

Paweł Małecki, Aleksandra Szewczyk, Jacek Pigłowski

Wrocław University of Technology, Polymer Engineering and Technology Division, ul. Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland
Corresponding author: pawel.malecki@pwr.wroc.pl

Received (Otrzymano) 31.01.2013

MAGNETOMECHANICAL PROPERTIES OF MAGNETORHEOLOGICAL COMPOSITES

According to Takagi's definition, an intelligent material is able to react to external stimulus by a significant change in its properties in order to make a proper and successful response to the stimulus. The rheological behaviour of magnetorheological composites (MRC) can be controlled continuously, rapidly and reversibly by an applied magnetic field. In this paper, an acrylic copolymer with carbonyl iron powder (CIP) is tested in conditions of mechanical and magnetic stimulations. Chitosan-coated magnetic particles are made in order to change the hydrophilic surface character of CIP to hydrophobic and as a result, obtain better compatibility between the particles and the matrix. The test samples are subjected to cyclic shearing with a constant frequency of 1 Hz. The change in the magnetomechanical properties is expressed by the relative change in hysteresis loop area δW and stress amplitude $\delta\tau$. An increasing content of carbonyl iron in the composites and the strength of magnetic field H causes an increase in the hysteresis loops area. Material containing modified particles has a significantly bigger hysteresis loop area than samples filled with unmodified carbonyl iron powder. Based on this knowledge, it can be concluded that this sample can dissipate much more mechanical energy.

Keywords: carbonyl iron powder, chitosan, magnetorheological composites

MAGNETOMECHANICZNE WŁAŚCIWOŚCI KOMPOZYTÓW MAGNETOREOLOGICZNYCH

Według definicji Takagiego, materiał inteligentny to taki, który jest zdolny do reagowania na bodźce zewnętrzne przez istotną zmianę swych właściwości dla pożądanego i skutecznego odpowiedzenia na te bodźce. Reologiczne właściwości kompozytów magnetoreologicznych mogą być kontrolowane w sposób ciągły, szybko i powtarzalny poprzez zastosowanie zewnętrznego pola magnetycznego. W pracy badano kompozyty kopolimeru akrylowego i proszku żelaza karbonylowego w warunkach stymulacji mechanicznej i magnetycznej. Przeprowadzono modyfikację powierzchni cząstek magnetycznych w celu zmiany jej charakteru z hydrofilowego na hydrofobowy oraz uzyskaniu lepszej kompatybilności między cząstkami a matrycą. Efekt modyfikacji potwierdza analiza FTIR. Próbkę badano w warunkach cyklicznego ścinania ze stałą częstotliwością 1 Hz. Zmianę właściwości magnetomechanicznych wyraża się poprzez zmianę pola pętli histerezy δW i amplitudy naprężenia $\delta\tau$. Wraz ze zwiększeniem zawartości żelaza karbonylowego w kompozycie i natężenia pola magnetycznego następuje zwiększenie pola pętli histerezy. Kompozyty zawierające 31% obj. cząstek magnetycznych modyfikowanych chitozaniem wykazują 4-krotnie większą pętlę histerezy niż odpowiednia próbka z żelazem bez modyfikacji. W warunkach badania, przy odkształceniu $25 \cdot 10^{-3}$ i polu $H = 100$ kA/m pole pętli wynosi 100 J/m³, gdzie dla próbki z modyfikowanymi cząstkami osiąga wartość 430 J/m³. Oznacza to, że materiał lepiej tłumí drgania, tj. rozprasza energię mechaniczną. Efekt ten związany jest ze wzrostem kompatybilności między cząstkami magnetycznymi a matrycą polimerową.

Słowa kluczowe: żelazo karbonylowe, chitozan, kompozyty magnetoreologiczne

INTRODUCTION

Magnetorheological elastomers (MRE) belong to a novel branch of materials referred to as "smart". They are the solid analogue of magnetorheological fluids (MRF) [1]. However, MRF have serious disadvantages, for example low durability (oil thickens after many cycles of work), moreover magnetically active particles tend to sedimentation and agglomeration. This phenomenon has a major influence on decreasing the magnetorheological effect. The use of thermoplastic elastomers as a matrix does not cause these defects. However, magnetorheological fluid (MRF) and com-

posites (MRC) work in different regions; MRF normally work in the post-yield regime but MRC have a working range in the pre-yield region. This means that they do not exclude but complement each other [2].

MRCs exhibit a reversible change in certain mechanical and rheological properties under the application of an external magnetic field. Their viscoelastic behavior is described by the Kelvin-Voight model, it is schematically represented by a spring and damper connected parallel. Two dynamic modulus: elastic (storage) modulus and viscous (loss) modulus can be distin-

guished. Furthermore, changes in certain mechanical properties can be expressed as hysteresis loops in the stress-strain (τ - γ) system. Typical magnetorheological composites consist of two main components: a non-magnetic polymer matrix and a magnetically active filler [2]. Moreover there is no compatibility between them, because of the difference in their surface character. Most polymers are hydrophobic but carbonyl iron is hydrophilic, this disadvantage can be overcome by polymer coating the particles.

In this work MRE composites were obtained from the water dispersion of an acrylic copolymer produced in the presence of an emulsifying system composed of ionic and non-ionic surface active agents. The solids content in the dispersion is evaluated as $58 \pm 2\%$ (PN-EN 827), therefore during the manufacture of composites, drying the materials in a vacuum is required. After the evaporation of water, we receive a transparent film [3]. As magnetic particles, carbonyl iron powder ($Fe_{min} = 95.5\%$) was used. Samples with different contents of particles were produced. Additionally, to improve the compatibility between the components, surface modification of the magnetic particles was executed.

According to the way in which the magnetic particles are dispersed in the matrix, specimens can be divided into two kinds: anisotropic (polarized) with particles aligned parallel to the direction of the external field and isotropic, where the particles are uniformly dispersed in the composites. In the current work, the authors have focused only to isotropic composites because they are simpler to manufacture than anisotropic ones, less expensive and more common in use [4].

EXPERIMENTAL DETAILS

Materials

1. Water dispersion of acrylic copolymer (Osakryl® AH 035, Synthos Dwory Poland).
2. Carbonyl iron powder (type CS, BASF Germany).
3. Chitosan (low molecular weight, 75÷85% deacetylated) and glutaraldehyde (Sigma - Aldrich).
4. Oleic acid and acetic acid (POCH S.A. Poland).

Preparation of chitosan coated magnetite CIP/CS

Carbonyl iron powder (6 g) was added to 150 ml of deionized water in a 250 ml three-necked flask. Then 12 ml oleic acid was poured under vigorous stirring at a temperature of 75°C. This reaction was carried out for 1 h under Ar protection. Then the solution was cooled to room temperature and the magnetic particles were selected through magnetic separation and washed several times with deionized water and ethanol. In the second stage, chitosan (2 g) in 400 ml of a 2.0 wt.% acetic acid solution and 6 g modified magnetic particles were put into three-necked flask. Finally 8 ml of glutaraldehyde solution (25 wt.%) was added to the mixture.

A crosslinking reaction was conducted for 3 h at 40°C. Finally, the particles were selected and washed as in the first part of the reaction.

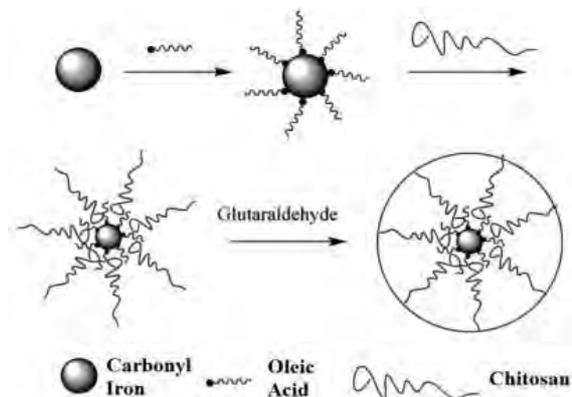


Fig. 1. Scheme of surface modification of magnetic particles [5]

Rys. 1. Schemat modyfikacji powierzchni cząstek magnetycznych [5]

Preparation of magnetorheological composites (MRC) and test samples

First of all, the magnetic particles were homogeneously mixed with the water dispersion of the acrylic copolymer by using ultrasound. Then mixture was poured into forms and dried in a vacuum dryer at 100°C during 72 hours. However, after evaporation of the water, the material was not homogeneous. In the next stage, the composites were homogenized using a laboratory two-roll-mill at room temperature. Then the samples were pressed at the temperature of 190°C in 50x50x4 mm aluminum forms.

In order to obtain a good magnetorheological effect, it is very important to determine the proportions of individual components of the composites. The most common way to obtain a maximum fraction value of carbonyl iron particles in the composite is to calculate the critical particle volume concentration (CPVC). Such an equation can be used:

$$CPVC = \frac{100 * \rho_n}{\rho_{Fe}} \quad (1)$$

where ρ_n is the bulk density of iron powder and ρ_{Fe} is the density of iron.

TABLE 1. Composition of particular magnetorheological composites samples

TABELA 1. Składy poszczególnych kompozytów magnetoreologicznych

Sample	Weight of acrylic copolymer	Weight of carbonyl iron powder	Contribution of carbonyl iron	Modification of magnetic particles	
	[g]	[g]	[wt.%]	[vol.%]	
I	18	10	35.7	6.6	-
II	18	20	52.6	12.3	-
III	18	45	71.4	24.0	-
IV	18	65	78.3	31.3	-
V	18	65	78.3	31.3	yes

The CPVC value for the applied carbonyl iron powder (type CS) is exactly 31 vol.%. This parameter is appropriate only for isotropic magnetorheological composites. In the case of anisotropic composites, we can obtain better magnetic properties with a lower amount of carbonyl iron.

Testing of MRC

The magnetorheological effect was evaluated by measuring the dynamic shear modulus in the presence/absence of an applied magnetic field. Examinations of the magnetorheological elastomers were carried out according to the program shown in Table 2. The samples were loaded cyclically with a constant frequency of 1 Hz. After the pressing stage, the elastomer composites were cut into 40 mm x 40 mm x 4 mm pieces. Two pieces of the materials were glued between clamping plates (fibreglass reinforced epoxy laminate). The test stand was equipped with a magnetic circuit so that the field going through (in the direction perpendicular to the specimen) the elastomer could be precisely controlled.

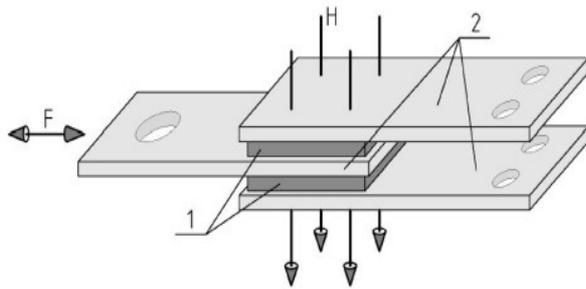


Fig. 2. Scheme of test sample for shear test: 1 - magnetorheological composite, 2 - claddings [6].

Rys. 2. Schemat próbki do badań: 1 - kompozyt magnetoreologiczny, 2 - okładziny [6]

TABLE 2. Testing program of MRC
TABELA 2. Program testowania MRC

Recorded Value	Intensity of magnetic field	Amplitude of displacement	Amplitude of deformation
Sign	H [kA/m]	x [mm]	$\gamma \times 10^{-3}$ [-]
Cycles			
0÷500	0,25,50,75,100	0.025	6.25×10^{-3}
501÷1000	0,25,50,75,100	0.05	12.5×10^{-3}
1001÷1500	0,25,50,75,100	0.075	18.75×10^{-3}
1501÷2000	0,25,50,75,100	0.1	25.00×10^{-3}

At the lowest strain amplitude ($6.25 \cdot 10^{-3}$), the samples were tested without any magnetic field. Every 100 cycles, field strength H was increased by 25 kA/m (25,50,75,100). After reaching 500 cycles, the displacement amplitude was changed to $12.50 \cdot 10^{-3}$ and the samples were tested in the same way. The testing program included four different strain amplitudes. The results were registered in the form of data containing

the displacement values and the resulting forces in the sample as a function of time.

RESULTS AND DISCUSSION

Morphology of CIP/CS nanocomposites

The FTIR analysis was made on a PE IR Spectrum ASCII PEDS 1.60 spectrometer, and the samples were prepared as KBr tablets. The spectra of pristine carbonyl iron powder (CIP) and chitosan coated CIP are presented in Figure 3. In the curve (line B), the peaks at around $4000 \div 3600 \text{ cm}^{-1}$ and $1300 \div 400 \text{ cm}^{-1}$, are due to the adsorbed water in the sample. At $2400 \div 2280 \text{ cm}^{-1}$ the peak from the CO_2 present in measuring chamber can be observed. The peaks at 2924 and 2856 cm^{-1} corresponded to the symmetric and asymmetric stretching vibration of the OH, CH_3 and CH_2 group, which is assignable to the oleic acid. The characteristic peaks for chitosan can be indicated above 3000 cm^{-1} and come from the stretching vibration O-H (above 3300 cm^{-1}) and N-H (above 3200 cm^{-1}) group. The results of the FTIR analysis suggest integration between the chitosan and oleic acid molecules, which creates an increase in transmittance.

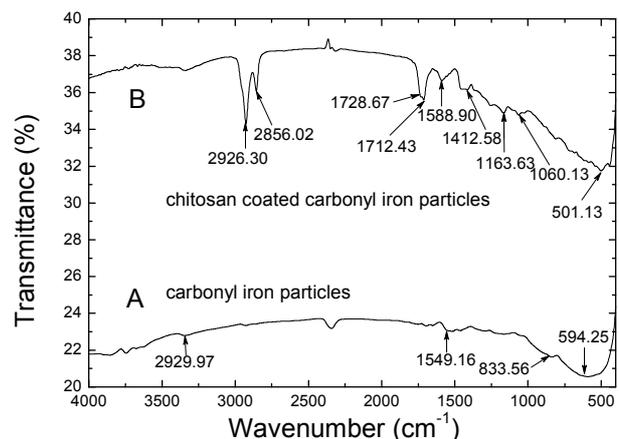


Fig. 3. FTIR spectra of carbonyl iron and magnetic chitosan nanoparticles

Rys. 3. FTIR żelaza karbonylkowego i cząstek modyfikowanych chitozaniem

Viscoelastic properties under magnetic field

The application of an external magnetic field induces the magnetic dipole μ in the ferromagnetic particles. This phenomenon makes them arrange themselves according to the field lines direction. The interaction between the carbonyl iron particles and their reorganization change the stiffness of the materials and in this way, the material is capable of damping vibration. The hysteresis loop is one of the most important parameters characterizing the viscoelastic behavior of magnetorheological composites under dynamic shear measurements. From the physical point of view, in a stress-strain curve, the area of this loop expresses the amount of energy dissipated in a single cycle. Several compos-

ite samples with different volume percentages of carbonyl iron (from 6 to 31 vol.%) were fabricated (Tab. 1). Additionally, the chitosan-coated magnetic particles were made for the sample with 31 vol.% CIP. According to CPVC formula (1), it can be expected that this sample should have the best magnetomechanical properties. The exemplary results for all the composites at a maximum amplitude of deformation ($\gamma_{max} = 25 \cdot 10^{-3}$) and intensity of magnetic field ($H = 100$ kA/m) are presented in Figure 4a. The hysteresis loop areas increase with an increasing content of carbonyl iron powder in the composites. In a higher magnetic field and at a higher amplitude of deformation, the material is stiffer and more rigid. This phenomenon makes a higher value of stress occur in the materials but the hysteresis loops are narrower. As can be indicated, after particles modification the composite exhibits a significant increase in the hysteresis loops area. A substantial difference is visible in Figure 4b. Respectively, the sample with the 31 vol.% CIP reaches a stress of about 6 kPa, however, the composite with the 31 vol.% chitosan-coated CIP has a stress of approximately 15 kPa. The reason for this difference is the better compatibility between the magnetic particles and the matrix. The changes in the shape of the hysteresis loops for these two kinds of samples during the whole testing program at $H = 100$ kA/m are presented in Figures 5 a, b. The loop of the composite containing the modified particles is much wider and bigger. That means that the material can dissipate much more energy.

The dependence area of the hysteresis loops versus the strain amplitude at 100 kA/m and as a function of magnetic field at the amplitude of deformation $\gamma = 25 \cdot 10^{-3}$ are presented respectively in Figures 6 a, b. The composites dissipate more energy with a higher volume content of carbonyl iron powder and at a higher amplitude of deformation. For the sample containing 31 vol.% chitosan-coated particles, hysteresis loop area

W [J/m^3] changes from 30 to 425 J/m^3 . What is more, increasing the strength of the magnetic field makes the value of W [J/m^3] increase, nevertheless, it is not a significant change. Moreover, in this investigation the samples with the modified nanoparticles have better magnetomechanical properties.

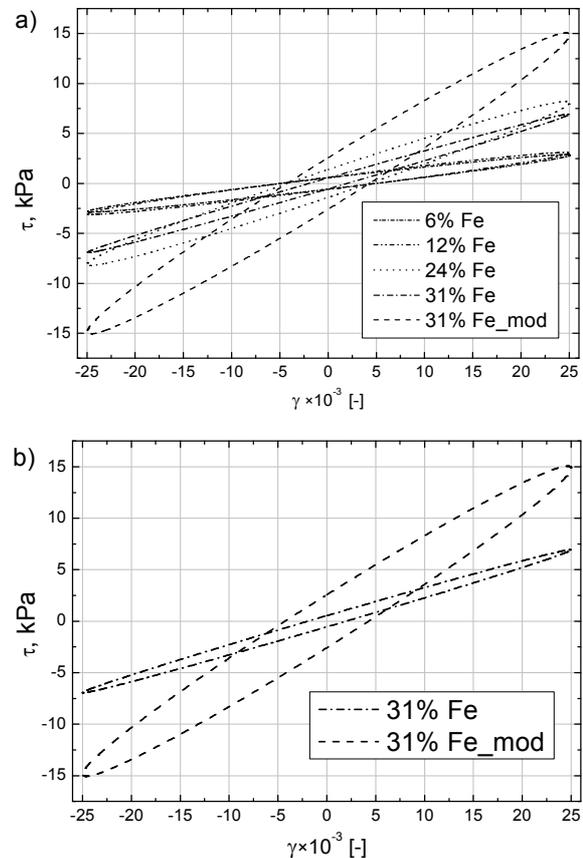


Fig. 4. Hysteresis loops at $\gamma_{max} = 25 \cdot 10^{-3}$, $H_{max} = 100$ kA/m: a) for all composites, b) for samples containing 31 vol.% carbonyl iron powder without and after modification of particles

Rys. 4. Pętle histerezy w warunkach: $\gamma_{max} = 25 \cdot 10^{-3}$, $H_{max} = 100$ kA/m: a) dla wszystkich kompozytów, b) dla próbek zawierających 31% obj. żelaza karbonylkowego, bez i po modyfikacji cząstek

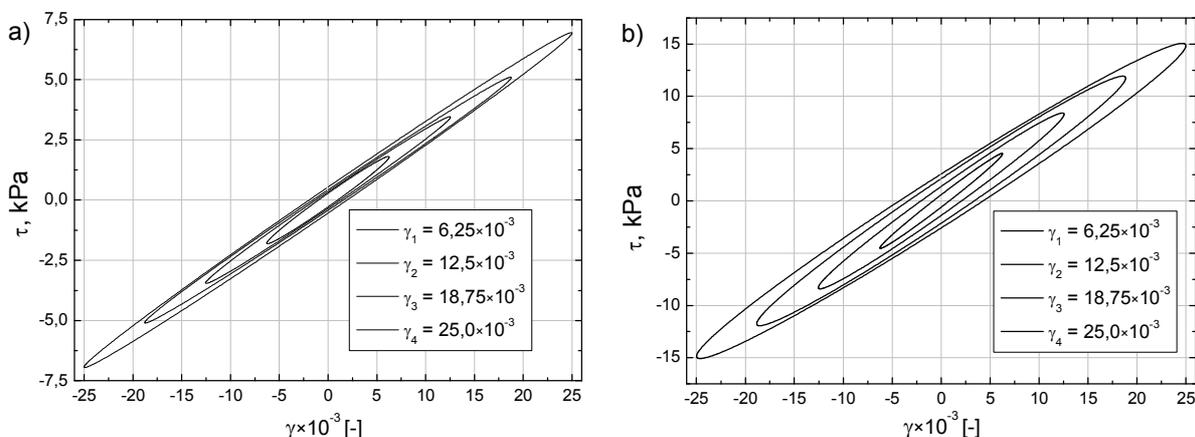


Fig. 5. Hysteresis loops during whole testing program for composites containing 31 vol.% CIP at 100 kA/m: a) without, and b) after modification

Rys. 5. Pętle histerezy podczas całego badania dla próbek zawierających 31% obj. żelaza karbonylkowego w polu 100 kA/m: a) bez modyfikacji oraz b) po modyfikacji

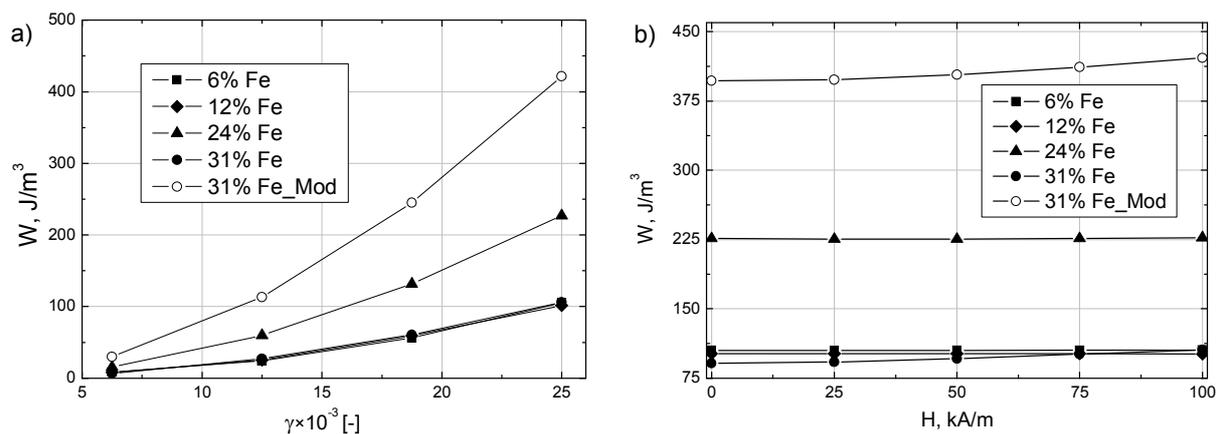


Fig. 6. Areas of hysteresis loops: a) versus strain amplitude $H = 100$ kA/m, b) in function of strength of magnetic field $\gamma = 25 \cdot 10^{-3}$

Rys. 6. Pola pętli histerezy: a) od amplitudy odkształcenia $H = 100$ kA/m, b) w funkcji natężenia pola magnetycznego $\gamma = 25 \cdot 10^{-3}$

SUMMARY

Structure core-shells are made in order to change the surface character of magnetic particles to hydrophobic. Covalently bonded chitosan on carbonyl iron powder improves the compatibility with the acrylic copolymer matrix. The research done in this work indicates that magnetorheological composites with modified particles have better magnetomechanical properties than the sample with unmodified magnetic powder. The results of this work show that this kind of materials can act as active damping elements and can be used in building dampers, sensors and actuators.

Acknowledgments

This research was supported by the statutory funds of the Polymer Engineering and Technology Division, Department of Chemistry, Wrocław University of Technology.

REFERENCES

- [1] Xiushou Lu, Xiuying Qiao, Hiroshi Watanabe, Xinglong Gong, Tao Yang, Wei Li, Kang Sun, Meng Li, Kang Yang, Hongen Xie, Qi Yin, Dong Wang, Xiaodong Chen, Mechanical and structural investigation of isotropic and anisotropic thermoplastic magnetorheological elastomer composites based on poly(styrene-*b*-ethylene-*b*-butylene-*b*-styrene) (SEBS), *Rheol. Acta.* 2012, 51, 37-50.
- [2] Boczkowska A., Awietjan S.F., Wróblewski R., Microstructure - property relationship of urethane magnetorheological elastomers, *Smart Mater. Struct.* 2007, 16, 1924-1930.
- [3] <http://synthosgroup.com/>
- [4] Hu Y., Wang Y.L., Gong X.L., Gong X.Q., Zhang X.Z., Jiang W.Q., Zhang P.Q., Chen Z.Y., New magnetorheological elastomers based on polyurethane/Si-rubber hybrid, *Polym. Test.* 2005, 24, 324-329.
- [5] Jingmiao Qu, Guang Liu, Yiming Wang, Ruoyu Hong, Preparation of Fe_3O_4 - chitosan nanoparticles used for hyperthermia, *Advanced Powder Technology* 2010, 21, 461-467.
- [6] Kaleta J., Królewicz M., Lewandowski D., Magnetomechanical properties of anisotropic and isotropic magnetorheological composites with thermoplastic elastomer matrices, *Smart Mater. Struct.* 2011, 20, 085006.