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Devulcanization of waste rubber powder using thiobisphenols as novel reclaiming agent

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ABSTRACT

In this study, thiobisphenols, 4,4′-dithiobis(2,6-di-t-butylphenol), was synthesized and used as novel reclaiming agent for the chemo-thermomechanical devulcanization process of waste rubber powder (WRP). The devulcanization process was carried out in an internal mixer at 180 °C and 200 °C using different content of reclaiming agent such as thiobisphenols. The degree of devulcanization was estimated by measuring sol content, crosslink density, and Mooney viscosity of the reclaimed rubber (RR). Devulcanization conditions have been studied further with respect to the processability, and the mechanical properties of the revulcanized reclaimed rubber (REVR). Photomicrographs from scanning electron microscopy (SEM) indicate the improvement of the coherency in the REVR with increasing degree of devulcanization. Dynamic properties were also studied for REVR. Again, in order to establish the effect of thiobisphenols as reclaiming agent, the devulcanization of WRP and revulcanization of RR were also evaluated in this study.

1. Introduction

In recent years, the automobile industry has been developed rapidly. As a result, the production of automobile tires also record a significant market growth. After a complete service span (six to ten years), the used tires need to be removed, due to their potentially hazardous effects resulted from the aging and subsequent degradation of waste tires. Every year, a large amount of replaced tires are being accumulated causing the main source of waste rubber. (Fang et al., 2001; Formela et al., 2016; Siddique and Naik, 2004; Zedler et al., 2017).

The problems associated with the waste disposal management have been considered as major issues in recent time. The disposal of waste rubber polymer is harmful to our environment due to its very low decomposition rate. The major portions of such waste rubber come from the tires are mainly stockpiled and dumped on the land, to create a serious environmental pollution. All these discarded portions of rubber are treated as waste rubber that does not degrade easily in the environment due to the presence of crosslinking agents, stabilizers, additives etc. So the probably the best solution would be to recycle and reuse of waste rubber and possibly to reclaim the raw rubber material with less environmental pollution (Adhikari et al., 2000).

The vulcanized rubber, based on three-dimensional crosslinked structures, belongs to non-environmentally friendly materials, is found difficult to degrade in natural or biological process (Chaubey and Arastoopour, 2011; Sienkiewicz et al., 2012). Devulcanization is a process of recycling waste rubber materials. Devulcanization is actually carried out through the cleavage of crosslinked sulfur bonds present in vulcanized rubber, without disrupting the polymer bonds. The disulfide and polysulphide bonds in vulcanized rubber are converted to monosulphide bonds by heating and thereafter those monosulphide bonds can be completely disintegrated by applying shear stresses. Finally, they are converted to recycled uncured rubber for further uses mostly through revulcanization process. Chemical vulcanization is usually carried out by heating the rubber with sulfur or added accelerators, activators for the formation of crosslink bonds between polymer chains of rubber. Such revulcanization is recommended for the addition of excellent resilience, improved mechanical properties, higher resistance to oxidation and organic solvents compared to unvulcanized rubber.

Until now, various methods (mainly physical and chemical processes including landfill, pyrolysis, combustion, retreading, ground rubber, reclaimed rubber, etc) have been suggested to recover the utilization of these discarded resources (Bandyopadhyay et al.,

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2008). The landfill is one of the widely used processes to dispose of waste rubber products. Ground rubber is made from waste rubber products that can be used in road paving application. At higher temperature (400 °C), the waste rubber products can pyrolyze into carbon black, oil etc. While comparing with upper methods, production of reclaimed rubber is now proving to be a great way to reduce atmospheric pollution and also is a very beneficial, cost-effective method to utilize waste rubber. A number of devulcanization techniques have been developed, involving mechanical, chemical, thermal, chemomechanical, thermomechanical, thermochemical, ultrasonic, microwave, biotechnological processes, etc (Adhikari et al., 2000; Molanorouzi and Mohaved, 2016).

In the thermal or mechanical process, waste rubber is devulcanized with external thermal energy or mechanical force (Edwards et al., 2016; Tao et al., 2013). These processes usually lead to the random cleavage of crosslinked network and the main chain of the polymer. In the chemical process, waste rubber is devulcanized with the help of a reclaiming agent (Meysami et al., 2017; Myhre and MacKillop, 2002). Several kinds of reclaiming agents have been reported to be used for the manufacture of reclaimed rubber, including several inorganic compounds (Adhikari et al., 2000).

A large number of studies are available focusing on organic compounds, such as benzoyl peroxide (Rooj et al., 2011), diallyl disulfide (De et al., 1999), tetrabenzylthiuram disulfide (Mandal et al., 2012), octylaminehexadecylamine, dioctylamine, trioctylamine, benzylamine (Van Duin et al., 2005), diphenyl disulfide (Kojima et al., 2004), thiosalicylic acid (Thaicharoen et al., 2010) for chemical devulcanization of natural and synthetic rubber. Chemo-thermomechanical process, which applies both thermal energy and mechanical force for devulcanizing rubber, has been found to be an efficient method compared to chemical devulcanization process only, as shown in other studies (Diaz et al., 2018; Formela and Cysewska, 2014; Warner, 1994). However, the effectiveness of chemo-thermomechanical process could be substantially enhanced further using a suitable reclaiming chemical agent.

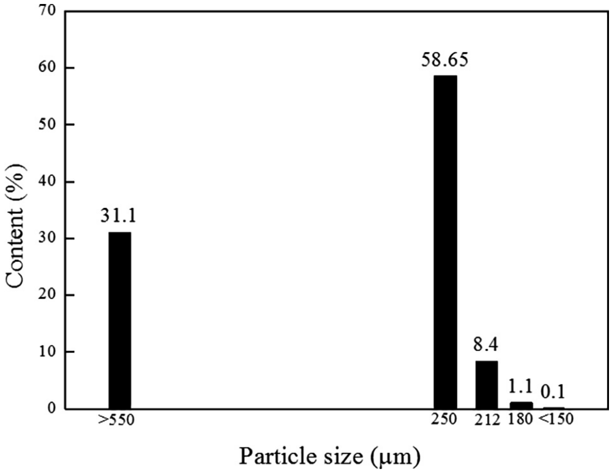


Fig. 1. Waste rubber powder particle size distribution.

Henceforth, in this study, we propose synthesis and subsequent use of thiobisphenols as a novel reclaiming agent for chemo-thermomechanical devulcanization of WRP for the first time. Thiobisphenols has been used here to break the crosslinked bonds of WRP. Moreover, the optimum condition for devulcanization was estimated by evaluating devulcanization temperatures and the content of thiobisphenols.

2. Experimental

2.1. Materials

WRP has been procured from Gangrim Fueltech (South Korea). The particle size distribution of WRP has been provided in Fig. 1. Typically, rubber tread waste from the tires of heavy truck has been used in this study which consist of natural rubber, zinc oxide, stearic acid, antioxidant agent 4010 (N-cyclohexyl-N′-phenyl-p-phenylenediamine), antioxidant RD (poly(1,2-dihydro-2,2,4-trimethyl-quinoline)), pine tar, carbon black, activator NOBS (N-(Oxidiethylene)-2-benzothiazolyl sulfenamide) and sulfur. Although the manufacturer did not reveal the composition due to their trade principle. 2,6-di-*tert*-butylphenol, sodium hydroxide, aromatic oil, zinc oxide, stearic acid, accelerator NS (N-*tert*-butyl-2-benzothiazylsulfonamide) and sulfur have been procured from Sigma Aldrich (South Korea).

2.2. Synthesis of thiobisphenols

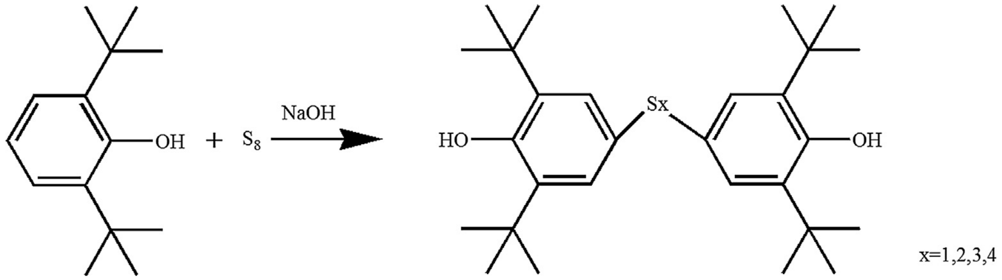
2,6-di-*tert*-butylphenol, sodium hydroxide and sulfur powder (mole ratio = 1:3:3) has been dissolved in ethanol followed by heating up to 80 °C, and keep refluxing for 4 h. The reaction mechanism has been elucidated in Scheme 1. The product was neutralized by adding hydrochloric acid and then extracted with xylene. After removing xylene, the thiobisphenols was obtained following the method (Fujisawa et al., 1974). 4,4′-dithiobis(2,6-di-t-butylphenol) was isolated by recrystallization from the ethanol.

2.3. Devulcanization process

WRP (100 g) were mixed with 10 g of aromatic oil and different content of thiobisphenols (0 g, 0.1 g, 0.3 g, 0.5 g, 1 g, 3 g) by blender at room temperature. Then the devulcanization process was carried out by an internal mixer with a speed 45 rpm at 180 °C and 200 °C for 10 min. The RPM value was selected based on subsequent trials in the laboratory to control the excess mechanical shearing and temperature increase.

2.4. Revulcanization process

About 100 g of RR was compounded with 2.5 g of zinc oxide, 0.3 g of stearic acid, 0.8 g of accelerator NS and 1.2 g of sulfur in



Scheme 1. Synthesis of thiobisphenols.