POLYMERS FOR ADVANCED TECHNOLOGIES
Polym. Adv. Technol. 2007; **18**: 513–518
Published online 1 May 2007 in Wiley InterScience (www.interscience.wiley.com) DOI: 10.1002/pat.923

PAT

Novel highly elastic magnetic materials for dampers and seals: part II. Material behavior in a magnetic field

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Received 30 November 2006; Revised 5 March 2007; Accepted 16 March 2007

The combination of polymers with magnetic particles displays novel and often enhanced properties compared to the traditional materials. They can open up possibilities for new technological applications. The magnetic field sensitive elastomers represent a new type of composites consisting of small particles, usually from nanometer range to micron range, dispersed in a highly elastic polymeric matrix. In this paper, we show that in the presence of built-in magnetic particles it is possible to tune the elastic modulus by an external magnetic field. We propose a phenomenological equation to describe the effect of the external magnetic field on the elastic modulus. We demonstrate the engineering potential of new materials on the examples of two devices. The first one is a new type of seals fundamentally different from those used before. In the simplest case, the sealing assembly includes a magnetoelastic strip and a permanent magnet. They attract due to the magnetic forces. This ensures that due to high elasticity of the proposed composites and good adhesion properties, the strip of magnetoelastic will adopt the shape of the surface to be sealed, this fact leading to an excellent sealing. Another straightforward application of the magnetic composites is based on their magnetic field dependent elastic modulus. Namely, we demonstrate in this paper the possible application of these materials as adjustable vibration dampers. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: composites; reinforcement; mechanical properties

INTRODUCTION

Composite materials consisting of rather rigid polymeric matrices filled with magnetic particles have been known for a long time and are called magnetic elastomers. These materials are successfully used as permanent magnets, magnetic cores, and connecting and fixing elements in many areas. These traditional magnetic elastomers have low flexibility and practically do not change their size, shape and elastic properties in the presence of an external magnetic field.

The new generation of magnetic elastomers (abbreviated as magnetoelasts) represents a new type of composite, consisting of small (mainly nano- or micron-sized) magnetic particles dispersed in a highly elastic polymeric matrix.[1–26] The combination of polymers with magnetic materials displays novel and often enhanced properties. The magnetic particles couple the shape of the elastomer to the external magnetic field. Combination of the magnetic and the elastic properties leads to a number of striking phenomena that are exhibited in response to an applied magnetic field. A giant deformational effect, tuneable elastic modulus, non-homogeneous deformation, and quick response to the magnetic field open new opportunities for using such materials for various applications. More information on the shape change induced by a non-uniform magnetic field can be found in our previous papers.[6,8–11,14]

It has only recently been accepted that the elastic properties of magnetic elastomers can be increased rapidly and continuously by application of external magnetic field.[4,5,7]

If the magnetoelast contains magnetic particles dispersed randomly, there are two basic experimental situations: the compressive force ($\mathbf{F}_x$) and the direction of magnetic field (characterized by the magnetic induction, $\mathbf{B}$) can be either parallel or perpendicular. In our previous papers, we found a 20% and even 100-fold increase of the modulus for magnetoelasts containing randomly distributed magnetic particles.[25,27]

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Elastic materials with tailor-made anisotropy can also be prepared under external field.[5,7,25,26] The anisotropy manifests itself both as a directionally dependent elastic modulus as well as a directionally dependent swelling. The anisotropic composite exhibited an increase of 21.5 kPa in shear storage modulus upon application of a 740 Oe magnetic field.[4,5] Jolly *et al.*[7] have found 0.6 MPa maximum increase in the shear modulus for iron loaded elastomer.

EXPERIMENTAL

Synthesis of composite materials

Type 1 materials

In order to prepare magnetic field responsive PDMS composites (magnetoelasts), carbonyl iron (BASF), Fe_3O_4 (Bayern), Fe, Fe_3O_4•Fe, and γFe_2O_3 particles (prepared by the Institute of Chemistry and Technology of Organoelement Compounds (GNIIChTEOS), Russia) were used as magnetic particles. The concentration of the filler particles was varied between 10 and 30 wt% in the polymer matrix. Poly(dimethyl siloxane) networks were prepared from a commercial product of a two component reagent (Elastosil 604 A and Elastosil 604 B) provided by Wacker Co. These chemicals were used without further purification. Component A contains the polymers and the catalyst with Pt content and component B provides the cross-linking agent. The magnetite particles were dispersed in the Elastosil 604 A. After mixing it up with the Elastosil 604 B component, the solution was transferred into cube shaped mould.

It has to be mentioned that it was not possible to prepare PDMS magnetoelasts with the same cross-linking contents which were prepared from carbonyl iron (BASF), Fe_3O_4 (Bayern) in case of the magnetic powder prepared by GNIIChTEOS. The Fe_3O_4•Fe and γFe_2O_3 magnetic powder retarded the cross-linking reaction. For this reason 20 and 3.5 wt% component B was used, respectively. Because of the retardation from the Fe_3O_4•Fe powder only 10 wt% could be used for the preparation with 20 wt% B component. The settlement of the magnetic particle was strong in these samples. In case of iron particles, 3 wt% B component was used for the preparation.

Type 2 materials

The second type of materials is based on polymer matrices of compounds 'SIEL' produced by GNIIChTEOS. The standard compound 'SIEL' consists of two components A and B. Component A is a mixture of low-molecular vinyl-containing rubber (VR) and a hydride-containing cross-linking agent. Component B is prepared from VR and a complex platinum catalyst.

Magnetic filler was a powder of iron particles with the average size of 2–4 μm. To prevent particle aggregation and to enhance their compatibility within the polymer matrix, magnetic powders have been preliminary processed by hydride containing silicone. As a result some moisture from the 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 under an electromagnetic field super high frequency (SHF) with the frequency of 2.4 GHz.

Materials of the Type 2 have a much lower elastic modulus than the materials of the Type 1.

In order to investigative the effect of a uniform magnetic field on the elastic modulus of the sample, isotropic and anisotropic elastomers were prepared. The synthesis of the elastomers in a uniform magnetic field can be used to prepare anisotropic samples. The detailed description of the preparation was explained in our previous paper.[25]

RESULTS

We have demonstrated that in the presence of built-in magnetic particles it is possible to modify the elastic modulus. The value of a magnetically induced excess modulus G_M^E depends on the concentration and spatial distribution of the magnetic particles as well as on the strength of the applied field. A more significant magnetic reinforcement effect was found for anisotropic samples containing oriented particle chains, instead of randomly distributed particles. If the mechanical stress and the direction of columnar structure as well as the magnetic induction are all parallel G_M^E approaches to 38.9 kPa when the PDMS sample contains 10 wt% iron.[25]

The analytic calculation of the magnetic modulus G_M^E is a rather complicated task due to the fact that the demagnetizing coefficient n_d cannot be given in an analytic form and it depends on the spatial distribution of the magnetic particles in the elastic matrix. We have calculated G_M^E by using an approximation formula for the demagnetizing coefficient and a simple linear relationship between magnetization and field intensity was considered: $M = \chi \cdot H_{eff}$. The proportionality factor χ denotes the magnetic susceptibility of the magnetoelast containing randomly dispersed solid particles.

It was found that at low field intensities the magnetic elastic modulus is proportional to the square of the magnetic induction: $G_M^E \propto B^2$. At high field intensities the magnetization saturates and as a result G_M^E approaches the maximum value $G_{M,\infty}$.

These two limiting cases can be phenomenologically described by the following equation:

$$G_M^E(B) = G_{M,\infty} \cdot \frac{B^2}{a_B + B^2} \tag{1}$$

where a_B represents a material parameter.

At small field intensities $B << a_B$ eqn 1 results in a parabolic dependence

$$G_M^E(B) \simeq \frac{G_{M,\infty}}{a_B} B^2 \tag{2}$$

At high field intensities $B >> a_B, G_M^E(B), G_M^E(B)$ saturates:

$$G_M^E \simeq G_{M,\infty} \tag{3}$$

The parameters of eqn 1 ($a_B$and$G_{M,\infty}$) can be determined by linearization of eqn 1

$$\frac{B^2}{G_M^E(B)} = \frac{a_B}{G_{M,\infty}} + \frac{1}{G_{M,\infty}} \cdot B^2 \tag{4}$$

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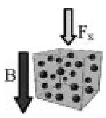
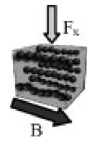
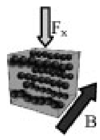
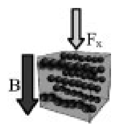
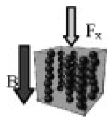
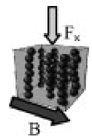
DOI: 10.1002/pat

Table 1. *Gm*, ∞ and a_B parameters for the magnetoelasts

Filler particles	Parameters[a]							
γ Fe_2O_3: 30 wt%, cross-linker: 3.5 wt%	$G_{M,\infty}$	1.85	13.84	4.45	8.78	6.24	**14.01**	13.85
	a_B	5095.31	19497.50	1854.45	6433.38	1024.04	1981.31	862.52
	G_0	46.46	45.70	52.34	52.95	53.26	110.58	112.01
Fe_3O_4•Fe: 10 wt%, cross-linker: 20 wt%	$G_{M,\infty}$	2.79	6.68	4.11	4.85	2.98	**14.09**	8.32
	a_B	2781.40	2425.02	2019.54	1981.82	773.43	1996.36	62200.44
	G_0	35.01	35.15	73.03	73.91	74.71	110.58	109.85
Fe: 10 wt%, cross-linker: 3 wt%	$G_{M,\infty}$	1.42	1.56	8.09	1.33	1.99	**45.71**	33.14
	a_B	1149.70	2317.88	3593.40	7384.30	657.80	1597.35	56369.51
	G_0	10.85	10.43	26.40	25.30	25.95	30.00	29.94
Carbonyl iron: 30 wt%, cross-linker: 3.5 wt%	$G_{M,\infty}$	2.67	2.41	9.19	2.38	2.03	**70.62**	8.55
	a_B	4144.65	4759.41	9065.44	3355.15	2928.52	11505.36	3995.14
	G_0	22.64	22.77	26.00	26.44	26.41	54.25	54.20
Fe_3O_4: 30 wt%, cross-linker: 3.5 wt%	$G_{M,\infty}$	2.02	3.11	5.65	2.27	2.01	**10.77**	5.57
	a_B	2924.77	1363.73	1713.13	831.92	714.00	2841.53	1128.53
	G_0	33.33	33.39	49.12	48.70	48.73	88.88	88.85

[a] $G_{M,\infty}$ [kPa], a_B [(mT)^2], G_0 [kPa].

By plotting the quantity of $B^2/G_M^E(B)$ against B^2, the slope provides the $1/G_\infty$ value, and the intercept gives the ratio $a_B/G_{M,\infty}$. We have determined the parameters $G_{M,\infty}$ and a_B by a linear least square method. We have summarized those data in Table 1 where the increment in the elastic modulus was the highest.

In Fig. 1, the experimental data and the phenomenological approach are presented. It is seen that the agreement between experimental data and phenomenological description is quite satisfactory.

Material behavior in alternating magnetic fields

To study the response of composites to alternating magnetic fields, the following preliminary studies were carried out. The sample of Type 2 material (based on 25 vol% of carbonil iron of 2 μm with the initial Young's modulus of 50 kPa) was placed inside a magnetic solenoid as shown in Fig. 2a. Under the influence of the solenoid magnetic field, the compression of the sample takes place and the position of the upper end of the sample changes. If the voltage and, thus, the magnetic field inside the solenoid is varied, the upper end of the sample vibrates.

The amplitude of this vibration is shown in Fig. 2b for various values of the field intensity and at different frequencies. One can see that the resonance effect is observed at frequencies of 20–30 Hz.

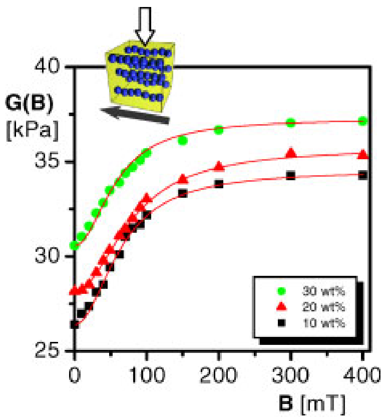


Figure 1. Effect of the elastic modulus on the magnetic field intensity. Solid lines were calculated on the basis of eqn 2. The cross-linker content is 3.0 wt% in every case. The iron content of the elastomers is indicated in the figure. The white and black arrows show the direction of the force and the uniform magnetic field, respectively.

Damping ability of magnetic composites

Two types of experiments were carried out. The first one was connected with damping of free oscillations.

We studied the periodical twisting oscillations of a spherical mass m hung on the end of a cylindrical magnetoelastic sample. A series of cylindrical samples of Type 2 materials with 6 mm diameter and volume concentration of magnetic particles $C_v = 10$, 14.5, 17.5, 21, 25, 30% were investigated. Mass concentration of the plasticizer was 75% and size of iron magnetic particles was 2 μm. A homogeneous magnetic field H was applied in the direction perpendicular to the longest axis of the sample.

As an example, Fig. 3 shows the dependence of the twisting angle α on time t for cylindrical samples with magnetic powder concentrations $C_v = 17.5$ and 30% measured in the absence of an external magnetic field and in a magnetic field of $H = 580$ Oe.

It was found that an increase in magnetic particle concentration or an increase of the intensity of the magnetic field results in a decrease of the oscillation period T (see Fig. 3).

Analysis of the experimental results shows that the magnetic field influences also the value of the logarithmic decrement of vibrations d. We calculated it as $d = \ln(A1/A2)$, where A1 and A2 are two nearest amplitudes of oscillations. The dependences of the decrement of attenuation on the magnetic field intensity, H, for samples with different magnetic particle concentrations are shown in Fig. 4.

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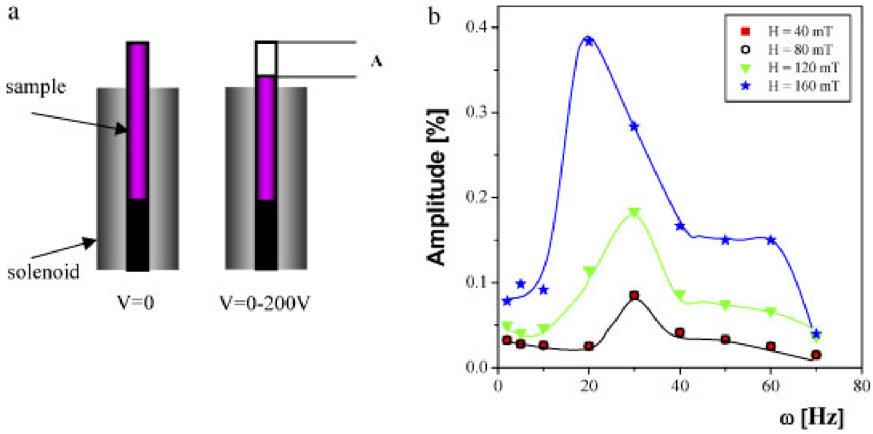

Figure 2. (a) Deformation of the sample inside the solenoid under the influence of the magnetic field and (b) amplitude of this vibration as a function of magnetic field frequency for various values of *H*.

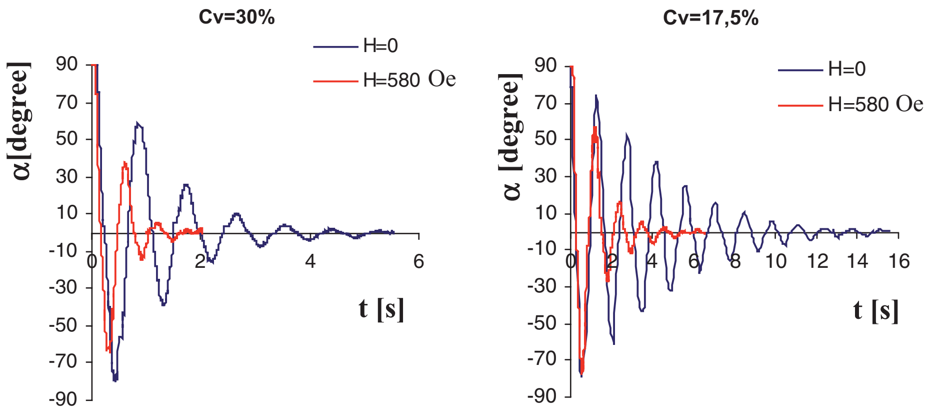

Figure 3. Dependence of the rotational angle α on time t for samples with two different values of magnetic particle content, C_v.

Damping of enforced oscillations were studied by another type of experiments.

In Fig. 5, we show the in-house built apparatus for the damping. With an electromotor an alternating up and down movement can be produced with constant frequency and amplitude on the anisotropic elastomer sample.

On applying the external magnetic field, the mutual particle interaction causes a large change in the elastic modulus of the elastomer. Due to the increased modulus, the frequency and the amplitude are also changed. Figure 6 shows few periods of this periodic movement of the sample of Type 1 material in the absence and presence of an external field. One can see in the figure the change in the height (h) of

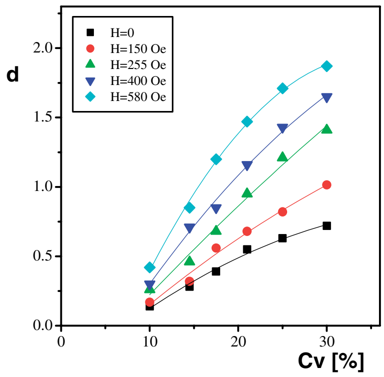

Figure 4. Dependences of the decrement of attenuation on the magnetic filler content for various values of *H*.

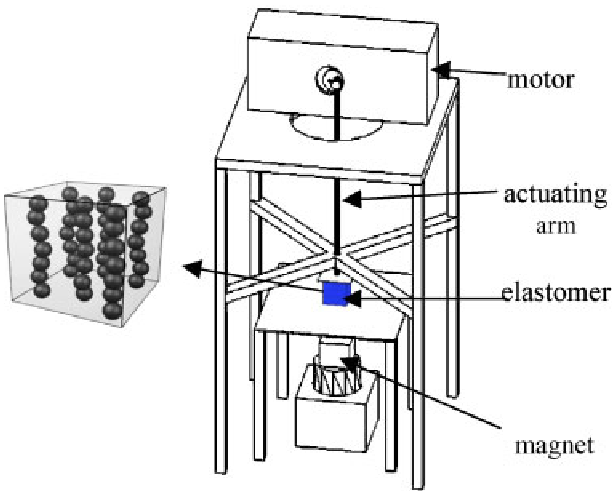

Figure 5. Damping machine.

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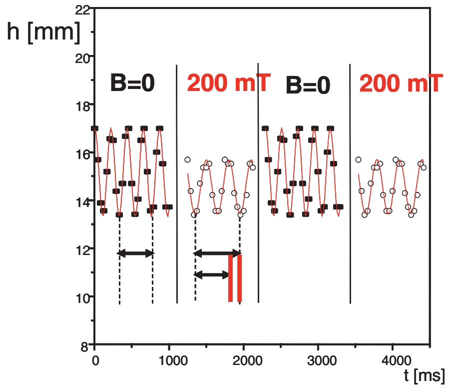


Figure 6. Periodic movement of the damping machine.

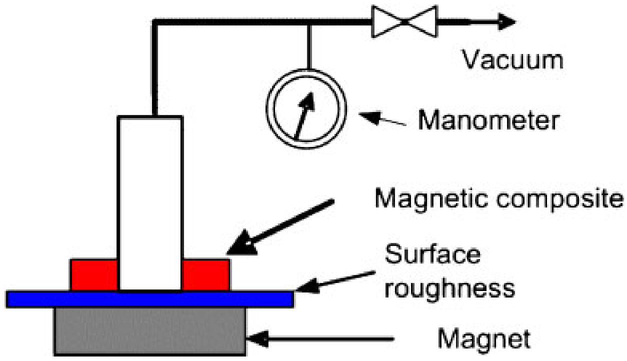


Figure 8. Scheme of the sealing set up.

the elastomer in the absence of an external field and in a 200 mT magnetic field.

Our preliminary experiments have given promising results to apply the anisotropic elastomers for dampers to modulate the amplitude and frequency.

Sealing experiments

Sealing experiments were performed and two types of surfaces with roughness have been produced. The roughness of the surfaces was characterized by the width, a, and the depth, b, of the wells. The photographs of the surfaces are presented in Fig. 7. For the first surface with fine roughness $a = 0.16$ mm, $b = 0.6$ mm. For the coarse roughness shown in Fig. 7b the values of $a = 0.3$ mm and $b = 1.4$ mm.

The scheme of the sealing set up is shown in Fig. 8. The surface to be sealed is shown by blue. The magnetic composite is shown by red. Vacuum was produced in the tube connected with the surface to be sealed. The pressure in the tube as a function of time was measured by a manometer. The dependence of the difference, p, between atmospheric pressure and the pressure in the tube for the two surfaces are shown in Fig. 9.

As it was expected, the rate of air leakage, $\mathrm{d}p/\mathrm{d}t$, is higher for the surface with higher roughness. But in both cases the value of $\mathrm{d}p/\mathrm{d}t$ decreases considerably when an external magnetic field is applied. For instance, from Fig. 9a one can see that the rate of leakage decreases by three orders of magnitude in the field of 95 mT.

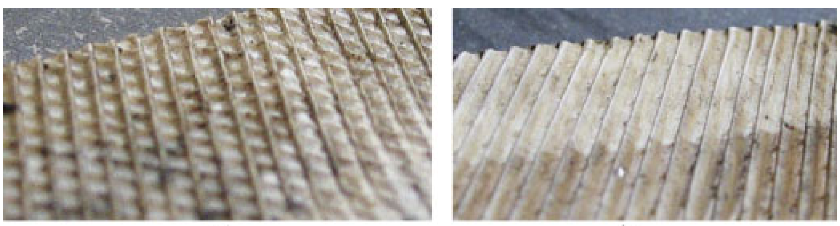
DISCUSSION

The main objective of this work was to develop new highly elastic magnetic field controlled materials and design a wide range of devices for industrial use on the basis of these materials. The novel feature of these materials is the ability to undergo quick and controllable large-scale deformations and essential changes in elastic and viscous properties in a magnetic field. These peculiar magnetoelastic properties can be used to create high-reliability seals with enhanced properties in comparison with existing analogues and tuneable vibration absorbers.

We prepared magnetoelasts and investigated their mechanical properties in a uniform magnetic field. We have shown that uniaxial field structured composites exhibit a much larger increase in the modulus than random particle dispersions. Mechanical properties like elastic modulus and stress–strain behavior of samples characterized by parallel and perpendicular chain-like structures are significantly different. It was found that the temporary reinforcement effect was most significant if the applied field, the particle alignment and the mechanical stress are all parallel to each other. A phenomenological approach was proposed to describe the dependence of elastic modulus on the magnetic induction. Within the experimental accuracy, the prediction of a phenomenological equation is supported by the experimental data.

Two types of damping experiments, that is, damping of free and enforced oscillations, were performed. It has been shown that in the case of free oscillations their period and logarithmic decrement decrease considerably in an external magnetic field. In the case of enforced oscillations, their amplitude decreases and the period changes significantly in the magnetic field. These results hold promise in developing tunable vibration devices and dampers based on our materials.

The experimental studies of the sealing abilities of the magnetic composites showed that these materials are effective for sealing of rough surfaces. It was found that



a b

Figure 7. Photographs of the surfaces to be sealed (a, surface with fine roughness; b, surface with coarse roughness).

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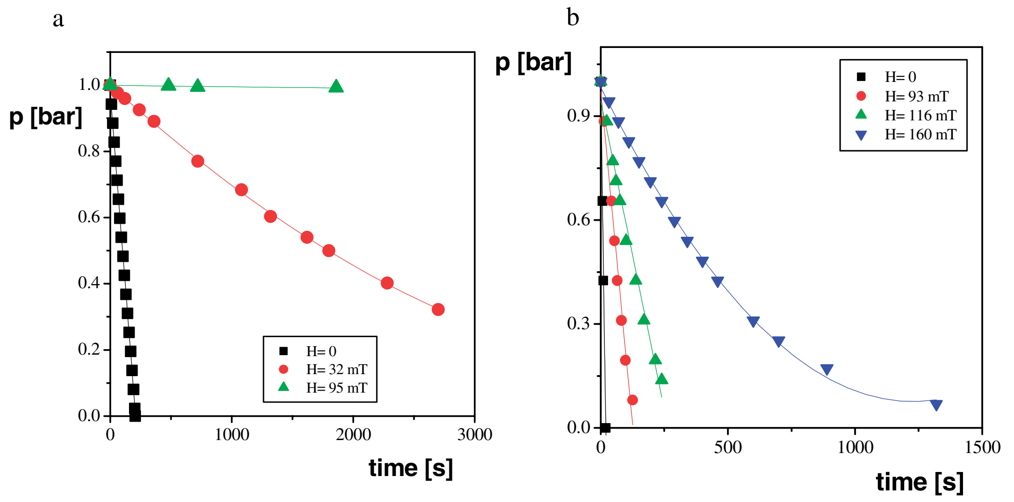

Figure 9. Functions $\Delta p(t)$ measured in the absence of a magnetic field and in the field of various intensities for a (a) surface with fine roughness (b) and a surface with coarse roughness.

the rate of air leakage can be reduced by three orders of magnitude by applying a magnetic field of 95 mT.

Acknowledgments

This research was supported by the Hungarian National Research Fund (OTKA, Grant No. T038228 and F046461) and sponsored by NATO's Scientific Division in the framework of the Science for Peace Programme (NATO SFP 977998). Elena Kramarenko and Gennady Stepanov are grateful to the Russian Foundation for Basic Research for financial support (grant 06-01-00723-a).

REFERENCES

1. Rosensweig RE, Jerauld GR, Zahn M. *Continuum Models Discrete Systems* 1981; **4**: 137.
2. Behroozi F, Orman M, Reese R, Stockto W, Calvert J, Rachfordt F, Schoen P. *J. Appl. Phys.* 1990; **68**: 3688.
3. Jin S, Tiefel TH, Wolfe R, Sherwood RC, Mottine JJ. *Science* 1992; **255**: 446.
4. Schiga M, Hirose M, Okada K.Japanese patent 4 266970, 1992.
5. Schiga M, Okada A, Karauchi T. *J. Appl. Polym. Sci.* 1995; **58**: 787.
6. Zrínyi M, Barsi L, Büki A. *J. Chem. Phys.* 1996; **104**(20): 8750.
7. Jolly MR, Carlson JD, Munoz BC, Bullions TJ. *J. Intell. Mat. Sys.* 1996; **7**: 613.
8. Zrínyi M, Barsi L, Büki A. *Polym. Gels Netw.* 1997; **5**: 415.
9. Szabó D, Barsi L, Büki A, Zrínyi M. *Models Chem.* 1997; **134**(2–3): 155.
10. Zrínyi M. *Trends Polym. Sci.* 1997; **5**(9): 280.
11. Zrínyi M, Barsi L, Szabó D, Kilian HG. *J.Chem. Phys.* 1997; **108**(13): 5685.
12. Bernadek S. *J. Magn. Magn. Mater.* 1997; **166**: 91.
13. Martin JE, Anderson RA. *J. Chem. Phys.* 1999; **111**(9): 4273.
14. Zrínyi M, Szabó D, Barsi L. Magnetic Field Sensitive Polymeric Actuator. In *Polymer Sensors and Actuators*, Osada Y, Rossi DE (eds). Springer Verlag: Berlin Heidelberg, 1999; 385.
15. Bernadek S. *Appl. Phys. A* 1999; **68**: 63.
16. Ginder JM, Nichols ME, Elie LD, Tardiff JL.*SPIE Conference on Smart Materials Technologies* 1999; 3675.
17. Carlson JD, Jolly MR. *Mechatronics* 2000; **10**: 555.
18. Borcea L, Bruno O. *J. Mech. Phys. Solids* 2001; **49**: 2877.
19. Ginder JM, Clark SM, Schlotter WF, Nichols ME. *Int. J. Mod. Phys. B* 2002; **16**(17–18): 2412.
20. Zrínyi M, Szabó D, Filipcsei G, Fehér J. Electric and magnetic field sensitive smart polymer gels. In *Polymer Gels and Networks*, Osada/Khokhlov (ed.). Marcel Dekker, Inc.: NY, 2002; **11**: 309.
21. Mitsumata TFurukawa KJuliac EIwakura KKoyamaK *Int. J. Mod. Phys. B* 2002; **16**17–18: 2419.
22. Zhou GY, Jiang ZY. *Smart Mater. Struct.* 2004, **13**: 309.
23. Zhou GY. *Smart Mater. Struct.* 2003; **12**: 139.
24. Ginder JM, Nichols ME, Elie LD, Tardiff JL. *SPIE Conference on Smart Materials Technologies* 1999; **3675**: 131.
25. Varga Zs, Filipcsei G, Zrínyi M. *Polymer* 2006; **47**(1): 227.
26. Varga Zs, Filipcsei G, Szilagyi A, Zrínyi M. *Macromol. Symp.* 2005; **227**: 357.
27. Abramchuk SS, Grishin DA, Stepanov GV, Kramarenko EYu, Khokhlov AR. *Polym. Sci. Ser. A* 2006; **48**(2): 138.

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