Polymer Degradation and Stability 128 (2016) 115–125

Contents lists available at ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

Reclaiming waste tire rubber by an irradiation technique

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A R T I C L E I N F O

Article history:
Received 14 January 2016
Received in revised form
8 March 2016
Accepted 9 March 2016
Available online 12 March 2016

Keywords:
Tire rubber
Devulcanization
Microwave
Reclamation
Devulcanization agent

A B S T R A C T

Tire rubber recycling reduces production costs, saves resources, and decreases the environmental issues. Waste tire rubber were devulcanized by a laboratory microwave oven with the aid of the devulcanizing agent and the oil. The effect of several devulcanizing agents, hexadecylamine (HDA), Diphenyl disulfide (DPDS), *N*-cyclohexyl-2-benzothiozyl sulfenamide (CBS) 2-mercaptobenzothiazole disulfide (MBTS) and two types of the oils, aromatic and paraffinic with various contents in different irradiation temperatures was studied. For homogeneous devulcanization, the waste rubber was ground to a median particle size of 319 μm before further treatment and subsequent irradiation process. The results showed that used waste rubber powder was devulcanized effectively. Among of the devulcanizing agents and based on Horikx analysis, formulated compound with DPDS with the sol fraction, crosslink density (CLD) and devulcanization percent of 16.5%, 85 mol/m^3 and 48%, respectively, was the most suitable compound for devulcanization when compared with formulated compounds with other devulcanizing agents. Among of compounds with different DPDS content, compound with 30 phr aromatic oil and 6 phr DPDS in formulation with devulcanization temperature of 240 °C, had the best devulcanizing parameters. Paraffinic oil had an adverse effect on devulcanization of the DPDS formulated compounds. For selected studied compounds, during microwave irradiation, a part or total amount of the polysulphides crosslinks were broken and the structure of the remained sulphur crosslinks were mostly mono sulphide. In the morphology study of the most devulcanized compounds, a coarse morphology of the non-devulcanized rubber covered by the devulcanized rubber were observed. The effect of the oil content was also obvious.

1. Introduction

Tire rubber recycling or reclaiming is the process of recycling vehicles' tires that are no longer suitable for use on vehicles due to wear or irreparable damages, i.e., punctures [1]. The demand for tire will grow by 4.3% yearly and will reach to 2.9 billion in 2017 [2]. As an estimation, over 17 and 3.3 million tons used tires are generated each year worldwide and in the EU, respectively [3]. Hence, end-of-life tires are a serious environmental concern and it's recycling is a must. Rubber reclaiming is one of the recycling methods applied to the waste rubber [4]. It uses thermal, mechanical and irradiation energies, with or without aid of devulcanizing chemicals (agents) to breakdown S–S bonds in vulcanized rubber networks. The product in most cases is a partially devulcanized rubber which can replace partially virgin rubber and can be revulcanized for manufacturing rubbery articles. A typical rubber composition of tire consists of natural rubber (NR, specially for heavy vehicles tires), styrene-butadiene rubber (SBR) and butadiene rubber (BR) [5]. Various attempts have been reported for reclaiming tire rubbers [4,6–16]. They used several strategies for reclaiming (devulcanization) tire rubbers. They were included mechanical shear by two roll mill and a chemical agent [10–12], mechanical shear by an internal mixer and a devulcanization aid [7,9,14,16] mechanical shear by a single or twin screw extruder [4,13] and miscellaneous techniques using supercritical carbon dioxide and a chemical agent [6]. However, the produced devulcanizates had low degree of devulcanization, resulting in poor mechanical and dynamical properties when they revulcanized.

The three dimensional rubber network can also broken down by irradiation (microwave) [17–19]. Garcia et al. [17] studied on the physical and chemical changes that occur in the ground tire rubber after different microwave exposure periods. For this purpose chemical, thermal, rheological and morphological analyses were performed on the tire rubber, which contained natural rubber (NR) and styrene-butadiene rubber (SBR) as polymeric material. The results showed that the microwave treatment promoted the

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http://dx.doi.org/10.1016/j.polymdegradstab.2016.03.009
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breaking of sulphur cross-links and consequently increased the rubber fluidity. However, long periods of exposure led to degradation and modification of some properties. De Sousa et al. [18] investigated on devulcanization of natural rubber (NR) by microwaves, as well as the influence of the amount of carbon black on this process through devulcanization of the NR with controlled composition on it. The results highlighted that the increase of the temperature is responsible for the occurrence of devulcanization, which is dependent on both the amount of carbon black present in the rubber and the time of exposure to microwaves. Zhang et al. [19] presented a paper in TMS annual meeting. They discussed about microwave absorption properties of the waste tire at various temperatures. They characterized the conditions favorable for the microwave heating of the waste tires. Karabork et al. [20] investigated on devulcanization of ground tire rubber by microwaves at the same heating rate (constant power) and different times of exposure. The devulcanized rubber (DV-R) and untreated GTR were characterized physically and thermally. The sol content and Fourier transform infrared spectroscopy (FTIR) analyses of the devulcanized samples were examined to define the efficiency of devulcanization. In another attempt, Poyraz and co-workers [21] studied on devulcanization of scrap ground rubber by short-term microwave irradiation and successive carbon nanotube growth.

Based on our knowledge, in most published reports, microwave irradiation has been used lonely for devulacanization of the waste rubber without using chemical agent. In addition, there is not any report that compares the effect of the various chemical agents on microwave devulcanization of the waste rubber. Authors [22,23] already studied the effect of various operative parameters including several devulcanizing agents on microwave devulcanization of ethylene-propylene-diene monomer (EPDM) and butyl rubber. In this study, the same parameters along with some more complementary aspects on tire rubbers will be considered and discussed.

2. Experimental

2.1. Materials: waste rubber, filler, and rubber chemicals

Passenger car waste tire rubber was obtained from local city sites and subsequently subsequently ground to particles with a median size of 319 μm (Fig. 1). Thermogravimetric analysis (TGA; STA 1500, Scinco Co., Ltd.) was subsequently used to determine the composition of the waste powder. TGA was performed in a nitrogen atmosphere below 550 °C and in air above 550 °C, respectively. The TGA curves and corresponding composition of the waste rubber powder are shown in Fig. 2 and Table 1. The other ingredients were aromatic and paraffinic oils with initial boiling points, 270 and 280 °C, respectively, as processing aids (Mehran Tyre 290 and Fariman), 2-propanethiol, hexylamine, cyclohexanethiol (Sigma Aldrich), diphenyl disulfide (DPDS, Sigma-Aldrich), *N*-cyclohexyl-2-benzothiozyl sulfenamide (Perkacit CBS, Flexsys), hexadecylamine (HDA, Cayman Chemical Co.),2-mercaptobenzothiazole disulfide (Perkacit MBTS, Flexsys), *N*-Cyclohexyl-2-benzothiazole sulfenamide (SANTACURE – CBS, Flexsys), zinc oxide (activator; Harcros Durham Chemicals, UK), stearic acid (activator; Anchor Chemicals Ltd., UK) and elemental sulphur (curing agent; Solvay Barium Strontium, Hannover, Germany), *N*-*tert*-butyl benzothiazole-2-sulfenamide (SANTACURE – TBBS, Flexsys).

2.2. Devulcanization of the waste powder and preparation of the rubber compounds

First, waste powder samples were extracted by acetone to remove low molecular substances, i.e. oils, residue of curing chemicals and un crosslinked rubbers, using a Soxhlet apparatus and 300 mL of acetone and 100 g of the rubber for 24 h at 70 °C, as described in ASTM D297-93. After extraction, the samples were dried in an oven with circulating air for 12 h. This material was used for devulcanization. Appropriate amount of CBS, DPDS, TMTD and HDA which were used as devulcanizing agents, were mixed with 30 g oil and then added to 100 g of above mentioned waste powder in a 500 mL glass beaker. The waste powder was soaked in the oil for 12 h at 80 °C in an oven to allow it to penetrate into the rubber fully. This produced four compounds (compounds A–D; Table 2). There was also a reference compound (RC), which was mixed with the aromatic oil and no chemical (Table 2).

Relatively, high level of the oil was incorporated in the formulation of the compounds. The oil dissolves the devulcanizing agent and simultaneously, helps the rubber to swell more effectively. The beaker was placed in a laboratory microwave oven (GMO-530, Gosonic) with an output power of 900 Watts, frequency of 2000 MHz, and internal capacity of 30 L for various final temperatures. The devulcanized rubber compounds were bulky in size after they were recovered from the microwave oven. They were subsequently processed on a laboratory two roll mills with cylinders 14 cm in diameter and 32 cm long with 4 mm nip width at ambient temperature for 2 min to produce sheets which were easier to work with.

To investigate the effect of various amounts of the devulcanizing agent (DPDS) and aromatic and paraffinic oils on the devulcanization of the waste tire powder, seven more compounds were prepared (compounds E,F,G and H; Table 3 and I,J and K; Table 4). Compounds in Table 4 had 2 phr DPDS as devulcanizing agent and all compounds in Tables 3 and 4 were devulcanized at 240 °C in the microwave oven as explained earlier. The radiation time was about 3 min.

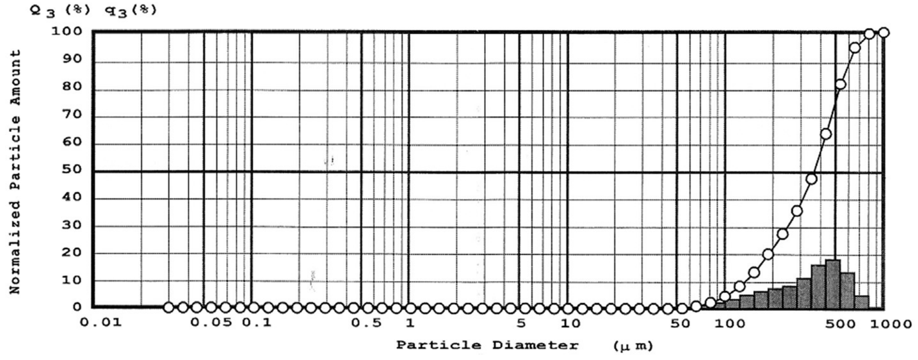

Fig. 1. Waste tire rubber particle size distribution.