

# Magnetoelectric properties of PVDF-CoFe<sub>2</sub>O<sub>4</sub> composite films obtained by 3D printing

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## Abstract

In this paper, we have investigated piezoelectric, magnetic and magnetoelectric properties of composite materials, consisting of polyvinylidene fluoride (PVDF) matrix and CoFe<sub>2</sub>O<sub>4</sub> nanoparticles in the form of filament extrusion and 3D printed films. We used PVDF powders from different manufacturers each with different molecular weights and phase compositions. For PVDF with lower molecular weight and higher electroactive phase content of the, we observed that approximately 80 % of the electroactive phase in the starting polymer was effectively transferred to the printed films through all technological stages. The composite filaments exhibited ferromagnetic behavior with a large coercive force of  $1.7 \pm 0.1$  kOe consistent with a particle size of about 20 nm. The magnetoelectric coefficient was about 2 mV/(Oe·cm) for printed composite films from both precursors, which is sufficient for a range of applications including microelectronics and tissue engineering using magnetically stimulated electric fields.

## Keywords

3D printing, PVDF, polymer composites, magnetic nanoparticles, magnetoelectric composites, fluoropolymer

## 1. Introduction

Magnetoelectric (ME) composites which are characterized by the induction of the electric polarization by a magnetic field, are of considerable interest for potential technological applications [1]. The typical architecture of ME materials includes a piezoelectric matrix and magnetic nanoparticles with large magnetostriction. ME coupling then results from the mechanical interaction between the magneto- and electroactive phases [2, 3]. Continuous improvements in technologies for obtaining ME

composites are expanding the range of applications of ME composites: sensors [4–8], 3D scaffolds for tissue engineering [9, 10], energy harvesters [11, 12], and storage devices [13–16].

A promising approach for the development of new ME composites is the use of additive manufacturing (AM). In this context, polymers are the preferred piezoelectric matrix material. AM technologies are particularly attractive for producing complex and customized structures, as they allow for precise control over dimensions and surface topography. The most widely used printing technology

is fused deposition modeling (FDM) [17], in which 3D objects are created by extruding layers of thermoplastic polymer. FDM has been successfully employed to print composite materials with various additives, including magnetic nano- and microparticle fillers [18, 19], which impart magnetic properties and other functionalities to the printed objects. However, current research on FDM printing of composites has primarily focused on commercial plastics commonly used in 3D printing, such as polylactic acid (PLA) and acrylonitrile butadiene styrene (ABS). Some studies have used piezopolymer filaments, both in their pure form and as composites filled with ferroelectric barium titanate particles to print vibration sensor elements and pressure sensors [20].

Polyvinylidene fluoride (PVDF) is one of the most studied homopolymers within the fluoropolymer class. Depending on its conformation, PVDF has four crystalline phases:  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$  [21]. The  $\beta$ - and  $\gamma$ -phases of PVDF exhibit pronounced piezoelectric properties, which are crucial for developing composites with magnetoelectric (ME) interaction. PVDF is biocompatible, mechanically flexible, and has good chemical resistance, making it suitable for biomedical and sensor applications [22]. CoFe<sub>2</sub>O<sub>4</sub> (CFO) is a magnetic material with a large magnetostrictive coefficient [23], and is widely used as a component in ME composites [24]. Due to their piezoelectric and mechanical properties, PVDF-based ME composites are promising materials for development of flexible sensors [25], a new type of magnetically stimulated scaffolds for tissue engineering [26], and ME converters for human condition monitoring [27].

While research on 3D printing with PVDF-based composites is currently limited, the potential to enhance properties through embedded particles, fibers, and filaments makes this area very promising. The influence of the molecular weight of polymer on the formation of the electroactive phase, which varies depending on the manufacturing method [28–29], and the mechanical properties that determine its applicability in wearable electronics [30] and tissue engineering [31], has not been fully explored. This work aims to study the effect of the molecular weight and phase composition of the starting PVDF material on the FDM printing of PVDF-CoFe<sub>2</sub>O<sub>4</sub> composites, focusing on their structural, mechanical, magnetic, and magnetoelectric properties.

## 2. Materials and methods

### 2.1. Materials

The reagents used were: Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, citric acid ( $\geq 98\%$ , from LenReactiv), 30% ammonia solution ( $\geq 98\%$ , from SigmaTek), N,N-Dimethylformamide ( $\geq 98\%$  from Ekos-1), and PVDF with two molecular weights.

The sol-gel self-combustion method was used to prepare CoFe<sub>2</sub>O<sub>4</sub> (CFO) magnetic nanoparticles. The initial components included metal salts Co(NO<sub>3</sub>)<sub>2</sub> and Fe(NO<sub>3</sub>)<sub>3</sub>, along with distilled water and aqueous solutions of ammonia and citric acid [23]. To obtain CoFe<sub>2</sub>O<sub>4</sub>, the metal salts have to be used in a molar proportion of Co<sup>2+</sup>:Fe<sup>3+</sup> = 1:2. A one molar solution of citric acid was added to the one molar aqueous solution of salts. Addition of aqueous ammonia keeps the pH level at approximately 7. The solutions were heated to 150 °C with intense stirring until they form a gel. The temperature was then increased to 300 °C to trigger the self-combustion reaction, resulting in the formation of nanopowders. The product was then ground in an agate mortar and washed several times with distilled water and acetone. The average size of the resulting crystallites does not exceed 20 nm [18].

A thin film of composites embedded in a piezoelectric polymer matrix was prepared by the solvent evaporation method using the Dr. Blade technique [32]. This blade coating method is a simple way to fabricate thin polymer composites on a laboratory scale. In this method, the polymer solution is placed on a substrate in front of a moving blade that smoothes it out. The thickness of the film was set at 100  $\mu\text{m}$  by adjusting the gap between the blade and the substrate.

Filament fabrication began with the preparation of the polymer precursor solution. PVDF powder from Sigma-Aldrich (Darmstadt, Germany) or PVDF granules from Halopolymer (Moscow, Russia) were dissolved in dimethylformamide (DMF) from Sigma-Aldrich at 40 °C, with continuous mixing until the polymer granules were completely dissolved. The concentrations were approximately 1 part PVDF to 6 parts DMF by weight. The total concentration of PVDF to DMF was adjusted to 1:8, because additional DMF was introduced along with the magnetic particles to achieve a final particle concentration of 10%.

Magnetic particles were incorporated into the polymer during the film formation stage. This helps to avoid their agglomeration near the metallic extruder screw and to achieve a uniform distribution of particles within the filament.

The composite CFO/PVDF filament was produced using a Twin Tech Screw (Rondol) microextruder. Uniform extrudate flow was observed at a temperature of 220 °C. The extruder speed was set at 12 rpm. The extruded filament was then cooled at room temperature.

At the initial and final stages of extrusion, the obtained filaments were discarded since their form was irregular and they contained higher concentration of additives. For the extrusion process, a nozzle was used that produces a standard filament with a diameter of approximately 1.75 mm, suitable for FDM printing.

Films (10 × 10 × 0.12 mm) were printed using an Ender S3 PRO FDM printer with nozzle and bed temperatures of 290 °C and 100 °C, respectively. The single-layer films were printed at 20 mm/s using a concentric infill pattern with 100% density.

Polymer precursors with different molecule weights (m.w.) were used to prepare two types of CFO/PVDF filaments. They were PVDF from Sigma-Aldrich with m.w. of 534 k and PVDF from Halopolymer with m.w. of 80 k. (referred to as SA and HP, respectively, in further analysis). These materials also differ in phase composition and crystallinity, as shown by our characterization.

## 2.2. Characterization

After each technological stage, we analyzed the crystallinity level using Differential Scanning Calorimetry (DSC, NETZSCH 204 F1 Phoenix, in nitrogen atmosphere), the phase composition using X-ray diffraction (XRD, Tongda TD3700 equipped with a Co X-ray tube) and Fourier-transform infrared spectroscopy (FTIR, FT-801 SIMEX-FTIR spectrometer).

The crystalline fractions ( $F_{cr}$ ), the heat of fusion and melting temperatures were determined by DSC analysis performed at a heating rate of 10 K/min. The extent of crystallinity was determined from the fusion heat of the sample with respect to a fully crystalline polymer. Under the assumption that the heat of fusion is the same for all crystalline forms of PVDF, its value for 100 % crystallinity is taken 104.6 J/g [33, 34].

The XRD patterns of all the samples were obtained covering  $2\theta$  angles from 15 to 70 deg. with an angular step ( $2\theta$ ) of  $0.02^\circ$ , corresponding to the diffractometer's resolution limit. To facilitate comparison with published data, the spectra were recalculated to a wavelength of 0.154 nm, corresponding to a  $\text{CuK}_\alpha$  radiation.

The infrared spectra were recorded in the 400–2000  $\text{cm}^{-1}$  range with 2  $\text{cm}^{-1}$  resolution in attenuated total reflection (ATR) mode. The filaments were cut lengthwise using a scalpel, and both filaments and printed films were examined by pressing their smooth surfaces against the spectrometer's diamond prism. Three spectra were acquired from each sample and averaged to produce a final spectrum. By analyzing exclusive peaks or common peaks with stronger absorption corresponding to certain phases, the obtained FTIR spectra can be used to identify the phase composition.

The samples containing CFO particles possess magnetic properties. Their hysteresis loops were measured at room temperature using a LakeShore 7400 vibrating

sample magnetometer. Segments of 4 mm long cut from filaments were used for measurements in orientation perpendicular to the magnetic field.

The magnetoelectric properties were studied after corona poling the samples for 1 h at  $80^\circ\text{C}$  under a 15 kV field using a custom-designed setup. The magnetoelectric voltage  $\Delta V$  was measured in an out-of-plane configuration with a lock-in amplifier (Model SR830, Stanford Research, Sunnyvale, CA, USA) at a frequency of 770 Hz [25]. The AC and DC magnetic fields were applied perpendicular to the surface, that is, along the polarization. The amplitude  $\Delta H$  of the AC field was 10 Oe, and the DC magnetic field varied up to 2 kOe. The ME coefficient  $\alpha_{\text{ME}}$  was defined using the following equation:

$$\alpha_{\text{ME}} = \frac{\Delta V}{b\Delta H}, \quad (1)$$

where  $\Delta V$  is the amplitude of the induced ME voltage,  $b$  is the thickness of the sample.

## 3. Results and discussion

### 3.1. Structure evolution

Initially, the differences between the PVDF materials from Sigma-Aldrich and Halopolymer were in molecular weight and phase compositions, as will be demonstrated below. Thus, the SA prevalent phase was  $\alpha$ , while in HP it was  $\beta$ -phase (Table 1).

After each technological stage, the melting peak position for both materials remained consistent, as indicated by the DSC curves in Fig. 1. However, for the SA material, an additional peak started forming after printing, indicating the formation of an electroactive phase ( $\beta+\gamma$ ) with a lower melting temperature [35]. In contrast, for the HP material, the melting temperature and the peak area remained the same, indicating greater stability at each stage, including filament extrusion and FDM printing.

The XRD patterns shown in Fig. 2 confirm the presence of CFO particles in the composite samples, exhibiting a cubic spinel structure of  $\text{CoFe}_2\text{O}_4$  consistent with COD card No. 00-153-5820. The calculated lattice constant is 0.8398 nm. The SA samples demonstrate two

**Table 1.** Crystallinity,  $\alpha$ ,  $\beta$ ,  $\gamma$ , and electroactive phase content for SA and HP materials

| Sample         | Material               | Crystallinity (%) | $F_{\text{ea}}$ (%) | $\alpha$ | $\beta$ | $\gamma$ |
|----------------|------------------------|-------------------|---------------------|----------|---------|----------|
| Powder         | Sigma-Aldrich          | 35                | 13                  | 22       | 8       | 5        |
|                | Halopolymer ( $F-2m$ ) | 34                | 32                  | 2        | 28      | 4        |
| Filament       | Sigma-Aldrich          | 27                | 18                  | 9        | 14      | 4        |
|                | Halopolymer ( $F-2m$ ) | 33                | 26                  | 7        | 21      | 5        |
| Printed object | Sigma-Aldrich          | 33                | 17                  | 16       | 16      | 1        |
|                | Halopolymer ( $F-2m$ ) | 33                | 24                  | 9        | 23      | 1        |

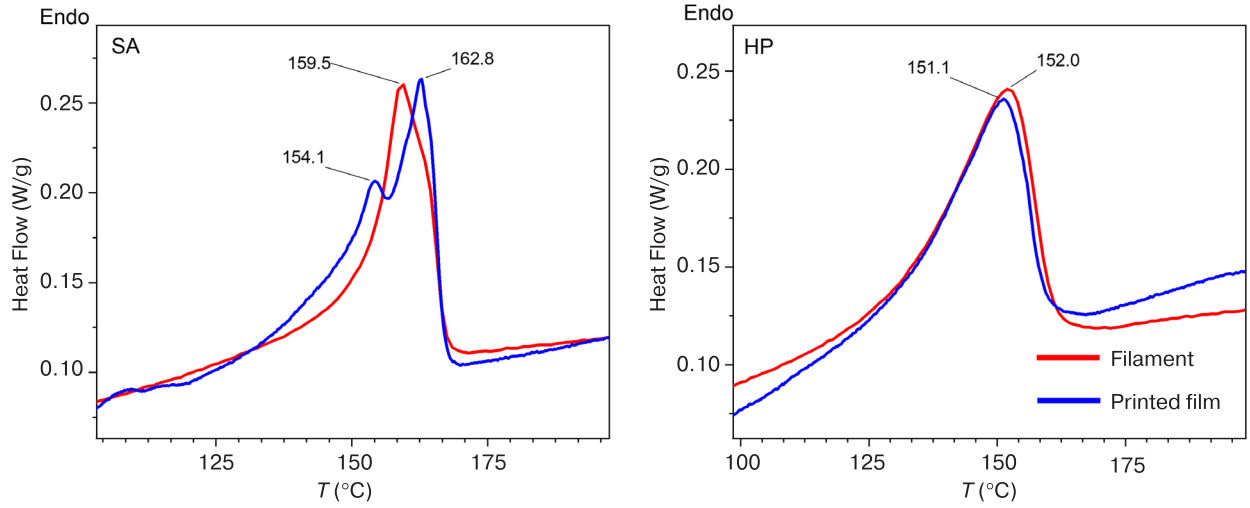


**Figure 1.** DSC data of melting peaks for composite CFO/PVDF filament (shown in red) and FDM-printed films (shown in blue). SA stands for Sigma-Aldrich, HP – for Halopolymer

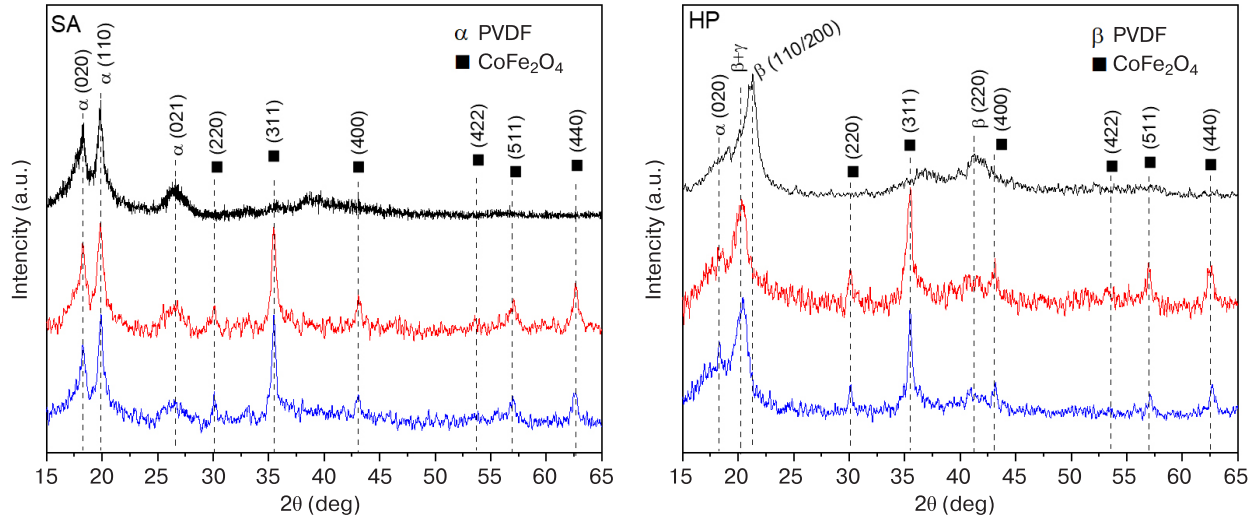


**Figure 2.** XRD patterns for raw PVDF powder (shown in black), composite CFO/PVDF filament (shown in red) and FDM-printed films (shown in blue). SA stands for Sigma-Aldrich, and HP – for Halopolymer

intensive peaks and one medium peak, corresponding to the 020, 110 and 021 reflections of monoclinic  $\alpha$ -phase crystal [22, 37]. In contrast, the main peak indicators for HP samples correspond to  $\beta$ -phase (110, 200, 220). A shift of the  $\beta$ -phase peak (110/200) towards smaller angles in filaments and printed films is observed, which can be interpreted as an increase in the content of the  $\gamma$ -phase.

The regions of interest (ROI) of the FTIR spectra are indicated in Fig. 3. Four peaks in the FTIR spectra can be selected to reliably identify the PVDF phase composition. The peak at 763 cm<sup>-1</sup> is one of the characteristic bands of the  $\alpha$ -phase, the peaks around 1275 cm<sup>-1</sup> and 1234 cm<sup>-1</sup> are indicative of  $\beta$ - and  $\gamma$ -phases, respectively. The electroactive phases ( $\beta$  and/or  $\gamma$ ) can be identified by a large peak at 840 cm<sup>-1</sup>, although this can be a common peak, but the absorbance for  $\beta$ - and  $\gamma$ -phases is much stronger [21]. Taking into account the total crystalline

fraction  $F_{cr}$ , the relative amount of the electroactive phase ( $\beta$  and/or  $\gamma$ ),  $F_{ea}$ , with respect to non-electroactive  $\alpha$ -phase, can be found from the following equation [21]:

$$F_{ea} = \left[ F_{cr} \frac{A_{840}}{\left( \frac{K_{840}}{K_{763}} \right) \cdot A_{763} + A_{840}} \right] \cdot 100\%, \quad (2)$$

where  $A_{840}$ ,  $A_{763}$  and  $K_{840}$ ,  $K_{763}$  are the experimentally obtained values of the intensity and the absorption coefficients for the corresponding phases at the wave numbers of 840 cm<sup>-1</sup> and 763 cm<sup>-1</sup>, respectively ( $K_{840} = 7.7 \cdot 10^4$ ,  $K_{763} = 6.1 \cdot 10^4$  cm<sup>2</sup>/mol).

It is also possible to estimate the relative  $\beta$ - and  $\gamma$ -phase content in samples. For this purpose, a parameter called the peak-to-valley height ratio (P2VHR) has been proposed in [21]. For the  $\beta$ -phase, the characteristic peak around 1275 cm<sup>-1</sup> with its nearest valley can be used.

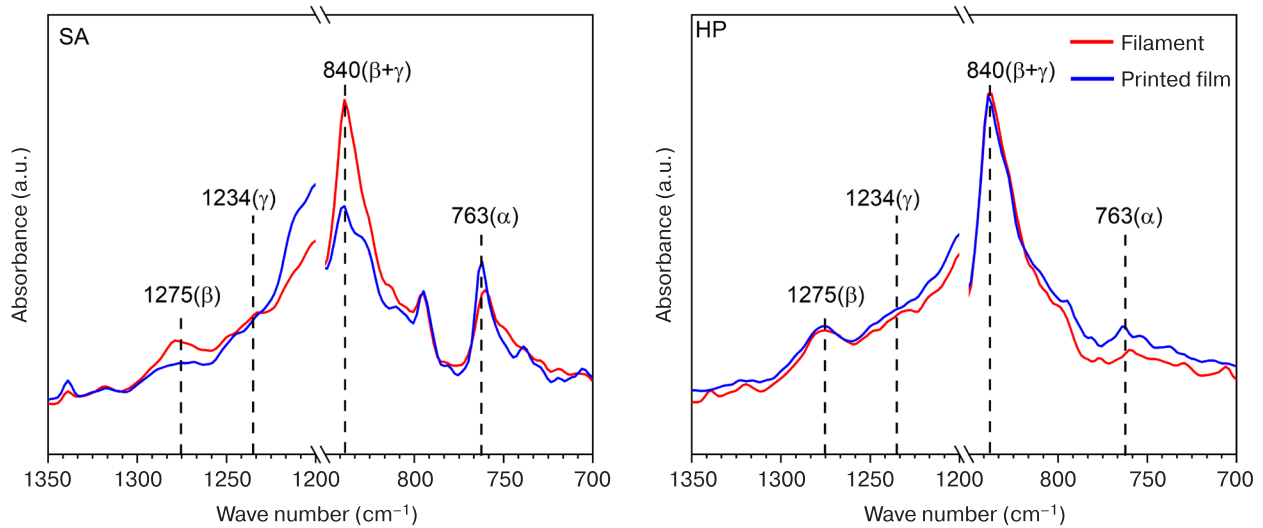


**Figure 3.** ROI of FTIR spectra for composite CFO/PVDF filament (shown in red) and FDM-printed films (shown in blue). SA represents Sigma-Aldrich samples, and HP represents Halopolymer samples

For the  $\gamma$ -phase, a suitable combination gives the peak at  $1234\text{ cm}^{-1}$ . The corresponding ratios are denoted as  $\Delta H_\beta$  and  $\Delta H_\gamma$ , respectively.

$$F_\beta = F_{\beta+\gamma} \frac{\Delta H_\beta}{\Delta H_\beta + \Delta H_\gamma} \cdot 100\%, \quad (3)$$

The quantitative analysis revealed that the materials underwent two different processes of phase transformations. For SA samples, there was an increase in the electroactive phase, while for HP samples, the relative amount of the electroactive phase decreased from its initial state. Significant changes in the phase composition for the materials occurred during filament extrusion (Fig. 4). Furthermore, the transition from the extrusion stage to the printing stage primarily affected the  $\beta$ - $\gamma$  phase contents (see Table 1).

The difference observed for the Sigma-Aldrich material between the filament and the printed object can be

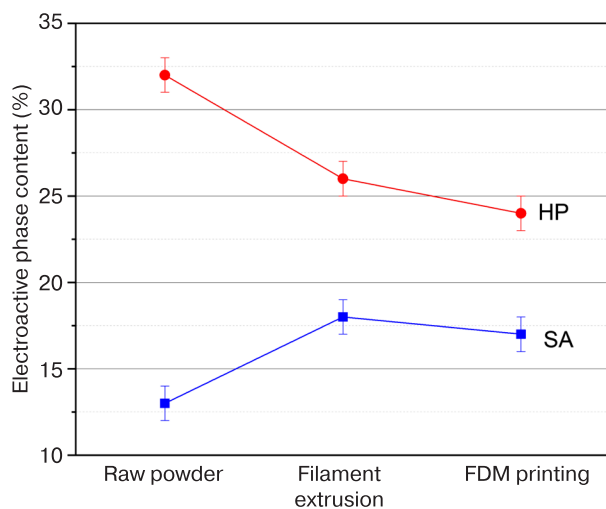


**Figure 4.** Relative electroactive phase content after each technological stage for SA and HP materials

explained by the likelihood of the  $\alpha$ -phase being converted to  $\beta$ - and  $\gamma$ -phases during extrusion, rather than the conversion of  $\beta$ -phase and  $\gamma$ -phase to  $\alpha$ -phase. This disparity is evident in the FTIR spectra (Fig. 3), where differences in the spectra are observed at each of the technological stages for the SA samples, while for the HP samples, the spectra of the filament and the printed film are very similar. Additionally, an increase in the  $\alpha$ -phase is observed after printing for the HP sample.

The phase transition diagrams between the  $\alpha$ -,  $\beta$ -, and  $\gamma$ -phases of PVDF are known, but none of the diagrams [35–39] consider the phase transitions during filament extrusion and FDM printing. Both extrusion and FDM printing surpass the melting point of PVDF, which is in the range of  $150\text{--}170^\circ\text{C}$ . However, based on the phase composition and thermodynamic properties, it is possible to determine from which Sigma-Aldrich or Halopolymer material the samples were obtained. This can be considered as a “memory” of the original state, despite dissolution, extrusion, and printing with the material.

### 3.2. Magnetic and magnetoelectric properties

The measured coercive force  $H_C$  of  $1.7 \pm 0.1\text{ kOe}$  is consistent with the values expected for CFO particles of relatively large size ( $\sim 20\text{ nm}$ ). The remanence magnetization  $M_r$  is also large: the ratio of  $M_r/M_m$  is about 0.5, where  $M_m$  is the magnetization value at the maximum applied field. The shape of the hysteresis loops and their similarity for samples made from both SA and HP filaments indicates that the magnetic particles are identical and uniformly distributed within the composite filaments. The magnetization curves allowed estimation of the actual nanoparticle weight concentration in the filaments by comparing the normalized magnetizations of the CFO nanoparticles and the filaments. This analysis revealed approximately 1 % loss of nanoparticles occurring during the composite synthesis, extrusion, and 3D printing processes. To com-

pensate, a 1 % increase in the nominal nanoparticle loading is recommended for future syntheses.

The dynamic method was used to estimate the magnetoelectric coefficient [25]. Measurements on two printed composite films in out-of-plane configuration of SA and HP PVDF, each 10 × 10 mm in size and 100 μm thick, showed maximum values around 2 mV/(Oe·cm) under DC bias field of 1.7 kOe (corresponding to the coercivity). The observed small values of ME voltage can be explained by several factors. The ME coupling arises from stress transfer at the interface between CFO particles and the electroactive phases of PVDF. When a magnetic field is applied, the shape of magnetostrictive CFO particles changes, creating strain. When these particles are surrounded by the electroactive phase, an induced voltage change occurs. The ME effect is a product property that requires a substantial amount of both the ferroelectric and magnetostrictive phases. In the printed samples the relative percentage of β and γ electroactive phases is moderate for both types of samples: 17 and 24 %, respectively for SA and HP samples (see Table 1). In addition, the content of CFO is also low, around 10 wt.%. Furthermore, the measurements were performed under non-resonant conditions, which also contributed to the reduced magnetoelectric response. In CFO/P(VDF-TrFE) composites, the ME coefficient can reach up to 40 mV/(Oe·cm) with 60 wt.% CFO [24]. However, a low concentration of CFO nanoparticles is required to ensure high polarization properties and a smooth surface of the printed objects. Nevertheless, the observed ME coefficients are sufficient for applications in magnetically stimulated scaffolds for tissue engineering [40].

## Conclusions

In conclusion, our research has shown that the molecular weight and phase composition of PVDF powder significantly influence the structural properties of CFO/PVDF composite filaments for 3D printing. Lower molecular weight PVDF composites have a lower melting tempera-

ture, which expands the range of 3D printers capable of printing this composite material.

Although filament extrusion and FDM printing have virtually no effect on the degree of crystallinity, the composite obtained from the Sigma Aldrich precursor (with higher molecular weight and initially in the dominant α-phase) undergoes a greater degree of transformation.

The prepared filament samples exhibit ferromagnetic behavior with a coercive force of 1.7±0.1 kOe, consistent with CFO particles of a relatively large size of ~20 nm. The hysteresis loops show no differences between samples made from SA and HP, indicating the same magnetic properties.

The magnetoelectric coefficient, estimated by the dynamic method, was approximately 2 mV/(Oe·cm) for printed composite films derived from both SA and HP samples. This relatively small value can be attributed to the low percentage of electroactive phase present in the printed samples, the low concentration of CFO particles in the initial PVDF composite filament, and non-resonant conditions of the measurements. However, such values are sufficient for magnetically stimulated scaffolds for tissue engineering.

From the perspective of 3D printing quality, the use of Halopolymer material appears to be the best option. Its lower melting point and higher β-phase content are critical for forming the piezoelectric and magnetoelectric properties.

The choice of precursor material for extruding the composite CFO/ PVDF filament is essential in determining the properties of both the filament and the resulting product after FDM printing. A precursor material with a higher β-phase will result in a greater β-phase content in the printed object.

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