The main goal of this project is to create a new generation of magnetoactive polymeric materials (MPM), capable of controlled changes of their physical properties under the influence of external magnetic fields. MPM are composites that contain ferromagnetic particles dispersed in liquid (magnetic fluids) or elastomeric (magnetic elastomers) media. Under the influence of an external magnetic field particles in magnetic fluids are arranged in so-called chain structures along the magnetic field lines, which leads to the appearance of a yield point and a very rapid (fractions of milliseconds) transition from a liquid to an almost solid state. In elastomeric media, the movement of particles is limited by the elasticity of the polymer matrix, and the resulting mesoscopic structures that magnetic particles form in magnetic field are determined by the balance of elastic and magnetic interactions. A change in the internal structure of an MPM in a magnetic field leads to a significant change in a number of physical properties of these materials, which opens up wide possibilities for their practical application.

The project was focused on developing (1) new polymer dispersed media based on comb-shaped polymers with a high grafting density of side chains (molecular brushes) and multichain star-shaped polymers, the regulation of the properties of which at the molecular level allows for the control of the level of filler microstructure restructuring in the presence of an external magnetic field, and, consequently, the physical properties of the composite material; and (2) new theoretical approaches to describing the properties of magnetoactive polymer materials.

Over the course of the third stage of the project, work on the synthesis of the main components of a new generation of MPM (magnetic fillers and dispersion media) was continued. A wide range of magnetic powders has been synthesized to create MPMs.

Methodology for the synthesis of anisotropic magnetic iron oxide by growing crystals of goethite FeOOH from an iron sulfate solution has been further developed and polished. The reduction of anisotropic goethite particles with hydrogen produced acicular magnetite particles with a particle size of 0.3–0.5 µm and a form factor of 5–7. Cubic magnetite with a particle size of 0.1-0.2 µm and metallic iron powder with a particle size of 0.2-0.3 µm were obtained. Cobalt ferrite with a high coercive force was obtained using coprecipitation of iron and cobalt sulfates from salts. Using the obtained cobalt ferrite, an iron-cobalt alloy powder with a particle size of 0.1-0.3 μm was obtained via reduction with hydrogen. All synthesized powders have good magnetic properties. Powders of cubic magnetite and metallic iron are soft magnetic materials with a coercive force of less than 10 mT, but the saturation magnetization of iron powder (160 G.cm3/g) is much higher than that of magnetite, while for magnetite the corresponding value is 70 G.cm3/g. Cobalt ferrite and cobalt iron alloy powders are magnetically hard materials with a coercive force of 150 and 100 mT, respectively. The saturation magnetization of the metal alloy is much higher than that of cobalt ferrite: 120 G.cm3/g and 30 G.cm3/g, respectively.

The following new dispersion media have been synthesized for the purposes of developing MPMs: 1) 128-chain PDMS stars with different chain lengths (33, 59, 87, 114). The range of molecular parameters of multichain PDMS stars that can be used as regular dispersion media for MPMs is determined; 2) a set of triblock copolymers with molecular brushes as middle blocks and linear end blocks. Such systems form microsegregated structures due to block incompatibility (linear blocks form spherical aggregates that play the role of physical stitches). During the synthesis, the length of the side chains, the length of the comb-shaped and linear blocks were varied; 3) brush elastomers based on chemically crosslinked molecular brushes.

Various MPMs were synthesized from the obtained components: magnetic fillers and widely used (cross-linked linear polymers) as well as novel matrices. The main focus of the study of their properties was the influence of viscoelastic properties of the MPMs on their magnetorheological (MR) response - the change in the elastic modulus in external magnetic field. A comparative analysis of a large number of samples with the same magnetic filling, but different elastic moduli was conducted, and it was shown that a significant MR effect can be achieved, if the elastic modulus of the composite is less than 100 kPa. In that case the MR effect can reach three to four orders of magnitude for materials with an elastic modulus of up to several kPa and concentration of magnetic iron particles close to 80 wt%. Magnetorheological fluids demonstrate the maximum effect of increasing the modulus, and the change in its magnitude with increasing magnetic field significantly depends on the type of dispersion medium, in particular, for MPMs based on multichain PDMS stars, the viscosity values ​​are saturated in relatively weak magnetic field of up to 300 mT, and the elastic modulus reaches saturation in the field of up to 100 mT.

The study of the structure, magnetic and viscoelastic properties of MPMs based on brush PDMS elastomers with different crosslinking densities and with different mass fractions of magnetic particles showed that, in contrast to traditional MAE based on linear polymers, brush elastomers demonstrate a strongly nonlinear elastic response. Due to the steric repulsion between the tightly grafted side chains, the brush elastomers are in the finite extensibility mode, when the mechanical properties are nonlinearly dependent on the crosslink density. The stiffening of the material with an increase in the amplitude of deformation increases with the concentration of crosslinks and the concentration of the magnetic filler. It has been shown that brush elastomers with high concentrations of magnetic particles are relatively “soft”, with an elastic modulus of less than 100 kPa, and reproduce the response of various skin tissues to deformation rather well (in particular, pig skin and human back skin). They demonstrate record values ​​of the MR effect, reaching three orders of magnitude. Repeated measurements of the components of the dynamic elasticity modulus 6 and 10 months after the synthesis of the samples show that the viscoelastic properties of the obtained composites do not undergo changes.

At this stage of work on the project one of the main focal points was the comparative analysis of the viscoelastic properties of elastomeric MPMs with isotropic and anisotropic distributions of magnetic filler in the polymer matrix, as well as MPMs based on spherical and anisometric particles. Anisotropic samples were obtained via synthesis in the presence of a magnetic field with the direction of the field chosen to be both perpendicular to the plane of the samples and parallel to it, which made it possible to study the effect of the relative orientation of the external mechanical force and the internal structure of the magnetic filler. It was shown that the elastic modulus of the material can vary depending on the direction of measurement in the range of 2-5 times. The most pronounced anisotropy of properties was obtained for composites with platelet particles.

Another important additional direction of work on the project has been the study of the dielectric properties of magnetoactive elastomers consisting of a soft silicone matrix and magnetically hard magnetic filler. It was shown that the presence of magnetically hard filler NdFeB makes it possible to passively control the dielectric response of MAEs by magnetizing the samples. The influence of the composition of the magnetic filler and the magnetization field on the dielectric properties of MAEs is important for the practical application of MAE as an element with a tunable dielectric response.

The motion of a system of spherical ferromagnetic particles in a viscoelastic medium in the presence of a magnetic field and the response of the medium to the motion of particles are studied. A model that connects the fractional Zener rheological model with the properties of the polymer matrix is proposed. It was shown that in a system of randomly distributed filler particles a tendency towards the formation of clusters is observed. It was also shown that the parameters of the fractional model influence the behavior of the system of particles in the magnetic field. For the case of ellipsoidal and cylindrical anisotropic inclusions-clusters, the response of a hyperelastic polymer medium to rotational and translational motion, as well as to an external load is calculated. It was demonstrated that the shape and size of anisotropic inclusions significantly changes the effective elasticity modulus of the material even in relatively weak magnetic fields, which is supported by experimental data.

Based on the results of the work on the project, three papers were written and were then published in the highly rated journals ACS Applied Materials and Interfaces, Polymers, Molecules. A chapter in Magnetic Materials and Technologies for Medical Applications has been prepared and published, it provides an overview of magnetoactive elastomers for biomedical applications. The results were reported at six conferences, three of which were international, and two of which included international participation. The research results were used for the lecture course "Fundamentals of Mechanics and Rheology of Polymers" (for graduate students of Moscow State University).