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Recycling of waste tire rubber: Microwave devulcanization and incorporation in a thermoset resin

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ABSTRACT

This study focused on the possibility of recycling Waste Tire Rubber (WTR) to be used as polymer modifier. Thus, WTR was grinded into powder, at ambient temperature, with a disc mill PQ500 and microwave electromagnetic energy was used to devulcanize this powder with the final aim of producing a new composite by its incorporation in a thermoset resin. The influence of the treatment microwave energy on the devulcanization ratio was investigated. FTIR analysis revealed that rupture of Sulfur-Sulfur (S—S) and Carbon-Sulfur (C—S) bonds have occurred during the treatment. Swelling analysis showed that the microwave treatment can lead to a very significant degree of devulcanization. The Ground Tire Rubber (GTR) and the Devulcanized Ground Tire Rubber (DGTR) were then separately used to prepare epoxy based composites. It appeared that epoxy composites filled with DGTR have better mechanical properties than those filled with untreated GTR. This result agrees with scanning electron microscopy observations which highlighted a better interface coherence between DGTR and epoxy. A complementary analysis pointed out a linear relationship between the rubber modulus and the number of crosslink per chain.

1. Introduction

Storage and elimination of used tires have become an urgent word preoccupation from the environmental point of view. In fact, each year, hundreds of used tires are generated and accumulated in many countries.

Among the waste treatment procedures for used tires, grinding is the most important method for converting the waste rubber into ground material. As such, it can be used in surfaces of athletic tracks or games, or in combination with other materials such as asphalts (Kocevski et al., 2012; Vazquez et al., 2016; Zhou et al., 2015; Shafabakhsh et al., 2014; Presti et al., 2012; Juganaru et al., 2015), concrete (Afshinnia and Poursaee, 2015; Gupta et al., 2016; Thomas et al., 2015,2016), mortars (Popovici et al., 2015), rubber and thermoplastic matrices (Mathew et al., 2001; Radhesh Kumar et al., 2002; Yagneswaran et al., 2008; Zhang et al., 2010a, 2010b; Xu and Li, 2012; Sivaraosa et al., 2013; Azeez et al., 2014), and epoxy resins (Chekanov et al., 1997; He et al., 1999; Harsch et al., 2007; Yagneswaran et al., 2008, 2013; Piszczyk et al., 2015).

Epoxy resins are well known to have good physicochemical, bonding, mechanical and thermal properties (Chozhan et al., 2007). However, their mechanical characteristics are not sufficient to meet the widespread applications. Thus, modification of epoxy resins becomes essential to improve their properties. One effective approach is to fill such polymers with reinforcing particles including silica (Jia et al., 2006), minerals (Jia et al., 2006), carbon fiber (Jia et al., 2006), fiberglass (Wingard, 2000) and Ground Tire Rubber (GTR) (Chekanov et al., 1997; He et al., 1999; Harsch et al., 2007; Yagneswaran et al., 2008, 2013; Piszczyk et al., 2015).

He et al. (1999) studied the influence of the concentration of preformed rubber (acrylic) particles on epoxy fracture behavior. Fracture results showed that toughness increased to a maximum and then decreased as the concentration was increased, suggesting an optimum concentration for toughening. These results were supported by micrograph observations. Yagneswaran et al. (2008, 2013) used mechanochemical devulcanized GTR powder to prepare epoxy composites. Structural and thermal analyses were performed with different techniques (SEM-EDX, FTIR, DSC and TGA). Results mainly showed an increase in thermal stability with increasing GTR content and good dispersion and interaction of GTR in the epoxy matrix (Yagneswaran et al., 2008). A dominant catalyzing effect of GTR on the curing reaction was highlighted

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since it was observed that the presence of GTR promotes the curing of epoxy resin (Yagneswaran et al., 2013). In the work reported by Piszczyk et al. (2015), flexible polyurethane foams were modified with two kinds of GTR, untreated and thermomechanically reclaimed. The impact of the rubber treatment on the mechanical and thermal properties of resulting polyurethane composites was analyzed. It appeared that the incorporation of rubber particles into polyurethane foam caused significant changes in the structure of this matrix. It particularly enhanced its cross-link density and had positive influence on its thermal stability and its compressive strength.

However, cross-linked structure of rubbers caused by the vulcanization process restricts the movement of rubber molecular chains and limits the interaction forces between GTR particles and the polymer matrix, resulting in a decrease of the composite's performance (Oliphant and Baker, 1993; Naskar et al., 2001, 2002). To obtain materials with improved properties, it seems useful to break the sulfur crosslinks formed during vulcanization. This process is named devulcanization.

Vulcanization is the thermo-chemical process mainly consisting of incorporating sulfur into a mixture of rubber to generate a 3D network, providing the elasticity and other properties desired in manufactured products. In fact, some degree of crosslinking in rubber phase is desired for its use alone or as a component in thermoplastics elastomers (Coran, 1995). In this process, sulfur atoms are chemically linked to rubber molecules to form Carbone-Sulfur-Carbon (C—S—C) and Carbone-Sulfur-Sulfur-...-Carbon (C—S_x—C) bonds. The vulcanization process is irreversible at standard atmospheric conditions of temperature and pressure.

Optimum devulcanization treatment, therefore, have to break C—S and/or S—S bonds without affecting hydrocarbon backbone chains. This operation occurs when the energy provided is higher than the link energies of C—S and S—S bonds, without reaching that of C—C bonds.

Several methods have been applied to devulcanize the Waste Tire Rubber (WTR) for reuse in rubber processing. Thermomechanical shearing devulcanization (Radhesh Kumar et al., 2002; Zhang et al., 2010a, 2010b; Sutanto et al., 2006a) is one of the most employed techniques. During this process, a strong rise in temperature occurs that can lead to the degradation of the rubber network. Most often, extruders are used to perform this procedure (Zhang et al., 2010a, 2010b; Sutanto et al., 2006a; Tao et al., 2013). Adding a chemical component defines a mechanochemical method (Yagneswaran et al., 2008; Sutanto et al., 2006a, 2006b; Dubkov et al., 2012). Various chemical compounds have been used in this method as devulcanizing agent. The main disadvantage of such compounds lies in their toxicity which pollutes the environment. Another process for rubber devulcanization is based on the use of high power ultrasound electromagnetic radiation (Li et al., 2004). Ultrasonic waves at certain level, can quickly break up the three dimensional cross-linked structure of vulcanized rubber in the presence of pressure and temperature. Ultrasonic devulcanization system is composed of an extruder and ultrasonic generator in order to combine the ultrasonic action with mechanical forces. There is also a devulcanization process based in the use of bacteria. Although vulcanized rubbers are not biodegradable, some microorganisms are able to attack the sulfur bonds of these materials, in order to remove the sulfur and oxidize it to sulfate (Li et al., 2011; Bredberg et al., 2002; Yao et al., 2013). The devulcanized powder obtained by this method could be incorporated in new rubber formulations, without significant loss in proprieties (Presti, 2013). However, the slowness of the devulcanization process, the necessity to treat the rubber in order to eliminate components that can kill bacteria and the difficulty of controlling the bacterial culture are the main factors that discourage the use of this method (Guo et al., 2010; Selbes et al., 2015).

Another method is microwave devulcanization that uses electromagnetic energy to break the cross-links of sulfur—sulfur (S—S) and carbon—sulfur (C—S) in rubbers. Microwave radiation can be absorbed by material through molecular interaction with the electromagnetic field and converted to heat. The material temperature increases quickly, reaching 260–350 °C during microwave treatment. This process promotes crosslink breaking while the chemical carbon—carbon bonds in the main chain are preserved (Rajan et al., 2006). However, several authors have found that long microwave exposure periods resulted in many structural changes and in breaking of the main polymer chain and the C=C chemical bonds, leading to lower molecular mass fractions (Garcia et al., 2015; Karger-Kocsis et al., 2013; Scuracchio et al., 2007; Isayev and Sujan, 2006). This can make the formation of new cross-links difficult in Devulcanized Ground Tire Rubber (DGTR) during their revulcanization in a following step for recycling. Among several techniques, microwave devulcanization presents some advantages that make it one of the most promising method for rubber recycling (Adhikari et al., 2000). These advantages include the ability to treat large amounts of material, the possibility of continuous processing and the easy adjustment of the process parameters, such as the power source and the time of treatment. Because microwave radiation can penetrate materials and deposit energy, heat can be generated throughout the volume of the material. The transference of energy does not rely on diffusion of heat from surfaces, and it is possible to achieve rapid and uniform heating of thick materials (Thostenson and Chou, 1999), i.e. this method enables to apply large amounts of energy rapidly and uniformly to the rubber, without using chemical reagents during the process (Isayev, 2005), which makes it an eco-friendly process (Hong et al., 2015).

In this study, microwave electromagnetic energy is used in an effort to break S—S and C—S bonds of powder rubber issued from WTR, leading to Devulcanized Ground Tire Rubber (DGTR). Crosslink densities of GTR and DGTR were estimated by swelling test in toluene. Analysis of bonds present in GTR and DGTR was performed by Fourier Transform Infrared analysis (FTIR). Then, GTR and DGTR were used to prepare epoxy based composites. Mechanical properties of these composites were evaluated by means of 3-point bending tests and fracture surfaces were observed by SEM, to correlate macroscopic properties with morphology. A complementary analysis was achieved to identify a relationship between the rubber modulus and the number of crosslink per chain.

2. Experimental procedures

2.1. Materials

GTR used in this study was kindly provided by Phenix Technologies (Sancheville 28800, France). It is mainly constituted of Styrene Butadiene Rubber (SBR) and originated from tire sidewalls. Its statistic size distribution was evaluated using an electrical sifter supplied by Retsch (France), with mesh sieves of 125 μm, 160 μm, 250 μm, 315 μm, 500 μm and 630 μm.

Composites were prepared by adding 10 wt% of GTR and DGTR powder to a mixture of a Bisphenol-A-(Epichlorhydrine) epoxy resin (molecular weight max 700) and bisphenol-F epoxy resin (molecular weight ⩽ 700/C13/C15 Alkyl glycidyl ether), by SOLOPLAST (Germany). A hardener of composition: 3 aminomethyl-3,5 ,5-trimethyl-cycloexyl amine, Bisphenol A-epoxy resin (molecular weight < 700) and alcohol benzyl, was used.

Unfilled material has been prepared by mixing for 15 min the epoxy resin with 45 wt% of hardener, in an internal propeller mixer. GTR or DGTR powder was added during mixing operation when preparing composites. The mixture is then poured into a