Atomic force microscopy and Mössbauer spectroscopy of magnetically active silicone elastomers

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Abstract. Elastomeric silicone composites with ferromagnetic filler are investigated. The distribution of carbonyl iron filler in the polymer matrix by scanning electron microscopy is visualized. Using atomic force microscopy the magnetostrictive characteristics of these materials are established. $^{57}$Fe nuclei hyperfine parameters of the iron filler atoms in the composites are determined by Mössbauer spectroscopy. The influence of the filler microparticles restructuring in external magnetic fields on the composites properties is discussed. The prospects for creating new materials and devices based on the characteristics of such magnetically active elastomers are revealed.

1. Introduction
To solve technical problems in modern highly organized technology, such as mechanical engineering, robotics, medical technology, space technology, etc., materials with a set of fundamentally new properties that could be controlled by external influences are required [1]. Magnetorheological elastomers (MRE) the rheological and mechanical properties of which vary greatly under the influence of an external magnetic field, attract great attention [2-3]. They consist of a non-magnetic polymer medium in which magnetic particles are dispersed. The balance between magnetic and elastic forces determine the resulting properties of the composites. This leads to numerous interesting effects that manifest in such magnetically active composites. In addition to the magnetorheological effect a magnetoelectro-rheological effect was also observed: a change in the viscoelastic properties of the composite under the simultaneous action of external magnetic and electric fields arising from the additional introduction of electroactive polymers into the material [4]. Significant magnetodeformation and magnetostrictive phenomena in external inhomogeneous magnetic fields have been established [5-7]. The phenomena of magnetic shape memory are discovered [8]. Magnetoresistive, piezoresistive, and magneto-piezoresistive properties were determined [9-12]. Magnetodielectric, magnetooptical, and magnetoacoustic effects were revealed [13–15]. Using the MRE dependence of
these elastic, rheological, electrical and other properties on the external magnetic field, magnetic and electric field sensors, controlled damping devices, and shock absorbers of engineering products are created [16-18]. However, many problems remain in the new generations effective MRE materials development. Of great interest is the internal microstructure of magnetically active composites changes that occur under such external influences [19]. In this work we further investigated the surface structure of a similar magnetically active composites using scanning electron (SEM) and atomic force (AFM) microscopy. $^{57}$Fe nuclei hyperfine parameters of the carbonyl iron filler atoms in the elastomeric matrix are determined using Mössbauer spectroscopy. The results obtained make it possible better understand the observed unique effects characteristic of such magnetically active composites.

2. Experimental technique

Powders of carbonyl iron grade P 10 as the magnetic filler of the silicone polymer matrix were used. The filler concentration in the composition was 75% mass. To ensure a more uniform distribution in the polymer binder the surface of the filler particles with a hydrophobizing organosilicon liquid 136-41 type was modified. Powders of such fillers with vinyl-containing and hydride-containing silicone oligomers in the presence of a complex platinum catalyst were mixed. The polymerization process was carried out first in a vacuum chamber, then at elevated temperature. The resulting materials have high elasticity with Young’s modulus of the order 50 kPa and heat resistance up to 200° C. Samples of rectangular composites with a length $L = 2$ cm, a width of 4 mm, and thicknesses of the order 2 mm were studied. The composites surface structure was studied using a Phenom ProX scanning electron microscope (SEM) (Phenom World BV, Netherlands) and an EasyScan atomic force microscope (AFM) (Nanosurf, Switzerland) operating in a semi-contact mode in air at room temperature. AFM protection against external excitations using a TS-150 dynamic anti-vibration table (Fabrik am Weiher, Switzerland) was applied. To visualize the filler particles in a silicone matrix, the AFM phase contrast mode was used. The neodymium magnet constant field influence on composites was effected in a specially designed construction, which allows AFM scans at a fixed position of the samples, eliminating the studied samples displacements when introducing and removing the magnet under the studied materials. The magnitude magnetic field induction of a disk shaped neodymium magnet directly at the scanning site of the composite under study was about 500 Oersted. The Mössbauer spectra were measured in the transmission geometry at room temperature using MS-1104Em electrodynamic spectrometer operating in the constant acceleration mode. $^{57}$Co(Rh) with an activity of 5 mCi was used as a source. Isomeric shifts were determined relative to $\alpha$-Fe. Spectra were recorded for samples both in an external magnetic field $H = 3.4$ kOe, applied in the transverse direction to the gamma-ray beam, and without a field.

3. Experimental results and discussion

An analysis of the composite surface structure obtained by SEM allowed us to determine a fairly uniform distribution of almost spherical filler micro- and nanoparticles aggregates (light objects) in an elastomeric matrix (dark background) with an average sizes carbonyl iron aggregates of 0.5 to 5 microns (figure 1). AFM data on the sizes of filler aggregates in the elastomer matrix are parallel to SEM data. Figures 2, 3 shows AFM phase contrast of surface images this magnetically active elastomer both in the absence and under the influence of a 500 Oersted magnet field. A significant restructuring of the composite surface arising under the influence such small external magnetic field is visualized. Control measurements of the AFM images show a complete return to the restoration the initial position of the filler particles in the rubber matrix after removing the magnet. The magnetostrictive transverse deformation of the composite reaches $\Delta L = 3$ microns. From this, the transverse magnetostriction constant of this composite is determined: $\lambda = \Delta L / L = 3$ microns / 2 cm = $1.5 \cdot 10^{-4}$. In most magnetic materials (for example, nickel, iron, cobalt and their alloys), the magnitude of magnetostriction constant is usually of the order of $\lambda \sim 10^{-7} - 10^{-5}$, and the highest
magnetostriction $\lambda \sim 10^{-3}$ is known in the Terfenol-D material [21]. Thus, a gigantic magnetostrictive effect in the studied sample can be stated upon application of a small constant external magnetic field.

The determination of the electronic structure and orientation of the carbonyl iron microparticles magnetization, used as a filler in the studied composites, is of great interest. Typical Mössbauer spectra of $^{57}$Fe nuclei in a filler composite matrix at room temperature are shown in figure 4 both in an external magnetic field $H = 3.4$ kOe, transverse to the direction of gamma quanta, and without a field. The abscissa axis represents the source velocity; the ordinate axis represents the relative intensities of gamma-ray absorption. The Mössbauer spectra demonstrate a well-resolved magnetic hyperfine structure: the sextet of absorption lines for $^{57}$Fe nuclei, corresponding to the Zeeman splitting of the nuclei energy levels in the iron atoms hyperfine magnetic field. Such spectra are characteristic of particles with sizes larger than a several nanometers, when the particle magnetization vector retains its
Figure 4. Room temperature Mössbauer spectra of a carbonyl iron filler in the magnetically active composite located: top - in the transverse external magnetic field $H = 3.4$ kOe; bottom - $H = 0$.

position during the Larmor precession period. The spectral parameters are characteristic of carbonyl iron: the absorption lines are relatively narrow ($\Gamma \approx 0.3$ mm / s), the isomeric shift is zero, and the average field on the iron nuclei is $H = 328.4(5)$ kOe. It is known that for a thin absorber with a random distribution of the direction of the hyperfine field on the iron nucleus, which coincides with the direction of the magnetization of the particle, the ratio of line intensities (from left to right) should be 3:2:1. And for magnetization in the plane of the sample should be 3:4:1. Since a thick absorber was used in the present experiments, there is a manifestation of the saturation effect, so the line shape deviates slightly from the Lorentzian one. Processing the spectra in the approximation of the Lorentz line shape gives the ratio of the intensities $A$ of the neighboring $A_2$ to $A_1$ lines: for the spectrum with $H = 0$ the value $A = 0.74$. This corresponds to the average angle of the magnetization to the sample plane $\Phi = 31^\circ$ (for the random distribution $\Phi = 35^\circ$). This is manifestation of the sample shape influence. The spectrum in the magnetic field $H = 3.4$ kOe gives the value $A = 1.00$ and $\Phi = 22^\circ$, i.e. the angle change $\Delta\Phi = 9^\circ$. Thus, Mössbauer investigations can provide valuable information about the electronic structure and orientation of the filler microparticles magnetization in the studied magnetoactive composites.

The experiments conducted at the vibration stands of IMASH RAS showed the possibility of a significant shift of the resonance frequencies of such composites under the action of magnetic fields of the same magnitude. It is planned to use these effects to create an actively controlled feedback damper by detuning a vibrating object from the resonant frequencies by changing the elastic-stiffness
characteristics of magnetoelastic supports. Therefore, it is possible to automatically control and maintain a minimum vibration level of practical scientific and technical objects.

4. Conclusions
Significant magnetostrictive deformations of the studied magnetoactive composites determined using AFM reveal the prospects of creating new materials and devices that provide significant advantages over currently used ones that are directly in demand in practice. Direct visualization of the restructuring of magnetically active carbonyl iron particles in a siloxane matrix under the influence of a small external magnetic field using an AFM and Mössbauer study data allow us better understand the reasons for the appearance of unique properties of such materials under low external influences. It can be assumed that the essential mechanism of these properties is due to the restructuring of the composite fillers in small external magnetic fields. The results obtained can be the basis for the design of actively controlled feedback dampers and promising new generation magnetostrictive engines with micro and nanoscale positioning accuracy and the ability to transfer significant force effects on the controlled objects.

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