MAGNETIC ELASTOMERS BASED ON NANOCRYSTALLINE MAGNETITE PARTICLES

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Abstract: *The superparamagnetic elastomers (which contain the magnetic 10 nm nanoparticles in size) are a new class of composite elastic material having controlled properties into magnetic field. This paper presents an artificial muscle obtained using common precursors (magnetite obtained in the laboratory, silicone rubber). The performance objectives was achieved a composite material with elastic properties that recommend it as being useful for making small magnetic muscle.*

Keywords: *magnetite, silicone rubber, elastomer, artificial muscles*

1. INTRODUCTION

Magnetic elastomers are a new class of composite materials that have elastic properties controlled by magnetic fields [1]. Because of their shape and the ability to modify the shape in a magnetic field, these types of composite materials can be used as artificial muscles, actuators and micro manipulators. Superparamagnetic elastomers (which contains the magnetic nanoparticles 10 nm in size) due to magneto-elastic properties can be used for the construction of sensors, switches, various separating membranes, etc [1].

2. EXPERIMENTAL

In the present paper, a method for obtaining magnetic rubbery silicone is presented, and its physical and mechanical properties are discussed. The objectives of the work were:
■ obtaining by chemical coprecipitation of magnetite nanocrystalline and its structural analysis by XRD, XRF, FTIR, UV-ViS, VSM;
■ incorporation of nanocrystalline magnetite in silicone matrix and analyzed by XRF, VSM;
■ experimental test of magnetic rubbery silicone under mechanical stress.

Nanocrystalline magnetite has been obtained by chemical co-precipitation from aqueous chlorides, ferric and ferrous, and precipitating agent used was sodium hydroxide, under reaction (1) [7,9]:

$$\mathbf{2FeCl_3 + FeCl_2 + NaOH \rightarrow 4HCl + 4NaCl + Fe_3O_4}\downarrow \quad (1)$$

To prevent magnetic agglomeration, the colloidal suspension can be stabilized by ultracentrifugation.

Silicone comes in liquid state, packaged in two separate containers: one (called A) contains silicone monomer and inhibitor, and the second container (called B) containing crosslink agent. Part A and part B are mixed with nanocrystalline magnetite. Thus, it was obtained a homogeneous black material. To remove air bubbles appeared during mixing, degassing is performed under a primary vacuum bell. Then, the mixture filled into the form, and silicone polymerization takes place at ambient temperature.

3. RESULTS AND DISCUSSIONS

3.1. X-Ray Diffraction

XRD analysis of the magnetite sample showed that it contains only nanocrystalline magnetite: the diffraction peaks are according to standard for magnetite 19-0629 - JCPDS (Joint Committee on Powder Diffraction Standards) [8].

The X-ray diffraction pattern (figure 1) is indicating a single phase of iron oxide (Fe_3O_4) with the grain size varying from 10–30 nm.

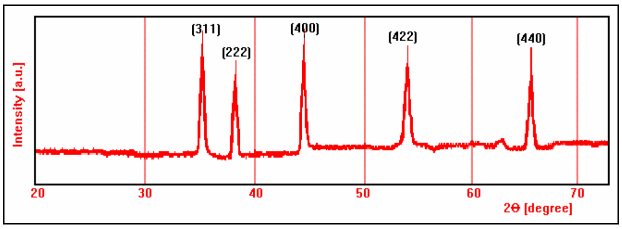


Figure 1. X-ray diffraction pattern of the magnetite sample

3.2. UV-Vis Spectroscopy

The UV-Vis spectrum of magnetite (figure 2) shows absorption maxima at 208, 220, 233 nm due to tetrahedral coordinated Fe^{3+} ions, and 278 nm due to octahedral coordinated Fe^{3+} ions.

The bands at 242 nm and 333 nm resulting from intervalence charge transfer transitions (IVCT) due to electronic delocalisation between Fe^{2+} şi Fe^{3+} ions.

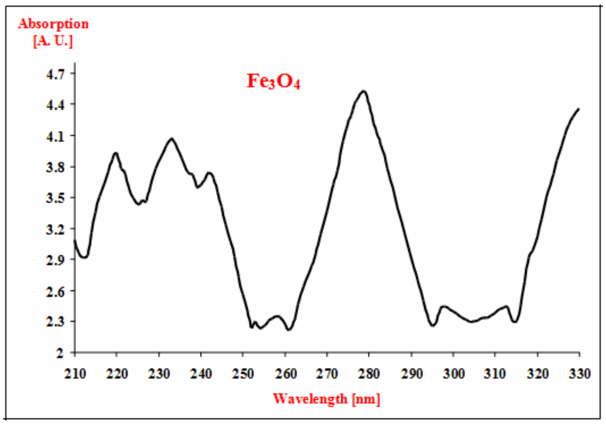


Figure 2. UV-Vis spectrum of the magnetite sample [7]

3.3. FTIR Spectroscopy

FTIR spectrum (IR transmission spectrum with Fourier transform) of the magnetite has two strong absorption bands 570 cm^{-1} (υ_1) and 390 cm^{-1} (υ_2), from Fe^{3+} vibrations. It also identified other bands in the range 3600-3100 cm^{-1} due to OH group: in the region 1670-1600 cm^{-1} (OH groups from water) and the band at 3394 cm^{-1} can be attributed to H_2O molecules or OH groups from magnetite particle surface; the band at 1547 cm^{-1} is attributed to change of OH vibrations from H_2O.

The IR bands at 795 cm^{-1} and 891 cm^{-1} assigned to the characteristic vibration of goethite, one of the hydrated forms of iron oxide. This is due to the presence of OH groups remaining related obtaining process of Fe_3O_4 and incomplete drying at the moment of IR analyse.

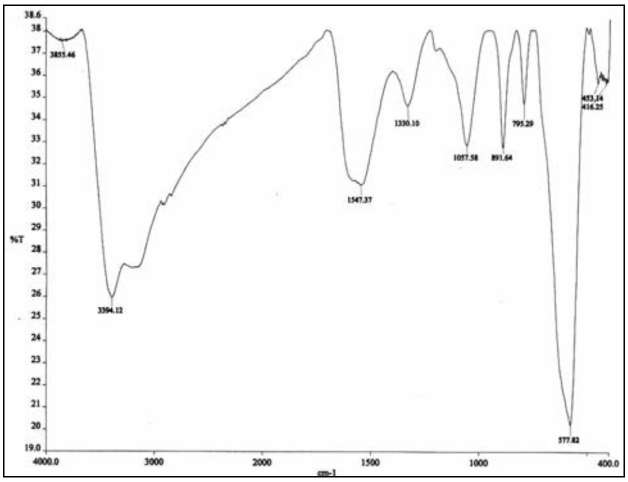
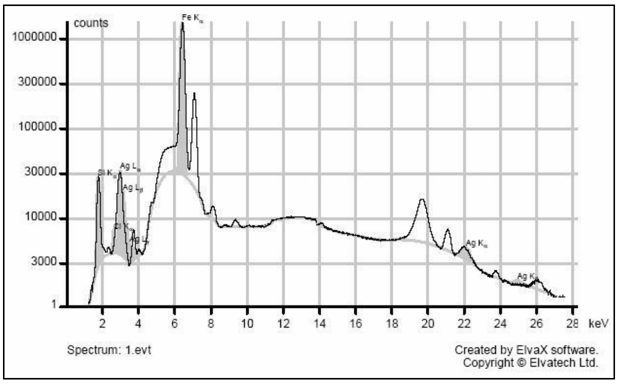


Figure 3. FTIR spectrum of magnetite sample

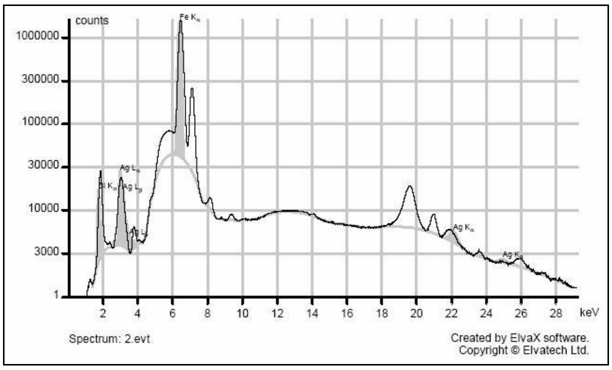
3.4. X-ray fluorescence spectrometry (XRF)

XRF analysis of silicone rubber – magnetite composites was performed on a X-ray fluorescence spectrometer with X-ray tube (Rh anode), Be window of 140 µm cooled, with the elemental analysis from Cl (17) to U (92).

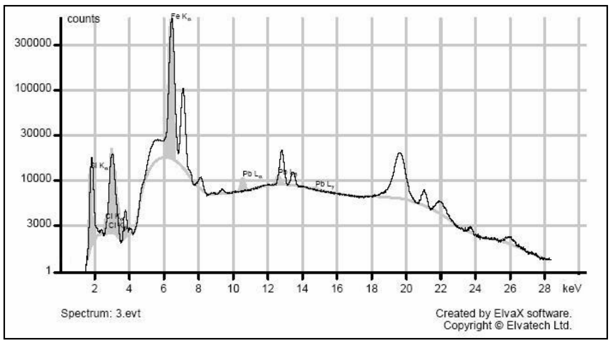
The ED-XRF spectra of magnetic silicone composite (Figure 4) highlights specific peaks of the iron from magnetite, the silicon from silicone rubber, and the silver from catalytic salt of silicone polymerization. Other elements are present only as impurities which come from iron chloride used in the preparation of magnetite.



a)



b)



c)

Figure 4. ED-XRF spectra of silicone rubber - magnetite nanocomposite samples with: a) 12% Fe_3O_4, b) 16% Fe_3O_4, and c) 24% Fe_3O_4

XRF analysis of the samples confirmed the chemical composition of the nanocomposite material, as shown in the graph from figure 5.

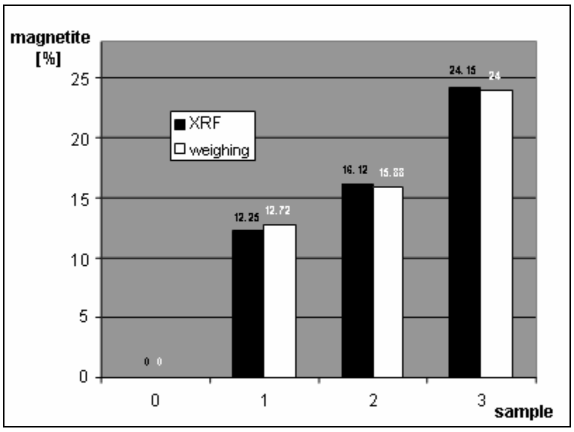


Figure 5. Comparison between the percentage of magnetite determined by weighing on analytical balance (white) and XRF (black), from silicone rubber - magnetite nanocomposite samples

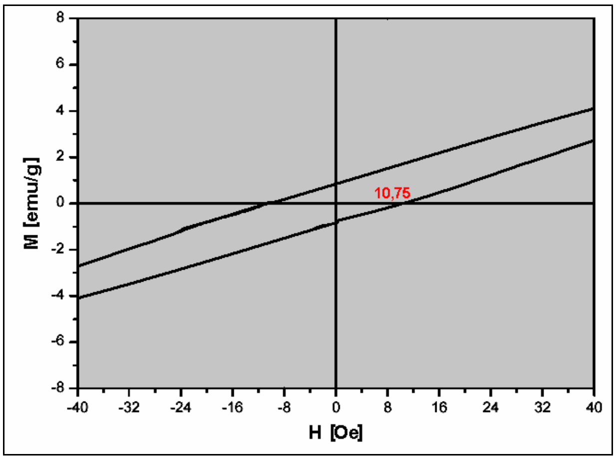


Figure 7. The hysteresis curve of composite silicone rubber - magnetite sample in ± 1000 Oe field

3.5. VSM

When the size of magnetic nanoparticles is sufficiently small, each particle is a single magnetic domain. Reduction of particle size makes the thermal vibrations lead to random variation in the timing of net spin and magnetic field unstable is considered.

While the spin magnetic moment of the particle is oriented randomly, their effects cancel each other and the effective magnetic moment of all particles becomes zero. If a magnetic field is applied, the particles produce an effective magnetic moment. This behavior is characteristic of paramagnetic materials and the difference is that each molecule has a big enough net magnetic field, for Fe_3O_4 was 4 μB. In 1956, Bean &. Jacobs have called this type of magnetism as *superparamagnetism* [3,4].

A necessary condition for superparamagnetism is that the particles are small enough so that its become single magnetic domains. Morrish and Yu determined that Fe_3O_4 particles are single domain when the shape is spheroid with diameter less than or equal to 50 nm [5].

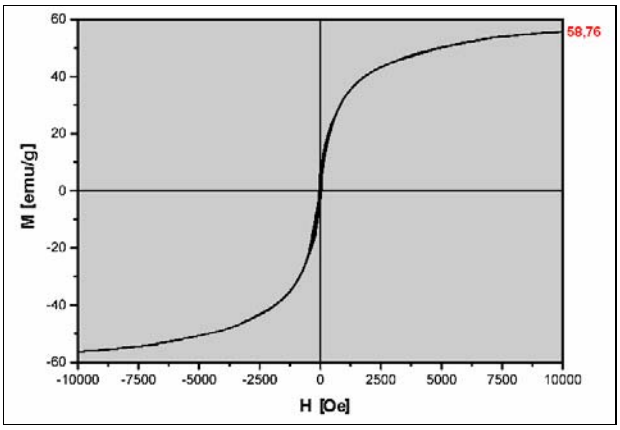


Figure 6. The hysteresis curve of magnetite sample in ± 10000 Oe field

The magnetic properties (coercitivity field H_c, remanent magnetization M_r, and saturation magnetization M_s) measured with VSM (at room temperature with applied field up to 10 kOe) demonstrated that the magnetic behavior of magnetite nanoparticles does not change significantly after encapsulation into silicone rubber.

The hysteresis curve of the magnetite sample is characteristic for magnetic nanoparticles with average diameter about 10 nm, and shows that the H_c value is less than 1 Oe (figure 6).

For all the samples with $H_c \leq 1$, was approximated $H_c \sim 0$. As a condition for superparamagnetism is $H_c \sim 0$, magnetite nanoparticles obtained can be considered superparamagnetic.

3.6. Tensile test

To measure the Young's modulus (E), also known as the tensile modulus or elastic modulus, is to compare the mechanical properties of the composite silicone rubber and Fe_3O_4 with commercial silicone rubber. It is defined as the ratio of the stress along an axis σ (MPa) to the strain ε(%) along that axis in the range of stress in which Hooke’s Law holds.

Tensile testing was performed on a Ametek Lloyd device (type LR10K PLUS 01/3052), according to the test standards: SR ISO 37/1997 and D41-1099.

The tests were performed on three samples of silicone rubber - magnetite composite (1,2,3) and one of silicone rubber, and reported stress-strain curves, as had tested the second criterion to be met: *elasticity*. The first criterion is met by obtaining ultrapure superparamagnetic magnetite powder.

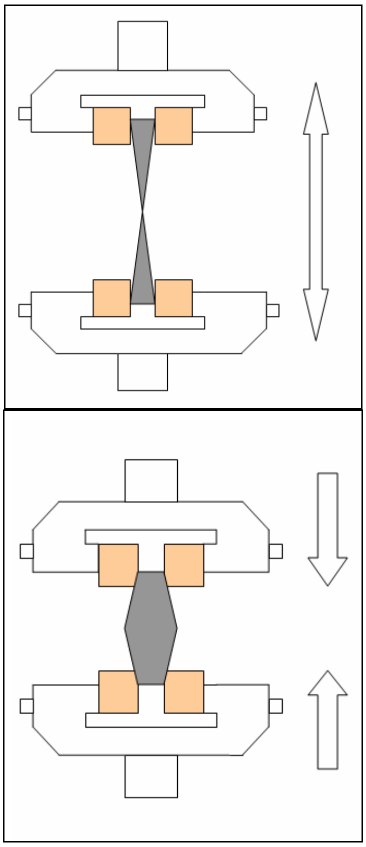


Figure 8. Scheme of tensile testing on silicone rubber

Table 1. The mechanical properties values determined for different composite samples relative to those of technical silicone rubber

sample	Measured mechanical properties / The composition of samples	σ [MPa]	ε [%]	E [Mpa]
0	Silicone rubber	8.54	280	3.05
1	Silicone rubber + 12% magnetite	7.50	260	2.88
2	Silicone rubber + 16% magnetite	6.80	240	2.83
3	Silicone rubber + 24% magnetite	5.10	198	2.58

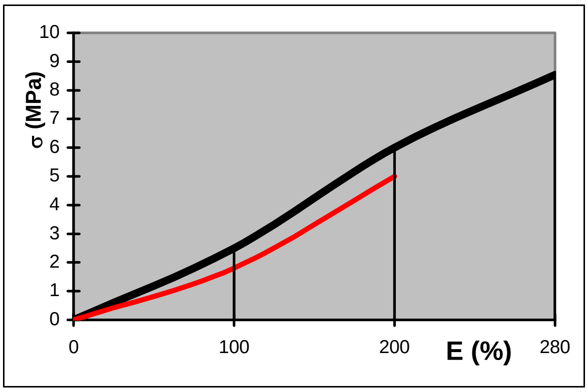


Figure 9. The stress-strain curve: silicone rubber (black curve) and silicone rubber – magnetite sample (red curve)

4. CONCLUSIONS

Synthesis of magnetic silicone rubber, based on nanocrystalline magnetite, was used to prepare anisotropic samples. The controlled magnetic field can orients the magnetite nanoparticles and a chain structure develops.

This composite material becomes anisotropic in terms of magnetic and mechanical properties. One can easily vary the direction of the particle chains by the direction of the applied magnetic field. In addition, the tensile strain of the material in relation to normal stress changes due to the existence of the magnetite nanoparticles is studied.

The contains of magnetite nanoparticles has a decisive effect on the stress-strain curve. Due to their shape and size distortion ability in a magnetic field, these magnetic stimuli-responsive materials have interest in artificial muscles, actuators, and micromanipulators.

5. ACKNOWLEDGMENTS

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6. REFERENCES

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