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# New ferrimagnetic biocomposite film based in collagen and yttrium iron garnet

*S. D. Figueiro[1], E. J. J. Mallmann[2], J. C. Góes[1], N. M. P. S. Ricardo[3], J. C. Denardin[4], A. S. B. Sombra[1], P. B. A. Fechine[2*]*

[1]Laboratory of Telecommunications and Materials Science and Engineering (LOCEM) – Physics Department, Federal University of Ceará – UFC, Campus do Pici, CP 12100, CEP 60451-970 Fortaleza – CE, Brazil
[2]Advanced Materials Chemistry Group (GQMAT) – Analytical and Physical-Chemistry Department, Federal University of Ceará – UFC, Campus do Pici, CP 12100, CEP 60451-970 Fortaleza – CE, Brazil
[3]Organic and Inorganic Chemistry Department, Federal University of Ceará – UFC, Campus do Pici, CP 12100, CEP 60451-970 Fortaleza – CE, Brazil
[4]Physics Department, Universidad de Santiago de Chile, USACH, Av. Ecuador 3493, Santiago, Chile

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**Abstract.** In recent years a great interest in the study of the association of magnetic with biological material for bioapplications has been observed in the literature. This work analyses the development of new magnetic biocomposite films from a magnetic ferrite and a biopolymer. Magnetic and dielectric properties of $Y_3Fe_5O_{12}$ (YIG)/collagen composite films were studied as a function of the YIG concentration. This biocomposite was also characterized by Infrared Spectroscopy (IR), Thermal Analysis (DSC and TG) and scanning electron microspcopic (SEM) methods. The magnetization and dielectric measurements were performed at room temperature. The results demonstrated that ferrimagnetic garnet (YIG) and collagen (Col) can be used to obtain a homogeneous composite. All the composite films showed a ferromagnetic behavior and they were characterized as a soft magnet material. These results show that Col-YIG biocomposites are biological films with magnetic properties that can be employed as a versatile performance materials, due to their flexible dielectric and magnetic features. They could be used as electronic devices in biological applications.

***Keywords:*** *thermal properties, polymer composite, biocomposite, magnetic properties*

## 1. Introduction

Magnetic particles have been studied due to their important versatility in bioapplications as magnetic resonance imaging (MRI) contrast agents, for cancer tumor detection, hyperthermia, drug delivery, selective separation and biomolecules detection [1]. For these applications, the particles must have combined properties of high magnetic saturation, biocompatibility and interactive functions at the surface [2]. The surfaces could be modified through the creation of few atomic layers of organic polymers, inorganic metallic or oxide surface.

This kind of material can also be used in electronic devices as magnetic recording, microwave components and permanent magnetic devices [3]. Magnetic ceramics are used in a number of applications such as radar-signal absorbing, magnetic printing, magnetic levitation etc. Yttrium iron garnet (YIG) is a good example of this. It is frequently used in microwave device applications such as mobile communication systems or satellite broadcast systems [4]. This ferrimagnetic garnet has cubic structure (space group Ia3d) and formula $Y_3Fe_5O_{12}$. A new generation of devices (such as delay lines, tun-

*Corresponding author, e-mail: fechine@ufc.br

ing filters and oscillators, isolators and bubble-storage memory units) has been developed on YIG basis [5, 6].

There is a lot of research on the association of magnetic with biological materials. For example, Kim and co-workers [7] have obtained microspheres of $Fe_3O_4$ encapsulated with chitosan as a MRI image contrast, while Jain and co-workers [8] obtained magnetic nanoparticles coated with Oleic-Pluronic for sustained delivery of cancer agents. Matsumine and co-workers [9] have developed a new hyperthermic treatment modality using magnetic materials (calcium phosphate cement containing $Fe_3O_4$) for metastatic bone tumors.

In this sense, biological molecules are important to change the magnetic component into a bio-inert composite. Collagen is the most abundant of the fibrous proteins and it constitutes more than 25% of the protein mass in the human body. It constitutes part of the fibrous connective tissues of skin, bones, tendons, cartilages, blood vessels, and teeth. Individual molecules of collagen, which are semi flexible rods ~280 nm in length and ~1 nm in diameter, undergo self-assembly to form interwoven network-like structures, ranging from long fibrils to complex structures [10]. They could be used to obtain magnetic composite films with new properties.

This study reports on the synthesis, structure and dielectric-magnetic behavior of the biocomposite material obtained from a ferrite (YIG) and a collagen membrane. Through experimentation we confirm the interaction between ferrite particles and collagen to obtain a natural composite with magnetic properties.

## 2. Material and methods

### 2.1. Ferrimagnetic particle

The preparation of the ferrimagnetic particles was performed by methods used by Fechine and co-workers [11], where stoichiometric amounts of $Y_2O_3$ (99.99%, Aldrich) and $Fe_2O_3$ (99.00%, Aldrich) were used in the YIG preparation. The material was grounded on a Fritsch (Idar-Oberstein, Germany) Pulverisette 6 planetary mill in sealed stainless steel vials (221.69 $cm^3$) and balls (ø10 mm) under air in weight ratio 1/9 (wt. of mixture powder/wt. of balls). Mechanical alloying was performed for 1h of milling with 370 rpm. After this, the powder was submitted to calcination in air at 1150°C for 5 h. The reaction occurring during calcination can be summarized as shown by Equation (1):

$$3Y_2O_3 + 5Fe_2O_3 \rightarrow 2Y_3Fe_5O_{12}\ (YIG) \quad (1)$$

### 2.2. Preparation of soluble collagen

The anionic collagen was prepared from intestinal bovine serosa by selective hydrolysis of amide groups using 50 g of intestinal bovine serosa, in the wet state and treated at 20°C for 72 h with an alkaline solution (3 ml of solution/g of tissue), salts (chlorides and sulfate), bases of alkaline ($K^+$ and $Na^+$) and alkaline earth metals ($Ca^{2+}$). The materials obtained were equilibrated with a solution containing $Na_2SO_4$, NaCl, KCl and $CaSO_4$ (6 ml of solution/g of tissue) for 12 h and the salt excess was removed as described earlier [12]. The materials was suspended in deionized water, had its pH adjusted at 3.5 with pure acetic acid and the mixture was homogenized in a blender. The soluble collagen gels concentration was 8 $mg \cdot g^{-1}$.

### 2.3. Preparation of collagen-YIG films (Col-YIG)

YIG ferrite mass (320, 480 and 640 mg) was dispersed in 40 g of the anionic soluble collagen (1:1, 1:1.5 and 1:2 Col:YIG proportions, respectively) by sonication for 3 min (1s on, 2s off) 70% in iced water bath, using a Branson (Danbury, CT, USA) Sonifier Model W-450D. The homogeneous emulsions were casted in acrylic mould and dried in laminar flow air. The samples were designed collagen, Col 1:1, Col 1:1.5 and Col 1:2.

### 2.4. Film thickness

The film thickness was measured using a Micrometer (Model 549E, Testing Machines Inc, Mineola, LI, NY). The thickness measurements were taken at 10 different points along the gauge length of each specimen and the main values were taken.

### 2.5. X-ray diffraction

The X-ray film diffraction (XRD) patterns were obtained at room temperature (300 K) in a Rigaku

(Tokyo, Japan) X-ray powder diffractometer operating at 40 kV/25 mA, using $CuK_\alpha$ radiation. The diffraction patterns were carried out using Bragg-Brentano geometry in continuous mode with speed of 0.5°/min and step size of 0.02° (2θ) in the angular range 20–60° (2θ).

### 2.6. FT-infrared spectroscopy

Fourier Transform Infrared (FTIIR) spectra were recorded using ATR regime using a SHIMATZU FTIR-283B spectrophotometer in the wave number region of 400–4000 $cm^{-1}$.

### 2.7. Differential scanning calorimetry

Differential scanning calorimetry was carried out using NETZSCH (Selb, Germany) DSC 204 F1 Phoenix® equipment. Accurately weighed (5–8 mg) dry material was placed in an aluminium cup and hermetically sealed. An empty cup was used as reference. Samples were analyzed under continuous flow of dry nitrogen gas at a heating rate of 20°C·$min^{-1}$ from 25 to about 200°C.

### 2.8. Thermogravimetric analysis

Thermogravimetric analysis (TG) of collagens and mineralized films was conducted by heating the sample up to 1000°C at the rate of 10°C·$min^{-1}$, using TGA Q5000 V2.1, TA Instruments (New Castle, DE, USA). The films were sealed in an aluminum pan and heated at the rate of 5°C·$min^{-1}$ in a $N_2$ atmosphere.

### 2.9. Scanning electron microscopy

Micrographs of collagen and collagen-YIG films were obtained by scanning electron microscope (SEM) (Vega XMU/Tescan, Bruker (Billerica, MA, USA)), operating with bunches of primary electrons ranging from 12 to 20 keV of rectangular samples, in samples covered with a 60 nm thick gold layer.

### 2.10. Dielectric and magnetic measurements

Dielectric measurements: real ($\varepsilon'_r$) parts of relative permittivity and loss tangent ($\tan\delta = \varepsilon''_r/\varepsilon'_r$) were performed using an Agilent (Santa Clara, CA, USA) 4294A precision impedance analyzer. It covered the region of 40 Hz–10 MHz at room temperature (300 K). This experimental part was performed in capacitors shape samples. The electrode material (Ag) was produced by the screen printing technique (Joint Metal-PC200).

The magnetization measurements were performed at room temperature with a home-made vibrating sample magnetometer (VSM). The VSM had been previously calibrated using a pure Ni wire, and after measuring the mass of each sample the magnetization was given in emu/g.

## 3. Results and discussion

All the composites (Col 1:1, Col 1:1.5 and Col 1:2) presented both crystalline and amorphous phases. For instance, Figure 1 shows the XRD obtained from composite Col 1:2. The crystalline phase is formed due to YIG (ICDD/PDF–70-0953) particles (ferromagnetic material) dispersed in the sample. It was also possible to identify a small fraction of an antiferromagnetic phase ($YFeO_3$-YFO-ICDD/PDF–86-0171). Ristić *et al.* [13] found the same result when they carried out the YIG synthesis by co-precipitation and calcination. This phase was also observed when the sol-gel method was used instead [14, 15]. In our previous work [16], we presented the YIG synthesis and made a complete structural characterization. Besides these magnetic phases, there was an amorphous phase characterized as collagen, where its major intensity was approximately in θ = 20°. This phase was identified as a broad region in the diffractogram and it was found in all the range.

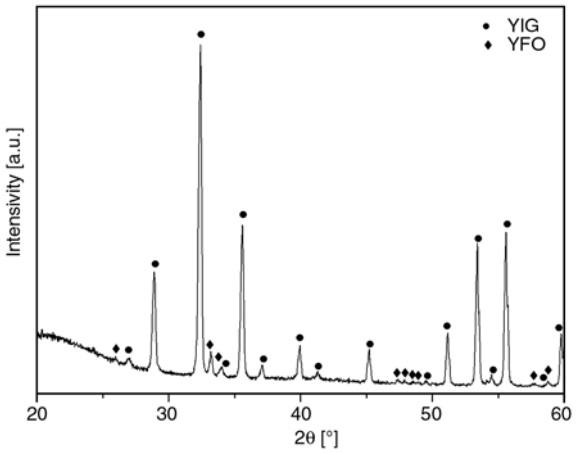


**Figure 1.** X-ray diffraction pattern of Col 1:2 biocomposite film

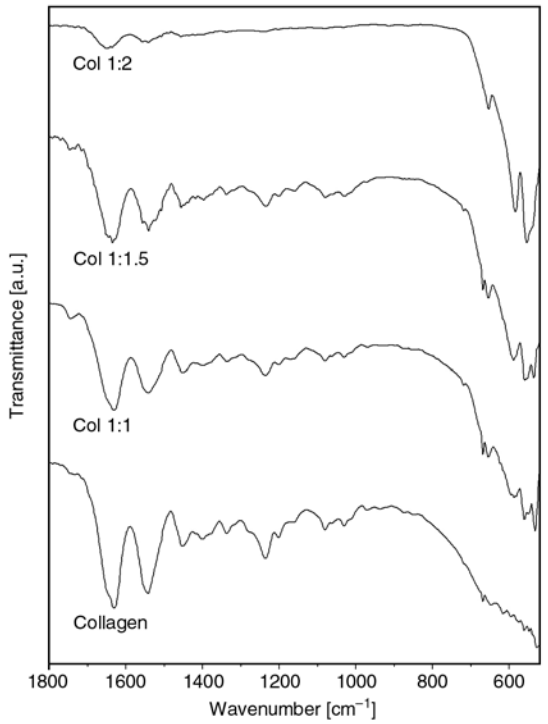


**Figure 2.** Infrared spectra of collagen and Col-YIG biocomposite films showing the finger print region

The IR spectra of the collagen and the Col-YIG composites films are shown in Figure 2. It can be observed that there are two distinct frequency regions where the bands happen for each phase of the composite. The main bands from collagen are located at 1651, 1543, 1338 and 1236 cm$^{-1}$, where the major feature of the IR spectrum of collagen film is the Amide I band between 1640 and 1660 cm$^{-1}$ [17, 18], which arises from the stretching vibration of C=O groups of amide groups in protein. The intense absorption observed at 1543 cm$^{-1}$ is due to the Amide II mode, which arises from N–H stretching vibration strongly coupled to the C–N stretching vibration of collagen amide groups. Signals in the spectral region of 1200–1400 cm$^{-1}$ absorption are generally attributed to the Amide III, arising due to the C–N stretching and N–H in plane bending from amide linkages. The C–N stretching vibration of the cyclic proline may also contribute for the absorption at 1454 cm$^{-1}$. The absorption seen at 1338 cm$^{-1}$ is attributed to $CH_2$ wagging vibration of the proline side chain.

The Col-YIG films presented the same bands observed for the collagen, as shown in Figure 2. However, one can observe three new bands in 654, 584 and 553 cm$^{-1}$. They belong to the ferrite ($Y_3Fe_5O_{12}$) used to perform the magnetic composite film. These modes are associated with the asymmetric stretching ($\upsilon_3$) of the tetrahedron (Fe–O bond) [16].

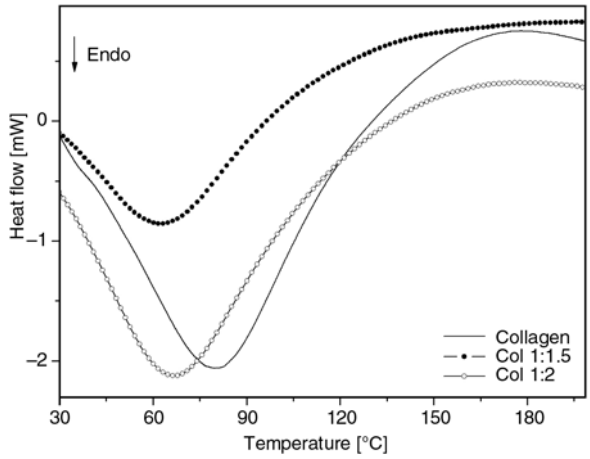


**Figure 3.** DSC curves of the Col-YIG biocomposite films

The DSC scans in Figure 3 show that collagen matrix of all samples are characterized by an endotherm peak. It is due to the denaturation process of collagen molecules and it is hydration dependant. For collagen film, the denaturation temperature is 79.7°C. For Col-YIG composites, Col 1:1.5 and Col 1:2, a decrease on this temperature was observed (62.3 and 66.7°C, respectively). These results show that YIG addition decreases the thermal stability of the collagen molecules. These results may be related to the shrinkage of the collagen matrix that is observed macroscopically.

As shown in Figure 4, the TG curves of collagen film were divided into three regions: Evaporation of absorbed water occurred from room temperature to 200°C, the thermal decomposition of collagen happened from 250 to 380°C, in which the weight

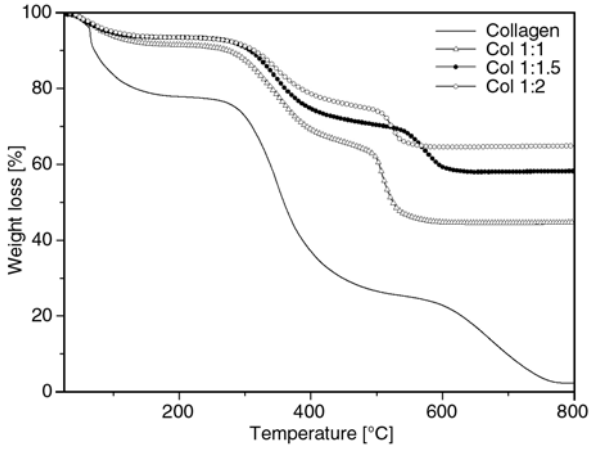


**Figure 4.** Thermogravimetric analysis of the Col-YIG biocomposite films

loss curve plateau appeared at over 550°C. The residue at 800°C was attributed to the weight of YIG in the sample. From Figure 4, one can see that the degradation temperatures vary from 351°C for collagen to 341°C for Col 1:1, 347°C for Col 1:1.5 and 346°C for Col 1:2, which suggests a decrease on thermal stabilization of collagen molecules. The amount of YIG in composite varies from 42.5% in Col 1:1 film to 56.5% in Col 1:1.5 and to 64,6 % in Col 1:2 composite. These results suggest that content higher of YIG in the composite tends to saturation.

Figures 5a, 5b and 5c show the SEM micrographs recorded on biocomposite films. The YIG particles were identified as almost uniform grains and exhibited a quasi-globular morphology. The presence of agglomerated grains was also observed in all samples. The microstructure of Col 1:1, Col 1:1.5 and Col 1:2 films were shown as particles dispersed in the polymeric matrix. Col 1:1 (Figure 5a), the sample with minor YIG quantity showed more dispersed grains than in the other films. It was also possible to observe composite phases (polymer and ferrite particles), i. e., YIG particles involved by collagen protein (or on its surface) to obtain the magnetic biocomposite film. As one can see, there were morphology changes due to the increase of YIG concentration in the film. The other samples (Col 1:1.5 and Col 1:2, Figures 5b and 5c, respectively) presented the same behavior, where the increase of the YIG concentration caused a rise of agglomerated regions.

In Figure 6, dielectric measurements ($\varepsilon'_r$ and tanδ) of the collagen and biocomposites films are shown. One can notice that the collagen presents a higher relative permittivity than other films until approximately 1 MHz (10.26), and that this value drops to 9.13 at 10 MHz (Table 1). Lima and co-workers [17] found a value of 2.60 for this same film at

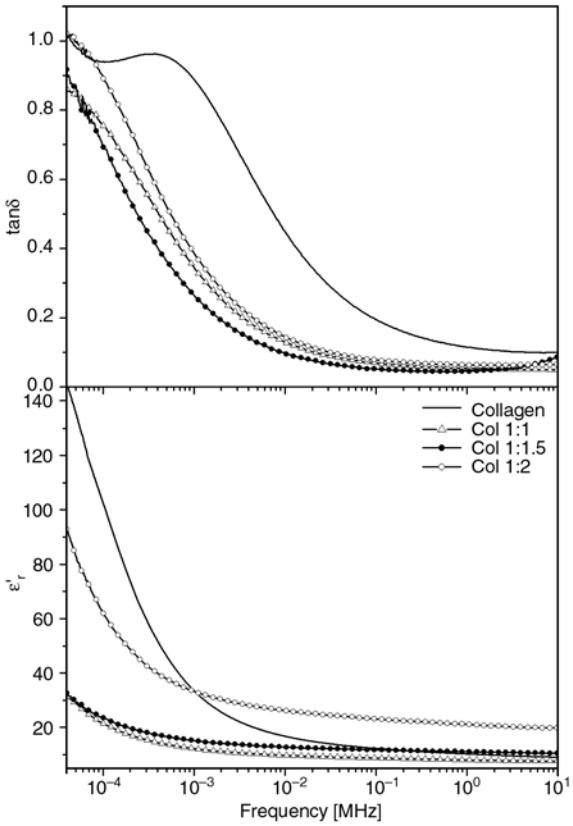


**Figure 6.** Dielectric measurements of the Col-YIG biocomposite films

**Table 1.** Thickness ($e$), relative permittivity ($\varepsilon'_r$) and loss tangent (tanδ) of the biofilms

| Samples | e [μm] | 1 kHz | | 10 MHz | |
|---|---|---|---|---|---|
| | | $\varepsilon'_r$ | tanδ | $\varepsilon'_r$ | tanδ |
| Collagen | 92.0 | 33.46 | 0.89 | 9.13 | 0.10 |
| Col 1:1 | 83.0 | 12.22 | 0.34 | 7.65 | 0.05 |
| Col 1:1.5 | 173.0 | 15.15 | 0.26 | 10.55 | 0.09 |
| Col 1:2 | 143.0 | 33.26 | 0.38 | 19.89 | 0.06 |

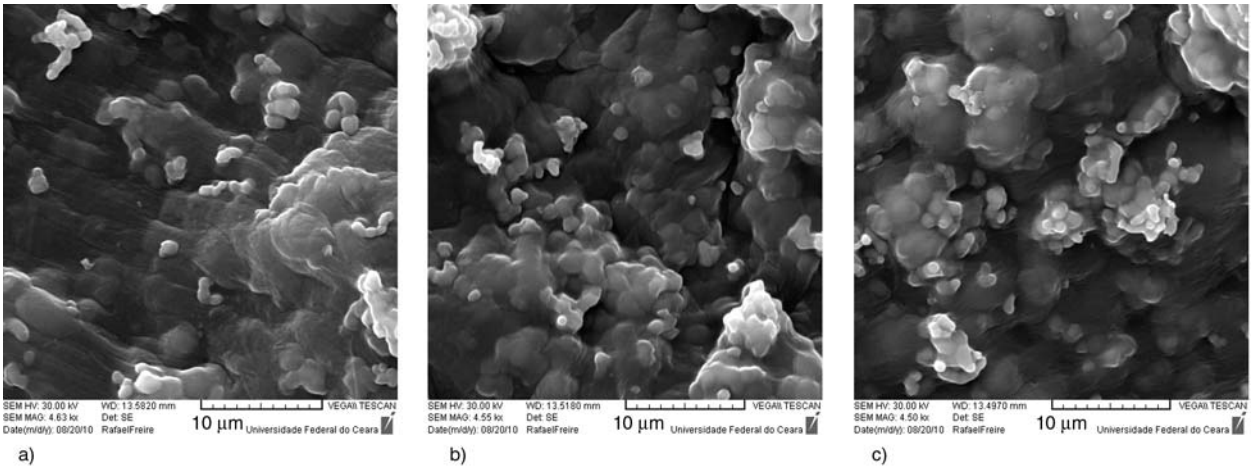


**Figure 5.** Scanning electron micrograph recorded from Col 1:1 (a), Col 1:1.5 (b) and Col 1:2 (c) films

1 MHz. This difference might have happened due to the synthetic route used to obtain the collagen, which resulted in a film with different dielectric properties. The collagen film also presented higher tanδ values when compared to biocomposites. This happens due to the large number of interfaces between the fibers and air pores that constitute the collagen network. It can also be observed that there was a shoulder at 370 Hz, which could be an evidence of the dielectric relaxation. It can be associated with the dipolar relaxation process, most probably due to the changes located at interfaces [19]. This behavior was also observed by Marzec and Pietrucha [20], when they studied the effect of different methods of collagen cross-linking on its dielectric properties as a function of the temperature.

As the biocomposites had YIG in variable proportions, it was expected a change in the dielectric behavior of the samples. Their profile was very similar to that of collagen, where the increase of the frequency decreased the $\varepsilon'_r$ and tanδ to the lowest values, when it was compared at 1 kHz and 10 MHz frequencies (Table 1). According to previous studies [11], YIG presented $\varepsilon'_r$ and tanδ values of 7.72 and 0.06 at 1 MHz, respectively. Therefore, due to the fact that the composite material had YIG and collagen, there was a modification of these dielectric features, as a result of a mutual influence (not necessarily linear). For Col 1:2, the YIG added caused a decrease of tanδ (0.06) and an increase of $\varepsilon'_r$ (19.89) at 10 MHz.

A study of the direct current (DC) magnetic features of the Col-YIG system was performed (Figure 7), where it was observed the variation in magnetization ($M$) versus the bias field ($H$) of the samples. The shape of hysteresis loops obtained from this experiment was attributed to soft ferrites due to their values of coercive field ($H_C$), remanent

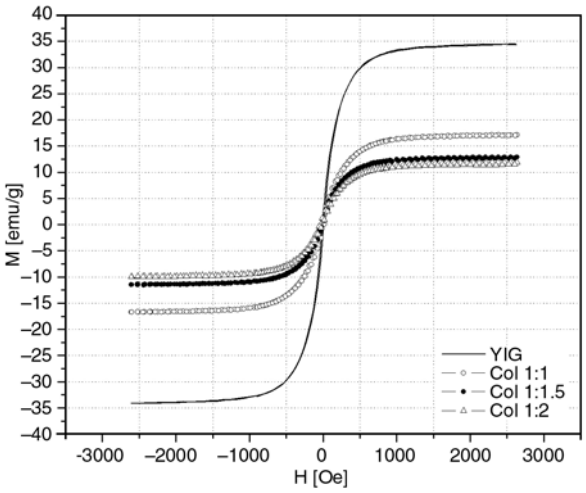


**Figure 7.** Hysteresis loop at room temperature for YIG and Col-YIG biocomposite films

($M_r$) and saturation ($M_S$) magnetization, as shown in Table 2. One can notice a decrease of the $M_S$ as a function of the collagen concentration due to the decrease of the ferrite material (YIG) in the film. For instance, the Col 1:2 film presented approximately half $M_S$ (17.12 emu/g) of the pure YIG (34.54 emu/g). However, all films presented magnetic features. The $H_C$ values showed that the increase of the collagen also makes the film harder than the ferrite alone (–11.13 Oe), where this value decreases to –40.21 Oe for the sample with minor YIG concentration (Col 1:1), see Table 2. The YIG presence in the collagen it changed into a new biocomposite with interesting magnetic behavior. Additionally, it was observed in some experiments

**Table 2.** Properties obtained from hysteresis loop for Col-YIG system

| Samples | $H_C$ [Oe] | $M_r$ [emu/g] | $M_S$ [emu/g] |
|---|---|---|---|
| YIG (26.53 mg) | –11.13 | 1.90 | 34.54 |
| Col 1:2 (10.90 mg) | –20.54 | 1.31 | 17.12 |
| Col 1:1.5 (12.27 mg) | –28.24 | 1.32 | 12.91 |
| Col 1:1 (6.84 mg) | –40.21 | 1.46 | 11.88 |


**Figure 8.** The Col 1:1 film (a) and the experiment carried out with a neodymium-iron-boron magnet; before (b) and after (c) magnetically attracted

that they were all magnetically attracted by a permanent magnet, as shown in Figures 8a–c. In this figure, one can see the Col 1:1 film (Figure 8a) before (Figure 8b) and after (Figure 8c) magnetically attracted by a neodymium–iron–boron ($Nd_2Fe_{12}B$) magnet. This film had the minor concentration of the ferrite material of the system Col-YIG and the phenomena occurred macroscopically. Thus, this kind of biocomposite could be used as a versatile magnetic-dielectric device at radio-frequency.

## 4. Conclusions

The results of our studies demonstrated that ferrimagnetic garnet ($Y_3Fe_5O_{12}$) and collagen fiber can be used to obtain a homogeneous composite. This new material presents magnetic properties due to magnetic phase concentration in the film, and this magnetic behavior was observed by the hysteresis loops measurement. All the composite films showed a ferrimagnetic behavior and they were characterized as a soft magnet material. These results show that Col-YIG biocomposites are biological films with magnetic properties and they can be employed as a versatile performance material, due to their flexible and magnetic features. They can be used, for instance as an electronic device and for biological applications.

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