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Magnetic properties of vulcanized natural rubber nanocomposites as a function of the concentration, size and shape of the magnetic fillers

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ABSTRACT

Nickel–zinc ferrites as well as their nanocomposites formed by natural rubber are desirable because they take advantage of the thermal, mechanical and magnetic properties of each component. However, to date, the effect of the size, shape and concentration of the magnetic fillers on the magnetic properties of nanocomposite has not been studied in detail. In this report, we are presenting results about the influence of the geometric characteristic of fillers on the magnetic parameters of nanocomposites. Nickel–zinc ferrite nanopowders (NZF) with stoichiometry $Ni_{0.5}Zn_{0.5}Fe_2O_4$ were synthesized by a chemical route named the Modified Polyol Method (MPM) and magnetic nanocomposites were prepared with concentrations between 1 and 10 phr of ferrite nanopowders by thermal compression and hot pressing. From TEM images of ferrite nanopowders aggregates and primary particles in the nanometric scale were identified with aspect ratio different from 1 (r = a/b = 0.99, 0.55 and 0.43). From VSM measurements and particle size, the NZF may be classified as a ferrimagnetic material in a paramagnetic state and the saturation magnetization (M_S) was equal to 36.4 emu/g. Performing VSM experiments with different degrees between the sample and the magnetic field, differences up to 9% were identified for the M_S indicating a dependence of magnetic parameters on the concentration and shape of particles and aggregates. Magnetization *versus* time assays were carried out via VSM and two distinct relaxation times were achieved and associated with different populations of size and/or shape for the magnetic fillers. These results point to the possibility of modulation of the magnetic properties of vulcanized natural rubber composites by means of a suitable engineering process to control the concentration, size and shape of magnetic nanoparticles and agglomerates.

1. Introduction

The nickel–zinc ferrites are isomorphic spinels to the $MgAl_2O_4$ mineral and they exhibit the molecular formula equal to $(Zn_x^{2+}Fe_{1-x}^{3+})[Ni_x^{2+}Fe_{1+x}^{3+}]O_4^{2-}$, where $(Zn_x^{2+}Fe_{1-x}^{3+})$ are tetrahedral sites and $[Ni_x^{2+}Fe_{1+x}^{3+}]$ are octahedral sites. This kind of ferrite is a technologically attractive material, which is used commercially used as high-frequency ferrites for radio frequency coils and transformer and motor cores [1–3]. In the last few years, theses oxides have been applied in biomedical systems mainly as carriers for drug delivery, contrast agents for magnetic resonance imaging (MRI) and hyperthermia fluid applications [4,5]. The natural rubber from latex is a natural polymer (*cis*-1,4-polyisoprene), its monomer is the 2-metil-1,3-butadieno (C_5H_8) and the main source of latex is *Hevea brasiliensis* [6]. There are many kinds of syntactical rubbers such as styrene-butadiene rubber (SBR), butadiene rubber (BR), ethylene propylene diene monomer (EPDM), chloroprene Rubber (CR) and nitrile butadiene rubber (NBR), but none exhibit a better combination of good elasticity, low mechanical hysteresis, excellent dynamic properties, good tensile, tear strength and abrasive resistance than natural rubber [7,8]. For this reason, natural rubber is widely used in the tire and automotive industries. These unique

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properties and applications of nickel–zinc ferrites and natural rubber can be combined generating a nanocomposite material providing the best of both worlds [9,10].

Nanocomposites formed by natural rubber and ceramic fillers are desirable, taking advantage of their thermal and mechanical properties from the elastomeric matrix and special function from the dispersed phase. Some examples are: (1) multiwalled carbon nanotubes were inserted in polymeric matrices producing significant mechanical improvements in the nanocomposites [11,12]; (2) barium strontium titanate embedded in a low-loss dielectric matrix that can be applied in microwave devices for wireless telecommunications [13]; (3) magnetic nanoparticles like nickel–zinc ferrite dispersed in vulcanized natural rubber forming rubber ferrite composites (RFCs) or magnetic polymer nanocomposites (MPNCs) that can be applied to various systems like electronic devices, integral circuits and magneto-optical media [14,15]; (4) flexible microwave absorbers based on nickel ferrite nanocomposites with a filler concentration of up120 phr were produced and they presented potential absorption at bands S and X [16]; (5) nickel–zinc ferrites and potassium strontium niobate were dispersed in vulcanized natural rubber forming magnetic and ferroelectric nanocomposites with low loss of mechanical properties [3]. In the last year, new preparation routes such as centrifugation of the latex and magnetic fillers formed *in situ* [17], thermal, dynamic mechanical, magnetic and dielectric properties have been the goal of investigation in the field of magnetic natural rubber nanocomposites [18,19]. However, reports on the influence of the size, shape, magnetic anisotropy and concentration of nickel–zinc ferrites on the magnetic properties of natural rubber nanocomposites are not abundant in scientific literature.

In this report, nickel–zinc ferrite nanopowders with magnetic properties and stoichiometry equal to $Ni_{0.5}Zn_{0.5}Fe_2O_4$ were synthesized by a chemical route named the Modified Polyol Method (MPM). Natural rubber nanocomposites with different concentrations of ferrite nanopowders were prepared by thermal compression and hot pressing. The influence of the size, shape and concentration of ferrite nanoparticles on the magnetic properties of natural rubber nanocomposites were identified and discussed.

2. Materials and methods

2.1. Synthesis of the ferrite nanopowders and preparation of the magnetic nanocomposites (NR/NZF)

The sample of nickel–zinc ferrite nanopowder with stoichiometry $Ni_{0.5}Zn_{0.5}Fe_2O_4$ (NZF) was synthesized by the Modified Polyol Method [20,21]. This chemical route is suitable for the synthesis of magnetic oxides because it permits an adequate control of shape, size and size distribution of the particles, parameters that influence their magnetic properties [22]. Starting reagents, chemical formula, molecular mass, purity and origin used were: nickel oxide (Ni_2O_3, 165.39 g/mol, analytical purity, VETEC), zinc oxide (ZnO, 81.38 g/mol, analytical purity, VETEC), iron oxide (Fe_2O_3, 159.69 g/mol, analytical purity, VETEC), ethylene glycol ($C_2H_4(OH)_2$, 62.07 g/mol, analytical purity, FMAIA) and nitric acid (HNO_3, 63.01 g/mol, 65%, NUCLEAR). Reagents were weighed to the $Ni_{0.5}Zn_{0.5}Fe_2O_4$ stoichiometry and they were dissolved in nitric acid and ethylene glycol, in continuous agitation until they were completely dissolved. During magnetic stirring, the temperature was increased to 180 °C. Afterwards, in a recipient, the material underwent a pre-calcination and a calcination, in a box type furnace.

The pre-calcination was carried out in two stages, under N_2 flux of 500 mL/min. In the first stage, the temperature was gradually increased from room temperature with a heating rate equal to 10 °C/min up to 150 °C and a soaking time of 2 h. In the second stage, at the same heating rate, the temperature was increased up to 300 °C for 1 h. Cooling was performed at a natural furnace rate under N_2 flux. The N_2 flux is utilized to minimize the presence of any possible levels of oxygen in the furnace chamber derived from the air atmosphere. An oxygen level is undesirable but it is expected because the furnace is not hermetically closed. After this process, a fragile and reddish-brown powder was obtained, which was called precursor nanopowders. This powder was deagglomerated in an agate mortar and sieved at 325 meshes.

The Calcination of the precursor was carried out at 450 °C for 3 h, under a dry air flux of 7 L/min. During the calcination, the heating and cooling rates were equal to 5 °C/min. The calcination temperature of 450 °C was selected to present an adequate combination of crystallinity, microstrain and saturation magnetization. More details about the method and other $Ni_{0.5}Zn_{0.5}Fe_2O_4$ synthesis can be provided by A. Daigle, (2011) and F. S. Bellucci (2012) [20,23].

Dry natural rubber was used for the preparation of the nanocomposites (cis-1,4-polyisoprene) of the commercial variety CCB (Crepe Claro Brasileiro – CCB), financed by the *DLP Industria e Comércio de Borracha e Artefatos* ® in the city of Poloni/SP. This rubber is obtained in processing plants by the coagulation of latex from the Hevea brasiliensis species, clones RRIM 600. Start reagents, chemical formula, purity and origin of the vulcanized system utilized were: zinc oxide (ZnO, 81.38 g/mol, analytical purity, VETEC), stearic acid ($CH_3(CH_2)_{16}COOH$, 284.48 g/mol, analytical purity, VETEC), mercaptobenzotiazol ($S_2NC_7H_5$, 167.25 g/mol, analytical purity, ORGANIC), sulphur (S_8, 256.52 g/mol, analytical purity, VETEC). 100 phr of dry natural rubber was mixed with an activation system made up of 4 phr of zinc oxide and 3 phr of stearic acid and the ferrite nanoparticles calcined at 450 °C in concetrantion of 1, 3, 5, 10, 20 or 50 phr in an open mixing mill or a rubber mixer (Makintec, model 379 m) at 40 °C. After 24 h, the vulcanized agents were made up of 2 phr of sulphur and then 1 phr of 2-mercaptobenzotiazol was added to these mixtures also using the same mill for 10 min at 40 °C. The samples named NR/NZF (1, 3, 5, 10, 20 or 50 phr) were thermal compression molded by hot pressing under 2.5 MPa, at 150 °C for 8 min and 30 s. The nanocomposites were conditioned, at least, 24 h prior to testing. Similar nanocomposites were produced with similar conditions by F. S. Bellucci et al. [24]. The vulcanized natural rubber and nanocomposites formulations are listed in Table 1 and the schematic representation of the general process of preparation is shown in Fig. 1.

2.2. Characterization of the ferrite nanopowders and magnetic nanocomposites

The structural characterization of ferrite nanopowders was carried out by infrared absorption spectroscopy (FTIR). The spectrophotometer FTIR used was a Bruker model Vector 22, in the region of 4000–400 cm^{-1}, with an accuracy of 2 cm^{-1} and

Table 1
The vulcanized natural rubber and nanocomposites formulations.

Components	Quantity (phr[a])
Dry natural rubber	100
Zinc oxide	4
Stearic acid	3
Sulphur	2
2-Mercaptobenzothiazol	1
$Ni_{0.5}Zn_{0.5}Fe_2O_4$	0, 1, 3, 5, 10, 20 and 50

[a] phr – Parts per hundred of rubber.