Thermomechanical devulcanization of waste rubber with supercritical CO₂

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1 Abstract

Approximately 70% of the rubber produced in the world is used in tires. The number of waste tires discarded worldwide each year is close to 330 million (approximately 4.4 million tons) and considering the average percent of natural and synthetic rubbers in tires is about 60%, 2.64 million tons of waste natural rubber are generated per year [1, 2]. In spite of all different ways of handling used tires, the most common is to deposit them in a landfill, creating a stock of tires. These stocks can cause fire danger and provide ambient for rodents, mosquitoes and other pests, causing health hazards and environmental problems [3].

Because of the three dimensional structure of the rubbers, and their specific composition that include several additives, their recycling is a current technological challenge. The technique which can break down the crosslink bonds in the rubber is called devulcanization. Rubber devulcanization is a process in which the waste rubber or vulcanized waste product is converted, using mechanical, thermal, or chemical energy, into the state in which it can be mixed, processed, and vulcanized again [4, 5]. Strictly, devulcanization can be defined as a process where poly-, di-, and mono-sulfidic bonds, formed during vulcanization, are totally or partially broken.

In the recent years, super critical carbon dioxide (scCO₂) was proposed as a green devulcanization atmosphere. This is because it is chemically inactive, nontoxic, nonflammable and inexpensive. Its critical point can be easily reached (31.1 °C and 7.38 MPa), and residual scCO₂ in the devulcanized rubber can be rapidly removed by releasing pressure [6].

In this study thermo-mechanical devulcanization of ground tire rubber (GTR) was performed in a twin screw extruder under diverse operation conditions. Supercritical CO₂ was added in different quantities to promote the devulcanization. Temperature, screw speed and quantity of CO₂ were the parameters that were varied during the process. The treated rubber was characterized by its devulcanization percent and crosslink density, by swelling in toluene. Infrared spectroscopy (FTIR) and Gel permeation chromatography (GPC) were also done, and the results were related with the Mooney viscosity of the material.

The results showed that the crosslink density decrease as the extruder temperature and speed increases, and, as expected, the soluble fraction increase with both parameters. The same behavior was found in the literature when devulcanization of GTR was done by extrusion [7].

Moreover, the Mooney viscosity of devulcanized rubber decreases as the extruder temperature increase. The reached values were in good correlation (R=0.96) with de the soluble fraction (Figure 1), as already found by M. Meysami et. al [8].

In order to analyze if the treatment causes main chains or crosslink scission, the Horikx's theory was used [9]. It can be seen from Figure 2 that all tests falls in the curve that corresponds to the sulfur bond scission, which suggests that the devulcanization was successfully happened, without degradation of the rubber; similar results were obtained previously by microwave vulcanization [10,11]. However, such devulcanization has not been revealed by FTIR analyses, since none of the FTIR characteristic peaks of GTR were modified by the devulcanization treatment.
Figure 1 – Mooney viscosity as a function of the soluble fraction of devulcanized rubber

Figure 2 – Soluble fraction of devulcanized rubber against relative decrease in crosslink density at different extrusion conditions

The lowest crosslink density was reached with 1 cm³/min of CO₂, and the power consumed in that process was also near to the minimum. These results encourage us to do further analyses to better understand the effect of the different conditions on the devulcanization process.

Références