Magnetorheological elastomers with efficient electromagnetic shielding

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ABSTRACT

This study is concerned not only with an investigation of rheological performance of magnetorheological elastomers (MREs) with random distribution based on modified magnetic particles, but also discusses their electromagnetic shielding properties for the first time. The current work further highlights the necessity of magnetic particles protection against oxidation species affecting them in real application conditions. Two kinds of MREs differing in matrix type represented by silicone elastomer and thermoplastic elastomer are prepared, and pristine carbonyl iron (CI) particles and siloxane-modified CI particles were used for each matrix. The difference in magnetic properties after the modification of particles is negligible while the modification significantly improves the anti-acid-corrosion properties. Moreover, modification of particles surface enhances their compatibility with silicone elastomer matrix which is evidenced by the measurements of viscoelastic properties under the external magnetic field applied. It is also shown that all the developed MREs can be successfully applied for the absorption of electromagnetic radiation in ultra-high frequency band, namely the frequency range from 700 MHz to 1.6 GHz can be readily covered by these materials.

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1. Introduction

Magnetorheological elastomers (MREs) are multi-phase composite materials frequently described as a solid analog to MR suspensions. Generally, MREs consist of an elastomeric matrix interspersed with micron sized ferromagnetic particles and hence combine the functionality of a highly elastic polymer matrix with the magnetic field-responsive properties [1–3]. The particles of choice for MREs are multi-domain iron particles satisfying requirements for soft magnetic material with high induced magnetic dipoles due to high magnetic permeability and high magnetization saturation while the residual magnetization is minimal. The magnetic particles can be incorporated into the elastic body either in random distribution or in ordered structures [4,5]. If a uniform magnetic field is applied to the reactive mixture during the cross-linking process, formed particle chains become locked in the elastomer. The resulting composites are called transversely isotropic MREs [6]. However, from a manufacturer's point of view it would be convenient if the use of magnetic field during cross-linking process could be avoided.

When the external magnetic field is applied to the MRE, the magnetic particles interact with the surrounding polymer chains and alter their positions. This results in an overall shape change of the composite. Thus, the coupling of magnetic field with the elastic response of reversible extend from 5% to 700% depending on the type of elastomeric matrix can result in powerful actuators such as artificial muscles and sensors [7,8]. Although the MREs are quite new materials, the giant deformational effects, high elasticity, and quick response to magnetic fields, *i.e.* field-dependent control of modulus, open new opportunities for using such materials for various applications [9,10]. However, there are still some limitations for their utilization such as corrosion of magnetic particles inside the systems due to the diffusion of corrosion agents through the polymeric matrix or insufficient wetting of magnetic particles with the matrix. Thus, the modification of particles surface is an effective tool for the improvement of MR performance in time due to the improved compatibility between magnetic particles and matrix [11], and improved oxidation and chemical stability.

Furthermore, the objective of the design of electromagnetic shielding materials (ESMs) widely used in civil and military fields due to their ability to absorb undesirable electromagnetic signals and wave pollution is to obtain the material having minimal thickness and the lowest possible reflectance within the widest possible operating bandwidth [12]. One of the possible ways providing these properties is the use of multi-component core–shell structured magnetic particles with magnetic core and electrically

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conducting shell dispersed in polymer matrix since the absorption of electromagnetic waves in such materials is governed by various loss mechanisms related to the magnetization and electric polarization processes [13].

Nanostructured tetraethylorthosilicate (TEOS) grafted onto the carbonyl iron (CI) magnetic particles was used in this study to evaluate the influence of siloxane-based coating of particles on their compatibility with two different elastomeric matrixes, namely thermoplastic and silicone elastomer matrix. Furthermore, this study will indicate a broadening in application spectrum of current MREs via the examination of their electromagnetic shielding properties.

2. Material and methods

2.1. Reagents

Carbonyl iron (ES grade, BASF, Germany) spherical particles with iron purity > 97.7% and size 2–3 μm were used as the magnetic agent in MREs under investigation. For the modification of CI particles, namely tetraethylorthosilicate (TEOS, purity = 98%) produced by Sigma–Aldrich (St Louis, USA), hydrochloric acid (HCl, ACS reagent, 37%) and toluene (anhydrous, 99.8%) both produced by Penta Chemicals (Czech Republic), were used. All the chemicals were used without further purification.

2.2. Coating of CI particles by 3APTS

Prior to the surface modification of the CI particles, their cleaning from any contamination and activation was performed via 0.1 M HCl according to the process described in the reference [14] in more details. The next step in the coating is the functionalization of the activated CI particle surface with TEOS polymer. Briefly, 100 g of activated CI particles were dispersed in 150 mL of a non-polar solvent toluene into a three-neck flask fitted with a mechanical stirrer and a reflux condenser. The entire assembly was placed into a heating mantle and stirred at 110 °C with sequential adding of TEOS (10 mL) for 20 min followed by the reaction under rigorous stirring (200 rpm) for additional 8 h at 110 °C. Afterward, the coated CI particles were separated from the toluene by sedimentation accelerated with a magnet, washed with distilled water (2 times, 200 mL each), ethanol (2 times, 200 mL each), and acetone (2 times, 200 mL each), and dried at a pressure of 200 mbar at 50 °C for 10 h.

2.3. Particles characterization

A Fourier transform infrared spectroscopy (FTIR, Nicolet 6700, Thermo Scientific, USA) was performed to verify the successful modification of the CI particles with TEOS. The FTIR spectra were recorded using the attenuated total reflectance (ATR) technique with Germanium crystal in a range of 680–4000 cm^{-1} at 64 scans per spectrum at a 2 cm^{-1} resolution. The magnetostatic properties of particles under investigation were measured at room temperature using a vibrating sample magnetometer (VSM 7407, Lakeshore, USA) in a magnetic field of up to 1200 kA m^{-1}. The measurements were carried out at a frequency of 82 Hz, and the vibration amplitude was 1.5 mm. In order to examine the resistance to corrosion by acids, the same amounts of pristine and TEOS-modified CI particles were dispersed in a hydrochloric acid solution of concentration 0.1 mol/L, and the increasing pH values due to the reduction of the acid solution oxidizing the iron-based particles as a function of time were recorded via pH-meter (Senso-Direct pH110, The Tintometer Ltd, United Kingdom).

2.4. MREs preparation

Two types of MREs differing in the matrix materials were prepared. The first matrix material was silicone elastomer represented

by Silgard 184 supplied by Dow Chemical Company (USA) while the second one was thermoplastic elastomer represented by Vistamaxx 61020FL supplied by ExxonMobil (USA). Furthermore, two types of MREs with 40 vol.% particles loading for each matrix material were investigated differing in the surface modification of CI particles, *i.e.*, the first was based on pristine CI particles and the second was based on CI particles modified with TEOS. Hence, four types of MREs were prepared and investigated to evaluate the MR performance as well as electromagnetic shielding properties dependence on the matrix material and particles modification used in detail.

The mixing of the two-component silicone elastomer (10:1) with the corresponding magnetic particles was carried out by mechanical stirring at room temperature until the mixture reached a homogeneous state. Then, the suspension was degassed at 300 mbar for 10 min. Afterwards the mixture was cast to a mould with the thickness of 0.5 mm, again degassed, and cured at 40 °C for 3.5 h.

In the case of thermoplastic elastomer, the mixing was carried out via a scientific twin screw extruder (Labtech Engineering Co. Ltd., Thailand) at 170 °C for 5 min. The compound was subsequently formed to plate of thickness 0.5 mm via compression molding at 170 °C for 5 min.

2.5. MREs characterization

Complex magnetic permeability and dielectric permittivity of MREs with randomly distributed particles (40 vol.%) in both types of matrix have been measured at the room temperature in the frequency range of 1×10^6–3×10^9 Hz by the impedance method with an impedance/material analyzer Agilent E4991A (Agilent Technologies, USA). The investigation of dielectric properties was carried out on circular samples with diameter of 15 mm, whereas the measurements of complex magnetic permeability were performed on toroidal samples with outer diameter of 8 mm and inner diameter of 3.1 mm. Specimens for both characterizations were cut out of previously prepared plates (thickness 0.5 mm) by a manual press. In order to estimate the absorbing properties of single-layer metal-backed ESMs based on investigated MREs, the frequency dependence of the reflection coefficient, R, representing the absorbing ability of ESMs in decibels, has been calculated. When the level of R is equal to −10 dB and the absence of transmitted energy is presumed, then 90% of absorption of incident energy by ESM is obtained. Given that an electromagnetic wave is incident on the ESM surface along the normal, R from the surface of such a material can be calculated according to [15]:

$$R_L(dB) = 20 \log \left| \frac{Z_{in} - 1}{Z_{in} + 1} \right|, \tag{1}$$

where

$$Z_{in} = \sqrt{\frac{\mu^*}{\varepsilon^*}} \tanh \left(j \frac{\omega}{c} \sqrt{\mu^* \varepsilon^*} d \right) \tag{2}$$

is the input impedance of the ESM, c is the velocity of light, $\omega(=2\pi f)$ is the angular frequency, $\mu^* = \mu' - j\mu''$ and $\varepsilon^* = \varepsilon' - j\varepsilon''$ are the complex permeability and permittivity of the material, respectively, and d is the thickness of the sample. The reflection from ESM is absent in case $Z_{in} = 1$ condition is met. However, the absence of reflection from the ESM in real materials is reached only approximately, and the frequency, f_0, and thickness, d_0, for which the above condition is satisfied with highest degree of accuracy, are called matching frequency and matching thickness, respectively. In practical calculations, the minimum of R is obtained only for complex values of thickness:

$$d = d' + jd'' = \frac{c}{2\pi f \sqrt{\mu^* \varepsilon^*}} \arctan \left(-j\sqrt{\frac{\varepsilon^*}{\mu^*}} \right) \tag{3}$$