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Preparation and characterization of flexible ferromagnetic nanocomposites for microwave applications

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ABSTRACT

Magnetic Fe_3O_4 nanoparticles (∼20 nm) were synthesized using the chemical co-precipitation method with a view of developing flexible and easily processable ferromagnetic materials with high mouldability to be used as microwave absorbers. The nanoparticles prepared were incorporated into natural rubber through latex stage processing. This novel processing method gives better dispersion of particles in the rubber matrix. The composites were characterized using XRD, SEM, vibrating sample magnetometer, dynamic mechanical analyzer, cavity perturbation, thermogravimetry (TGA), and Fourier transform infrared photoacoustic spectroscopy (FTIR-PAS). A notable improvement in the mechanical properties of composites was observed upon adding Fe_3O_4 particles. Magnetic and microwave characteristics of the composites indicate the formation of a flexible ferromagnetic material with good microwave absorption characteristics.

1. Introduction

Rubber-ferrites, i.e. rubber filled with magnetic materials are an important class of composite materials that are useful in various applications such as microwave absorbers and flexible magnets [1–3]. Mouldability of these composites into complex shapes is another advantage. Metals and metal oxides are commonly incorporated into the rubber or thermoplastic rubber matrices to obtain composites with improved magnetic properties. When metal oxides are used as magnetic materials, large volumes are necessary to yield the required magnetization. However, large amounts of fillers in the rubber matrix may impair their mechanical properties. One possible way to overcome this problem is the use of nanometer-sized magnetic oxides in the composites which will impart good magnetic properties even at moderate loading. For example, Jamal et al. [4] prepared nickel nanocomposites of natural and chloroprene rubbers and Kong et al. [5] used thermoplastic natural rubber (NR) as the matrix for commercially available Fe_3O_4 nanoparticles through a melt blending process.

An important problem encountered while preparing rubber nanocomposites is to obtain a homogenous distribution of fillers throughout the rubber matrix. Nanoparticles, due to their high surface activity, exhibit a tendency to agglomerate into clusters in the matrix leading to poor mechanical and electromagnetic properties of composites. In order to exploit the full potential of nano-sized fillers, homogenous dispersion in the composite is necessary. Standard rubber composite preparation methods are solution casting or shear mixing of dry filler particles in the dry rubber on a two-roll mill or internal mixer. These processing methods are ineffective for the optimum distribution of filler particles in the rubber matrix. In solution casting, high specific gravity magnetic materials will settle to the bottom of the solution rendering inhomogeneity in the composite. In the latter method, shear forces generated during mixing may not be sufficient to break down the agglomerates.

Latex stage processing is an efficient method to obtain better dispersion of nanoparticles in the rubber, if water-dispersed nanoparticles are available. Latex is a colloidal dispersion of

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rubber particles in water. The nanoparticle dispersion can be mixed well with the latex and coagulated immediately so that the coagulum contains the particles in the dispersed state. The coagulum is then dried to remove water and mixed in a mill or internal mixer with other compounding ingredients. This second shear mixing will remove any inhomogeneity remaining in the mix. In this paper latex stage processing is utilized as the composite preparation method.

Iron ferrite, Fe_3O_4, is a traditional magnetic material used in electronics, magnetic storage media, ferrofluids and catalysis [6–10]. Among the several methods proposed for the preparation of Fe_3O_4, plasma procedures [11–14] and chemical co-precipitation [15] are effective in synthesizing Fe_3O_4 in nanometric dimensions. Of these, chemical co-precipitation was selected because of its simplicity and low cost. In this work, Fe_3O_4 nanoparticles synthesized by co-precipitation method are incorporated into natural rubber. To achieve better dispersion, latex stage incorporation of the magnetic materials was utilized. The NR-Fe_3O_4 composites thus synthesized were characterized using SEM, vibrating sample magnetometer, dynamic mechanical analyzer, thermogravimetry (TGA), and Fourier transform infrared photoacoustic spectroscopy (FTIR-PAS). On the lines of earlier studies on the microwave characteristics of filled polymers [16–18] the prepared NR-Fe_3O_4 nanocomposites were tested for their permeability in the microwave frequencies to see the feasibility of the composites to be used as microwave absorbers.

2. Materials and methods

2.1. Preparation of composites

Concentrated natural rubber latex (60 DRC) was procured from Njavally Latex Pvt Ltd. Ferrous sulphate ($FeSO_4$), ferric Chloride ($FeCl_3$), and ammonia solution (NH_4OH) were supplied by Merck Specialties Pvt. Ltd., Mumbai, India. Zinc oxide, stearic acid, 1,2-dihydro2,2,4-trimethylquinoline (TQ), zinc dibutyldithiocarbamate (ZDBC) and sulfur used were of commercial grade.

$FeCl_3$ and $FeSO_4$ dissolved in water were mixed in a beaker by keeping the molar ratio of Fe^{3+} and Fe^{2+} in the mixture to be 2:1. The mixed solution was stirred well and an excess amount of NH_4OH solution was added. The solution turned to black brown as Fe_3O_4 precipitate was formed *in situ*. The principal reaction is:

$$Fe^{2+} + 2Fe^{3+} + 8OH^- \rightarrow Fe_3O_4 + 4H_2O$$

The Fe_3O_4 dispersion obtained was added to concentrated latex (60 drc), and diluted to twice its volume. The amounts of $FeCl_3$ and $FeSO_4$ were varied to get 15, 30, 45 and 60 phr of Fe_3O_4 in the latex. The latex was coagulated using 8% acetic acid. Numerous local coagulations were formed throughout the bulk of the mix to form a flocculated system. These flocs were filtered and washed with distilled water until free from acid. The crumbs obtained were squeezed to remove water and dried. The dried rubber was mixed with other compounding ingredients in a Brabender plastograph as per the formulation given in Table 1. The final mixing was carried out on a two-roll mill. Since an accelerator capable of curing the rubber stock at room temperature was used, all the mixes were vulcanized at 90 °C for 1 h in an electrically heated hydraulic press under 180 kg/cm^2 pressure. The samples cut from the vulcanized sheets were used for characterization.

Table 1
Formulation of the composites.

Ingredients	Phr
NR	100
Fe_3O_4	15, 30, 45 and 60
ZnO	4
Stearic acid	2
TQ	1
ZDBC	1.5
Sulphur	2

2.2. Magnetic parameters

Magnetic measurements of the pristine Fe_3O_4 nanoparticles and the natural rubber composites were made at room temperature using a PAR EG&G 4500 Vibrating Sample Magnetometer (VSM). Magnetization was measured as a function of applied field in the range ±15,000 Oe.

2.3. Morphology

Scanning electron microscope (SEM) studies were carried out using SEM model 6390LA JEOL instrument. The samples were sputter coated with gold to suppress specimen charging.

TEM images were taken with a Hitachi model H-800 transmission electron microscope.

2.4. X-ray diffraction

High resolution XRD was done using the instrument PANAlyticalXPert Pro High Resolution X-ray diffractometer. The scan range was from 20 to 80 (2θ) using Cu Kα radiation.

2.5. Dynamical mechanical analysis

Tensile properties of the composites were determined according to ASTM D412. TA Instruments DMA Q800 was used to conduct dynamic mechanical analysis. Test specimens having a dimension of 30 mm × 3 mm × 2 mm were used in tension mode. Frequency sweep experiments were conducted over a frequency range of 1–30 Hz at 40 °C. The amplitude was fixed at 15 μm.

2.6. Thermogravimetry

Thermogravimetric analyses of the gum and composites were carried out on TA Instruments TGA Q50 with a heating rate of 20 °C/min under nitrogen atmosphere.

2.7. Microwave analysis

The microwave characteristics of the prepared conducting polymer composites were studied using cavity perturbation technique. The experimental set up consists of a ZVB20 vector network analyzer, sweep oscillator, S-parameter test set and rectangular cavity resonator. The measurements were done in S (2.5–4 GHz) band frequencies at room temperature (25 °C). The dimensions of S band rectangular wave-guide used in the measurements were 34.5 cm × 7.2 cm × 3.4 cm.

2.8. FTIR-photoacoustic spectra

In the present studies, the Fourier transform infrared (FTIR) photoacoustic spectra (PAS) in the 400–4000 cm^{-1} were acquired by co-adding 384 scans at a resolution of 8 cm^{-1} using a Varian 7000 FTIR spectrometer equipped with a MTS300 photoacoustic module from MTEC Photoacoustics, Inc. The photoacoustic module consisted of a microphone with a nominal sensitivity of 50 mV/Pa and a sample cup of 10 mm diameter. The sample cup contained helium gas to enhance the signal amplitude. The spectrometer included a water cooled mid-IR source and KBr beamsplitter. Rapid scan was used to obtain the spectra of fiber samples in the solid state. The samples were used as it is without mixing it with KBr.