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Polymer composites with magnetostrictive properties

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The synthesis, characterization and evidence of magnetostrictive properties of blends between one ionic polyurethane with carboxylic units and magnetostrictive micropowders ($Fe_{78}Si_9B_{13}$), as well as nanopowders ($Fe_{68,5}Co_{10}Sm_{1,5}B_{20}$) is reported. The incorporation of magnetic particles in the polyurethane matrix lead to a magnetic behavior directly dependent on their density and dimensions. The best response was achieved for the micropowders with the diameter within 100 – 150 μm range. A good behavior was also evidenced for the compact system composed of microparticles with the diameter less than 60 μm.

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1. Introduction

Magnetostriction is the phenomenon of strong coupling between magnetic properties and mechanical properties of some ferromagnetic materials: strains are generated in response to an applied magnetic field, while conversely mechanical stresses in the materials produce measurable changes in magnetization. This phenomenon can be used for actuation and sensing. Furthermore, newer magnetostrictive materials provide strains, forces, energy densities, and coupling coefficients which compete advantageously with transducer technologies such as those based on piezoelectric materials [1].

Ionic polymers comprise the active layer in ionic polymer-metal composites (IPMCs), and due to the generation of a large strain in response to low electric field stimulation and high gravimetric energy density, there has been considerable conjecture over the potential applications of these soft transducers [2,3] and substantial fruitful investigations towards these ends [4,5]. Usually, IPMC's are actuators constructed from an anionic perfluorinated polymer membrane (e.g., modified PTFE (Teflon) with perfluorinated sulfonate anion side groups) with surface electrodes. These materials are the key component in proton exchange membrane fuel cells, and are commercially available (e.g., DuPont Nafion). Being actionless, ionomeric composites have been proved to be efficient for biomedical applications due to their flexibility, miniaturization and stability in liquid media. Also, actuator-based ionic polymers were used for drug delivery, medical micro-pumps activated through a polymeric diaphragm, as well as sensors that allow sanguine pressure and cardiac beat recording. Moreover, these actuators can stimulate biological muscles and arms functions [6].

In recent years, the use of polyurethane-metal composites has grown, especially of those attained through carbamate hydrogen replacement with picolyl units, where Ni (II) complex exhibit better mechanical properties as compared with the Co ones, due to different metal-ligand interaction strength [7]. An improvement of mechanical properties has been obtained for polyurethanes blends that contain acetates of transitional metals and pyridine as pendant units, with an increase of modulus of 10-35% related to precursor [8]. Polyurethanes that contain metal-metal bonds in the polymeric chain are photodegradable, both in solution and solid state, being characterized by „trap" structures formation that binds metal radicals in order to prevent metal-metal linkage restoration due to radical recombination. Poly(ether urethane)s with ionic structures based on calcium and magnesium salts of mono(hydroxyethyl)ftalate have proved to be biocompatible and biodegradable on short term when used in blood-contacting device, such as artificial heart components. Other ionomeric polyurethanes were obtained through quaternization of N-methyldiethanolamine with alkyl halide or metal (II) sulphates, as well as metals incorporation in polymeric siloxane networks [9]. Previously, polyurethane ionomers bearing carboxylic or other specific units have been reported that can function as potential sensors for transitional metals and actuators [10-12].

The present study provides experimental data on the formation of polymer–magnetostrictive material composites in an attempt to integrate the investigation in the current research on multifunctional magnetostrictive materials. The paper reports the synthesis, characterization and properties of blends between an ionic polyurethane with carboxylic units and magnetic micropowders ($Fe_{78}Si_9B_{13}$), or nanopowders ($Fe_{68,5}Co_{10}Sm_{1,5}B_{20}$). The resulting intelligent hybrid systems could serve as useful probes for obtaining sensors, actuators and assemblers of multifunctional magnetostrictive materials type.

2. Experimental

Positive magnetostrictive micropowders ($Fe_{78}Si_9B_{13}$, $\lambda_s \cong +36$ ppm) were obtained *via* atomization method. Thus, alloys were melted in a quartz melting-pot and then ejected by the appliance of an additional pressure in two Fluxes (argon and water). Thereafter, the magnetic micropowders were collected using a magnet. Depending on the micropowder diameters ((i) d < 60 µm; (ii) 60 µm < d < 100 µm; (iii) 100 µm < d < 150 µm), these ones were incorporated in a polyurethane matrix in a 20% w/w concentration. The thickness of the polymeric films was between 0.1 – 0.4 mm. Also, a nanopowder ($Fe_{68,5}Co_{10}Sm_{1,5}B_{20}$) as-quenched (Co20 Sm aq) was obtained by arc discharge method (Huffman-Kratschmer modified method). The basis alloy was mixed with the electrode material and, through appliance of a voltage pulse, an arc was generated with nanopowder attainment.

In order to obtain ionomeric composites based on ionic polyurethanes and magnetic particles, a mixture of polyurethane in anhydrous DMF (c = 10 $g \cdot dl^{-1}$) and magnetic particles with different dimensions (100 µm < d < 150 µm, 60 µm < d < 100 µm, d < 60 µm) was sonicated for 5 minutes, in the presence of 1 % didodecyl or dilauryl sulphate dispersants. The polymeric films were obtained through depositing the blends on a glass surface in the presence of particles (20 %), evaporated and dried at 60-65 °C to eliminate the solvent. With this technique, three polymeric films were prepared, with a thickness of 0.2-0.4 mm.

3. Results and discussion

3.1. Obtaining and characterisation of magnetostrictive composites

The magnetostrictive nanopowders of composition ($Fe_{68.5}Co_{10}Sm_{1.5}B_{20}$) were characterized through thermo-magnetic analysis (Fig. 1). Such nanopowders exhibit high Curie temperatures, as well as large differences between the heating/cooling curves. This behavior can be attributed to sample degradation (decomposition) during heating.

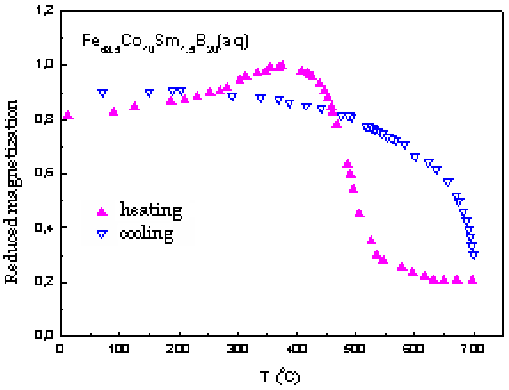


Fig. 1. Thermo-magnetic analysis for $Fe_{68,5}Co_{10}Sm_{1,5}B_{20}$ nanopowders.

The first magnetization curve (Fig. 2), registered at room temperature, evidence for the same type of compounds a decrease of the magnetic saturation.

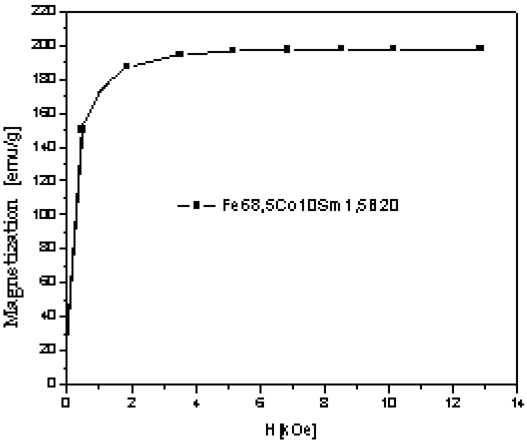
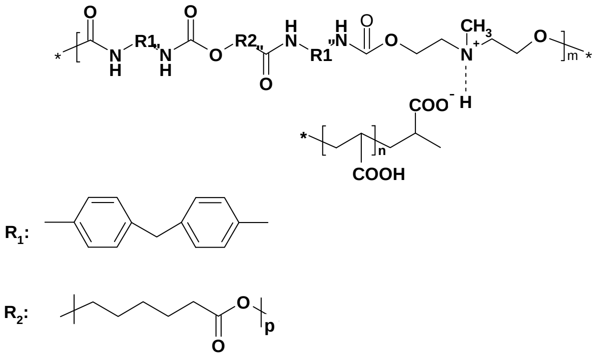


Fig. 2. The first magnetization curves for $Fe_{68,5}Co_{10}Sm_{1,5}B_{20}$ nanopowders.

The obtaining of the magnetostrictive composites implied the use of an ionic polyurethane with carboxylic groups in blending with magnetic particles of Fe-Si-B type. The polyurethane precursor is based on poly(caprolactone) diol of 2000 $g \cdot mol^{-1}$, 4,4'-methylene diphenyl diisocyanate (MDI) and *N*-methyldiethanolamine (1:3:2 molar ratio). The synthesis of the ionomeric structure was performed through acrylic acid *in situ* polymerization in the presence of benzoyl peroxide. The structure of the ionic polymer with polyacrylic acid chains complexed with nitrogen tertiary atoms from polyurethane backbone is presented in Scheme 1.



Scheme 1. Ionic polyurethane structure.

The resulting polymer has a typical elastomeric block-copolymer structure with polyether long soft segments (67.7%) and hard segments comprising both urethane and ionic units (32.2%). One can mention that the presence of polyacrylic acid chains (10% w/w) does not affect the elastomeric properties of the polymers. The molecular characterization by ^{1}H-NMR and IR spectroscopy, and viscosity measurements ($\eta_{red.}$ = 0.58 dl·g^{-1} in DMF, c = 0.35 g·dl^{-1}) clarified the structure of the polymer, where the spectroscopic characterizations yielded results in full agreement with the proposed structure. The IR spectrum of polymeric film show characteristic bands due to NH urethane stretching at 3300 cm^{-1}, CH groups at 2870-2900 cm^{-1}, hydrogen-bonded carbonyl bonded at 1710 cm^{-1}, while hydrogen-unbounded carbonyl group band located at 1725 cm^{-1} is overlapping with the one from polyacrylic acid.

3.2. Magnetic and magneto-elastic characterization of the composites obtained through magnetostrictive powder inclusion into polymer matrix

Hysteresis is a property of systems that do not instantly follow the forces applied to them, but react slowly, or do not return completely to their original state, this property helping to keep the components in a particular state while the other components change the state. From a device implementation standpoint, magnetostrictive materials exhibit significant nonlinearities and hysteresis to a degree which other smart materials, for instance electrostrictives, typically do not [13]. The deleterious effects due to these behaviors can be circumvented through feedback control techniques. However, the development of broadband feedback control solutions that do not degrade in performance over a large performance range has been elusive in many magnetostrictive systems, because in these systems the efficacy of real-time monitoring and feedback control is diminished by noise inherent to hysteresis, thermal creep, and strong material property variations. Important advances on the modeling of magnetostrictive materials and structures have been achieved recently, and as transducer designers find opportunities to develop new applications, model completeness and accuracy will surely follow. In addition, recent advances in materials science research have enabled more capable magnetostrictive materials in various forms, including amorphous or crystalline thin films, magnetostrictive particle-aligned polymer matrix composite structures, and sintered powder compacts suitable for mass production of small irregular shapes. The latest research on magnetostrictive materials includes the development of new compounds to minimize magnetic anisotropy and hysteresis [14].

In Figs. 3-5 are presented the magnetic hysteresis cycles for composite thin films that contains $Fe_{78}B_9Si_{13}$ magnetostrictive micropowders of different dimensions: 100 μm < d < 150 μm, 60 μm < d < 100 μm and d < 60 μm. The loops are distant and symmetrical *versus* origin of the coordinate system. The shape of the loops evidences the magnetic character of the samples. It can be observed a significant modification of the magnetic response of the system depending on the micropowder density incorporated in the polyurethane matrix, as well as their dimensions. The best magnetic response was achieved for the micropowders with the diameter within 100 – 150 μm range, with also a superior behavior of the compact system composed of microparticles with the diameter less than 60 μm. The reduction of the powder concentration results in the diminishing of the magnetic response of the composite system.

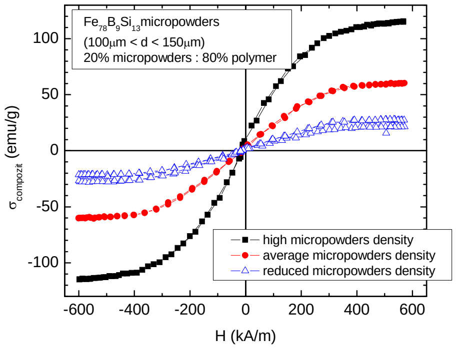


Fig. 3. Variation of hysteresis cycles as a function of micropowders density and dimensions (100 μm < d < 150 μm).

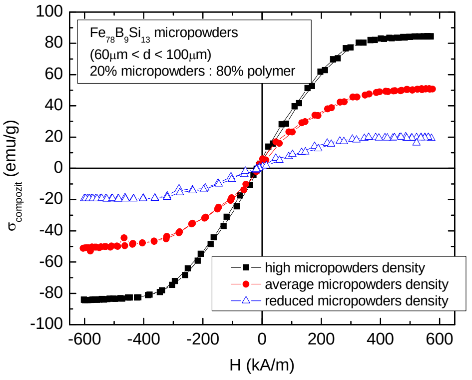


Fig. 4. Variation of hysteresis cycles as a function of micropowders density and dimensions (60 μm < d < 100 μm).

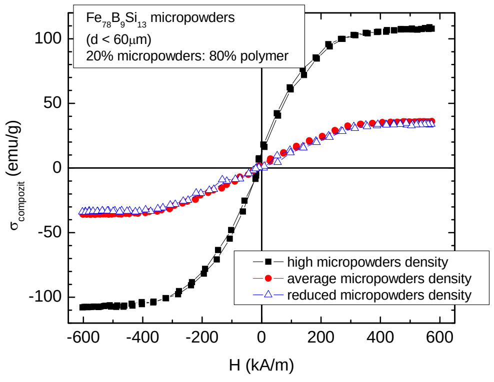


Fig. 5. Variation of hysteresis cycles as a function of micropowders density and dimensions (d < 60 μm).

In Fig. 6 is ilustrated the magnetostriction variation as a function of an applied magnetic field for one composite material including $Fe_{78}Si_9B_{13}$ micropowders (d < 60 μm, 8 % percentage) incorporated into the polyurethane matrix, with a desirable magnetoelastic response.

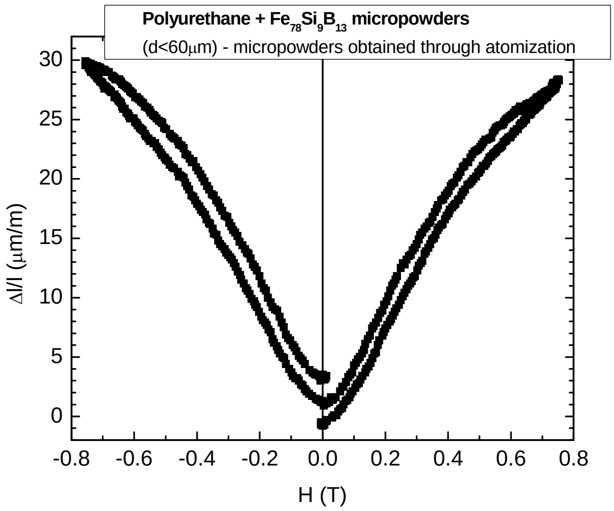


Fig. 6. Magnetoelastic response of composite material including $Fe_{78}Si_9B_{13}$ micropowders (d < 60 μm, 8 % percentage) incorporated into the polyurethane matrix.

Due to the high value of the hard segment content in the polyurethane matrix (32.2%), the magnetostriction increases slightly, probably due to the fact that rigidity and crystallinity of polyurethane increase. In a random polycrystalline sample, the polycrystalline saturation magnetostrictive may be derived from averaging cubic single crystal theory [15] and we can consider an isotropic magnetostriction for these types of randomly composites, where the whole magnetostriction is an average of the magnetostriction of each grain in a composite under a magnetic field.

In order to ilustrate the magnetoelastic behavior of the polyurethane composite comprising 20% $Fe_{68.5}Co_{10}Sm_{1.5}B_{20}$ nanopowders, the hysteresis cycle was registered (Fig. 7). Taking into account of the good magnetic response, a good magnetoelastic one for the studied system it is expected likewise. Moreover, in the Fig. 8 is shown the variation of magnetostriction of the probes as a function of nanopowder density. It is important to be mentioned for the composites of Fe-Co-Sm-B type the reversed magnetic response as compared with the magnetoelastic one.

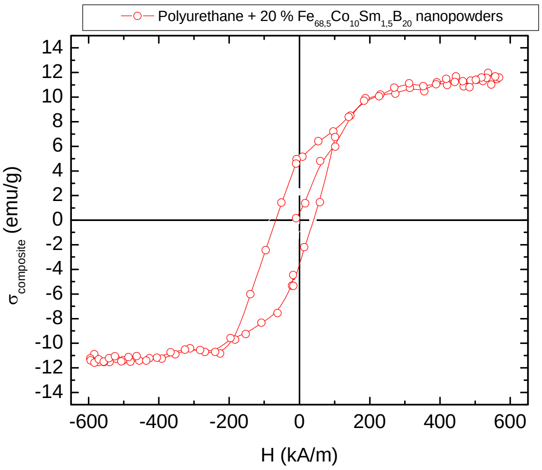


Fig. 7. Variation of hysteresis cycle as a function of $Fe_{68,5}Co_{10}Sm_{1,5}B_{20}$ nanopowders density included in polyurethane matrix.

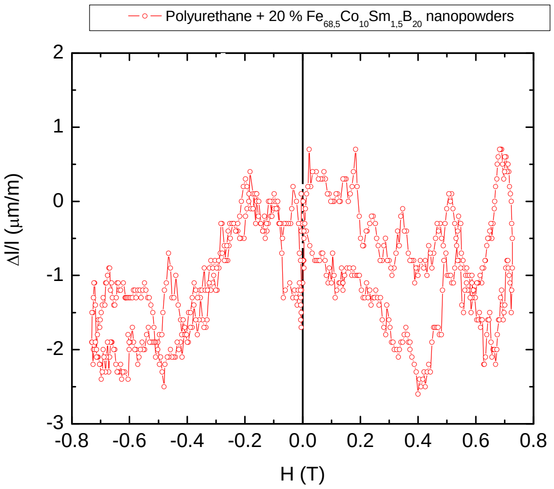


Fig. 8. Variation of magnetostriction as a function of $Fe_{68,5}Co_{10}Sm_{1,5}B_{20}$ nanopowders density included in polyurethane matrix.

4. Conclusions

The incorporation of magnetic micro- or nanopowder in a polyurethane matrix lead to a magnetic behavior of the resulting composites. As follows, the magnetostrictive properties of the resulting composites depend on the magnetostrictive powder mass and the distribution on the surface/volume unity. The best magnetic response was achieved for the micropowders with the diameter within 100 – 150 μm range, and a compact system composed of microparticles with the diameter less than 60 μm exhibits also improved properties.

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