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Mechanical and rheological properties of natural rubber compounds containing devulcanized ground tire rubber from several methods

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ABSTRACT

In the recent past we reported the investigation of different devulcanization processes of a ground tire rubber (GTR) such as supercritical fluid, ultrasonic and biological technologies. Each of these techniques had been previously optimized, focusing on the experimental combination of parameters providing the best devulcanization conditions. The present study aims to extensively compare the optimal conditions of these three different techniques for the devulcanization of a GTR. In particular the GTR and the devulcanizates by each technique were blended into raw natural rubber at a concentration of 10 phr. The rheological and mechanical properties of their vulcanizates were investigated and compared to find out the rubber providing the highest compatibility for compounding and revulcanization. In addition, a comparison of these results was made with the ones of raw natural rubber compound and vulcanizate.

1. Introduction

The last years have seen an increase of the amount of tires arriving to the end of their life. According to a 2008 survey [1] approximately 900 million of End of Life Tires (ELTs) are generated each year around the world. Scrap materials consume landfill space, spoil soil, groundwater and surface water. They also represent threats for public health and safety because of the risk for diseases and fires that may release toxic chemicals into the air. ELTs recycling represents a main concern to the industrial world.

Waste rubber represents a potential “green” source of rubber, replacing the raw natural and synthetic rubber. The increasing quality requirements of rubber products and the high costs of the reclaiming processes are two of the main limiting factors for the application of rubber recycling. Nevertheless, the more stringent environmental regulations and the fluctuating price of raw materials have become driving forces for the development of several innovative technologies for the recycling. Over the last 15 years, recovery rates for ELTs have tremendously increased in Europe, Japan and United States. Japan started recycling programs even earlier. Rubber recovery is not an easy matter due to the presence of three-dimensional chemical crosslinks. Generally, the modern approaches that allow recycling ELTs as a source of new material and not as a fuel can be divided into two categories. The first approach involves grinding process leading to a reduction of the rubber particle size without significant rupture of the chemical bonds. The second approach attempts to devulcanize the waste rubber by breaking the three-dimensional network. The most studied devulcanization strategies involve mechanical, chemical, physical and biological processes [2–5].

Most of the chemical techniques are dangerous for health and environment since they require reactions that involve organic compounds, oils and solvents. On the other hand, thermal and mechanical techniques require large amount of energy and are generally expensive. A microbial desulfurization was suggested over the last years as an alternative with respect to the methods that require hazardous chemicals or energy consuming operation conditions.

Out of all existing devulcanization technologies, supercritical fluid, ultrasonic and biological techniques were chosen as focus of the present paper. These three devulcanization technologies were

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primarily chosen considering their impact on the environment and in particular their tendency to minimize the use of solvents, chemicals or energy.

The supercritical carbon dioxide devulcanization was first proposed by Kojima et al. [6]. In this technique the supercritical CO_2 ($scCO_2$) has been used as a reaction medium for some devulcanizing agents, in particular diphenyl disulfide (DD). Supercritical fluids, in particular $scCO_2$, show the ability to permeate into polymers and represent excellent solvents for these materials. $ScCO_2$ has high diffusivity, low viscosity and high thermal conductivity depending on temperature and pressure. This fluid is non-toxic, inexpensive, nonflammable and easily removable from rubber and it has an accessible critical point (temperature and pressure is, respectively, equal to 31.1 °C and 7.38 MPa). As a result, $scCO_2$ represents an ideal "green" solvent [7]. This technique minimizes the use of swelling agents, generally required for chemical techniques and leads to a bulk treatment. Nevertheless, this technique requires both energy to reach supercritical fluids conditions and chemicals as devulcanizing agents. As just mentioned, this technology is based on a well-studied process in scientific and patent literature [6–8]. Most of the previous studies investigated this process on several types of rubber, in particular, natural rubber and synthetic rubber [6,9–11]. Some studies were also performed on ground tire rubber (GTR) [12,13]. This technique has been also investigated on GTR by an experimental design approach in order to gain information regarding how the processing parameters can influence the devulcanization process [14].

The ultrasonic devulcanization, which has been widely investigated and patented by Isayev et al. [2], is carried out without involving any chemical, since ultrasounds can generate cavitation leading to the rupture of three-dimensional network in the rubber matrix within a time of several seconds. The incorporation of an ultrasonic device in twin-screw extruder makes this process continuous. This technology avoids the usage of any devulcanizing or swelling agents, generally required for chemical techniques. It is a continuous process that allows to treat large amount of material and it is a bulk treatment. However, this technique requires energy to reach the treatment temperatures and to generate the ultrasonic waves.

Most of the previous studies investigated this devulcanization process using an ultrasonic single-screw extruder on several types of rubber, in particular, GTR, natural rubber (NR) and various synthetic rubber [2]. Ground rubber represents an ideal raw material for the ultrasonic devulcanization, since it can be fed directly into the extruder. Recently, the incorporation of an ultrasonic device in a twin-screw extruder made the process more efficient [15]. The resulting devulcanized tire rubber can be directly compounded with curatives without adding virgin rubber and the revulcanized showed good mechanical properties [2,15]. In addition, the ultrasonic devulcanization of GTR in a twin-screw extruder was also investigated using the response surface methodology (RSM) [16]. This study mainly pointed out that temperature, screw shape, screw speed and flow rate have significant effect on the devulcanization process, however, the ultrasonic amplitude (US) was found to be the most influencing process variable. In particular, it is necessary to keep a relatively low value of US, sufficient to reduce the network density and to increase the number of active sites, without introducing an excessive degradation.

The third considered devulcanization technology is the biological one, involving microorganism strains able to metabolize the sulfur present in the rubber matrix. Just few microorganisms were found with the ability to devulcanize waste rubber and ground tire rubber, due to their complex structure. This process was reported in 1997 by Romine and Romine [17]. They used *Sulfolobus acidocaldarius* on GTR and proposed a "4s"-like mechanism for the desulfurization. Other studies were successively carried out on other microorganisms. One of the most efficient chemo-organotroph bacterium described in literature was reported by Christofi et al., in 2006 [18]. This bacterium is *Gordonia desulfuricans* 213E (NCIMB 40816) that is reported to be able to reduce the content of sulfur between 23% and 35%.

Out of all known technologies, the biological devulcanization one seems to be the greenest since no swelling or chemical devulcanizing agents are required and it is a low energy consumption technique. It has been proven that this process is highly selective towards sulfur, however the treatment is limited to the surface and has low reaction yields. Therefore, long treatment time is generally required.

In order to reuse end-of-life tires it is important to evaluate and set up an efficient process. To do this we compare three different devulcanizing processes (the supercritical carbon dioxide, ultrasonic and biological devulcanization) on ground tire rubber that comes from truck tires, rich in natural rubber. To evaluate the usefulness of these processes we compare the mechanical and rheological properties of natural rubber compounds containing the devulcanized GTR obtained from these processes.

The aim of the present study is to provide an extensive comparison of the optimal conditions for these three different devulcanization techniques on a GTR by compounding the devulcanized tire rubber derived from each technique with raw natural rubber and testing the properties. In particular, the GTR and devulcanizates by each technique were compounded into the raw NR at a concentration of 10 phr to find out the rubber providing the highest compatibility for compounding and revulcanization. The rheological and mechanical properties of their vulcanizates were investigated and compared. In addition, a comparison of these results was made with the ones of virgin NR compounds and vulcanizates. Each of the studied technique had previously been studied and optimized, therefore only the best conditions were considered in this study. It should be noted that this is the first study where such extensive comparison of various techniques of devulcanization was made.

2. Experimental

2.1. Materials and equipment

The GTR used in the present study was a cryo-ground rubber from truck tires, the same used and characterized in our previous paper [13]. 95 wt % of particles were smaller than 0.4 mm, the majority of which having dimensions between 0.15 and 0.4 mm. The rubber fraction was 53% of the total weight and was made up of 70% NR and 30% of synthetic rubber. The DD (99% assay) was purchased from Sigma Aldrich (Germany), carbon dioxide (99.995% assay) from Sapio (Italy), acetone and toluene (>99% assay) were purchased from Panreac (Spain). The constituents of mineral salt medium (MSM) were purchased from Sigma Aldrich (Germany).

N-Cyclohexylbenzothiazole-2-sulfenamide was Vulkacit CZ/EG-C from Lanxess (Germany); stearic acid was Stearina TP8 from Undesa (Italy); sulfur was from Zolfoindustria (Italy), zinc oxide was from Zincol (Italy), NR was STR20 1,4-cis polyisoprene from Von Bundit (Thailand) and carbon black was N330 from Cabot Corporation (USA).

2.2. $scCO_2$ process

This devulcanization technique has previously been extensively studied and optimized on GTR using the experimental design approach [14]. In this paper, we demonstrated that the only significant processing variables are temperature, amount of DD and