CHAPTER 1

STATE OF THE ART: RECYCLING OF EPDM RUBBER Vulcanizates

1. Introduction

A rubbery material is composed of macromolecules (polymers), the behavior of which is influenced by their long-chain character. The chains are flexible; the carbon atoms are able to rotate around their axis, enabling the macromolecular chains to twist into various conformations. Consequently, entanglements can occur between these chains. The material is considered as a liquid, but a very viscous one that even may have the appearance of a solid. Curing (or vulcanization) is a process of forming a network between the macromolecular chains by crosslinking. After curing, the rubber has a fixed shape and cannot flow anymore, owing to the crosslinks, which anchor the polymer chains to each other and prevent them from slipping alongside. Therefore, in contrast to what happens in thermoplastic recycling processes, it is not possible to process the cured rubber only by heating and to give it a new shape.

Approximately 70% of the rubber produced worldwide is used in tires. Among all possible ways of handling post-consumer tires (such as shredding and energy reclamation), a common one is to dump them in a landfill, creating a stockpile of tires. These stockpiles can cause fire danger and provide breeding grounds for rodents and other pests, causing health hazards [1]. An environmental-friendly method of recycling is therefore strongly desired.

EPDM rubber is a copolymer of Ethylene and Propylene, with a diene as a co-monomer, which introduces unsaturation into the macromolecule. The last letter “M” refers to the polymethylene-(CH$_2$)- type backbone according to the nomenclature given by ISO1629. EPDM is usually produced in a hydrocarbon solvent (e.g. hexane) or in a suspension (in propene). The manufacturing of EPDM is based on Ziegler-Natta catalysis, using Vanadium compounds (VCl$_4$ or VOCl$_3$) as catalyst with alkylaluminiumhalogene (Et$_2$AlCl or Et$_3$Al$_2$Cl$_3$) as co-catalyst. The average molecular weight of EPDM lays between 30000 and 150000, depending on the polymerization variables and the ethylene:propylene:diene ratio. The molecular structure of EPDM is shown in Figure 1.1 [2,3].
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A wide range of dienes have been investigated as the third monomer(s), of which only two are used commercially nowadays [2,4]: 5-ethylidene-2-norbornene (ENB) and dicyclopentadiene (DCPD). The diene(s) are so structured that only one of the double bonds will polymerize, while the remaining double bond will act as a site for sulfur cross-linking [2]. This latter double bond will remain pendant from the chain backbone. Accordingly, EPDM shows an excellent resistance to heat, oxygen, and ozone. The research on EPDM still continues, aiming for higher quality products and lower price. Recently, there is a tendency of producing EPDM using metallocene catalyst technology, which results in a greater product cleanliness and higher production efficiency [5].

EPDM is the fastest growing elastomer among the synthetic rubbers since its introduction in 1963 (Figure 1.2) [2,5-7]. It represents 7% of the world rubber consumption and it is the most used non-tyre rubber. This is generally due to its excellent ozone resistance as compared to natural rubber and its synthetic counterparts (Isoprene rubber/IR, Styrene Butadiene rubber/SBR, and Butadiene rubber/BR). Besides, EPDM can also be extended with fillers and plasticizers to an extremely high level and still give good processability and properties in its end products, which is a matter of price advantage. Moreover, it has an outstanding oxygen resistance, good electrical properties, little moisture adsorption, excellent resistance to weathering and...
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chemicals, a good compression set and a very good dynamic fatigue resistance. The main use of EPDM (over a third of its global output [8]) is in automotive applications such as in the production of profiles, hoses and seals; in building and construction as profiles, roofing foil, and seals; in cable and wire as insulation and jacketing. EPDM is also used in blends with general-purpose rubbers to improve the ozone and weathering resistance in products such as in cover strips and thermoplastic material used for exterior automotive applications (bumpers and panels) [2]. Contrary to the other rubber parts of cars, namely tires, EPDM rubber has received much less attention concerning the recycling issue.

2. Rubber recycling processes

Ever since tires and other rubber products have been produced and used, there has been the problem of scrap or used rubber parts. A recognizable example is the post-consumer tires. Moreover, the waste of rubber during the production process of several products (sometimes in the order of 10 wt %) constitutes a big problem. Because of changing legislation, the rubber-producing and –consuming society is more and more urged to consider the possibilities of recycling in one form or the other. This legislation imposes the automobile-industry, for example, to recycle 95% of the overall weight of the car wrecks from 2015 onwards. As a result, the rubber industry cannot escape from recycling the rubber products used in cars.

Rubber recycling nowadays includes all processes where rubber scrap is transformed into a re-usable form to produce new articles or services. One of the oldest rubber recycling processes, the so-called “Heater/Pan Process”, was invented around 14 decades ago by Hall (1858) [9,10]. Since then, numerous methods have been proposed and studied in the rubber recycling field [11,12]: repeat use (re-use and re-treading), physical recycling (reclaiming, grinding and surface activation), recovery of base chemicals (pyrolysis, gasification and hydrogenation) and energy recycling (incineration). High temperature and pressure are applied in most of the recycling methods studied.

Grinding is considered a physical recycling method of rubber. The ground rubber can be used as a reinforcing filler in new products. In this respect, surface activation of the rubber crumbs has been found useful in improving the bond strength with other rubber particles or the surrounding matrix. On the other hand, the repeated use constitutes, due to the very low price of new tires, hardly a solution for the waste problem and retreading only happens at very small scale [13].

Rubber recycling processes keep developing, aiming at the re-utilization of rubber as close as possible to its virgin form. This type of recycling method where rubber is re-used like in its virgin form is called devulcanization (or reclaiming). During devulcanization, the rubber network is broken down, often by chain scission. The product can be revulcanized/recured to form new rubber articles. Unfortunately, a selective process that only breaks the cross-links without main chain scission is still unavailable at the moment. The devulcanized rubber will have a different molecular structure compared to the unvulcanized rubber (see Fig. 1.3). Due to the broader molecular weight distribution, the revulcanized product will have lower mechanical
properties in comparison with the product from virgin rubber. Moreover, the revulcanization conditions might also be influenced by the change in molecular weight.

![Diagram of molecular structures](image)

Figure 1.3. The difference of molecular structures between virgin raw rubber, vulcanizate and devulcanized rubber [14]

The devulcanization processes, where the destruction of the rubber network takes place, can be classified into 5 groups:

1. **Chemical Processes.** A typical process is mixing of the rubber powder with a peptizer and a reclaiming agent [15]. The latter is used in breaking the rubber network. Most of the time, this method is combined with thermal and/or mechanical energy to accelerate the process. The most common reclaiming agents are disulfides, e.g. aryl disulfides such as diphenyl disulfide, thiophenols and their zinc salts and mercaptanes. These compounds are radical scavengers: they react with the radicals generated by chain or crosslink scission and prevent recombination of the molecules [11],[16]. Typical concentrations for the reclaiming agents are 0.5 to 4 wt %. Suitable peptizers are mainly aromatic oils with high boiling points.

Other compounds used for sulfur-crosslink scission are 1,8-diazabicyclo(5,4,0)undecane with p-toluene sulfonic acid or with tetraethyl thiuram disulfide, triphenyl phosphine, dipentene with cobalt or manganese compounds, redox systems, vulcanization accelerators and antioxidants [9,11]. Other chemicals, which are able to selectively break mono-, di- and polysulfidic crosslinks, are chemical probes. Examples of such compounds are: 2-propanethiol/piperidine and triphenylphosphine to break polysulfidic bonds; 1-hexanethiol and piperidine, lithium aluminiumhydride, phenyllithium, sodium dibutylphosphite, sodium-di-n-butylphosphite to break poly- and disulfidic bonds; methyl iodide to break monosulfidic bonds. The disadvantage of chemical probes is, nevertheless, the toxicity of the chemical compounds and the difficult reclaiming conditions [17]. Polysulfidic crosslinks can also be broken up by hydroxyl ions in a two phase system. The rubber powder is dispersed in basic water, and a quaternary ammonium chloride acts as a phase-transfer catalysts and transports the hydroxyl ions into the rubber phase where the scission takes place [11]. Another chemical reclaiming method is the De-Link process [9,18] that involves mixing of finely ground rubber powder of about 40 mesh with 6 part per hundred rubber (phr) material called De-Link in a two roll mill or an internal mixer at ambient temperature. De-Link is composed
of zinc salt of dimethyldithiocarbamate and mercaptobenzothiazole in the molar ratio of 1:1 to 1:12 dispersed in diols and activated by stearic acid, zinc oxide, and sulfur. The tensile properties and tear resistance achieved by mixing 30% of this reclaim into the virgin rubber were claimed to be very similar to those of the virgin material.

2. Thermo-chemical processes. For this kind of processes, the effect of heat is combined most of the times with the chemical one to break the crosslinking points, thereby to plasticize the rubber scrap. The heater or pan process (Hall, 1858) is one of the oldest ones in the rubber reclaiming industry [9,10], where ground rubber is subjected to steam pressure for around 48 hours. Further development of this batch process with the help of reclaiming agents enables shorter reaction times (5-10 hours at 180°C), which are still however too long for practical applications. This process is applicable to a large number of polymers: NR (natural rubber), SBR (styrene/butadiene rubber), CR (chloroprene rubber), NBR (Nitrile rubber), and IIR (Butyl rubber). Moreover, the required equipment is relatively inexpensive. The Digester or Alkali process (Marks, 1899) became very important to produce reclaimed rubber [10], because of its ability to recycle reinforced scrap rubber. The fiber from reinforced coarse ground scrap material is first removed by mixing it with alkali, water, plasticizing oil (and chemical peptizers). The mixture is heated up in a jacketed, agitator equipped autoclave to 180-210°C for 5-24 hours [9]. The disadvantage of this process is the long cycle time and the pollution generated from the chemicals used. The digester solution must be disposed off after each cycle; the washing water with its contamination of fine rubber material also causes water pollution; drying and dehydrating causes air pollution and requires large amounts of energy. Nevertheless, this process is attractive regarding its ability to remove the fiber from the rubber without grinding down to extremely small sizes so that relatively inexpensive equipment can be used. A modification of this process uses a paddle stirred, horizontal autoclave in which the finely ground rubber scrap, mixed with reclaiming agents, is treated with steam. Heat transfer in this system takes place more evenly throughout the particles; pollution and costs are diminished since the process requires no digester solutions, no washing and no extensive drying.

Recent developments were aimed at shorter reaction times. In the high pressure steam process [9,10], fiber-free coarse ground rubber scrap is mixed with reclaiming agents and reclaimed in a high pressure autoclave at 5.6 to 6.9 MPa and temperature around 280°C for about 5 minutes. The rubber blend is then collected, dried, and milled. The Engelke process mixes coarse ground rubber scrap with plasticizing oils and peptizers; the resulting blend is lowered in cages into small autoclaves. This is heated to very high temperatures for just 15 minutes, after which refining and straining takes place [9,11].

3. Mechanical processes. In the mechanical process, shearing action is applied to the material, tearing the rubber network. The Lancaster-Banbury process is one of the oldest examples [9] in which fiber-free coarse ground rubber scrap is mixed with reclaiming agents and sheared in a high speed, high pressure internal batch
mixer. The material reaches high temperatures (around 250°C) in 3-12 minutes and is then cooled, refined, and strained. The Ficker reclaiming process uses the same concept but is carried out in a continuous, twin-screw devulcanizer instead of an internal mixer [9].

One of the first continuous reclaiming processes developed made use of a “reclaimator”, which in essence is a single screw extruder with a feedstock of 0.6 mm ground, fibre-free rubber scrap. The rubber is subjected to high shearing action between the screw and the wall of the extruder barrel. Temperatures between 175-205°C are applied and the residence time is between 1 and 3 minutes [10]. The end of the extruder is cone shaped. Only the material that has been well plasticized will be able to pass this cone.

Toyota developed a process in which, according to the corresponding paper [19], unvulcanized rubber, ground rubber, reclaiming oil and devulcanizing agent (in 100:30:10:1 weight ratio) are masticated together in a mixing mill (batch process) or an extruder (continuous process) to produce a compound that contains devulcanized rubber. Using the extruder for continuous operation, the production steps, labor cost and time can be reduced. Rubber is fed at about 10 kg/h, extruded and cooled in a water bath. Screw rotation speeds of 100-400 rpm and temperatures between 50-400°C were applied. Temperatures lower than 50°C will slow down the devulcanization rate of the waste vulcanized rubber, while temperatures above 400°C will cause main chain scissions, i.e. degradation of the rubber. Various reclaiming agents can be used for this process, as long as they are able to partly break the sulfur crosslinks to such an extent that both the unvulcanized and the waste rubber can be well mixed. Toyota developed another continuous process combining pulverization, reclaiming and deodorization [20]. This type of process has been tested for 4 kinds of rubber: NR-based, SBR-based, and IIR-based tire rubber and EPDM. For this process, rubber has to be ground first to a particle size of less than 5 mm. The rubber particles are crushed to smaller ones in the initial zone of the extruder and heated up to the reaction temperature quickly.

4. Irradiation processes [9,21-25]. Microwave devulcanization is one of the possible methods involving the use of irradiation techniques [9,24,26]. The principle of microwave heating of rubber is discussed thoroughly by Suryanarayanan [27]. Material is heated in the microwave field only if it can absorb microwaves via dipole rotation or ionic conduction. Dipole rotation plays a role in the heating of polar materials such as nitrile or polychloroprene rubber. In contrast, the heating of non-polar materials such as natural rubber, EPDM and SBR is an indirect heating process. The presence of carbon black in those non-polar rubbers makes them receptive to microwave energy. The free ions, which exist at the interface between carbon particle and rubber, are attracted by electrical fields. Their velocity represents the kinetic energy given by the microwave field. When the free ions collide with non-polar molecules, the energy is converted into heat energy that is transferred to the non-polar molecules.
The devulcanization method using microwave was first described in a patent from the Goodyear Tire & Rubber Co. [24] Coarse ground rubber of 6-10 mm (preferably fiber-free) is transported in a transparent tube system through a microwave device. The material rapidly heats up to 260-350°C in seconds. In a subsequent publication, Fix [28] discussed the advantages of this method and pointed out that the costs to devulcanize hose and inner tube material is only a fraction of the costs of the original compound. In addition, the transformation from waste to refined stock, ready for remixing, takes place in only five minutes with usually 90-95% recovery of the rubber. However, the plant is no longer operational, reportedly due to heat control problems [9].

It has also been discovered [29,30] that through the application of certain levels of ultrasonic waves at certain amplitudes in the presence of pressure, and optionally heat, the three-dimensional network of vulcanized elastomers can be broken down. As a consequence, ultrasonically treated rubbers become soft and can be reprocessed and shaped in a manner similar to that employed with uncured elastomers. This process is suitable for the recycling of various rubbers including those from used tires. Ultrasonic devulcanization can be conveniently carried out in an extruder equipped with an ultrasonic device placed in a cross-head or coaxial die [21,31-34]. Ground rubber particles of about 0.5 mm size are extruded and then flow through the die, where a horn gives ultrasonic energy to the material. The devulcanization takes place in the gap between the die and the horn. Here the material turns soft and is able to flow again. The horn vibrates longitudinally at a frequency of 20 kHz with an amplitude between 5 and 10 microns, which is provided by a 3000 W ultrasonic power supply equipped with a converter and a booster. Ultrasound amplitude, screw speed, feeding speed, cooling capacity and die gap have been tested with this set-up. Higher flow rates and smaller die gaps result in an increase in molecular weight of the soluble part and increased gel content. Increasing flow rate results in a lower decrease of crosslink density. The amount of main chain breakage is a controllable parameter and is dependent on pressure and residence time. Devulcanization occurs very fast, typically within 0.1-10 seconds. The type of rubber, which can be devulcanized, can be of the polar or non-polar type. The mechanism of rubber devulcanization under ultrasonic treatment is presently unclear [35].

5. Biological processes. Biological devulcanization is usually attractive regarding its high selectivity. Nevertheless, a lot of effort is needed to find the suitable culture for a process, where high conversion can be achieved. Chemolithiotropic microorganisms have been tested for devulcanizing rubber [9,11,36], namely NR and SBR. Bacteria from the genus Nocardia and Thiobacillus have been used to devulcanize NR and SBR, respectively. The devulcanization was only observed on the rubber particle surface and only 4.7% of the total sulfur was oxidized to sulfate within 40 days [37]. Due to these constraints, this process is still far from application in industry.
3. EPDM recycling

Recycling of EPDM rubber might involve reprocessing it into its virgin form by breaking the crosslinks between the polymer chains (devulcanization) or reusing the EPDM waste in usable form, as will be discussed in the following paragraphs.

3.1. Developments in Reclaiming EPDM Rubber

Efforts to recycle EPDM rubber are derived from tire recycling process. Unfortunately, the recycling process of tire rubber, which is a mixture of NR and SBR, cannot be applied directly to EPDM. Heat and pressure are enough to reclaim NR. The addition of plasticizers plays a role in reducing the cycle time and giving uniform and highly devulcanized product. Plasticizers (as alkyl phenol sulfides, aromatic amines, chlorinated mercaptans) are able to penetrate evenly into the NR and bond cleavage is uniform [10]. On the contrary, recycling of EPDM displays several problems due to the low solubility of the devulcanizing agent in the rubber. Another obstacle might be the presence of a higher percentage of more stable monosulfidic crosslinks in EPDM [38]. Indeed, the energy required to break monosulfidic bonds is approximately 20% higher than what is needed to break the polysulfidic bonds (Table 1.1). More details on several studies on EPDM recycling will be discussed in the following paragraphs.

<table>
<thead>
<tr>
<th>Type of vulcanizates</th>
<th>Type of bonds to be broken</th>
<th>Energy required (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur vulcanizate</td>
<td>- C – S –</td>
<td>270</td>
</tr>
<tr>
<td></td>
<td>- S – S –</td>
<td>240</td>
</tr>
<tr>
<td>Peroxide vulcanizate</td>
<td>- C – C –</td>
<td>345</td>
</tr>
</tbody>
</table>

3.1.1. ‘Fundamental’ or ‘small scale’ investigations

Verbruggen et al. investigated the effect of amines as devulcanization agent for EPDM rubber [40]. They found that EPDM successfully could be devulcanized with several types of amines. In the series primary, secondary, and tertiary aliphatic amines as well as benzylic amines almost no difference in reactivity was found. The relative decrease in crosslink density obtained with amines was comparable with the results obtained with disulfides. The reactivity of the amines was neither influenced by the basicity nor by the number of protons attached to the nitrogen atom. The presence of an α-H was however suggested as the determinative factor for the reactivity. The relative decrease in crosslink density reached in devulcanization was reported to depend on the concentration of the devulcanization chemicals. A higher concentration of amines led to a higher decrease in cross-link density.

3.1.2. Thermal-Mechanical Process

Toyota developed a technology for continuously reclaiming EPDM-rubber within a short time (10 minutes) using a twin screw extruder [14,41-44]. The
continuous devulcanization processing using the extruder was made possible by optimizing the various conditions, which include the reaction temperature, screw geometry, rotational speed and the amounts of additives such as devulcanizing agent and reclaiming oil. The rubber material was typically cut into 1 cm² pieces and fed into the extruder. Oil and devulcanizing agent were added to the rubber in a weight ratio of 20:6:1 (rubber/oil/devulcanizing agent), and the mixture was swollen for at least 24 hours at room temperature. The twin screw extruder used was 1.2 meter long, with an output capacity of 5-20 kg/h. The screws had a diameter of 3 cm and rotated up to 500 rpm. The rubber temperature was increased quickly to the devulcanization temperature of 300°C during the process. A temperature within the range of 280°C to 330°C was claimed to be most preferable for sulfur vulcanized EPDM, while the shear stress applied was preferred to be between 1 and 15 MPa [45].

However, this reclaimed EPDM rubber can only be used for parts, which do not require a high function or high quality appearance, such as luggage door weather strips, hose protectors, or headlamp cover seals. A maximum addition of 25% of the reclaimed EPDM to virgin one was possible from a processability and performance point of view.

3.1.3. Microwave Devulcanization of EPDM

The Goodyear Tire & Rubber Company tried to devulcanize EPDM rubber waste with microwave energy [24,28]. A microwave frequency of 915 or 2450 MHz and energy between 325 and 1404 kJ/kg was generated. The heating mechanism of EPDM rubber by microwave is an indirect heating mechanism. EPDM itself is a non-polar rubber; hence, it does not absorb the microwave energy. The latter is absorbed by the carbon black in the EPDM rubber product, which in turn heats up the molecules in its surrounding by conduction. Since the EPDM is usually highly loaded with carbon black, it can be heated rapidly in the microwave field. The mechanical properties after blending microwave devulcanized EPDM with virgin one were claimed not to deviate much from that of the virgin rubber as shown in Table 1.2 [24,28]. In addition, it is also mentioned in the patent that the material produced by this method can be devulcanized and revulcanized for the second time without significant loss of physical properties.

<table>
<thead>
<tr>
<th>Physical Properties</th>
<th>% devulcanized EPDM</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0%</td>
</tr>
<tr>
<td>Tensile strength (MPa)</td>
<td>8.6</td>
</tr>
<tr>
<td>Elongation at break (%)</td>
<td>315</td>
</tr>
<tr>
<td>Hardness (Shore A)</td>
<td>73</td>
</tr>
</tbody>
</table>
3.1.4. Ultrasonic Devulcanization of EPDM

An investigation into the ultrasonic devulcanization of sulfur cured EPDM rubber was conducted by Isayev et al. [46]. EPDM was fed at a flow rate of 0.63 g/s to an extruder, which was preheated to 120°C. An ultrasonic device was mounted in the gap between the horn and the die plate of the extruder. The EPDM vulcanizate was loaded into the hopper. In the extruder, the material was compressed and conveyed by the screw to the devulcanization zone. The ultrasonic treatment of the rubber occurred in the gap between the horn and the die plate of the reactor. Gap size and ultrasonic wave amplitude were processing parameters and had an influence on the degree of devulcanization. An increase of the ultrasonic amplitude and a decrease of the gap size increased the degree of devulcanization of EPDM.

The devulcanized EPDM rubbers were revulcanized by using the same recipe and cure conditions as the virgin rubber. Concerning the dynamic visco-elastic properties, it was found that devulcanized EPDM was a more elastic material than uncured virgin EPDM and revulcanized EPDM is a less elastic material than virgin EPDM vulcanizate at the same loss modulus level. It was also found that the tensile strength of revulcanized EPDM was much higher than that of the original vulcanizates with elongation at break being practically the same.

Crosslink density and gel fraction measurements indicated that more devulcanization was achieved at higher amplitude for all compositions of filler. However, less devulcanization of carbon black filled rubbers was obtained, because a certain portion of ultrasonic energy was consumed to break the physical and chemical bonds between EPDM rubbers and carbon black, which possibly displays a lower bond energy than the chemical bonds in polymer chains and cross-links. Mechanical properties of the revulcanizates deteriorated with an increase in carbon black concentration since the fillers became deactivated under ultrasonic treatment.

Considerably better mechanical properties were obtained in blend vulcanizates containing various amounts of devulcanized rubber and virgin rubber. By adding 25% of devulcanized EPDM rubber into virgin filled one, better mechanical properties were obtained with respect to revulcanizates of 100% devulcanized EPDM rubber, at any content of filler.

3.2. Ground EPDM rubber waste as filler

Ceni Jacob et al. looked at the effect of ground EPDM vulcanizate on properties of EPDM rubber [47,48]. Given that EPDM products contain high oil and filler loadings, EPDM powder may act as a low-modulus reinforcing filler. The EPDM waste was ground at room temperature using a bench grinder with a silicone abrasive wheel rotating at 2950 rpm. They found that ground EPDM vulcanizate (W-EPDM) acts as a filler in raw EPDM (R-EPDM) and its addition results in an increase of Mooney viscosity, but a decrease of scorch time, presumably as a result of the accelerator migration from W-EPDM to the matrix R-EPDM. At higher loadings of vulcanizate powder, the maximum rheometric torque decreased, which may be attributed to the sulfur migration from the matrix to W-EPDM, and caused a decrease
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of the cross-link density of the matrix. The tensile strength, tear strength, hysteresis and elongation at break improved indicating the reinforcing nature of the carbon-black containing W-EPDM powder. In the case of low-strain modulus and hardness, the filler effect was counterbalanced by the crosslinking effect. The marginal increase in heat build-up and drop in resilience were attributed to the filler effect.

Replacing virgin EPDM by W-EPDM in blends with other polymers [49] was also studied and it was found that, although addition of W-EPDM to R-EPDM/PP blends causes an initial drop in the mechanical properties, thermoplastic elastomers with enhanced properties were obtained at higher loadings of W-EPDM. Up to 45% of R-EPDM could be replaced by W-EPDM without significantly affecting the physical properties. The utilization of waste EPDM in making thermoplastic elastomers offers a potential means to recycle waste polymers, keeping economic as well as environmental factors in mind.

4. Final Remarks

Re-using EPDM in its vulcanized form is one option of EPDM recycling. The major disadvantage is that the changes in product properties are significant. Moreover, the amount of waste EPDM that can be blended with the virgin one is very limited, since it only acts as a filler. The ideal way to recycle a material is always to re-use it in its original form, meaning for EPDM a recycling process in which the crosslinking points are selectively broken. However, in this respect, EPDM is more difficult to devulcanize than NR as the result of the difficult penetration of the devulcanization agent into the rubber matrix.

When heat is applied to EPDM sulfur vulcanizates, the di- and polysulfidic bonds change into stronger monosulfidic bonds. Shear stress is necessary to break these monosulfidic bonds. Unfortunately, scission by shear is not a selective process. It breaks molecular bonds randomly, which means it may also break the main chain of the polymers. This will result in shorter polymer chains, which in turn will reduce the mechanical properties of the reclaim.

Although the results of microwave devulcanization seem promising, the processing line for this process has been stopped by Goodyear Tyre Rubber & Co., probably due to problems with the heat control. The EPDM devulcanization method using a ultrasonic reactor, which was investigated by Isayev et al. [46], also seems promising. This method does not require addition of chemicals and temperatures higher than 120°C. Unfortunately, only unfilled EPDM vulcanizate has been tested. The presence of fillers might influence the process largely, considering the ultrasonic effect towards the filler and the interactions between the components in the compound. Further research still needs to be conducted to judge the applicability of this method for filled EPDM compounds.

Looking at these results, the EPDM recycling field still needs further research in order to achieve an effective and reliable process, which results in high quality recycled EPDM rubber. Moreover, big scale applications of available methods still have to be tested extensively. The best way of recycling rubber is to decrosslink it
back to its polymer form (devulcanization) so that it can be revulcanized and reshaped as a new product. The studies up to date have only been able to devulcanize EPDM up to a given fraction, so that a maximum of 25% can be introduced in automotive parts that do not require a high quality appearance and function. It is still a big challenge to find an effective and reliable process for EPDM recycling, where the product can be used in high quality compounds with or without a little addition of virgin EPDM.

5. Research Scope

The technology proposed in this current EPDM recycling project is based on the previous work of Verbruggen et al. [40] and Mouri et al. [14,41,42]. Mouri et al. [14] proposed a possible devulcanization reaction mechanism under shear field, depicted in Figure 1.4. It was suggested that the polysulfidic and disulfidic bonds are converted initially by the action of heat into monosulfidic bonds and release low-molecular sulfide compounds (such as hydrogen sulfide, sulfur dioxide and carbon disulfide). These monosulfidic bonds are then broken under shear force. Subsequently, the remaining sulfur atoms in the broken sulfur crosslinks react with neighbouring H-atoms to form a stable state (low-reactivity) sulfur functional groups. This was supported in the literature by following the amount of monosulfidic, disulfidic, and polysulfidic bonds during the process. Verbruggen et al. showed the prospect of α-H aliphatic amines as devulcanizing agent to restore EPDM vulcanizates in their virgin vulcanizable form, which has been shown by the authors by comparing the NMR spectra between the virgin rubber, vulcanizate and devulcanizate.

![Figure 1.4. Mechanism of crosslinking breakdown reaction proposed by Mouri et al. [14]](image-url)

The novel aspect of the current research is the combination of shearing and the use of α-H aliphatic amines as devulcanizing agent to obtain revulcanizable EPDM rubbers and the modelling of the process. In order to achieve a feasible EPDM recycling, the corresponding process parameters in the extruder, such as the shear stress, the temperature, and the screw configuration, have to be optimized. For this optimization, a satisfactory model for the process in TSE is required, which in turn necessitates the development of a kinetic model on EPDM devulcanization reaction.
An engineering type of kinetic model was derived for this purpose. A suitable screw configuration and operating conditions for the continuous system would be designed using this engineering kinetic model.

This research is a joint project with the University of Twente, department of Rubber Technology. The research conducted at University of Groningen has been focused on the technical part of the process, i.e. finding the suitable setup and operating conditions to devulcanize the EPDM. The research at University of Twente is focusing on the chemistry of the devulcanization and revulcanization.

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