Dynamic behavior of magnetic hybrid films of polyvinyl butyral/iron oxide nanoparticles (PVB/Fe_2O_3) for their control as microactuators

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Polymeric magnetic hybrid materials (PMHM) are a motivating research topic for microactuator technologies, as flexible magnetic devices or contactless manipulation, useful for many applications. However, the control of these microactuators remains a challenge due to the severe performances required and the nonlinear dynamics that typify them. This study performs an exhaustive experimental characterization of the nonlinear dynamics of a PMHM-film as a cantilever actuator. The PMHM-film consists of polyvinyl butyral (PVB) with iron oxide (Fe_2O_3) nanoparticles synthesized *in-situ*, at two different nominal concentrations of $FeCl_2{\cdot}4H_2O$. This work presents the synthesis of the PMHM-films (PVB/Fe_2O_3), their magnetic and morphological characterization, and the dynamic characterization at constant and sine magnetic fields. Magnetic characterization showed a superparamagnetic-like behavior of the material at room temperature, in accordance with previous works. A damped-like behavior is exposed with a maximum displacement of 0.99 mm when a constant magnetic field of 0.96 kOe is applied. In the sine magnetic field test, a nonlinear response and rate-dependent behavior when the frequency is increased were observed. Future work will consider the physical model of the dynamic behavior of the (PVB/Fe_2O_3) films and a control system to reduce the hysteresis nonlinearities.

Keywords: Hysteresis, modeling, magnetic polymers, smart materials, dynamics

1.- INTRODUCTION

Hybrid materials are widely studied nowadays due to the combination of desirable properties that could be profitable for specific applications. A polymeric hybrid material can be defined as a material having one or more inorganic phases dispersed in an organic phase (usually a polymer matrix). Interface interactions on a hybrid material could be stronger than the interactions in composite materials [1].

Some polymeric hybrid materials may be considered as *stimuli-responsive* polymers. *Stimuli-responsive* polymers significantly change their properties with a variation of environmental conditions, returning to its original state on termination of the stimulus [2]. *Stimuli responsive* polymers, operating in response to external magnetic fields are called *magneto-active* polymers.

One line of research for the application of *magneto-active* polymers are the *microactuators*, due to their flexibility, low weight, low density and relative low cost of processing. Moreover, they could be controlled without any physical contact, helpful for some applications [3].

Many applications have been previously reported in the literature, for example, micromanipulators [4], micropumps [5], biomedical devices [6], researches in biomimetics [7,8], and so forth. However, the control of these microactuators remains a challenge due to the high positioning accuracy and precision required and, at the same time, to the nonlinear dynamics that typify this materials [9].

The aim of this work is to present the experimental characterization of the dynamic response of a PMHM-film (PVB/Fe_2O_3) as a cantilever actuator when it is submitted to an external magnetic field. This work deals first with the *in-situ* synthesis of the PVB/Fe_2O_3 films, their magnetic characterization, and then the dynamics characterization at constant and sine magnetic fields. The main motivation is to propose, as future work, a physical model of the dynamic behavior based on these results and a control system to reduce the hysteresis nonlinearities.

2.- EXPERIMENTAL PROCEDURE

2.1 Synthesis of the PVB/Fe_2O_3 films

The synthesis process to obtain the PMHM-films of PVB/Fe_2O_3 is based on the synthesis described by Puente-Córdov*a* [10]. This process was performed in two stages. In the first stage, a precursor hybrid material (PVB-Fe(II) is obtained (Figure 1a). In the second stage, first, the precursor hybrid material is submerged in an aqueous solution of NaOH 6.7 M at 55ºC. During this process, we noticed a change in color, from yellow to dark brown (Figure 1b). Next, 30 ml of H_2O_2 are added causing another change in color, from dark brown to copper red (Figure 1c). This change can be related to the presence of iron oxide nanoparticles into the polymer matrix PVB. When the process ends, the material is washed with unionized water to eliminate residues, obtaining finally the polymeric magnetic hybrid material PVB/Fe_2O_3 as films.

To know the influence of the variation of Fe_2O_3 content into the PVB matrix, the films of PVB/Fe_2O_3 were obtained at two different nominal concentrations of precursor salt, $FeCl_2{\cdot}4H_2O$, with respect to PVB content. Specifically, 40%wt and 50%wt of $FeCl_2{\cdot}4H_2O$. The thickness of both obtained films was about 0.018 mm.

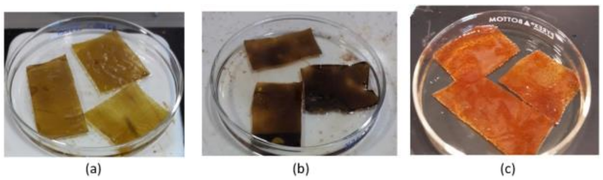

Figure 1.- *Evolution of the color in films (a) precursor PVB-Fe(II) (b) PVB-Fe(II) after adding NaOH (c) PVB/Fe_2O_3 films after adding H_2O_2*

2.2 Characterization

The evaluation of magnetic properties of the PVB/Fe_2O_3 samples was realized in a Vibrating Sample Magnetometer (VSM). The measurements of the magnetization (M) of the material versus an applied magnetic field (H) were taken at room temperature, with a magnetic field sweep of -70 kOe to 70 kOe at a rate of 12 kOe/s. Transmission Electron Microscopy (TEM) images were obtained in an equipment model JEOL JEM-2100 using an operation voltage of 200 kV. The samples were a section of the PVB/Fe_2O_3 films.

The experimental analysis of the dynamic behavior of the PMHM-films PVB/Fe_2O_3 under magnetic fields was evaluated by considering them as a rectangular cantilever beam (Figure 2). The external magnetic field was generated by using an electromagnet, positioned at the free end of the cantilever at 1 mm of separation. The input signal applied to the electromagnet was controlled by a Matlab/Simulink program. A voltage amplifier was used to obtain the input values which the electromagnet demands to generate the required magnetic field. A laser sensor (by Keyence, model LK G152) was used to take the measurements of the displacement of the PVB/Fe_2O_3 films in the +x axis when the magnetic field is applied. The same software was used to read the results on the PC.

Tests were performed using two regimes of voltage/current input: step mode and oscillatory mode. In the step mode a constant input of 30 V (0.73 A) was applied, corresponding to 0.96 kOe of magnetic field (measured by a gaussmeter model HIRTS-GM08). Oscillatory mode was performed applying a sinusoidal input with different frequency and constant amplitude corresponding to 0-30 V (0 to 0.96 kOe) sine voltage. The aim of the oscillatory mode is to evaluate the presence of hysteresis in the response.

Tests for each sample of different content of precursor salt (40%wt and 50%wt $FeCl_2{\cdot}4H_2O$) were done using the same geometry: 15 mm in length, 2 mm in width and 0.018 mm in thickness. For the only case of the sample with 50%wt $FeCl_2{\cdot}4H_2O$, additional tests were performed using a width of 4 mm and maintaining the length constant (15 mm). The aim is to analyze the influence of changing the total volume.

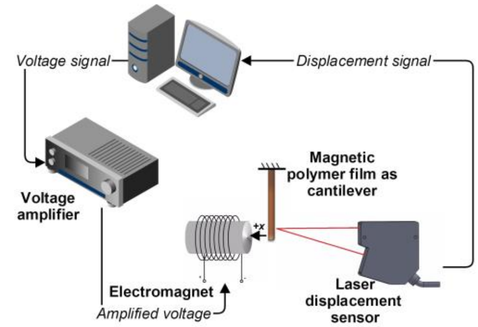

Figure 2.- *Schematic diagram of the setup to perform the displacement measurements of the PVB/Fe_2O_3 films*

The used diagram of experiments to take the displacement measurements of the PVB/Fe_2O_3 films in function of an applied magnetic field is shown in figure 3.

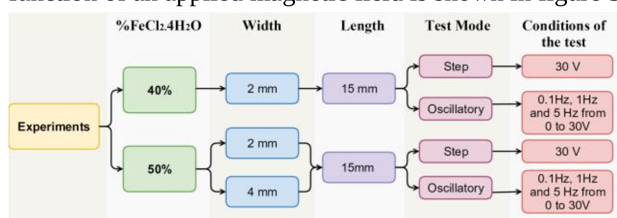

Figure 3.- *Experimental design for the dynamic characterization*

All the obtained results for magnetic, morphological and dynamic characterizations are presented in the next section.

3.- RESULTS AND DISCUSION

3.1 Magnetic and morphology results

The results of magnetometry tests for the samples with 40%wt and 50%wt of precursor salt ($FeCl_2{\cdot}4H_2O$) are shown in figure 4. For both samples the shape of the obtained experimental curves are typical in superparamagnetic behavior. These superparamagnetic curves are a consequence of magnetic nanoparticles with characteristic size less than 20 nm.

It is worth to notice that the magnetic saturation of the samples increases when the nominal concentration (of the precursor salt) increases. A similar behavior was reported by Nabiyouni and Ghanbari [11] for a ABS/Fe_2O_3 nanocomposite, when an increment of 5% to 20% of Fe_2O_3 concentration increased the magnetic saturation about 240%. Nanoparticles size distribution and stoichiometry must be analyzed more in depth in future works in order to have better control of the behavior of the actuator itself.

Figure 5 shows a HRTEM image of the sample of PVB/Fe_2O_3 with a nominal concentration 50%wt of $FeCl_2{\cdot}4H_2O$. This result corroborates that magnetic nanoparticles of Fe_2O_3 were synthetized *in-situ* into the polymer matrix, PVB. In addition, there is possible to see a section of well-defined lattice prints corresponding to crystal of nanoparticles of Fe_2O_3 embedded into PVB matrix.

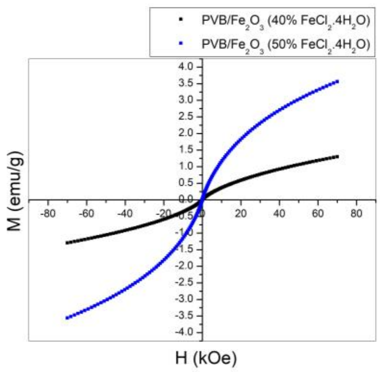

Figure 4.- *Magnetization curve at room temperature*

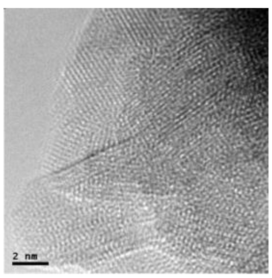

Figure 5.- *HRTEM image of sample PVB/Fe_2O_3 with 50%wt $FeCl_2{\cdot}4H_2O$*

3.2 Tests results at step mode input voltage

The displacement responses of the PVB/Fe_2O_3 films for each concentration and each used geometry are shown in figure 6. These responses correspond to a magnetic field step input of 0.96 kOe (30 V) to the free end of the cantilever situated at 1 mm of separation to the electromagnet. An oscillatory behavior is observed when applying the step voltage and before reaching settling time. This kind of damped-like behavior is associated to the typical damping behavior of the polymer matrix and the cantilever structure configuration. By increasing the precursor salt $FeCl_2{\cdot}4H_2O$ from 40%wt to 50%wt the maximum displacement of the PVB/Fe_2O_3 film also increases, from 0.089 mm to 0.99 mm, with the same geometry. These results agree with the magnetic properties previously discussed: the displacement increases when the magnetization value (the precursor salt concentration) increases and the PVB concentration decreases.

The maximum displacement to the PVB/Fe_2O_3 sample with 50%wt $FeCl_2{\cdot}4H_2O$ and 4 mm of width is 0.65 mm. The diminish in the displacement with respect to the sample with the same composition and different width (50%wt $FeCl_2{\cdot}4H_2O$, 2 mm) is attributed to the increase in stiffness through the increment in the area moment of inertia. Moreover, it is possible to see a decrease in the oscillations when the magnetic field is applied, because of the increase in the total mass.

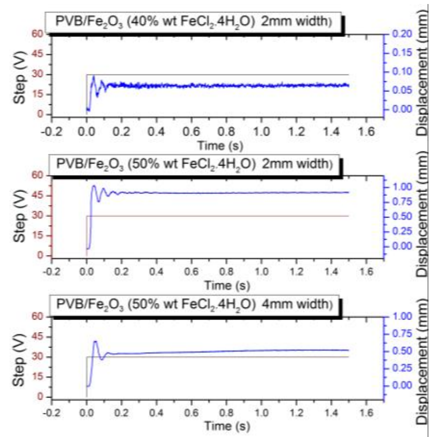

Figure 6.- *Step mode results at 30V for both geometries and different precursor salt concentrations.*

To evaluate the response at different frequencies, oscillatory tests were performed in the next section.

3.3 Test results at sine mode input voltage

Figures 7, 8 and 9 show the obtained results when applying a sine voltage with 30 V of maximal amplitude, at 0.1, 1 and 5 Hz of frequency (10, 1 and 0.2 seconds for cycle, respectively), as input to the electromagnet. A nonlinear response of displacement with a frequency-dependent hysteresis are observed. This is caused by the relaxation times of the polymeric matrix and the magnetic dipoles of the nanoparticles. Relaxation time is associated to molecular weight. For thermoplastics (PVB), this time is about 1 s [12,13]; for nanoparticles, it must correspond to a lower value. For times > 1 s, almost all the molecular motions are achieved. In addition, an external magnetic field tends to align the magnetic dipoles. When the magnetic field is removed, dipoles rearrange to reach a stable configuration. At low frequencies (0.1 Hz), there is enough time to this movements, obtaining small hysteresis. The contrary occurs at higher frequencies (5 Hz), causing bigger hysteresis.

The highest magnetization and the greatest displacement is shown by sample of 50%wt $FeCl_2{\cdot}4H_2O$ and 2 mm in width. This may cause a longer time for the magnetic dipoles to regain their stable arrangement once the magnetic field is removed. The above can be reflected in larger hysteresis loops (figure 7) in comparison with samples of 50%wt $FeCl_2{\cdot}4H_2O$ and 4 mm width (figure 8) and 40%wt $FeCl_2{\cdot}4H_2O$ (figure 9).

Further, for all cases, the phase-lag starts to affect the response from about 1 Hz, which is low in frequency. This could be due to the high length of the cantilever and, in consequence, induces a low bandwith of the actuator.

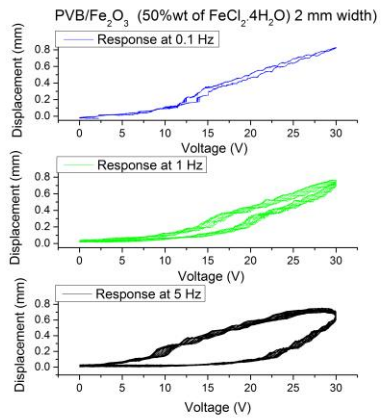

Figure 7.- *Sine mode results at 0-30 V and 0.1 Hz, 1 Hz and 5 Hz for the sample PVB/Fe_2O_3 with 50%wt $FeCl_2$·$4H_2O$*

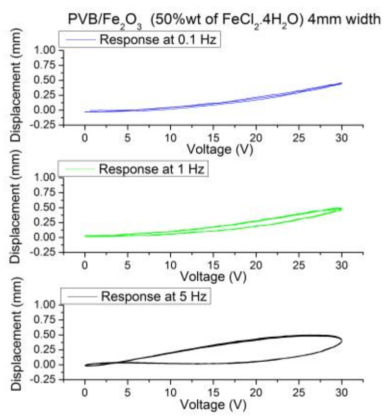

Figure 8.- *Sine mode results at 30 V and 0.1 Hz, 1 Hz and 5 Hz for the sample PVB/Fe_2O_3 with 50%wt $FeCl_2$·$4H_2O$, 4 mm width*

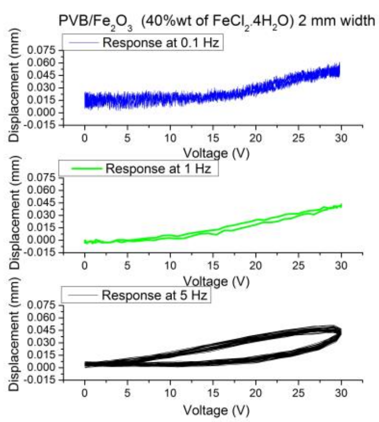

Figure 9.- *Sine mode results at 30 V and 0.1 Hz, 1 Hz and 5 Hz for the sample PVB/Fe_2O_3 with 40%wt $FeCl_2$·$4H_2O$*

Considering these data, a physical model of the dynamic behavior of the (PVB/Fe_2O_3) films will be proposed in future work.

CONCLUSIONS

PVB/Fe_2O_3 films at nominal concentrations of 40%wt and 50%wt of its precursor salt $FeCl_2$·$4H_2O$ were obtained. Magnetic properties tests exhibit a superparamagnetic behavior of the films at room temperature. TEM images showed the apparently embedded iron oxide nanoparticles into the PVB matrix. The measured responses of the films showed a damped-like behavior in the step voltage tests, proper of this kind of cantilever configuration. With a magnetic field of 0.96 kOe, a maximum displacement of 0.99 mm was obtained for the sample of PVB/Fe_2O_3 with 50%wt $FeCl_2$·$4H_2O$, 2 mm width. By increasing the width of the cantilever from 2 mm to 4 mm, the displacement at the same applied magnetic field decreases but also diminish the oscillations in the response. The sine mode test showed a rate dependent and nonlinear behavior of the response.

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