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### RESEARCH ARTICLE

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# Processability and properties of cubic-BaTiO<sub>3</sub>/poly (vinylidene fluoride) composites for additive manufacturing: From powder compounding to 3D-printed parts

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#### Abstract

Poly(vinylidene fluoride) (PVDF) is a piezoelectric and thermoplastic material with great potential for additive manufacturing (AM) applications. Using barium titanate (BaTiO<sub>3</sub>) as filler, PVDF-based composite materials were developed, characterized, and processed by AM material extrusion (MEX). The morphological features and phase transformations occurring throughout the processing of BaTiO<sub>3</sub>-filled PVDF, from the compounding to the printed part, were analyzed. The morphology of the powder feedstock after dispersion in a high-energy ball mill changed from spheroidal to laminar and β-phase formation was favored. Microhardness gradually increased with the BaTiO<sub>3</sub> content, obtaining an enhancement of  $\sim 60\%$  for a content of 25 vol%, and supported the good dispersion of the filler. A  $\sim$ 48% increase of the dielectric permittivity was also achieved. After extrusion, filaments with a filler content of 15 vol% showed a more stable diameter, as well as higher crystallinity and surface roughness, compared with those with lower BaTiO<sub>3</sub> contents. Material extrusion of filament and direct printing of pellets based on MEX were successfully used to obtain AM parts. Composite parts showed enhanced surface roughness, hydrophilicity, and flexural modulus (up to  $\sim$ 33% for the 7 vol% composite compared with the PVDF), thus leading to superior mechanical characteristics and potential biomedical applications.

### Highlights

- Dry high-energy ball milling was a suitable greener dispersion approach.
- MEX processes were successfully used to obtain 3D-printed parts.
- The use of direct printing of pellets/powder improved the 3D printability.
- The surface roughness and hydrophilicity increased with the filler content.
- The permittivity and elastic modulus increased with the filler content.

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additive manufacturing, barium titanate, filament extrusion, material extrusion (MEX), PVDF

# **1** | INTRODUCTION

During last decades, poly(vinylidene fluoride) (PVDF) has attracted the attention of the research community for its use as matrix in composite materials due to the piezoelectric and pyroelectric properties that shows when the electroactive phases, polar  $\beta$  and  $\gamma$ , are formed. Nevertheless, the  $\beta$  phase is more polar than the  $\gamma$  one and, consequently, achieving the electroactive  $\beta$  phase in this polymer plays a key role in achieving high piezoelectric coefficients  $(d_{33})$ . Different approaches have been carried out to maximize this phase.<sup>1,2</sup> As an example, Bae et al.<sup>3</sup> analyzed three different processes in poly(vinylidene fluoride-trifluoroethylene) (PVDF-TRFE) polymers: (1) annealing and cooling, (2) cold and hot pressing, and (3) electrical poling. In this work, the maximum  $\beta$  fraction (62.80%) was found for hot pressing with a pressure of 30 MPa at a temperature of 140°C. Additionally, spontaneous polarization due to the electroactive fluorine atoms in the polymer chains and the relatively high dielectric permittivity, compared with other polymers, contributes to the increasing interest in PVDF.<sup>4</sup>

Although the dielectric properties of PVDF makes it a potential candidate for electromechanical devices, such as microelectromechanical systems (MEMS) and nanogenerators, an enhancement of the dielectric permittivity would be advantageous.<sup>5</sup> For this purpose, the addition of different fillers has been proposed, one of them being BaTiO<sub>3</sub> (BT) nanoparticles.<sup>6</sup> To disperse these nanofillers in the PVDF matrix, organic solvents are commonly used to dissolve the polymeric matrix. Among others, one of most frequently used for PVDF is N,Nthe dimethylformamide (DMF).<sup>5,7</sup> After solution, the nanofiller is incorporated forming a suspension and subjected to magnetic stirring or sonication.<sup>5</sup> Nevertheless, the use of organic solvents can be environmentally detrimental. Consequently, one of the main aims of this work is to avoid the use of organic solvents to pursue a greener approach into the processing route. For this purpose, high-energy ball milling is used as dispersion process in this work, as among the advantages of this method, the avoidance of organic solvents and scalability are two of the main.

Additionally, the resulting material from this method is in powder form, which is beneficial if additive manufacturing (AM) is considered as the processing route, that is the powder obtained directly from the highenergy ball milling can be fed directly to an extruder to produce filaments for AM material extrusion (MEX); commonly known as fused deposition modeling (FDM). It is well known that during last years, the manufacturing industry has been focused on AM and the adaptability of materials to these techniques due to the low manufacturing restrictions and, consequently, high design freedom. In this regard, processing parameters plays a significant role in the final properties of PVDF<sup>8,9</sup> and related nanocomposites<sup>10</sup> as changes in crystallinity and  $\beta$  phase concentration occurs.<sup>11</sup>

In the last decade, the development of customized nanocomposites has been sparked by a growing demand for 3D printable materials with superior functionalities and enhanced physicochemical and mechanical properties.<sup>12</sup> Specifically, polymer-based composite filaments for 3D printing have recently garnered considerable attention.<sup>13–20</sup> Nanoscale interactions between the matrix and the fillers have a significant effect on the mechanical performance and durability of the final 3D-printed composite part.<sup>21</sup>

In this work, the operational parameters of filament extrusion and MEX of BT-reinforced PVDF nanocomposites were optimized, analyzing morphological features and phase transformations that occur throughout the processing from powder compounding to 3Dprinted parts. Filaments were characterized in terms of surface morphology and uniformity, calorimetric properties, and FTIR analysis. Furthermore, the surface roughness, hydrophilicity, and mechanical properties under bending load of the 3D-printed composite parts were evaluated. The influence of the BT content on the quality of the dispersion,  $\beta$  formation, microhardness, and dielectric permittivity of the powders developed were also analyzed.

# 2 | MATERIALS AND METHODS

## 2.1 | Materials

Commercially available cubic BT with an average particle size lower than 100 nm was purchased from Sigma-Aldrich (Darmstadt, Germany). The polymer matrix used in this work was PVDF Kynar 711 from Arkema (Colombes, France).

#### 2.2 Methods 1

#### 2.2.1Dispersion method

The as-received powders of the polymer matrix and BT filler were mixed in a high-energy planetary ball mill (Pulverisette 7, Fritsch classic line, Fritsch, Germany) using a steel jar and WC balls. The ball-to-powder ratio was 13 and the speed was set to 500 rpm. Milling was conducted for 20 cycles using cycles of 10 min alternating with 10 min pause to avoid heating of the mixture.

## 2.2.2 | Characterization of the powder produced

Changes induced in the as-received polymeric powder during the dispersion process were evaluated by scanning electron microscopy (SEM) in a TENEO. Additionally, the particle size was measured by granulometry in a Mastersizer 2000 from Malvern. The microstructure of the composite powder was also analyzed by SEM. The cross section of the prepared powder was polished and the distribution of the ceramic filler through the polymer matrix was evaluated.

Microhardness tests were also used to evaluate the homogeneity of the materials in a Wilson Hardness VH1150 durometer. A matrix of  $6 \times 6$  indentations was created on the polished surfaces with a Vickers indenter using a force of 0.3 kg (HV0.3).

The presence of the electroactive  $\beta$  phase in the processed PVDF was analyzed by attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR) in an Invenio-X from Bruker. The average spectra for each group tested were the result of 16 scans per measurement. The fraction of electroactive phase  $(F_{EA})$  was calculated from peaks located close to  $840 \text{ cm}^{-1}$  ( $\beta$  and  $\gamma$ ) and 763 cm<sup>-1</sup> ( $\alpha$ )<sup>22</sup>:

$$F_{\rm EA} = \frac{A_{840}}{(K_{840}/K_{763})A_{763} + A_{840}},\tag{1}$$

where  $A_{840}$  and  $A_{763}$  are the absorbance intensities of electroactive and  $\alpha$  phases, respectively, and  $K_{840}$  and  $K_{763}$ , the absorption coefficients,  $7.7 \times 10^4$ , and  $6.1 \times 10^4 \,\mathrm{cm}^2 \,\mathrm{mol}^{-1}$ , respectively.

The  $\beta$  phase ( $F_{\beta}$ ) is obtained from  $F_{EA}$  and the height ratio of the absorbance at  $\sim 1275 (\Delta H_{\beta})$  and  $1232 \,\mathrm{cm}^{-1}$  $(\Delta H_{\gamma})$ , corresponding to the  $\beta$  and  $\gamma$  phase, respectively:

$$F_{\beta} = F_{EA} \cdot \frac{\Delta H_{\beta}}{\Delta H_{\beta} + \Delta H_{\gamma}}.$$
 (2)

The glass transition temperature was determined by differential scanning calorimetry (DSC) by using a SDT Q600II from TA Instruments. The study was conducted in a temperature range between room temperature and 600°C with a heating rate of 10°C/min in air. Simultaneously, thermogravimetric analysis (TGA) was used to characterize the thermal degradation of the PDVF and the influence of the addition of BT as filler.

From the calorimetric data, the following information was obtained: peak melting temperature  $(T_{peak})$ , and the melting enthalpy  $(\Delta H_{\rm f})$ . From the latter parameter, the degree of crystallinity ( $\% X_c$ ) of the sample was calculated by  $^{23,24}$ :

$$\% X_{\rm C} = 100 \cdot \left[ \frac{\Delta H_{\rm f}}{\Delta H_{\rm f}^{\rm o} \cdot W_{\rm PVDF}} \right],\tag{3}$$

where  $\Delta H_{\rm f}$  is the melting enthalpy of the sample,  $\Delta H_{\rm f}^{\circ}$  is the melting enthalpy of 100% crystalline PVDF (104.7 J/g according to Ref. [25]), and  $W_{PVDF}$  is the net weight fraction of the polymer in the tested sample.

The permittivity ( $\varepsilon$ ) and dielectric loss (tan  $\delta$ ) were obtained by electrical impedance spectroscopy in compression molded samples (200°C at 15 MPa, 15 min) using an Agilent 4294A analyzer in the frequency range of  $10^3 - 10^7$  Hz.

#### 2.2.3 Filament extrusion

Composite mixtures of PVDF and BT were fed into a lab prototype extruder to produce continuous filaments suitable for MEX processes. This extruder consists of an 8-mm screw, a cylinder with an L/D ratio of 10, and a nozzle tip of 1.6 mm diameter (smaller than the filament diameter due to swelling effect). The equipment was preheated for 1 h prior to the extrusion process. By setting the temperature at the nozzle tip to 200°C and using a rotation speed of 7 rpm, filaments with a mean diameter of 1.75 mm were obtained. No water-cooling stages were needed airor after extrusion.

As the lab prototype extruder was not adequate to work with the PVDF nanopowder, the filaments without BT filler were produced using a Filament Maker Composer 450/350 (3devo, Utrecht, Netherlands). In this equipment, the temperature is controlled in four different zones. The heaters were set to 188 (feed zone), 178, 183, and 163°C (nozzle tip). The extrusion was carried out at a rotation speed of 3.5 rpm and the fan speed was set to 50%. A spool of 1.75 mm diameter PVDF filament was obtained.

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# **TABLE 1** Operational parameters for additive manufacturing parts.

Material	Equipment	Layer thickness (mm)	Layer width (mm)	Deposition speed (mm/s)	Temperature nozzle tip (bed) (°C)	Motor step (steps/mm)
PVDF	Prusa i3 (Filament)	First layer: 0.4 Other layers: 0.3	0.45	10	260 (90)	-
PVDF	Creality Ender 3	First layer: 0.4	0.45	10	230 (90)	269
7 vol%	(Pellets)	Other layers: 0.3				269
10 vol%						236
15 vol%						236

Abbreviation: PVDF, poly(vinylidene fluoride).



**FIGURE 1** Morphology of the poly(vinylidene fluoride) (PVDF) (A) and as-milled barium titanate-filled PVDF composites: 10 vol% (B) and 20 vol% (C); and particle size distribution (D).



FIGURE 2 Microstructure of the as-milled powder of composite materials: 10 vol% (A), 15 vol% (B), 20 vol% (C), and 25 vol% (D).

# 2.2.4 | Characterization of the filaments produced

The morphological characterization of the PVDF-based filaments manufactured included the evaluation of their uniformity in terms of diameter, measured with an electronic digital micrometer ( $\pm 0.001$  mm). Furthermore, the surface morphology of the filaments was evaluated by optical microscopy using an Olympus BX51 optical microscope (Olympus Co., Ltd., Tokyo, Japan).

The filaments obtained were also characterized by ATR-FTIR using an IR Spectrum Two<sup>TM</sup> (PerkinElmer, Waltham, MA, USA) in the range of 4000–500 cm<sup>-1</sup> at a resolution of 8 cm<sup>-1</sup>. The average spectra for each group tested were the result of 12 scans per measurement. The  $F_{\beta}$  was calculated by Equations (1) and (2).

Small fragments (n = 4) of each type of filament produced were used for DSC analysis in a DSC 4000 (PerkinElmer, Waltham, MA, United States). The samples (weight around 10 mg) were placed in aluminum crucibles and subjected to a heating/cooling/heating cycle from 30 to 230°C. Heating and cooling rates of 10 and 20°C/min were used, respectively. A nitrogen flow of 20 mL/min was set. From the calorimetric data, the onset temperature ( $T_{\text{onset}}$ ), peak melting temperature  $(T_{\text{peak}})$ , and the melting enthalpy  $(\Delta H_{\text{f}})$  were determined. From the latter parameter, the degree of crystallinity (%  $X_{\text{c}}$ ) of the samples was calculated by Equation (3).

# 2.2.5 | Manufacturing of test specimens by AM

Standard solid samples were obtained by AM using the composite filaments developed with BT contents of 7 vol%, 10 vol%, and 15 vol%. The samples were designed to have dimensions of  $40 \times 5 \times 2$  mm, which are half the values of standard UNE-EN ISO 178:2020 bending specimens. Two different techniques were used to manufacture the AM parts. First, by using a Prusa i3 (Prusa Research, Prague, Czech Republic), which is based on a MEX process, according to ISO/ASTM 52900:2021, using filaments as feedstock. Also based on a MEX process, a Creality Ender 3 (Shenzhen Creality 3D Technology Co., LTD., China) coupled with a pellet extruder (PX0850 V4 Pellet Extruder, Mahor·xyz, Spain) was used for direct printing of pellets, which were obtained from the PVDF-based filaments using a pelletizer (VariCut Pelletizer, Thermo Fisher Scientific, Karlsruhe, Germany).



FIGURE 3 Microhardness maps (HV0.3, in MPa) of the as-milled powder of composite materials: PVDF (A), 10 vol% (B), 15 vol% (C), 20 vol% (D), and 25 vol% (E); and microhardness (HV0.3, in MPa) as a function of the barium titanate (BT) content (F).

TABLE 2 Properties of poly(vinylidene fluoride) (PVDF) and barium titanate (BT)-reinforced nanocomposites.

				Degradation temperature			
Material	$T_{\text{peak}}$ (°C)	$\Delta H_{\rm f}$ (J/g)	%X <sub>c</sub>	$T_{\rm d,onset}$ (°C)	T <sub>d,peak</sub> (°C)	Microhardness (MPa)	$\varepsilon$ (1 kHz)
PVDF	167.9	31.1	29.7	428.9	463.84	$131 \pm 17$	37.6
10 vol%	168.8	27.9	36.6	466.8	520.07	$138 \pm 28$	43.3
15 vol%	169.6	35.4	54.0	470.1	525.11	$151 \pm 28$	43.8
20 vol%	169.2	32.0	56.4	466.0	526.18	191 ± 17	48.5
25 vol%	170.3	23.2	47.0	453.9	519.64	$210 \pm 10$	55.7



**FIGURE 4** Fourier transform infrared spectroscopy of poly(vinylidene fluoride) (PVDF) and as-milled barium titanate (BT)-filled PVDF (20 vol% BT).

The samples were 3D-printed with 3 perimeters, 0 bottom/top layers, and 100% linear infill printed in parallel direction to the specimen, while retraction settings included a distance of 3 mm at a speed of 40 mm/s. The other main printing parameters used are summarized in Table 1. Pure PVDF specimens were obtained using both 3D printers, but only the Creality 3D printer equipped with the pellet extruder was used to manufacture composite parts. The direct printing of composite pellets made it possible to produce parts with adequate quality while avoiding the handling of highly fragile filaments (especially those with high content of BT).

# 2.2.6 | Characterization of the samples obtained by AM

A roughness meter (SJ-201P, Mitutoyo, Japan) was used to analyze the surface of the PVDF-based specimens. A total of 6 measures were performed per sample (n = 4), using a sampling length (cutoff) of 0.8 mm, a R profile, and a 2CR75 filter.

The hydrophilicity of the sample's surface was evaluated by measuring the water contact angle (WCA) through the sessile drop method. The static contact angle of 2  $\mu$ L distilled water droplets (n = 5) was determined at room temperature using an Ossila WCA measuring device (Ossila Ltd., Sheffield, UK) and the opensource software ImageJ.

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Finally, their mechanical properties were determined under bending load in a LIYI (LI-1065, Dongguan Liyi Environmental Technology Co., Ltd., China) testing machine in displacement control mode. A three-point flexural test was carried out (n = 5) following ISO 178 standard and using a crosshead speed of 1 mm/min and a distance between supports of 32 mm. Maximum flexural stress, flexural modulus and offset flexural yield strength (2% deviation from linearity) were calculated in accordance with ISO 178.

The statistical analysis of the results obtained was carried out using MATLAB software (MATLAB and Statistics Toolbox Release 2021a, The MathWorks, Inc., Natick, United States). Specifically, the Kruskal–Wallis test (when comparing more than two groups) and the Wilcoxon two-sided rank sum test (when comparing only two groups) were used. The significance levels were set to \*p < 0.05, \*\*p < 0.01, and \*\*\*p < 0.001, for statistically significant, highly statistically significant, and very highly statistically significant differences, respectively.

## 3 | RESULTS AND DISCUSSION

# 3.1 | Morphological and size changes induced by the dispersion process

The morphology of the powder used as feedstock in filament extrusion for AM plays a key role in the quality of the filaments, as well as in mechanical properties and processability. Additionally, the size of the particles forming the powder strongly influences the operational parameters and can limit the processability of the material.

To explain the morphological changes induced by the dispersion process proposed in this work, Figure 1A–C show representative SEM micrographs of the as-received PVDF powder (Figure 1A) and the composite materials



FIGURE 5 Permittivity (A) and dielectric loss (B) of poly(vinylidene fluoride) (PVDF) and barium titanate-based nanocomposites.





incorporating contents of 10 vol% and 20 vol% of BT (Figure 1B,C, respectively). The morphology of the powder drastically changed. Initially, the PVDF particles presented spherical geometry, and the presence of agglomerates forming spheroidal forms constituted by a significant number of particles is clearly appreciated.

After dispersing the BT nanoparticles by dry highenergy ball milling, the spheroidal form of the powder was lost, showing laminar structures with lateral sizes ranging from 10 up to 165  $\mu m$  and thicknesses in the range of 2–20  $\mu m.$ 

Although the addition of higher contents of BT seems to not significantly affect the geometry and particle size of the composite powder, the granulometric analysis (Figure 1D) showed a slight reduction of the average particle size ( $d_{0.5}$ ) as the BT content increases up to 20 vol%, from 140.8 down to 101.1 µm. For contents of 25 vol%, the average particle size ( $d_{0.5}$ ) increases again up to





FIGURE 7 Diameter analysis of the poly(vinylidene fluoride) (PVDF)-based filaments produced.

**FIGURE 8** Fourier transform infrared spectroscopy spectra of poly(vinylidene fluoride) (PVDF) extruded filaments and its composites.

 $135.0 \ \mu$ m. It is important to note that, although it can be used for comparison, the particle size obtained by granulometry is approximated as the particles are not spherical.

Another issue to consider is that the size distribution is wide in all the cases. This fact can contribute to enhance the accommodation of the different particles during filament extrusion as smaller particles can occupy spaces between the bigger ones.

Figure 2 shows representative SEM micrographs of the powder after the dispersion process, where the ceramic filler can be differentiated as the bright phase. In all the composite materials, the BT nanoparticles were well distributed throughout the PVDF matrix, and no agglomeration was found. For samples with a BT content of 25 vol% some linear pattern was observed, which could be related to a higher friction caused by the high content of the ceramic filler. Olmos et al.<sup>6</sup> also used dry high-energy ball milling as dispersion method and obtained good quality dispersions, but they did it under cryogenic conditions to efficiently disperse submicrometric BT particles.

To corroborate the goodness of the dispersion, Figure 3 shows microhardness maps in an area of  $5 \times 5 \text{ mm}^2$  for all the materials. The obtained values are homogeneous along the analyzed region for all the nanocomposites, which supports that the BT nanoparticles are well distributed throughout the polymeric matrix. Additionally, as expected, the microhardness gradually increases with the BT content (Table 2), obtaining an increase of ~60% for a filler content of 25 vol%.

The presence of the different phases after the dispersion process was evaluated by FTIR-ATR. As marked in Figure 4, the bands located at 615, 764, 854, and 974 cm<sup>-1</sup> correspond to the formation of the  $\alpha$ -phase. In contrast, the presence of  $\beta$  and  $\gamma$ -phases can be identified by the band located at 842 cm<sup>-1</sup>. Additionally, bands

positioned at 1279 and 1431 cm<sup>-1</sup>, and 776, 833, and 1242 cm<sup>-1</sup>, are attributed to  $\beta$  and  $\gamma$ -phases, respectively.<sup>22,26</sup> In the FTIR spectrum of the as-received PDVF powder, the peaks attributed to the presence of polar and nonpolar phases were identified, being the fraction of the electroactive phase  $\sim 23\%$ , mainly corresponding to  $\beta$ phase. In contrast, after the dispersion process,  $\beta$  phase is dominant (~100%), as no peak associated with the  $\alpha$  or  $\gamma$ phases was found. The promotion of the  $\beta$  phase during dispersion is related to the high shear forces and, consequently, the strain induced by planetary ball milling; like the effect of calendering.<sup>27</sup> This fact makes planetary ball milling a potential candidate to disperse the ceramic particles promoting  $\beta$  phase without using solvents. Although melt blending could also be considered as an alternative green approach, Chiolerio et al.<sup>28</sup> confirmed that it induces the formation of  $\alpha$  phase.

Table 2 shows the results obtained from the DSC and TGA analysis. The melting temperature ( $T_{\text{peak}}$ ) increases with the addition of the ceramic filler from 167.9 up to 170.3°C for a BT content of 25 vol%. The degree of crystallinity ( $%X_c$ ), calculated from the melting enthalpy, also increases with BT content due to the nucleation effect of the particles added to the PVDF matrix<sup>29,30</sup> and the high strain during the process.

All the materials presented thermal stability for temperatures below 420°C. The degradation of the PVDF started at a temperature of 428.9°C ( $T_{onset}$ ). Nevertheless, when BT nanoparticles were incorporated, the temperature at which the degradation started increased in all the cases, reaching a maximum value of 470.1°C ( $T_{onset}$ ). Although there is an enhancement on the  $T_{onset}$  for all the nanocomposites, a maximum was found at a BT content of 15 vol%.

The permittivity ( $\varepsilon$ ) and the dielectric loss (tan  $\delta$ ) of the PVDF and composite materials are shown in

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Group ( <i>n</i> = 4)	$T_{\text{onset}}$ (°C)	$T_{\mathrm{peak}}$ (°C)	$\Delta H_f$ (J/g)	%X <sub>c</sub>
PVDF	$160.6\pm0.2$	$169.3\pm0.1$	$45.3\pm0.2$	$43.3\pm0.2$
7 vol%	$160.4\pm0.3$	$168.9\pm0.3$	$31.7 \pm 0.6$	$37.8\pm0.7$
10 vol%	$161.1\pm0.2$	$168.4 \pm 0.2^{a}$	$32.5 \pm 1.2$	$42.6 \pm 1.6$
15 vol%	$161.1 \pm 0.3^{b}$	$168.0 \pm 0.6^{\circ}$	$30.7 \pm 0.1$	$46.5\pm0.2$

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**TABLE 3**Properties ofpoly(vinylidene fluoride) (PVDF) andbarium titanate (BT)/PVDF filaments.

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 $a_{**}p < 0.05$  compared with PVDF group.  $b_{*}p < 0.05$  compared with 7 vol% group.

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 $c_{***}p < 0.01$  compared with PVDF group.



**FIGURE 9** Use of additional material to improve adhesion: sample printed without extra bases (A); printing model of the solid samples manufactured (B); and sample printed with extra bases (C).

Figure 5. The dielectric permittivity of the material increases with the BT content up to  $5 \times 10^{10}$  Hz, which is attributed to the higher permittivity of BT compared with PVDF and the interfacial interaction filler-matrix.<sup>31</sup> The value of the dielectric permittivity (also presented in Table 2) increases up to 55.7 with the addition of a 25 vol % of BT, which is ~48% above the one of the PVDF (37.6). Yang et al.<sup>32</sup> obtained a similar value, of ~45, incorporating a content of 30 vol% into spin-coated nanocomposite films. Above this frequency, the variation is not significant. The decrease in the dielectric permittivity at higher frequencies is attributed to the loss of space and dipolar polarization.<sup>33</sup>

The tan  $\delta$  also increases with the addition of BT, but it remains below 0.05 at frequencies between 10<sup>4</sup> and 10<sup>6</sup> Hz.

# 3.2 | Composite filament production and characterization

Figure 6 shows the different PVDF-based filaments manufactured. As can be seen in the images, composites filaments showed no significant defects that can hinder their use in MEX processes. Pure PVDF filaments had a smoother surface than the composite ones, for which the roughness also seems to increase with increasing BT concentration (Figure 6). Petousis et al.<sup>13</sup> obtained similar results when analyzing their polylactic acid/titanium nitride (PLA/TiN) composite filaments. Atomic force microscopy tests revealed that filaments developed with concentrations up to 6 wt% TiN showed higher surface roughness, compared with pure PLA filaments, but were still adequate for MEX 3D printing.

In terms of dimensional analysis, the diameter of the produced filaments was within the acceptable range for their application in 3D printing. No statistically significant differences were observed (p > 0.05) when comparing the diameter (n = 20) of the different filaments developed. Although the PVDF filament group is the only one whose average diameter coincides with the target value of 1.75 mm, the different composite groups were at values of 1.74  $\pm$  0.02 for the 7 vol% and 10 vol% groups, and of 1.74  $\pm$  0.01 mm for the 15 vol% group. The smaller deviation in the results of the composite group with the highest BT concentration can be seen more clearly in Figure 7.

The stretch induced during filament extrusion and printing at the nozzle as well as the high pressure may contribute to enhance the  $\beta$ -phase crystallization.<sup>8</sup>



(A)

**(B)** 



**FIGURE 10** Prusa i3 3D printer for the filament printing (A); Creality Ender 3 3D printer with pellet extruder (B); and 3D printed samples with the different materials (C).

Additionally, the cooling rate is a key point in maximizing the  $\beta$ -phase fraction. de Neef et al.<sup>27</sup> reported that  $\beta$ -phase crystallization starts around 400°C/s and the necessity of cooling rates above 1000°C/min to achieve 100%.

The FTIR analysis did not reveal appreciable differences between the spectra of the manufactured filaments, being the fraction of electroactive phase was  $\sim$  38%, dominantly  $\beta$  phase (Figure 8). Only minor differences were found between PVDF and BT/PVDF composites FTIR spectra, including some peaks with slight shift in position (i.e., 1380, 1183, 1064, and 873  $\text{cm}^{-1}$ ) and a general slight decrease in peak intensity for the composite groups compared with the pure PVDF filaments. Besides, no new absorption peaks were observed. Thus, overall, no significant changes were found due to the incorporation of BT

particles to the PVDF matrix, indicating good blending between the materials<sup>18</sup> but a lack of intermolecular interaction that could potentially lead to the formation of agglomerates.<sup>20</sup>

The calorimetric characterization of the filaments led to the results summarized in Table 3. The introduction of the piezoelectric BT particles in the formulation of the filaments generated an increase in the onset melting temperature  $(T_{onset})$ , with a statistically significant difference for the 15 vol% group. For this last group, as well as the 10 vol%, significant differences were also obtained with respect to the PVDF control group in terms of peak melting temperature  $(T_{\text{peak}})$ . In this case, a reduction of this parameter was observed in the composite groups. By determining the melting enthalpy for each group of filaments, the degree of crystallinity ( $\%X_c$ ) could be calculated. Although no significant differences were found (p > 0.05), it was observed that the increase in BT concentration leads to an increase in crystallinity, which is due to the above-mentioned nucleation effect of the additive particles into the PVDF matrix.<sup>29,30</sup>

# 3.3 | Manufacturing and characterization of composite test specimens

As PVDF has shown to be prone to warping,<sup>34–36</sup> an adhesion platform (similar to the standard brims, but specifically designed) was necessary to ensure the adhesion of the parts to the print bed (Figure 9A). Warping takes place because of relaxation of the internal stress accumulated by the parts during printing and cooling and is favored by the anisotropic shrinkage and relatively high coefficient of thermal expansion of PVDF.<sup>34</sup> The specifically designed brim provided the samples with a greater surface area to adhere to the print bed (Figure 9B,C). These 3D-printed borders, commonly known as "mouse ears," were connected to the part extending from its edges, and were easily detached after printing. Apart from the brim, other strategies to reduce or completely avoid warping involves the use of lower temperature and printing speed, as well as the application of specialized 3D printing adhesives.<sup>36</sup> In this work, the implementation of this specific brim was sufficient to avoid warping.

Figure 10 shows the AM equipment used for the 3D printing of filament and pellets, and the obtained samples.

Surface roughness measurements (Figure 11) revealed an increase in this parameter, in terms of the arithmetic average roughness  $(R_a)$ , as the concentration of BT increases in the sample; PVDF group had a value of 8.4  $\pm$  2.6 µm, while the 15 vol% group showed the highest



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FIGURE 11 Set up for surface roughness analysis (A), positions on the part where roughness measurements were conducted (B), and results obtained from the test (C). \*(*p* < 0.05).

value at  $11.2 \pm 1.1 \,\mu\text{m}$ . Thus, statistically significant differences were observed for groups 10 vol% and 15 vol% compared with the PVDF group. On the other hand, PVDF specimens manufactured by using the Prusa i3 printer (from filament) showed a value significantly higher (p < 0.05) than that obtained for the samples manufactured by using the Creality 3D printer (from pellets).

The introduction of BT particles into the PVDF matrix affected not only the surface roughness of the parts, but also their surface hydrophilicity. The WCA decreased significantly (p < 0.05) for all composite groups compared with the control PVDF group of samples. In contrast to the low hydrophilicity of the PVDF group, which showed a WCA value of  $80.5 \pm 2.6^{\circ}$ , BT/PVDF composites groups had a value of  $53.6 \pm 3.6^{\circ}$ (no significant differences between the groups). The use of BT nanoparticles as an additive to PVDF matrices has already been confirmed in the literature<sup>37,38</sup> to substantially reduce the WCA of the polymeric material. The increased hydrophilicity of the surface, coupled with

the increase in its roughness, give these 3D-printed composite samples the potential to provide improved cell adhesion and proliferation under in vitro or in vivo applications,<sup>39,40</sup> which is interesting for tissue engineering applications.

In terms of mechanical properties, the increase in BT content led to a decrease in the maximum flexural stress for the 15 vol% group (with high dispersion of results) and in terms of the offset flexural yield strength for all the composites. The loss of mechanical properties was statistically significant for the 15 vol% group, as shown in Figure 12 for the specimens manufactured using the Creality 3D printer (from pellets). The introduction of BT ceramic particles into the matrix limits the flexibility of the polymer chains along the printed layers,<sup>14</sup> so that the abovementioned reductions were anticipated. In contrast, the flexural modulus of the 7 vol% and 10 vol% composite groups significantly increased by up to 33% and 29%, respectively, compared with the PVDF control group.

Other authors have reported similar results from the mechanical evaluation under bending load of



**FIGURE 12** Mechanical properties of the different groups tested under bending load: maximum flexural stress (A); flexural modulus (B); offset flexural yield strength (C); and specimen during flexural test (D). \*(p < 0.05) \*\*(p < 0.01).

polymer-based parts obtained by 3D printing.13,14,41 Khatri et al.,<sup>14</sup> for example, observed a reduction in flexural strength with increasing BT content (up to 30 vol%) in 3D-printed parts based on acrylonitrile butadiene styrene (ABS). Pure ABS samples showed a flexural strength of 74.14 MPa, whereas this parameter was 35.18 MPa for the 30 vol% BT composite. In contrast, the flexural modulus increased from 1.97 GPa for the ABS group to a maximum of 2.97 GPa for composite with 20 vol% BT composition. Liu et al.<sup>41</sup> also found that, after an initial increase in mechanical properties due to the introduction of BT nanoparticles into the formulation of polycaprolactone (PCL) composites, flexural strength and modulus significantly decreased after a certain composition; specifically, the 25 vol% BT composite showed a flexural modulus of only 2 GPa, compared with values of around 3.5 GPa for BT concentrations ranging from 5 vol% to 20 vol%. To explain these results, the authors have pointed out the interaction between the additive and the matrix<sup>13,41</sup> or changes in the rheology of the base material<sup>42</sup> as causes of the increase in mechanical properties.

**TABLE 4** Mechanical properties under bending load of poly(vinylidene fluoride) (PVDF) specimens manufactured using different 3D printers.

Group ( <i>n</i> = 5)	Flexural modulus (MPa)	Maximum flexural stress (MPa)	Offset flexural yield strength (MPa)
PVDF Ender 3 (pellets)	1594.0 ± 79.3	$60.0 \pm 1.7$	45.4 ± 2.2
PVDF Prusa i3 (filament)	1570.6 ± 63.0	62.0 ± 2.7	43.7 ± 2.7

On the other hand, the decrease in flexural properties observed at relatively high concentrations of BT is considered to be related to the reduced mobility of polymer chains<sup>17</sup> together with the agglomeration of nanoparticles,<sup>41</sup> which are then converted into stress concentration points (and later on fracture points) that can reduce the mechanical properties of the composite. While the nanocomposite powders developed in this work Polymer COMPOSITES

showed adequate distribution of the BT particles, as stated in Section 3.1, and no agglomeration was found, the enhanced stiffness of the printed composite layers still had a significant effect on the mechanical properties when the filler content reaches 15 vol%. On the other hand, no statistical differences (p > 0.05) were found between PVDF samples manufactured by the different printers (and, consequently, with the different format of the feedstock material: filaments and pellets) used in this work (Table 4).

#### CONCLUSIONS 4

Dry high-energy ball milling was demonstrated to be a suitable greener approach to obtain good quality and homogeneous dispersions in BT/PVDF composites. After the dispersion process, the morphology of the powder significantly changed to lamellar structures with a wide size distribution, which could be advantageous to enhance the accommodation of the different particles during filament extrusion. As expected, the microhardness and dielectric permittivity gradually increased with the BT content, obtaining an enhancement of  $\sim 60\%$  and  $\sim 48\%$  for a filler content of 25 vol%, respectively. Additionally, the fraction of the electroactive phase significantly increased due to the induced strain from  $\sim 23\%$  to  $\sim 100\%$ .

Composites filaments with a maximum of 15 vol% were successfully obtained for their use in MEX processes. With increasing BT concentration, surface roughness increased, and the diameter of the composite filaments was slightly smaller but more stable due to lower swelling. No significant differences in  $\beta$ -phase formation were observed between PVDF and composite filaments, but crystallinity was promoted by the presence of BT.

AM MEX with filaments and direct printing of pellets (also based on MEX) were successfully used to obtain 3Dprinted parts. The use of pellets instead of filament improved the 3D printability. The surface roughness and hydrophilicity of the parts increased with the filler content, which can be interesting for tissue engineering applications. The increase in BT content led to a decrease in the maximum flexural stress and offset flexural yield strength. The flexibility was limited by the presence of BT particles and the flexural modulus significantly increased (33% and 29%, for 7 vol% and 10 vol%, respectively, compared with the PVDF).

## **AUTHOR CONTRIBUTIONS**

Rocío Moriche: Conceptualization; methodology; investigation; writing-original draft; writing-review & editvisualization; project administration; funding ing;

acquisition. Ricardo Donate: Conceptualization; methodology; investigation; writing-original draft; writingreview & editing; visualization. Andrea Otero: Investigation; visualization. Lucía Santiago-Andrades: Investigation. Elena Monzón: Investigation. María Jesús Sayagués: Methodology; investigation; writing-review & editing. Mario Monzón: Conceptualization; writingreview & editing; supervision; project administration; funding acquisition. Rubén Paz: Methodology; writing-review & editing; supervision; project administration; funding acquisition.

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### DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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