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INVESTIGATION OF MAGNETORHEOLOGICAL ELASTOMER SURFACE PROPERTIES BY ATOMIC FORCE MICROSCOPY

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Якобеску Г. Е., Балашою М., Бика И. E14-2012-54
Исследование свойств поверхности магнетореологического эластомера
методом атомной силовой микроскопии

Магнитореологические эластомеры состоят из натуральной или синтетической резиновой матрицы с внедренными вкраплениями ферромагнитных микрочастиц. Магнитно-эластичные свойства таких композитов являются не просто суммой эластичности полимера и жесткости и магнитных свойств наполнителя, а результатом сложных совместных взаимодействий и эффектов на разных шкалах размеров и детектируемых различными экспериментальными методами. В представленной работе исследуются микроструктура, поверхностные магнитные и упругие свойства нового изотропного и анизотропного магнитореологического эластомера, приготовленного из силиконовой резины и «мягких» микросфер из карбонильного железа. Измерения были выполнены методом атомной силовой микроскопии в следующих модах: (i) стандартное отображение — бесконтактная атомная силовая микроскопия; (ii) магнитная силовая микроскопия и (iii) «наноиндентирование». Проведено сравнительное исследование образцов с различными концентрациями частиц и интенсивностью магнитного поля, примененного во время процесса полимеризации.

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Iacobescu G. E., Balasoiu M., Bica I. E14-2012-54
Investigation of Magnetorheological Elastomer
Surface Properties by Atomic Force Microscopy

Magnetorheological elastomers consist of a natural or synthetic rubber matrix interspersed with micron-sized ferromagnetic particles. The magnetoelastic properties of such a composite are not merely a sum of elasticity of the polymer and stiffness and magnetic properties of the filler, but also the result of a complex synergy of several effects, relevant at different length scales and detectable by different techniques. In the present work we investigate the microstructures, the surface magnetic properties and the elastic properties of new isotropic and anisotropic magnetorheological elastomer prepared using silicone rubber and soft magnetic carbonyl iron microspheres. The measurements were performed by atomic force microscopy in the following modes: standard imaging — non-contact atomic force microscopy, magnetic force microscopy and nanoindentation. A comparative study for the samples with different particle concentrations and strength of magnetic field applied during the polymerization process is developed.

The investigation has been performed at the Frank Laboratory of Neutron Physics, JINR.

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INTRODUCTION

Magnetorheological (MR) materials belong to a class of functional materials with smart behaviour, due to the fact that their physico-mechanical properties can be controlled by external magnetic fields [1–6]. MR elastomers (MREs) are composites where magnetic particles are suspended in a nonmagnetic solid or gel-like matrix. The particles inside the elastomer can be homogeneously distributed (isotropic MRE) or they can be grouped (anisotropic MRE) depending on the fact that the polymerization is performed in the absence or in the presence of the magnetic field, respectively [7, 8]. Mechanical characteristics, viscoelastic properties, and magnetostrictive effect of the MREs make them susceptible for various applications as electric current passive and active elements, adaptive tuned vibration absorbers, resonator absorber, seismic protection devices and, as shown in [9], also for electric capacitors.

In order to point out the variations in the magnetorheological elastomer's microscopic properties as a result of filling the polymer matrix with magnetic microparticles, MREs composed from Fe particles, obtained by thermal decomposition of $Fe_2(CO)_9$ and a polymer matrix formed from dimethylsiloxane and dibutyltindilaurate benzyl silicate, were investigated by means of X-ray diffraction (XRD) and small-angle neutron scattering (SANS) [10].

The new samples studied in this paper are based on a magnetorheological elastomer containing Fe microparticles, prepared as shown in [11, 12].

The main purpose of the present work is to investigate the microstructure, the surface magnetic domains and the elastic properties of the samples, at nanoscale level, using the atomic force microscopy technique (AFM).

EXPERIMENTAL DETAILS

The materials used to prepare the MREs samples include silicone rubber (RTV3325, Rhône–Poulenc), catalyst (60R, Rhône–Poulenc), silicone oil (Merck), and stearic acid (S4641773, Merck). Soft magnetic carbonyl iron (CI) from Sigma with average diameter of 5.0 μm was used as a dispersible microparticle. The preparation procedure is described in detail in [9]. At the end of the polymerization, MR elastomers are achieved as disks with diameter of 20 mm and thickness of 1 mm.

The MRE samples were denoted as follows: S_{o1} and S_{m1} (75% silicone rubber, 20% MR suspension, and 5% catalyst), S_{o2} and S_{m1} (55% silicone

rubber, 40% MR suspension and 5% catalyst), S_{o3} and S_{m1} (35% silicone rubber, 60% MR suspension and 5% catalyst). The indexes «o» denote the isotropic MREs, while the indexes «m» denote the anisotropic MREs.

Earlier investigations of magnetorheological elastomers composed from Fe particles, obtained by thermal decomposition of $Fe_2(CO)_9$ and a polymer matrix formed from dimethylsiloxane and dibutyltindilaurate benzyl silicate by means of X-ray diffraction (XRD) and small-angle neutron scattering (SANS), are described in detail in [12].

For imaging the surface topographies we used non-contact operating mode (NC-AFM). The cantilever had a nominal length of 125 mm, a nominal force constant of 40 N/m, and oscillation frequencies in the range of 275–373 kHz. We used horizontal «line-by-line» flattening as planarization method.

For magnetic surface properties characterization we used the Magnetic Force Microscopy (MFM) module (pre-magnetized tip, sensitivity 1–2 Oe) in two-pass technique.

The elastic properties of the samples were measured using both force/distance spectroscopy and the nanoindentation modes (down/up speed of Z scanner extension is 0.3 μm/s).

RESULTS AND DISCUSSION

XRD and SANS Investigations. Analysis of XRD relative intensity modifications of different lattice planes with Fe microparticle concentration variation and polymerization applied magnetic field (Fig. 1) showed that a small crystallographic texture effect takes place in the sample for higher

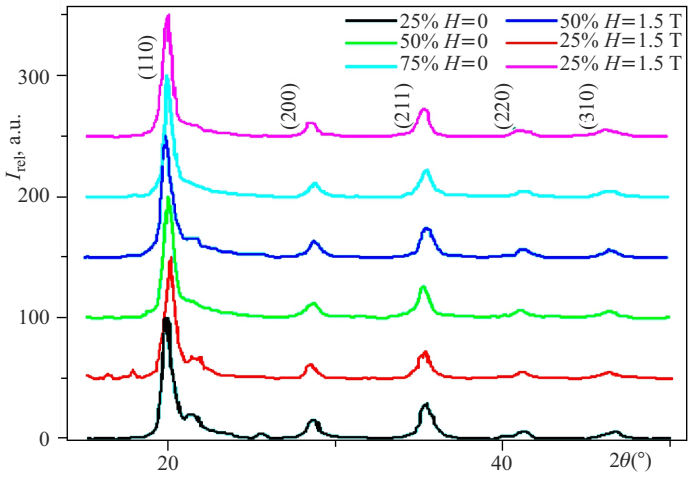

Fig. 1. Diffractograms of elastomers with Fe microparticles (in various concentrations) by using MoKα radiation

Fe concentrations. For the samples polymerized in magnetic field a larger texture effect is detected due to a more uniform relative orientation of the particles.

The SANS scattering in the samples revealed a power-law behaviour $I(Q) \sim Q^{-\alpha}$ with the exponent $3 < \alpha < 4$. Thus, at all microparticle concentrations, the elastomer is characterized as a surface fractal with the dimension D_s as shown in Table 1.

Table 1. Dimension of the surface fractal for different microparticle concentrations in MRE

Particle concentration, %	D_s	Reference
25	2.3 ± 0.1	[12]
50	2.2 ± 0.1	[12]
75	2.1 ± 0.1	[12]

Surfaces Topographies and MFM Images. The magnetorheological elastomer surfaces were already investigated by other authors using tapping mode AFM (T-AFM) technique in order to detect the magnetic regions from the phase signals [13]. In phase images obtained by T-AFM, a higher modulus material typically induces a higher phase offset and appears lighter as opposed to a softer phase that appears darker. But this method is indirect and less accurate than the MFM method which could provide images of the differences between the regions with different magnetic properties. In Fig. 2 are shown the MFM images of MRE samples.

The images of the magnetic domains at the surfaces of the samples show the tendency of agglomeration of the magnetic particles in the case of anisotropic MREs with high concentration (40 wt%, 60 wt%). This is in good agreement with the results reported by Fuchs et al. [14] who found that the effect appears for microparticles with small diameters, and it is less evident for the diameters higher than 9 μm. We notice that the ferromagnetic clusters tend to align in a preferential direction for the sample with concentration of 40 wt%, while for the sample with higher concentration, a relative distorted alignment was detected at long distances.

The MFM images allow us to measure the average diameters of the ferromagnetic particles, using the line profile scan mode of the AFM data acquisition programme applied for 20 different regions of the samples. It was found that the average diameter of the microparticles for the isotropic samples was 4.7 μm, while for the anisotropic samples it was 5.1 μm. We consider that the difference appears due to the fact that the agglomeration of ferromagnetic particles in the anisotropic samples produces «ghost» magnetization in the space between particles. They distort the MFM images affecting the accuracy of the measurements.

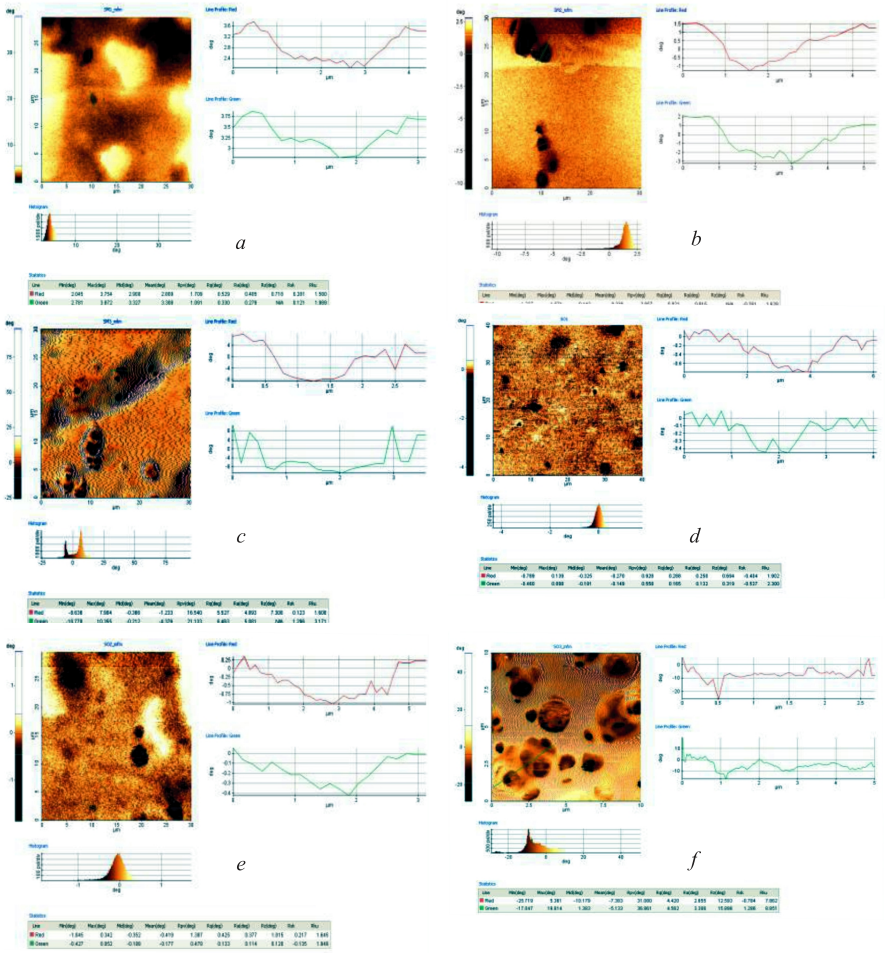

Fig. 2. MFM images of the surfaces of anisotropic (a–c) and isotropic (d–f) MR elastomer samples with different MR suspension concentrations of 20% (a, d), 40% (b, e), and 60% (c, f). The scanned areas are 30×30 μm and 10×10 μm

Nanoindentation Data. As reported in [15], AFM was already successfully used to probe the mechanical behavior of polymers with widely different properties, and then we expected to obtain useful and accurate data for the MREs also. Following the steps proposed in [16–18] we recorded the force/distance (F/D) curves and load/unload vs. displacement curves for the pure elastomer matrix and the MRE samples (Fig. 3). Generally, the hysteresis of the loading/unloading curves indicates that the deformation is not fully elastic and partially inelastic. In the case of investigated MREs

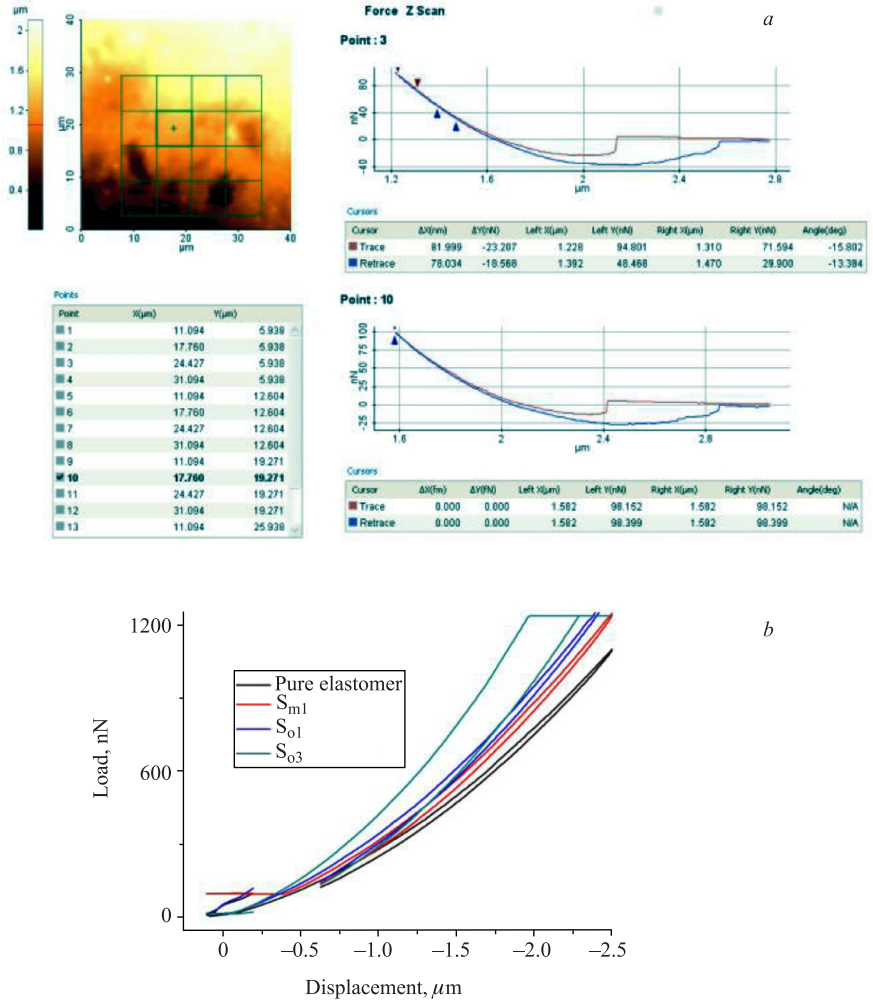

Fig. 3. F/D spectroscopy curves of pure elastomer matrix (*a*) and nanoindentation curves for the matrix and the samples S_{m1}, S_{o1}, S_{o3} (*b*)

the hysteresis is very narrow and it shows that the elastomers have a predominant elastic behaviour.

Adhesion energies for each sample were calculated from F/D data as proposed in [18]. The average values over 16 data points are summarized in Table 2.

As can be noticed from Table 2, the adhesion energy is affected by the ferroelectric particle concentration and by the isotropic or anisotropic

Table 2. Adhesion energy obtained from F/D curves when considering the contact area of the tip on the MRE surface with a normal vector

	Matrix	S_{o1}	S_{o2}	S_{o3}	S_{m1}	S_{m2}	S_{m3}
Adhesion energy (J)	$194 \cdot 10^{-15}$	$188 \cdot 10^{-15}$	$181 \cdot 10^{-15}$	$175 \cdot 10^{-15}$	$78.5 \cdot 10^{-15}$	$33 \cdot 10^{-15}$	$21 \cdot 10^{-15}$

character of the MRE. In addition, it was found that in the regions with high ferroelectric particle accumulations the adhesion energy is with two orders of magnitude lower than in the regions with pure elastomer.

CONCLUSION

Using AFM images of MREs and MFM and nanoindentation data we were able to: detect the dispersion of the magnetic particles embedded in the elastomeric matrix, measure the diameters of the magnetic particles, observe morphological features such as interdomains of soft and hard segments, mapping the regions with different hardness, measure the adhesion forces.

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