Study of filler microstructure in magnetic soft composites

Study of filler microstructure in magnetic soft composites

H H Valiev[1], A Ya Minaev[2], G V Stepanov[3], Yu N Karnet[1]

[1]Federal budget - funded research Institute of applied mechanics of the Russian Academy of Sciences, 7 Leningradsky prospekt Moscow, 125040, Russia

[2] Federal budget - funded research Institute of Machines Science named after A.A. Blagonravov of the Russian Academy of Sciences, 4 Maly Kharitonyevsky Pereulok Moscow,101990, Russia

[3] State Research Institute for Chemical Technologies of Organoelement Compounds, 38 Shosse Entuziastov Moscow, 111123, Russia

E-mail: hhvlv@mail.ru

Abstract. Electron and atomic force microscopy were used for the study of magnetoactive filler surface microstructure in a magnetorheological composite. The particles redistribution phenomena of filler aggregates on the surface of elastomers under the action of a small external applied constant magnetic field are visualized. A model is proposed for the interaction of a magnetoactive filler with an elastomeric matrix of the composite, which explains the observed experimental results.

1. Introduction

At present, a fundamentally new class of intelligent or "smart" materials — magnetoactive elastomers with a giant magnetic response [1–15] is being intensively studied. These numerous studies have revealed, for example, the properties of these composites, such as magneto-rheological, magneto-deformation, magnetostrictive, magneto-electrorheological, magnetoresistive, piezoresistive, magnetoresistive, magneto-optical, magnetodielectric, magnetoacoustic, piezoelectric effects, as well as the shape memory effect. Such materials are characterized by the ability to control the oscillatory or vibrational processes occurring in the studied samples when exposed to them by small magnetic fields. Such magnetorheological dampers can be used in active vibration protection systems. For various areas of engineering, great interest is the possibility of controlling the dynamic properties of such materials by external influences. The elasticity and deformation of such rubber-like materials can be controlled using permanent magnetic fields. This class of materials is characterized by a change in dynamic properties, i.e. offset resonance characteristics in the region of higher frequencies with increasing exposure to magnetic fields. It is shown that, depending on various types of loading, it is possible to smoothly control the resonant frequencies of prototypes from 35 Hz to 150-170 Hz, i.e. it is possible to change the resonant frequencies of magnetorheological elastomers by almost 5 times [16-17]. Also installed are good dynamic impact characteristics of these materials. By adjusting the elastic-rigid characteristics of the magnetically controlled supports, you can rebuild the damped product from the resonant frequencies that occur during the operating modes of the products. Of great interest is the study of changes in the internal microstructure of such materials occurring under such external influences. In the development of joint studies of IPRIM and IMASH RAS and FSUE GNIIHTEOS in this work, further study of the surface structure of an analogous magnetic composite using the scanning electron (SEM) and atomic force (AFM) microscopy was carried out, which will allow a better understanding of the observed unique effects characteristic of such magnetoactive elastomers.

2. Experimental technique and materials

The magnetoactive materials studied in this work were synthesized according to the method developed at the FSUE GNIIHTEOS. Magnetoactive elastomers were synthesized on the basis of carbonyl iron powder P-20, previously reduced in hydrogen, and an elastic polymer matrix. Silicone oligomer of the "SIEL" brand, manufactured by SSC RF GNIIHTEOS, was used as a polymer base. The technology for producing a composite consisted of mixing the modified iron powder with the liquid components of a silicone oligomer, casting the composition into molds of a given size, and temperature polymerizing the silicone matrix. The iron powder was previously coated with a layer of silicone oil from a solution of petroleum ether at the rate of 0.5% oil per powder. Thus, the effect of wetting the surface of the magnetic component with silicone rubber was achieved. Silicone oligomer brand "SIEL" is a two-component system: component A: $(CH_3)_3SiO$ {[$(CH_3)_2SiO$] a - - [CH_3 (H) SiO] b} x – Si $(CH_3)_3$ and $(CH_2 = CH)_3SiO$ [CH_3 SiO] y - - Si $(CH = CH_2)_3$, component B: $(CH_2 = CH)_3SiO$ [CH_3 SiO] y - - Si $(CH = CH_2)_3$, reacting with the addition of a platinum catalyst. After mixing all the components, the process of polymerization of oligomers begins, which consists in the interaction of the vinyl groups with the hydride-containing component in the presence of a platinum catalyst. To accelerate the polymerization, the composition was heated to 100–150 ° C. The concentration of the magnetic component in the composite was 75 wt.%. The resulting samples have a high elasticity with a Young's modulus of elasticity of the order of 50 kPa.

The surface structure of the composites was studied using Phenom XL scanning electron microscopes (Phenom World BV, the Netherlands) and an EasyScan atomic force microscope (AFM) (Nanosurf, Switzerland), which worked in semi-contact mode in air at room temperature [18]. The protection of the AFM against external excitations with the help of a dynamic anti-vibration table TS-150 (Fabrik am Weiher, Switzerland) was also used. Cantilevers SuperSharpSilicon (Nanosensors, Switzerland) with a probe radius of about 2 nm were used. For visualization of filler particles in a rubber matrix, the phase contrast mode was additionally used. Processing of the obtained AFM images was carried out using the computer program SPIP (Image Metrology, Denmark). Changes in the surface topography of composites under the influence of an external constant magnetic field were also investigated. The use of a permanent magnet has various advantages in the practical use of such magnetic elastomers. In an atmosphere with volatile organic substances, the use of electricity to drive an electromagnet is problematic. The use of a magnetic field from permanent magnets can be effective also for various power failures. We used a disc-shaped permanent neodymium NdFeB magnet 6 mm in diameter and 3 mm high. The magnetic field strength was approximately 200 mT at the center of the upper surface of the magnet. The impact of the magnet on the composites under study was carried out in a specially designed snap-in that allows you to perform AFM measurements at a fixed position of the samples, eliminating the shift of the entire sample from the fixed position during the input and output of the magnet during filming. In all experiments, the vertical distance from the magnet mounted in the horizontal plane under the sample to the horizontal plane of the sample under study was about 1 cm.

3. Experimental results

Figure 1 shows a SEM image of the surface of a synthesized magnetoactive elastomer. A fairly uniform isotropic distribution of the filler aggregates (light particles) in the rubber matrix (dark background) is determined. AFM surface images of this composite are shown in figure 2 (topography on the left, phase contrast on the right). The top scan a) represents the topography of the composite, which is under the action of magnetic field, and the bottom scan b) when the magnetic field from the sample has been removed.

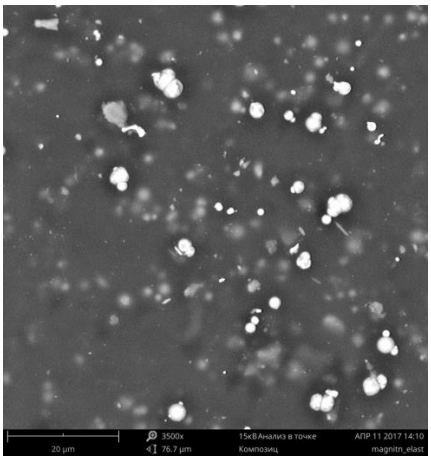

Figure 1. SEM image of the magnetic elastomer surface structure.
Scan: 76.7 x 76.7 microns.

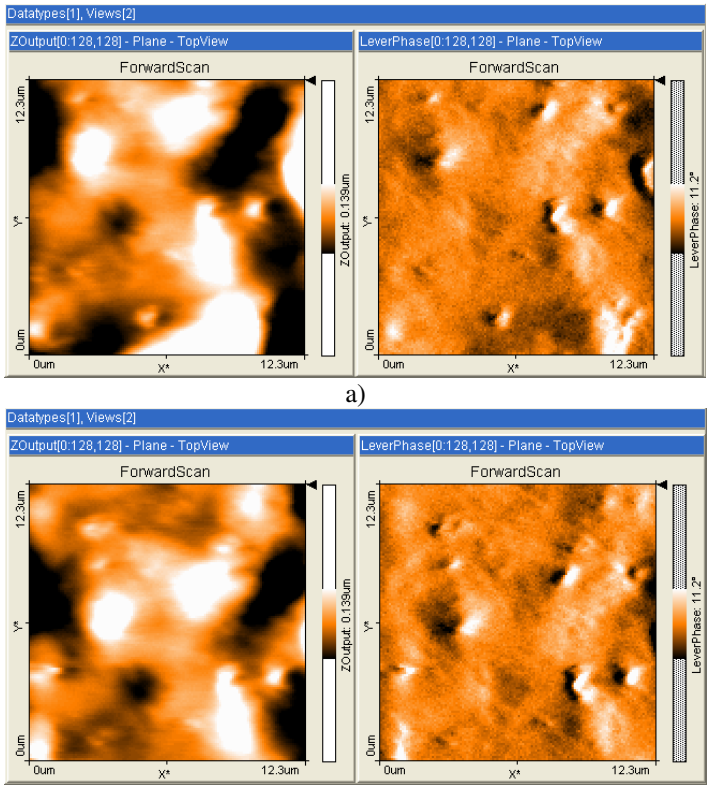

Figure 2. AFM images of the surface structure of a magnetoactive elastomer
(topography on the left, phase contrast on the right)
a) in a magnetic field (top scan); b) without magnetic field (bottom scan).
Scans 12.3 x 12.3 microns.

The analysis of the images made it possible to determine the size distribution of micro and nanoparticles of aggregates of the filler in an elastomeric matrix with an average value of nano and microaggregates of the order of 0.5–5 μm (figures 1–2). The distance between the aggregates of the filler is about 10 microns. Additionally, the phenomena of restructuring the aggregate particles of the filler on the surface of the composites under the action of an external applied constant magnetic field of about 0.2 tesla were directly visualized (figure 2a). In a specially designed system, a magnetic field of a disk-shaped neodymium magnet was applied from the underside of the sample under study parallel to the microscope probe, and AFM surface scanning was performed from the top. This

allowed the introduction and removal of the magnetic field acting on the sample under study, without disturbing the position of the analyzed surface under the AFM probe. The microstructure of the filler particles was completely restored after removing the magnet effect to its original state. The lateral displacements determined by AFM on the surface of composites of aggregates of the filler under the influence of a magnetic field were about 2 μm (figure 2a, b).

4. The discussion of the results

The microstructure of the filler particles in the composition of the elastomeric matrix, especially in rubbers with a small Young's modulus, significantly affects the properties of magnetoactive composites. Here the interaction of the elastic and magnetic subsystems of the magnetoactive composite is essential. The redistribution of the magnetic filler observed in the AFM together with the elastomer matrix can be represented graphically in figure 3.

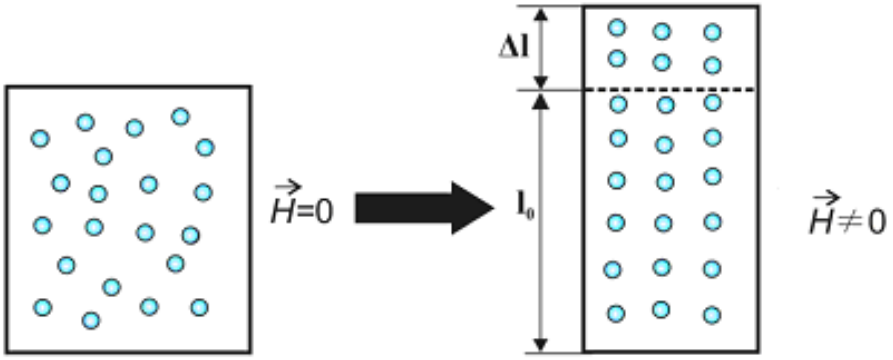

Figure 3. Redistribution of isotropic superparamagnetic iron filler on the background of an elastomeric matrix in the absence (left) and when an external magnetic field H is applied (right).

Here, on the left is the initial distribution of the isotropic superparamagnetic iron filler on the background of the elastomer matrix in the absence of an external magnetic field H, and on the right, when an external magnetic field is applied. Due to the smallness of the Young's modulus of the elastomer matrix during interaction of iron magnetic moments with a superimposed magnetic field, the sample is compressed in a direction parallel to the field and stretched accordingly in the perpendicular direction, which is directly visualized by AFM images. We can offer the following explanation for the occurring interactions leading to the observed magnetorheological effects. When a composite is formed, the electrons of carbonyl iron atoms, which act as electron donors, interact with silicon ions Si 4+ of the main siloxane chain, which serves as electron acceptors. This forms the interfacial polymer – filler layer, which provides the interconnection of the elastic and magnetic subsystems of the composite. The arising superparamagnetic state of iron atoms is due to the appearance of two energy-equivalent ionic oxidation states Fe 2+ and Fe 3+ with a fast electronic exchange between them. When an external magnetic field is applied, the degeneracy of these states is lifted with stabilization of a certain electronic configuration, which is accompanied by the appearance of a stable magnetic moment of iron ions, and, consequently, the magnetic moment stabilization of the filler single aggregate. Then immediately a cooperative exchange interaction of all magnetic moments in these iron aggregates in the composite arises due to their super-exchange spin interaction with the siloxane segments (Si - O - Si) of the silicone matrix. In turn, this leads to the observed unique effects characteristic of such magnetic elastomers.

5. Conclusion

The use of the SEM and AFM methods made it possible to determine the microstructure of magnetic active filler on the surface of the magnetorheological composite. With the help of AFM was directly visualized the phenomenon of redistribution of particles of aggregates of the filler on the surface of elastomers under the action of a small external applied constant magnetic field. These restructuring of the aggregates of the magnetoactive filler in the rubber matrix, due to the strong interaction of the elastic and magnetic subsystems of the composite, are presented as the reason for the appearance of huge magnetorheological and magnetostrictive effects in the synthesized samples of magnetoactive

elastomers. A model is proposed for the interaction of a magnetoactive filler with an elastomeric matrix of the composite, which explains the observed experimental results.

Acknowledgments
The work was performed on the state assignment in the Institute Applied Mechanics RAS for the period 2019-2021. State number Registration: AAAA-A19-119012290177-0.
The work was also supported by the RFBR № 19-53-12039\19

6. References

[1] Jolly M R, Carlson J D, Munoz B C and Bullions T A 1996 The magnetoviscoelastic response of elastomer composites consisting of ferrous particles embedded in a polymer matrix *J. Intell. Mater. Syst. Struct*. **7** 613-22

[2] Filipcsei G, Csetneki I, Szilgyi A and Zrinyi M 2007 Magnetic field-responsive smart polymer composites *Adv. Polym. Sci*. **206** 137-89

[3] Ubaidillah, Sutrisno J, Purwanto A and Mazlan S A 2015 Recent progress on magnetorheological solids: materials, fabrication, testing, and applications *Adv. Eng. Mater.* **17** 563-97

[4] Sorokin V V, Stepanov G V, Shamonin M, Monkman G J, Khokhlov A R and Kramarenko E Yu 2015 Hysteresis of the viscoelastic properties and the normal force in magnetically and mechanically soft magnetoactive elastomers: effects of filler composition, strain amplitude and magnetic field *Polymer* **76** 191-202

[5] Kramarenko E Yu, Chertovich A V, Stepanov G V, Semisalova A S, Makarova L A, Perov N S and Khokhlov A R 2015 Magnetic and viscoelastic response of elastomers with hard magnetic filler *Smart Mater. Struct.* **24** 035002

[6] Zrinyi M, Barsi L and Buki A 1996 Deformation of ferrogels induced by nonuniform magnetic fields *J. Chem. Phys*. **104** 8750-6

[7] Abramchuk S, Kramarenko E, Stepanov G, Nikitin L V, Filipcsei G, Khokhlov A R and Zrinyi M 2007 Novel highly elastic magnetic materials for dampers and seals I.: preparation and characterization of the elastic materials *Polym. Adv. Technol.* **18(11)** 883-90

[8] Abramchuk S, Kramarenko E, Grishin D, Stepanov G, Nikitin L V, Filipcsei G and Zrinyi M 2007 Novel highly elastic magnetic materials for dampers and seals II.: material behaviour in a magnetic field *Polym. Adv. Technol.* **18(7)** 513-8

[9] Li Y, Li J, Li W and Du H 2014 A state-of-the-art review on magnetorheological elastomer devices *Smart Mater. Struct.* **23** 123001

[10] Chertovich AV, Stepanov GV, Kramarenko EY, Khokhlov AR 2010 New composite elastomers with giant magnetic response Macromol Mater Eng **295** 336-341

[11] Sorokin V V, Stepanov G V, Shamonin M, Monkman G J, Khokhlov A R, Kramarenko E Yu 2015 Hysteresis of the viscoelastic properties and the normal force in magnetically and mechanically soft magnetoactive elastomers: effects of filler composition, strain amplitude and magnetic field *Polymer* **76** 191-202

[12] Becker T L, Zimmermann K, Borin D Y, Stepanov G V, Storozhenko P A 2018 Dynamic response of a sensor element of magnetic hybrid elastomer with controlled properties *Journal of magnetism and magnetic materials* **449** 77 -82

[13] T A Nadzharyan, S A Kostrov, G V Stepanov, E Yu Kramarenko 2018 Fractional rheological models of dynamic mechanical behavior of magnetoactive elastomers in magnetic fields *Polymer* **142** 316-329

[14] Alekhina Yu A, Makarova L A, Rusakova T S, Semisalova A S, Perov N S 2017 Properties of magnetorheological elastomers in crossed ac and dc magnetic fields, *Journal of the Siberian Federal University. Series: Mathematics and Physics* **10** 45-50

[15] Mikhailov V P, Bazinenkov A M, Dolinin P A, Stepanov G V 2018 Dynamic modeling of an active damper *Vestnik Mashinostroenia* **3** 34-36

[16] Korovkin YuV, Minaev AYa, Stepanov GV Dynamic properties of magnetically active elastomer composites in laboratory tests *Russian Engineering Research* vol 34 no 5 pp 299–302

[17] Minaev A Ya, Korovkin Yu V 2018 Study of the dynamic properties of magnetoactive elastomers and the development of damping supports *Assembly in machine building, instrument making* no1 pp 10-12

[18] Valiev HH, Vlasov AN, Vorobyev VV, Karnet YuN, Kornev YuV and Yumaschev OB 2019 Atomic force and electron scanning microscopy of silicone composites http:dx.doi.org10.5772 intechopen.79537