Particle concentration effects on the ferrofluids based elastomers microstructure

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Combination of magnetic and elastic properties of magnetic elastomer leads to diverse phenomena exhibited by this material in magnetic fields and opens new possibilities for technological applications. Various structures could be formed inside the material or the already existing structures would be changed due to the application of a magnetic field. A new rubber material containing magnetized anisotropic nanoclusters with the use of ferrofluids is proposed. By means of small angle neutron scattering specific variations of the structure factor and interparticle correlation length with the particle concentration and the magnetic field imposed during polymerization are found and discussed.

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1. Introduction

Magnetic elastomers (ME's) represent a specific class of smart materials responding in a complicated way to the changes of external conditions. ME's are composed of magnetic nanoparticles and a low magnetic permeability polymer matrix. These composites are quite new, and the work on understanding their properties in dependence on the synthesis processes, composition, mechanical and magnetic fields, etc. is nowadays extensively progressing with regard to nano- or microtechnology [1-14].

Employing modern techniques, rubber materials containing anisotropically magnetized particles and/or their clusters could be produced with unique prospects for the use in robotics and biomechanics as functional or model artificial muscles. A new material containing anisotropically magnetized nanoclusters with the use of ferrofluids is proposed.

The ferrofluids (or magnetic fluids) are colloidal dispersions of ferro- and ferri- magnetic nanoparticles stabilized by means of steric or electrostatic methods [15, 16]. The investigations of their structure by means of neutron methods more than 30 years are attracting the interest of specialists [17-22].

The possibility of quasi-equilibrium transformation of a ferrofluid into a solid substance by means of carrier liquid polymerization has been for the first time experimentally verified by Martinet at al. [23]. The ferrofluid polymerized in the presence of an external field forms a texture, the anisotropy of which is a function of polymerization field. A number of measurements of initial susceptibility [24] and magnetization curves [25] and the theoretical analysis of their experimental data [26, 27] have shown this fact.

In the present paper the microstructure properties of a rubber elastomer polymerized with ferrofluid are investigated and modeled by means of small-angle neutron scattering experimental data.

2. Experimental

Preparation of magnetic elastomer (ME)

The magnetic elastomer (ME) is produced by using the procedure described in Ref.[7]. It is composed from (in vol. %): 60%-70% silicone rubber (SR) (RTV 3325PC-Bluestar Silicones SAS); 1% silicone oil (SO), Merk type, with viscosity of ~200 mPas and density of ~ 1040 kg $\cdot$ m^{-3}; 5% catalyst (C), 60R (Rhone-Poulenc) type; 34%-24% Fe_3O_4 ferrofluid [15, 16] based on transformer oil.

A mixture composed of SR and SO is homogenized for 600s with the Silent Crusher apparatus (Heidolph Instruments GmbH and CoKG) at 5000 rpm. Then, at the chamber temperature the ferrofluid is introduced into the mixture and is homogenized for 120 s. Then the catalyst (C) is introduced and the homogenization continues for 60 s, at 6000 rpm.

The polymerization of the magnetic elastomers was realized at several values of the magnetic field induction: B=0.0 T; B=28 mT; B=56 mT; B=112 mT (polymerization in a magnetic field transversal to the sample surface).

The SANS measurements have been performed at the small angle neutron scattering instrument (SANS II) at SINQ (PSI, Villigen, Switzerland). A detailed description of the instrument can be found elsewhere [28].

3. Results and discussion

Small angle scattering is a well-established technique suitable for studies of the microstructure in the nanometer length range of condensed matter objects.

The scattered intensity on an absolute scale for any interacting particulate systems of scatteres can be expressed as:

$$I(Q) = \phi P(Q) S(Q) \quad (1)$$

where: Q is the modulus of the scattering vector defined as $Q = (4\pi/\lambda)\sin(\theta/2)$, with the scattering angle being θ; $\phi = N/V_0$ is the density of particles in the volume V_0 of the sample, $P(Q)$ concerns each particle and is related to its form factor, $F(\vec{Q})$, by

$$P(Q) = \left\langle \left| F(\vec{Q}) \right|^2 \right\rangle$$

with

$$F(\vec{Q}) = \int_{\text{Volume of particle}} (\rho - \rho_0) \exp(i\vec{Q}.\vec{r}) dV$$

ρ and ρ_0 are the coherent lengths densities of the particle and respectively of the polymer matrix.

$S(Q)$ is the interparticle term-the structure factor-related to the spatial distribution of the centres of mass

$$S(\vec{Q}) = \left\langle \sum_{\alpha,\beta} \exp i\vec{Q}(\vec{R}_\alpha - \vec{R}_\beta) \right\rangle$$

$\langle \ldots. \rangle$ denotes a statistical average and is taken over the available positions and orientations of the particles.

In Fig. 1 the experimental curves are shown for the magnetic elastomer samples with 5.88%, 3.9% and 1.27% particle volume concentrations, polymerized in zero magnetic field (P12, P22, P32), in 28 mT (P13, P23, P33), and in magnetic field of 56 mT (P14, P24, P34), respectively.

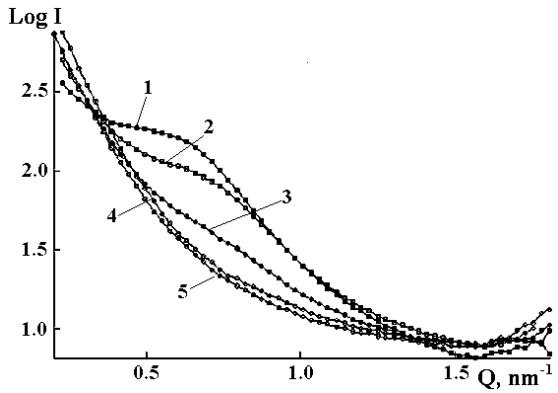

Fig. 1. SANS experimental curves for magnetic elastomer samples with particle volume concentrations 5.88% (1), 3.9% (2), 1.27% (3), polymerized in zero field, for elastomer matrix (4) and the calculated $P(Q)$ factor (5) obtained with PRIMUS program.

Using PRIMUS program [29] from curves 1, 2; 3 and 4, by means of data extrapolation to zero concentration, is obtained the $P(Q)$ factor (curve 5) (Fig.1).

Using the FITTER program [30] to model the extrapolated curve (5), it was found for the averaged form factor of an ellipsoid model:

$$P(Q) = A\int_0^1 \Phi^2 \left[Qa\sqrt{1 + x^2\left(v^2 - 1\right)} \right] dx + B$$

where,

Q is the modulus of the scattering vector;

A is the value of $P(Q)$ for $Q = 0$;

$$\Phi(x) = 3\frac{\sin(t) - t\cos(t)}{t^3}$$

B is the background;

with a and va the half axis and v eccentricity, having the following values $a = 10.61 \pm 0.07 nm$ and, $v = 0.30 \pm 0.002$.

Knowing the form factor from relation (1), the structure factor for each concentration can be obtained. In Fig. 2 experimentally obtained structure factor curves for the ME samples with varying particle concentration are presented for zero magnetic field applied during polymerization.

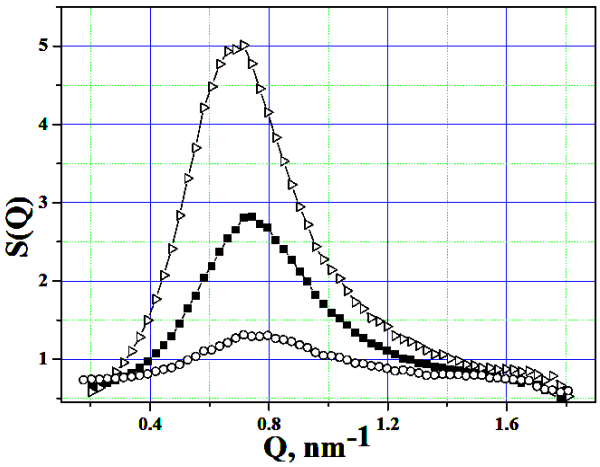

Fig. 2. Structure factor curves of the magnetic elastomer samples with the particle volume concentrations: 5.88% (P12, empty triangles), 3.9% (P22, solid squares) and 1.27% (P32, empty circles) polymerized under zero field.

Similar structure factor curves for magnetic elastomer samples with particle volume concentrations of 5.88%, 3.9%, and 1.27% polymerized under 28 mT and 56 mT are obtained.

From the mean peak position of Gauss fit the interparticle correlation distances are obtained (Table 1).

Table 1. Mean peak position of Gauss fit and correlation distances.

Sample	Particle volume concentration [%]	Polymeriz field [mT]	Gauss fit mean peak position [nm^{-1}]	Correlation length [nm]
P12	5.88	0	0.69+/-0.003	9.10
P22	3.9	0	0.74+/-0.004	8.49
P32	1.27	0	0.75+/-0.013	8.37
P13	5.88	28	0.70+/-0.003	8.93
P23	3.9	28	0.74+/-0.002	8.49
P33	1.27	28	0.79+/-0.007	7.94
P14	5.88	56	0.70+/-0.003	8.97
P24	3.9	56	0.74+/-0.003	8.45
P34	1.27	56	0.77+/-0.006	8.15

The small asymmetry of the structure factors can be explained by the incomplete background matching of scattering intensity.

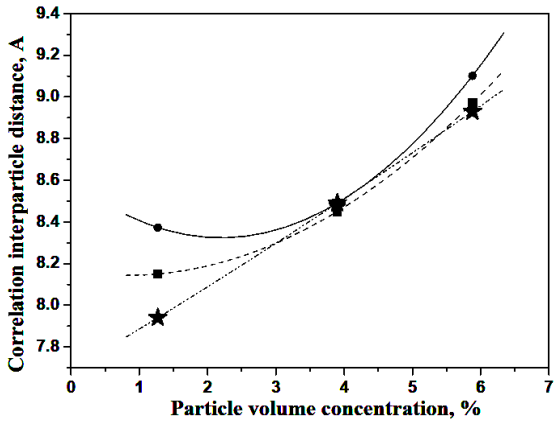

Fig. 3. Variation of the interparticle correlation distance with the particle volume concentration for different values of the polymerization magnetic field: B = 0 (solid circles), 28 mT (solid stars) and 56 mT (solid squares).

In Fig. 3 the interparticle correlation distance obtained by means of small angle neutron scattering measurements is plotted versus the particle volume concentration for each value of the polymerization magnetic field induction. The following dependences of the interparticle correlation distance on the particle volume concentration varying with the induction of the magnetic field applied during polymerization are found:

(a) B=0, $y = 8.6 - 0.025x + 0.057x^2$;

(b) B=28mT, $y = 7.7 + 0.194x + 0.002x^2$;

(c) B=56mT, $y = 8.16 - 0.05x + 0.032x^2$

The results presented in Fig. 3 infer that the particle concentration greater than 3% affects the interparticle correlation distance to a higher extent than the magnetic field in the 28-56 mT range applied during the polymerization process.

On the other hand, for small particle volume concentrations (below 3%) the magnetic field during the polymerization process seems to be a major factor influencing the interparticle correlation length.

In the case of high particle volume concentrations the multi-particle aggregates are forming even if the sample is polymerized under zero field. The aggregate size and the interparticle correlation length increase with the overall particle concentration in the sample. Consequently, the attained structural equilibrium of the system is not influenced by application of the magnetic field with B = 28 mT; however, the field B = 56 mT is able to produce important changes. In the case of small particle volume concentrations the application of the employed magnetic fields affects specifically the local distribution of the particles.

Further analysis will be directed to the clarification of the experimentally detected specific effects of the imposed during polymerization magnetic field upon the interparticle correlation distance in function of the particle volume concentration.

4. Conclusions

Combination of magnetic and elastic properties of magnetic elastomers leads to various phenomena which these composites display under an applied magnetic field. Various structures could be formed inside the material or the already existing structures would be changed due to the magnetic field. By means of small angle neutron scattering, variation of the structure factor with particle concentration and the induction of the magnetic field applied during polymerization are found. The results show that at the particle concentrations greater than 3 vol. % has a stronger effect on the interparticle correlation distance than that of the magnetic field up to 56 mT imposed during the polymerization process. Contrary to this fact, for small particle volume concentrations (of the order of 1 vol. %), the magnetic field applied during the polymerization process affects the interparticle correlation distance to a considerable extent. Further investigations of the magnetic SANS and magnetization measurements are required for the description of the magnetic microstructure and properties of the textured magnetic elastomers.

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