Available online at www.sciencedirect.com
ScienceDirect
Polymer 48 (2007) 488–495
polymer
www.elsevier.com/locate/polymer

Effect of a homogeneous magnetic field on the viscoelastic behavior of magnetic elastomers

G.V. Stepanov [a], S.S. Abramchuk [b], D.A. Grishin [c], L.V. Nikitin [c], E.Yu. Kramarenko [b,c,*], A.R. Khokhlov [b,c]

[a] *State Scientific Center of the Russian Federation, Institute of Chemistry and Technology of Organoelement Compounds, sh. Entuziastov 128, Moscow 111123, Russia*
[b] *Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Science, ul. Vavilova 28, Moscow 119991, Russia*
[c] *Physics Department, Moscow State University, Moscow 119992, Russia*

Received 3 August 2006; received in revised form 13 October 2006; accepted 16 November 2006
Available online 13 December 2006

Abstract

Viscoelastic behavior of highly elastic magnetic elastomers has been studied by three different experimental techniques: elongation, static and dynamic shears. It has been shown that the elastic modulus of the materials increases considerably in an external homogeneous magnetic field of up to 0.3 T (100-fold increase of the tangential modulus has been observed at small 1–4% deformations). The appearance of the new effect of pseudo-plasticity induced by the magnetic field has been observed leading to a considerable (up to 100-fold) increase in the shear loss modulus of the composites.

Keywords: Magnetorheological elastomers; Mechanical properties; Pseudo-plasticity

1. Introduction

''Soft'' magnetic elastomers called magnetoelastic [1–6] or magnetorheological elastomer [7–12], or elastomer–ferromagnetic composite [13], or magnetic gel [14,15] are composites based on highly elastic polymer matrices filled with magnetic particles. The main feature of these materials is their ability of changing mechanical and rheological properties under the action of an external magnetic field. That is why these materials are often referred to as magnetorheological (MR) elastomers. Considerable interest to these materials is due to their high potential for various applications as smart materials, i.e. materials capable to change their properties in a controlled manner.

Tens of papers have appeared during the last few years reporting on the MR elastomers differing in composition and synthetic conditions. They are usually based on silicone polymers and iron particles of nano- or microsizes. In most of the papers the anisotropic or structured materials are studied. These anisotropic samples are usually obtained when the polymerization reaction is carried out in a homogeneous magnetic field. The chain-like structures formed due to interactions of magnetic dipoles are fixed in polymeric matrix. It was reported that these anisotropic materials show a change (up to 60% [9,10,13,16,17]) in the mechanical properties in magnetic fields.

In this paper we study and compare the mechanical behavior of isotropic and anisotropic ''soft'' MR elastomers in homogeneous magnetic fields of various intensities. Three different experimental methods have been used, namely, the behavior of magnetic elastomers at elongation, static and dynamic shears. Both storage and loss moduli of the materials have been measured as functions of material composition and magnetic field intensity at various frequencies of shear oscillations. In contrast

* Corresponding author. Physics Department, Moscow State University, Moscow 119992, Russia.
E-mail address: kram@polly.phys.msu.ru (E.Yu. Kramarenko).

0032-3861/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2006.11.044

to previous reports [9,10,13,16,17] the MR elastomers under investigation show tremendous (up to 100-fold) increase not only in storage but also in loss modulus in the magnetic field of up to 300 mT.

One of the most interesting new phenomena revealed is the appearance of induced pseudo-plasticity of the MR elastomers under the action of the magnetic field. It is found that in some cases the deformation of the material is virtually fixed by the magnetic field. One may say that the material ''remembers'' its shape in the presence of magnetic field.

2. Experimental

Magnetic field responsive elastomers used in this work consist of a highly elastic polymeric matrix filled with magnetic particles. Polymer matrices were synthesized on the basis of compounds ''SIEL'' produced by GNIIChTEOS. Standard compound ''SIEL'' consists of two components A and B. The component A is the mixture of low-molecular vinyl-containing rubber (VR) and a hydride-containing cross-linking agent:

$(CH_3)_3SiO\{[(CH_3)_2SiO]_a-[CH_3(H)SiO]_b\}_x-Si(CH_3)_3$ and
$(CH_2{=}CH)_3SiO[CH_3SiO]_y-Si(CH{=}CH_2)_3$

The component B is prepared from VR and a complex platinum catalyst:

$$(CH_2{=}CH)_3SiO[CH_3SiO]_y-Si(CH{=}CH_2)_3 + \text{Pt-catalyst}.$$

The mechanism of reaction :

$$\equiv SiO-CH{=}CH_2 + HSi\equiv \rightarrow -OSiCH_2CH_2Si\equiv$$

Two types of magnetic filler have been used. The first one was the powder of iron particles with the average size of 2–4 μm. The second one was the powder of iron particles with a wide size distribution of 2–70 μm. To prevent particle aggregation and to enhance their compatibility with the polymeric matrix, magnetic powders have been preliminarily processed by hydride-containing silicone. As a result some moisture from particle surface was removed and the surface became more hydrophobic.

Processed magnetic particles were further dispersed in the compound SIEL. Composition polymerization was performed at 100–150 °C at additional effect of electromagnetic field SHF with the frequency of 2.4 GHz. As a result, the isotropic samples with homogeneous filler distribution have been obtained. This type of materials is called here and below as ''isotropic''.

Another type of materials studied in this work has been obtained when the polymerization reaction was carried out in an external homogeneous magnetic field of 40 mT. Magnetic particles tend to form chain-like structures under the influence of a uniform magnetic field and columnar particle aggregates parallel to the field direction are fixed in the course of polymerization. As a result, materials thus obtained have highly anisotropic properties. We will call this type of materials as ''structured''.

The main characteristics of the samples used in this work are summarized in Table 1. The magnetic filler content is shown in the second column. Composition of the filler was varied. Sample 1 is based on smaller magnetic particles of 2–4 μm while samples 2, 3 and 4 contain mixtures of two magnetic powders in various proportions (see Table 1).

Viscoelastic properties of magnetic elastomers in an external magnetic field were studied by three different techniques. First, the elastic modulus of the materials was determined under sample elongation. Samples with the size of $3 \times 3 \times 10$ mm were placed between the poles of an electromagnet [see Fig. 1(A)]. The upper part of the sample is fixed. The elongation force was applied to the lower part of the sample in the direction perpendicular to the field (the horizontal field lines are schematically shown in Fig. 1(A)). The stress–strain curves have been measured in the magnetic fields of various intensities.

Second, shear modulus of materials has been determined by the standard shear test [9,10], namely, two pieces of the material of the size $10 \times 10 \times 5$ mm were placed between three non-magnetic plates [see Fig. 1(B), these plates are shown by two white vertical rectangles placed on the magnetic pole surfaces and a white thin rectangle in the middle]. The positions of two plates on the magnet S and N surfaces were fixed and the plate in the middle was moving. The direction of the external magnetic field was perpendicular to the shear force during the experiment. The values of the shear modulus in the magnetic fields of various intensities have been calculated from the dependence of the displacement of the middle plate on the shear force.

Third, viscoelastic behavior of the magnetic elastomers has been studied with the use of the rotational rheometer Rheostress RS 150L (HAAKE GmbH). Samples were placed in the measuring unit with the plane–plane configuration [see Fig. 1(C)]. The measuring unit is made from titanium. All measurements were performed at the temperature of 20 ± 0.5 °C. To study the behavior of samples in external homogeneous magnetic field permanent magnets with uniform magnetic field of 0.03 and 0.07 T were placed at a stationary bottom plate of the measuring unit. A rotating moment was acting on the moving upper part of the measuring unit. Magnetic field was directed perpendicular to the shear plane. The measurement of the storage modulus, G', and the loss modulus, G'', has been performed on cylindrical samples of 10 mm in diameter and of 3–5 mm in height at fixed amplitude of deformation.

For all measurements magnetic field was uniform with the accuracy of 97% in the whole volume of the samples.

Table 1
Sample composition

Sample	Magnetic filler content, C_v (vol%)	Fillers (% mass)	
		2–4 μm	2–70 μm
1	30	100	0
2	37	50	50
3	35	75	25
4	35	50	50

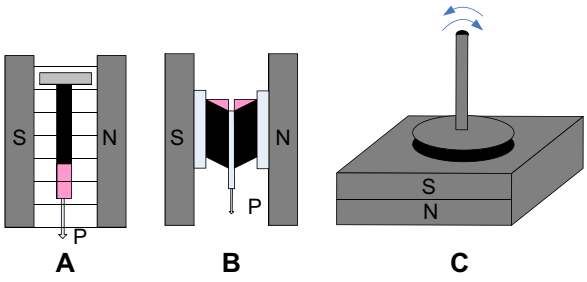

Fig. 1. The schemes of experiments for investigating the stress–strain properties of magnetic elastomers. (A) Elongation test: the initial sample shape is shown in black, the difference between the initial sample length and the length after loading in the magnetic field is shown in pink. (B) Shear test: two deformed samples are shown in black, the difference between the initial and deformed sample shapes is shown in pink; the field direction is the same as in A. (C) Dynamic shear test at oscillation regime, samples were placed between the rotating plate and the upper magnetic surface. The field lines are perpendicular to the upper magnetic surface. S and N are magnetic poles. *P* is the external mechanical force. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3. Results and discussion

3.1. Elongation

The stress–strain curves obtained for the samples 1 and 2 under elongation at various magnetic field intensities are shown in Fig. 2(a) and (b), respectively. Sample 1 is based on small microparticles while sample 2 contains some fraction of larger particles (Table 1).

One can see that the dependence of the stress, σ, on the relative sample elongation, ε, is practically linear in the absence of an external magnetic field for both samples. From the slope of the curve $\sigma(\varepsilon)$ we can define the Young's modulus of the material, E_0. For sample 1 it is equal to 25 kPa and for sample 2 it is equal to 13 kPa.

Under the influence of the field the linearity of the dependence σ on ε is violated for both samples. With an increase in the field intensity non-linear behavior becomes more pronounced, in the range of small elongations (1–5%) the stress increases faster than that at higher elongations.

To characterize this non-linearity one can introduce the tangential Young's modulus that is defined as the derivative of the stress with respect to the strain, $E = \mathrm{d}\sigma/\mathrm{d}\varepsilon$, at every value of ε. As an example, the function $E(\varepsilon)$ for sample 2 in the field of $H = 245$ mT is plotted in Fig. 3. First, one can see that in the magnetic field some stiffening of the material takes place, i.e. the values of E in magnetic field are always higher than the value of E_0 (Young's modulus measured in the absence of any magnetic field). Furthermore, E is a decreasing function of ε. There is a huge (two orders of magnitude) increase of the tangential modulus in the magnetic field at small deformations, while at higher ε the increase in E is only 10-fold. Similar phenomenon has been observed in Refs. [9,11], however, they observed only 2-fold increase in the tangential modulus at small deformations of up to 4%, at higher deformations the increase was even smaller.

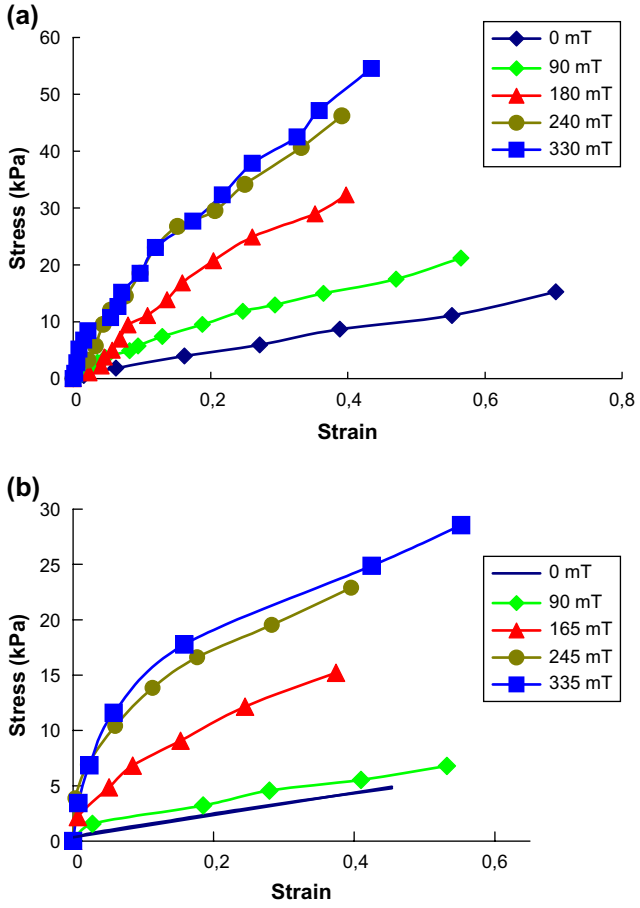

Fig. 2. Stress–strain dependences for samples 1 (a) and 2 (b) measured in uniform magnetic fields of various intensities.

This unusual behavior of magnetic elastomers can be explained as follows. In the absence of the magnetic field the magnetic particles are distributed more or less homogeneously within the material. As soon as an external field is applied, the magnetic moments tend to align with the field to produce a bulk magnetic moment. Besides, the magnetic particles start to interact and tend to form chain (columnar) structures as in

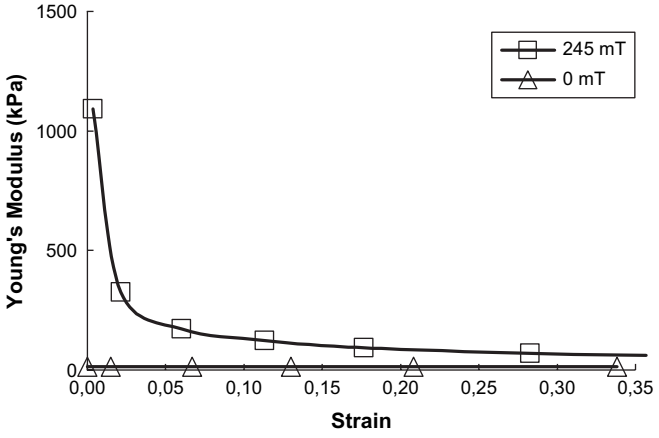

Fig. 3. Dependence of the tangential Young's modulus, $E = \mathrm{d}\sigma/\mathrm{d}\varepsilon$, on the strain, ε, for sample 1 measured without applied magnetic field and in the presence of the magnetic field of 245 mT.

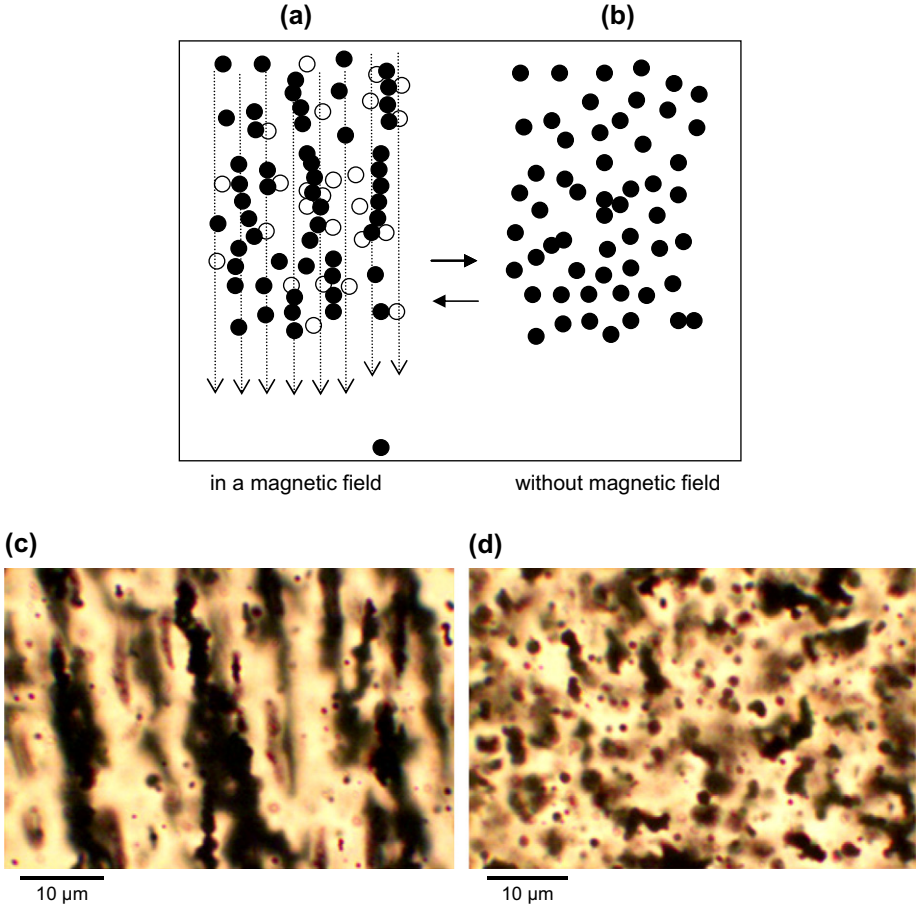

Fig. 4. Schematic representation of magnetic particle displacements under the action of the external magnetic field: (a) in the presence of magnetic field; (b) without field. Photos obtained with the help of optical microscope in through-passing light, demonstrate displacements of magnetic particles under the action of the external magnetic field; (c) in magnetic field of 0.02 T; (d) without field.

ordinary magnetic fluids. The difference is that in fluids the particles can move freely while in elastomers they are connected with the polymeric matrix and their displacements lead to some local deformations of the matrix.

The phenomenon of magnetic particle displacements under the action of a magnetic field has been observed by us in a thin film of composite with the use of metallographic optical microscope. Schematic representation of this phenomenon is shown in Fig. 4(a,b) while in Fig. 4(c,d) we present the photos obtained by optical microscopy. In the absence of the field the particles in isotropic composites are distributed randomly [Fig. 4(b,d)]; under the influence of the field they move to new positions [Fig. 4(a,c)], their initial positions are shown by open circles in Fig. 4(a). The displacement is completely reversible, i.e. when the magnetic field is switched off the particles return to their initial positions. It should be noted that structuring of magnetic particles within composites under the influence of a magnetic field can be also confirmed by the material surface structuring [3].

The equilibrium distribution of particles in the magnetic elastomer in a homogeneous magnetic field is defined by the balance between elastic and magnetic forces. If we increase the intensity of the magnetic field, the displacements of the particles as well as the local deformations of the polymer increase. As a result the microstructure of the material changes, this fact leads to some changes in the mechanical properties.

If the intensity of the magnetic field is fixed, the value of magnetic moment of the particles is also fixed and so are the forces of their interaction. In the absence of any external deformation of the material the particles adopt some equilibrium positions to build the columnar structures within the materials. At small deformations this structure is only slightly disturbed, so that every particle retains its neighbors, and the material shows the elastic behavior. At large deformations particles can change irreversibly their neighbors, this fact leads to the appearance of inelastic deformations due to the presence of the magnetic field (to be discussed later). Non-linear behavior of the stress–strain curves (decrease of the tangential modulus) in magnetic field seems to be connected with the appearance and accumulation of inelastic strains.

The dependences of the tangential Young's modulus, E, on the magnetic field intensity, H, for samples 1 and 2 are shown in Fig. 5. The moduli were calculated at 50% deformations.

The functions $E(H)$ are S-shaped. We believe that the considerable elasticity growth in the field of about 200 mT is connected with the structuring of magnetic powder within the material. Saturation of the $E(H)$ dependences can result

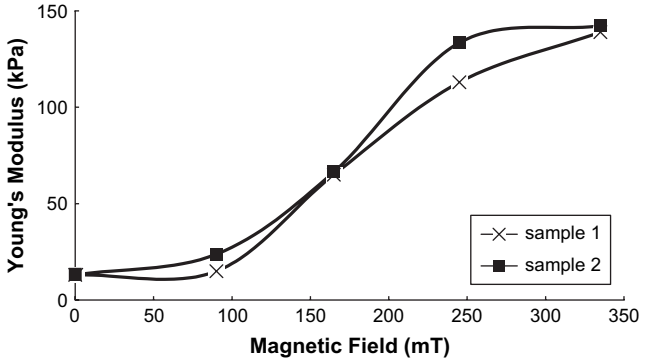

Fig. 5. Dependence of the Young's modulus of samples 1 (cross) and 2 (squares) calculated for 50% deformations on the intensity of the external uniform magnetic field.

from the saturation of particle magnetization. Indeed, according to the literature data the saturation of iron is achieved in magnetic field of 400 mT. Similar behavior of elastic modulus has been observed by us for materials based on other fillers, i.e. magnetite [6].

3.2. Shear

In Fig. 6 we present dependences of the stress on the shear strain for isotropic samples 3 and 4 measured without magnetic field and in the presence of the field $H = 80$ mT. Both samples contain 35 vol% of magnetic filler but the composition of the filler is different. Sample 4 is based on the magnetic powder with higher fraction of large particles (see Table 1).

As can be seen from the slope of the stress–strain curves, the shear moduli of both samples increase with the magnetic field. This behavior is similar to that observed for the elastic modulus of sample 1 measured at sample elongation. And again the value of the tangential modulus depends on the deformation. As an example, in Fig. 7 we show the dependence of the tangential shear modulus on the shear strain obtained for sample 4 under shear for various values of H.

Another conclusion that can be drawn from Fig. 6 is that sample 4 is more rigid than sample 3 both in the absence of

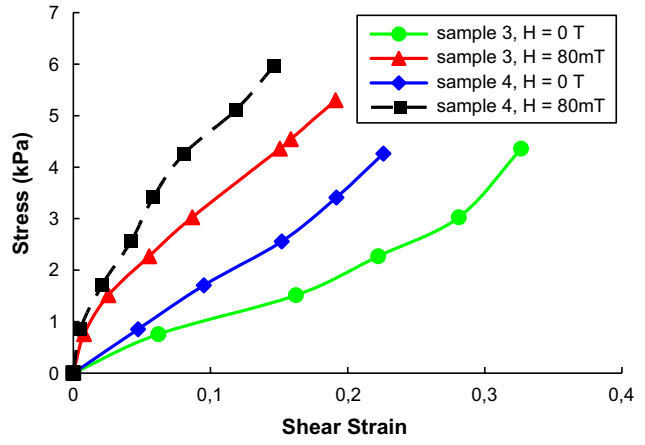

Fig. 6. Dependences of the stress on the shear strain for samples 3 and 4 measured in the absence of the magnetic field and in the field of $H = 80$ mT.

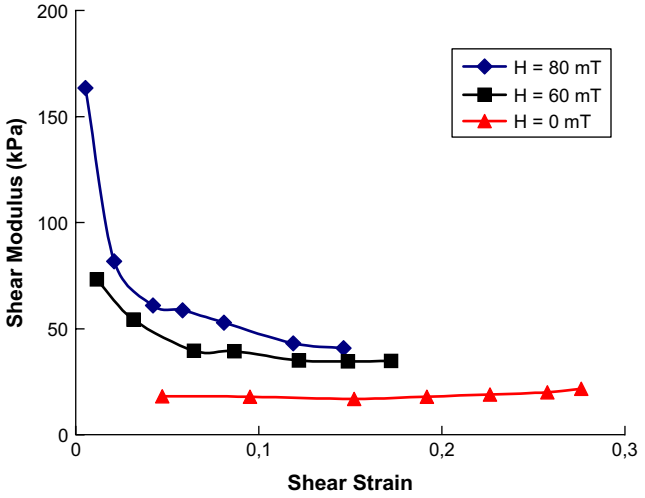

Fig. 7. Dependences of the tangential shear modulus on the shear strain measured in the absence of any magnetic field and in the field of various intensities, sample 4.

any magnetic field and in the presence of magnetic field. This seems to be due to the different compositions of magnetic fillers of samples 3 and 4 (see Table 1). Sample 4 contains a higher fraction of magnetic powder with a wider size distribution, leading to different packing conditions.

Fig. 8 shows the results of the continuous loading–unloading experiments. The shear stress was first increased from zero in a stepwise mode. Once a certain maximum stress was attained (corresponding to the maxima of the stress–strain curves in Fig. 8), stress was stepwise decreased down to zero. In Fig. 8 we present the loading–unloading curves measured in the magnetic field of two different intensities.

One can see that in magnetic field the stress–strain curves show very pronounced hysteresis behavior. It should be noted that without magnetic field the material shows practically elastic response. The area of loading–unloading hysteresis becomes larger with an increasing value of the magnetic field intensity. Similar phenomenon was observed by us for magnetic composites under elongation and compression [6].

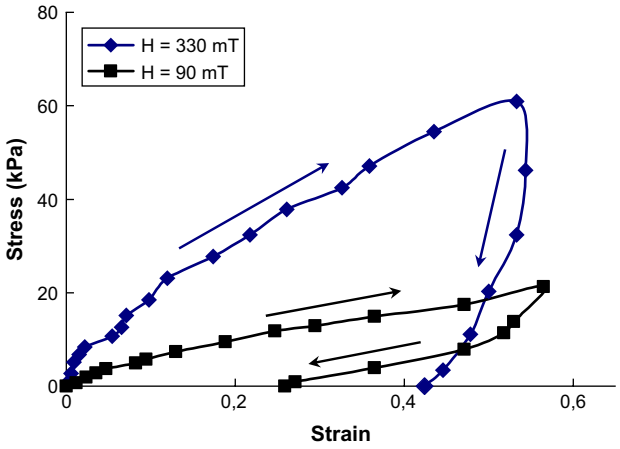

Fig. 8. Loading–unloading curves of sample 3 measured in the magnetic field of various intensities (arrows show the experimental procedure: loading and subsequent unloading).

As can be seen from Fig. 8, the behavior of magnetic composites in external magnetic fields is characterized by a marked residual deformation of the samples after unloading. In the presence of the magnetic field deformation of the sample after complete shear stress release remains practically unchanged with time. At fixed maximal strain its value depends on the field intensity, increasing with the field strength growth. This deformation totally disappears once the magnetic field is switched off. One may conclude that the new effect of pseudo-plasticity induced by magnetic field takes place. This phenomenon may also be called as the shape memory effect since the material ''remembers'' its shape.

The appearance of pseudo-plasticity or memory effect may be explained as follows. Under applied homogeneous magnetic field the magnetic particles within composites tend to align into chains. As a result, internal deformations of the polymer matrix between magnetic particles increase. The filler particles change their initial positions with respect to the state without magnetic field and each of them falls into an equilibrium state due to dipole–dipole forces and internal stresses of the polymer matrix. The whole sample of the composite appears in one of the local energy minimum of the system. Every time an applied external mechanical force breaks the initial chains of magnetic particles in the magnetic field. However, after the rearrangement of magnetic particles new chains are formed and each filler particle falls into a new equilibrium state. Due to dipole–dipole interactions of magnetic particles the sample maintains its new shape in the magnetic field and the whole system appears in a new local energy minimum of the system. If we reduce the external mechanical force to zero without changing the magnetic field we observe some residual strain of the sample. Only when the magnetic field is switched off, the forces of dipole–dipole interaction decrease and the initial shape of the sample is restored due to elastic forces of polymer matrix.

The increase in elastic modulus of the composite can be related with mechanical rearrangement of filler particles under the influence of magnetic field. Average distance between particles along the formed chain decreases significantly and this results in an increase in mechanical stiffness along the chain due to high rigidity of the filler particles with respect to the polymer matrix. These chains play the role of reinforcement fibres of the composite such as high modulus fibres do in usual polymer composites.

We should expect that these chains of magnetic particles form three-dimensional network within polymer matrix, because of the significant increase in its elastic modulus at all stress–strain experiments carried out in our work.

3.3. Rheometric studies

In Fig. 9 the frequency dependences of the storage and loss moduli of sample 3 measured in the absence of the field and in the presence of the magnetic field of $H = 0.07$ T are shown. One can see that both moduli increase significantly under the influence of the field. The behavior of the storage modulus G' in the magnetic field is consistent with the behavior of the elastic modulus measured for samples at elongation and static shear (see the previous sections). As was mentioned above the increase in the elastic modulus can be explained by the structuring of the magnetic particles in the magnetic field with the formation of three-dimensional network of chain-like aggregates.

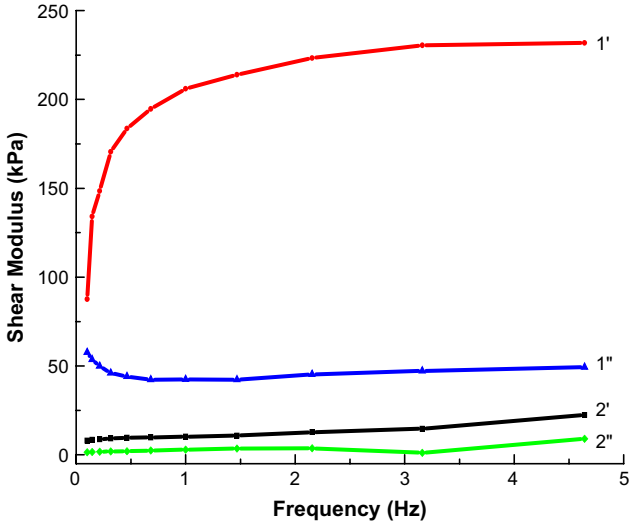

Fig. 9. Dependences of the storage, G′ (1′, 2′), and loss, G″ (1″, 2″), moduli on the frequency of shear oscillations measured for sample 3 without applied magnetic field (2′, 2″) and in the magnetic field of $H = 0.07$ T (1′, 1″).

An increase of the loss modulus G'' in the magnetic field can be explained by the new effect of pseudo-plasticity described above. The strain–stress curves show considerable hysteresis with large residual deformations after the stress release (see Fig. 8). The energy loss in the loading–unloading process is proportional to the area between the loading and unloading curves. This area increases considerably with increasing intensity of the external magnetic field at fixed maximum strain.

On the other hand the value of the loss modulus, G'', is defined by the area of the hysteresis loop of cyclic loading–unloading process. The observed growth of G'' in the course of the torsion oscillations in the magnetic field is a manifestation of an increasing hysteresis loop area which in turn is a manifestation of the effect of pseudo-plasticity.

The phenomenon of increasing G' and G'' with an increase in the magnetic field intensity can be also seen from Fig. 10. In this figure we present the results of the measurements of G' and G'' without magnetic field and in the presence of the field of two different intensities.

The curves 3 and 4 correspond to samples 4 and 3 (see Table 1). Sample 4 contains a larger fraction of 2–70 μm particles. One can see that an increase of both moduli is slightly more pronounced for this sample, however, the difference in modulus values is not significant. This result is consistent with the data obtained in the shear experiments (see Section 3.2).

The curves 1 and 2 are obtained for the samples of the same material composition but synthesized in the presence of uniform magnetic field. Thus, these samples have some anisotropic internal structure already in the absence of the magnetic

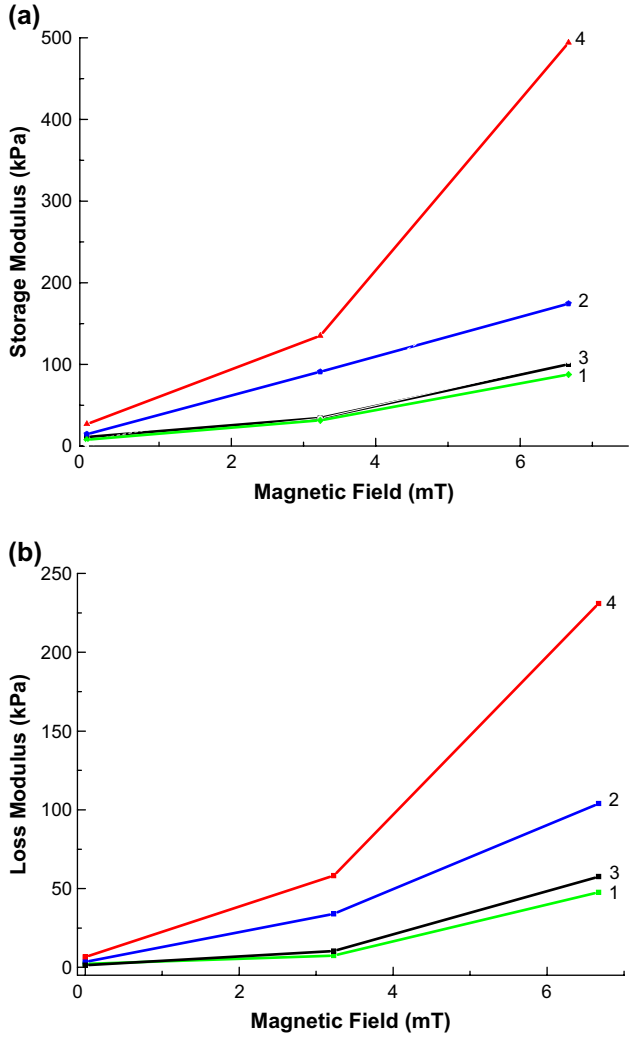

Fig. 10. Dependences of the storage (a) and loss moduli (b) on the field intensity for sample 3, isotropic (1), structured (2); sample 4, isotropic (3), structured (4), stress = 1 Pa, $f = 0.1$ Hz.

field. These structured materials show much more pronounced response to the magnetic field. This phenomenon may be connected with the presence of chain-like structures within the material from the beginning, in this case applied magnetic field causes further strengthening of these structures.

Besides, the largest modulus increase is observed for structured sample of material based on magnetic filler with wider particle size distribution. This is likely due to a higher degree of particle packing in chain-like aggregates for this case. In the case of monodisperse magnetic particles, the chains formed by these particles in the magnetic field have some fraction of regions filled with pure elastomer. We expect that in the case of polydispersed magnetic powders the fraction of these regions in the chains is lower. This is because smaller particles can fill easily the areas between larger particles which are unreachable for large ones. As a result, three-dimensional network of the magnetic chains formed by a polydispersed powder appears to be more rigid than that formed by a monodispersed powder. The same tendency is observed for composites synthesized in the absence of a magnetic field but it is much less pronounced because of the absence of specific interactions induced by magnetic field.

4. Conclusions

In this paper the viscoelastic behavior of "soft" magnetic elastomer has been studied by means of three types of experiments: elongation, static and dynamic shears. The main results are:

- giant increase of the elastic modulus in the external homogeneous magnetic field for both isotropic and structured composites;
- pronounced effect of pseudo-plasticity has been observed in all the experiments;
- giant increase in the loss modulus of the material has been observed.

Under the influence of the magnetic field some structuring of the magnetic particles within the composite takes place. We suppose that chain-like aggregates of magnetic particles form three-dimensional network leading to self-reinforcement of the material and thus, to a considerable increase in its elastic properties. In the course of the mechanical loading of composites some rearrangement of particles takes place leading to the effect of pseudo-plasticity. This effect is manifested by a considerable increase in shear loss modulus. We believe that such considerable increase of both moduli in the magnetic field (100-fold instead of several fold obtained in the literature) is connected with the fact that the initial elastic modulus of our samples was very small (several kPa), much smaller than that of materials studied by other authors [9,10,13,16,17]. Particles can easily move under the influence of the field to form magnetic structures of denser chains.

Some effect of the size distribution of magnetic particle on the viscoelastic behavior of composites has been found. The detailed study of this effect will be reported elsewhere.

Acknowledgement

The financial support of the NATO Science for Peace program (SfP-977998) is gratefully acknowledged.

References

[1] Levina EF. Russian Patent 2157013; 2000.
[2] Nikitin LV, Kornev L, Mironova LS, Stepanov GV, Samus AN. In: Proceedings of the Moscow international symposium on magnetism. Moscow; 1999. Part 2, p. 231.
[3] Nikitin LV, Stepanov GV, Mironova LS. Polym Sci Ser A 2001;43:443–50.
[4] Nikitin LV, Stepanov GV, Mironova LS. Polym Sci Ser A 2004;46(3):489–509.
[5] Nikitin LV, Stepanov GV, Mironova LS, Gorbunov AI. J Magn Magn Mater 2004;2072–2073:272–6.
[6] Abramchuk SS, Grishin DA, Stepanov GV, Kramarenko EYu, Khokhlov AR. Polym Sci Ser A 2006;48(2):138–45.
[7] Stewart WM, Ginder JM, Elie LD, Nichols ME. US Patent 5,816,587; 1998.

[8] Jolly MR, Carlson JD, Munoz BC. Smart Mater Struct 1996;5:607.
[9] Jolly MR, Carlson JD, Munoz BC. J Intell Mater Syst Struct 1996;7:613.
[10] Shen Y, Golnaraghi MF. J Intell Mater Syst Struct 2004;15:27–35.
[11] Bellan C, Bossis G. Int J Mod Phys B 2002;16(17–18):2447–53.
[12] Bossis G, Abbo C, Cutillas S, Lacis S, Metayer C. Int J Mod Phys B 2001;15:564.
[13] Zhou GY, Jiang Z. Smart Mater Struct 2004;13:309–16.
[14] Zrinyi M, Gacs J, Simon C. WO Patent 9702580; 2006.
[15] Szabo D, Szeghy G, Zrinyi M. Macromolecules 1998;31:6541–8.
[16] Carlson JD, Jolly MR. Mechatronics 2000;10:555–69.
[17] Demchuk SA, Kuzmin VA. J Intell Mater Syst Struct 2002;75: 396–400.