phosphite; $X \geqslant 0$, Bu″ = *n*-butyl, R = rubber polymer (adapted from Ref. [59]).

create a major disposal problem for the rubber industry. At the same time, the local authorities prohibit open burning of this waste due to environmental pollution. As latex product waste represents a source of high-quality rubber hydrocarbon it is a good candidate for generating reclaimed rubber of superior quality.

The Rubber Research Institute of India (RRII) reported a method for reclaiming latex products [70]. In this process, waste condoms were powdered initially by passing them through a hot two roll mill at 80–90 °C to a size of about 40 mesh. The powdered material was admixed with 10 phr of naphthenic oil and 1 phr of pentachlorothiophenol (PCTP) on a cold mill. The resulting compound was heated in an air oven at 140 °C for 30 min. The reclaimed rubber obtained by this process was found to form a smooth band on the mill and contained about 82% of rubber hydrocarbon. However, it was found that only a small amount of this reclaim could be added to raw rubber without adversely affecting the mechanical properties. The addition of 25% reclaimed rubber to filled NR caused a decrease in tensile strength, elongation at break, resilience, tear strength and abrasion resistance. The compression set of the raw rubber was not much affected, but an increase in heat built-up and hardness was observed. A compound containing this reclaim showed better processing characteristics.

From the foregoing it is clear that the utilization of reclaimed rubber is at present limited to the preparation of elastomer blends. Reclaim is added only in a very small percentage of the raw rubber in high-quality products or in high percentages in low-quality products. This is mainly due to the degradation of the rubber hydrocarbon during the reclaiming process.

The utilization of cross linked waste latex rubber (WLR) as a potential filler in epoxidized natural rubber (ENR) deserves much attention [71]. The cross linked WLR was powdered and screened into different fractions. The ground vulcanizate preparation was done on a fast-rotating corrugated mill. The particle size distribution of the powder rubber was found to be polydispersed. With increasing filler content in a blend with virgin compound, curing characteristics like optimum cure time, scorch time and induction time decreased. The cure-activating nature of the filler is obvious from the increase in the rate constant values. The filler helps in reducing the sticky nature of the ENR compound during mixing. These observations are advantageous as far as processability and productivity are concerned. When the vulcanization system is a conventional one, the finest size filler shows superior mechanical performance while the order of performance is reversed when the vulcanization mode changes to efficient. As far as tear strength is concerned, a particle size of 0.3–0.5 mm was found to be the best. In every case, the properties degrade at a loading of 40 phr. The swelling index values register a constant increase with an increasing loading of the filler, and this increase is lowest for fine fillers. In addition to this, the reduction in crosslink density with increasing filler loading is also lowest for smaller particle size filler. The scanning electron micrographs of the fractured surfaces clearly support the good particle–matrix adhesion in the case of fine fillers. The phase-separated nature of the coarse filler particles in the ENR matrix classifies these materials as a filled ENR composite, rather than a blend system.

In another study diphenyldisulfide is found to be effective for the reclamation of WLR in a thermomechanical process [72]. A stronger reduction of the crosslink density was observed at temperatures of 170 and 180 °C when reclaimed with diphenyldisulfide compared to hexadecylamine. In the present study all poly- and disulfidic cross links were broken during reclaiming with disulfide at the temperatures mentioned above, indicating that after reclamation the cross links present in WLR are mainly the monosulfides. Main-chain scission to crosslink scission studies showed that reclamation has mainly occurred through the scission of cross links rather than by main-chain scission.

On the other hand, hexadecylamine is found to be ineffective as reclaiming agent, because it results in the formation of additional cross links rather than

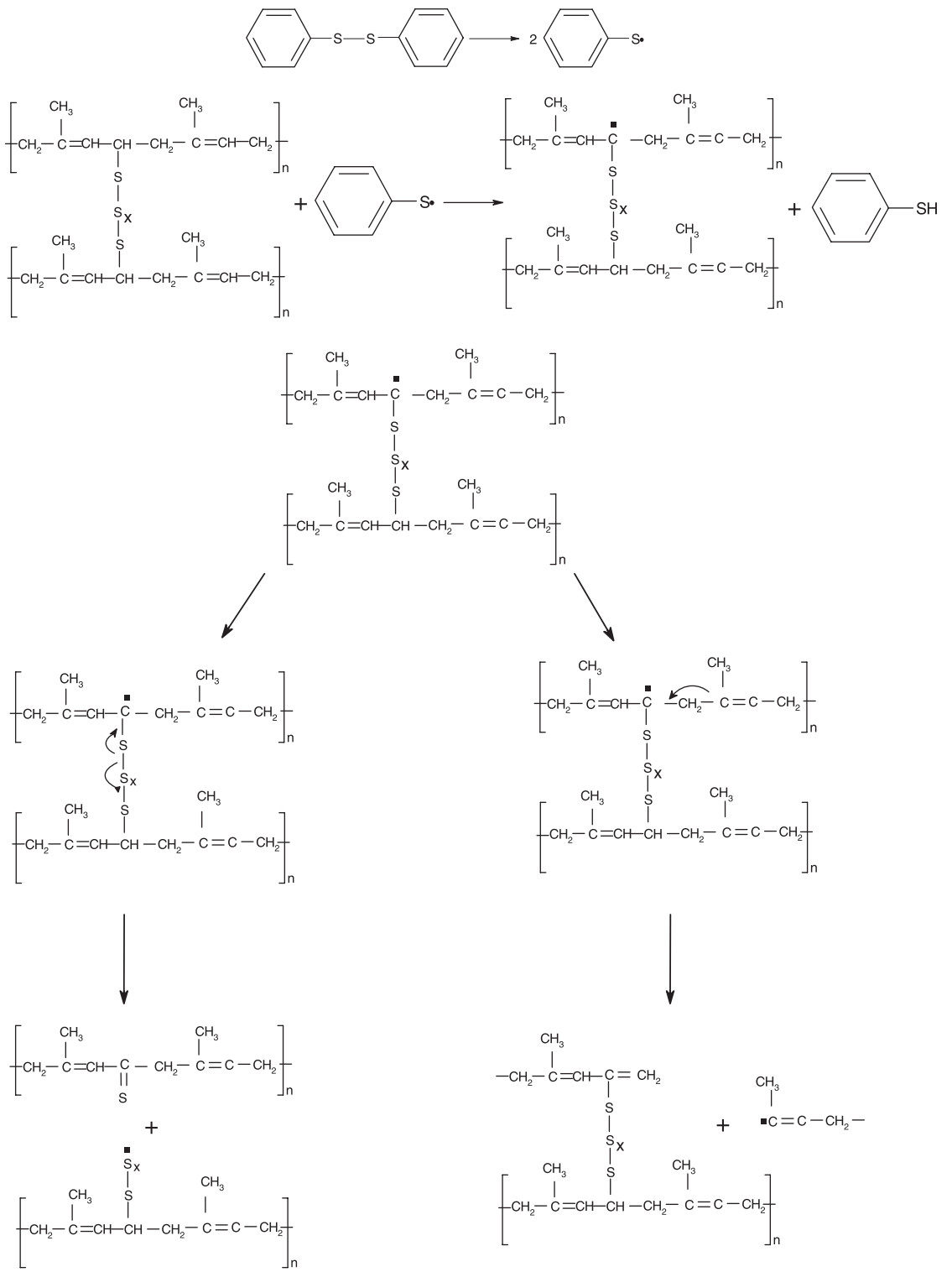


Fig. 19. Simplified reaction scheme proposed for the reclamation of natural rubber by diphenyldisulfide (adapted from Ref. [73]).

reclaiming. The crosslink distribution studies showed that some of the polysulfidic cross links remain in the sample after the treatment with hexadecylamine whereas no polysulfides were found in the samples treated with diphenyldisulfide. This again proves the fact that diphenyldisulfide more effectively breaks the polysulfidic cross links in latex vulcanizate compared to hexadecylamine.

A simplified reaction scheme proposed for the reclamation of natural rubber with diphenyldisulfide is given in Fig. 19 [72]. The radicals formed by scission of the disulfide are capable of hydrogen abstraction or addition to the double bonds in natural rubber [73]. Hydrogen abstraction is relatively easy because the protons in an allylic position are activated by the double bond (the resulting carbon radical is resonance stabilized). The benzene-sulfide radical, therefore, abstracts the allylic hydrogen from the natural rubber vulcanizate to form benzenethiol and a natural rubber vulcanizate radical. The presence of benzenethiol in the acetone extract of natural rubber, reclaimed with diphenydisulfide detected by gas chromatography mass spectrum (GC-MS), supports the above reaction mechanism. The polymer radical can now undergo main-chain scission and/or crosslink scission.

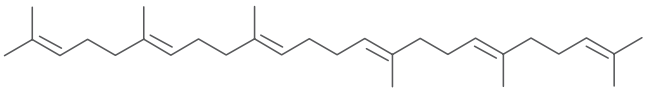
7. Model compound studies on the devulcanization of natural rubber using 2,3-dimethyl-2-butene

A model compound study has been used successfully to elucidate the mechanism of the devulcanization of natural rubber with an aromatic disulfide and an aliphatic amine. A model compound study instead of an in-rubber study has been chosen, because it gives a more detailed picture of the devulcanization characteristics of the various sulfur ranks of a vulcanizate. Model compound studies, in which the rubber polymer is replaced by a reactive low-molecular weight compound, have proven to be a suitable method for the study of vulcanization reactions and this technique has been extended in this paper for the study of devulcanization reactions as well. Model compounds are easier to analyze than their polymeric counterparts due to their low-molecular weight. Nieuwenhuizen, Haasnoot and Reedijk have given a comprehensive review of the technique of model compound vulcanization (MCV) [74].

The low-molecular weight compound used should be representative of the reactive unit of the polymer, ensuring comparable chemical behavior during their reactions. Therefore, these compounds contain C=C unsaturation. It is further essential, that the model compounds have at least one allylic hydrogen atom, since crosslink formation involves the substitution of an allylic hydrogen for a sulfur link. Tetrametyl-ethylene (TME) is used as a model molecule for natural rubber in the present study, as a clear picture of the structure of the vulcanized and devulcanized products can be obtained [75,76], Table 2. This compound is a general model for different types of rubber and commonly used for model compound studies. The advantage of TME is that it has only one type of allylic moiety and therefore, the reaction products have only few isomers. Furthermore, the cross linked products can be separated by HPLC from the crosslink precursors and the unreacted TME. At a wavelength of 254 nm the crosslink precursors and the products can be detected.

An aromatic disulfide and an aliphatic amine were chosen as devulcanization agents for the present study, because historically these two have most prominently been used as devulcanization agents for natural rubber [77].

Table 2
Chemical structure of common model compounds for natural rubber

Model	Chemical structure
Squalene (410.72 g/mol)	
2,3-Dimethyl-2-butene (TME) (84.16 g/mol)	

In Fig. 20 the peak areas of the monosulfidic compounds are shown against reaction time of devulcanization at 200 °C, for various concentrations of diphenyldisulfide and hexadecylamine, especially after thermal devulcanization. The latter indicates the absence of devulcanization agent. In all cases monosulfides are formed, but again the large difference between diphenyldisulfide and hexadecylamine is conspicuous. The higher the amount of diphenyldisulfide added, the more monosulfidic compound is formed. For hexadecylamine the opposite applies; the more diphenyldisulfide added the less monosulfidic compound is formed. The thermal treatment, without either of the two devulcanization agents present, clearly falls in between. Once formed, there is little decrease of the monosulfidic compound anymore, later on in the process.

Fig. 21 shows the peak areas of the disulfidic compound after the thermal devulcanization with diphenyldisulfide or hexadecylamine, resp. thermally at 200 °C, for various concentrations of devulcanization agents. Again, large differences are seen between the use of diphenyldisulfide and hexadecylamine. For diphenyldisulfide the concentration of disulfidic cross links reaches a maximum after approximately 5 min and then decreases with increase of time: all at a level higher than for the case where no devulcanization agent has been used at all. However, only a relatively small amount of disulfide compounds is formed for the amine as

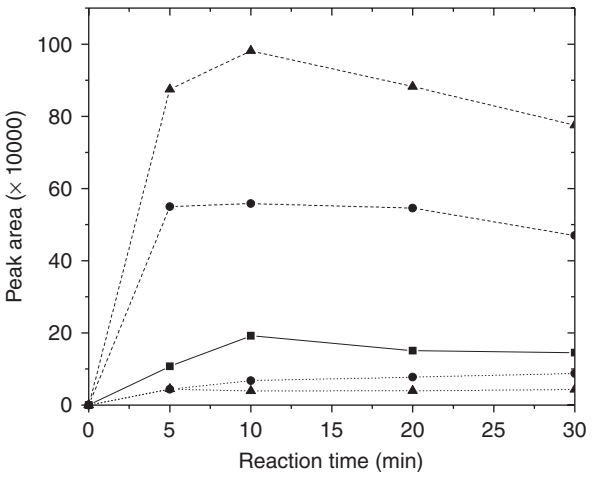


Fig. 20. Peak areas of monosulfide crosslinks devulcanized with diphenyldisulfide (------), hexadecylamine (……) and thermally (——) at various concentrations of devulcanization agents as a function of reaction time at 200 °C; (■): 0 phr; (●):1 phr; (▲): 2 phr (adapted from Ref. [77]).

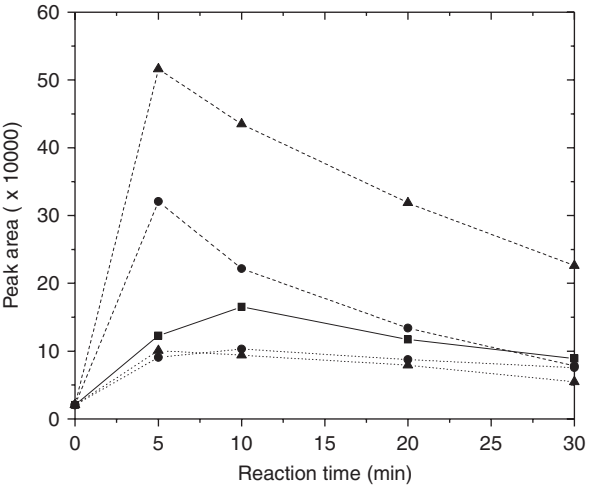


Fig. 21. Peak areas of disulfide crosslinks devulcanized with diphenyldisulfide (------), hexadecylamine (……) and thermally (——) at various concentrations of devulcanization agents as a function of reaction time at 200 °C; (■): 0 phr; (●): 1 phr; (▲): 2 phr (adapted from Ref. [77]).

devulcanization agent, more or less irrespective of its concentration, at a level below the thermal devulcanization.

The peak areas of trisulfidic compounds obtained for devulcanization are shown in Fig. 22. All curves now show the same trend of an initial increase, followed by a decrease in time. The curves for diphenyldisulfide as well as for hexadecylamine all fall below the line for thermal treatment. Diphenyldisulfide forms the least amount of trisulfides, and the amount decreases slightly with increasing concentration, whereas for hexadecylamine little effect of concentration is seen. Thermal devulcanization leads to the maximum amount of trisulfides. There is not much difference in rate of decomposition of trisulfides after the initial increase, for both diphenyldisulfide and hexadecylamine.

Fig. 23 shows the peak areas of the polysulfidic compounds against reaction time. The amounts of polysulfides decrease with increasing concentration of both diphenyldisulfide and hexadecylamine. Both the devulcanization agents decompose the polysulfides in the same fashion; both have a similar reactivity towards the polysulfide cross links. The decomposition of the polysulfide in the thermal treatment is much slower, particularly in the beginning.

The well-known fact that the two reclaiming agents used in this study act according to different mechanisms is clearly proven by the results. For

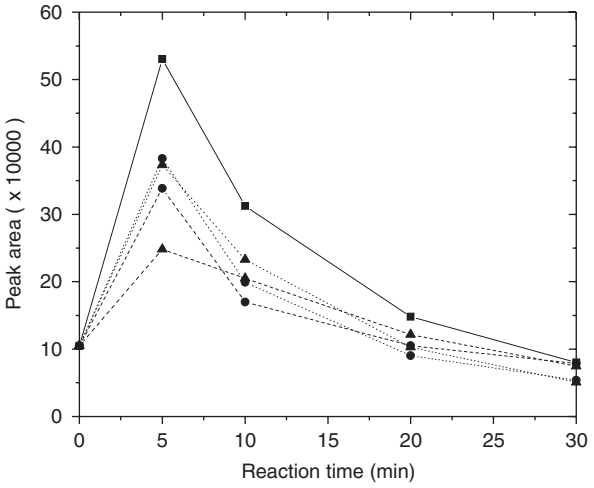


Fig. 22. Peak areas of trisulfide crosslinks devulcanized with diphenyldisulfide (------), hexadecylamine (……) and thermally (———) at various concentrations of devulcanization agents as a function of reaction time at 200 °C; (■): 0 phr; (●): 1 phr; (▲): 2 phr (adapted from Ref. [77]).

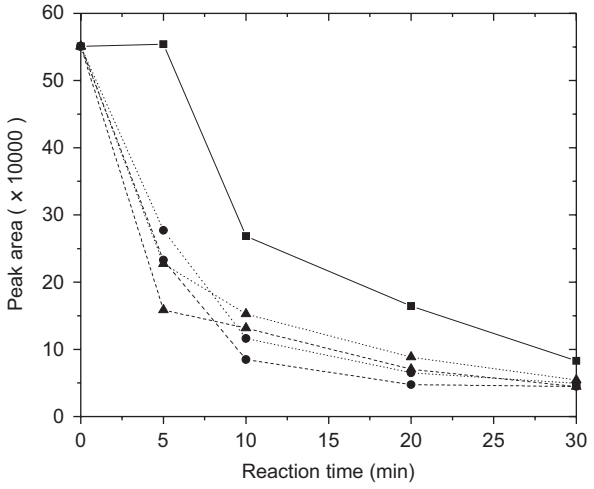


Fig. 23. Peak areas of polysulfide crosslinks devulcaniszed with diphenyldisulfide (------), hexadecylamine (……) and thermally (———) at various concentrations of devulcanization agents as a function of reaction time at 200 °C; (■): 0 phr; (●): 1 phr; (▲): 2 phr (adapted from Ref. [77]).

diphenyldisulfide as devulcanization agent there is a clear increase in the amount of mono- and disulfides observed, compared to thermal devulcanization, and the amount increases with increasing concentration of the diphenyldisulfide. For hexadecylamine, an increase in the concentration of the devulcanization agent results in a decrease of the amount of mono- and disulfidic cross links relative to the case where no devulcanization agent is present: The amine inhibits the formation of mono- and disulfides during the devulcanization reaction.

Bis-(2,3-dimethyl-2-butene-1-yl)-polysulfide, TME-S_x-TME, is known to undergo further reactions after formation, described as maturation of the vulcanizate. The most important reactions in this context are:

(i) disproportionation or S–S bond interchange reactions;
(ii) decomposition reactions; and
(iii) desulfuration reactions.

The disproportionation reactions may occur by a free radical mechanism [78–80] or by an ionic mechanism [80]. In polar media the reactions are unlikely to proceed rapidly. This reaction as such does not yield any new carbon–sulfur bonds and will therefore not change the total number of cross links. The decomposition of a polysulfide can lead to the liberation of elemental sulfur and to modification of the olefinic fragment. The desulfuration reactions are of a much greater influence on the product distribution than the other two reactions. In the presence of a zinc-accelerator complex the extracted sulfur can even be used for additional crosslink formation [81]. The formation of these new cross links is then accompanied by a shortening of the average length of the sulfur bridges [29]. The most conspicuous result is, that during the devulcanization reaction with diphenyldisulfide large amounts of mono- and to a lesser extent disulfides are formed (Figs. 20 and 21). Cross linked products with higher sulfur ranks decompose to a large extent into di- and monosulfides. The monosulfides do not disintegrate further under these circumstances due to the high bond energy of the carbon–sulfur bond [82].

In the other case, with hexadecylamine present, the amount of di- and monosulfides is reduced relative to the thermal treatment where no devulcanization agent is used (Figs. 20 and 21). Hexadecylamine stabilizes the reaction mixture against these short sulfides formation.

The fundamentally different behavior between the two devulcanization agents can be explained by side reactions, which diphenyldisulfide provokes by virtue of its sulfur content. Besides the breakdown of diphenyldisulfide into sulfide radicals (thiyl radicals), it may liberate sulfur: it acts as a sulfur donor. The sulfur can react with still unreacted

TME to form mono- and disulfidic cross linked products. Another mechanism is diphenyldisulfide exchanges its sulfur moiety via thiyl-radicals with polysulfidic cross links to preferably short cross links.

Once monosulfides are formed, they are not broken anymore under the conditions of devulcanization. The high bonding energy of monosulfidic cross links compared to the bonding energies of poly- or disulfidic cross links prevents this from happening. In that perspective, hexadecylamine and diphenyldisulfide perform equally well as devulcanization agents for the higher sulfide ranks: three and more. But hexadecylamine is greatly preferred, because it prevents the formation of large amounts of di- and monosulfides, which eventually survive the devulcanization and lowers the efficiency of the process.

8. Model description of main-chain scission and crosslink scission

Relations between the degree of cross linking and gel fraction in a polymer have been derived by several authors [83,84]. An important parameter in these relations is the cross linking index, γ, the average number of cross links to which one original polymer molecule is linked. Vulcanized rubbers are an example of a three-dimensional polymer network in which the branching units or crosslink sites are commonly taken as tetra-functional [85]. The relations have been applied to the determination of the degree of cross linking in linear polymers, but they can be used as well to calculate the soluble fraction of the network in a cross linked polymer that has been subjected to a degradation process. The analysis of the amount of soluble polymeric material generated during the degradation process, sol–gel analysis, can be used to investigate the ratio of main chain to crosslink scission during devulcanization.

8.1. Chain scission at random

In case of random main-chain destruction it is commonly assumed that a Poisson-type molecular size distribution of fragments is formed. The Poisson distribution is defined as a special case of the Schultz–Flory distribution:

$$N_x = N\beta(1-\beta)^{x-1} \approx \frac{N\beta e^{-\beta x}}{(1-\beta)} \approx N\beta e^{-\beta x} \text{ for } \beta \ll 1, \tag{1}$$

where N is the total number of polymer molecules in the distribution, x is the number of monomer units in a fragment, N_x is the number of fragments with length x, and $1/\beta$ is the number-average length of fragments.

On the basis of this distribution the following relationship for the sol fraction s and gel fraction g is derived by Charlesby [84]:

$$s = 1 - g = \frac{1}{(1+\gamma-\gamma s)^2}. \tag{2}$$

An implicit equation for s, which can be made explicit to read

$$s = \frac{\left[(2+\gamma) - \left(\gamma^2+4\gamma\right)^{1/2}\right]}{2\gamma}, \tag{3}$$

in which γ is the cross linking index of the whole polymer defined as the average number of cross linked units per original length (of average length $1/\beta$). It can also be shown, that the number-average molecular weight M_{gel} of the primary molecule, incorporated in the gel, is given by

$$M_{gel} = M_0 \frac{[(1+\gamma-\gamma s)]}{\gamma}, \tag{4}$$

M_{gel} is the number-average molecular weight for all primary molecules. The cross linking index of the gel fraction equal to

$$\gamma_{gel} = (1+s)(1+\gamma-\gamma s) \quad \text{for } \gamma > 0.5. \tag{5}$$

v_0 is defined as the number of elastically effective polymer network chains per unit volume of network and represents a measure of the crosslink density, as commonly employed for gel measurements. For the sake of easiness, in the following the term elastically effective polymer network chain per unit volume will be used inter-changing with the term crosslink density. The latter is related to the former by a constant determined by the crosslink functionality:

$$\gamma = \frac{v_0}{N}. \tag{6}$$

It follows from Eq. (4) that the number of primary molecules per gram of network is given by

$$N_{gel} = \frac{\gamma N}{(1+\gamma-\gamma s)} = \frac{v_0}{(1+\gamma-\gamma s)}. \tag{7}$$

By combining Eqs. (5) and (7) it follows that the number of chains in the network can be calculated as follows:

$$v_{0,gel} = \gamma_{gel} N_{gel} = v_0(1+s). \tag{8}$$

Horikx assumed, that the number of network chains v_0 is only given by chains, which are chemically cross linked. Using Eqs. (2) and (7), the following relation is obtained:

$$N_{gel} = v_0 s^{1/2}. \tag{9}$$

According to Flory [86], the number of elastically effective polymer chains in the network, v, as determined by mechanical measurements and swelling measurements, requires a correction on v_0 to account for dangling chain ends:

$$v = v_0 - 2N \tag{10}$$

for tetra-functional cross links, v is determined by swelling experiments using the well-known Flory–Rehner equation:

$$v = \frac{-\left[\ln(1-v_r) + v_r + \chi v_r^2\right]}{V_s(v_r^{1/3} - 0.5v_r)}, \tag{11}$$

where v_r is the volume fraction of the polymer in the vulcanizate swollen to equilibrium, χ is the polymer–solvent interaction parameter, v is the number of elastically active network chains per unit volume and V_s is the solvent molar volume.

The number of elastically effective chains per unit volume of network is then given by combining (8)–(10)

$$v_{gel} = v_{0,gel} - 2N_{gel} = v(1+s) - 2v_0 s^{1/2}, \tag{12}$$

$$v_{gel} = v_0\left(1 - s^{1/2}\right)^2. \tag{13}$$

During the random scission process the number of cross links v_0 remains constant and soluble matter is created by randomly detaching small molecular fragments out of the network. By virtue of Eq. (6), γ decreases as much as N increases. If Eq. (13) is formulated before and after the network scission and the ratio of both is taken as the relative decrease in cross-link density, v_0 disappears from the equation and the remaining can be expressed as a function of the soluble fractions before and after scission of the sample:

$$1 - \left(\frac{v_f}{v_i}\right) = 1 - \left[\frac{\left(1 - s_f^{1/2}\right)^2}{\left(1 - s_i^{1/2}\right)^2}\right] \tag{14}$$

with s_i the soluble fraction of the still untreated vulcanizate, v_i the number of elastically effective network chains of the still untreated vulcanizate, and s_f and v_f correspond to the situation after the treatment.

8.2. Crosslink scission

To determine the soluble fraction in the case of crosslink scission, N is taken as a constant and γ decreases. In this case, v_0 remains in the equation. The relative decrease in crosslink density is now dependent on the cross-link index γ:

$$v_{gel} = v_{0,gel} - 2N_{gel} = v_0\left(1 - s^{1/2}\right)^2 = N\gamma\left(1 - s^{1/2}\right)^2. \tag{15}$$

The relation between the effective number of network chains before and after treatment reads now:

$$1 - \left(\frac{v_f}{v_i}\right) = 1 - \left[\frac{\gamma_f\left(1 - s_f^{1/2}\right)^2}{\gamma_i\left(1 - s_i^{1/2}\right)^2}\right] \tag{16}$$

with γ_i the cross linking index before treatment, and γ_f the cross linking index after treatment.

Horikx used the measurement of the network chain density in the gel by equilibrium swelling together with the value measured for M_n with GPC to calculate γ_i:

$$\gamma_i = \frac{v_i M_n}{\rho}. \tag{17}$$

Another way to determine γ_i is by measuring the residual sol content immediately after vulcanization and then making use of Eq. (3).

8.3. Intermediate stages between crosslink scission and main-chain scission

The disadvantage of the Horikx treatment is that it explains only the two limiting cases: crosslink scission or main-chain scission. For intermediate cases, Yashin and Isayev [87] used the model of Dobson and Gordon to describe the sol–gel formation of devulcanized rubber. On the basis of simulations of branched polymers, Dobson and Gordon [88–90] developed a model for a rubber network. This network is represented by a tree, starting from a primary chain or first generation—the stem—to which chains of second generation—the branches—are attached followed by further branches of the third generation, etc. Cross links connect pairs of chains of succeeding generations.

Yashin and Isayev state that under random chain scission conditions a Poisson distribution of chain fragments is generated, and for the parameters p

and q they propose an exponential decay as given by

$$1 - p(t) = (1 - p_0)e^{-k_p t}, \quad (18)$$

$$q(t) = q_0 e^{-k_q t}, \quad (19)$$

where p is the probability of breaking a given bond linking two monomers in the infinite chain, constituting the cross linked network, q is the probability of creating a bond or crosslink between two polymers. k_p and k_q are the scission rate constants for chain scission and crosslink scission, respectively. In the same way as Horikx did, Yashin and Isayev normalized v to the network chain density for the still fully vulcanized sample and they did the same with the gel fraction $g = (1-s)$. By simulating network degradation in time and adjusting the ratio of the scission constants, the same type of curves can be constructed as those of Horikx. When k_p/k_q approaches ∞, only rubber chains are broken and when k_p/k_q approaches 0, only cross links are broken.

9. Advantages of reclaimed rubber

Although reclaimed rubber is a product of discarded rubber articles it has gained much importance as additive in various rubber article formulations. It is true that mechanical properties like tensile strength, modulus, tear strength, storage modulus and other properties are all influenced with increasing amounts of reclaim rubber in virgin rubber formulations. But at the same time the reclaim rubber provides many advantages.

9.1. Easy breakdown and reduced mixing time

During the reclamation process the material is plasticized due to a large amount of mechanical energy input. Therefore, it mixes faster than pure virgin rubber with less heat generation. In addition to the reduced mixing time there is a sizable reduction in power consumption during mixing.

9.2. Easy calandering and extrusion

Reclaimed rubber provides faster processing during extrusion and calandering. When the vulcanized rubber is reclaimed, it is softened by scission of the cross links and main chains in the polymer network. The result is a system of cross linked fragments that is more three dimensional in nature than the original polymer. The three-dimensional structure gives dimensional stability to the compound. Extruder die swell and calender shrinkage are reduced due to the lower nerve of the blend containing reclaimed rubber.

9.3. Influence on ageing properties

During vulcanization, reclaimed rubber containing compounds show fewer tendencies to reversion indicating better ageing resistance. Ball and Randall, as well as Dierkes [91] observed anti-aging characteristics of reclaimed rubber. Ball and Randall explained the improved aging resistance by the severe treatment of oxidation, heating, digestion and mechanical shearing during the reclaiming process to stabilizes the hydrocarbon chains against further changes.

10. Uses of reclaimed rubber

Reclaim can be used in many different applications. Where cost is a primary consideration and quality requirements are not particularly demanding, reclaim can be the sole source of polymer. Examples of such products are mats and massive tires. In other cases, reclaim is blended with virgin synthetic and natural rubber. The virgin polymer adds strength and the reclaim contributes to improved processing and better mixing. Such applications include most of the constituent parts of both passenger and truck tires, bias and radial ply.

Formulating with reclaim is comparable to formulating with virgin rubber, except for its influence on the curing characteristics. The optimum cure system of virgin compound has to be adjusted when reclaim is added. The material, mixing and energy consumption savings associated with reclaimed rubber are but a part of the total benefit of its use. These savings are substantial and significant, but there are further positive aspects to the use of reclaim, which accrue to our society as a whole. They include the employments of hundreds of people in the reclaim industry and the alleviation of solid-waste-disposal problems, as well as the conservation of petrochemical raw materials and of the energy required to convert the petrochemicals into synthetic rubber.

The major uses of reclaimed rubber are

(i) carcass, sidewall and under-tread of passenger, light-truck and off-the-road tires;
(ii) tubeless passenger-tire inner liner;

(iii) inner tubes;
(iv) semi-pneumatic tires;
(v) automotive floor mats;
(vi) mechanical goods;
(vii) adhesive, sealing and tape compounds;
(viii) rubberized asphalt.

Acknowledgments

The authors are indebted to the Directorate General for International Co-operation of the Dutch Ministry of Foreign Affairs for the financial support of the project, NUFFIC and Eindhoven University of Technology for the co-ordination.

References

[1] Schidrowitz P, Dawson TR. History of the rubber industry, institute of rubber industries. Cambridge: Heffer & Sons; 1952.
[2] Hoffmann W. Rubber chemicals and additives. In: Hoffmann W, editor. Rubber technology handbook. New York: Hanser Publishers; 1994. p. 320–5.
[3] Singleton R, Davies TL. Ground vulcanized rubber and reclaimed rubber. In: Blow CM, Hepburn C, editors. Rubber technology and manufacture. London: Butterworth; 1982. p. 237–42.
[4] Ball JM. Reclaimed rubber. New York: Rubber Reclaimers Association Inc.; 1947.
[5] Blackley D C. Latex-dipping processes. In: Blackley DC, editor. Polymer lattices—science and technology. London: Chapman & Hall; 1997.
[6] Jumpasut P. Asia's amazing growth in latex products industry. Paper presented at the Latex conference. Hamburg, Germany, April 2004.
[7] Beswick RHD, Dunn D. Global latex industry: Technology and markets. Paper presented at the Latex conference. Hamburg, Germany, April 2004.
[8] Scheirs J. Rubber tyre recycling. In: Scheirs J, editor. Polymer recycling: science, technology and applications. London: Wiley; 1998. p. 125–37.
[9] Mark HF, Bikales NM, Overberger CG, Menges G. Rubber reclaiming. In: Mark HF, editor. Encyclopedia of polymer science and engineering. New York: Wiley; 1998. p. 787–91.
[10] Crane G, Elefritz RA, Kay EL, Laman JR. Scrap tire disposal procedures. Rubber Chem Technol 1978;51:577–99.
[11] Beckman JA, Crane G, Kay EL, Laman JR. Scrap tire disposal. Rubber Chem Technol 1974;47:597–624.
[12] Klingensmith B. Recycling, production and use of reprocessed rubbers. Rubber World 1991;203:16–9.
[13] Myhre MJ, MacKillop DA. Rubber recycling. Rubber Chem Technol 2002;75:429–74.
[14] Manuel HJ, Dierkes W. Recycling of rubber. Rapra Rev Rep 1997;9.
[15] Dunn XR, Recycling, resource reduction, sustainable developments. Global actions. Paper presented at Recycle '93, Davos international forum and exposition, March 1993. p. 22–6.
[16] Le Beau DS. Science and technology of reclaimed rubber. Rubber Chem Technol 1967;40:217–37.
[17] Warner WC. Methods of devulcanization. Rubber Chem Technol 1994;67:559–66.
[18] Yamashita S. Reclaimed rubber from rubber scrap (2). Int Polym Sci Technol 1981;8(12):T/77–93.
[19] Schaefer R, Isringhaus RA. Reclaimed rubber. In: Morton M, editor. Rubber technology. Dordrecht: Kluwer Academic Publishers; 1999.
[20] Mayo FR, Heller J, Walrath RL, Irwin KC. Accelerated oxidation of polyisoprene II: effects of hydrazines, sulfur compounds and phenyl-β-napthylamine in solution. Rubber Chem Technol 1968;41:289–95.
[21] Bolland JL. Kinetic studies in the chemistry of rubber and related material I: the thermal oxidation of ethyl linoleate. Proc R Soc 1943;186:218–36.
[22] Poshkus AC, Herweb JE. The reaction of triarylphosphite with sulfonyl chlorides. J Am Chem Soc 1957;79:4245–6.
[23] Makarov VM, Drozdowskii VF. Reprocessing of tires and rubber waste. In: Horwood E, editor. Recycling from the rubber products industry. New York: Prentice -Hall; 1991.
[24] Knorr K. Reclaim from natural and synthetic rubber scrap for technical rubber goods. Kautsch Gummi Kunstst 1994;47:54–7.
[25] Saeki Y. Methodology, technology and economy of polymer recycling. Proceeding of the international rubber conference, 1995. p. 594–601.
[26] Hader RN, LeBeau DS. Chemistry of reclaimed rubber. Ind Eng Chem 1951;43:250–63.
[27] Sekhar BC, Subramaniam A. Improvements in and relating to the reclaiming of natural and synthetic rubbers. Malaysia: STI-K Polymers SDN BDH; 1996 [EP:0748837].
[28] Onouchi Y, Inagaki S, Okamoto H, Furukawa J. Reclamation of scrap rubber vulcanizates III: reclamation of crushed tire scrap with dimethylsulfoxide. Int Polym Sci Technol 1982;55:T/58–62.
[29] Horikx MM. Chain scission in polymer network. J Polym Sci 1956;19:445–54.
[30] Tyler KA, Cerny GL. Method of reducing pollution in microwave devulcanization process. USA: Goodyear Tire and Rubber; 1984 [US:4459450].
[31] Novotny DS, Marsh RL, Masters FC, Tally DN. Microwave devulcanization of rubber. USA: Goodyear Tire and Rubber; 1978 [US:4104205].
[32] Fix SR. Microwave devulcanization of rubber. Elastomerics 1980;112(6):38–40.
[33] Fix SR. Microwave devulcanization of rubber. Proceedings of the international institute of synthetic rubber producers, 1980.
[34] Pelofsky AH. Rubber reclamation using ultrasonic energy. USA: Cities Service Oil Co; 1973 [US:3725314].
[35] Okuda M, Hatano Y. Method of desulfurizing rubber by ultrasonic wave. Japan: Yokohama Rubber Co. Ltd; 1987 [JP:62121741].
[36] Mangaraj D, Senapathi N. Ultrasonic vulcanization. USA: Battelle Memorial Institute; 1985 [US:4548771].
[37] Levin VY, Kim SH, Isayev AI, Massey J, Von Meerwall E. Ultrasound devulcanization of sulfur vulcanized SBR: Crosslink density and molecular mobility. Rubber Chem Technol 1996;69:104–14.

[38] Levin VY, Kim SH, Isayev AI. Vulcanization of ultrasonically devulcanized SBR elastomers. Rubber Chem Technol 1997;70:120–8.
[39] Isayev AI, Chen J, Tukachinsky A. Novel ultrasonic technology for devulcanization of waste rubber. Rubber Chem Technol 1995;68:267–80.
[40] Yashin VV, Isayev AI. A model for rubber degradation under ultrasonic treatment: Part I. Acoustic cavitation in viscoelastic solid. Rubber Chem Technol 1999;72:741–57.
[41] Isayev AI, Yushnov SP, Chen J. Ultrasonic devulcanization of rubber vulcanizates I. Process model. J Appl Polym Sci 1996;69:803–13.
[42] Isayev AI, Yushnov SP, Chen J. Ultrasonic devulcanization of rubber vulcanizates II: simulation and experiments. J Appl Polym Sci 1996;69:815–24.
[43] Isayev AI, Kim SH, Levin VY. Superior mechanical properties of reclaimed SBR with bimodel network. Rubber Chem Technol 1997;70:194–201.
[44] Johnston ST, Massey J, Meerwall EV, Kim SH, Levin VY, Isayev AI. Ultrasonic devulcanization of SBR: molecular mobility of gel and sol. Rubber Chem Technol 1997;70: 183–93.
[45] Tukachinsky A, Schworm D, Isayev AI. Devulcanization of waste tire rubber by powerful ultrasound. Rubber Chem Technol 1996;69:92–103.
[46] Diao B, Isayev AI, Levin VY. Basic study of continuous ultrasonic devulcanization of unfilled silicone rubber. Rubber Chem Technol 1999;72:152–64.
[47] Yushanov SP, Isayev AI, Kim SH. Ultrasonic devulcanization of SBR rubber: experimentation and modeling based on cavitation and percolation theories. Rubber Chem Technol 1998;71:168–90.
[48] Hong CK, Isayev AI. Ultrasonic devulcanization of unfilled SBR under static and continuous conditions. Rubber Chem Technol 2002;75:133–42.
[49] Yun J, Isayev AI. Superior mechanical properties of ultrasonically recycled EPDM rubber. Rubber Chem Technol 2003;76:253–70.
[50] Campbell DS, Saville B. Current principles and practices in elucidating structure in sulfur vulcanized elastomers. In: Proceeding of the international rubber conference. Brighton, UK, 1967. p. 1–14.
[51] Campbell DS. Structural characterization of vulcanizate Part X: thiol-disulfide interchange for cleaving disulfide cross links natural rubber vulcanizates. J Appl Polym Sci 1969;13:1201–14.
[52] Kiroski D, Sims J, Packham DE, Gregory AL. The use of thiol–amine chemical probes in network characterization of NBR vulcanizates. Kautsch Gummi Kunstst 1997;50: 716–20.
[53] Saville B, Watson AA. Structural characterization of sulphur vulcanized rubber networks. Rubber Chem Technol 1967;40:100–48.
[54] Meyer KH, Hohenemser W. Contribution to the study of the vulcanization reaction. Rubber Chem Technol 1936;9: 201–5.
[55] Moore CG. The nature of the cross links in tetramethylthiuram disulfide-zinc oxide-natural rubber vulcanizates. J Polym Sci 1958;32:503–6.
[56] Humphey RE, Hawkins JM. Reduction of aromatic disulfide with triphenylphosphine. Anal Chem 1964;36: 1812–4.
[57] Humphey RE, Potter JL. Reduction of disulfide with tributylphosphine. Anal Chem 1965;37:164–5.
[58] Moore CG, Trego BR. Structural characterization of vulcanizates Part IV: use of triphenylphosphine and sodium-di-*n*-butyl phosphite to determine the structure of sulfur linkages in natural rubber, cis-1,4-polyisoprene and ethylene–propylene rubber vulcanizate networks. J Appl Polym Sci 1964;8:1983.
[59] Gregg Jr EC, Katrenick SE. Chemical structures in cis-1,4-polybutadiene vulcanizates: model compound approach. Rubber Chem Technol 1970;43:549–57.
[60] Gregg Jr EC. Sulphur cross links in polybutadiene vulcanizates. Rubber Chem Technol 1969;42:1136–46.
[61] Miller GW. The chemistry and technology of rubber. NewYork: Reinhold Publishing corporation; 1937.
[62] Nicholas PP. The scission of polysulfidic cross links in scrap rubber particles through phase transfer catalyst. Rubber Chem Technol 1981;55:1499–515.
[63] Nicholas PP. Devulcanized rubber composition and process for preparing same. USA: B.F. Goodrich company; 1979 [US:4161464].
[64] Dinsmore HL, Smith DC. Analysis of natural and synthetic rubber by infrared spectroscopy. Anal Chem 1948;20:11–24.
[65] Straube G, Straube E, Neumann W, Ruckaet H, Forkmann R, Loffler M. Method of reprocessing scrap rubber. Germany: Hoelzemann Metallverarbeitung; 1994 [US:5275948].
[66] Tsuchii A, Suzuki T, Takeda K. Microbial degradation of natural rubber vulcanizates. Appl Environ Microbiol 1985;50:965–70.
[67] Tsuchii A, Takeda K, Tokiwa Y. Degradation of the rubber in truck tires by a strain of Nocardia. Biodegradation 1997;7:405–13.
[68] Tsuchii A, Takeda K, Tokiwa Y. Rubber-degradation enzyme from a bacterial culture. Appl Environ Microbiol 1990;56:269–74.
[69] Kojima M, Ogawa K, Mizoshima H, Tosaka M, Kohjiya S, Ikeda Y. Devulcanization of sulfur-cured isoprene rubber in supercritical carbondioxide. Rubber Chem Technol 2003;76:957–68.
[70] Thomas KT, Claramma NM, Kuriakose B, Thomas EV. Recycling of natural rubber latex waste. In: Paper presented at the International conference on rubber and rubber-like materials, Jamshedpur, India, November 1986.
[71] Mathew G, Singh RP, Nair NR, Thomas S. Recycling of natural rubber latex waste and its interaction in epoxidised natural rubber. Polymer 2001;42:2137–65.
[72] Rajan VV, Dierkes WK, Joseph R, Noordermeer JWM. Comparative investigation on the reclamation of NR based latex products with amines and disulfides. Rubber Chem Technol 2005;78:855–67.
[73] Kuzmiski AZ. Developments in polymer stabilization. London: Applied Science Publishers; 1981. p. 71.
[74] Nieuwenhuizen PJ, Haasnoot JG, Reedijk J. Model-compound vulcanization: an established technique for the next century. Kautsch Gummi Kunstst 2000;53: 144–52.
[75] Dierkes W, Rajan V, Noordermeer JWM. Model compound studies on the de-vulcanisation of natural rubber at different temperatures. Kautsch Gummi Kunstst 2005;58:312–6.
[76] Rajan VV, Dierkes WK, Joseph R, Noordermeer JWM. Model compound studies on the devulcanization of natural

rubber using 2,3-dimethyl-2-butene. Rubber Chem Technol 2005;78:572–87.
[77] Verbruggen MAL, van der Does L, Noordermeer JWM, van Duin M, Manuel HJ. Mechanism involved in the recycling of NR and EPDM. Rubber Chem Technol 1999;72:731–40.
[78] Kende I, Pickering TL, Tobolsky AV. The dissociation energy of the tetrasulphide linkages. J Am Chem Soc 1965;87:5582–6.
[79] Pickering TL, Saunders KJ, Tobolsky AV. Disproportionation of organic polysulfides. J Am Chem Soc 1967;89: 2364–7.
[80] Pickering TL, Saunders KJ, Tobolsky AV. The chemistry of sulfides. New York: Interscience Publishers; 1968.
[81] Milligan B. Vulcanization accelerator and activator complexes 2: chemistry of amine and zinc carboxylate complexes of zinc and cadmium benzothiazolyl mercaptides. Rubber Chem Technol 1966;39:1115–26.
[82] Kok CM, Yee VH. The effects of crosslink density and crosslink type on the tensile and tear strengths of NR, SBR and EPDM gum vulcanizates. Eur Polym J 1986;22:341–5.
[83] Charlesby A. Gel formation and molecular weight distribution in long-chain polymers. Proc Roy Soc (London) 1954;A222:542–57.
[84] Charlesby A. Solubility and molecular size distribution of cross linked polystyrene. J Polym Sci 1953;11(6): 513–20.
[85] Flory PJ. Molecular size distribution in three dimensional polymers III: tetrafunctional branching units. J Am Chem Soc 1941;63:3096–100.
[86] Flory PJ, Rehner Jr J. Statistical mechanics of swelling network structures. J Chem Phys 1950;18:108–11.
[87] Yashin VV, Isayev AI. A model of rubber degradation under ultrasonic treatment: part II. Nature of rubber network and comparison with experiments. Rubber Chem Technol 2000;73:325–39.
[88] Gordon M. Good's theory of cascade process applied to the statistics of polymer distribution. Proc Roy Soc London 1962;A268:240–56.
[89] Dobson GR, Gordon M. Configurational statics of highly branched polymer systems. J Chem Phys 1964;41: 2389–98.
[90] Dobson GR, Gordon M. Theory of branching processes and statistics of rubber elasticity. J Chem Phys 1965;43: 705–13.
[91] Dierkes W. Rubber re-use is best all round. Eur Rubber J 1996;169:36–8.