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MAGNETIC ELECTROSPUN COMPOSITE FIBERS

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Abstract: *This work is focusing on electrospinning polyethylene oxide (PEO) with incorporated barium ferrite nano-particles (BaFe) and the characterization of the magnetic properties of the obtained composites fibers. The barium ferrite powders used belong to a group of ferrites with hexagonal crystal structure. PEO has low toxicity, is water soluble, and is available in a variety of molecular weights of which 600.000 g/mol was used in this study. Following successful electrospinning of magnetic composite fibers, we have selected two samples, denoted as S1 and S2, for further investigation. The process parameters corresponding to the production of S1 and S2 differ only by the needle tip-to-collector distance which is larger for S2 (70 mm as compared to 50 mm). SEM images and fiber diameter distributions reveal that, as previously shown for pure PEO electrospun fibers, the average fiber diameter is decreasing with decreasing tip-collector distance. In addition, the distribution of the fiber diameters for the S1 sample is wider than the one for S2. This is indicative of a less controlled electrospinning process in the case of the S1 sample. Magnetic measurements on composite fibers reveal an expected ferrimagnetic behavior and no major differences between the magnetic properties of S1 and S2.*

Key words: *electrospinning, polyethylene oxide, barium ferrite nano-particles, composite fibers, magnetic properties*

1. INTRODUCTION

Current society increasingly requires innovative materials and associated technologies to answer its demands. In this context, nanotechnologies foster the creation, through structural control at nano level, of nano-structured materials with exceptional performance and innovative new functions. Nano-structured organic materials and biomaterials are finding diverse industrial applications while expanding as a major field of material research. Semiconductor related materials are both socially and economically important as information communication and energy transformation materials.

Composite materials made of various organic and inorganic materials hold a huge potential for intelligent structures.

In order for nano-structured materials to develop entirely new functions, it is important to design and control the technologies which allow their production. Among the many promising ones, electrospinning is actively pursued both at research and at industrial level for its capability of producing nano-sized polymer fibers which can be easily functionalized with various nano-particles for added properties. In this paper, we are focusing on conferring magnetic properties to polymeric fibers obtained through electrospinning. Magnetic fibers are manufactured by introducing ferrimagnetic nano-particle powders into the polymer solution prior to electrospinning. The resulting polymer fibers are composite fibers, as the polymer (the matrix) together with the magnetic powder filler make a discontinuous phase. These composites have many potential applications in microelectronics as nano-electronic micro-mechanical systems (MEMS) and bio-micro-mechanical systems (BioMEMS).

Prior work on electrospun magnetic nano-fibers has mainly involved electrospinning combined with the sol-gel method [1-4]. Various authors have also reported on the electrospinning of polymer and nano-particles mixtures. However, in this case, the affinity between the inorganic and the organic materials may complicate fiber synthesis. However, the large range of potential applications such as electromagnetic interference (EMI) shielding, electrically conducting materials, super-capacitors and filters has motivated research in this direction. For example, $BaFe_{12}O_{19}$ nano-particles incorporated in poly (vinyl alcohol) were electrospun with the purpose of producing filters for the effective separation of Fe_3O_4 nanoparticles and removal of arsenic from waste water [4]. Cobalt ferrite/polyacrylonitrile and cobalt ferrite/carbon nano-fibers were electrospun and characterized by Chen *et al.* [5].

We are focusing in this work on: (a) electrospinning polyethylene oxide (PEO) with incorporated barium ferrite (BaFe) nano-particles and (b) characterization of the magnetic properties of the obtained composite fibers. The barium ferrite powders used belong to a group of ferrites with hexagonal crystal structure. PEO has low toxicity, is water soluble and available in a variety of molecular weights of which the 600.000 g/mol is used in this study. The wide variety of molecular weights available for PEO confer significant versatility to its usage but the real benefit is its water solubility which provides a more sustainable less hazardous route to nano-fiber production [6]. BaFe on the other hand, is attracting significant scientific and technological interest because of its relatively high Curie temperature, high coercive force and high magnetic anisotropy field, as well as its excellent chemical stability and corrosion resistivity [7]. Thus, composite electrospun fibers obtained from PEO and BaFe can exhibit important properties for a wide field of applications.

2. EXPERIMENTAL

2.1. Materials

Polyethylene oxide (PEO) from Sigma-Aldrich with a molecular mass of 600.000 g/mol was used to prepare PEO solutions. Deionized water and ethanol (> 99%, PanReac &AppliChem IWT Reagents) were used as solvent without any further purification and sodium chloride as additive to improve the electric conductivity of the polymer solution. Magnetic nano-barium ferrite particles with a diameter of less than 100 nm were supplied by Sigma-Aldrich. Some of the properties of the BaFe nano-particles include saturation magnetization 5.2801 emu/g, remanent magnetization 2.2174 emu/g and coercivity 4141.4 G. All solutions and samples were stored at room temperature.

The SEM images of the nano-barium ferrite particles obtained at different magnifications with a SEM-EDX VEGA II LSH TESCAN are shown in Fig. 1. They reveal particle agglomeration due to magnetic nature of the hard magnetic materials.

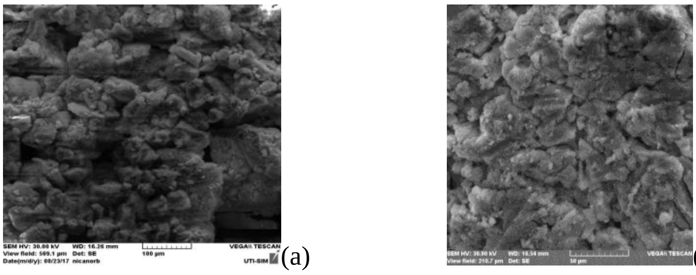

(a) (b)

Fig. 1: *SEM images of barium ferrite nano-particles (a) 500x magnification (b) 1000x magnification.*

A VSM Vibrating Sample Magnetometer (VSM model 7410 Lake-Shore) was used for measuring the hysteresis loops of barium ferrite nano-particles (see Fig. 2). The hysteresis loops indicate a behavior specific to hard magnetic materials with a high coercive field value.

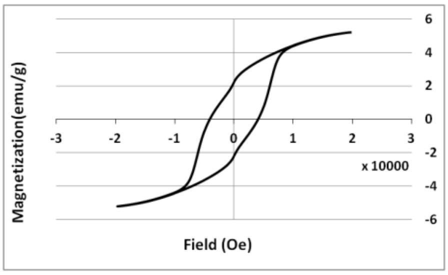


Fig. 2: *Magnetic loops of magnetizing barium ferrite nano-particles.*

2.2. Solution preparation

The solvent used to prepare the polymer solution is a mixture of ethanol and water in a weight ratio of approximately 4:1. The PEO powder (600.000 g/mol, 5.5 wt %) was dissolved in this solvent mixture by stirring vigorously using a magnetic stirring rod. An amount of 0.8 wt% of NaCl was added to the mixture to improve the conductive properties of the polymer solution.

An amount of 1.0 wt% barium ferrite nano-particles was dispersed in the PEO solution and subjected to ultrasonication at room temperature to obtain a homogeneous suspension. The obtained ferrite particle polymer suspension was used for electrospinning with different process parameters.

2.3. Electrospinning process

A 3 ml syringe with a needle inner diameter of 0.4 mm was used for feeding the polymer suspension. The syringe was fixed horizontally on the syringe pump (Model: KDS 100, KD Scientific) and the solution was electrospun by using a standard high voltage power supply (Matsusada HER 20R3) on a rotating drum. An external magnetic field produced by two permanent NdFeB magnets placed next to the electrospun area was applied in order to orient the nano-particles within the polymeric fibers. Several tests with different process parameters were performed and the once presented in Table 1 were selected for further investigation due to their improved fiber properties, *i.e.* absence of beads and smaller fiber diameters.

Table 1: *Process parameters for the selected samples S1 and S2.*

Sample	**Flow rate (ml/h)**	**Voltage (kV)**	**Tip-collector distance (mm)**	**Tip speed (mm/s)**	**Temperature (^{0}C)**	**Humidity (%)**	**Deposition time (s)**
S1	1	20	70	50	26	35	120
S2	1	20	50	50	26	35	120

2.4. Characterization

The electrospun fibrous mats were deposited on aluminum foil. A small piece of the foil was cut to obtain a suitable sample for imagistic investigation. The sample was placed in a SEM VEGA II LSH TESCAN and imaged with different magnification for dimensional characterization. For each image, at least 50 different points were randomly chosen to measure the average diameter of the fibers. A Lake Shore 7300 Vibrating Sample Magnetometer operating up to a maximum field of 30kG was used to obtain data for saturation magnetization, magnetic remanence and coercivity. This data was used to generate the hysteresis loops of the magnetic composite fibers.

3. RESULTS AND DISCUSSION

Fig. 3 shows, for each of the selected samples, SEM images at 500x, 2000x and 5000x magnification. The 500x magnified SEM images reveal a non-uniform structure of the fiber network which contains twisted fibers and also fiber agglomerations. The 2000x magnification is revealing, at closer inspection, some of the magnetic nano-particles which become clearly visible at higher magnifications. However, it is hard to draw a comparative conclusion between the two samples just by visual inspection. This is better evidenced through the investigation of the fiber diameter distribution.

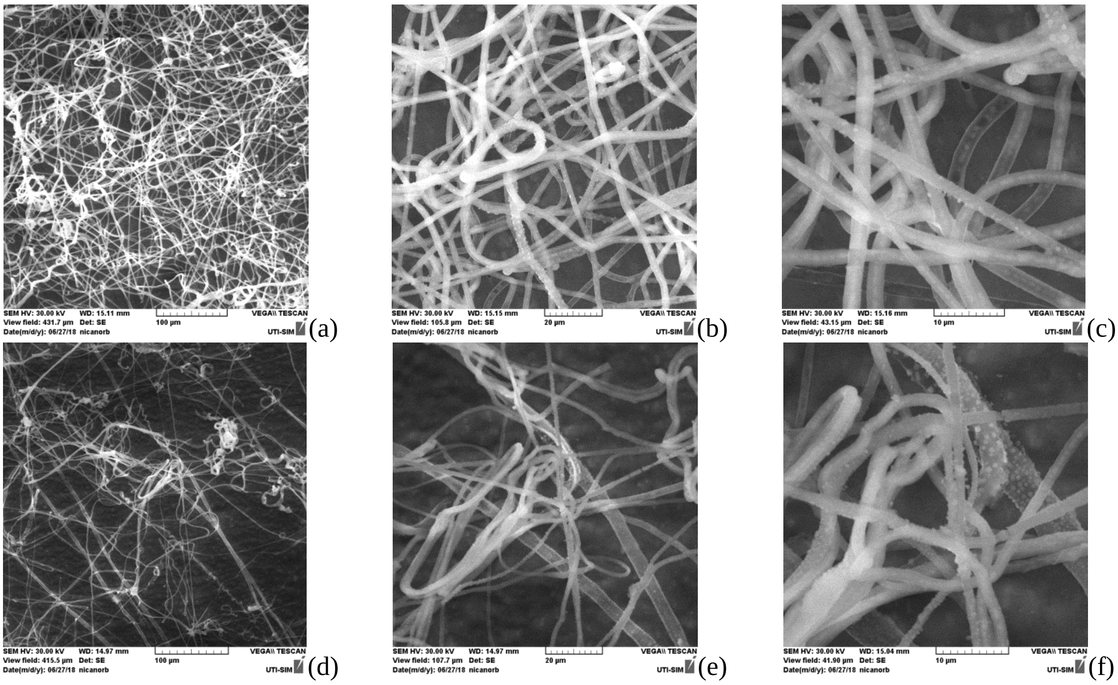
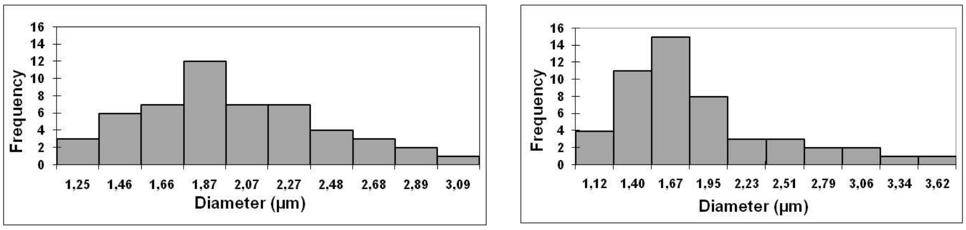


Fig. 3: *SEM images of sample S1 at 500x (a), 2000x (b), 5000x (c) magnification and of sample S2 at 500x (d), 2000x (e), 5000x (f) magnification.*

A series of 50 measurements were performed on the 2000x magnification SEM images of the samples in order to determine the diameter distribution presented in Fig. 4. The average fiber diameters for S1 and S2 are 1.89 µm and 1.75 µm, respectively. The peak of the distribution is at 1.87 µm and 1.67 µm for S1 while the diameter varies between 1.05 and 3.09 µm. For S2, the peak of the distribution is at 1.67 µm but the variation limits are larger, *i.e.* 0.84 to 4.64 µm. These values are in line with previous studies, including our own [8], which are revealing that the average electrospun fiber diameter is decreasing with decreasing tip-collector distance from 70 mm in S1 to 50 mm in S2. Our studies reveal, albeit on a small number of samples, that this behavior is preserved also upon incorporation of magnetic nanoparticles. In addition, the distribution of the fiber diameters for the S1 sample is wider than the one for S2. This is indicative of a less controlled electrospinning process in the case of the S1 sample.



(a) (b)

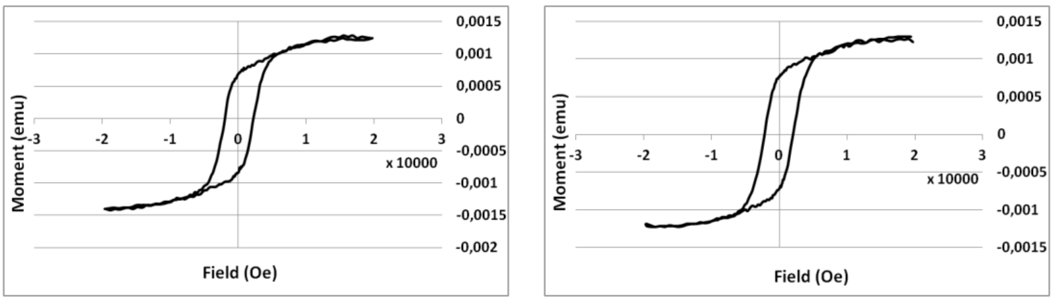
Fig. 4: *Fiber diameter distribution for S1 (a) and S2 (b).*

The magnetic properties of the electrospun S1 and S2 were measured at room temperature. Typical magnetization hysteresis loops are shown in Fig. 5. Table 2 is presenting the magnetic coercivity (H_c) values, the saturation magnetization (M_s) and the remanent magnetization (M_r). The coercivity (H_c) is the external applied magnetic field necessary to return the material to a zero magnetization condition, and the remanent magnetization (M_r) is the residual magnetization after the applied field is reduced to zero.

Table 2: *Magnetic properties of electrospun composites.*

Characteristic	**S1**	**S2**
Coercivity H_c (G)	2097.0	2102.1
Saturation magnetization M_s (emu/g)	1.24E-3	1.27E-3
Remanent magnetization M_r (emu/g)	6,893E-4	7.713E-4

Comparison of the hysteresis loops in Fig. 5 and magnetic properties in Table 2 reveals that there are no significant differences between the investigated samples. The magnetic coercivity decreases from 4141.4 G for pure barium ferrite nano-particles to around 2100 G after the nano-particles were dispersed in the polymer matrix. This decreased coercivity is due to the smaller amount of nano-particles in the polymer solution (1.0 wt %) and the increased nano-particles distance for the single-domain nano-particles, as compared to the close contact of the pure barium ferrite nano-particles. Also, the remanent magnetization for both electrospun composite decreased compared to the remanent magnetization of the pure nano-powder. Again, this is related to the weight percentage content of the nano-particles in the polymer fibers.



(a) (b)

Fig.5: *Magnetic hysteresis loops of the electrospun fibers S1 (a) and S2 (b).*

5. CONCLUSIONS

Polyethylene oxide-based fibers containing magnetic $BaFe_{12}O_{19}$ nano-particles have been successfully produced through electrospinning. Two samples, denoted as S1 and S2, were selected for further investigation of their structural and magnetic properties. The process parameters corresponding to the production of S1 and S2 differ only in the tip-collector distance which is larger for S2. SEM images and fiber diameter distributions reveal that, as previously shown for pure PEO electrospun fibers, the average fiber diameter is decreasing with decreasing tip-collector distance. In addition, the distribution of the fiber diameters for the S1 sample is wider than the one for S2. This is indicative of a less controlled electrospinning process in the case of the S1 sample. Investigation of the magnetic properties of the composite fibers, reveal as expected a ferrimagnetic behavior for both samples. No major differences between the magnetic properties of S1 and S2 were observed in terms of hysterezis loops, coercivity and remanent magnetization. However, both the magnetic coercivity and the remanent magnetization are smaller in the electrospun samples compared to the pure barium ferrite nanoparticles.

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