

On the Improvement of Magnetorheological Elastomer Oxidation Stability

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ABSTRACT

The objective of this study was to prepare nanostructured tetraethylorthosilicate grafted onto the carbonyl iron magnetic particles as a dispersed phase in magnetorheological elastomers and to evaluate the influence of siloxane-based coating of particles on their resistance against chemical oxidation caused in real applications for example by acid rains or sea humidity as well as their compatibility with silicone matrix.

INTRODUCTION

Magnetorheological elastomers (MREs) are multi-phase composite materials frequently described as solid analogues to MR suspensions¹. 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. 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 random distribution or in ordered structures².

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 usage of such materials for various applications³. However, there are still some limitation 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, and improved oxidation and chemical stability⁴.

MATERIALS AND METHODS

Commercially available carbonyl iron (CI, ES grade, BASF, Germany) spherical particles with declared iron purity > 97.7 % and size 2–3 μm were used as the magnetic agents 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. The modification of CI particles was performed according to the reference⁵ with only small modification in the type of siloxane monomer.

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 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. In order to examine the resistance to corrosion by acids, the same amounts of pristine and TEOS-modified CI particles were dispersed in HCl of concentration 0.1 mol/L, and the pH values of the solutions as a function of time were recorded via pH-meter (Greisinger electronic, GPRT 1400, AN, Germany).

The mixing of the two-component silicone elastomer represented by Silgard 184 supplied by Dow Chemical Company (USA) in a ratio of elastomer:hardener 10:1 with the corresponding magnetic particles (40 vol.%) 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.

The MR properties of MREs under investigation were measured using a rotational rheometer Physica MCR502 (Anton Paar GmbH, Austria) with a Physica MRD 170/1T magneto-cell at 25 °C. True magnetic field intensity (0 – 691 kA/m) was measured using a Hall probe. A parallel-plate measuring system with a diameter of 20 mm and a gap of 0.5 mm was used. The small-strain oscillatory tests were carried out through dynamic strain sweeps and frequency sweeps. The strain sweeps were performed in the applied strain range 0.01 – 1 % at a fixed frequency of 1 Hz in order to get the position of the linear viscoelastic region (LVR). Afterwards, the viscoelastic moduli were obtained from frequency sweep tests (0.1 – 10 Hz) at a fixed strain

amplitude in the LVR ($\gamma = 0.1\%$ in all of our experiments).

RESULTS AND DISCUSSIONS

The typical FTIR spectrum of pristine CI particles (Fig. 1a) illustrates, that no characteristic bands are observed because of their composition consisting of more than 97.7 % of iron. After the reaction with TEOS, the characteristic peaks of Si–O bonds were observed, which indicates that the siloxane was fabricated on the surface of CI. The band at 1105 cm^{-1} attributed to the (Si–O–C/Si–O–Si) asymmetric stretching appeared. Additionally, the peaks at 796 cm^{-1} and 937 cm^{-1} are assigned to the stretching vibration of Si–OH as matching with the structure of TEOS.

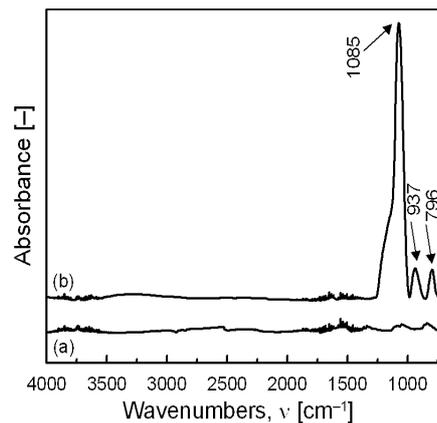


Figure 1. FTIR spectra of pristine CI particles (a), their TEOS-modified analogues (b).

The dependence of the magnetization saturation on the magnetic field strength can be seen in Fig. 2. The pristine CI particles exhibited only slightly higher magnetization saturation compared to their TEOS-modified analogues which is very positive for the potential applications since the magnetic performance of the particles sustains on the same level after the coating procedure.

For practical applications of MREs it is very important to improve their durability

by suppressing the chemical reaction of iron particles due to the diffusion of acidic reactive species coming from e.g. acid rains or sea humidity through the matrix material resulting in chemical reduction of iron followed by decreased magnetic parameters such as saturation magnetization or magnetic permeability.

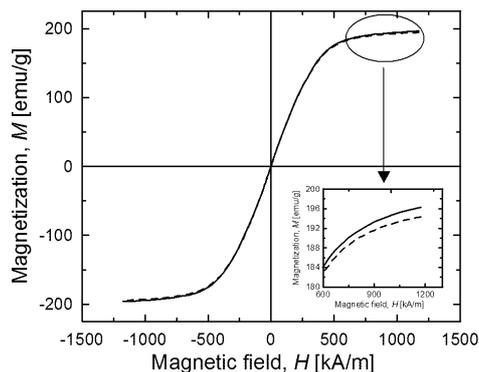


Figure 2. Magnetization curves of pristine CI particles (solid line) and TEOS-modified CI particles (dashed line).

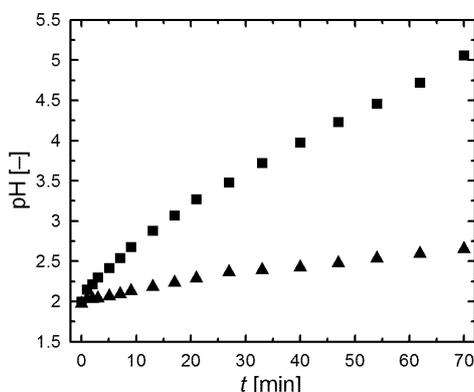


Figure 3. Resistance to corrosion of pristine CI particles (■) and TEOS-modified CI particles (▲) at acidic conditions.

The trends of pH values of acidic (HCl) dispersions of pristine and TEOS-modified CI particles over time were used to compare the anti-acid-corrosion properties (Fig. 3). Evidently, the surface of pristine CI particles reacts strongly with HCl while only

moderate pH increase was observed for TEOS-modified CI particles resulting in the improved anti-acid-corrosion properties important for real applications.

In general, the mechanical properties of materials depend on frequency of deformation. A good understanding of the influence of frequency on a material is therefore very important for its practical use. An oscillatory test for MREs should be performed within the LVR that the chain-like structure of the system is being maintained. To ensure validity of the oscillatory test, the amplitude sweep test was always carried out first in our case. After the LVR has been defined by a strain sweep for each sample separately, its structure was further characterized using a frequency sweep at a strain value from LVR. This provides more information about the interactions between particles and matrix.

The response of MREs under frequency sweep test is shown in Fig. 4. Evidently, the storage modulus, G' , characterizing the elastic component of MRE, is nearly independent of frequency, as would be expected from behaviour of structured or cured gels. The modification of magnetic particles via TEOS has an impact on their extremely improved compatibility with the silicone matrix. Almost one order of magnitude increase of, G' , is probably due to the chemical bonding of TEOS coating with siloxane group of the matrix. The loss modulus, G'' , characterizing the viscous component of MRE, changes comparatively with, G' , in almost all conditions applied. This trend is different only for TEOS-modified CI particles under the application of external magnetic fields of high intensity (○ and ▷ symbols in Fig. 4b). The interpretation of, G'' , is complicated here since it linearly decreases in log-log coordinates with increasing frequency. This can be caused due to the internal movement of magnetic particles bonded to the matrix and such relative movement of particles can

create some friction between neighbouring particles⁶.

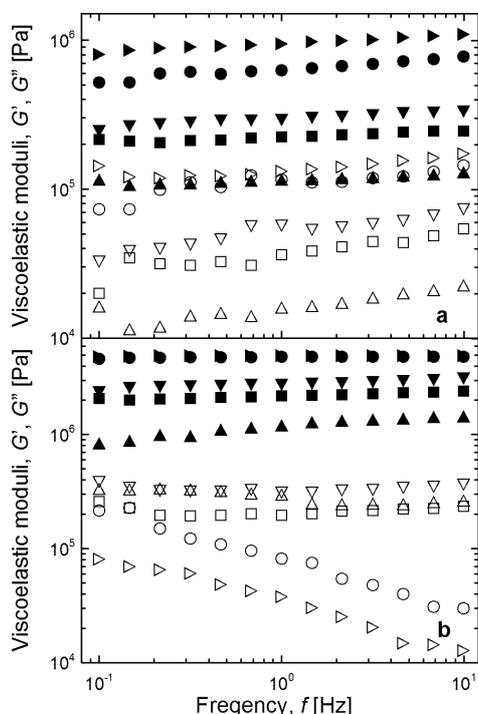


Figure 4. Storage, G' , (solid) and loss, G'' , (open) moduli dependence on frequency, f , for MRE based on pristine CI particles (a), and TEOS-modified CI particles (b) randomly dispersed in silicone elastomer at various magnetic field intensity, H , (kA/m): 0 (\blacktriangle , \triangle), 171 (\blacksquare , \square), 343 (\blacktriangledown , \triangledown), 464 (\bullet , \circ), 691 (\blacktriangleright , \triangleright).

CONCLUSIONS

In this study, a detailed experimental study on the oxidation stability and viscoelastic properties under an external magnetic field of MREs based on pristine CI or TEOS-modified CI particles was presented. The polysiloxane surface layer greatly improved the resistance to corrosion by acids as was proved via pH development in time when particles were dispersed in hydrochloric acid. Moreover, the coating also enhanced the interactions, and subsequently compatibility, of magnetic particles to

silicone matrix as was demonstrated by increased storage modulus for MRE based on siloxane-modified particles compared to that based on mere particles.

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