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Microstructure and Properties of Magnetorheological Elastomers

Anna Boczkowska and Stefan Awietjan

1. Introduction

Magnetorheological elastomers (MREs) belong to the new group of the functional materials called “smart”. Although smart materials are known since long time, their intensive development started in the end of the XXth century. The term smart materials, intelligent materials or less frequently used adaptive materials or multifunctional materials, was introduced in the eighties of the twentieth century, when some materials, which were included in the group were already known. Till today there is no accepted universal definition of smart material, it is also not included in the encyclopedia devoted to these materials, published in 2002 [1, 2].

The term smart material generally refers to material which changes its properties under the influence of various external stimuli [3]. However, it seems that this approach is too simplistic. Much more precise description of smart material is given by Takagi in his work [4]. According to him, smart material is capable of reacting to external stimuli by changing its material properties for the desired way and effectively responds to these stimuli. Such material should therefore be some kind of sensor, processor, and actuator. These attributes should be looped, and the effect of changing the properties of the material should be done in real time.

Among smart materials, magnetorheological materials (MR) are an important group. They are a class of materials with rheological properties rapidly varied by the application of a magnetic field (Fig. 1). The change in their properties is in the proportion to the magnitude of the magnetic field applied and is immediately reversible. The Bingham plastic model is often used to model the behaviour of MR materials [1].

Research focussing on magnetorheological materials was initiated by Jacob Rabinow at the National Bureau of Standards, now the National Institute for Science and Technology, in the
United States in the 1940s and early 1950s. His early works on magnetorheological fluids led to a host of devices and products based on dry magnetic powders, for example the magnetic, powder brake. In addition to MR fluids, the MR materials also contain magnetic field responsive gels [5], foams, powders, and elastomers. The comparison of the most typical magnetorheological materials is shown in Table 1.

![Figure 1. Magnetorheological material A- before, B – and after the application of an external magnetic field.](image)

<table>
<thead>
<tr>
<th></th>
<th>Magnetorheological fluid MRF</th>
<th>Ferrofluid</th>
<th>Magnetorheological elastomer MRE</th>
</tr>
</thead>
<tbody>
<tr>
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<td>iron</td>
</tr>
<tr>
<td>Particles size</td>
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<td>2 –10 nm</td>
<td>10 – 50 μm</td>
</tr>
<tr>
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<td>oils</td>
<td>oils, water</td>
<td>elastomers</td>
</tr>
<tr>
<td>Volume fraction</td>
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<td>0,02 – 0,2</td>
<td>0,1 – 0,5</td>
</tr>
<tr>
<td>Additives</td>
<td>surfactants, thicsotropic agents</td>
<td>surfactants</td>
<td>none</td>
</tr>
<tr>
<td>Viscosity without external magnetic field [mPa·s]</td>
<td>100 - 1000</td>
<td>2 - 200</td>
<td>none</td>
</tr>
<tr>
<td>Change of properties in an external magnetic field</td>
<td>Yield stress $\tau_y$ up to $\sim$100 kPa</td>
<td>Relative viscosity $\Delta \eta / \eta \sim$1</td>
<td>Storage modulus $\Delta G' \sim$20 kPa</td>
</tr>
</tbody>
</table>

Table 1. Composition and properties of typical magnetorheological materials [6].

The interest in magnetorheological elastomers (MREs) has recently increased because of their prospects for application in various smart systems. They are still much less known than magnetorheological fluids. The MREs are smart materials, analogues of the magnetorheological fluids (MRFs), in which the fluid component is replaced by a cross-linked material like rubber or silicone. They consist of micron sized magnetically permeable particles in non-magnetic matrix. In a similar way, as in the case of MRFs, the particles tend to align themselves in the direction of the magnetic field, but after curing of the matrix such microstructure is fixed. Magnetorheological materials change their rheological properties under the influence of an external magnetic field. Their rheological properties can be changed continuously, rapidly and reversibly by changing an external magnetic field. This behaviour is described by the magnetorheological effect.
In this chapter the overview on magnetorheological elastomers is given, as well as basic knowledge about rheology and magneto-rheology. Also the effect of the amount, size and orientation of the particles on the microstructure and properties of MREs is discussed, as well as the influence of magnetic field on the compressive characteristics and rheological properties of developed MREs.

2. Magnetorheological elastomers

The MREs consist of magnetically permeable particles (such as iron or other ferromagnetic particles) added to a viscoelastic polymeric material prior to crosslinking. The MREs contain ferromagnetic particles having sizes from few to few hundreds of μm. Pure iron has the highest saturation magnetization of known elements and it has also high permeability and low remanent magnetization, providing high, short-term inter-particle attraction. It is known from available literature that the amount and the shape of the particles, as well as the type of the polymer matrix influence the MREs properties.

MREs can be classified according to several parameters like: particles type, matrix, structure and distribution of particles [7].

MREs classification:

1. Particles magnetic properties
   a. Soft magnetic particles
   b. Hard magnetic particles
   c. Magnetostrictive particles
   d. Magnetic shape-memory particles
2. Matrix structure
   a. Solid matrix
   b. Porous matrix
3. Matrix electrical properties
   a. Isolating matrix
   b. Conductive matrix
4. Distribution of particles
   a. Isotropic
   b. Anisotropic

Usually magnetic field is applied to the polymer composites during crosslinking of the matrix. Such treatment locks the columnar particle chain structures during the final cure giving special anisotropic properties. The formation of columnar particle structures within the elastomers corresponds to a low dipolar energy state. Shearing of the cured composite under applied magnetic field requires additional energy because of the particles displacement from this low energy state. The amount of work required and the field dependent shear modulus increase steadily with the applied magnetic field [8, 9, 10].

Changes of the properties in MREs under the influence of the magnetic field depend strongly on the microstructure formed during the curing of elastomer matrix, also as a result
of magnetic field. Interactions between particles in a magnetic field bring them closer, resulting in increased stiffness of the material. This changes the stress-strain curves [11]. The magnetic field causes a shift towards higher stresses. The same mechanism is responsible for the effect of "magnetostriction", shortening of length of the cylindrical sample in the presence of an external magnetic field [12], as schematically shown in Figure 2A, or its extension, the MRE when the particles are distributed isotropically [13]. Under the influence of the field the particles move in the direction of the field, as shown in Figure 2B. This effect is possible when the adhesion between the particles and the matrix is large enough so that the movement of particles leads to deformation of the elastomeric matrix, which is has such low stiffness that such deformations can occur. A similar phenomenon occurs in the MREs, in which the particles are spherical and have an elongated shape [14]. Then, under the influence of the magnetic field they become dipoles, rotating in the direction of the magnetic field vector, which also leads to deformation of the elastomer and thus increase in the length of the sample (Fig. 2C). In all cases, these changes are rapid and fully reversible.

**Figure 2.** Magnetostriction effect in MREs under external magnetic field.

Under the influence of magnetic field rheological properties of MREs change [15], mainly shear modulus, but also the modulus of elasticity determined in a compression test [11]. These properties are strongly dependent on a magnetic field strength. Shearing of MREs in the presence of a magnetic field displaces the particles from the position of minimum energy state, which requires additional work increasing monotonically with increasing magnetic field strength. Therefore, shear modulus depends on the field and is a characteristic feature of the MREs [10, 16]. Changes of the module in the magnetic field also depend on the content of ferromagnetic particles in the elastomer matrix.
The vast majority of MREs described in the literature contain soft magnetic particles, mainly iron, cobalt and their oxides [17,18,19,20]. There is a group of magnetorheological elastomers with hard magnetic fillers like BaFe$_{12}$O$_{19}$ or SrFe$_{12}$O$_{19}$ [21]. These materials, like permanent magnets remain magnetized after turning off the external magnetic field [22,23]. For the fabrication of MREs also magnetostrictive particles are used, usually Terfenol D - a material with giant magnetostriction [24,25] and the particles with magnetic shape memory (MSM), such as Ni-Mn-Ga [26,27,28].

The matrix of magnetorheological elastomers can be solid or porous. MREs with porous matrix, also called magnetorheological foams, have foamed matrix in order to increase the abilities to change their properties. Majority of magnetorheological elastomers have a matrix with electrically insulating properties. In some cases magnetorheological elastomers, which were doped with electrically conductive particles such as graphite or silver and their percolation threshold has been reached, become electric conductors [29]. Conductive polymers such as polypyrrole, polyacetylene, polyaniline can also be used for matrix [30,31]. However, using a conductive matrix has no significant effect on changes in the rheological or mechanical properties in a magnetic field, and raises costs.

The spatial distribution of the particles is determined during curing process. In the presence of a magnetic field during curing, the obtained elastomer has anisotropic, oriented structure, consisting of chains of particles [10,6,7,8,32,33,34,35,36] as schematically shown in Figure 3B. Magnetorheological elastomer cured without the magnetic field allows to receive isotropic structure, which is shown on a schematic diagram in Figure 3A [11,20,21,37,38,39,40,41,42].

![Figure 3. Schematic microstructure of MRE: A - isotropic, B - anisotropic spatial distribution of particles.](image-url)
3. The rheological properties and magnetorheological effect of magnetorheological elastomers

Many materials, especially polymers and their composites are characterized by viscoelastic properties [43]. This means that they combine the features of elastic solids and viscous liquids, as schematically shown in Figure 4. Their behavior is between the ideal solid described by Hooke’s law, in which the stress is always directly proportional to the strain and is independent of strain rate, and a viscous liquid, in which according to Newton’s law, stress is always directly proportional to the strain rate and does not depend on the strain. Viscoelastic materials under rapid deformation behave more like elastic body, and under very slow - as viscous liquid. Rheology describes the flow and deformation of solids and liquids under the influence of an external forces.

![Viscoelastic properties of materials.](image)

For a perfectly elastic solid when the force is applied, strain occurs immediately, and it is linearly proportional to the applied force. The ratio of stress to strain is a measure of elasticity of the material. After unloading deformed body immediately returns to its initial state. The applied force can cause the shear stress ($\tau$) and shear modulus ($G$). $G$ modulus determines the resistance of the solid to deformation and is expressed by the ratio of shear stress ($\tau$) to the shear strain ($\gamma$):

$$G = \frac{\tau}{\gamma} \quad (1)$$

For an elastic solid, both stress and strain are independent on time. For the viscoelastic solid, rheological parameters are dependent on the time and described by Kelvin-Voight model for linear viscoelasticity:

$$\tau = G \cdot \gamma + \eta \frac{d\gamma}{dt} \quad (2)$$

where:
- $\eta$ – dynamic viscosity,
- $t$ – time.

Deformed material can undergo relaxation when the applied force is maintained, which results in a decrease in the stress in time, until its complete disappeared, as schematically shown in Figure 5. When the force is removed, the disappearance of deformation is delayed. This delay is given by the relaxation time $\lambda$: 
\[ \lambda = \frac{\eta}{G} \]  \hspace{1cm} (3)

In the area of linear viscoelasticity delay times during creep and recovery are the same. Usually solids are more complicated and to describe the viscoelastic behavior during the creep and recovery it is necessary to use the whole spectrum of relaxation times. In most testing methods of viscoelastic materials, instead of constant stress, dynamic strain measurements in the form of an oscillating sinusoidal function of time is used (Fig. 6):

\[ \tau = \tau_0 \cdot \sin(\omega \cdot t) \]  \hspace{1cm} (4)

where: \( \tau_0 \) - applied stress,
\( \omega \) - angular velocity [1/s or rad/s],
\( \phi \) - angle.

\[ \omega = 2\pi \cdot f, \text{ } f \text{ } - \text{ frequency } \text{[Hz]} \]  \hspace{1cm} (5)

Figure 5. Stress relaxation (\( \tau \)) at time (t).

Figure 6. Dynamic measurements: a - deformation of the angle \( \phi \), b - sinusoidal strain or stress.
The course of deformation and the induced stress in the perfectly elastic solid is in-phase, as shown schematically in Figure 7. However, in the viscoelastic material phase shift angle $\delta$ occurs in the range $0 - 90^\circ$, between the stress and strain that induces it (Fig. 8). It is the result of delayed reaction of the material to an applied strain. The response to an applied strain consistent with the phase is called the elastic (material entirely elastic - behaves according to Hooke's law), shifted in phase by $90^\circ$ - viscous (material entirely viscous - behaves like a Newtonian fluid), and between $0$ and $90^\circ$ - viscoelastic (viscoelastic material).

To combine the elastic and viscous properties the complex shear modulus $G^*$ has been introduced. It is the total resistance of the solid to the applied strain and is defined as:

$$G^* = \frac{\tau_0}{\gamma_0}$$

(6)
For viscoelastic materials, both complex modulus and phase angle is frequency dependent. For easy distinction between elastic and viscous behavior of the material complex numbers were introduced, so that the complex shear modulus can be described as follows:

\[ G^* = G' + iG'' \]  \hspace{1cm} (7)

where:
- \( G' \) - storage modulus, or elastic (the real part of complex modulus \( G^* \)),
- \( G'' \) - loss modulus, or viscous (imaginary part of complex modulus \( G^* \)).

The term storage modulus indicates that the strain energy is temporarily stored during deformation, and can be later recovered, and the loss modulus term means that the energy is irretrievably lost and converted to shear heat. Modules \( G' \) and \( G'' \) are described by the following relations:

\[ G' = G^' \cdot \cos \delta = \frac{\tau_0}{\gamma_0} \cdot \cos \delta, \]  \hspace{1cm} (8)

\[ G'' = G^' \cdot \sin \delta = \frac{\tau_0}{\gamma_0} \cdot \sin \delta. \]  \hspace{1cm} (9)

Storage modulus \( G' \) and loss modulus \( G'' \) are parameters describing the rheological properties of viscoelastic polymeric materials. Storage modulus \( G' \) defined by the ratio of elastic stress to strain, describes the amount of stored (saved) energy during shear, and refers to the elastic properties of the material. Loss modulus \( G'' \) expressed by the ratio of viscoelastic stress to strain, shows how much energy was dissipated in a cycle of deformation in the form of heat and defines the viscous properties of the material [44].

If the complex modulus value is equal to the storage modulus \( G^* = G' \), the loss modulus \( G'' \) is equal to zero and the material is completely elastic - the whole cycle of deformation energy is stored and then released, and the deformation is completely reversible. When the complex modulus is equal to the loss modulus \( G^* = G'' \), storage modulus \( G' \) is equal to zero and the material is completely viscous. Modules \( G' \) and \( G'' \) are dependent on the frequency of oscillation and the temperature. The higher the frequency of oscillation, the higher the value of the modules \( G' \) and \( G'' \). A rise in temperature causes a decrease in storage modulus \( G' \) and increase of loss modulus \( G'' \) [44].

The ratio of loss modulus \( G'' \) to the storage modulus \( G' \) is called the loss angle (damping) and is expressed by the tangent of the phase angle \( \delta \) [45].

\[ \tan(\delta) = \frac{G''}{G'} \]  \hspace{1cm} (10)

The loss angle \( \tan(\delta) \) is the ratio between the energy lost and stored during the deformation and determines the viscoelastic material’s ability to dissipate (damp) energy [45].
Case of completely viscous material value of \(\tan(\delta)\) is greater than 1, and the loss modulus values are higher than the storage modulus \(G'' > G'\). When the value of \(\tan(\delta)\) is less than 1 it means supremacy of the elastic properties over the viscous, which means higher values of storage modulus in relation to the loss modulus \(G' > G''\). The lower the value of the \(\tan(\delta)\), the more elastic the material. A zero value of \(\tan(\delta)\) indicates that the material is perfectly elastic [46].

To describe the damping properties of the material parameters such as the loss angle \(\tan(\delta)\) and the complex shear modulus \(G^*\) are used [47,48]. Damping of vibration or the damping of cyclic deformation is related to a non-reversible absorption of the deformation energy and its conversion into heat that is dissipated by the material [49].

Magnetorheological elastomers are viscoelastic materials, which because of their potential applications are subjected to dynamic loads. Characteristic MREs work area is in the range of small deformations below the yield stress. Under the influence of the magnetic field MREs change their stiffness over a wide range, allowing customization for effective vibration damping. MREs properties are studied and described by the equations typical for viscoelastic materials, with the parameter describing the influence of the external magnetic field on the rheological properties of MREs.

Change in the properties of MREs under the magnetic field is called the magnetorheological (MR) effect and is the most important and most extensively studied property of magnetorheological composites.

The term “magnetorheological” is used only in relation to a group of magnetorheological materials. It describes the reversible properties changes under the magnetic field in comparison to the material properties without the presence of the field. Changes in the rheological properties are usually described by the shear modules: storage \(G'\) and loss \(G''\) [10,50,51,52,53,54,55]. The magnetorheological effect is also associated with increased stiffness (modulus of elasticity, measured in compression test for example) and the change in damping of magnetorheological materials [11].

Changes in the properties of MREs under the magnetic field, described as the MR effect are related to the magnetic particles tendency to change their position under the influence of an applied magnetic field. The magnetic field induces dipole moments in the ferromagnetic particles, which tend to obtain the positions of minimum energy state. Particles movement introduce deformations in the elastomer matrix, resulting in the increase of shear modulus and stiffness of the MREs. Secondly, the interactions between particles in a magnetic field causes their attraction to each other, which also introduces a deformation in the elastomeric matrix and, consequently, increases the stiffness of the material and shear modules [56]. We can conclude that due to efforts of magnetic particles to change the position in a magnetic field, the elastic matrix is deformed, which leads to an increase in the shear modules (\(G^*\)) [20].

The creation of oriented chains of particles in the elastomer leads to a state of minimum magnetic energy [10]. Such MREs under shear deformation in the presence of an external
magnetic field losses the low-energy state and requires additional work associated with the movement of entire chains of particles that oppose the deformation and tend to return to equilibrium state. Deformation of the matrix leads to an increase in the value of shear modules $G'$ and $G''$ and increase in the stiffness of the elastomer. MREs properties strongly depend on the magnetic field strength. Studies of the MREs magnetorheological effect are usually carried out at relatively small frequencies (from 1 to 20 Hz) [8,10,57,58,59,60].

Changes of the properties of magnetorheological composites in the magnetic field are usually described by absolute and relative magnetorheological effect [61].

The absolute magnetorheological (MR) effect is the difference between the maximum value of shear modulus $G_{\text{max}}$ achieved in a magnetic field, and the value obtained without a magnetic field $G_0$ (called zero field modulus). The absolute magnetorheological effect is described by the equation:

$$\Delta G = G_{\text{max}} - G_0 \text{ [MPa]}.$$  \hspace{1cm} (11)

The relative magnetorheological (MR) effect is the ratio of the absolute magnetorheological effect to the zero field modulus $G_0$, expressed in percents:

$$\frac{\Delta G}{G_0} \cdot 100\%.$$  \hspace{1cm} (12)

As it is shown in the literature the absolute and relative MR effects depend on the content of magnetic particles, the frequency of oscillations and the magnetic field strength [20,32,40,42,57,61].

According to reports relative magnetorheological effect can be of 30-40% on average [62], and even 60% for MRE containing 30% vol. iron particles [63]. With the increase in the frequency in the range from 100 to 1400 Hz, shear modulus increases up to four times for MRE containing 27% vol. iron particles. An increase in shear modulus (about 2 MPa) under the influence of the magnetic field of 0.56 T, as well as significant MR effect has been obtained [8,58,60,64].

In most studies, the magnetic field is applied parallel to the chains with iron particles, in order to increase the interaction between particles inside chains [8,57,62].

The MR effect is also influenced by the amplitude of the applied strain, and this is because forces of the magnetic interaction strongly depend on the distance between the dipoles (the iron particles) [20,58]. Magnetorheological elastomers are characterized by a greater strain at which the MR effect is significant than the corresponding MR fluids [10,20,57].

In [65], an increase in storage modulus of 100% in a magnetic field of 670 mT for the MRE based on silicone rubber matrix containing 20 vol.% of iron particles has been reported. The authors of [66] recorded the relative MR effect reaching 878% under 1 T magnetic field (800 kA/m), the MRE was based on silicone rubber (10 wt.%), plasticized with silicone oil (10 wt.%), containing 80 wt.% of particles and cured in 1.5 T magnetic field (1200 kA/m).
Beneficial effects of plasticizers, causing a reduction of material matrix stiffness, on the magnetorheological effect is shown in other papers [20].

Most of the results presented in the literature describes the MREs with isotropic distribution of particles. In [20,61] it was found that larger relative MR effect can be achieved in materials with softer matrix. Therefore, plasticizers are often added in order to increase the relative MR effect. The increase in the relative MR effect is obtained in this case, but the zero field modulus (without magnetic field) is lower.

Also reports can be found about the influence of the anisotropic microstructure on the properties of magnetorheological elastomers. The static and dynamic tensile testing of MREs with particles oriented in the form of chains have shown that they exhibit much higher Young’s modulus in comparison to MREs with the isotropically distributed particles [67], which is explained by the presence of column-like structure formed by the particles. Stiffness of the chains depends on the distance between the particles within them, and increases with the applied magnetic field due to the dipole formation and dipole-dipole interactions.

There is also a significant effect of particle size on the MR effect. In order to achieve a significant MR effect, particles should contain at least several magnetic domains [10]. The shape of particles can also have influence on the MR effect, it is better if they have an asymmetric shape with the main axis of anisotropy [63]. Few works have reported positive effect of surface modification of particles on the growth of magnetorheological effect [68], although others show clearly that due to the better adhesion particle-matrix boundary region occurs and the ability of particles to move is reduced, which leads to a reduction of MR effect [69,70].

4. Experimental results

4.1. Materials characterisation

In our study, the selection of composite matrix was carried out to produce MREs with mechanical properties, which can be varied widely under the influence of the magnetic field.

Magnetorheological elastomers were manufactured using:

- soft polyurethane (PU), denoted here as PU 70/30, obtained from polyether polyols VORALUX® HF 505 used in a blend with 14922, with the average molecular weight respectively 3596 and 4350 g/mol, and isocyanate compound HB 6013, supplied by Dow Chemical Company,
- segmented urea-urethane elastomer (EPU), obtained from 4,4’-diphenylmethane diisocyanate (MDI), ethylene oligoadipate (OAE) with the average molecular weight about 2000 g/mol and dicyandiamide (DCDA) as a chain extender.

PU substrates were mixed in the weight ratio, respectively 30:70:23. Mixing and curing process were conducted at room temperature.
EPU with molar ratio of MDI:(OAE+DCDA) equal to 2.5 was synthesized by one-shot method. The curing process was carried out at temperature of 150°C, what makes technology aspects of MRE manufacturing more complicated. The existence in every short hard segment of strong polar urea group and strong polar nitrilimide side-group increases the urea-urethane thermal and mechanical properties, as well as stiffness and hardness in comparison to soft polyether polyurethane (see Table 2).

<table>
<thead>
<tr>
<th>Material</th>
<th>Viscosity (mPas)</th>
<th>Density (g/cm³)</th>
<th>Glass transition temperature (°C) Soft segments</th>
<th>Hard segments</th>
<th>Hardness (°ShA)</th>
<th>Young’s modulus (MPa)</th>
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</thead>
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<tr>
<td>PU 70/30</td>
<td>8000</td>
<td>1.03</td>
<td>-64</td>
<td>41</td>
<td>&lt; 10</td>
<td>0.1</td>
</tr>
<tr>
<td>EPU 2.5</td>
<td>1400</td>
<td>1.26</td>
<td>-23</td>
<td>165</td>
<td>87</td>
<td>14</td>
</tr>
</tbody>
</table>

Table 2. Selected physical and mechanical properties of elastomers used for MREs fabrication.

As shown in Table 2 polyurethane PU 70/30 is characterized by lower density and mechanical properties than EPU 2.5. Low hardness and stiffness of the polyurethane matrix can lead to the higher relative property changes of the MRE under an external magnetic field. On the other hand, the EPU 2.5 is distinguished by lower viscosity of reactive mixture of substrates and good mechanical properties. Low viscosity during the processing of the MRE makes the arrangement of the particles into aligned chains very easy.

During the fabrication of MRE, two polyols were mixed first and then carbonyl iron was added. This mixture was subsequently put under vacuum to remove trapped air bubbles. After de-gassing the isocyanate compound was added and the reactive mixture was poured into moulds. The mixing of substrates and curing processes were carried out at room temperature, without or with application of magnetic field.

Three iron powders, which differed in size and shape of the particles, were used as magnetocactive component of MREs:

- carbonyl-iron powder, produced by Fluka, containing spherical particles with average diameters in the range 6-9 μm, Fe > 99.5 wt.%,
- carbonyl-iron powder HQ, produced by BASF, containing spherical particles with average diameter 1.4 μm, Fe > 97.5 wt.%.
- iron powder, produced by PYRON, containing irregular particles of a diameter of 70 μm.

Images of the particles and particle size distribution histograms are presented in Fig. 9, particles characteristics are shown in Table 3.

All the particles used for the study are characterized by their high saturation magnetization, which has a positive effect on the properties of MREs by increasing the strength of interaction between particles in a magnetic field. Moreover, they are commercially available and relatively inexpensive. A variety of MRE samples were produced:

a. pure elastomers (without particles),
b. elastomers with randomly dispersed iron particles,
c. elastomers with aligned iron particles.

Figure 9. SEM images and particle size distribution histograms A - carbonyl iron Fluka, B - carbonyl iron HQ, C - Iron PYRON.
<table>
<thead>
<tr>
<th>Particle’s type</th>
<th>Manufacturer</th>
<th>Designation</th>
<th>Shape</th>
<th>Particle size (manufacturer’s data) [μm]</th>
<th>Average particle size (Horiba LA-950) [μm]</th>
<th>Saturation magnetization [emu/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>carbonyl iron</td>
<td>Fluka</td>
<td>Fe</td>
<td>spherical</td>
<td>6-9</td>
<td>9</td>
<td>217</td>
</tr>
<tr>
<td>carbonyl iron</td>
<td>BASF</td>
<td>Fe HQ</td>
<td>spherical</td>
<td>1-2</td>
<td>1.4</td>
<td>215</td>
</tr>
<tr>
<td>iron</td>
<td>PYRON</td>
<td>Fe PYRON</td>
<td>irregular</td>
<td>no data</td>
<td>74</td>
<td>209</td>
</tr>
</tbody>
</table>

Table 3. Characteristics of ferromagnetic particles used for MREs fabrication.

The carbonyl iron particle volume fractions were 1.5, 11.5, 18, 25 and 33.0 vol. %. The samples were subjected to a magnetic field during curing, to produce aligned chains in the elastomer matrices. Two magnetic field strengths were used: 80 and 240 kA/m. Samples with different orientation of the particle chains to the long sample axis (30, 45, 60 and 90 degree) were produced.

4.2. Microstructure-properties relationship in MRE

The spatial distribution of particles in the magnetorheological elastomer matrix depends on the curing conditions. It is known [6,7,8,10,32,33,34,35,36] that curing in the presence of a magnetic field, allows to obtain magneto-anisotropic structure, consisting of chains of particles, as shown in the example of MRE with PU matrix and 11.5 vol.% carbonyl iron particles (Fig. 10A and C). The cross-section parallel to the direction of the magnetic field shows the arranged paths (chains) of Fe particles, clearly indicating the orientation of the particles in a magnetic field (MF). The curing of magnetorheological elastomer without application of magnetic field, leads to the isotropic structure of Fe particles uniformly distributed throughout the volume of the matrix (Fig. 10D).

As it is seen in the cross-section of the composite, perpendicular to the direction of the magnetic field (Fig. 10B), the distribution of chains is relatively uniform, moreover, most of them consist of more than one row of particles.

The viscosity of the reactive mixture is a technological parameter, which turned out to have an significant influence on the ability of particles to create a structure oriented along the magnetic field direction. The viscosity is not constant over time, but increases as the reaction follows, to the principle of doubling the length of the molecules in each act of addition, often starting during mixing of liquid substrates. The lifetime of the mixture is the period in which it is liquid, until the gel formation. The movement of particles in a reactive mixture of substrates is possible until it is liquid.
Observations of the brittle fractures of produced MREs, as shown in Figure 11, show that too high viscosity of the reactive mixture inhibits the movement of particles and the applied magnetic field does not allow to obtain the oriented structure of particles chains. This is the case for the silicone rubber matrix (Fig. 11C), which has a viscosity before curing of 30 000 mPa·s and is nearly four times greater than the viscosity of the PU 70/30 mixture and up to 20 times than EPU. Even a relatively short time of gelling (about 10 min for the PU 70/30) is not an obstacle for obtaining oriented structure of particle chains. It is sufficient for particles to shift the position to obtain the lowest Zeeman energy and arrange along the lines of magnetic field.

Another important parameter that affects the microstructure and consequently the properties of MREs is the magnetic field strength during curing. At higher magnetic field strengths the formed chains are thicker, consisting of more than 1-2 rows of particles.
Figure 11. Microstructure of MREs with 11.5 vol.% of Fe particles, cured in the 80 kA/m, matrix: A - EPU 2.5, B - PU 70/30, C - silicone rubber. Arrows show the direction of the magnetic field during curing.

Figure 12. Model of MRE microstructure dependently on the magnetic field strength during the matrix curing: A - 80 kA/m, B - 240 kA/m.

The structural anisotropy was confirmed by the Vibration Sample Magnetometer (VSM) studies. Tests were carried out parallel (II) and perpendicular (L) to the direction of particles
chains, corresponding to the magnetic field direction during curing. The example of the hysteresis loops obtained for the MREs is shown in Fig. 13A. From the hysteresis loops the anisotropy coefficient ($A_b$) was calculated at the selected value of magnetic field strength of 160 kA/m. It was expressed by the ratio of magnetization measured at 160 kA/m, respectively parallel and perpendicular to the particles alignment direction. The $A_b$ values are shown in Fig. 13B.

Figure 13. (A) Magnetization curves as a function of a magnetic field in the direction parallel (II) and perpendicular (L) to the chains of particles for the MRE containing 11.5 vol. % Fe particles, cured in the 240 kA/m magnetic field. (B) A change in the magnetic anisotropy $A_b(160)$ for MRE with different particle amount and magnetic field during curing (80 and 240 kA/m).

It was found that there is a maximum value of the anisotropy coefficient corresponding to 11.5 vol.% of carbonyl-iron. The anisotropy coefficient decreases with further increase in the volume fraction of particles. Moreover, for the sample with the highest $A_b$ a significant effect of the aligning magnetic field is visible; higher magnetic field leads to a better alignment. Structural and magnetic anisotropy has not been found in the specimens having 33 vol. % of carbonyl-iron, therefore, the anisotropy coefficient is equal to 1 for these specimens. The result can be attributed to the formation of the network of particles, in contrast to the chains of particles that characterize anisotropic composites. This was also observed on SEM images.

The anisotropy of MRE microstructure, obtained due to the magnetic field during curing has a significant influence on the changes of their mechanical properties in the magnetic field. Also the field strength applied during manufacture influences the mechanical properties of the MREs. This was confirmed by the results of mechanical and rheological tests presented in this chapter.

4.2.1. Compression tests

Compression tests were performed using a specially designed magnetic coil device for the MTS tensile tester. The study was conducted on samples with different particle volume...
content (1.5, 11.5 and 33%), produced in a magnetic field of 80 and 240 kA/m. Samples with dimensions of $\phi = 20$ mm and $h = 25$ mm, with particle chains parallel to the axis of the sample, were compressed uniaxially without and with a magnetic field strength of 240 kA/m. The obtained stress-strain curves are shown in Figure 14.

The compressive curves recorded without magnetic field are marked with a dashed line, while with MF using the solid line. It is clear that in each case MREs in a magnetic field are characterized by higher stiffness and compressive strength than without magnetic field. MREs with a higher content of particles are characterized by higher stiffness and

![Figure 14](Image)
compressive strength both without and with the magnetic field. Moreover, in a magnetic field, obtained stress-strain curves are at a higher level for MREs with higher structural and magnetic anisotropy, those cured in a magnetic field of greater intensity, even when no field curve was at a similar level, as for the MRE containing 1.5% vol. Fe particles (Fig. 14A).

Changes of the properties of magnetorheological elastomers in the magnetic field are described by absolute and relative MR effect, which in this case is expressed by the relative and absolute change in compressive modulus. Based on the compressive curves, the absolute and relative change of the compressive modules in the field of 240 kA/m, at the deformation of 0.1 mm/mm has been calculated and presented in Table 4.

<table>
<thead>
<tr>
<th>Fe particles fraction [vol. %]</th>
<th>Magnetic field during curing [kA/m]</th>
<th>ΔEc(240) [MPa]</th>
<th>ΔEc(240) / Ec(0) * 100 % [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,5</td>
<td>80</td>
<td>0,03</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>240</td>
<td>0,05</td>
<td>51</td>
</tr>
<tr>
<td>11,5</td>
<td>80</td>
<td>0,17</td>
<td>86</td>
</tr>
<tr>
<td></td>
<td>240</td>
<td>0,23</td>
<td>100</td>
</tr>
<tr>
<td>33</td>
<td>80</td>
<td>0,72</td>
<td>56</td>
</tr>
<tr>
<td></td>
<td>240</td>
<td>0,75</td>
<td>55</td>
</tr>
</tbody>
</table>

Table 4. Comparison of absolute (ΔEc (240)) and relative (ΔEc(240) / Ec(0) * 100 %) changes in the compressive modules in the magnetic field of 240 kA/m, under the deformation of 0.1 mm/mm.

The absolute MR effect is greater with the higher content of iron particles and depends on the applied magnetic field strength during curing. The higher the magnetic field during curing, the larger the absolute MR effect. The relative MR effect is not directly proportional to the particle content and reaches the highest value for contents of 11.5 vol.% Fe. Relative MR effect for the largest particle content, as well as magnetic anisotropy coefficient is practically the same regardless of the magnetic field during manufacture. Moreover, it is worth noting that the relative MR effect reaches its maximum for the MRE with the highest values of the coefficient of magnetic anisotropy.

4.2.2. Rheological properties

The knowledge of dynamic properties is needed especially for materials that are used in equipment subjected to vibration such as in aerospace and automotive industries. To describe the efficiency of damping, parameters such as the loss angle tan (δ) and shear modulus G*, consisting of the storage modulus G’ and loss modulus G” are used, determined by rheological tests [47,48].
MREs cured at different magnetic field strengths, tested without magnetic field have a similar storage (elasticity) modulus, loss (viscosity) modulus and the loss angle, which increases with increasing oscillation frequency of deformation. This pattern is characteristic for viscoelastic materials for which the higher the frequency of oscillation, the higher the value of the modules $G'$ and $G''$ [44]. The sharp increase in $\tan(\delta)$ as a function of oscillation frequency shows an increase in the share of the viscous properties of MREs.

The increase in the magnetic field causes an increase of both modules $G'$ and $G''$, much higher values were obtained in 160 kA/m for the MRE with a higher magnetic and structural anisotropy (cured in the 240 kA/m). For larger magnetic field the difference is not so evident. In a magnetic field damping is characterized by smaller changes in the function of frequency, but its value clearly depends on the magnetic field strength ($\tan(\delta)$ increases with increasing field) and to a lesser extent, but also depends on the microstructure formed during curing. MREs cured in the field of higher intensity are characterized by higher values of $\tan(\delta)$. With increasing magnetic field, the share of the viscous properties is greater, and increases with the structural and magnetic anisotropy. The material absorbs more energy which is dissipated as heat.
Figure 16. Changes in modules $G'$ and $G''$ and damping factor $\tan(\delta)$ as a function of oscillation frequency (at constant strain of 0.1%) for the MREs with PU matrix and different content of Fe particles without and in the field 160 kA/m. Particle chains parallel to the MF in rheometer.
Selected plots of rheological properties as a function of frequency of oscillation, described by the storage modulus $G'$, loss modulus $G''$ and loss angle $\tan(\delta)$ without field and in a magnetic field of 160 kA/m, for MREs with a polyurethane matrix and different content of carbonyl iron particles, are shown in Fig 16. The samples were cured in the magnetic field of 240 kA/m, and the particle chains were oriented parallel to the direction of the MF applied in rheometer.

It can be concluded that the increase in the particle content causes a slight increase in both modules in the initial state (without magnetic field) and they are dependent on the frequency of oscillation. Modules (storage and loss) in the initial state increase with increasing frequency of oscillation. Loss angle also depends on the content of particles and is greater with the higher particle content. The higher the value of $\tan(\delta)$, the greater the ability to absorb energy. However, note that the values obtained for the studied MREs are well below 1, which means a significant advantage of the elastic properties over the viscous.

In the magnetic field storage and loss modulus increase, and this increase depends on the content of the particles. The more particles the greater the value of the modules, and both increase with increasing frequency. For high frequencies, a decrease in loss modulus is observed, inversely proportional to the particle content.

Increase of loss angle as a function of frequency in the magnetic field is much smaller, except for the MREs with very low amount of particles 1.5 vol.%, for which the $\tan(\delta)$ in the MF is the same as without magnetic field. The values of $\tan(\delta)$ clearly increase for the low oscillation frequency, and rise with the rising particle content. The higher the value of $\tan(\delta)$, the greater the share of energy dissipated, and the material exhibits better damping properties.

The influence of the size of particles on the microstructure and rheological properties of MREs has also been investigated. The particle size does not affect the possibility of obtaining anisotropic structure consisting of chains of particles. In case of irregularly shaped particles (PYRON iron) during curing in magnetic field, they turn so their long axis is parallel to the direction of the magnetic field, which is consistent with the direction of easy magnetization and the tendency to minimize the energy associated with the shape anisotropy.

Rheological parameters were measured for a selected frequency of 10 Hz, the parameters $G'$, $G''$, and their absolute ($\Delta G'$, $\Delta G''$) and relative ($\Delta G'/G'_0$, $\Delta G''/G''_0$) changes describing absolute and relative MR effect are shown in Figure 18 as a function of magnetic field strength. Compared MREs have parallel arrangement of particles chains to the magnetic field in rheometer, the same content of particles but different sizes.

Storage modulus, loss modulus, and their absolute and relative changes increase with increasing magnetic field to the value of 320 kA/m, above the increase is weaker, which is associated with reaching a saturation magnetization of particles. In case of loss modulus $G''$ and the absolute and relative changes, significantly higher values as a function of field were obtained for the largest particles, with an average size of ~74 microns and irregular shapes.
Storage modulus $G'$ values were clearly lower for MRE with particles of small diameter (~1.4 μm), while for other types of particles are similar. Noticeable difference in favor of larger particles occurs in the field of 320 kA/m, which comes from the fact that particle size affects the strength of magnetic interactions between them. The bigger they are the stronger the interactions, the particles are attracted to each other in a chain with higher force, which ultimately leads to a greater MR effect. The maximum relative MR effect for the MREs with 11.5 vol.% of particles is 760% of the relative change in storage modulus, and 770% for the loss modulus. For this field strength these values are much higher than the values found in the literature.

The alignment of particle chains within the matrix may have a significant effect on the performance of the MREs. In order to investigate this effect, samples with different alignment of particles were produced and tested. A schematic representation of the samples, which contained 11.5 vol.% of Fe particles (Fluka, 9 μm), is shown in Fig. 19.
Figure 18. Changes of the storage modulus $G'$ (A), loss modulus $G''$ (B) and the absolute (C, D) and relative (E, F) magnetorheological effects as a function of magnetic field for the MRE with polyurethane matrix and content of 11.5 vol.% of particles. Sizes of particles: Fe ~ 9 μm, Fe HQ ~ 1.4 μm, Fe PYRON ~ 74 μm. Magnetic field in rheometer parallel to the chains of particles.
Figure 19. Schematic representation of the particle distribution with respect to the magnetic field direction.

Figure 20. The effects of different orientation of carbonyl iron particles in elastomer matrix, changes of relative MR effect as a function of the magnetic field.
It can be concluded that the values of storage and loss modules, and their absolute and relative changes strongly depend on the orientation of the particles chains. The largest absolute and relative MR effects were obtained for the arrangement of particles at an angle of 60° to the direction of the magnetic field. Under the influence of a magnetic field the direction of easy magnetization comes along the chains of ferromagnetic particles. To minimize the Zeeman energy the chains tend to set to the direction of the magnetic field, which involves the displacement of particles. Because they are embedded in the elastomer matrix and restrained by interactions at the interface, their displacements will introduce additional shear stress into the matrix, causing increased stress concentration in the matrix between the particles [71]. This does not take place when the particles chains are perpendicular to the direction of the field, and the resulting MR effect is much higher than for the isotropic structure. The lowest MR effect as a function of the field, both absolute and relative has been obtained in isotropic MREs.

The properties of the elastomeric matrix have also a great influence on MREs rheological properties. Rheological properties measured for the MREs fabricated from elastomers with different stiffness and hardness are shown in Fig. 21. Elastomer matrix with higher stiffness and hardness (EPU 2.5) leads to the higher storage and loss modulus of the MREs measured without magnetic field, while under the magnetic field the values are significantly lower in comparison to MREs obtained from soft elastomer (PU 70/30). As a result the absolute and relative MR effect is much higher in MREs obtained from the soft elastomer.

MREs with the stiffer matrix (EPU 2.5) exhibit significant lower MR effect because the stiffer matrix makes impossible the particles to displace when they are subjected to the magnetic field [72].

Developed magnetorheological composites belong to a group of smart materials, and under the influence of the magnetic field changes of the properties should be fully reversible. It is a complete reversibility of change in modules $G'$ and $G''$, as shown in Fig. 22 for the MRE.
containing 11.5 vol.% Fe particles oriented at an angle of 45 degrees in the increasing magnetic field, which was alternating turned on and off. Each time after switching off the magnetic field the modules immediately returned to initial state.

![Figure 22. The changes of rheological properties of MRE in the magnetic field alternating switched on and off.](image)

5. Conclusions

Studies on fabrication of MREs were carried out using different elastomers as a matrix, ferromagnetic particles with various shape and size. Samples with isotropic and anisotropic particles arrangement, were examined. Particles were oriented into chains under external magnetic field. Special attention was put on fabrication of samples with different orientation of chains to the magnetic field direction.

It was found that the microstructure of the MREs depends on the amount of ferrous particles and manufacturing conditions. The orientation of the iron particles into aligned chains is possible for lower volume content of the ferromagnetic fillers. High carbonyl-iron volume content in the matrix leads to the formation of more complex three-dimensional lattices. Also the magnetic measurements confirmed the existence of the microstructure anisotropy for the lower volume content of the iron particles. The structural and magnetic anisotropy has not been found in the MREs with 33 vol. % of particles. To evaluate the effect of the external magnetic field on the magnetorheological properties compressive strength, storage and loss modulus, as well as loss factor were measured. Both, the content of particles and their arrangement have significant effect on the properties of magnetorheological
urethane elastomers. Compression test results showed that under external magnetic field samples are distinguished by a higher compressive strength.

Rheological properties of magnetorheological urethane elastomers also depend on the content of particles and their arrangement. Application of an external magnetic field leads to a significant increase in elastic modulus. Absolute and relative changes of storage modulus, calculated from obtained curves, show that the microstructure of the samples has a significant effect on their magnetorheological effect. Magnetorheological effect, expressed by relative change of storage modulus under magnetic field, is the highest for the sample with the highest magnetic and structural anisotropy.

The aligned particle network structure has a significant influence on the elastic properties of the composite material. Inside the chains the effective filler content is higher than the average filler content. By optimizing the content of particles and their alignment, either the stiffness or the damping properties of MREs can be increased by applying a magnetic field.

As a result of the studies it was also found, that the MREs having anisotropic microstructure exhibit, for the same particles content, much higher magnetorheological effect in comparison to the isotropic ones. The non-linear change of the rheological properties versus particles fraction was found. It is due to structural and magnetic anisotropy of the MREs, which has the greatest influence on the changes of the properties under the magnetic field, i.e. magnetorheological effect. Moreover, it was found that the magnetorheological effect can be controlled by the particles alignment to the magnetic field lines. It means that it is possible to obtain high magnetorheological effect not by increasing of the particles volume fraction, but by the formation of appropriate microstructure. It can be achieved for lower particles volume fraction, what advantageously decreases weight of devices based on the MREs. As a result of this work the new MREs, with application capabilities, characterized by extremely high magnetorheological effect (900% in MF of 480 kA/m), were elaborated.

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