APPLICATION OF ATOMIC FORCE MICROSCOPY FOR MAGNETIC AND MECHANICAL INVESTIGATION OF NEW MAGNETORHEOLOGICAL ELASTOMERS

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In this paper, we present the investigation of topographic, magnetic and nanoelastic properties of new magnetorheological elastomers by using atomic force microscopy techniques (AFM): standard imaging Non-contact AFM, Magnetic Force Microscopy and Nanoindentation. The scanning modes were adapted in order to observe the specific morphological features induced by the presence of the magnetic dopants, while the Nanoindentation was used to study the differences in hardness and elasticity between the magnetic domains and the polymeric matrix.

Keywords: atomic force microscopy, nanoindentation, magnetorheological elastomers, nanofluids, carbonyl iron.

1. Introduction

Atomic Force Microscopy (AFM) describes a group of techniques used for non-destructive surface studies at the nanoscale level. They have a resolution of three orders of magnitude better than optical microscopy, and they were proved to be powerful and versatile techniques to investigate the surface properties, at sub-nanometer scale resolution, for different kind of materials, from thin films to biological samples [1-10].

In the last decades, since the AFM technology had started to be used in investigation of a larger classes of materials, new imaging modes were designed and created to overcome all the limitations of the former ones. From the first Contact mode to the Dynamic modes, and more recently developed multi-parametric, molecular recognition, multi-frequency and high-speed imaging modes, all efforts were focused to address outstanding questions of materials properties.

Depending on the surface characteristics, the set-up should be customized in order to obtain an accurate representation of the desired surface property. For example, while the sharp tips are appropriated to investigate surfaces with smooth aspect (low roughness) and resistant to the action of external forces, soft materials, like biological sample, may be irreversible destroyed by hard and sharp tips/probes.

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Our days, nanoindentation and nanomechanical force spectroscopy by using an Atomic Force Microscope, became more and more reliable methods in fields like mechanobiology, the development of smart materials, energy storage, nanomedicine or clinical diagnosis [11].

Magnetorheological elastomers (MREs) represent a specific class of smart soft materials, which respond in a complex way to the external actions. Due to their unique combination of good magnetic controllability and elastic properties,[12-15] these materials are designed and intensively studied as materials for robotics, biomechanics industries, etc. [16,17].

Previous studies reported the investigation of MREs by using Tapping Mode AFM (T-AFM) technique to identify the interdomains of soft and hard segments [18] and Nanoindentation for the study of mechanical properties [19].

The Non-contact mode (NC-AFM) is very appropriate for investigation the surface properties of the elastomeric sample due to the fact that the tip is at a higher distance from the scanned surface and the viscosity of the material doesn't affect the accuracy of the attractive atomic force induced by the dipole-dipole interaction between the tip atoms and the sample atoms (Van der Waals force).

More difficult to be used in the case of elastomers was MFM method, because it was necessary to find the proper distance to avoid the stickiness of the sample, but to still detect the magnetic force of the magnetic surface domains.

2. Experimental details

Our studies were performed using an XE-100 AFM system (Park, South Korea). The investigated areas were $20\times20\mu m^2$, $30\times30\mu m^2$ and $45\times45\mu m^2$, the scan rate was 0.2Hz, and 0.3Hz and the set point (the force applied by the end of the tip to the sample surface when the system is in feedback) was 5nN for NC-AFM and 1.47μN for MFM.

2.1 Noncontact mode for surface investigations

NC-AFM is one of several vibrating cantilever techniques in which an AFM cantilever which carries the probe is vibrated near the surface of a sample. In the case of NC-AFM, the spacing between the tip and the sample is usually on the order of tens to hundreds of angstroms. At these distances, the van der Waals interatomic force is attractive. Due to the attractive force between the probe tip and the surface atoms, the cantilever which vibrates at its resonant frequency near the sample surface experiences a shift from its intrinsic spring constant. The new value is known as the effective spring constant.

When the attractive force is applied, the effective spring constant becomes smaller than the resonant one. Accordingly, the stronger the interaction between the surface and the tip (in other words, the closer the tip is brought to the surface), the

smaller the effective spring constant becomes. Then, the AFM system detects changes in the resonant frequency or vibration amplitude as the tip comes near the sample surface.

If the change in the effective resonance frequency, resulting from the interaction between the surface atoms and the probe, or the change in amplitude at a given frequency can be measured, the NC-AFM mode feedback loop will then compensate for the distance change between the tip and the sample surface. Thus, by maintaining constant the amplitude and distance, one can measure the topography of the sample surface.

The NC-AFM operating mode for imaging the surface topographies of MRE samples had the following parameters: cantilever nominal length of 125 mm, nominal force constant of 40 N/m, and oscillation frequencies in the range of 275–453 kHz. We used horizontal line-by-line flattening as the images planarization method.

2.2 Magnetic force microscopy

For the magnetic surface properties characterization of MREs we used a MFM module (pre-magnetized tip, sensitivity 1–2Oe) in a two-pass technique. The surface topography was obtained in Non-Contact mode and the MFM images were generated by measuring either the amplitude or the phase change of the cantilever oscillation from the magnetic force between the surface and the magnetized MFM cantilever.

During the MFM measurements, there are two forces acting on the tip: magnetic and Van der Waals forces. The dominating force depends on the distance between the tip and the sample surface. The inter-atomic magnetic force persists for greater tip-to-sample separations than the van der Waals force. If the tip is close to the surface, in the region where standard Non-Contact AFM is operated, the image will be predominantly topographic. As you increase the separation between the tip and the sample, magnetic effects become apparent. Collecting a series of images at different tip heights is one way to separate magnetic from topographic effects.

MFM images contain information on magnetic domain distributions on the sample surface. In order to in separate the magnetic signal from the entire signal we used ‘Two Pass’ technique, when in the first scan, the tip scans the surface as in Non-Contact AFM to obtain the topography of the sample, and in the second scan, the tip-sample distance is increased and the biased tip is scanned along the topography line obtained from the first scan. At the second pass, the tip is affected only by the magnetic force and MFM image is obtained as a result [20].

In the case of the studied MREs, the magnetic signal is quite poor. To increase the accuracy the second scan was set to be closer to the scanned surface and the set point for the NC-AFM was lowered not to interfere with the magnetic

signal. When shorting the scan distance the influence of adhesion forces substantially increased. Then, in order to balance between a poor signal and a distorted one, all the distance parameters were set manually for each sample, in a pre-scaling phase of the measurements.

2.3 Nanoindentation

By Nanoindentation one can determine the hardness of a local region and other properties as elasticity, adhesion, creep, and tribology of different materials. Force-Distance Spectroscopy is used to measure the vertical force that the tip applies to the surface while a contact-AFM image is being taken. This technique are used to analyse surface contaminants' viscosity, lubrication thickness, and local variations in the elastic properties of the surface [20].

As reported in [21], AFM was already successfully used to characterize the mechanical behaviour of polymers with widely different properties, and then we expected to obtain useful and accurate data for the MREs also.

The elastic properties of MRE samples were measured using both force/distance spectroscopy and nanoindentation (down/up speed of Z scanner extension 0.3 μm/s). Each sample was subjected to a network of 12 points of indentation, in 20 different regions of $20\times20\mu m^2$ areas.

Following the steps proposed in [22,23] we recorded the Force/distance (F/D) curves and load/unload vs. displacement curves for the pure elastomer matrix and the MRE samples. Generally, the hysteresis of the loading/unloading curves indicates that the deformation is not fully elastic and partially inelastic. In the case of MREs the hysteresis is very narrow showing that the elastomers have a predominant elastic behaviour.

2.4 Sample preparation

MRE are composites where magnetic particles are suspended in a non-magnetic solid or gel-like matrix.

In the present work we study two new classes of MRE containing: anisotropic magnetized ferrofluid nanoclusters together with Fe microparticles dispersed in the elastomer matrix, and carbonyl iron microparticles dispersed in an elastomer matrix.

The materials used for the MREs preparation include silicone rubber (SR) RTV3325 type, from Bluestar Silicones, catalyst (Ca) 6H type from Bluestar Silicones, a ferrofluid (nFe) with Fe_3O_4 nanoparticles (10 nm average diameter) with kerosene based carrier fluid, and magnetization saturation 150Gs, from Politechnical University-Timisoara, and carbonyl iron microparticles (CI) from Sigma-Aldrich, with average diameter between 4.5 μm and 5.4 μm.

Pre-established amounts of nFe and CI microparticles were introduced in SR and then mixed in the presence of the Ca (Table 1).

Table 1

Magnetorheological elastomers composition

Sample	SR (vol.%)	Ca (vol.%)	nFe (vol.%)	CI (vol.%)
P_0	95	5	0	0
P_1	90	5	5	0
P_2	89	5	5	1
P_3	88	5	5	2
P_4	85	5	5	5
P_5	80	5	5	10
V_1	86	10	0	4
V_2	83	10	0	7
V_3	80	10	0	10

After 24 hours the samples polymerize and the discs from Figure1 are obtained.

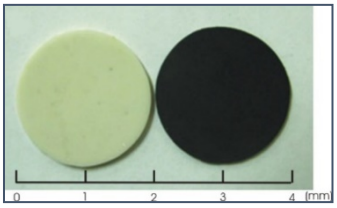


Fig.1. Matrix (left) and MRE (right) disk-shaped samples for AFM investigations.

3. Results and discussions

As mentioned above, the investigation of MRE's surface and magnetic surface properties were performed using the 'Two Pass' scanning techniques.

At the first scan, the topography images of the samples were recorded in the Non-contact mode. The second pass was set at a higher distance from the sample, and we obtained the magnetic map of the domains with different magnetizations. In order to separate the topographic signal (van der Waals force) from the magnetic signal, the scanning distances were manually set for each sample. Figure 2 presents the topography and the MFM images for the sample P1. Both adhesion influence and signal interferences were eliminated by proper setting the scanning distances (10nm and respectively 20nm) and frequencies (0.3Hz). No artefacts affected the images.

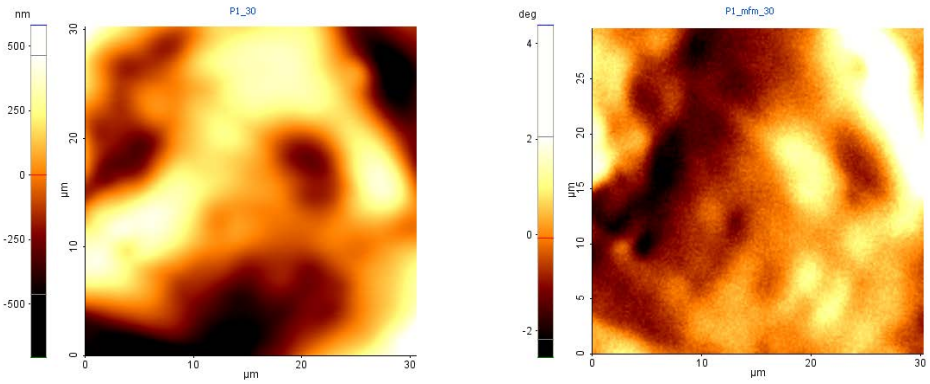
In order to measure the dimensions of the magnetic domains, we used Line view analysing tool of the Image processing program XEI 1.7.1 (Figure 3), and the Grain view image processing of the same program, for obtaining the histograms of areas, volumes and perimeters (Figure 4).

For samples P1-P4, we noticed a homogenous distribution of the magnetic fillers in the polymeric matrix. The conglomerations appear in less than 0.1% of the scanned samples and can be associated to possible frictions acting in the process of surface preparation.

For the sample P5, as shown in Figure 4, the percent of conglomerations of the magnetic fillers became important (25%). From the shape of the magnetic regions we can conclude that at this concentration, the conglomerations consist of a very few number of microparticles surrounded by ferrofluid.

The tendency of conglomerations at a specific concentrations and descriptions of different aspects of the magnetic filler arrangement in the elastomeric matrix (elastomer shells as ”third phase”) were already reported for some MREs [24].

For the samples V1-V3 any conglomeration was visible for the studied concentration of the magnetic nanoparticles. When the size of particles is very small, the impact of the van der Waals force on the behaviour of particles becomes significant.



(a) (b)

Fig. 2. Topography (a) and MFM image (b) of sample P1 (90vol.% SR, 5vol.% nFe and 5vol.% Ca), scanned over an area of 30×30µm^2.

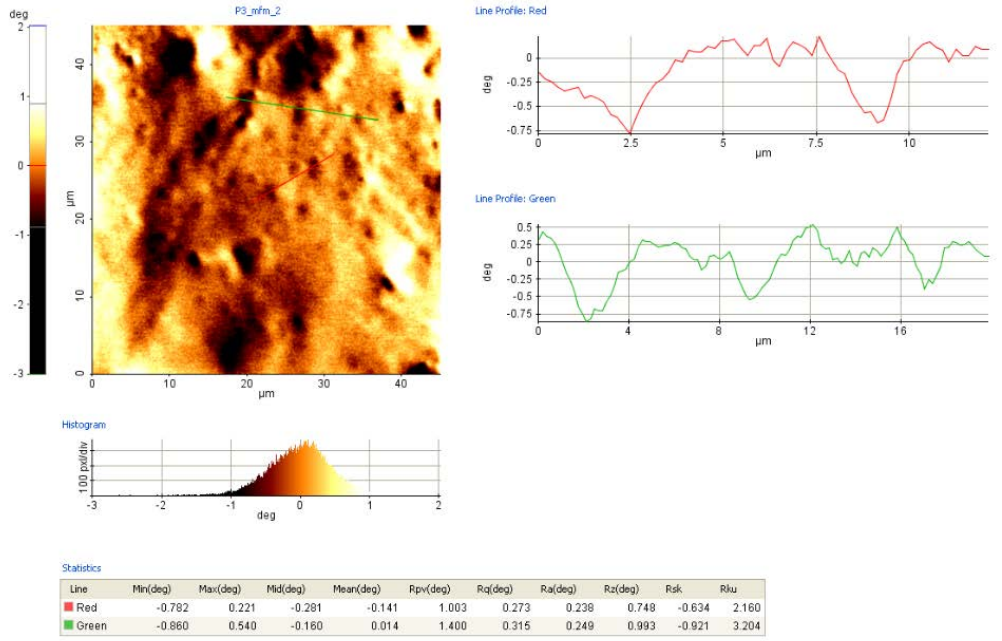


Fig. 3. MFM image in Line view tool of the Image Processing Program, for sample P3 (88 vol.% SR, 5vol.% nFe, 2vol.% CI and 5vol.% Ca), scanning area of 45×45µm^2.

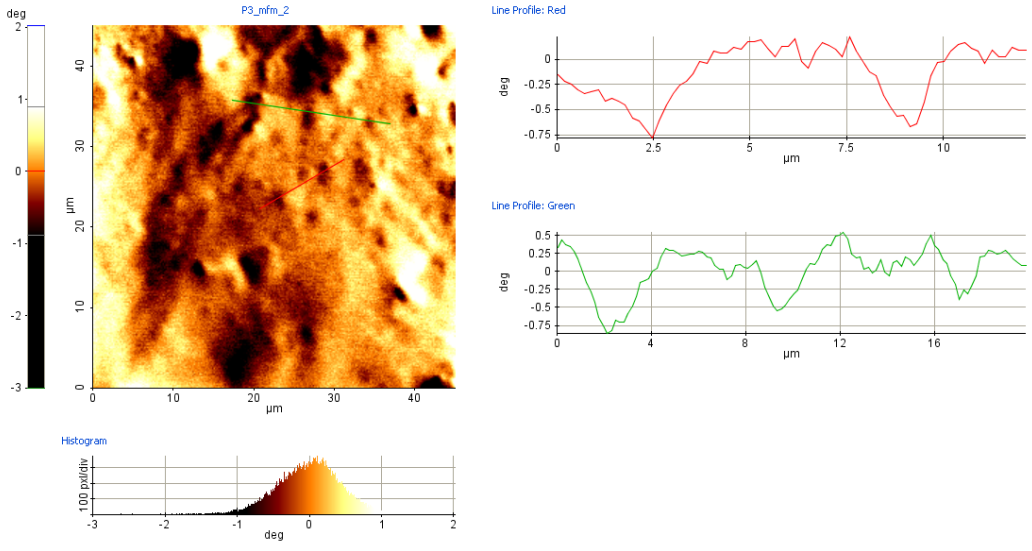
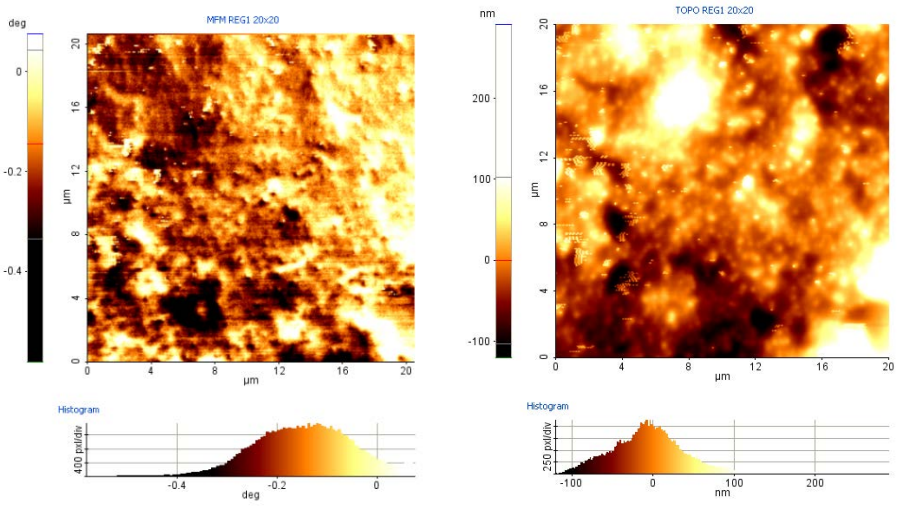


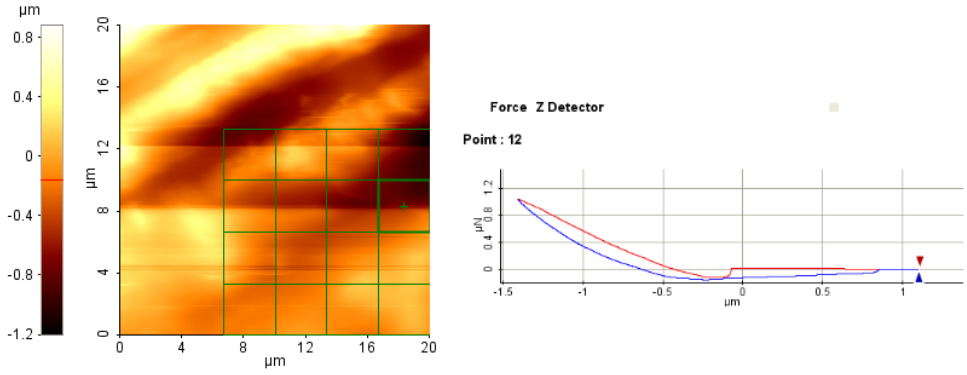
Fig. 4. Magnetic regions and their histograms for the sample P5 (80vol.% SR, 5vol.% nFe, 10vol.% CI and 5vol.% Ca), scanning area of 45×45µm^2.



(a) (b)

Fig. 5. Surface topography (a), and MFM images (b) of the sample V1 (86 vol.% SR, 4vol.% CI, 10 vol.% Ca), scanned area of 20×20µm^2.

As reported before, for nanoparticles imbedded in the elastomeric matrix the interaction between different particles is the most significant, therefore favouring good particle mixing [25]. Figure 5 presents a comparative study of the topographic and MFM signals, which validates the uniform distribution of the magnetic fillers into the elastomeric matrix.



Cursors

Cursor	ΔX(fm)	ΔY(fN)	Left X(µm)	Left Y(nN)	Right X(µm)	Right Y(nN)	Angle(deg)
Trace	0.000	0.000	1.113	0.370	1.113	0.370	N/A
Retrace	0.000	0.000	1.103	-1.605	1.103	-1.605	N/A

Fig. 6. F/D spectroscopy curves for sample V3 (80 vol.% SR, 10 vol.% CI, 10 vol.% Ca), 12 points of indentation.

The mechanical behaviour of the MREs depends of the matrix properties and of the filler properties, the adhesion and wetting of the surface of the filler by the matrix polymer influencing the behaviour of the composite. The concentration of the filler has a strong influence on the MRE mechanical properties [17,19].

Adhesion energies for each sample were calculated from F/D data as proposed in [23].

Table 2 shows the adhesion energies obtained from F/D curves when considering the contact area of the tip on the MRE surface with a normal vector.

Table 2

	Matrix	P1	P2	P3	P4	P5	V1	V2	V3
Adhesion energy (J)	$2.084\cdot 10^{-11}$	$0.25\cdot 10^{-11}$	$1.72\cdot 10^{-12}$	$1.26\cdot 10^{-12}$	$0.44\cdot 10^{-12}$	$1.47\cdot 10^{-12}$	$0.73\cdot 10^{-12}$	$0.54\cdot 10^{-12}$	$0.12\cdot 10^{-12}$

Correlating the results from Table 2 with the MRE compositions, we notice that the adhesion energy is affected by the ferrofluid concentration (decrease by one order of magnitude for the doped matrix), by the concentration of the ferrous microparticles (decrease when increasing the microparticles concentration), by the simultaneously presence in the matrix of ferrofluid and magnetic microparticles (lower when both dopants are present), and the type of the magnetic particles (lower for nano- than for microparticles).

The unusual behaviour of P5, when the adhesion energy is increased at a high concentration of the filler is another evidence of the tendency of the microparticles to form clusters in the elastomer matrix, during polymerization. A similar tendency was reported for microparticles with small diameters, and also for anisotropic megnetorehological elastomers with high concentration microparticles [16,19].

4. Conclusions

Using Non-contact atomic force microscopy and magnetic force microscopy modes, we succeeded to detect the dispersion of the magnetic particles embedded in the elastomeric matrix of magnetic elastomers, and to measure the diameters of the magnetic particle and/or the magnetic clusters. Using nanoindentation and Force-distance Spectroscopy, we measured the adhesion energies for different concentrations of the magnetic fillers. Atomic Force Microscopy techniques proved to be reliable methods for investigation of magnetic and nanomechanical properties of magnetorheological elastomers.

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REFERENCES

[1] *Giessibl, F. J.*, Reviews of Modern Physics, 75/3 (2003) 949–983.
[2] *Phillips R. W.*, Surface and Coatings Technology, 68–69 (1994) 770-775,
[3] *Jepu I., Porosnicu C., Lungu C.P., Mustata I., Luculescu C., Kuncser V., Iacobescu G., Marin A., Ciupina V.*, Surface and Coatings Technology, 240 (2014) 344-352, https://doi.org/10.1016/j.surfcoat.2013.12.050
[4] *Samide A., Iacobescu G. E., Tutunaru B., Grecu R., Tigae C., Spinu C.*, Coatings, 7/11 (2017) Article Number: 181, doi: 10.3390/coatings7110181
[5] *Dufrêne Y. F., Ando T., Ricardo Garcia R., Alsteens D., Martinez-Martin D., Engel A., Gerber C., Müller D. J.*, Nature Nanotechnology, 12 (2014) 295–307.
[6] *Amrein M.W., Stamov D.* (2019) Atomic Force Microscopy in the Life Sciences. In: Hawkes P.W., Spence J.C.H. (eds) Springer Handbook of Microscopy. Springer Handbooks. Springer, Cham. https://doi.org/10.1007/978-3-030-00069-1_31
[7] *Galvanetto N.*, Biochimica et Biophysica Acta (BBA) – Biomembranes, 1860/12 (2018) 2532–2538, doi:10.1016/j.bbamem.2018.09.019
[8] *Moldovan A., Bota P.-M., Poteca T. D., Boerasu I., Bojin D., Buzatu D., Enachescu M.*, Eur. Phys. J. Appl. Phys. 64 (2013) 31302, https://doi.org/10.1051/epjap/2013130235
[9] *Moldovan A., Bota M., Dorobantu D., Boerasu I., Bojin D., Buzatu D., Enachescu M.*, J Adhes Sci Technol, 28/13 (2014) 1277-1287, doi: 10.1080/01694243.2014.900907
[10] *Buzatu, F. D., Lungu R. P., Buzatu D., Sartorio R., Paduano L.*, J Solution Chem., 38 (2009) 403–415, doi: 10.1007/s10953-009-9384-5
[11] *Garcia R.*, Chem. Soc. Rev., 49 (2020) 5850-5884, https://doi.org/10.1039/D0CS00318B
[12] *Bica I., Anitas E.M.*, Nanomaterials, 10 (2020) 1783.
[13] *Bunoiu M, Anitas E.M., Pascu G., Chirigiu L.M.E., Bica I.*, International Journal of Molecular Sciences 21 (2020) 4785.
[14] *Gavrilovici A.M., Anitas E.M., Chirigiu L., Bica I., Negrutiu M.L.*, Advances in Polymer Technology, Vol. 2019 (2019) Article ID 1983547, https://doi.org/10.1155/2019/1983547.
[15] *Bica I., Bunoiu M.*, International Journal of Molecular Sciences 20 (2019) 4201.
[16] *Bica I., Liu Y.D., Choi H.J.*, Colloid Polym Sci 290(12) (2012) 1115-1122
[17] *Ruddy, C., Ahearne, E., Byrne, G.*, A review of magnetorheological elastomers: Properties and applications. Advanced Manufacturing Science (AMS) Research Centre, Mechanical Engineering, University College Dublin, Belfield, Dublin 4, Ireland.
[18] *Fuchs, A., Zhang, Q., Elkins, J., Gordaninejad, F., Evrensel, C.*, J. Appl. Polym. Sci. 105 (2007) 2497–2508, https://doi.org/10.1002/app.24348
[19] *Iacobescu G. E., Balasoiu M., I Bica I.*, Journal of superconductivity and novel magnetism, 26/4 (2013) 785-792, doi: 10.1007/s10948-012-1903-8
[20] Park Systems XE Mode Notes: Magnetic Force Microscopy (MFM) High Resolution and High Sensitivity Imaging of Magnetic Properties, Force-distance Spectroscopy, Nanoindentation.
[21] *Fan, Y., Gong, X., Xuan, S., Zhang, W., Zheng, J., Jiang, W.*, Smart Mater. Struct. 20 (2011) 035007, doi: 10.1088/0964-1726/20/3/035007
[22] *Hengsberger, S., Kulik, A., Zysset, Ph.*, European Cells and Materials 1, 12-17 (2001), doi: 10.22203/eCM.v001a02
[23] *Pauschitz, A., Schalko, J., Koch, T., Eisenmenger-Sittner, C., Kvasnica, S., Roy, M.*, Sci. 26(6) 585–591 (2003)
[24] *Kallio M.*, The elastic and damping properties of magnetorheological elastomers, PhD Thesis, VTT PUBLICATIONS 565, 2005
[25] *Li H.*, Impact of cohesion forces on particle mixing and segregation. PhD Thesis, University of Pittsburgh, 2005.