Tunable properties of magnetoactive elastomers for biomedical applications

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Abstract

The remote controllable magneto-mechanical devices based on MAEs (magnetoactive elastomers) can be obtained through variation of magnetic parameters of MAEs. Such devices can be used as the elements of peristaltic systems, artificial muscles, hyperthermia or drug delivery. MAEs with different matrix rigidity and filler particles type were investigated with VSM Lakeshore 7400 series and immittance meter Aktakom AM-3016 model. The dependencies of magnetostatic and magnetodynamic properties of MAEs with different types of magnetic particles on concentration of the magnetic filler and DC magnetic field strength were studied. There is a possibility to control the “magnetic hardness”, energy absorption and heating, relaxation properties of MAEs which allow to use MAEs as the main element of the tunable devices for biomedical applications.

Keywords: magnetoactive elastomer, tunable properties, magnetic hardness, hyperthermia, drug delivery, peristaltic system, artificial muscle;

1. Introduction

The development of “smart materials” is of high relevance nowadays due to their tunable properties (mechanical, magnetic, electrical and so on). Magnetoactive elastomers (or magnetorheological elastomers, or magnetoactive elastomers, or MAEs) are the unique type of smart materials. Under the applied magnetic field the changes of such properties as size, shape, Young’s modulus, permittivity (Semisalova et al., 2013), permeability, energy absorption, etc. occur. The reverse effect is also possible, for example, mechanical deformations lead to magnetization changes.

The particular attention is paid to aspects of biomedical applications of MAEs (V. Q. Nguyen et al. (2012), R. Fuhrer et al. (2013)). It was found by V. Q. Nguyen et al. (2012) that MAEs have the actuation properties close to...
those of natural muscles. The magneto-mechanical properties can also be utilized in peristaltic devices like micropumps according to R. Fuhrer et al. (2013). It is known that the skeletal-muscle pumps aid in the blood circulation by venous contraction (C. F. Rothe et al. (2005) and D. Sheriff et al. (2005)). In order to demonstrate the application of magnetic particles doped silicone tubes as a magnetic pump, a magnetic peristaltic pump similar to the skeletal-muscle pump was designed and operated by R. Fuhrer et al. (2013).

The area of drugs delivery is also attractive for biomedical applications of MAEs. The principle mechanisms of the drug delivery devices are based on the fluid pumps functioning. The recent research in the drug delivery has focused on the controlling the time and amount of drug released from a reservoir. The pioneering works about control of the drug delivery with magnetic field belong to R. Langer (1990) and H. Chen et al. (1997). The deformation (caused by external magnetic field) of the MAE membrane causes a pressure change which results in the controlled drug delivery (X. Zhao et al. (2011), Y. Zhou and F. Amirouche (2011), F. N. Pirmoradi et al. (2011)).

The oncology issues, especially large tumors, can be treated by hyperthermia. The inductive heat property of magnetic elastomer composite in an alternating current (AC) magnetic field was investigated recently by L. Zhao et al. (2011). The authors showed the hyperthermia effect of the composite under the ac magnetic field. The development of the composite material for hyperthermia as a polymeric stent coating was reported by C.-Y. Kim et al. (2013).

To develop the use of MAEs in biomedical devices and applications, the certain properties of such composite materials are required. MAEs are usually based on elastic matrix and ferromagnetic particles. The variation of the matrix polymer (S. Abramchuk et al. (2007), Kallio et al. (2005)), and the type, sizes, concentration of magnetic particles (S. Bednarek (1998), N. Guskos et al. (2010), P. Siegfried et al. (2014)) leads to tunable mechanical, magnetic and electrical characteristics.

For example, the MAE combination of flexibility and tunability has attracted significant interest as soft actuators for controlled movement or positioning. The required stiffness, shape memory effect, flexibility can be provided not only by the polymer properties. Carbonyl iron microparticles have enabled the preparation of magnetic elastomers that combine the use of the highest possible saturation magnetization (pure metallic iron) and high particle loading of up to 75 wt% with respect to polymer without negatively affecting mechanical stability and integrity. The optimal particle amount for the application as soft, magnetic pump (mechanical stability and flexibility) is about 67 wt% according to R. Fuhrer et al. (2013).

It was earlier formulated by V. Q. Nguyen et al. (2012) that representative characteristics of artificial muscles include stress, strain, strain rate, bandwidth i.e., the frequency at which strain drops to half of its amplitude, work density (the amount of work generated in one actuator cycle normalized by the actuator volume), specific power, efficiency, electromechanical coupling, cycle life and elastic modulus of the material. The silicone-50 wt% Fe composite can exhibit several actuation modes (V. Q. Nguyen et al. (2012)). The dependence of saturation magnetization on the filler concentration was presented by V. Q. Nguyen et al. (2012): the saturation magnetization increased linearly with particle concentration increasing. The soft magnetic and soft mechanic elastomer with 50 wt % Fe exhibited 90 emu/g saturation magnetization and 80% elongation in magnetic field of 1 T and stronger.

Additional interest in varying of the MAE properties is an obtainment of homogeneous heat distribution under the external AC magnetic field for hyperthermia. It is of great importance to enhance the dispersion stability of particles in the matrix by heating (C.-Y. Kim et al. (2013)). The magnetic hysteresis loops, the stress-strain curves, the temperature dependences of magnetic and mechanical properties are of a great importance in the investigation of MAEs for hyperthermia. The composite film with 30 wt % of magnetite exhibits the value of saturation magnetization of 4 emu/g. The composite film showed the thermal stability up to 400°C, about 4.4% weight loss until 408°C (C.-Y. Kim et al. (2013)).

Sensitivity to the magnetic field is important for the description of the elastomer behavior, thus it is of particular interest to compare susceptibilities (or permeabilities) of different types of magnetic elastomers obtained by different methods. The differences between magnetic properties of the elastomers with magnetic particles and magnetic properties of the powder of the same particles can indicate the phase composition of the composite material under investigation according to P. S. Antonel (2015). The magnetic susceptibility of MAEs is the characteristic of its sensitivity to the external magnetic field. As mentioned above, the using MAEs with Fe or magnetite particles for hyperthermia processes became possible due to their heating via the absorption of AC
magnetic field energy (D. Diaz-Bleiset al. (2014), T. Mitsumata et al. (2009)). But in technical purpose devices (sensors, pumps, actuators) the heating of the MAE part is a disadvantage that reduces the lifetime of the device. Iron particles are conductive, that leads to heating of devices because of induced by AC magnetic field currents inside the particles. Therefore the use of nonconductive magnetic particles (for example barium ferrite particles) will be convenient for pump devices.

By J.-H. Koo et al. (2012) it was shown, that unlike traditional MAEs with iron particles, a dispersion of hard magnetic materials will produce the MAE with magnetic poles. The magnetic field that was applied perpendicularly to these poles, caused the sample bending, similar to a cantilevered beam or bending-type actuators in small mechanical systems and devices.

In this study, the magnetic properties of MAEs with conductive and nonconductive particles for possible biomedical application were investigated. The dependence of magnetostatic and magnetodynamic properties on concentration of the filler particles was also studied. It was found that in DC magnetic field MAEs with hard magnetic filler changed its anisotropic properties (coercivity) with the change of matrix elasticity. The results obtained allow to extend the area of MREs applications as the elements of peristaltic systems, hyperthermia or drug delivery and also to concretize the requirements for the materials for biomedical purposes.

2. Materials and methods

2.1. Materials

For the magnetic properties investigation the samples of magnetorheological elastomers with different types of filler particles were prepared. Soft magnetic iron particles (5µm), hard magnetic NdFeB particles (50µm and 2µm), hard magnetic barium ferrite (BaO 6Fe₂O₃) particles (100µm and 10µm) were used as a magnetic component of MAEs. The synthesis technology of MAEs with magnetic particles was described in one of the previous articles by G.V. Stepanov et al (2008). Matrix rigidity of the obtained by this technology MAEs was medium or soft.

MAEs with barium ferrite particles were prepared using two-part silicone compound Dow Corning. The barium ferrite powder (similar to Vinnik et al., 2014) was mixed with the liquid A-part of the compound in a cylindrical glass placed in an ultrasonic bath for the homogeneous particle distribution. The precursor was mixed with the second B-part of the compound, and the mixture was molded into the Petri dish. The polymerization process of the undoped compound occurred during 10 min. The polymerization time of the compound with particles increased. The rigid MAEs were obtained.

The mass fractions of the filler varied from 25% to 85%. The magnetic properties dependence on the matrix stiffness was also investigated. All the MAE samples are counted in Table 1.

2.2 Magnetodynamic method

The measurements of the dynamic magnetic permeability of MAEs were conducted using a coil with a core made of material under investigation by immittance meter Aktakom (model AM-3016) at the room temperature. The MAE impedance characteristics were defined at different frequencies and external magnetic field applied to the coil with a sample. The maximum applied DC field was ±5 kOe and it was applied perpendicular to the coil axis.

2.3 Magnetostatic method

Measurements of magnetostatic properties of MAEs were conducted using Vibrating Sample Magnetometer LakeShore (7407 System). The magnetometer allows to obtain the hysteresis loop and to determine the principal magnetic characteristics of the sample. For each type of the measurement a disk with a diameter of 3-4 mm and a thickness of ~ 1mm was made from the elastomer sample. The disk was fixed on a holder by the Teflon tape and was placed between electromagnet poles with the sample plane being parallel to an external magnetic field. The maximum fields was ±16 kOe.
3. Results and discussions

3.1. Magnetostatic measurements

The hysteresis loops of two types of MAEs are presented at the fig. 1 and 2. All MAEs contain the system of interacting multi-domain magnetic particles. The remagnetization processes of each type of MAEs are different. The magnetostatic characteristics of different types of MAEs are shown in the Table 1.

| The sample (the number means the weight concentration in MAE) | Matrix rigidity | Particle size, μm | Saturation magnetization*, emu/g | Coercivity, Oe | Remanent magnetization, emu/g |
|-------------------------------------------------------------|----------------|-------------------|---------------------------------|---------------|-----------------------------|
| Fe85-s medium 2 180 11 0,6 | Fe77-s medium 2 166 12 0,6 | Fe68-s medium 2 163 12 0,7 |
| NdFeB75-l medium 2 110 1236 64 | NdFeB75-s medium 2 93 671 36,4 | NdFeB69-s medium 2 80 499 21,5 |
| NdFeB60-s medium 2 73 398 26,1 | Ba-Fe61 medium 2 10 36 238 8,5 | Ba-Fe40 medium 2 100 18 650 4,7 |
| Ba-Fe25 medium 2 100 11 1062 4,7 | Ba-Fe64 medium 2 100 34 539 16,4 | Ba-Fe60 medium 2 100 27 561 11,8 |
| Ba-Fe55 medium 2 100 27 448 11,9 | Ba-Fe48 medium 2 100 24 415 9,3 | Ba-Fe38 medium 2 100 16 372 6,2 |

* For NdFeB filler the magnetization in the maximum field of 16 kOe.

There are three types of hysteresis loops of MAEs which associated with the magnetic filler. The iron particles are soft magnetic material, so the coercivity is small enough, and saturation magnetization is the largest (Fig.1, Table 1). The elastic polymer matrix can affect the coercivity of MAE with iron particles compared with iron powder. But the coercivities of MAEs with different concentrations of iron particles are approximately the same. In small particles the shape anisotropy dominates what is reflected in such coercivity of the MAEs. The saturation magnetization of MAEs increased with particle concentration increasing (Fig. 3a). Use of the MAEs with the high concentration of iron particles also provides a strong response to the magnetic field due to the high susceptibility. This effect allows to construct the devices for the flow pressure measurement based on the tonometer operating principle or valves with the remote control.

Fig.1. The hysteresis loops of MAEs with 5 μm sized iron particles (85 wt%, 77 wt%, 68 wt%).
The neodymium-iron-boron magnetic filler affects the magnetic properties of MAEs. The obtained hysteresis loops of MAEs with NdFeB particles are minor (Fig. 2). The saturation was not achieved in the maximum value of magnetic field 16 kOe. The magnetization in maximum field of MAEs increased with particle concentration increasing (Fig. 3b). The magnetizations in the maximum field 16 kOe of MAEs-NdFeB with 50 mkm and 2 mkm sized particles differ despite the same mass concentration 75 wt % (Table 1). Perhaps this feature can be explained by the fact that the larger particles have the larger torque, thus the probability of the particle turning and the ordering of magnetic moments in the field direction larger than those of the small particles. Moreover there are the isotropic, but probably not homogeneous distribution of the particles in the matrix. This peculiarity was partially discussed in recently published paper Kramarenko et all (2015). The inhomogeneity and the magnetization differences can be associated with the deviation of properties through the large prepared MAE sample.

The switching field of the single domain particle is known to be dependent on the angle between easy axis of the particle and the direction of the external magnetic field (Chikazumi S. (1997)). It has the maximum value at 0° and 90° angles, and the minimum value at 45° angle. It was found, that the one 50 mkm NdFeB filler particle had a large magnetocrystalline anisotropy, and the model of coercivity by Stoner-Wohlfarth can be even used to describe the remagnetization characteristics of such large particles as 50 mkm particles. The similarity of large NdFeB particles characteristics to those of single domain particles were probably associated with the pretreatment (annealing) of the particles before filling the matrix. As it was mentioned above, the larger particles have the larger ordering on the easy axis in the field direction, thus the coercivity of MAE with large particles is more than the coercivity of MAE with small particles with the same mass concentration 75wt% (Table 1). The most of the magnetic moments of small particles of MAEs was oriented at some angle to the magnetic field, thus they were remagnetized in the field considerably less than critical, which corresponds to the smaller coercivity. The increasing of concentration of small particles can lead to their agglomeration, hence the coercivity of MAEs with higher concentration of small neodymium-iron-boron particles is larger (Fig. 3c). The lower concentration of particles means the lower agglomeration and leads to the smaller coercivity of MAE.

![Graph](image_url)

Fig. 2. The hysteresis loops of MAEs with 2 µm sized neodymium-iron-boron particles (75 wt%, 69 wt%, 60 wt%).
The hysteresis loops of MAEs with barium ferrite particles (10 mkm and 100 mkm) also exhibit the large coercivities (Fig.4a,b, Table 1) and rather the large saturation magnetization. As mentioned above, the remagnetization processes are caused by turning of the particles. Comparing the coercivities of MAEs with the large particles in the soft (38wt%) and rigid (40wt%) matrix, the remagnetization of such MAEs was concluded to occur due to rotation of the large particles. The coercivity of MAE with the rigid polymer is significantly larger than one of MAE with the soft polymer (as the elastic modulus and therefore the elastic force (resistance to the rotating) are significantly larger in the rigid polymer) (Table 1).
Thus the possibility to control the “magnetic hardness” of the MAE appears with varying the rigidity of polymer matrix. Variation of the type of magnetic filler allows to tune the magnetic characteristics of MAE and adjust their magneto-mechanical properties, extending the area of their application in actuators (micropumps, muscle analogies, positioners) based on MAEs.

3.2. Magnetodynamic measurements

The most important dynamic properties of the MAEs are the field dependencies of the real and imaginary part of magnetic permeability. The imaginary part of the permeability associates with the energy loss (Fiolillo F. 2004). For the MAEs with conductive particles both components of the permeability decrease with field increasing (Fig.5). The field dependency of the imaginary part of the permeability can have the peak at the certain external magnetic field value. This means that the additional DC magnetic field, applied perpendicularly to the AC magnetic field direction, causes the extra absorption of the AC magnetic field energy by MAE. This effect allows to improve heating properties of the hyperthermia materials, which now have the same operating principle.

![Graphs showing field dependencies of the real and imaginary part of magnetic permeability for different iron particles concentrations.](image)

**Fig.5(a).** The dependence of the real part of the magnetic permeability on the external magnetic field for the MAE with iron particles 5µm.

**Fig.5(b).** The dependence of the imaginary part of the magnetic permeability on the external magnetic field for the MAE with iron particles 5µm.

4. Conclusions

Magnetic properties of MAEs with soft magnetic iron particles, hard magnetic NdFeB, and barium ferrite particles were investigated. Their dependencies on concentration of the magnetic filler and DC magnetic field value were studied. The change of the magnetic filler allows to tune the magnetic characteristics (saturation magnetization, coercivity, magnetic permeability) of MAE and to adjust the magneto-mechanical properties. It was found that in DC magnetic field, there is a possibility to control the anisotropic properties and the coercivity of MAEs with the hard magnetic filler by varying the rigidity of the polymer matrix (“magnetic hardness”). Coercivity of the magnetic elastomers with iron particles decreased with the filler concentration increase. The heating properties and energy absorption can be improved by the applying the DC magnetic field. The remote controllable magneto-mechanical devices based on MAEs can be obtained through variation of magnetic parameters of MAEs and can be applied for different biomedical purposes. The results obtained allow to extend the area of MREs applications as the elements of peristaltic systems, artificial muscles, hyperthermia or drug delivery and to concretize the requirements for the materials for biomedical purposes.
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