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2008 J. Phys.: Condens. Matter 20 204121

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# Motion of ferroparticles inside the polymeric matrix in magnetoactive elastomers

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Received 5 April 2008

Published 1 May 2008

Online at [stacks.iop.org/JPhysCM/20/204121](http://stacks.iop.org/JPhysCM/20/204121)

## Abstract

Ferroelastic composites are smart materials with unique properties including large magnetodeformational effects, strong field enhancement of the elastic modulus and magnetic shape memory. On the basis of mechanical tests, direct microscopy observations and magnetic measurements we conclude that all these effects are caused by reversible motion of the magnetic particles inside the polymeric matrix in response to an applied field. The basic points of a model accounting for particle structuring in a magnetoactive elastomer under an external field are presented.

## 1. Introduction

Highly elastic matrices filled with micro- or nanodisperse ferromagnets make a novel class of smart magnetically controlled materials which have been investigated extensively in recent years. As the subject is rather new, in the literature these composites are referred to under a variety of names, e.g. magnetorheological (MR) elastomers, magnetic gels, magnetoelastics, ferroelasts etc. In our opinion, an adequate term retaining all the essential meanings is *magnetoactive elastomers* (MAEs) [1].

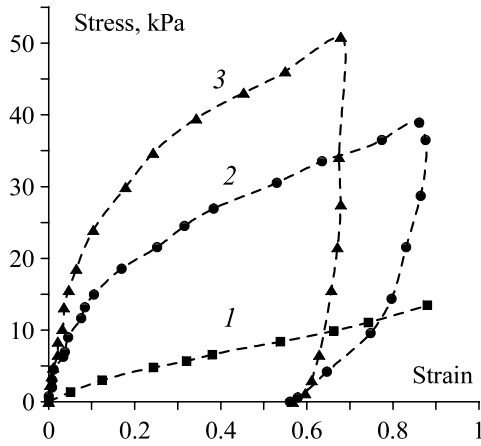
Initially MAEs were obtained and investigated as prospective MR-elastomers, i.e. substances whose elastic properties depend importantly on the applied magnetic field [2–5]. Later on, an understanding came, however, that in fact an essentially new class of functional materials had been born. In the late 1990s new interesting species were added to this stock. One, dubbed *magnetic gels*, was obtained [6–8] by swelling up polymer gels with magnetic fluids. Another, called *magnetoelastics* was prepared by mixing highly elastic polymers with magnetically soft (iron) grains [9, 10].

In the present paper we carry on the studies of a remarkable combination of properties of MAE of the latter

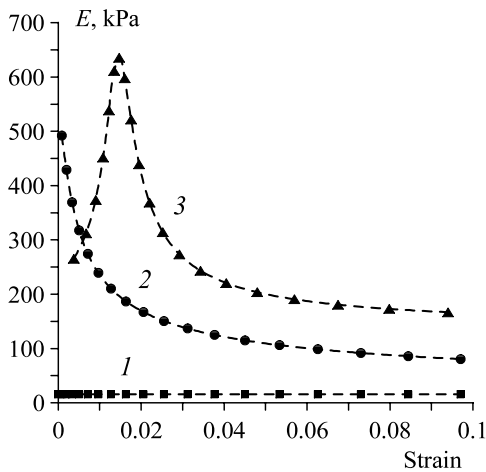
type. Namely: (i) when subjected to a uniform field under zero stress, the samples behave magnetostrictively; they elongate along the field direction by up to 18% [11], (ii) in a non-uniform field the deformations are huge, reaching 300%, (iii) at small strains a large (about hundred times) field-induced enhancement of elasticity occurs. Recently in MAEs a magnetic shape memory effect was discovered [11, 12]. Under a uniform magnetic field a sample loses its elasticity and behaves as a plasticine. After switching off the field, the plasticity disappears, and the sample ‘recollects’ its initial shape. In our opinion, all these effects occur as a result of field-induced motion of the particles inside the matrix. This hypothesis, put forward previously [11, 13, 14], is here supported by direct microscopy observations, magnetic measurements and computer simulations.

## 2. Experimental details

To obtain isotropic MAEs, the components, carbonyl iron with dispersity 2–4  $\mu\text{m}$  and liquid silicone caoutchouc, are mixed in a roller machine, poured out in a mold and polymerized at 120–150 °C; the volume fraction of magnetic phase is 30–35 vol%.



**Figure 1.** Stress–strain dependence for an isotropic MAE at  $H = 0$  (1), 1.2 (2), 2.6 (3) kOe.



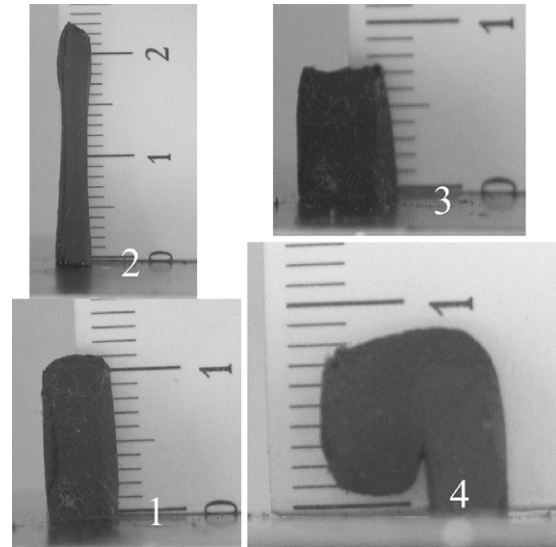
**Figure 2.** Young's modulus as a function of elongation at  $H = 0$  (1), 1.2 (2), 2.6 (3) kOe.

The elastic properties are modified by adding SIEL silicone oil manufactured by GNIICHTEOC. For test purposes, anisotropic MAE samples are prepared by the same procedure but with polymerization carried out under a magnetic field of 800 Oe.

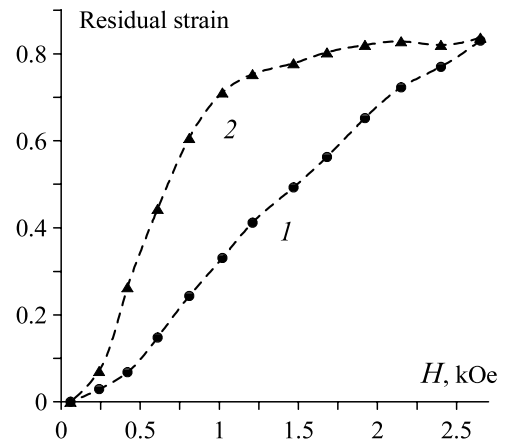
### 2.1. Mechanical behavior

Elastic properties are measured by stretching cylindrical samples under a constant magnetic field imposed along the axis. Figure 1 shows a typical stress–strain dependence. As seen, with the field growth the stress generated by the sample increases, and the rate of this growth is higher at low strain. In figure 2 the measured strain dependence of Young's modulus  $E$  for the same sample is presented. The value in zero field is  $E_0 = 16$  kPa but in a field  $\sim 0.3$  T the effective modulus  $E$  of our MAE exceeds  $E_0$  by about hundred times. This result is in agreement with the evidence of [1, 4]. In [15] similar results were obtained and explained by breaking up of pre-existing particle chains.

As mentioned, a unique feature of MAEs is the magnetic shape memory effect. Qualitative illustration is given in



**Figure 3.** MAE sample in a uniform magnetic field (1) retains its shape after stretching (2), contraction (3) and inflection (4).



**Figure 4.** Residual strain of a sample with  $E_0 = 16$  kPa stretched under magnetic field: after unloading (1), and on diminution of the field strength (2).

figure 3 and quantitative characterization in figure 4. As seen from curve 1, a sample magnetized at 2.6 kOe, stretched by 80% and then unloaded, keeps the acquired strain during the whole time of observation (hours). When the field is decreased, the residual strain goes down along curve 2. The loop formed by these two lines evidences a considerable lag between the residual strain attained with an outright increase of the field and that obtained by first going to a higher field and then reducing it to a given value. Notably, our MAEs display exactly the same qualitative behavior when instead of stretching the sample is contracted. For the particular tested sample this means that under 2.6 kOe it is capable of retaining any once-created strain by up to 80%.

In a uniform magnetic field under zero stress the same cylindrical sample displays magnetostriction up to 18%, as shown in figure 5. The origin of this giant effect we associate with re-structuring of the material. Under the field, the magnetically soft particles acquire magnetic moments and due

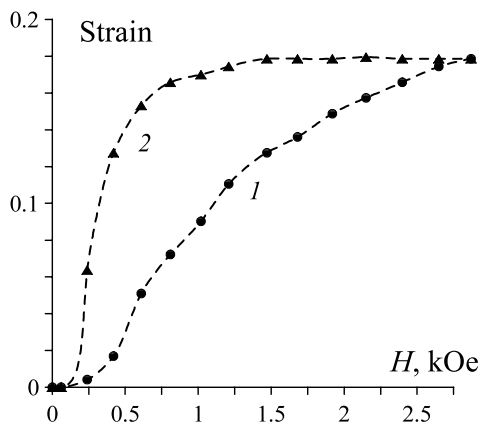


Figure 5. Magnetostriction of MAEs with  $E_0 = 16$  kPa under increased (1) and decreased (2) field.

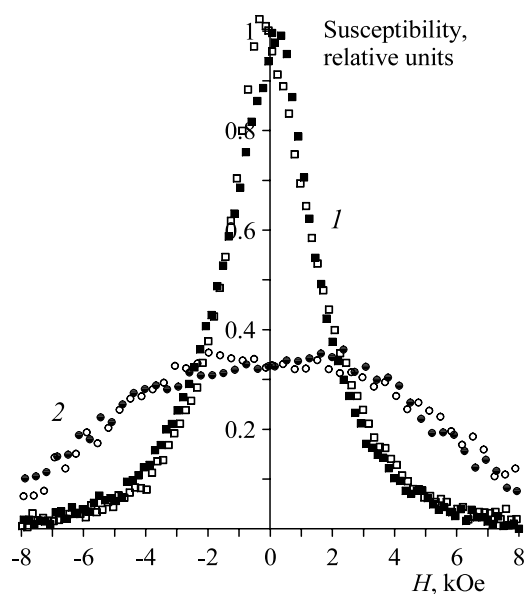


Figure 6. Magnetic susceptibility of a sample along (1) and across (2)  $H_p$  at increase/decrease of the applied field (solid/empty symbols);  $E_0 = 400$  kPa along  $H_p$ .

to the occurring dipole–dipole forces tend to aggregate along  $H$ . As a result, deformation of the sample as a whole occurs. If after that, keeping the field constant, the sample is stretched and then unloaded, it enhances its length, as shown in figure 4. On reducing the field, the strain goes down similarly to curve 2 in figure 4.

### 2.2. Magnetic behavior

Magnetization curves are measured with a vibrating-sample magnetometer Lake Shore VSM 7400s (Department of Magnetofluidynamics, Technische Universität Dresden) and cross-checked with an original set-up (Department of Magnetism, Moscow State University). To estimate the structure effect, anisotropic samples prepared under  $H_p = 0.8$  kOe are taken; their longitudinal modulus is about 400 kPa. Figure 6 presents the effect of structure on the

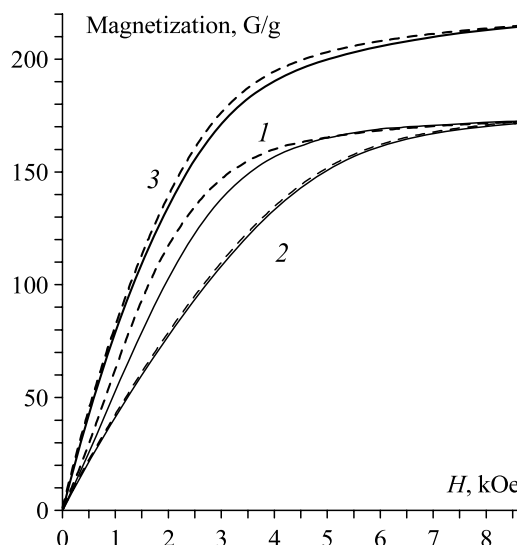


Figure 7. Hysteresis loops of MAE with  $E_0 = 60$  (1) and 400 (2) kPa and of carbonyl iron powder (3) upon increase (solid) and decrease (dashed) of the field.

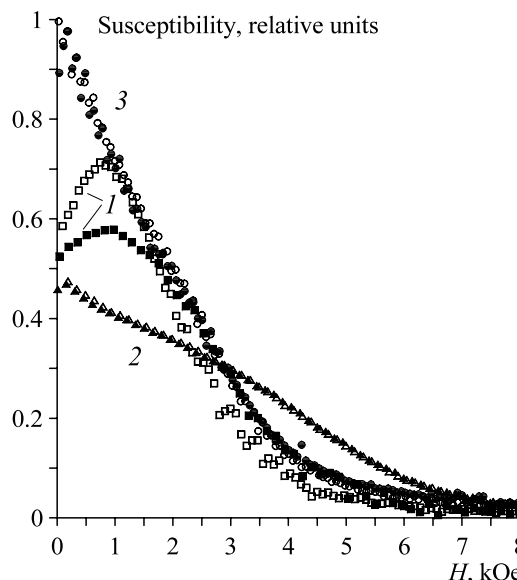
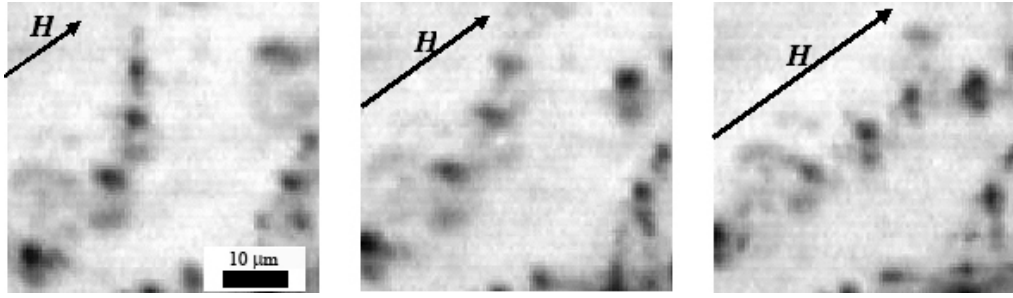


Figure 8. Magnetic susceptibility at increase/decrease of the field (solid/empty symbols) for MAE with  $E_0 = 60$  (1),  $E = 400$  (2) kPa, and carbonyl iron powder (3).

magnetic susceptibility defined as the ratio of the increments of the magnetization  $M$  and field strength  $H$ . As seen, the susceptibilities along and across  $H_p$  differ by about three times; the curve of an isotropic sample lies in between those shown in figure 6.

The magnetic anisotropy, being ‘frozen’ in intentionally formed structures, should manifest itself as an induced one in isotropic MAE. Following this idea, a series of measurements on samples with the same magnetic content but different elastic moduli is performed. The obtained hysteresis loops are shown in figures 7 and 8. For comparison, the loop for carbonyl iron powder (filler) is presented. Note that the curves for MAE (2 and 3) are lower than those for the filler (1) in proportion to



**Figure 9.** Microscope observations: formation of chains under a quasistatic field, the arrow length is proportional to the field strength and the process is fully reversible.

the powder content. Differing appreciably in steepness at weak to moderate fields, in a strong field lines 2 and 3 get closer due to the equal quantity of the magnetic filler.

Of all the loops, the widest one pertains to the softest sample, that is yet more evident from the differential curves of figure 8. There the magnetic susceptibility has a maximum around 1 kOe, which for the decrease of  $H$  (line 1, empty symbols) is greater than that for its increase (line 1, solid symbols). Comparison of these curves and those of figure 6 proves structuring of isotropic MAE under magnetization. A possible mechanism for the effect is as follows. As the field grows, the neighboring particles approach each other, grouping in chains. This aggregation yields enhancement of the susceptibility which in a certain interval exceeds the usual diminution due to magnetic saturation. As a result, a maximum of susceptibility occurs. On decreasing the field, the structures survive until lower values of  $H$  than those at which they had once emerged.

Notably, the above-mentioned hysteresis curve resembles qualitatively the one obtained for a mechanical cycle of MAE, see figures 4 and 5. We surmise that this resemblance is not occasional. Indeed, when forming structures, the particles move to closer distances. This process locally deforms the matrix and changes the overall shape of the sample and macroscopic elasticity modulus of the material. Mutual attraction of magnetized particles makes the new state quite stable since the negative gain in magnetic energy is much higher than the increment of the elastic one. If such a magnetized MAE is mechanically deformed, the multi-particle aggregates have a plethora of ways to regroup without enhancement of their joint free energy. As a result, no restoring bulk forces are generated, and the sample behaves as a plastic material. When the field is turned off, the magnetic interparticle forces vanish, and the formerly ‘frozen’ elasticity of the matrix becomes the main driving factor. It makes the polymeric network go back to the initial configuration so that the sample ‘recollects’ its shape. Measurements of this kind on MAE samples differing in the elastic modulus (not presented here) show that the softer the material the more pronounced are the magnetic and mechanical hystereses.

### 2.3. Optical observations

Qualitative evidence of particle motion is obtained with the aid of a metallographic microscope. The test MAE sample is

polymerized on the object-plate, on which around the focus spot magnetic conductors are fixed. The latter transfer the field created by a DC coil and direct it perpendicular to the line of observation. By a rough estimate, the only way possible under such circumstances, the maximal field strength ranged from 2–3 kOe. The pictures obtained with this set-up are shown in figure 9. As seen, on the increase of  $H$  the embedded particles (dark objects) form chains in the direction of  $H$  (arrow). The optical evidence obtained points out two main facts. First, in a MAE with Young’s modulus  $\sim 10$  kPa under a magnetic field of 2–3 kOe a considerable regrouping of particles occurs. Second, in an elastic matrix the particle regrouping process is always reversible.

### 3. Model considerations

To account for the above-mentioned effects in MAEs, the following model is proposed. A sample contains  $N$  identical spherical magnetically soft particles of radii  $a$  positioned at the points  $r_i$ . Each particle magnetizes isotropically and linearly along the local field:

$$\begin{aligned} \mu_i &= (4\pi\chi a^3/3)\mathbf{H}_l(r_i), \\ \mathbf{H}_l(r_i) &= \mathbf{H}_0 + \sum_{j \neq i}^N \frac{3(\mu_j \mathbf{n}_{ij})\mathbf{n}_{ij} - \mu_j}{r_{ij}^3}, \end{aligned} \quad (1)$$

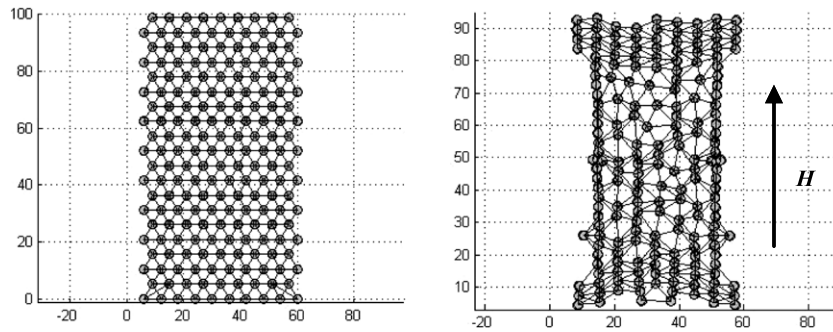
here  $\mathbf{H}_0$  is the external field,  $r_{ij}$  the center-to-center vector of the particles and  $\mathbf{n}_{ij} = r_{ij}/r_{ij}$ . Thence the magnetic part of the energy can be written:

$$U = - \sum_{i=1}^N \mu_i \mathbf{H}_l(r_i). \quad (2)$$

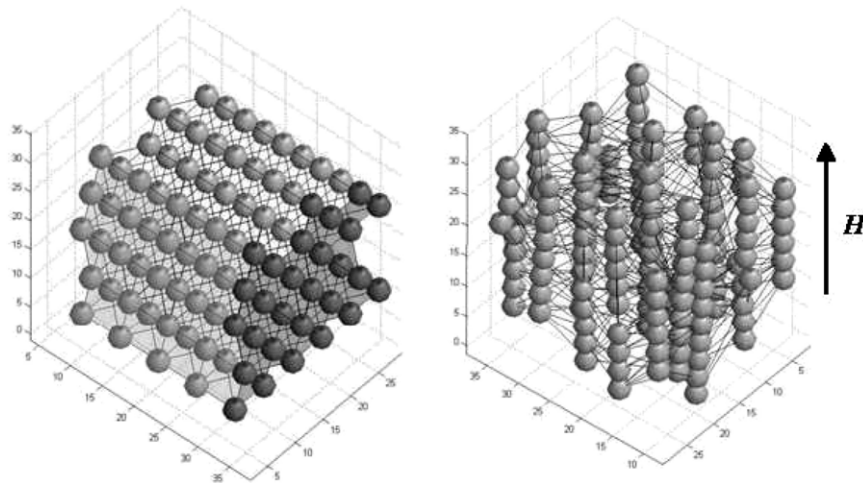
Since the internal magnetic susceptibility of iron particles is high, the external one,  $\chi$ , is close to  $3/4\pi$ . Estimation of the interparticle fields under this assumption shows that they are much lower than  $\mathbf{H}_0$ . Substituting the second of equations (1) into the first, one arrives at a linear set of relations for the components of  $\mu_i$ .

To deal with the elasticity aspect, we use a model [16] developed for granular composites. In that context, the continuum material is replaced by a set of elastic rods connecting particles, so that the force exerted on the  $i$ th particle is written as

$$\mathbf{F}_i^{(el)} = \sum k_{ij}(\mathbf{r}_{ij} - \mathbf{r}_{ij}^0), \quad (3)$$



**Figure 10.** Initial (hexagonal lattice,  $H_0 = 0$ ) and final equilibrium structures of a plane model with  $N = 190$ ; the magnetic field parameter  $aH_0^2/k = 20$ , here  $k$  is the reference value of  $k_{ij}$ ; the coordinate axes are scaled in units of the particle radius.



**Figure 11.** Initial (hexagonal lattice,  $H_0 = 0$ ) and final equilibrium structures of a 3D model with  $N = 125$ ; the magnetic field parameter  $aH_0^2/k = 30$ .

where  $k_{ij}$  is the rigidity coefficient of a rod connecting particles  $i$  and  $j$ . Keeping one boundary of the sample in a fixed position, the set of non-stationary equations

$$\zeta \, dr_i/dt = -\nabla U + \mathbf{F}_i^{(el)} \quad (4)$$

is integrated to  $t \rightarrow \infty$  with  $\zeta$  being the auxiliary viscosity. As a result, one obtains equilibrium spatial configurations occurring in such bead-and-rod systems under static field; examples for plane and 3D model samples are presented in figures 10 and 11, respectively. The simulations show that under a field the particles first group in short (2–4 grains) chains which further on lengthen and, if being parallel, repel each other. Maximal distortions occur at the sample boundaries. The calculations give also the distribution of the particle magnetic moments. As expected, in model MAEs the field-induced growth of chains in weak-to-moderate fields enhances the magnetic susceptibility while at strong fields the latter goes down due to magnetic saturation.

This effect resembles the one inherent to magnetization of solid multi-domain ferromagnets but is essentially different in nature. In a solid ferromagnet the enhancement is due to domain-wall motion while in MAE this is the mechanical motion of the particles already magnetically saturated. The

signs of the mentioned solid-state effect could be noticed in curve 1 of figure 8 at very low field.

#### 4. Conclusions

Basic magnetomechanical properties of MAE are analyzed. Evidence is provided that all the effects essentially originate from regrouping of the magnetic particles inside the elastic matrix. A fundamental proof of that is the established fact of a correlation between magnetic and mechanical hysteresis behavior of the samples studied.

#### Acknowledgments

The work was done under the auspices of RFBR project 06-01-00723. The authors thank V V Rusakov for fruitful discussions.

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