**Silicone rubber based magnetorheological elastomer: magnetic structure tested by means of neutron depolarization and magnetic force microscopy methods**

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**Abstract.** Magnetorheological elastomer samples (MREs) prepared using silicone rubber and spherical Fe microparticles have been investigated by means of neutron depolarization (ND) and magnetic force microscopy (MFM). From MFM analysis it was found the average diameter of the microparticles in the case of the isotropic samples to be 4.85 µm, while for the anisotropic ones, 5.1 µm. It was applied and examined the neutron depolarization process in function the microparticle concentration variation and the sample anisotropy.

**1. Introduction**

It is well known that by introducing magnetic nano or microparticles in an elastic matrix, materials with tunable properties in the presence of external magnetic fields can be produced [1–5]. Based on the deformations and stresses induced in magnetorheological elastomers (MRE) [6-15], different application can be developed: giant magnetoresistors [7], quadrupolar magnetoresistors [7,8], Hall probes [8], deformation sensors [9,10], etc. Magneto-elastic properties of MRE are of high importance in defining their application areas [10]. The combination of different kinds of elastomers, magnetic particles and processes of manufacture may result in the obtaining of materials with a wide variety of properties [11-17].

The properties of these composites are the result of several effects, observable at different length scales and by different techniques. From small angle neutron scattering (SANS) data it was obtained earlier that doping with Fe₃O₄ nanoparticles and applying of a magnetic field during the polymerisation process led to a significant change in the local structure of the elastomer [18–23]. For an elastomer filled with a large amount of Fe microparticles a texture effect is observed by means of SANS, and this effect is larger for the samples polymerised in a magnetic field [19].

In the present paper results on the magnetic structure of a MRE investigated using magnetic force microscopy (MFM) and the neutron depolarization methods are reported.

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2. Experimental

2.1. Samples preparation

The materials used in this study are 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 5.0 μm was used as a dispersible microparticles. Using these materials, three different types of anisotropic MR elastomers were prepared. At first, the mixture of CI and silicone oil was heated and maintained at the temperature of 573 K (±10 % error range) for about 10 min, while the mixture was being homogenized. Stearic acid was then introduced in the mixture when its temperature dropped to 370 K (±10 % error range) with stirring. The as-obtained MR suspension contained 80 % CI, 15 % silicone oil, and 5 % stearic acid in weight. Pre-established amounts of MR suspension were introduced in silicone rubber and then mixed in the presence of the catalyst. A homogenous paste was then achieved containing 75 % silicone rubber, 20 % MR suspension, and 5 % catalyst for the S01 sample, 55 % silicone rubber, 40 % MR suspension and 5 % catalyst for the S02 sample, and 35 % silicone rubber, 60 % MR suspension and 5 % catalyst for the S03 sample with all in a weight fraction.

The following step was the introduction of the samples between two parallel glass plates; the distance between the plates was fixed at the 1 mm (±10 % error range). Further, the formed ensemble was introduced for 24 hours between the magnetic poles of a Weiss electromagnet (Phylatex type, Germany) of 50 0 kA/m fixed magnetic field intensity. The direction of the magnetic field intensity was perpendicular to the surface of the samples (SM1, SM2, SM3). At the end of the polymerization, MR elastomers stripes were obtained. For the investigations disks were cut out from the stripes. Each disk has a diameter of 20 mm and thickness of 1 mm [6].

2.2. Magnetic force microscopy

Magnetic force microscopy (MFM) is based on the magnetostatic interaction between the magnetic sample and a magnetic tip placed over the sample surface. The method has high spatial resolution (routinely better than 100 nm) and high surface sensitivity. MFM measurements are carried out using two-pass method. For each raster line, the first pass is made very close to the sample surface (AFM - atomic force microscopy) and yields knowledge of the surface topography. The second pass then follows the recorded topography but at an increased scan height. Obviously, the tip-sample distance must be large enough (usually 50-100 nm) to eliminate (or minimize) the short-range van der Waals' forces that provide the topographic contrast. Then in the second pass the tip is affected only (mainly) by long-range magnetic forces and corresponding MFM image of the sample surface is obtained.

For imaging the surface topographies of samples S01, S02, S03, SM1, SM2, SM3 the noncontact operating mode AFM (NC-AFM) it was used. 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. A horizontal line-by-line flattening planarization method was applied. The MFM images permitted to determine the average ferromagnetic particles diameter, using the line profile scan mode of the AFM data acquisition program applied for 20 different regions of the samples over an area of 500 μm [24].

2.3. Neutron depolarization

Polarized neutrons are useful to extract the magnetic contribution from the total result of the neutron interaction with magnetic media. A neutron technique for direct measurement of the magnetic induction from experimental data is the Larmor precession method. The polarization degree of a neutron beam is depicted by the following relationship

\[ P = \frac{N^+ - N^-}{N^+ + N^-} \]  

(1)
where, $N^+$ and $N^-$ represent the neutrons number with the parallel spin, respectively antiparallel to the external applied magnetic field. The beam polarization degree reducing process is named as depolarization. The theory of depolarization of the neutron beams transmitted through ferromagnetic media was developed by Halpern and Holstein [25]. First experimental application of the neutron depolarization was done by Burgy et al. [26] and Drabkin et al. [27]. This method was developed and applied by Rekveldt [28,29] for the investigation of ferromagnetic materials. At present, this method is exploited at a few neutron centres in the world [30-38]. When the neutron passes through a magnetic cluster, the neutron spin is subjected to the Larmor precession around the local magnetic induction vector. Therefore, from the exponential depolarization curve, the dispersion of the magnetic induction inside the sample may be extracted.

In the present paper a time of flight (TOF) depolarization at Larmor [31,35,38,39] precession experiment, accomplished for testing the magnetic structure of silicone-rubber MRE’s samples, is reported.

The neutron depolarization measurements were carried out on the polarized neutron spectrometer REMUR (see figure 1) installed at the pulsed reactor IBR-2 operated by the Frank Laboratory of Neutron Physics of JINR.

**Figure 1.** The REMUR spectrometer scheme for the polarized neutrons transmission mode experiment.

In figure 2 the geometrical features of the Larmor precession in a basic experiment are presented. A rectangular sample of a soft magnetic plate is placed under an angle $\beta$ to the external applied magnetic field $\vec{H}$. The angle between the external applied magnetic field $\vec{H}$ and the average magnetic induction $\langle \vec{B} \rangle$ in the sample is $\alpha$. The neutron path through the ferromagnetic plate is $d$. The initial polarization of the neutron spin, $\vec{P}_0$ is directed along the applied magnetic field $\vec{H}$ and the angle between the vectors $\vec{P}_0$ and $\langle \vec{B} \rangle$ is $\alpha$. The existence of perpendicular polarization component of $\langle \vec{B} \rangle$ results in the Larmor precession of the neutron spin in the local mean field $\langle \vec{B} \rangle$. The Larmor precession frequency is defined by the absolute value of magnetic induction through the relationship:
\[ \omega_L = \gamma_n < B > \]  

where, \( \gamma_n = 1.83 \cdot 10^8 \text{s}^{-1} \cdot \text{T}^{-1} \) is the gyromagnetic ratio of the neutron. The Larmor precession angle in the sample is given by the expression:

\[ \phi = \omega_L t = \gamma_n < B > \frac{d}{v} \]

where, \( t \) is the time that the neutrons of velocity \( v \) cross the distance \( d \) inside the sample. Using the expression of the momentum, \( p = \frac{h}{\lambda} \), would mean that

\[ \frac{1}{v} = \frac{m}{h} \lambda \]

where, \( m \) is the mass of the neutron, \( h \) is the Plank’s constant and \( \lambda \) is the neutron wavelength [38]. Therefore, the angle of precession can be expressed as \( \phi = \omega_L \lambda \), where \( \omega_L = 0.04633 < B > \cdot d \) (\( \omega_L \) in [Å^{-1}], \( < B > \) in [T], \( d \) in [µm]).

![Figure 2](image)

**Figure 2.** The geometrical features of the Larmor precession in a basic experiment are presented. A soft magnetic plate is placed in an external applied magnetic field \( \vec{H} \). The angle between the external applied magnetic field \( \vec{H} \) and the average magnetic induction \( < \vec{B} > \) in the sample is \( \alpha \). The neutron path through the ferromagnetic plate is \( d \). The initial polarization of the neutron spin, \( \vec{P}_0 \) is directed along the applied magnetic field \( \vec{H} \) and the angle between the vectors \( \vec{P}_0 \) and \( < \vec{B} > \) is \( \alpha \). The perpendicular polarization component of \( < \vec{B} > \) determines the Larmor precession of the neutron spin in the local mean field \( < \vec{B} > \).

In the case of magnetic fluctuations arising along the neutron path through a magnetorheological membrane (see Fig. 3) the following relation is obtained using the depolarization coefficient expression of Halpern and Holstein [25]:
\[ \frac{P}{P_0}(\lambda) = \exp(-A\lambda^2) \]  

(3)

**Figure 3.** The geometry of the depolarization experiment in the isotropic magnetorheological elastomer sample S01 (P₀ and P denotes the initial and respectively final neutron spin polarization; d is the particle diameter; L is the thickness of the sample).

3. Results and Discussions

In figure 4 MFM images from the surface of the isotropic MRE samples with different concentration of carbonyl iron (CI) suspension: (a) 20%; (b) 40%; (c) 60%, are presented. MFM method, provide images of the differences between the regions with different magnetic susceptibility.

In figure 5 MFM images from the surface of isotropic MRE samples, S01 (a) and anisotropic, SM1 (b) samples with 20% particle concentration and respectively 60% (S03, SM3) are given. The images show the tendency of magnetic particles agglomeration in the case of anisotropic MREs with high particle concentration (40 wt%, 60 wt%).

The MFM images can provide the average diameters of the ferromagnetic particles. It was found the average diameter of the microparticles in the case of the isotropic samples to be 4.85 µm, while for the anisotropic ones, 5.1 µm.

**Figure 4.** MFM images from the surface of the isotropic MRE samples with different concentration of carbonyl iron (CI) suspension: (a) 20% (S01); (b) 40% (S02); (c) 60% (S03).
Figure 5. MFM images from the surface of isotropic MRE samples S01 (a) and anisotropic SM1 (b) (75% silicone rubber, 20% MR suspension, and 5% catalyst).

Figure 6. MFM images of the surface of isotropic MRE sample S03 (a) and anisotropic SM3 (b) (35% silicone rubber, 60% MR suspension and 5% catalyst).

The neutron depolarization experimental data and the fitting curves of the normalized polarization versus the wavelength for the isotropic samples S01, S02, S03 and the elastomeric matrix are depicted in figure 7.

Figure 7. Experimental data (symbols) and the fitting curves (lines) of the normalized polarization versus the wavelength for the isotropic samples S01, S02, S03 and the elastomeric matrix.
It can be seen that there is no depolarization effect through the elastomeric matrix. For the isotropic samples S01, S02, S03 the depolarization enhancement with the particle concentration increase is observed.

![Graph showing normalized polarization as a function of neutron wavelength](image)

**Figure 8.** Experimental data and fitting curves of the normalized polarization as a function of the neutron wavelength from isotropic and anisotropic samples S01, SM1 and S03, SM3.

The comparison of the experimental data and fitting curves of the normalized polarization as a function of the neutron wavelength from isotropic and anisotropic samples S01, SM1 and S03, SM3 is presented in figure 8. For low particle concentration, the depolarization in the case of anisotropic sample overcomes the depolarization in isotropic one. On the contrary, for the highest particle concentration the depolarization for the anisotropic sample is lower than in the anisotropic one.

In table 1 the results of the neutron depolarization curve fits are given. The parameter A describes the magnitude of depolarization process.

| No. | Sample | A   |
|-----|--------|-----|
| 1   | S01    | 0.21|
| 2   | S02    | 0.59|
| 3   | S03    | 0.93|
| 4   | SM1    | 0.25|
| 5   | SM3    | 0.58|

The depolarization process depends on the number of the magnetic fluctuations arising along the neutron path (through the mean square induction fluctuations) and the mean size of the magnetic inhomogeneities.

Modelling the depolarization process through the magnetorheological isotropic and anisotropic membrane details on the magnetic particles distribution and particle mean size can be obtained.

**4. Conclusions**

Magnetorheological elastomer samples (MREs) prepared using silicone rubber and spherical Fe microparticles have been investigated by means of neutron depolarization (ND) and magnetic force microscopy (MFM). From MFM analysis it was found the average diameter of the microparticles in the case of the isotropic samples to be 4.85 µm, while for the anisotropic ones, 5.1 µm.
Further it was examined the depolarization process with the microparticle concentration variation and with the sample anisotropy. The development of a model for processing de neutron depolarization data is in progress.

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References
[1] Abramchuk S, Kramarenko E, Stepanov G, Nikitin L, Filipcei G, Khokhlov A, Zrinyi M 2007 Polym. Adv. Technol. 18 883
[2] Stepanov GV, Chertovich AV, Kramarenko EYu 2012 J. Magn. Magn. Mat. 324 3448
[3] Lopez-Lopez MT, Durán Juan DG, Iskakova, LYu, Zubarev AYu 2016 Journal of Nanofluids 5(4) 479
[4] Stolbov OV, Yu L. Raikher YuL, Balasoiu M 2011 Soft Matter 7 8484
[5] Andriushchenko P, Nefedev K & Stepanov G 2014 Eur. Phys. J. B 87 11 doi:10.1140/epjb/e2013-31097-1
[6] Bica I, Liu Y D, Choi H J 2012 Colloid. Polym. Sci. 290 1115
[7] Bica I 2010 Mater. Sci. Eng. B 166 94
[8] Bica I 2012 J. Ind. Eng. Chem. 18 483
[9] Bica I 2012 J. Ind. Eng. Chem. 18 1666
[10] Bica I, Balasoiu M, Kuklin A I 2012 Solid State Phenom. 190 645
[11] Chertovich AV, Stepanov GV, Kramarenko EYu, Khokhlov AR, 2010 Macromol. Mater. Eng. 295 336
[12] Philippova O, Barabanova A, Molchanov V, Khokhlov A 2011 Eur. Polym. J. 47(4) 542
[13] Bica I, Anitas EM, Bunoiu M, Vatzulik B, Juganaru I 2014 J. Ind. Eng. Chem. 20 3994
[14] Bica I, Balasoiu M, Bunoiu M, Iordaconi M 2016 Rom. Journ. Phys. 61(5–6) 926
[15] Balasoiu M and Bica I 2016 Results in Phys. 6 199
[16] Bunoiu M, Bica I 2016 J. Ind. Eng. Chem. 37 312
[17] Bica I, Balasoiu M, Bunoiu M, Iordaconi M, Cirtina G 2015 J. Optoelectron. Adv. Mater. 17 (9-10) 1379
[18] Balasoiu M, Craus ML, Kuklin AI, et al 2008 J. Optoelectron. Adv. Mater. 10(11) 2932
[19] Balasoiu M, Craus ML, Anitas EM, Bica I, Plestil J, Kuklin AI 2010 Phys. Solid State 52(5) 917
[20] Balasoiu M, Lebedev VT, Orlova DN, Bica I 2011 *Crystallogr. Rep.* **56**(7) 93

[21] Balasoiu M, Bica I, Raikher Yu L, Dokukin E B, Almasy L, Vatzulik B, Kuklin A I 2011 *Optoelectron. Adv. Mater.* **5**(5) 514

[22] Balasoiu M, Lebedev VT, Orlova DN, Bica I, Raikher YL 2012 *JPCS* **351**(1) 012014

[23] Balasoiu M, Lebedev VT, Raikher YuL, Bica I, Bunoiu M 2017 *Journ Magn. Magn. Mater.* **431** 126-129

[24] Iacobescu GE, Balasoiu M, Bica I 2013 *J Supercond Nov Magn* **26** 785

[25] Halpern O, Holstein T 1941 *Phys. Rev.* **59** 960

[26] Burgy M, Hughes DJ, Wallace RJ, Heller RB, Woolf WE 1950 *Phys Rev. B* **80** 953

[27] Drabkin GH et al. 1965 *JETP* **20** 1548

[28] Rekveldt M Th 1973 *Z. Phys.* **259** 391

[29] Kraan W, Rekveldt M Th 1978 *J. Magn. Magn. Mater.* **8** 168

[30] Maleyev SV 1982 *J. de Physique* **43** (C7) 23

[31] Dokukin E, Korneev D, Loebner W, Pasjuk V, Petrenko V, Rzany H, 1988 *J. Phys. Coll.* **49** (C8) 2073

[32] Taketomi S, Itoh S, Endoh Y, Ogawa S, Miyajima H, Chikazumi S 1988 *J. Appl.Phys.* **64**(10) 5849

[33] Mitsuda S, Yoshizawa H, Endoh E 1992 *Phys. Rev. B* 45(17) 9788

[34] Rekveldt M. Th. in Studies of Magnetic Properties of Fine Particles and their Relevance to Material Science (J. L. Dorman and D. Fiorani, eds.). 1992. Amsterdam: Elsevier Science Publishers B.V. pp. 445

[35] Krezhov K, Lilkov V, Konstantinov P, Korneev D 1993 *J. Phys.: Condens. Matter* **5** 9277

[36] Thibaudeau P, Ott F, Thiaville A, Dubuget V, Duverger F, *EuroPhys. Lett.* 93 (2011) 37003.

[37] Rekveldt M Th, Kraan WH 2013 *J. Magn. Magn. Mater.* **329** 105

[38] Kozhevnikov SV, Ott F, Radu F 2016 *Journ Magn. Magn. Mater.* **402** 83

[39] Balasoiu M, Dokukin E B, Kozhevnikov S V, Nikitenko Yu V 1999 *Proceedings of the international school and symposium on small angle scattering* (Book series:KFKI Preprint/Report Series vol 1999 issue 2) part E pp 90-94