The main goal of this project is the design of novel magnetoactive polymer materials (MPM), which are capable of changing their physical properties under external magnetic fields. MPMs are composites based on ferromagnetic particles dispersed in liquid (magnetic fluids) or elastomeric (magnetic elastomers) media. Under an external magnetic field, magnetic particles inside the magnetic liquids aggregate in chain-like structures aligned with magnetic field, which leads to the appearance of the yield stress and a very rapid (fractions of milliseconds) transition from a liquid to an almost solid state. In elastomeric medium, particles’ motion is constrained by an elastic polymer matrix, and the resulting mesoscopic structures formed by magnetic particles in a magnetic field are affected by balance between elastic and magnetic interactions. The lower the elastic modulus, i.e., the softer the matrix, the larger the particles’ displacement from their initial equilibrium position can be realized in an external magnetic field. Change of internal structure of elastomeric materials in a magnetic field leads to significant changes in a number of physical properties of these materials, in particular, to a significant increase in the elastic modulus, to large deformations, etc. Due to their unique properties, magnetoactive materials are promising for a wide range of practical applications.

The aims of this project are the following. (1) Development of new polymer dispersion media based on bottlebrush polymers with a high grafting density of side chains (molecular brushes) and multiarmed stars. Regulation of their properties will allow one to control the restructuring degree of the filler microstructure under an external magnetic field on the molecular level, and, hence, the physical properties of the composite material. (2) Development of new theoretical approaches to describe the properties of magnetoactive polymer materials.

At the second stage of the project, we continued synthesis work and focused on the main components of a new generation MPMs: magnetic fillers and dispersion media. New methods for the synthesis and surface modification of magnetic nanoparticles of magnetite of various sizes and shapes have been tested out. A laboratory setup was made for the production of nano-iron powders by the decomposition of gaseous iron pentacarbonyl in silicone oil, which prevents the initial iron particles from sticking together. The size of the obtained powder was estimated by SEM and was less than 100 nm. The decomposition of nickel acetylacetonates, cobalt, iron at temperatures of 215 - 290 ° C in ethylene glycol and glycerin has been performed. Also, a method for obtaining magnetite nanoparticles by the solvothermal method was developed. The technology of coating the surface of nanoparticles with carbon has been developed; depending on the modification conditions, the size of the particles and their magnetic properties can change 10 times.

As new dispersion media for the development of MPMs with a high response to magnetic fields we synthesized and characterized 1) multiarmed polydimethylsiloxane stars with 16, 32, and 64 arms and an average arm length of 32 to 120 dimethylsiloxane monomers and 2) bottlebrushes based on poly(dimethylsiloxane) (PDMS) with different ratios of the length of the main chain and side chains. Their rheological and viscoelastic properties, depending on the structure were studied.

Unlike the first stage, where attention was paid to liquid-based MPMs, at the second stage elastomeric compositions based on bottlebrush PDMS were obtained for the first time. Special injection method for rapid mixing of components and prevention of sedimentation of magnetic particles in the liquid composition before the completion of the polymerization processes was developed. Elastomeric MPMs based on bottlebrushes with varying degrees of crosslinking and carbonyl iron microparticles concentration from 10 to 80 wt.% were obtained. Their mechanical and viscoelastic properties were studied by static tension and dynamic mechanical analysis. It was shown that a decrease in the molar fraction of side chains with terminal OH groups from 1.5 to 0.5 leads to a gradual softening of the MPM matrices in the absence of magnetic particles. Young's modulus values as low as 1000 Pa are achieved, which corresponds to the elastic modulus of soft biological tissues, such as lungs, kidneys and brain. When magnetic particles are added, the elastic modulus increases with an increase in the volume fraction of magnetic particles. Nevertheless, MPM composites remain relatively soft with E <100 kPa, i.e. within the range of biological softness. Due to the combination of solvent-free synthesis and tissue mimetic mechanical properties, these materials have high potential for biomedical applications. It was shown that the relative growth of the storage modulus of composites based on the softest matrices (0.5 mol% of PDMS-OH) in a magnetic field of 1 T reaches two orders of magnitude, which is typical for MPMs based on standard silicone compositions with a low molecular weight plasticizer content of up to 70 wt%. Thus, the use of bottlebrushes made it possible to exclude the low molecular weight component without losing the value of the magnetorheological effect.

Work on the creation of MPMs based on amphiphilic polymer matrices has been started in three different ways. 1) Samples of magnetoactive elastomers containing carbonyl iron as a magnetic filler and PDMS with glycerol as a dispersed medium were obtained. The ratio of components in the system was varied. The obtained samples demonstrate moderate values ​​of the storage modulus in the range of 7-20 kPa. The relative increase in the storage modulus in a magnetic field is several times. 2) Series of LBL triblock copolymers with a polydimethylsiloxane (PDMS) bottlebrush block (B-block) and two polymethyl-methacrylate (PMMA) linear end blocks (L-blocks) were synthesized. This series contains LBL triblocks with various polymerization degrees of the bottlebrush backbone (nbb = 100-1100) and L-block PMMA (nL = 50-1300). The next step is to characterize the mechanical properties of these compounds as pure material and with different fractions of magnetic particles. 3) PEG monoallyl ethers of various molecular weights have been synthesized. They are supposed to be used to obtain hydrophilic matrices based on polymethylhydride siloxane oligomers.

The synthesis methods of elastomeric MPMs with anisotropic distribution of magnetic filler in the polymer matrix deserved a great attention at this stage. Molds for polymerization in a confined volume in magnetic fields of different magnitudes were designed. Anisotropic elastomeric MPMs with chain aggregates of magnetic particles, predominantly aligned with the magnetic field in which the synthesis was carried out, were obtained. The mechanical properties of the material are studied depending on the mutual orientation of the external mechanical force and the internal structure of the filler; it was shown that the effect of anisotropy of mechanical properties can reach several hundred percent.

Another important area of ​​the work was to study the phenomenon of magnetodeformation (magnetostriction) in elastomeric MPMs. The effect is that significant elongation of the samples occurs in an external uniform magnetic field. In contrast to traditional magnetostrictive materials, the physical basis of magnetostriction in elastomeric MPMs relates to significant rearrangement of the filler structure and the resulting deformations of the polymer matrix, while the magnetostriction value can reach 20%. To study the dependence of the the effect magnitude on the structure and composition of the MPMs, materials with a wide set of fillers and various elastic moduli of the matrix were synthesized, and two methods to study the magnetic response of samples were applied. The first method is direct measurements of the elongation of the samples in a magnetic field. During the second one, the stresses occurring in confined sample in response to the applied field were measured. It was shown that structured samples (synthesized in a magnetic field) exhibit a significantly higher effect than isotropic samples with the same content of magnetic filler. The relative elongation of the samples increases (a) with an increase of magnetic filler concentration due to the enhancement of magnetic interactions and (b) with a decrease in the elastic modulus of the polymer matrix, since the restructuring degree is greater in softer matrices. The magnetostrictive behavior of all samples in ascending-descending magnetic fields was characterized by significant hysteresis characteristic of the magnetomechanical properties of soft magnetoactive elastomers. Measurements of stresses in confined MPM specimens and interpretation of the results within the framework of theoretical consideration made it possible to distinguish two different contributions to magnetostriction one of which is the macroscopic effect associated with the value of the sample’s aspect ratio and the second one if the microstructure of the filler.

Two theoretical models that describe the processes occurring in magnetoactive elastomers have been proposed and studied. A one-dimensional fractional differential equation of motion of a viscoelastic medium is solved. This equation describes the response of a polymer matrix to the motion of ferromagnetic filler particles in an external magnetic field. Various initial conditions as well as solution stability are considered. It is shown that the proposed model can describe the viscoelastic properties of a polymer medium. A model that describes the restructuring of a cluster of ferromagnetic particles in a magnetoactive elastomer as a rotation of a ferromagnetic ellipsoid in a cell was developed. The dependences of the elastic response of the medium to the ellipsoid rotation caused by the magnetic field on the geometric anisotropy of the aggregate, filler concentration in the material and the direction of the magnetic field were calculated.

Three papers where prepared based on the obtained results. Two of them are published in high-rated journals Soft Matter and Materials. The third one is accepted for publishing in Polymer Sciences. Results were reported at 3 international conferences. Moreover, one of the project members used results obtained during this project in Master’s dissertation, which was graded with an excellent mark. Materials of this work were also used in PhD thesis, which is going to be defended in December. Research results were used in lecture course «Introduction to polymer mechanics and rheology» (for postgraduate students).