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Development of passenger tire treads: reduction in zinc content and utilization of a bio-based lubricant

S. Moresco [a], M. Giovanela [a], L.N. Carli [b, **], J.S. Crespo [a, *]

[a] Centro de Ciências Exatas e da Tecnologia, Universidade de Caxias do Sul, Rua Francisco Getúlio Vargas, 1130, Caxias do Sul, 95070-560, RS, Brazil
[b] Campus Blumenau, Universidade Federal de Santa Catarina, Rua Pomerode, 710, Blumenau, 89065-300, SC, Brazil

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ABSTRACT

The present study aimed to characterize and determine the technical viability of using vegetable oil as a lubricant and vulcanization activator with low zinc content in a natural rubber tire tread as additives. These additives were used to replace traditionally used components in the rubber industry. The chemical and thermal characterizations of each alternative additive were performed using thermogravimetric analysis, Fourier transform infrared spectroscopy, and atomic absorption spectrometry. Nine samples were prepared with various vegetable oil contents (3, 4, 6, and 8 parts per hundred of rubber – phr) and vulcanization activators with lower zinc content (2, 3, 4, and 5 phr). The compositions were characterized using rheometry and physico-mechanical analyses. The obtained results were compared to the standard formulation of tire treads using naphthenic oil and zinc oxide. The thermal and chemical characteristics suggest that the vegetable oil has the typical structure of a phenol. The low-zinc-content vulcanization activator has the typical structure of an aromatic zinc carboxylate. The physico-mechanical properties of the samples indicate that the best performance was achieved with 3 phr of the low-zinc-content vulcanization activator and 3 phr of vegetable oil, which reduced the lubricant content by 50% and zinc content by 75% without unfavorably affecting the properties of the final product.

1. Introduction

The tire industry is constantly developing so that their products are more secure, durable, ecological and energetically economical. Each part of a tire requires a specific compound with particular physical and chemical properties. Several studies have been conducted to replace various components of these formulations with renewable and/or less environmentally harmful additives, thus aiming to the adoption of cleaner production by the rubber industries (Dasgupta, 2008; Gujel et al., 2014a).

The elastomer compositions use vulcanization activators, which generally consist of a metal oxide (usually zinc oxide, ZnO) at a ratio of up to 5 phr (parts per hundred of rubber) and a fatty acid at a ratio of 0.5–3 phr. Because of environmental concerns, the zinc content in rubber compounds is the subject of extensive research (Chapman, 1997). Zinc can be released into the environment from the rubber during production, through recycling and in rubber powder from tire wear during the life cycle of the tire. Cations such as Zn^{2+} and Cu^{2+} cause mucus coagulation in fish gills, which leads to asphyxia (Branco, 1974). Thus, some studies have been performed to reduce the zinc content in elastomeric compounds (Gujel et al., 2014a; Heideman et al., 2006; Henning, 2007a; Pysklo and Pawlowski, 2007).

Henning (2007b) used zinc monomethacrylate as the activator in vulcanization compounds with sulfur. Compared with ZnO in equivalent molar quantities, zinc monomethacrylate produces higher crosslink density. The molar concentration of zinc in the formulation decreases by 80%. Heideman et al. (2006) and Pysklo and Pawlowski (2007) used alternative zinc complexes and metal oxides as vulcanization activators in the presence of sulfur and ZnO nanoparticles. The study demonstrates that zinc glycerate is a potential substitute for ZnO as the activator in vulcanization systems with sulfur without damaging the cure characteristics and increasing the compound crosslink density, even when the zinc content is reduced by 10–20%. In 2014, Gujel et al. (2014a, 2014b) analyzed the use of a zinc stearate as a substitute to the standard ZnO for the bus body profiles of ethylene propylene diene rubber

* Corresponding author. Tel./fax: +55 54 3218 2159.
** Corresponding author. Tel./fax: +55 47 3232 5187.
E-mail addresses: larissa.carli@ufsc.br (L.N. Carli), jscrespo@ucs.br (J.S. Crespo).

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(EPDM), in which it was possible to reduce 60% of the zinc content without damaging the technical performance of the final product.

Lubricants are used to make the elastomeric-compound processing easier. Today, most used lubricants in the industries have high contents of polycyclic aromatic compounds (PCA), many of which have been identified as suspected carcinogens. During their use, passenger car tires and truck tires lose up to 2 kg and 12 kg, respectively, of their mass from abrasion. Most of the material spreads over the ground near roads and is removed by runoff, which causes water contamination (Dasgupta et al., 2009).

Vegetable oils from renewable sources are possible substitutes for lubricants from petroleum for rubber compounds, mainly because of the absence of PCA and the increasing demand for eco-friendly, renewable, less toxic and readily biodegradable products. These intrinsic characteristics promote the application of the concepts of cleaner production when vegetable oils are used in substitution to the aromatic oils. In this regard, Shashidhara and Jayaram (2010) depict the potential applications for various vegetable oils, e.g. soybean oil, jojoba oil, and tallow oil for application as lubricants and plasticizers, linseed oil for coatings and paints, among others.

Some studies have evaluated soybean oil (Dasgupta et al., 2007, 2009), palm oil (Ismail et al., 1999, 1997; Ismail and Tajur, 1997) and castor bean oil (Costa et al., 2004) in elastomeric-compound applications. Dasgupta et al. (2007) performed physical and chemical characterizations of compounds from petroleum oils and vegetable oils in natural rubber (NR) for truck tire treads. It was observed that the compounds containing vegetable oils presented a higher vulcanization rate. In 2008, 2009, these authors (Dasgupta et al., 2008; Dasgupta et al., 2009) characterized compounds produced with NR and vegetable oils in comparison to aromatic, naphthenic and paraffinic oils. They observed that the mechanical properties, particularly with the use of soybean oil, exhibited a reduction in modulus at 300% and a reduction in tensile strength. Thus, the elongation at break increased because the elastomer chain has greater mobility as a result of the use of vegetable oils. In 2014, Gujel et al. (2014a, 2014b) also used soybean oil as the lubricant in a formulation for the bus body profile of EPDM and observed that the cure characteristics were affected: the vulcanization time was shortened when the lubricant from soybean oil was used.

This brief review shows that several researches were performed with the aim to use vegetable oils and alternative zinc compounds in rubber compositions. However, the use of cashew nut oil, which presents a phenolic structure, was not described in the literature. Moreover, no reports were found regarding the decrease of the zinc content using Zn org.

Considering these facts, the present study aimed to prepare and characterize NR tread compounds that incorporated cashew nut oil and vulcanization activator with low zinc content (Zn org) as alternative raw materials aiming to reduce the environmental impact of this product. Furthermore, this work presented for the first time the results of Zn^{2+} release in water from elastomeric compositions.

2. Experimental section

2.1. Materials

The materials in this study were as follows: NR (SMR 5L, Malaysia), ZnO (with 80% wt. of Zn) (Votorantim Metais, São Paulo, Brazil), naphthenic oil (NO, Nynas, Three Rivers, United States of America), carbon black N-330 (CB, Columbian Chemicals Company, São Paulo, Brazil), sulfur (S, Intercuf Indústria e Comércio Ltda, São Paulo, Brazil), and *N*-cyclohexyl-2-benzothiazole-sulfenamide (CBS, Lanxess Indústria Produtos Químicos e Plásticos Ltda, São Paulo, Brazil). The rubber additives were Zn org (with 33% wt. of Zn) (LT Químicos, São Paulo, Brazil) and lubricant from cashew nut oil (VO) (Resibrás, Fortaleza, Brazil).

2.2. Characterization of the rubber additives

The rubber additives were characterized by thermogravimetric analysis (TGA) using a TA Instruments Q500 equipment to determine the partial composition of Zn org and VO. The analyses were performed from 25 to 900 °C at a heating rate of 20 °C min^{-1} under a nitrogen flow of 50 mL min^{-1}.

The functional groups of Zn org and VO were evaluated by Fourier transform infrared spectroscopy (FTIR) using a Spectrum 100 spectrophotometer (Perkin Elmer) with a resolution of 9 cm^{-1} from 4000 to 670 cm^{-1}.

The zinc content in the Zn org was determined by atomic absorption spectrometry (AAS) using a Perkin Elmer Analyst 200 spectrometer after acid digestion, which was performed with 1.0 g of Zn org in 100 mL of an HNO_3 solution (10% v/v) during 6 h.

2.3. Preparation of the elastomeric compositions

The standard formulation with conventional additives was based on a typical composition of a passenger tire tread based on Babbit (OHM, 1990). This formulation and the compositions with different contents of Zn org and VO are shown in Table 1.

The compositions were prepared in an internal mixer (Banbury, Copé) at 50 rpm and 125 °C. Then, the mixture was accelerated in an open-roll mixing at 80 °C for 3 min and a friction ratio of 1:1.25.

The specimens for the physico-mechanical characterization were fabricated by compression molding at 150 °C under a pressure of 15 MPa in a Shultz electrically heated hydraulic press according to ASTM D3182 at the optimum vulcanization time, which was determined by the rheometric analysis (Section 2.4.2).

2.4. Characterization of the elastomeric compositions

2.4.1. Mooney viscosity

The Mooney viscosity was determined in a MV-2000 Mooney viscometer (Alpha Technologies) using a large rotor at 100 °C and a test time of 5 min with 1 min of preheating according to ASTM D1646. Two samples were analyzed and the average and standard deviation were calculated.

2.4.2. Curing characteristics

The curing characteristics were determined using an MDR 2000 oscillating disk rheometer (Alpha Technologies) at the vulcanization temperature (150 °C) according to ASTM D2084.

2.4.3. Thermal characterization

Differential scanning calorimetry (DSC) analysis was performed to determine the glass transition temperature (T_g) of the cured compositions according to ASTM D3418. The analysis was performed using a TA Instruments Q 2000 from − 90 °C to 150 °C at a heating rate of 20 °C min^{-1} under a nitrogen flow of 50 mL min^{-1}. Two samples were analyzed and the average and standard deviation were calculated.

2.4.4. Average interchain separation

The average interchain separation (R) was evaluated using X-ray diffraction (XRD). The analysis was performed for the pristine NR and cured compositions (standard and VO 6 phr) at room temperature in a Shimadzu 600 diffractometer using Cu$K\alpha_1$ radiation ($\lambda = 1.54$ Å). The measurements were performed in reflection mode

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