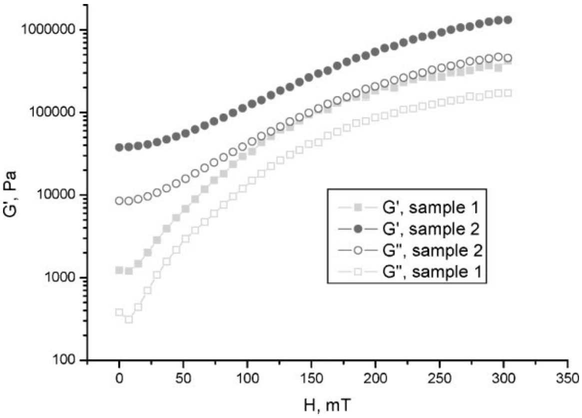
New Composite Elastomers with Giant Magnetic Response

A. V. Chertovich, G. V. Stepanov, E. Yu. Kramarenko,* A. R. Khokhlov

Novel magnetorheological elastomers (MRE) based on a highly elastic silicone rubber filled with carbonyl iron magnetic particles of 3–5 and 3–50 μm are synthesized. The effect of an external homogeneous magnetic field on the viscoelastic properties of these materials is studied by dynamic experiments (shear oscillations on a rheometer). It is shown that the magnetic response of the MRE increases with a decrease of the strain. At 1% deformation both the storage and loss moduli of the new MRE demonstrate a giant response to the magnetic field, namely, an increase of more than two orders of magnitude in both moduli in a field of 300 mT is observed. In addition, these new MREs show a twofold increase of the damping ratio, which is important for their application as tunable vibration absorbers.



Introduction

Magnetorheological (MR) materials – that is, materials whose rheological properties can be varied by application of a magnetic field – find nowadays a wide range of applications, in particular, in intelligent systems of shock absorbers, playing an important role in automotive vehicle, aviation, vibration controls, etc. Traditional MR materials are magnetorheological fluids (MRF), being micron-sized magnetic particles dispersed in non-magnetic viscous media such as oil. They undergo rapid, reversible and huge (of the order of 10^6 times) changes in apparent viscosity under application of a magnetic field. A new type of MR material – magnetorheological elastomers (MRE) – has appeared quite recently and already received considerable interest.[1–23] In MREs, magnetic particles are dispersed in a highly elastic polymeric matrix; this matrix keeps its shape, providing some advantages to MREs in comparison with MRFs, in particular, there being no particle sedimentation and material leakage. In addition, the combination of magnetic and elastic forces within the MRE leads to the appearance of some unique properties, in particular, a huge increase of the modulus in magnetic fields[8–11] and the shape memory effect.[8,9] The main findings on the influence of magnetic fields on static mechanical properties of MREs and gels are reviewed in Ref.[12]

Recently, a number of studies have been performed on the dynamic mechanical behavior of MRE materials.[19–23] In particular, in Ref.[21] the effect of the magnetic field on storage and loss moduli has been studied at various strain amplitude and frequencies. An increase of around 50% in the storage modulus in a field of 800 mT was found, while the loss modulus was shown to decrease in a magnetic field.

A. V. Chertovich, E. Yu. Kramarenko, A. R. Khokhlov
Physics Department, Moscow State University, Moscow, 119991, Russia
Fax: +7 (495) 939-2988; E-mail: kram@polly.phys.msu.ru
G. V. Stepanov
State Scientific Center of the Russian Federation, Institute of Chemistry and Technology of Organoelement Compounds, sh. Entuziastov 128, Moscow, 111123, Russia

Macromol. Mater. Eng. **2010**, *295*, 336–341

DOI: 10.1002/mame.200900301

The novelty of our work is that we report on MREs demonstrating a tremendous magnetic response. Dynamic shear tests of viscoelastic properties of the materials show that both the storage and the loss moduli of the new composite materials increase by more than 100 times in a relatively weak field of 300 mT. The influence of the field on the material elasticity and internal friction is analyzed simultaneously.

Experimental Part

Materials

The magnetic field responsive elastomers used in this work consisted of a highly elastic polymeric matrix filled with magnetic particles. Polymer matrices were synthesized on the basis of the compound "SIEL" produced by GNIIChTEOS.[24] The standard compound "SIEL" consists of two components, A and B. Component A is a mixture of low-molecular-weight vinyl-containing rubber (VR) and a hydride-containing cross-linking agent:

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

Component B was prepared from VR and a complex platinum catalyst:

$$(CH_3{=}CH)_3SiO[CH_3SiO]_y{-}Si(CH{=}CH_2)_3 + \text{Pt-catalyst}$$

The mechanism of reaction is: $\equiv SiO{-}CH{=}CH_2 + HSi\equiv \rightarrow -OSiCH_2CH_2Si\equiv$

It has been shown previously[25] that the degree of crosslinking of the polymer matrix varies with the ratio between components A and B in the polymerization mixture. In addition, to decrease the Young's modulus of the polymeric matrix, 75% of the plasticizer, silicone oil, was added.

Two types of magnetic filler were used. The first was a powder of iron particles with average size 3–5 μm. The second was a powder of iron particles with a larger size of 40–50 μm. To prevent particle aggregation and to enhance compatibility with the polymeric matrix, the magnetic powders were preliminary processed by hydride-containing silicone. As a result, some moisture from the particle surfaces 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 with the additional effect of electromagnetic field SHF at the frequency of 2.4 GHz to enhance the polymerization rate and to avoid filler sedimentation. As a result, isotropic samples with homogeneous filler distribution were obtained.

Two types of MRE have been studied in this work. The first one (Sample 1) contains 70 wt.-% carbonyl iron particles of 3–5 μm in size. It has a rather low Young's modulus and we call it the "soft" sample. The second (Sample 2) has a higher fraction of magnetic filler (85 wt.-%) and thus is more rigid. In addition, the magnetic filler used was a mixture of small and large iron particles, in the amount of 50 and 35 wt.-%, respectively. Large magnetic particles were added to enhance the structural properties of the material. Besides, as it has been shown previously,[9] introduction of a fraction of large particles increases the magnetic response of the MRE material.

Measurement of Moduli

The viscoelastic behavior of the magnetic elastomers was studied with the use of a rotational rheometer Rheostress RS 150L (HAAKE GmbH). The scheme of the experimental setup is shown in Figure 1. Samples were placed in the measuring unit, made from titanium, in the plane–plane configuration. A rotating moment was imposed on the moving upper part of the measuring unit. Measurements of the storage modulus, G', and the loss modulus, G'', were performed on cylindrical samples of 10 mm in diameter and of around 5 mm in height in the regime of dynamical oscillations under controlled stress. The frequency and amplitude of the external stress were varied. All measurements were performed at a temperature of 20 ± 1 °C.

To study the influence of the external homogeneous magnetic field, the measuring unit with a sample was placed inside a home-made solenoid fixed on a special stationary table. The internal diameter of the solenoid was 20 mm. The magnetic field within the solenoid was directed perpendicular to the shear plane and was varied via the electric field in the range 0–300 mT. For all measurements, the magnetic field was uniform with an accuracy of 97% in the whole volume of the samples.

In most of the experiments for the softer sample (Sample 1) the amplitude of the harmonic stress was equal to 100 Pa. For the more rigid sample (Sample 2) it was equal to 1 000 Pa. These values of the stress were chosen according to the results of the static measurements (see Figure 2), so that the corresponding deformations were below 10%.

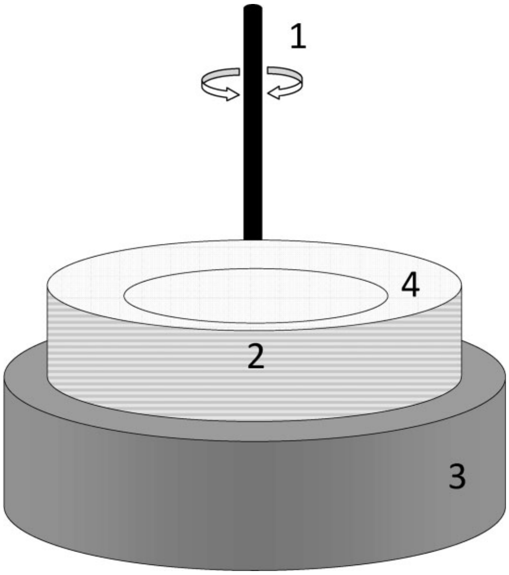


Figure 1. Scheme of the rheometer measuring unit; *1* — actuator of enforced torsion oscillations, *2* — MRE sample, *3* — stationary fixed table, 4 – electromagnet.

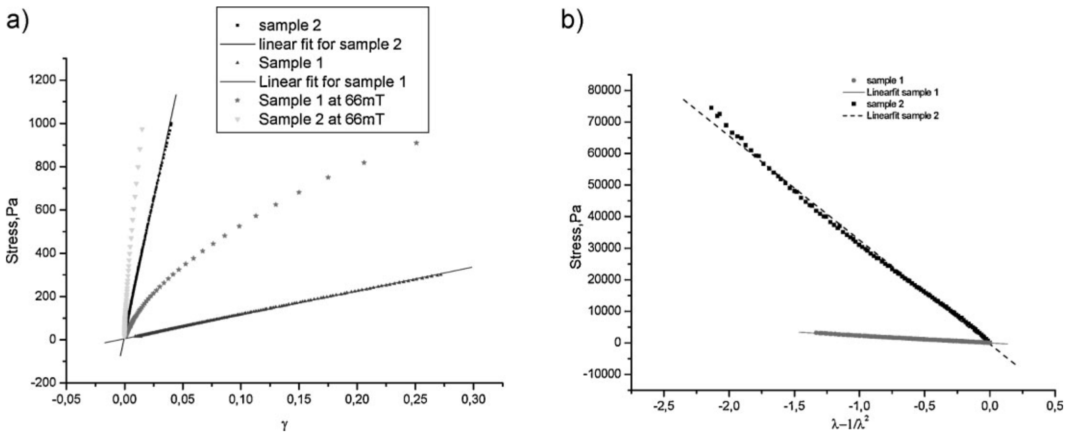


Figure 2. Stress–strain curves measured by two experimental techniques: a) static shear experiments on the rheometer Haake, γ is the shear angle; and, b) uniaxial compression experiments, λ is the relative deformation.

The shear modulus of the MRE in the absence of the magnetic field was also measured by two methods: under static shear and in uniaxial compression. The static shear test was performed in the static regime on the rheometer; the obtained dependencies of the stress on the shear angle are shown in Figure 2a. The uniaxial compression experiment was carried out on a TAPlus setup (Lloyd Instruments Ltd.) with the use of the plane–plane cell. Figure 2b shows the dependence of the stress on the relative compression function λ, defined as a ratio between the length of the deformed sample, l, and its initial length, l_0: $\lambda = l/l_0$. The shear modulus of highly elastic composites under compression can be calculated according to the following well-known relation for elastomers:[26]

$$\sigma = G(\lambda - 1/\lambda^2) \tag{1}$$

Where σ is the nominal stress and G is the shear modulus. Thus, in our experiments the values of the shear modulus were defined as the slopes of the stress–strain curves in Figure 2b.

Values of the shear moduli of the two samples obtained by two different static methods are shown in Table 1. The quite large difference in G of Sample 1 measured under uniaxial compression and shear seems to be because the sample is very soft and barrel-type shapes are formed under uniaxial compression. Some discrepancy between G measured by static and dynamic methods can be due to a dependence of the modulus on the oscillation frequency. As expected, Sample 2, containing a larger amount of magnetic filler, is more rigid – its modulus is approximately 20 times higher than that of the soft sample.

In Figure 2b we plot also the stress–strain curves measured in an external magnetic field of 66 mT. It should be noted that the functions $\tau(\gamma)$ are nonlinear in the external field. This behavior is quite different from that in the absence of the field, when linearity of the stress–strain curves is fulfilled for rather large ranges of deformation. We have observed this phenomenon previously[8,9] and it is connected with structuring of the magnetic filler under the action of the magnetic field. An analogous strong dependence of the shear modulus on deformation was found in dynamic experiments, as discussed below.

Table 1. Shear modulus of MRE measured by three different experimental methods.

Sample	Shear modulus under:		
	Uniaxial compression	Static shear	Dynamic oscillation at low frequencies
	kPa	kPa	kPa
1	2.3	1.2	1.5
2	31	25	19

Results and Discussion

Frequency Dependence of the Moduli

In Figure 3 we plot the dependencies of G' and G'' on the frequency of oscillations measured in the absence of magnetic field and in a field of 80 mT. In agreement with general considerations, the values of both the storage modulus, G', and the loss modulus, G'', are practically constant, increasing only slightly with frequency. At frequencies higher than 10 Hz the quality of measurements is not high, in particular because of a significant contribution from the rotor moment of inertia. In the magnetic field the dependencies $G'(f)$ and $G''(f)$ do not change qualitatively, they only shift to higher values. It should be noted that the frequency dependence of the loss modulus is more pronounced for the more rigid Sample 2, which contained a mixture of small and large magnetic particles.

Strain Dependence of the Moduli

We have found previously that, in magnetic fields, our MREs demonstrate a strong dependence of the static shear

DOI: 10.1002/mame.200900301

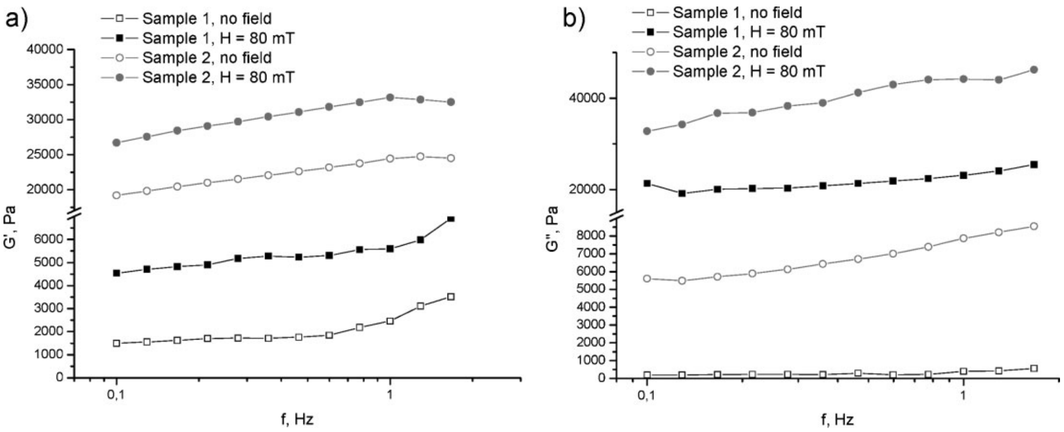


Figure 3. Dependences of G' (a) and G'' (b) on the oscillation frequency for two samples of MRE measured without magnetic field and in a field of 80 mT.

modulus G' on the strain amplitude.[9] The largest magnetic response (increase of the modulus in magnetic field) was observed for small relative deformations of less than 1%.[9] We have found a similar behavior in dynamic experiments. In Figure 4 we plot the stress amplitude dependences of the storage modulus for Sample 1 and 2 measured without magnetic field and in a field of 80 mT (it should be noted that we measure the values of the moduli at a fixed amplitude of the stress defining the amplitude of the deformation). One can see that both samples demonstrate significant stress and, thus, strain dependence of the modulus. All the curves are decreasing functions of τ. However, the rate of the decrease depends on the material composition and also strongly increases when the external magnetic field is applied.

The field influence is more pronounced for the softer sample: its modulus without the field is nearly constant while in the field it rapidly decreases with τ. As a result, the field response of the material is strongly strain dependent. For instance, at a stress amplitude of 15 Pa an approximately 100 times increase of G' is observed, while at a stress amplitude of 1 000 Pa the value of G' increases by only 6 times. The dependence of the modulus on the oscillation amplitude was studied in Ref.[23] and a more recent paper.[19] The deformation was varied in the range 1–10% (this range approximately corresponds to our experiments), however, any strong strain dependence of the magnetic response was not been mentioned. The loss modulus also decreases with increasing strain, similarly to the storage modulus behavior and in contrast to the results obtained in Ref.[21]

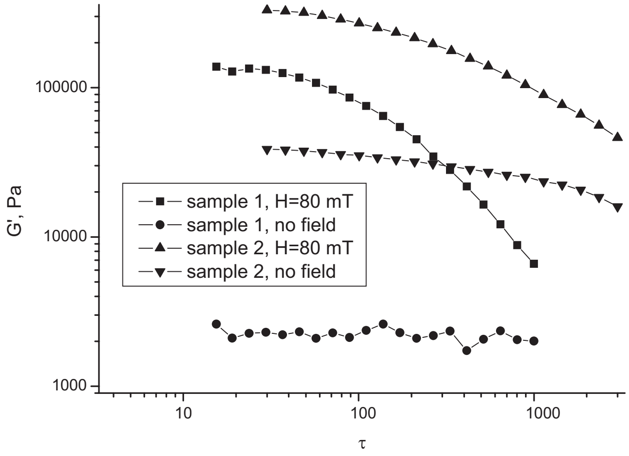


Figure 4. Dependences of the storage modulus, G', on the stress amplitude, τ, measured without magnetic field and in a field of 80 mT.

Magnetic Field Dependence of the Moduli

In Figure 5 we present the dependences of G' and G'' on the magnetic field measured at the oscillation frequency 0.5 Hz for the Sample 1 and 2 (at fixed stress amplitudes of 100 and 1 000 Pa, respectively). At lower frequencies the dependencies are analogous, for higher frequencies (10 Hz and higher) the dependence of both G' and G'' on the field is much less pronounced, perhaps because of the significant experimental error caused by the moment of inertia of the rotor.

One can see that both samples demonstrate huge magnetic response. In a field of 300 mT the storage modulus and the loss modulus increase by two orders of magnitude. The highest difference in the modulus values without the field and in the maximum field is observed for the soft sample (G' increases from 1 to 420 kPa), mainly due to a low initial value of G'; in the maximum magnetic field, the difference in the rigidity of Sample 1 and 2 is much smaller than at $H = 0$. The largest increase of the modulus is observed in a field range of 30–70 mT, at higher values of H

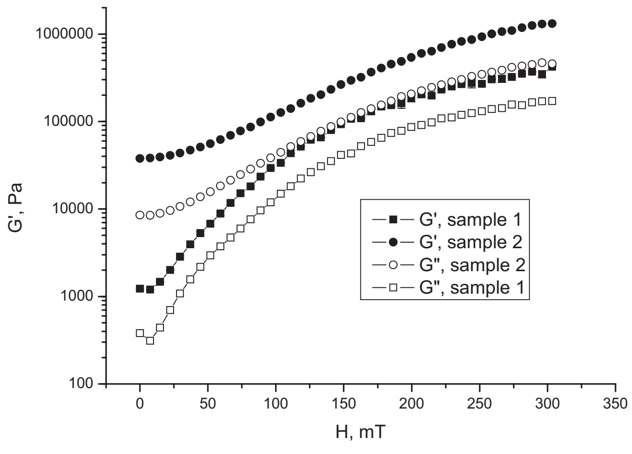


Figure 5. Dependences of G' and G'' on the magnetic field for Sample 1 and 2 at an oscillation frequency of 0.5 Hz.

there is a tendency of the both $G'(H)$ and $G''(H)$ dependencies to saturation.

At first glance the behavior of the storage and loss moduli is quite similar, since both of them are increasing functions of the field. However, it appears that the rate of this increase is different for the two moduli. As a result, the ratio G''/G' is found to grow with the field. The corresponding curves for Sample 1 and 2 are shown in Figure 6. The ratio G''/G' defines the damping properties of the material: it shows how much energy the material absorbs in the form of internal friction and how much elastic energy it conserves. For the soft Sample 1 this ratio increases faster with the field in the range of 0–100 mT. The increase is rather large: from 0.25 at zero field to 0.45 in a field of 150 mT. At higher fields the damping ratio stays practically constant. For the more rigid sample the behavior of G'/G'' is slightly non-monotonous: initial rapid growth from 0.22 to 0.38 over the range $H = 0$–150 mT is followed by a slower decrease to 0.34 at the maximum value of H. A possible explanation of this phenomenon is that initial growth of the field influences at first the viscosity of the plasticizer (silicone oil) within the swollen polymer matrix. Similar to the processes in magnetic fluids, where the viscosity can drop several orders of magnitude under the action of an external magnetic field, the formation of chain-like structures of magnetic particles within MRE hinders the shear flow of plasticizer and influences the elastic modulus, but to a much lesser extent. This phenomenon is more pronounced for the softer sample. At high field, deformations of the matrix are smaller and new chains are not formed; however, the chains themselves become denser, this trend causes the slight decrease of G''/G'.

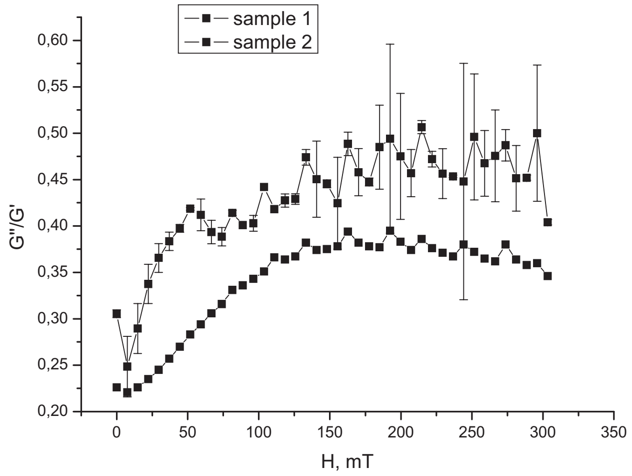


Figure 6. Dependences of the ratio G''/G' on the magnetic field at an oscillation frequency of 0.5 Hz.

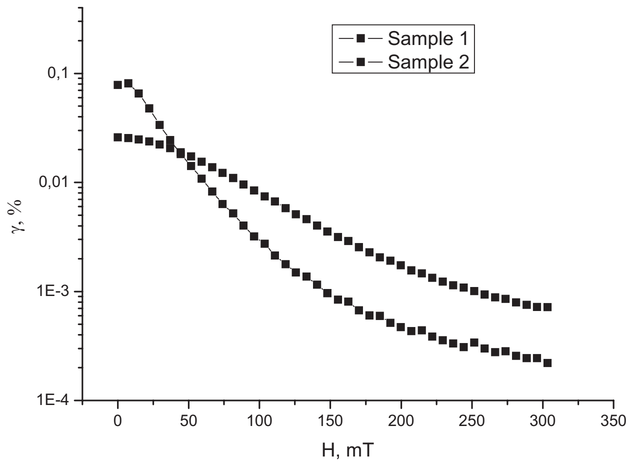


Figure 7. Dependences of the shear angle γ on the magnetic field at a constant stress (100 Pa for Sample 1 and 1 000 Pa for Sample 2) at an oscillation frequency of 0.5 Hz.

The damping properties of our MRE are demonstrated in Figure 7 where the field dependencies of the sample deformation measured at fixed stress are shown. A decrease of more than two orders of magnitude in shear angle amplitude γ is observed. These data are very promising for application of the new MRE for tunable dampers.

Conclusion

The main objective of the paper is the development of the new magnetic field-controlled materials on the basis of highly elastic polymer matrices filled with magnetic particles. The novel feature of these materials is the ability to undergo essential controllable changes in elastic and viscous properties in magnetic field. These peculiar magneto-elastic properties can be used to create new generation of tunable vibration absorbers.

DOI: 10.1002/mame.200900301

We report on the dynamic behavior of new type of magnetorheological elastomers. We have shown that the both storage and loss moduli of the new MRE increase tremendously under the action of the magnetic field. The main novelty of this work is that we obtain for the first time MRE materials demonstrating a huge (up to 400 times) increase of the storage and loss moduli. The ratio between the two moduli defining the damping properties of the material also increases with the field.

Acknowledgements: Financial support from the *Federal Agency of Science and Innovation* and the *Federal Agency of Education* is gratefully acknowledged.

Received: September 24, 2009; Published online: February 16, 2010; DOI: 10.1002/mame.200900301

Keywords: composites; elastomers; modulus; stimuli-sensitive polymers; viscoelastic properties

[1] M. R. Jolly, J. D. Carlson, B. C. Munoz, *Smart Mater. Struct.* **1996**, *5*, 607.
[2] M. R. Jolly, J. D. Carlson, B. C. Munoz, *J. Intell. Mater. Syst. Struct.* **1996**, *7*, 613.
[3] US 5816587 (1998), W. M. Stewart, J. M. Ginder, L. D. Elie, M. E. Nichols.
[4] RU 2157013 (2000), E. F. Levina.
[5] L. V. Nikitin, G. V. Stepanov, L. S. Mironova, *Polym. Sci. Ser. A* **2001**, *43*, 443.
[6] L. V. Nikitin, G. V. Stepanov, L. S. Mironova, *Polym. Sci. Ser. A* **2004**, *46*, 489.
[7] L. V. Nikitin, G. V. Stepanov, L. S. Mironova, A. I. Gorbunov, *J. Magn. Magn. Mater.* **2004**, *2072-2073*, 272.
[8] S. S. Abramchuk, D. A. Grishin, G. V. Stepanov, E. Yu., Kramarenko, A. R. Khokhlov, *Polym. Sci. Ser. A* **2006**, *48*, 138.
[9] G. V. Stepanov, S. S. Abramchuk, D. A. Grishin, L. V. Nikitin, E. Yu. Kramarenko, A. R. Khokhlov, *Polymer* **2007**, *48*, 488.
[10] S. Abramchuk, E. Kramarenko, G. Stepanov, L. V. Nikitin, G. Filipcsei, A. R. Khokhlov, M. Zrinyi, *Polym. Adv. Technol.* **2007**, *18*, 883.
[11] S. Abramchuk, E. Kramarenko, D. Grishin, G. Stepanov, L. V. Nikitin, G. Filipcsei, M. Zrinyi, *Polym. Adv. Technol.* **2007**, *18*, 513.
[12] G. Filipcsei, I. Csetneki, A. Szilgyi, M. Zrinyi, *Adv. Polym. Sci.* **2007**, *206*, 137.
[13] Y. Shen, M. F. Golnaraghi, *J. Intell. Mater. Syst. Struct.* **2004**, *15*, 27.
[14] C. Bellan, G. Bossis, *Int. J. Mod. Phys. B.* **2002**, *16*, 2447.
[15] G. Bossis, C. Abbo, S. Cutillas, S. Lacis, C. Metayer, *Int. J. Mod. Phys. B.* **2001**, *15*, 564.
[16] G. Y. Zhou, Z. Jiang, *Smart Mater. Struct.* **2004**, *13*, 309.
[17] WO 9702580 (2006), M. Zrinyi, J. Gacs, C. Simon.
[18] J. D. Carlson, M. R. Jolly, *Mechatronics* **2000**, *10*, 555.
[19] J. Li, X. Gong, H. Zhu, W. Jiang, *Polym. Test.* **2009**, *28*, 331.
[20] L. Chen, X. Gong, W. Li, *Chin. J. Chem. Phys.* **2008**, *21*, 581.
[21] L. Chen, X. L. Gong, W. H. Li, *Polym. Test.* **2008**, *27*, 340.
[22] T. L. Sun, X. L. Gong, W. Q. Jiang, J. F. Li, Z. B. Xu, W. H. Li, *Polym. Test.* **2008**, *27*, 520.
[23] M. Kallio, T. Lindroos, S. Aalto, E. Jarvinen, T. Karna, T. Meinander, *Smart Mater. Struct.* **2007**, *16*, 506.
[24] DD 297178 C08L83/06; C08L83/00 (1992); NUENCHRITZ CHEMIE GMBH [DE], invs: E. Alekseeva, S. Nanuschjan, KOMPOSITION AUF DER GRUNDLAGE VON FLUESSIGEN METHYLPHENYLVINYLSILICONKAUTSCHUKEN 01.02.1992.
[25] G. V. Stepanov, E. I. Alekseeva, A. I. Gorbunov, L. V. Nikitin, ‘‘Silicone Magnetoelastic Composite’’, in: *Organosilicon Chemistry VI – From Molecules to Materials*, N. Auner, J. Weis, Eds., Wiley-VCH, Weinheim 2005, Vol. 2, p. 779 ff.
[26] A. Yu. Grosberg, A. R. Khokhlov, *Statistical Physics of Macromolecules*, Nauka, Moscow 1989, English translation: AIP, New York 1994.