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Recycling of rubber wastes by devulcanization

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ABSTRACT

Disposal of used tires and rubber wastes is one of the biggest challenges of the 21st century waste management. One of the environmentally friendly possibilities of recycling this type of material is to go through the breaking of their three-dimensional structure. This treatment, called the devulcanization, can be defined as a process that causes the selective breakup of the sulfur-sulfur (S-S) and carbon-sulfur (C-S) chemical bonds without breaking the backbone network and without degrading the material. The devulcanized rubber can be mixed with virgin rubber or with other kinds of matrices to give new compounds without generating a significant decrease in mechanical and physical properties. Many devulcanization process types are presented in the literature: chemical, ultrasound, microwave, thermomechanical, etc. The thermomechanical devulcanization based on extrusion seems to be the more suitable to be applied on an industrial scale. The supercritical CO_2 has been proposed as a green atmosphere that can be used to improve this type of devulcanization. In fact, it seems that in supercritical conditions, the CO_2 swells the rubber and stretches the sulfide links, making them easier to break.

This paper presents a literature review on rubbers recycling by devulcanization. It is focused on the different devulcanization techniques used in the last decades. Particular attention is paid to the thermomechanical method, those in the presence of supercritical CO_2 and, finally, the combined thermomechanical process with supercritical CO_2 atmosphere.

1. Introduction

Nearly 70% of the rubber produced in the world is used in tires. The amount of waste tires discarded worldwide each year is approximately 800 million (~10 million tons) and taking into account that the quantity of natural and synthetic rubber in tires is around 60%, 6 million tons of tire scraps are produced each year (Rozada et al., 2005; Mui et al., 2008; Pehlken and Müller, 2009). In spite of all different ways of handling used tires, the most common is to deposit them in a landfill, resulting in a stock of scraps. These stocks represent a fire danger and produce an enabling ambient for rodents, mosquitoes and other plagues, causing health and environmental problems (Snyder et al., 1977; Smith, 1999; Adhikari et al., 2000; Isayev, 2003).

The landfilling of end-of-life tires was forbidden by the European Commission since 1999 (Landfill of Waste Directive, 1999). Because of that, the recycling and reutilization of waste tires are being deeply studied in many countries.

Some applications of the waste rubbers are sports and playing surfaces, floor and walkways tiles, concrete, thermal isolation, acoustic isolation, footwear, road and rail equipment, activated carbon production, etc (Myhre and MacKillop, 2002; Smith et al., 1995; Molino et al., 2018). However, the best way to carry out the disposal of rubber wastes is through recycling, including all methods where rubber waste is converted to make new commodities (Fix, 1980; Nicholas, 1982; Accetta et al., 1982; Phadke et al., 1983; Warner, 1994; Myhre and MacKillop, 2002; Ghorai et al., 2016). Further, it was pointed in the literature that rubber recycling is more energy efficient than, for example, burning (Burlakovs et al., 2017).

Because of the three-dimensional structure network of rubbers, the vulcanization process which produces strong bonds and the specific composition that includes several additives, the recycling of such materials is a current technological challenge. In fact, a tire is a composite made up of several types of synthetic and natural rubbers, particulate fillers (silica, carbon black, etc.), chemical additives (sulfur, oils, etc.), and textile and/or metal reinforcements (Fang et al., 2001; Shulman, 2011; Sienkiewicz et al., 2012; Karger-Kocsis et al., 2013). Fig. 1 shows the composition, in percentage by weight, of the different tires components, for passenger's vehicles (PV) and for truck vehicles (TV). The major difference between the composition of the PV and TV tires lies mainly in the metal reinforcement. In the example, 27% of the weight of a TV tire is steel versus 15% for a PV tire. Another difference, not shown in the plot, is the proportion of natural rubber used. Indeed, tires

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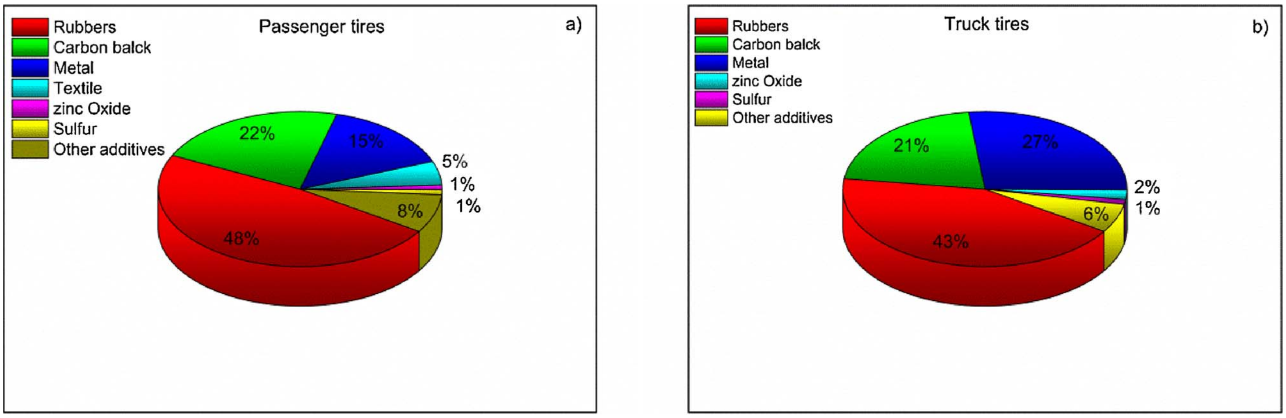

Fig. 1. a) Passenger tires and b) truck tires composition in percentage by weight.

for TV, being more mechanically stressed, contain a larger proportion of natural rubber, while PV has a higher percentage of synthetic rubber (Pehlken and Müller, 2009).

Regarding the useful life, there are two types of tires: the reusable tires and the non-reusable tires. The first ones are tires which are sent to retreading companies that gives them a second life. The second ones are tires that cannot be retreaded due to an advanced damage, structural deformation or high degradation. These tires are starting materials for recycling. The proportion of reusable and non-reusable tires in Europe during 2013 is presented in Fig. 2 (ETRMA, 2015).

With the aim of recycling and reusing the vulcanized rubbers, it is crucial to find a safety way for their devulcanization, i.e. a way to cleave their crosslink bonds. Rubber devulcanization is a process in which the vulcanized waste rubber is transformed into the state in which it can be revulcanized, after its mixing and processing (Franta, 1989; Rader et al., 1995; Isayev, 2001; Isayev, 2005; Isayev, 2013). Strictly, devulcanization can be defined as a process where poly-, di-, and mono-sulfidic bonds, formed during vulcanization, are totally or partially broken. This means that devulcanization can be defined as a process that causes the selective breakup of sulfidic bonds without main chain scissions and degradation of the polymer.

Regardless of the devulcanization method, some of the main polymer chains are broken during devulcanization and, thus, the properties of the treated material are different compared to the original rubber. The use of devulcanized rubber can reduce the cost of final products. Depending on the desired application, the devulcanized rubber can be reused as obtained or mixed in different amounts with virgin rubber or other polymers. Some of the properties of recycled rubber blends that were published in the last years are presented in Table 1 (Ramarad et al., 2015). Also, the effects of kinds of components, and ratio and size of reclaimed rubber particles on the mechanical properties of composites, are summarized in Table 2.

This paper summarizes some research studies concerning rubbers recycling by devulcanization. It will be focused on the different devulcanization techniques used in the last decades. Particular interest will be attached to the thermomechanical method, those in the presence of supercritical CO_2 and, finally, the combined thermomechanical process with supercritical CO_2 atmosphere.

2. Methods for devulcanization of rubbers

2.1. Pre-process treatment

Indistinctly of the type of devulcanization process, the first step consists of, generally, reducing the tire rubber size by grinding (Karger-Kocsis et al., 2013). In some cases, depending on the desired reutilization of the waste rubbers, several grindings are required (Pehlken and Müller, 2009).

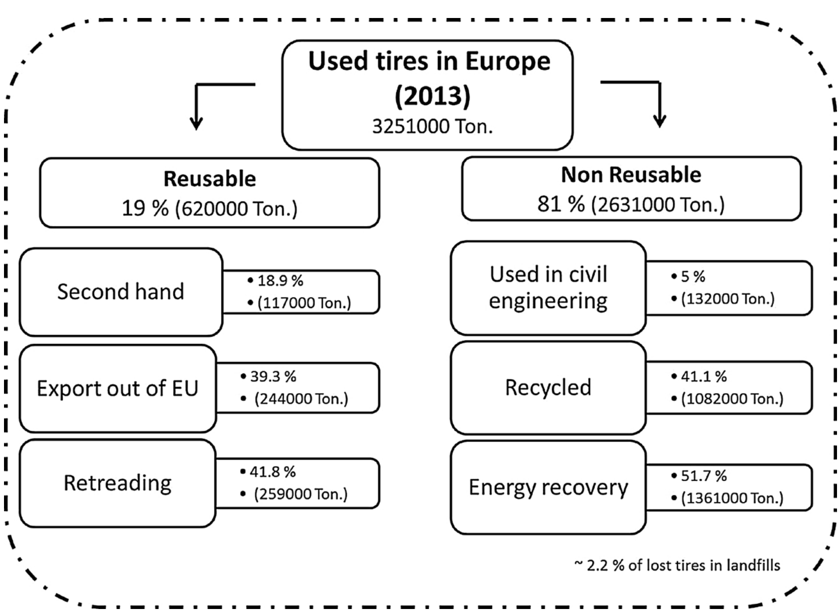

Fig. 2. Discrimination between reusable and non-reusable tires in the EU, during 2013.