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A novel industrial technique for recycling ethylene-propylene-diene waste rubber

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ABSTRACT

Recycling waste rubber has gained importance in recent years. Ethylene-propylene-diene rubber (EPDM) is used to manufacture various automotive parts. Reclaiming EPDM rubber waste is a major problem. Waste powder from discarded EPDM automotive parts was devulcanized using an industrial autoclave which provided both heating and high pressure steam. To aid the devulcanization process, 2-mercaptobenzothiazoledisulfide (MBTS) and tetramethylthiuram disulfide (TMTD) devulcanizing agents, and aromatic and aliphatic oils were also used. A portion of the virgin EPDM rubber in a common formulation for the automotive rubber strips was replaced with the devulcanized product to produce blends, which were revulcanized using a semi-efficient (SEV) vulcanization system. The viscosity, cure and mechanical properties of the blends were subsequently determined.

This study showed that the oils had different effects on the devulcanization of the waste powder and MBTS was more efficient than TMTD. Replacing 60 wt% of the virgin rubber in the automotive rubber strips with the devulcanized powder had no adverse effect on the scorch and optimum cure times, crosslink density, rate of cure, and viscosity. Also, when 20 wt% of the virgin rubber was replaced, the hardness, compression set, and modulus at 20% elongation were unaffected. It was concluded that the reclaimed rubber could be used in low percentage in order not to extremely deteriorate the mechanical properties of the virgin rubber. This provided a new effective recycling route for the waste EPDM powder in the automotive rubber strips.

1. Introduction

The automotive sector relies heavily on the use of rubbers such as ethylene-propylene-diene rubber (EPDM) to manufacture parts. Consequently, this creates a large volume of waste that must be recycled eventually. Polymeric materials do not decompose easily, and therefore, disposal of waste polymers is a serious environmental concern. Rubber recycling is growing in importance worldwide because of increasing raw material costs, diminishing resources, and the growing awareness of environmental issues and sustainability [1]. One of the major problems until now has been the limited use of waste rubber in real recycling loops, i.e., reuse in new rubber products. Improvement of the properties of waste rubber by developing a more selective breakdown process is an important issue and a global challenge [2]. ASTM STP 184 A [3] defines devulcanization as “a combination of depolymerization, oxidation, and increased plasticity” because each of these processes usually occurs during reclamation. Actually, devulcanization is the reverse of vulcanization.

In sulfur vulcanization, the formation of both C—S and S—S bonds takes place, and it is thus expected that during devulcanization, only C—S and S—S bonds cleavage should occur. In fact, in an ideal devulcanization process, crosslinks should be broken without main-chain scission. Ethylene-propylene-diene rubber (EPDM; Scheme 1) was first introduced in the USA, in limited commercial quantities, in 1962 [4]. EPDM is a copolymer of ethylene and propylene with a diene monomer which introduces unsaturation sites or double bonds into the macromolecule. Currently, EPDM is the fastest-growing general purpose rubber. This is because EPDM′ has excellent properties, particularly its resistance to ozone and oxygen and ability to tolerate high loading of filler. In automotive applications, about 3 wt% of the total weight of a vehicle is made of non-tire rubber products, namely, weather-strips, hoses, vibration insulators, and miscellaneous parts [5]. Since the start of its

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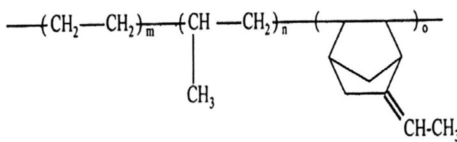
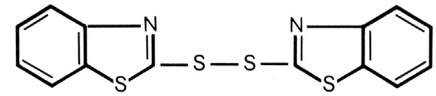


Scheme 1. Chemical structure of EPDM rubber with ENB monomer.



Scheme 2. 2-mercaptobenzothiazoledisulfide (MBTS).

production and use in these products, the disposal of scrap or used rubber parts has been a problem. Devulcanization processes, during which the destruction of the rubber network takes place, may be classified into five groups [6]: chemical processes, thermochemical processes, mechanical processes, irradiation processes, and biological processes.

Several studies have reported devulcanization of waste rubber by different methods and assessed effect of the devulcanization process on the properties of reclaimed rubber. A typical chemical process for devulcanizing waste rubber involves the mixing of rubber scrap powder with reclaiming agents such as disulfides, thiophenols and their zinc salts, and mercaptans [7]. The reclaiming agent breaks down the rubber network. In thermochemical processes, a combination of heat and reclaiming agents is used to break the cross-linking points [8,9]. In mechanical processes, a shearing action is applied to the rubber which breaks down the rubber network. Shearing can be created on a two roll mill [10–12], in a batch mixer [4], or in a single- or twin-screw extruder [13–17]. Irradiation processes include microwave [18–22] and ultrasonic wave devulcanization [23,24]. The three-dimensional rubber network can be broken down by microwaves and ultrasonic waves. Debnath and co-workers [25] reclaimed GRT mechanochemically and then revulcanized it in combination with virgin natural rubber (NR). Reclaiming of GRT was carried out by tetra benzyl thiuram disulfide (TBzTD) in the presence of spindle oil at around ambient temperature. Increasing the reclaimed rubber (RR) content in the blend decreased the optimum cure time without altering the scorch time. Furthermore, the equilibrium swelling of the NR vulcanizates was reduced with increasing reclaimed rubber content. Thermal stability of the blend was raised with increase in reclaimed rubber content. Also, the elastic and storage modulus of the NR/RR vulcanizates improved with increasing reclaimed rubber content. Isayev and co-researchers [26] devulcanized tire rubber particles of 10 and 30 mesh by means of a new ultrasonic twin-screw extruder. The ultrasonic amplitude and devulcanization temperature were varied at a fixed frequency of 40 kHz. Revulcanizations with a greater degree of devulcanization exhibited a higher elongation at break, whereas those with a lower degree of devulcanization exhibited higher strength and modulus. Revulcanizates of rubber with larger mesh size exhibited a consistently higher elongation at break.

In terms of environmental conservation, biological processes (microbial metabolism) are useful for devulcanization [27,28]. Some microbes exhibit biological activity toward sulfur and break the sulfur crosslinks in rubber by oxidizing sulfur to sulfate, waste rubber products are also devulcanized by various *Thiobacillus* species. However, this method is slow, time consuming, and has low conversion efficiency. Other miscellaneous methods such as devulcanization in supercritical materials are also available but are not of industrial importance at the present time [29]. Zhao and co-workers [30] used non-ionic surfactants to improve affinity between lipophilic ground tire rubber (GTR) and hydrophilic microbes. The growth characteristic of the *Sphingomonas* in the co-culture process and effects of different surfactants on the bio-desulfurization of GTR were investigated. One of the surfactants showed best effect on enhancement of biosulfurization. Moreover, the mechanical properties of desulfurized-GTR/styrene-butadiene rubber composite were improved. In another study [31], GTR was devulcanized in supercrtitical CO_2 in the presence of diphenyl disulfide (DD) as devulcanizing agent. Temperature and pressure were kept respectively at 180 °C and 15 MPa and the ratio between rubber and DD was 10 wt%. The process produced 50% devulcanization with a low amount of sol fraction. It also emerged that the un-reacted DD affected the revulcanization process and the mechanical properties of the blend containing devulcanized rubber. This was the only limiting factor for the application of this devulcanization process.

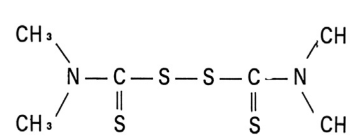
1.1. Recycling of the EPDM waste rubber

Recycling of EPDM waste rubber can involve reprocessing it into its virgin form by breaking the crosslinks between the polymer chains (devulcanization), or, reusing the waste rubber in a new form. There are various difficulties associated with recycling EPDM rubber. These include the low solubility of most devulcanizing agents in rubber and presence of a higher percentage of stable monosulfidic crosslinks in the network [32]. The energies required to break monosulfidic C–S, polysulfidic S–S and peroxide C–C bonds are 270, 240 and 345 kJ/mol, respectively [33]. Isayev et al. [34,35] investigated the devulcanization of various rubbers, including EPDM in a reactor consisting of a single screw extruder and an ultrasonic source on the die. The effect of processing parameters and ultrasonic conditions on devulcanization were reported. Mouri et al. [36] used a chemicomechanical method, involving simultaneous use of devulcanizing chemical agents and shear action. The devulcanization efficiency was increased by the addition of the devulcanizing agents during the shearing action [14,32,36,37]. The devulcanizing agents were organic disulfides, mercaptanes and aliphatic amines.

1.2. Recycling of the waste rubber powder in autoclave

Recycling of waste rubber in autoclave is classified as a thermochemical process. In this process, high pressure steam (heating source) having a temperature around 280 °C, and pressures around 5.6–6.9 MPa, and a devulcanizing agent is used [7,8,38]. This method was primarily used by certain researchers for devulcanizing natural rubber, butyl, and silicone rubbers [7].

The primary objective of this study was to devulcanize waste EPDM rubber powder obtained from residues of discarded automotive parts, using a high pressure steam industrial autoclave. To assist the process, 2-mercaptobenzothiazoledisulfide (MBTS, Scheme 2) and tetramethylthiuram disulfide (TMTD, Scheme 3) organic disulfide devulcanizing agents were also used. The waste powder was first soaked in aromatic and aliphatic oils for some time and then devulcanized. In the second stage, the devulcanized powder was mixed with virgin EPDM, carbon black and oil at two



Scheme 3. Tetramethylthiuram disulfide (TMTD).