



MAGNETICALLY ACTIVE SILICONE ELASTOMERS: TWENTY YEARS OF DEVELOPMENT

Cite this: *INEOS OPEN*,
2019, 2 (6), 178–184
DOI: 10.32931/io1926r

Received 23 December 2019,
Accepted 27 January 2020

<http://ineosopen.org>

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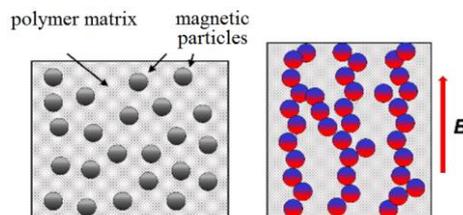
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Abstract

The main objectives of this highlight are to give an overview of major achievements in the field of soft magnetoactive elastomers based on silicone rubbers over the past twenty years and to demonstrate the prospects for their further development.



Key words: magnetoactive elastomers, magnetorheological elastomers, magnetic elastomers, silicone rubbers, polymer composites.

Introduction

The year 2019 was rich in significant anniversaries: the 150th anniversary of the Mendeleev Periodic Table, the 120th anniversary of the birth of a genius Soviet scientist—full member of the Academy of Sciences of USSR Alexander N. Nesmeyanov, and, finally, the 65th anniversary of our Institute—INEOS RAS. This is always a good reason to step back and take stock. This review is devoted to a small anniversary: twenty years since the creation of new promising materials—magnetoactive silicone elastomers featuring strong responses to magnetic fields.

Since their inception, silicone elastomers have played a special role among a great variety of elastomers based on organic rubbers. They could not compete with organic derivatives on their physico-mechanical properties and cost, but multiply outperformed the competitors in the width of a temperature range, biological inertness, and biocompatibility. For a long time, they have been afflicted with a sense of inferiority and restrictions in some application fields, until new technologies have come to turn their drawbacks into advantages. The low level of intermolecular interactions of liquid PDMS rubbers enabled the development of a broad family of sealing compositions on their base, which can provide sealing materials for any purposes and, even more, offer opportunities to proceed to new technologies for the production of silicone elastomers, featuring short curing times and ensuring the use of high-performance equipment for obtaining mass-produced articles from silicone rubbers, such as cable insulation, tubes and pipes, baking tins, and many others.

The research area highlighted in this review is concerned just with the seemingly main drawback of silicone elastomers—low physico-mechanical characteristics, in particular, low elastic moduli. This area studies magnetoactive elastomers (MAEs)

based on silicone rubbers with embedded magnetic particles (Fig. 1a). An idea to combine the properties of elastomers with the properties of magnetic materials is not new. The conventional rigid magneto-polymer composites have been known for a long time. We encounter these materials in machines and household, where their application enables a reduction in the mass of permanent magnets for different magnetic spacers and latches—devices that provide fixation of one or another movable joint, permanent magnet cores. One of the popular application fields of magneto-polymer composites involves the tapes that ensure snug engagement of doors in common domestic refrigerators. However, rigid magnetic elastomers do not display smart properties, which are characteristic for magnetic fluids; they can be magnetized, but their shape and mechanical properties are hardly affected by magnetic fields. To make such a composite material smart, in particular, to make it demonstrate a considerable magnetic response, a polymer matrix should be soft enough (with the elastic modulus of up to several tens of kPa). In a soft matrix, the elastic forces appear to be comparable to the dipole–dipole interactions between magnetic particles in a magnetic field, which allows a magnetic filler to be structured along the magnetic field lines (Fig. 1b), as it happens in magnetic fluids, in which the liquid serves as a dispersing medium for magnetic particles. However, unlike magnetic fluids, where particles can move freely, in magnetic elastomers a particle shift from the initial equilibrium positions gives rise to local strains of the matrix, which hamper the particle motion. As a result, the structure formed by the filler in a magnetic field is determined by the balance of magnetic and elastic interactions. Using the external magnetic field, it is possible to change the degree of interaction of magnetic particles in the material, and consequently, to shift this balance by regulating the material's internal structure and physical properties, which depend on this structure.

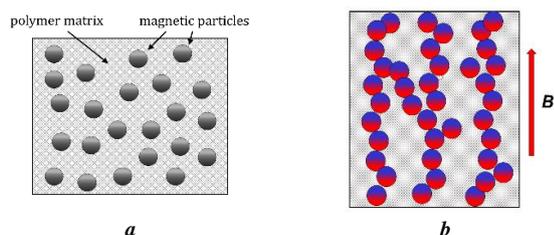


Figure 1. Schematic representation of the structure of an isotropic magnetoactive elastomer—magnetic nano- or microparticles dispersed over a polymer matrix (a) and the change of the filler structure in an external magnetic field (b).

In Russia, the first examples of magnetoactive elastomers, which was called initially "magnetoelastic", were obtained as a result of collaborative efforts of the scientists from Lomonosov Moscow State University (MSU) and Institute of Chemistry and Technology of Organoelement Compounds (GNIKhTEOS) over 20 years ago. The properties of this material were reported for the first time at a scientific conference at MSU—MISM-2009 [1] and described in the journal "Nauka i Zhizn" ("Science and Life", in Russian) [2]. The elastic modulus of this silicone elastomer, bearing iron magnetic particles with sizes of 11 nm and 2 μm , increased in several times from 16 to 100 kPa in the magnetic field of 160 mT. It should be noted that, in parallel with the Russian research group, magnetoactive elastomers were developed and studied by the groups of Prof. T. Mitsumata in Japan and Prof. M. Zrinyi in Hungary [3]. However, their material was based on aqueous polyacrylamide gels and nanomagnetite particles [3]. They also detected that the elastic moduli of the composites increase with the growth of the magnetic field. However, the average and maximum absolute changes of the modulus at 400 mT composed 31 and 71 Pa, which corresponds to the relative increases by 19% and 46%, respectively [3]. These values were much lower than those achieved with the silicone matrices. Furthermore, the silicone elastomers were more stable than the aqueous gels. In recent years, MAEs have been produced all over the world based on different polymers, in particular, natural [4] or butadiene rubber [5], urethane [6], *etc.* However, according to the data of a recent review [7], over 51% of all the investigations have been conducted with silicone MAEs. Therefore, silicone MAEs became dominant in this field.

Magneto-responsive properties of MAEs

Among the most interesting and striking effects displayed by MAEs, of note is, first of all, the above-mentioned magnetorheological effect—a significant change of the viscoelastic properties in magnetic fields (see, for example, reviews [7–12]). In particular, the elastic modulus of such a composite based on soft silicone matrices can increase by 1–4 orders of magnitude in relatively weak magnetic fields of up to 300 mT [8, 13–18], which offers ample opportunities for the creation of controllable damping devices, compactors, shutters, and so on. A maximum value of the elastic modulus of the material in a magnetic field is mainly determined by the strength of a three-dimensional network of magnetic particles, which is formed in highly filled composites and exhibits a marked orientation of the magnetic particle chain aggregates along the lines of the

magnetic field [19, 20]. Therefore, the relative growth of the elastic modulus depends on the initial modulus of the polymer matrix: the softer the matrix in the absence of a field, the higher a relative increase of its rigidity in the magnetic field. Our German colleagues suggested the use of soft composites with the initial moduli of about several hundreds of Pa as substrates for cell cultivation [17]. The mechanical properties of these substrates are immeasurably closer to the natural conditions than the conventional surfaces for cell cultivation (glass, solid polymers). At the same time, these cell substrates enable tuning of their rigidity *via* the applied field and, thus, the variation of the conditions for cell adsorption.

Our investigations performed for the last twenty years show that, besides the magnetorheological effect, MAEs possess a whole series of other new unique features, which include the following unusual mechanical properties:

- the magnetodeformation effect which is a unique propensity to rapid and controlled deformation of a material in magnetic fields [8, 9, 16, 21]. In gradient magnetic fields, magnetic particles strive to shift to a higher field; owing to the low elastic modulus of a matrix, the magnetic forces prevail and cause deformation of the whole sample. Already the first works [1, 2, 16] showed that the material can deform up to 300% in nonuniform fields, which immediately opened prospects for their use as operating elements in microactuators, compactors, and even artificial muscle. It was demonstrated that the frequencies of a varying magnetic field, at which the material can operate effectively, range from 30 to 50 Hz [16]. A surprising feature of MAEs appeared to be their ability to deform not only in gradient but also in uniform magnetic fields [9, 22–25]. This effect appeared to be analogous to magnetostriction, which is observed in strong magnetic materials. However, unlike conventional magnetostriction materials, in which the changes in sizes are connected with deformation of a crystal lattice of the magnetized sample owing to the changes in magnetic (dipole–dipole and spin–orbit) and exchange forces and do not exceed 0.01%, a working element in MAE is the polymer matrix, and the elongation of samples along the lines of the magnetic field can reach 20% owing to the rearrangement of a magnetic filler in the polymer [22].

- the shape memory effect or the plasticity effect which is induced by the magnetic field. This interesting effect is manifested in the fact that an initially elastic material converts to something like plasticine in a magnetic field, and it can be used to mold figures of various shapes within 100% strain, which are fixed by the magnetic field [14]. After switching off the magnetic field, the initial shape of the sample is recovered. The shape memory is manifested in highly filled soft composites in not so low magnetic fields of 300 mT. However, its manifestations associated with considerable hysteresis phenomena are characteristic also for MAE in weak magnetic fields. The stress–strain curves demonstrate remarkable nonlinearity and feature high residual strains after the removal of a load in the magnetic field [15] (see Fig. 2). These phenomena are explained by the formation of magnetic clusters under simultaneously acting external mechanical force and magnetic field, in which magnetic interactions between particles retain them from decomposition after removal of the mechanical load.

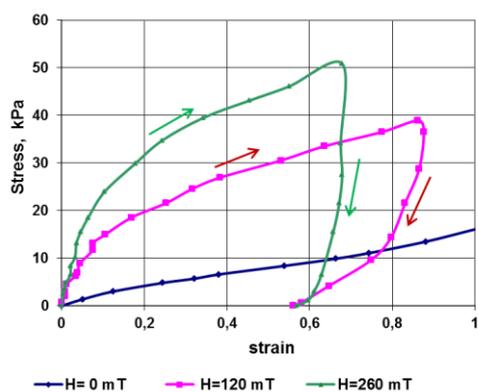


Figure 2. Results of cyclic uniaxial tension of a MAE sample in zero and permanent fields of 120 mT and 260 mT; the strain value is calculated based on the size which the sample acquires after magnetization in this field without loading; arrows indicate a deformation direction.

– the Payne effect which consists in the dependence of an elastic modulus of a filled elastomer on the strain value; it increases many times in MAE when the magnetic field is switched on [26–28]. However, it should be noted that the region of linear viscoelasticity extends with an increase in the magnetic field owing to the strengthening of magnetic interactions and the formation of stronger clusters of magnetic particles, which can be decomposed at higher strains.

All the mentioned mechanical effects are considered in greater detail in our recent review [9].

Besides the mechanical effects, MAEs feature controllable electromagnetic characteristics:

– the magnetodielectric effect, namely, effective dielectric permittivity and conductivity of magneto-polymer compositions controlled by the magnetic field [29–31]. The magnetodielectric effects are more pronounced in the samples which have high concentrations of the magnetic filler (up to 80% by mass) and display low elastic moduli; a relative change in the effective dielectric permittivity reaches 1000% in the magnetic field of up to 0.6 T. A considerable hysteresis of the magnetodielectric effect in the external magnetic field is also observed. These results are explained by the rearrangement of the magnetic filler under the action of the magnetic field [30]. The magnetodielectric effect can be used as a basis for different sensor devices.

– the piezoresistive effect which represents a change in the electrical conductivity under the action of external pressure [32].

– the magnetically controlled radio absorbing properties of magneto-polymer composites: it was shown [33, 34] that both reflection and transmittance coefficients of a material at gigahertz frequencies essentially change upon application of the magnetic field; moreover, their values strongly depend on the direction of the magnetic field as well as on the internal structure of the filler, which is formed in the samples during synthesis. These effects can be used to create radioprotective or polarization coatings based on MAE, which will be controlled by external magnetic fields.

In general, it was noted [35] that any property of a soft magneto-polymer composite, sensitive to the distribution of a magnetic filler in the polymer matrix, can be controlled by the external magnetic field over a wide range. It should be indicated

that the anisotropy of the material properties can be produced during the synthesis of MAE [8, 9, 20, 26, 35, 36]. If the synthesis is carried out in the magnetic field, then the oriented structures formed owing to the interaction of magnetic particles appear to be fixed in the matrix during polymerization. As a result, the materials obtained in this way display anisotropy, for example, the anisotropy of mechanical properties even in the absence of an external magnetic field. The intrinsic anisotropy of the material enables the diversity of possible mutual orientations of the composite internal structure, the external mechanical force, and the external magnetic field, and each configuration is characterized by a certain magnetic response of the material. It was shown that the maximum effects are observed when the force and the field act codirectionally with the internal structure of the filler [8, 26].

According to the Web of Science database, the number of publications in the field of magnetoactive elastomers increases exponentially every year. Such an interest is connected with a wide range of new fundamental phenomena, which are exhibited by MAEs, as well as the potential of their application in different devices. Possible applications of the above-mentioned properties are aligned with applications of other widely known materials, which include piezoelectrics, piezoelectric polymers, magnetostriction materials, and shape memory alloys. Combining a series of unique features, magnetoactive elastomers can accomplish the functions of several materials and elements simultaneously, thus, simplifying the construction of a device and reducing the number of its components, which are subjected to wear or breakage. A detailed review of the technical solutions for different devices developed in recent years using MAEs can be found in Ref. [37].

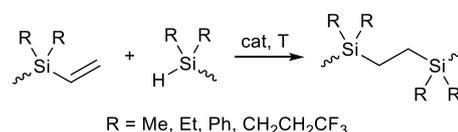
Effect of MAE composition on its magnetic response

It should be noted that the composition of MAE offers ample opportunities for the production of materials featuring high variability of physical properties. Two main components of MAE are a polymer matrix and a magnetic filler. Variation of the properties of these components can afford the materials with optimal characteristics for various applications.

Polymer matrices

The first samples of MAE, which demonstrated a large increase in the elastic modulus in the magnetic field, were obtained based on a SIEL silicone compound [38]. Different modifications of this compound, as most versatile and convenient in handling, were used for further synthesis of materials, which properties have been studied in our research group for the last twenty years. Owing to the directed synthesis and advanced methods for analysis, the resulting compounds featured the given properties.

One of the basic mechanisms of polymerization is polyaddition which scheme is presented below.



As can be seen from the scheme, polymerization proceeds without release of side products, which allows one to use the resulting compositions not only as film or coating ones, but also as potting compositions for closed vessels of any configurations.

Depending on the problem, silicone polyaddition compounds can be cured at moderate temperatures—from room temperature to 160 °C—with the duration from a day to 30 minutes. These materials can be polymerized in layers of various thicknesses. They feature good adhesion to surfaces such as metal, glass, ceramic, and so on.

Investigation of the processes of thermal aging showed [39] that silicone compositions possess thermal stability for continuous periods, retaining the main parameters at a satisfactory level: strength and relative elongation for elastomer compositions and Brinell hardness for glassy ones.

Polydimethylsiloxane compounds feature an operating temperature range from –60 to +200 °C. An extension of the temperature range to the negative or positive region is achieved by the modification of the main siloxane chain. The polyaddition compounds can be filled with different magnetic powders: both metallic and oxide ferrites.

However, to reach a high magnetic response of MAE, the elastic modulus of a weakly cross-linked silicone composition had to be reduced by introducing nonfunctional oligomers, which are not involved in the cross-linked structure but play the role of a diluting agent for the system and, thus, reduce its elastic modulus. The concentration of a low-molecular plasticizing agent, a silicone oil, had to be level to 70% by mass to achieve a significant magnetic response of the material. Nowadays, certain laboratories from all over the world produce highly efficient MAEs based on silicone matrices analogous to SIEL with the addition of a low-molecular-mass diluting agent [17].

Reduction of the elastic modulus of a composition without addition of a liquid filler was crucial for the expansion of a spectrum of materials which can be combined with MAE, since upon contact with the surfaces that absorb oil, a filler could flow out from the system during exploitation, which inevitably caused inconveniences in the form of fatty spots or drops and also led to changes in the technical characteristics of the composition; this, of course, was unacceptable for most practical applications. A solution was found by a purely polymer method: the required liquid was grafted on a siloxane matrix in the form of the so-called dangling tails. Thus, siloxane compositions included, besides bifunctional oligomers and a highly functional cross-linking agent, monofunctional oligomers, which provided a reduction in the network elastic modulus [40]. Only the introduction of side chains into the composition of a polymer network afforded soft samples with low elastic moduli (about 2 kPa). It was demonstrated that MAEs on their base display a high response to the magnetic field: relative growth of the real part of the dynamic elastic modulus of these samples reaches the value of 400 in the magnetic field of 1 T, which is comparable with the results obtained previously for the silicone MAEs with high contents of the low-molecular-weight oil.

In this respect, of particular interest as potential matrices are the so-called molecular brushes—the macromolecules with densely engrafted side chains [41, 42]. As it was mentioned above, the side chains essentially reduce the density of chemical cross-links in polymer networks and the physical entanglements,

affording a strong reduction in the material elastic modulus. The presence of several independently variable architectural parameters of molecular brushes, including the length of side chains and the density of their grafting, allows one to control the elastic moduli of the resulting networks at the molecular level. Currently, investigations on the creation of MAEs based on molecular brushes are carried out within the project of the Russian Science Foundation.

Magnetic filler

Another main component of MAEs, the magnetic filler, offers even more opportunities for the control of composite properties. Of note is the possibility of application of particles of variable chemical nature, in particular, those featuring hard magnetic and soft magnetic properties. The former include iron carbonyl, which, being cheap and available in different sizes, is the most popular filler for MAEs. A narrow magnetic hysteresis loop of soft magnetic materials, which is characterized by the low values of remanent magnetization, allows one to control the properties of MAEs on their base in the real-time mode, for example, by increasing and reducing the material elastic modulus *via* increasing or reducing the magnetic field.

Unlike soft magnetic fillers, hard magnetic fillers afford an opportunity to significantly change the material properties one time *via* application of a magnetic field. MAE based on hard magnetic particles retains its magnetization after switching off the magnetic field [43, 44]. A typical example of hard magnetic fillers is the particles of neodymium–iron–boron alloy. A powder from irregularly shaped particles can be obtained by crushing an amorphous fast-quenched tape of the NdFeB alloy. The photographs of typical particles are presented in Fig. 3a; spherical particles may also occur (Fig. 3b).

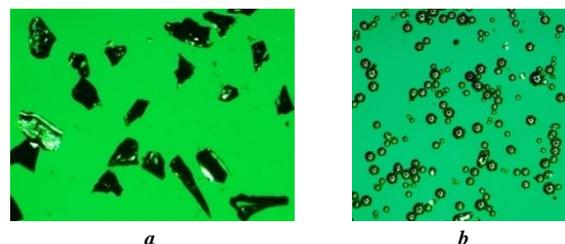


Figure 3. NdFeB magnetic particles of two types: irregular-shaped (*a*) and spherical (*b*) ones.

A hard magnetic filler can be combined with soft magnetic particles to create hybrid magnetic elastomers [45–49]. The idea is to produce a material that would possess a self-magnetic field after magnetization and, consequently, no external heavy magnets and electromagnets would be required to endow this material with the desired viscoelastic properties. Of course, these properties cannot be regulated during exploitation of the material, for example, in an actively controlled damper, but it provides a good advantage for mass-dimensional characteristics of the damper, since it can serve as an efficient working body in passive and semiactive damping devices even in the absence of magnetization systems. It should be noted that the effects of variation of the viscoelastic properties in these materials are lower than those in the composites with soft magnetic fillers, and the efficiency of its application will be defined by the technical features of constructed damping devices. Investigation

of the structural and magnetic characteristics of such a material showed that, after magnetization, it cannot be demagnetized by the reverse magnetic field. Upon application of the reverse magnetic field, a part of particles of the hard magnetic filler start to turn inside the soft polymer matrix [47] and, consequently, continue to be magnetized in the same direction, in which they were initially magnetized. This is evident from the magnetic hysteresis loops and can be observed with an optical microscope. The magnetization and magnetic susceptibility curves of such a composite have complex characters; this is explained by the parallel processes of remagnetization and turning of the particles inside the magnetic elastomer during magnetization and remagnetization [47–50].

Another parameter of magnetic particles is their shape. To date, most of the works were concerned with spherical particles; however, anisotropy is expected to significantly affect the magnetic response of a material, in particular, to reduce the content of the magnetic filler in the polymer matrix while retaining the values of magnetic effects. Nowadays, the effect of particle shape on the properties of MAE is actively studied and MAEs based on both spherical and cubic, needle- and plate-like magnetic particles are synthesized.

An important step in the synthesis of MAE is the modification of the surface of magnetic particles in order to reduce the aggregation of powders, to endow them with hydrophobic properties, and to improve their compatibility with a liquid silicone rubber [20, 43]. For these purposes, the magnetic powder can be treated with a mixture of a GKZh-94 water-repellent agent ($\text{Me}_3\text{Si}-\text{O}-[\text{MeSi}(\text{H})-\text{O}]_n-\text{SiMe}_3$) with a PMS silicone oil in hexane. For iron powders with particle sizes of 2–5 μm , the concentration of the modifying agent is 1% of the powder mass. A mixture of the iron powder with the solution of the modifying agent is passed through a roller and dried; as a result, the filler particles appear to be separated from each other and coated with a double layer of the silicone molecules. This modified powder is readily distributed in the liquid silicone rubber.

Another method for modification is the chemical grafting to the surface of silicone chain particles. Recently, it was suggested [51] to use different methods for modification of iron carbonyl with carboxy-containing siloxane oligomers and the efficiency of the processing of particles was evaluated based on the measurement of the main rheological and viscoelastic parameters of magnetofilled polydimethylsiloxane liquid and elastomer compositions.

New directions of practical application of MAEs

With the improvement of structures and compositions of magnetoactive siloxane elastomers, the search for new application fields is still continuing. In particular, the coatings based on MAE (Fig. 4a) with the controlled microrelief have been created [52–56], which is very important, in particular, for the realization of a superhydrophobicity effect. It was revealed that the oriented chain structures from magnetic particles, which are formed in the MAE bulk upon application of the magnetic field, can grow to the material surface as is shown schematically in Fig. 4b. In the magnetic field, directed perpendicular to the

MAE surface, the initially smooth surface immediately bristle up with an array of needle or brush formations that completely disappear upon switching off the field. The formation of the hierarchical structured surface leads to an essential increase in the water contact angles. Recently, the silicone matrices filled with magnetic iron microparticles have been used to obtain the materials which contact angles in the relatively low magnetic field of 600 mT reach 160° [52]; this allows one to speak about the potential superhydrophobicity of the MAE surface induced by the magnetic field.

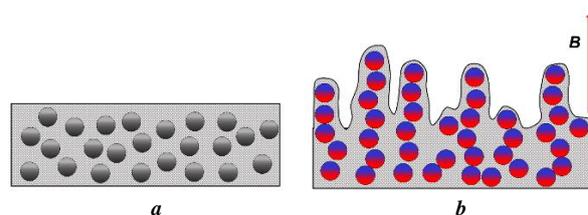


Figure 4. Schematic representation of the MAE surface relief in the absence (a) and in the presence (b) of a magnetic field.

Recently, the structuring of spherical magnetic particles at the interface of a viscoelastic medium with air has been studied by molecular dynamics, and the dependences of the parameters of surface relief on the concentration of magnetic particles, the elastic modulus of a polymer matrix, and the external magnetic field were determined [57]. It was shown theoretically and experimentally that a reduction in the matrix elastic modulus leads to the growth in the surface roughness at the optimal filling degrees of 70–80 wt %. Moreover, the theoretical calculations performed within a mesoscopic model [58] showed that the essential roughness of MAE can be achieved using anisometric particles as the filler. In this case, the low concentrations of the particles, which turn in the magnetic field, are enough to afford significant strains in the material surface.

The magnetic sensitivity of the MAE relief offers also opportunities for the creation of a dynamic surface, which relief is controlled in the contact-free mode through the variation of the magnetic field in space and application of the time-varying magnetic field. This can become a promising route for the directed transport of liquids and the creation of devices for microfluidics. The control of the dynamic coating relief can be significant also for the application of these materials as antifreezing coatings. The coatings based on MAEs are likely to find further application as antiadhesive and antistick coatings—yet another traditional field of application of silicone coatings.

Of special note are the potential medical applications of MAEs. One of them, connected with the treatment of a serious ophthalmic disease—retinal detachment, has been developed in our group for the last three years [59–67]. This refers to the creation of an eye retina fixator which pressing force stems from magnetic interactions. Owing to their unique properties, MAEs are especially promising elements for the fixators which are placed inside an eye on a retina surface and are fixed owing to the attraction to an external magnetic seal. The latter represents a silicone tape with inserted permanent magnets, which is attached to a sclera outside an eye ball. A soft internal seal from MAE (the Young modulus of *ca.* 1–100 kPa) can be readily deformed and is inserted through a narrow incision, which represents a medium close to natural tissues and does not

traumatize them. However, upon interaction with a magnet, the elasticity of MAE increases by several orders of magnitude, which provides the required pressure for retina fixation. The hydrophobicity of MAE also plays an essential role, preventing the penetration of an aqueous medium under the seal and isolating it from tissue in the place of a retinal break. A series of experiments with isolated donor eye balls on the development of a technology for the retina retention in the desired anatomic position using the designed fixator demonstrated high potential for the application [63, 64]. To define optimal configurations of the magnetic field in the fixator, a theoretical model was created and the distribution of the mechanical pressure in the seal projection was calculated for different geometrical dimensions and shapes of the internal and external magnetic elements of the fixator depending on the distance between them. It was shown that variation of the concentration of the magnetic filler in MAE and the sizes of the internal seal gives quite a high degree of variability of the fixator configuration while retaining the possibility of creation of the required level of a pressing force at the miniature sizes of the seal. Moreover, to improve the construction of the fixator, the method for producing external magneto-polymer seals from neodymium-iron-boron alloy via pressing the samples with a high degree of filling with the magnetic component and silicone binder was developed [60]. It was demonstrated that these composite materials can serve as an alternative to commercially available permanent magnets as the materials for the eye retina fixator elements, since the composite materials enable the synthesis of samples of any shapes. In the case of application, for example, of a thermoplastic acrylic polymer, the seal can be provided with the desired shape upon heating on a bend former under the required curvature of the eye surface.

Conclusions

In summary, it should be noted that the investigations in the field of MAEs over the past twenty years showed that these materials exhibit an extremely wide spectrum of new physical properties and phenomena, which arise under the action of external magnetic fields. It feels like we are still on the way to new discoveries in this area, in particular, owing to the high variability of the composite formulation. In our opinion, the effects of shape and dispersity of the magnetic filler particles on the material properties are still almost unexplored; new architectures of polymer matrices can introduce specific characteristics into the magnetic response of MAE. On the other hand, the level of understanding of the main aspects of magnetochemical phenomena, which arise upon magnetization of MAEs, achieved so far has created a foundation not only for the further advancing of their properties but also for their practical application, which realization requires the development of schemes for controlling the magnetic response of MAE. In general, the progress in this area leads to the extension of the silicone market as one of the most versatile elastomer materials.

Acknowledgements

This work was supported by the Russian Science Foundation, project no. 19-13-00340.

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References

1. L. V. Nikitin, L. S. Mironova, K. G. Kornev, G. V. Stepanov, A. N. Samus, *The Magnetodeformational Effects and Other Properties of Magnetoelastics*, Proc. Moscow International Symposium on Magnetism, Moscow, **1999**, part 2, p. 231.
2. For the first report on the properties of magnetoactive elastomers, see: *Nauka i Zhizn* (Life and Sciences), **2001**, <http://nauka.relis.ru/17/0002/17002078.htm>
3. T. Mitsumata, K. Ikeda, J. P. Gong, Y. Osada, D. Szabó, M. Zrínyi, *J. Appl. Phys.*, **1999**, 85, 8451. DOI: 10.1063/1.370626
4. J. M. Ginder, M. E. Nichols, L. D. Elie, J. L. Tardiff, *Proc. SPIE, Smart Struct. Mater. 1999: Smart Mater. Technol.*, **1999**, 3675, 131–138. DOI: 10.1117/12.352787
5. T. Mitsumata, T. Okazaki, *Jpn. J. Appl. Phys.*, **2007**, 46, 4220–4224. DOI: 10.1143/JJAP.46.4220
6. A. Boczkowska, S. F. Awietjan, R. Wroblewski, *Smart Mater. Struct.*, **2007**, 16, 1924–1930. DOI: 10.1088/0964-1726/16/5/049
7. Ubaidillah, J. Sutrisno, A. Purwanto, S. A. Mazlan, *Adv. Eng. Mater.*, **2015**, 17, 563–597. DOI: 10.1002/adem.201400258
8. G. Filipcsei, I. Csetneki, A. Szilágyi, M. Zrínyi, *Adv. Polym. Sci.*, **2007**, 206, 137–189. DOI: 10.1007/12_2006_104
9. M. Shamonin, E. Y. Kramarenko, in: *Novel Magnetic Nanostructures*, Amsterdam, Elsevier, **2018**, pp. 221–245. DOI: 10.1016/B978-0-12-813594-5.00007-2
10. A. M. Menzel, *Phys. Rep.*, **2015**, 554, 1–45. DOI: 10.1016/j.physrep.2014.10.001
11. S. Odenbach, *Arch. Appl. Mech.*, **2016**, 86, 269–279. DOI: 10.1007/s00419-015-1092-6
12. M. T. Lopez-Lopez, J. D. G. Durán, L. Yu. Iskakova, A. Yu. Zubarev, *J. Nanofluids*, **2016**, 5, 479–495. DOI: 10.1166/jon.2016.1233
13. L. V. Nikitin, L. S. Mironova, G. V. Stepanov, A. N. Samus, *Polym. Sci., Ser. A.*, **2001**, 43, 443–450.
14. S. S. Abramchuk, D. A. Grishin, E. Yu. Kramarenko, G. V. Stepanov, A. R. Khokhlov, *Polym. Sci., Ser. A*, **2006**, 48, 138–145. DOI: 10.1134/S0965545X06020064
15. G. V. Stepanov, S. S. Abramchuk, D. A. Grishin, L. V. Nikitin, E. Yu. Kramarenko, A. R. Khokhlov, *Polymer*, **2007**, 48, 488–495. DOI: 10.1016/j.polymer.2006.11.044
16. S. Abramchuk, E. Kramarenko, D. Grishin, G. Stepanov, L. V. Nikitin, G. Filipcsei, A. R. Khokhlov, M. Zrínyi, *Polym. Adv. Technol.*, **2007**, 18, 513–518. DOI: 10.1002/pat.923
17. A. Stoll, M. Mayer, G. J. Monkman, M. Shamonin, *J. Appl. Polym. Sci.*, **2014**, 131, 39793. DOI: 10.1002/app.39793
18. A. V. Chertovich, G. V. Stepanov, E. Yu. Kramarenko, A. R. Khokhlov, *Macromol. Mater. Eng.*, **2010**, 295, 336–341. DOI: 10.1002/mame.200900301
19. H.-N. An, S. J. Picken, E. Mendes, *Soft Matter*, **2012**, 8, 11995–12001. DOI: 10.1039/C2SM26587G
20. S. Abramchuk, E. Kramarenko, G. Stepanov, L. V. Nikitin, G. Filipcsei, A. R. Khokhlov, M. Zrínyi, *Polym. Adv. Technol.*, **2007**, 18, 883–890. DOI: 10.1002/pat.924
21. L. V. Nikitin, L. S. Mironova, K. G. Kornev, G. V. Stepanov, *Polym. Sci., Ser. A*, **2004**, 46, 301–309.
22. G. V. Stepanov, A. V. Chertovich, E. Yu. Kramarenko, *J. Magn. Magn. Mater.*, **2012**, 324, 3448–3451. DOI: 10.1016/j.jmmm.2012.02.062
23. E. Galipeau, P. Ponte Castañeda, *Proc. R. Soc. A*, **2013**, 469, 20130385. DOI: 10.1098/rspa.2013.0385
24. X. Guan, X. Dong, J. Ou, *J. Magn. Magn. Mater.*, **2008**, 320, 158–163. DOI: 10.1016/j.jmmm.2007.05.043

25. G. V. Stepanov, E. Yu. Kramarenko, D. A. Semerenko, *J. Phys.: Conf. Ser.*, **2013**, *412*, 012031. DOI: 10.1088/1742-6596/412/1/012031
26. V. V. Sorokin, E. Ecker, G. V. Stepanov, M. Shamonin, G. J. Monkman, E. Yu. Kramarenko, A. R. Khokhlov, *Soft Matter*, **2014**, *10*, 8765–8776. DOI: 10.1039/c4sm01738b
27. H. An, S. J. Picken, E. Mendes, *Polymer*, **2012**, *53*, 4164–4170. DOI: 10.1016/j.polymer.2012.07.023
28. V. V. Sorokin, I. A. Belyaeva, M. Shamonin, E. Yu. Kramarenko, *Phys. Rev. E*, **2017**, *95*, 062501. DOI: 10.1103/PhysRevE.95.062501
29. A. S. Semisalova, N. S. Perov, G. V. Stepanov, E. Yu. Kramarenko, A. R. Khokhlov, *Soft Matter*, **2013**, *9*, 11318–11324. DOI: 10.1039/c3sm52523f
30. I. A. Belyaeva, E. Yu. Kramarenko, M. Shamonin, *Polymer*, **2017**, *127*, 119–128. DOI: 10.1016/j.polymer.2017.08.056
31. S. A. Kostrov, M. Shamonin, G. V. Stepanov, E. Yu. Kramarenko, *Int. J. Mol. Sci.*, **2019**, *20*, 2230. DOI: 10.3390/ijms20092230
32. I. Bica, *J. Ind. Eng. Chem.*, **2012**, *18*, 483–486. DOI: 10.1016/j.jiec.2011.11.067
33. I. E. Kuznetsova, V. V. Kolesov, A. S. Fionov, E. Yu. Kramarenko, G. V. Stepanov, M. G. Mikheev, E. Verona, I. Solodov, *Mater. Today Commun.*, **2019**, *21*, 100610. DOI: 10.1016/j.mtcomm.2019.100610
34. I. E. Kuznetsova, V. V. Kolesov, B. D. Zaitsev, A. S. Fionov, A. M. Shihabudinov, G. V. Stepanov, E. Yu. Kramarenko, *Bull. Russ. Acad. Sci.: Phys.*, **2017**, *81*, 945–949. DOI: 10.3103/S1062873817080184
35. V. V. Sorokin, G. V. Stepanov, M. Shamonin, G. J. Monkman, A. R. Khokhlov, E. Yu. Kramarenko, *Polymer*, **2015**, *76*, 191–202. DOI: 10.1016/j.polymer.2015.08.040
36. L. V. Nikitin, G. V. Stepanov, L. S. Mironova, A. N. Samus, *J. Magn. Magn. Mater.*, **2003**, *258–259*, 468–470. DOI: 10.1016/S0304-8853(02)01099-5
37. Y. Li, J. Li, W. Li, H. Du, *Smart Mater. Struct.*, **2014**, *23*, 123001. DOI: 10.1088/0964-1726/23/12/123001
38. E. I. Alekseeva, S. R. Nanush'yan, I. Yu. Ruskol, E. V. Sokolyuk, *Polym. Sci., Ser. D*, **2010**, *3*, 244–248. DOI: 10.1134/S1995421210040076
39. G. V. Stepanov, E. I. Alekseeva, A. I. Gorbunov, *Catal. Ind.*, **2009**, *1*, 278–284. DOI: 10.1134/S2070050409040035
40. S. A. Kostrov, V. V. Gorodov, A. M. Muzafarov, *Vysokomol. Soedin., Ser. A*, **2020**, *62*, 1–9. DOI: 10.31857/S2308112020040082
41. W. F. M. Daniel, J. Burdyńska, M. Vatankhah-Varnoosfaderani, K. Matyjaszewski, J. Paturej, M. Rubinstein, A. V. Dobrynin, S. S. Sheiko, *Nat. Mater.*, **2016**, *15*, 183–189. DOI: 10.1038/nmat4508
42. Z. Cao, W. F. M. Daniel, M. Vatankhah-Varnoosfaderani, S. S. Sheiko, A. V. Dobrynin, *Macromolecules*, **2016**, *49*, 8009–8017. DOI: 10.1021/acs.macromol.6b01358
43. G. V. Stepanov, D. Yu. Borin, E. Yu. Kramarenko, V. V. Bogdanov, D. A. Semerenko, P. A. Storozhenko, *Polym. Sci., Ser. A*, **2014**, *56*, 603–613. DOI: 10.1134/S0965545X14050149
44. E. Yu. Kramarenko, A. V. Chertovich, G. V. Stepanov, A. S. Semisalova, L. A. Makarova, N. S. Perov, A. R. Khokhlov, *Smart Mater. Struct.*, **2015**, *24*, 035002. DOI: 10.1088/0964-1726/24/3/035002
45. D. Yu. Borin, G. V. Stepanov, S. Odenbach, *J. Phys.: Conf. Ser.*, **2013**, *412*, 012040. DOI: 10.1088/1742-6596/412/1/012040
46. D. Yu. Borin, G. V. Stepanov, *J. Optoelectron. Adv. Mater.*, **2013**, *15*, 249–253.
47. G. V. Stepanov, D. Yu. Borin, P. A. Storozhenko, *J. Magn. Magn. Mater.*, **2017**, *431*, 138–140. DOI: 10.1016/j.jmmm.2016.07.051
48. G. V. Stepanov, D. Yu. Borin, A. V. Bakhtiarov, P. A. Storozhenko, *Smart Mater. Struct.*, **2017**, *26*, 035060. DOI: 10.1088/1361-665X/aa5d3c
49. J. M. Linke, D. Yu. Borin, S. Odenbach, *RSC Adv.*, **2016**, *6*, 100407–100416. DOI: 10.1039/C6RA23435F
50. M. V. Vaganov, D. Yu. Borin, S. Odenbach, Yu. L. Raikher, *Soft Matter*, **2019**, *15*, 4947–4960. DOI: 10.1039/c9sm00736a
51. V. V. Gorodov, S. A. Kostrov, R. A. Kamyshinskii, E. Yu. Kramarenko, A. M. Muzafarov, *Russ. Chem. Bull.*, **2018**, *67*, 1639–1647. DOI: 10.1007/s11172-018-2271-8
52. V. V. Sorokin, B. O. Sokolov, G. V. Stepanov, E. Yu. Kramarenko, *J. Magn. Magn. Mater.*, **2018**, *459*, 268–271. DOI: 10.1016/j.jmmm.2017.10.074
53. S. Lee, C. Yim, W. Kim, S. Jeon, *ACS Appl. Mater. Interfaces*, **2015**, *7*, 19853–19856. DOI: 10.1021/acsami.5b06273
54. G. Glavan, P. Salamon, I. A. Belyaeva, M. Shamonin, I. Drevenšek-Olenik, *J. Appl. Polym. Sci.*, **2018**, *135*, 46221. DOI: 10.1002/app.46221
55. R. Li, X. Li, Y. Li, P.-a. Yang, J. Liu, *Friction*, **2019**. DOI: 10.1007/s40544-017-0309-0
56. G. Glavan, W. Kettl, A. Brunhuber, M. Shamonin, I. Drevenšek-Olenik, *Polymers*, **2019**, *11*, 594. DOI: 10.3390/polym11040594
57. P. A. Sánchez, E. S. Minina, S. S. Kantorovich, E. Yu. Kramarenko, *Soft Matter*, **2019**, *15*, 175–189. DOI: 10.1039/C8SM01850B
58. T. A. Nadzharyan, O. V. Stolbov, Yu. L. Raikher, E. Yu. Kramarenko, *Soft Matter*, **2019**, *15*, 9507–9519. DOI: 10.1039/c9sm02090j
59. Yu. A. Alekhina, L. A. Makarova, S. A. Kostrov, G. V. Stepanov, E. G. Kazimirova, N. S. Perov, E. Yu. Kramarenko, *J. Appl. Polym. Sci.*, **2018**, *136*, 47425. DOI: 10.1002/app.47425
60. Yu. A. Alekhina, L. A. Makarova, T. A. Nadzharyan, N. S. Perov, G. V. Stepanov, E. Yu. Kramarenko, *Bull. Russ. Acad. Sci.: Phys.*, **2019**, *83*, 801–803. DOI: 10.3103/S1062873819070049
61. L. A. Makarova, T. A. Nadzharyan, Yu. A. Alekhina, G. V. Stepanov, E. G. Kazimirova, N. S. Perov, E. Yu. Kramarenko, *Smart Mater. Struct.*, **2017**, *26*, 095054. DOI: 10.1088/1361-665X/aa82e9
62. T. A. Nadzharyan, L. A. Makarova, E. G. Kazimirova, N. S. Perov, E. Yu. Kramarenko, *J. Phys.: Conf. Ser.*, **2018**, *994*, 012002. DOI: 10.1088/1742-6596/994/1/012002
63. E. G. Kazimirova, V. V. Shiryayev, P. V. Lyskin, E. Yu. Kramarenko, *Vestn. Oftal'mol.*, **2017**, *5*, 24–30. DOI: 10.17116/oftalma2017133524-30
64. E. G. Kazimirova, V. V. Shiryayev, P. V. Lyskin, G. V. Stepanov, E. Yu. Kramarenko, *Modern Technol. Med.*, **2018**, *10* (4), 15–25. DOI: 10.17691/stm2018.10.4.02
65. RU Patent 169560 U1, **2017**.
66. RU Patent 2628652 C1, **2017**.
67. RU Patent 2628651 C1, **2017**.