## ARTICLE

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# Poly(vinylidene fluoride)/thermoplastic polyurethane flexible and 3D printable conductive composites

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#### Abstract

This work focus on the development of polymeric blends to produce multifunctional materials for 3D printing with enhanced electrical and mechanical properties. In this context, flexible and highly conductive materials comprising poly(vinylidene fluoride)/thermoplastic polyurethane (PVDF/TPU) filled with carbon black-polypyrrole (CB-PPy) were prepared by compression molding, filament extrusion and fused filament fabrication. In order to achieve an optimal compromise between electrical conductivity, mechanical properties and printability, blends composition was optimized and different CB-PPy content were added. Overall, the electrical conductivities of PVDF/TPU 50/50 vol% co-continuous blend were higher than those found for PVDF/TPU 50/50 wt% (i.e., 38/62 vol%) composites at same filler content. PVDF/TPU/CB-PPy 3D printed samples with 6.77 vol% filler fraction presented electrical conductivity of 4.14 S m<sup>-1</sup> and elastic modulus, elongation at break and maximum tensile stress of 0.43 GPa, 10.3% and 10.0 MPa, respectively. These results highlight that PVDF/TPU/CB-PPy composites are promising materials for technological applications.

### KEYWORDS

carbon black, co-continuous polymer blends, fused filament fabrication, polypyrrole

#### 1 INTRODUCTION

Additive manufacturing (AM), also called 3D printing, has recently attracted great attention in the field of prototyping due to its low cost, reduced lead time and production of complex structures without a mold tooling.<sup>1-3</sup> There are various different AM technologies and fused filament fabrication (FFF) is the most popular between them due to its simplicity, the possibility of large scale production, large materials selection and reduced cost.<sup>4</sup> In this technique, a thermoplastic filament is extruded through a heated nozzle and the material is deposited layer by layer on a heated bed. The most common commercial filaments employed in FFF are poly(acrylonitrile-co-butadiene-co-styrene) (ABS), poly(lactic acid) (PLA), polyamide and glycol-modified

polyethylene terephthalate (PETG).<sup>1-4</sup> Recent advances in this technology have also allowed to use highperformance materials with functional properties.<sup>5-10</sup> In this framework, the development of electrically conductive polymer composites (ECPCs) filaments are an important example for the manufacturing of multi-functional components using FFF technique. The addition of carbonaceous nanofillers in materials for additive manufacturing has been recently explored.<sup>11</sup> Various fillers, such as carbon nanotubes (CNT),<sup>5,6,9,12-14</sup> carbon black (CB),<sup>8</sup> graphene (GR)<sup>15-17</sup> and others, have been added to polymer matrices to improve the electrical and thermal conductivity, mechanical strength, modulus of elasticity and toughness of components fabricated by FFF. These materials have the potential to be used in several technological applications, including chemical sensors,<sup>6</sup> flexible electronic devices,<sup>1,5,9,15,18</sup> electrical circuit printing,<sup>8,19</sup> electromagnetic interference (EMI) shielding.<sup>20–23</sup>

In order to minimize the cost and to avoid loss of mechanical properties and printability of the insulating polymer matrix, one of the challenges in the development of ECPCs filaments is to achieve the highest conductivity values at the lowest conductive filler concentration. When a conductive filler is added into the insulating polymer matrix, the melt flow index (MFI) of the material filament decreases abruptly.<sup>13,20,21,23</sup> Furthermore, with increasing of the conductive filler content, a ductile to brittle transition for specimens produced by FFF have been reported.<sup>13,24–26</sup> In general, the tensile modulus and strength values increase with increasing the conductive filler content, while the elongation at break decreases. In fact, Dorigato et al.<sup>13</sup> have demonstrated that the printability of the ABS/CNT composites was partially impaired for conductive filler concentration above 4 wt%. Moreover, the mechanical properties and electrical resistivity of the ABS/CNT composites depend on the growing direction.<sup>22</sup> Anisotropy of the objects produced using FFF technique has been demonstrated in the open literature.<sup>13,24–28</sup> In addition, due to the presence of voids, the electrical conductivity and mechanical properties of samples prepared via FFF are most often lower than those of specimens produced by using compress-molding process.

A great effort has been made to overcome printing limitation and to improve the quality and properties of the conducting polymer components fabricated via FFF.<sup>5,10,13,17,20–23,26,29</sup> For this purpose, in several works the optimization of the 3D printing parameters has been investigated.<sup>7,13,24–28</sup> On the other hand, the production of filaments containing two or more conductive fillers into an insulating polymer matrix $^{20,22}$  or a modified conductive filler<sup>5</sup> have been demonstrated to be quite efficient to overcome these problems. For example, Schmitz et al.<sup>22</sup> and Dul et al.<sup>30</sup> reported results on the production of hybrid composites with good printability, mechanical properties and electromagnetic shielding efficiency. On the other hand, Ahmed et al.<sup>5</sup> have produced conductive polymer composites of polymethylmethacrylate (PMMA) and CNTs physically modified with an ionic liquid (IL), which acts as a plasticizer and dopant for the CNTs. The PMMA/CNT composites exhibited strain at break varying between 50% and 250% and electrical conductivity depending on the conductive filler content. The highest conductivity of 520 S m<sup>-1</sup> was achieved by using 15 wt% CNT content.

In this context, the preparation of polymer blends to be used as matrix in polymer composites has been used as a strategy to improve mechanical and electrical properties.<sup>31–34</sup> Recently, many works have been focused on the preparation of co-continuous immiscible polymer blends to reduce percolation threshold in ECPCs and to improve mechanical properties and printability of

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composites filaments.<sup>22,32–35</sup> The development of a material filament based on co-continuous polymer blends containing conductive filler can be an interesting alternative for the production of structural and highly conductive components by FFF. A potential advantage of cocontinuous blends is the reduction of the percolation threshold because the particles of the conductive filler could be preferentially localized in one of the two phases or at the interface (double percolation). In fact, conductive fillers, as carbon nanotubes and carbon black, have been found to be selectively distributed in one of the cocontinuous phase or at the interface of the phases in polymeric blends.<sup>29,34,36-38</sup> The localization of the conductive filler in co-continuous polymer blends is affected by thermodynamic, kinetic factors and melt viscosity. To the best of our knowledge, the production of insulating polymeric blends to control morphology and properties have been already proposed,<sup>32-35,38-40</sup> however, only a few studies are reported on its use in FFF.<sup>31</sup>

Moreover, among polymer blends, composites based on poly(vinylidene fluoride) (PVDF) and thermoplastic polyurethane (TPU) have been reported due to the possibility of producing high-performance engineering materials for various industrial applications,<sup>41,42</sup> such as electromagnetic interference (EMI) shielding<sup>32</sup> and energy harvesting.<sup>43</sup> In fact, PVDF can display piezoelectric behavior under proper crystalline conditions,<sup>44</sup> and some researchers claim that blending PVDF with TPU is an efficient way to prepare materials with an excellent combination of mechanical flexibility and properties.41-43 pvroelectric/piezoelectric Additionally. Menon et al.<sup>32</sup> showed a good improvement in EMI shielding capability by adding alloy particle/multi-walled carbon nanotubes (MWNT) localized in one phase of PVDF/TPU cocontinuous blends. Although the addition of conductive filler into PVDF/TPU co-continuous blends are an interesting strategy to combine the good mechanical properties of polymeric blends to electrical properties of the conductive filler, only one study has been found in the open literature<sup>32</sup> and it is not related to the development of material filament.

To overcome the above mentioned limitations and the lack of studies on the production of flexible and highly electrical conductive filaments for fused filament fabrication, this study proposes the preparation of a polymeric blend composed of PVDF and TPU as matrix comprising different volume fractions of carbon black doped with polypyrrole (CB-PPy) as conductive filler.

#### 2 | EXPERIMENTAL

#### 2.1 | Materials

The poly(vinylidene fluoride) used in this study, (PVDF 24), was purchased from Amboflon<sup>®</sup> with a relative

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density of 1.78 g cm<sup>-3</sup>, melt flow index of 22 g 10 min<sup>-1</sup> and electrical conductivity of  $10^{-13}$  S cm<sup>-1</sup>. The thermoplastic polyurethane is a Desmopan<sup>®</sup> DP 6064 A, from Covestro, with relative density of 1.09 g cm<sup>-3</sup> and electrical conductivity of  $10^{-11}$  S cm<sup>-1</sup>. Carbon black doped with polypyrrole was purchased from Sigma Aldrich (80 wt% of carbon black) with electrical conductivity 3 x  $10^{1}$  S cm<sup>-1</sup>.

### 2.2 | Sample preparation

### 2.2.1 | Preparation of PVDF/TPU blends

PVDF/TPU blends were produced by melt mixing using a Thermo-Haake Polylab QC Rheomix internal mixer (Thermo Haake, Karlsruhe, Germany) consisting of an internal volume of 50 cm<sup>3</sup>. The polymers were dried overnight at 60°C and the processing was carried out with a rotor speed of 50 rpm, at 180°C for 15 min. The compositions of the blends are shown in Table 1. The blends composed of 50/50 and 38/62 vol% of PVDF/TPU were selected as matrix for the composites preparation due to the formation of a co-continuous phase and high flexibility, respectively.

# 2.2.2 | Preparation of composites containing CB-PPy

The carbonaceous filler carbon black doped with polypyrrole (CB-PPy) was incorporated into the selected matrices by melt mixing using the internal mixer. First, previous defined amounts of PVDF and TPU were added in the mixing chamber and after 2 min, the conductive filler was introduced and left mixing for 13 min more. The composition of each mixture is shown in Table 1. For compression molded samples, different filler contents were selected up to 10 vol% (the percolation threshold is expected to be in this range) to evaluated the effect of the filler quantity on the materials properties. According to the electrical conductivity measurements and calculation of the percolation threshold, three compositions were selected to be printed via FFF.

### 2.2.3 | Compression molding

The mixtures reported in Table 1 were compression molded in square plaques  $(120 \times 120 \text{ mm}^2)$  with a thickness of 2 mm by a Carver Laboratory press (Carver, Inc. Wabash, IN, USA) at  $180^{\circ}$ C applying a pressure of

**TABLE 1** Formulations of PVDF/TPU blends, PVDF/TPU/CB-PPy blend composites, and their processing technique: Compression molding (CM), filament and 3D printing

	Material composition		Processing technique			
Sample	PVDF (vol%)	TPU (vol%)	CB-PPy (vol%)	СМ	Filament	3D printing
TPU	100	0	-	Х	-	-
PVDF	100	0	-	Х	Х	Х
PVDF/TPU	59	41	-	Х	-	-
PVDF/TPU	50	50	-	Х	-	-
PVDF/TPU	48	52	-	Х	-	-
PVDF/TPU	38	62	-	Х	Х	Х
PVDF/TPU/CB-PPy-1.83% (38/62 vol%)	37.30	60.87	1.83	Х	-	-
PVDF/TPU/CB-PPy-3.12% (38/62 vol%)	36.81	60.07	3.12	Х	Х	Х
PVDF/TPU/CB-PPy-3.74% (38/62 vol%)	36.58	59.68	3.74	Х	Х	Х
PVDF/TPU/CB-PPy-4.39% (38/62 vol%)	36.33	59.28	4.39	Х	-	-
PVDF/TPU/CB-PPy-6.33% (38/62 vol%)	35.59	50.08	6.33	Х	-	-
PVDF/TPU/CB-PPy-9.71% (38/62 vol%)	34.31	55.98	9.71	Х	-	-
PVDF/TPU/CB-PPy-0.64% (50/50 vol%)	49.68	49.68	0.64	Х	-	-
PVDF/TPU/CB-PPy-1.30% (50/50 vol%)	49.35	49.35	1.30	Х	-	-
PVDF/TPU/CB-PPy-1.96% (50/50 vol%)	96.04	96.04	1.96	Х	-	-
PVDF/TPU/CB-PPy-3.29% (50/50 vol%)	48.35	48.35	3.29	Х	-	-
PVDF/TPU/CB-PPy-3.96% (50/50 vol%)	48.02	48.02	3.96	Х	-	-
PVDF/TPU/CB-PPy-6.77% (50/50 vol%)	46.61	46.61	6.77	Х	Х	Х



**FIGURE 1** Filaments of the blend PVDF/TPU 38/62 vol% and composites comprising different amount of conductive filler [Color figure can be viewed at wileyonlinelibrary.com]

3.9 MPa for 10 min and after samples characterization, specific compositions were selected to prepare the filaments for posterior fused filament fabrication.

### 2.2.4 | Filaments extrusion

The selected mixtures prepared by melt mixing were immersed in liquid nitrogen before grinding. Then the obtained powders were extruded using a Estru 13 single screw extruder (Friul Filiere SpA, Udine, Italy) with four temperature zones, 130, 170, 175, and 180°C and screw speed of 30 rpm. The final filament diameter was set to  $1.75 \pm 0.10$  mm (Figure 1).

#### 2.2.5 | Fused filament fabrication

The filaments with composition displayed in Table 1 were used to feed the 3D printing machine and the samples were printed by a prototype 3D printer, Sharebot Next Generation desktop 3D printer (Sharebot NG, Nibionno, LC, Italy) based on the fused filament fabrication technology. The design and parameters were settled using the open source software Slic3r and the printing parameters are shown in Table 2. The specimens were build-up along horizontal alternate (H45) direction, as shown in Figure 2, where the first layer was  $45^{\circ}$  to the origin and the following layers were deposited  $90^{\circ}$  with respect to the previous one. The specimens were printed in circular format (diameter 15 mm and thickness 2 mm) and dumbbell format according to ISO 527 type 1BA (Figure 3) (gauge length 30 mm, width 5 mm and thickness 2 mm).

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**TABLE 2** fused filament fabrication printing parameters

Parameter	Value
Nozzle temperature	230°C
Bed temperature	$40^{\circ}C$
Nozzle diameter	0.4 mm
Nozzle speed	$16 \text{ mm s}^{-1}$
Layer height	0.2 mm
Number of layers	10
Infill density	100%

## 2.2.6 | Testing techniques

The electrical conductivity of the high-conductive samples was measured according to the ASTM D4496-04 standard with a four-probe configuration. The voltage source was a DC power supply produced by ISO-TECH IPS303DD (ISO-TECH, Milan, Italy) and the current flow was measured between external electrodes by a pocket multimeter electrometer ISO-TECH IDM 67 (ISO-TECH, Milan, Italy) with an internal electrode (i.e., 3.69 mm). The samples were cut in regular specimens of  $36.9 \times 5 \times 2 \text{ mm}^3$  and the measurements were taken on both side of three specimens. For the high-resistive samples a two-probe standard method was performed by a Keithley 6517A electrometer/high resistance meter (Beaverton, OR, USA) connected to a resistivity test fixture Keithley 8009. The thickness of the samples was 2.0 mm and the tests were performed on both sides of each sample.

Mechanical properties were measured by tensile test using an electromechanical testing machine, Instron<sup>®</sup> 5969 (Norwood, MA, USA) with a 50-kN load cell. The elastic modulus of the specimens was evaluated using an electrical extensometer model 2620–601 with a gauge length of 12.5 mm at a crosshead speed of 1 mm min<sup>-1</sup> until 1% of deformation. Fracture properties were determined at a crosshead speed of 100 mm min<sup>-1</sup>. Five specimens of each composition were analyzed in dumbbell format, according to ISO 527 type 1BA (gauge length 30 mm, width 5 mm and thickness 2 mm).

Dynamic mechanical analysis (DMA) was carried out under tensile mode using a Netzsch DMA 242 E (Netzsch, Germany) device in order to obtain the storage (E') and loss (E'') modules curves as a function of temperature. Also, the  $T_g$  values were calculated from the tan  $\delta$ maximum peak (ratio between E'' and E') for neat polymers, blends and composites to evaluate the fillers effect on PVDF/TPU  $T_g$  value. Rectangular specimens with 20 x 5 x 2 mm<sup>3</sup> with a gauge length of 10 mm were tested. The tests were performed for one sample of each composition from -80 to  $100^{\circ}$ C applying a maximum

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**FIGURE 2** Schematic representation of dumbbell specimens ISO 527 type 1BA for (a) the first layer and (b) after the deposition of the second layer [Color figure can be viewed at wileyonlinelibrary.com]



**FIGURE 3** 3D printed samples of the blend PVDF/TPU 38/62 vol% and the composite PVDF/TPU/CB-PPy 6.77 vol% (50/50 vol%) [Color figure can be viewed at wileyonlinelibrary.com]

dynamic strain of 50  $\mu$ m at a heating rate of 3°C min<sup>-1</sup> and frequency of 1 Hz.

Scanning electron microscopy (SEM) observations were performed to investigate the morphology of the blends and the conductive composites. Also, the fillers dispersion and distribution in the PVDF/TPU matrix was investigated. SEM coupled with energy dispersive X-ray spectroscopy (EDS) was also performed to assist in the phases identification. The analysis was carried out on different regions of fractured surfaces of one sample of each composition using a Tescan VEGA3 field emission scanning electron microscope (Tescan, Czech Republic) at an acceleration voltage of 5.0 kV coupled with an Oxford Instrument X-act model 51-ADD0007 (Oxford Instruments, United Kingdom). In addition, SEM and EDS analysis were also performed after etching out the TPU phase. Composites samples of 20 x 20 x 2 mm were immersed in THF and let for 4 h in a sonication bath and then dried at room temperature for 24 h.

The density of 3D printed samples was experimentally measured by weighting circular samples (15x2 mm) in the air and calculated according to Equation (1):

$$\rho_{ex} = \frac{m}{V}, \qquad (1)$$

where d is the experimental density  $(g \text{ cm}^{-3})$ , m is the weight (g) and V the calculated volume (cm<sup>3</sup>). Three



**FIGURE 4** Tensile curves for PVDF/TPU blends with different proportions of each component [Color figure can be viewed at wileyonlinelibrary.com]

specimens of each sample were measured. The theoretical density was predicted based on the rule of mixtures following the Equation:

$$\rho_{th} = \rho_{p1} \times V_{p1} + \rho_{p2} \times V_{p2} + \rho_{p3} \times V_{p3}, \qquad (2)$$

where  $\rho_{p1}$ ,  $\rho_{p2}$ , and  $\rho_f$  are the densities of polymer 1, polymer 2, and conductive filler, respectively, and  $V_{p1}$ ,  $V_{p2}$ ,  $V_f$  are the volume fraction of each of these materials. In addition, the content of voids (*V*%) was measured according to Equation (3):

$$V\% = \frac{\rho_{th} - \rho_{ex}}{\rho_{th}} \times 100. \tag{3}$$

### 3 | RESULTS AND DISCUSSION

# 3.1 | PVDF/TPU blends produced by compression molding

Tensile tests were carried out in order to investigate the mechanical properties of the PVDF/TPU blends and the

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TABLE 3 Mechanical properties of PVDF/TPU blends including average values and standard deviation

PVDF/TPU (vol%/vol%)	Elastic modulus (MPa)	Maximum tensile stress (MPa)	Elongation at break (%)
100/0	$2424.7 \pm 74.2$	$56.9 \pm 1.2$	$21.4 \pm 8.4$
59/41	733.4 ± 70.6	$19.8 \pm 0.9$	$38.9 \pm 26.1$
50/50	$287.8 \pm 39.1$	$10.9 \pm 0.9$	$27.5 \pm 6.4$
48/52	87.6 ± 19.9	$13.1 \pm 0.8$	$117 \pm 22.2$
38/62	$41.2 \pm 14.8$	$5.5 \pm 1.1$	$153 \pm 81.4$
0/100	$7.0 \pm 0.4$	n.m.	n.m.

Abbreviation: n.m., not measureable.



**FIGURE 5** SEM images at 1000 x of magnification of (a) neat TPU; (b) neat PVDF; PVDF/TPU: (c) 38/62 vol%, (d) 50/50 vol% and (e) 59/41 vol%. Red arrows indicate PVDF phase in the blends [Color figure can be viewed at wileyonlinelibrary.com]

tensile stress and tensile strain curves obtained from the fracture test are shown in Figure 4. The tensile strength decreases proportionally to the amount of TPU in the blends. The highest strength is achieved in neat PVDF, 56.9 MPa, and it significantly drops to 5.5 MPa (i.e., 90%) as increasing the TPU content to 62 vol %. In addition, the tensile properties, which are summarized in Table 3, show that increasing the TPU content in the PVDF leads to reduce the elastic modulus and increase elongation at break due to the elasticity of TPU. The most flexible blend was that one with higher amount of the elastomeric component, (PVDF/TPU 38/62 vol%), thus this composition was selected to be used as matrix for the conductive composites production. However, some

studies claim that to achieve a co-continuous phase, which assists in the reduction of the percolation threshold in conductive composites, a concentration of 50 vol% of each polymer is necessary.<sup>33</sup> For this reason, the blend PVDF/TPU 50/50 vol% was also selected as matrix to prepare the composites.

In order to investigate the formation of a cocontinuous phase, the microstructure of prepared blends was analyzed by scanning electron microscopy. As reported in the SEM images of Figure 5, all samples present gross phase-separated morphology, which is typical of heterogeneous incompatible blends.

The micrograph of the blend with 38 vol% of PVDF (see Figure 5(c)) shows that PVDF is in smaller volume



**FIGURE 6** (a) EDS mapping and (b) EDS spectrum of PVDF/TPU 50/50 vol% at x1000 magnification; SEM images of the etched blend at magnifications of (c) x150 and (d) x500; (e) EDS mapping and (f) EDS spectrum of the etched blend at x1000 magnification [Color figure can be viewed at wileyonlinelibrary.com]

amount and thus dispersed in the TPU phase. Nevertheless, when the PVDF content in the blend is raised to 50 vol% of (see Figure 5(d)), it is possible to observe the presence of a co-continuous morphology as the two polymers are present in the blend in the same volume quantity. When PVDF becomes the prevalent phase in the blend (Figure 5(e)) the microstructure becomes more homogeneous. Furthermore, the blend PVDV/TPU comprising 50 vol% of each polymer was analyzed by SEM coupled with EDS to investigate the composition of each phase. Figure 6(a) shows the EDS mapping image of the blend, where the green color represents regions containing fluorine (present in PVDF), oxygen (present in TPU) is indicated in blue and nitrogen in pink. The EDS spectrum for the blend is presented in Figure 6(b). In addition, the blend was etched with tetrahydrofuran

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**FIGURE 7** DMA results (a) storage modulus and (b) loss tangent as function of temperature for neat TPU, neat PVDF and blends with different compositions [Color figure can be viewed at wileyonlinelibrary.com]

**TABLE 4**  $T_g$  values for neat TPU, neat PVDF and PVDF/TPU blends

Sample	$T_g$ value (°C)
TPU	-25.0
PVDF/TPU 38/62 vol%	-29.4
PVDF/TPU 50/50 vol%	-32.4
PVDF/TPU 59/41 vol%	-36.1
PVDF	-39.2



Sample	С	$f_p$	t	$R^2$
PVDF/CB-PPy	0.44	0.80	3.86	0.99
TPU/CB-PPy	0.47	3.04	2.21	0.99
PVDF/TPU/CB-PPy (38/62 vol%)	0.73	3.10	2.19	0.99
PVDF/TPU/CB-PPy (50/50 vol%)	0.45	1.30	3.10	0.99



**FIGURE 8** Electrical conductivity of PVDF/CB-PPy, TPU/CB-PPy, PVDF/TPU/CB-PPy 38/62 and 50/50 vol% as function of filler volume fraction [Color figure can be viewed at wileyonlinelibrary.com]

(THF) to remove the TPU phase. Figure 6(c),(d) show the SEM images for the etched blend supporting the claim of a blend with co-continuous morphology. Moreover,



**FIGURE 9** Tensile curves for PVDF/TPU/CB-PPy composites with different proportions of each component [Color figure can be viewed at wileyonlinelibrary.com]

Figure 6(e) displays the EDS mapping of the etched blend confirming that most part of TPU phase was removed and Figure 6(f) containing the EDS spectrum for the etched blend shows the reduction in the amount of oxygen presenting in the sample related to the TPU phase.

**TABLE 6** Mechanical properties of PVDF/TPU blends and composites from compression molding including average values and standard deviation

Matrix: PVDF/TPU (38/62 vol%)	Elastic	Maximum tensile	Elongation at
CB-PPy (vol%)	modulus (MPa)	stress (MPa)	break (%)
0	$41.2 \pm 14.8$	$5.5 \pm 1.1$	153 ± 81
3.74	125.9 ± 7.2	$7.0 \pm 0.7$	$22.0 \pm 9.1$
6.33	$210.0 \pm 18.4$	$8.0 \pm 0.4$	$16.0 \pm 3.8$
Matrix: PVDF/TPU (50/50 vol%)	Elastic	Maximum tensile	Elongation at
CB-PPy (vol%)	modulus (MPa)	stress (MPa)	break (%)
Matrix: PVDF/TPU (50/50 vol%)	Elastic	Maximum tensile	<b>Elongation at</b>
CB-PPy (vol%)	modulus (MPa)	stress (MPa)	<b>break (%)</b>
0	287.8 ± 39.1	10.9 ± 0.9	27.5 ± 6.4
Matrix: PVDF/TPU (50/50 vol%)	Elastic	Maximum tensile           stress (MPa)           10.9 ± 0.9           9.0 ± 1.5	Elongation at
CB-PPy (vol%)	modulus (MPa)		break (%)
0	287.8 ± 39.1		27.5 ± 6.4
3.96	259.1 ± 34.6		10.3 ± 3.9

The storage modulus E' and loss tangent (tan  $\delta$ ) as measured from dynamic mechanical thermal analysis are reported in Figure 7. The storage modulus (E') as function of temperature is displayed in Figure 6(a). Neat PVDF shows higher storage modulus then those found for the blends containing TPU and neat TPU. The storage modulus decreases with the increasing of TPU in the blends leading to a more flexible material, as expected. The trend of storage modulus is the same previously observed for the tensile Young's modulus. Moreover, the glass transition temperature  $(T_g)$  determined as a peak of tan  $\delta$  values are presented in Table 4. For neat TPU and neat PVDF the  $T_g$  are -25.0 and -39.2°C, respectively. For immiscible polymer blends, it is expected two distinct  $T_g$  values. However, the  $T_g$  of PVDF and TPU are in a narrow temperature range and the results show only one  $T_g$  value between those observed for the neat polymers. The blend  $T_g$  is related to the amount of each polymer present in the blend. The blend composed of 38 vol% of PVDF shows a  $T_g$  value of  $-29.4^{\circ}$ C. When the PVDF percentage is increased to 50 vol% the  $T_g$  decreases down to -32.4°C. Also, the blend containing higher amount of PVDF (59 vol%) presents a lower  $T_g$  at -36.1°C. This means that increasing the percentage of PVDF in the blends, which has lower  $T_g$  than TPU, the blends  $T_g$ decreases proportionally.

# 3.2 | PVDF/TPU/CB-PPy samples produced by compression molding

According to the above mentioned analysis and the potential achievement of a co-continuous phase, the blends PVDF/TPU 38/62 vol% and PVDF/TPU 50/50 vol% were selected to be used as matrix to produce the electrically conductive polymeric composites.

Electrical resistivity tests were performed to evaluate the electrical conductivity of the materials as function of volume fraction of conductive filler. The curves of electrical conductivity versus content of filler for the different composites (PVDF, TPU and PVDF/TPU composites) are summarized in Figure 8.

As reported in Figure 8, the electrical conductivity of the composites increases with the content of CB-PPy. According to the classical percolation theory, the dependence of the electrical conductivity ( $\sigma$ ) of composites on the electrically conductive filler concentration (f) above the percolation concentration threshold ( $f_p$ ) can be described by a scaling law in the form of the following power law equation<sup>45</sup>:

$$\sigma = c \left( f - f_p \right)^t, \tag{4}$$

where *c* is a fitting constant and *t* the critical exponent. These values are presented in Table 5. The theoretical predictions of *t* are related to the system dimension and the calculated *t* values are in agreement to the classical theory for tridimensional systems ranging from 2 to  $4.^{46,47}$ 

The percolation threshold for PVDF/CB-PPy and TPU/CB-PPy composites resulted to be 0.8 and 3.04 vol%, respectively. On the other hand, the electrical percolation threshold for CB-PPy in a PVDF/TPU 50/50 vol% matrix and in a PVDF/TPU 38/62 vol% matrix were 1.3 and 3.1 vol%, respectively. According to Bizhani et al.,<sup>40</sup> a co-continuous immiscible polymer blend decreases the electrical percolation threshold due to the selective localization of the filler in one of the phases or at the interface of phases. Our results show that blending PVDF and TPU can improve the percolation threshold of the mixtures when both components are present in 50 vol% in the composite and a co-continuous structure is formed.

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**FIGURE 10** SEM images of: (a) and (b)TPU/ CB-PPy 3.04 vol%; (c) and (d) PVDF/CB-PPy 4.86 vol% and (e) and (f) PVDF/TPU/CB-PPy 3.96% (50/50 vol%) at different magnifications (a, c, e: x5000 and b, d, f: x10000)

According to the electrical conductivity values, some composites were selected to perform further characterizations. Tensile curves for composites with 38/62 and 50/50 vol% of PVDF/TPU as matrix are represented in Figure 9 and mechanical properties of the samples are shown in Table 6. The results indicate that the incorporation of the filler into the blends rises the rigidity of the mixtures, increasing the elastic modulus and reducing the elongation at break. In addition, the same occurs when comparing the composites comprising the different matrices: PVDF/TPU 38/62 and 50/50 vol%. The blends comprising higher amount of PVDF (50 vol%), at the same filler concentration, show higher elastic modulus and lower elongation at break due to the presence of less quantity of the elastomeric component (TPU).

SEM images of the conductive composites are displayed in Figure 10. Figure (a) and (b) show the morphology of TPU comprising 3.04 vol% of CB-PPy and Figure (c) and (d) of PVDF comprising 4.86 vol% of the filler. The SEM pictures reveal that the microstructure of the investigated materials is not substantially affected by the introduction of the CB-PPy conductive filler.

Furthermore, Figure 11(a)–(c) show the SEM image, EDS mapping and EDS spectrum of the composite PVDF/TPU/CB-PPy 3.96% (38/62 vol%). In the EDS mapping image is possible to see that the phases are present in a co-continuous morphology and the composition of each phase, where the green color represents the atoms of fluorine present in PVDF and the blue and pink color the atoms of oxygen and nitrogen, respectively, present

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**FIGURE 11** (a) SEM image at x5000 of magnification; (b) EDS mapping and (c) spectrum at x1000 of magnification of PVDF/TPU/CB-PPy 3.96% (50/50 vol%); (d) SEM image and (e) EDS spectrum of PVDF/TPU/CB-PPy 3.96% (50/50 vol%) etched with THF to remove TPU phase at x500 magnification showing the presence of PVDF in the unetched phase [Color figure can be viewed at wileyonlinelibrary.com]

in TPU. Since the conductive filler is composed of carbon black-polypyrrole, it is not possible to observe using this technique where the filler is localized. In addition, the composites were immersed in THF to remove the TPU phase. The SEM image of the etched composite is displayed in Figure 11(c) showing the remaining PVDF continuous phase and its composition can be confirmed by the EDS spectrum present in Figure 11(d).

# 3.3 | PVDF/TPU/CB-PPy composites by fused filament fabrication

After electrical conductivity measurements and calculation of the percolation threshold, the composites comprising 3.12 and 3.74 wt% of conductive filler were extruded into filament format and subsequently 3D printed using FFF technique. Those were the

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TABLE 7	Mechanical properties of selected compositions of 3D printed parts via fused filament fabrication including average values
and standard c	deviation

Matrix: PVDF/TPU (38/62 vol%) CB-PPy (vol%)	Elastic modulus (MPa)	Maximum tensile stress (MPa)	Elongation at break (%)
0	$35.8 \pm 0.1$	$3.1 \pm 0.2$	$261 \pm 89.4$
3.12	$179.9 \pm 46.6$	$6.7 \pm 0.3$	38.6 ± 9.8
3.74	$301.3 \pm 32.7$	$8.6 \pm 0.8$	35.5 ± 17.1
Matrix: PVDF/TPU (50/50 vol%) CB-PPy (vol%)	Elastic modulus (MPa)	Maximum tensile stress (MPa)	Elongation at break (%)
6.77	430.6 ± 13.0	$10.0 \pm 2.2$	$10.3 \pm 1.5$



**FIGURE 12** Tensile curves of PVDF/TPU composites 3D printed via fused filament fabrication comprising different amounts of conductive filler [Color figure can be viewed at wileyonlinelibrary.com]

compositions that achieved good electrical conductivity values at lowest filler concentration for compression molded samples. However, after the printing process the electrical conductivity of the specimens decreased significantly. In order to prepare highly conductive printed parts, the composite comprising 6.77 vol% of CB-PPy was also selected for the 3D printing process.

The mechanical properties of 3D printed parts were analyzed by tensile tests and the results are presented in Table 7. As expected, the composites with higher amount of filler showed higher elastic modulus and lower elongation at break. Furthermore, the tensile curves from fracture tests of 3D printed specimens are displayed in Figure 12. For samples with same composition, the maximum tensile stress is higher in compression molded than in 3D printed specimens due to the less amount of defects presented in the compressing molded final parts. It is well known that FFF printed parts often show lower mechanical performance when compared to compression or injection molded parts because of porosity and poor interlayer bonding.

The micrographs of the cross-sections of 3D printed specimens are presented in Figure 13. The images exhibit the boundaries between the layers deposited during the FFF process. It is also possible to see the presence of voids, mainly in Figure 11(a),(b) between the layers. Moreover, according to the images, with the increasing in the filler content there is an increasing in the layer adhesion and decreasing in the quantity of voids leading to a better compacted material. However, according to the measurement of percentage of voids (see Table 8), the increasing in the filler content leads to higher quantity of voids. It can be explained because the cross-section fractures show only the morphology between the layers and they do not show the voids present between the deposited filaments on a single layer. As the addition of conductive filler rises the viscosity of the composite filaments causing a reduction in the filament flow through the extruding nozzle, less amount of material is deposited in the printing process leading to higher porosity in a single laver.

For all composites, the 3D parts presented an electrical conductivity lower than the compression molded samples with same composition. The presence of voids and defects in 3D printed parts may explain the significant drop observed in the electrical conductivity values. Although the compression molded samples containing 3.74 vol% of CB-PPy showed an electrical conductivity of  $1.94 \times 10^{-1}$  S m<sup>-1</sup>, the 3D printed samples with same composition presented a significant lower value of electrical conductivity. On the other hand, for the composite containing 6.77 vol% of CB-PPy and a co-continuous PVDF/TPU matrix, even after the 3D printing process the electrical conductivity was  $4.14 \times 10^{0}$  S m<sup>-1</sup>, only one order of magnitude lower than the compression molded counterparts (as shown in Table 9), thus indicating a promising use of this filaments for technological applications that require electrical conductivity.

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FIGURE 13 SEM images at

(50/50 vol%)

200x of magnification of 3D printed specimens of: (a) PVDF/TPU 38/62 vol%, (b) PVDF/TPU/CB-PPy 3.12% (38/62 vol%), (c) PVDF/TPU/ CB-PPy 3.74% (38/62 vol%) and (d) PVDF/TPU/CB-PPy 6.77% (a) 200 µm (b) 200 µm (c) 200 µm 200 µm 200 µm 200 µm

**TABLE 8**Experimental and theoretical density and % of voidsfor 3D printed parts

Sample: PVDF/ TPU/CB-PPy	Experimental density (g.cm <sup>-3</sup> )	Theoretical density (g.cm <sup>-3</sup> )	% of voids
3.12% (38/62 vol%)	1.18	1.38	15
3.74% (38/62 vol%)	1.09	1.38	21
6.77% (50/50 vol%)	1.13	1.49	24

A comparison of the electrical conductivity of 3D printed nanocomposites comprising different polymers as matrix and containing carbon nanofillers is shown in Table 10. Most of the studies that present values of electrical conductivity as high as we obtained in this work report the addition of at least 3 vol% of CNT. CNT have shown to be more effective in creating a conductive network in polymeric matrices due to its higher aspect ratio, however, composites comprising CNT leads to a greater increase in the materials viscosity and are more difficult to be processed at the same filler concentration than CB-PPy composites.<sup>53</sup>

**TABLE 9** Comparison of electrical conductivity of compression molded and 3D printed samples including average values and standard deviation

Matrix: PVDF/TPU (38/62 vol%) CB-PPy (vol%)	σ compression molded (S m <sup>-1</sup> )	σ 3D printed (S m <sup>-1</sup> )
0	$(1.60 \pm 0.03) \times 10^{-11}$	$(5.90 \pm 0.30) \times 10^{-12}$
3.12	$(7.95 \pm 4.82) \times 10^{-7}$	$(9.74 \pm 7.78) \times 10^{-8}$
3.74	$(1.94 \pm 1.04) \times 10^{-1}$	$(6.01 \pm 3.72) \times 10^{-8}$
Matrix: PVDF/TPU (50/50 vol%) CB-PPy (vol%)	σ compression molded (S m <sup>-1</sup> )	σ 3D printed (S m <sup>-1</sup> )
6.77	$(1.70 \pm 0.24 \ 10^0) \times 10^1$	$(4.14 \pm 0.08) \times 10^{0}$

### 4 | CONCLUSIONS

Flexible and high electrically conductive composites comprising a co-continuous blend of PVDF/TPU as matrix and CB-PPy as conductive filler were used to produce

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Nanofiller content Matrix Type of nanofiller Electrical conductivity (S m<sup>-1</sup>) References 22 ABS CB 3 wt%  $10^{-12}$ 22 ABS CNT 3 wt%  $10^{-7}$ 20 ABS MWCNT 6 wt%  $10^{-2}$  $10^0$ 48 ABS MWCNT 10 wt% ABS  $10^{-13}$ 20 GNP 6 wt% 30 ABS GNP/CNT 6 wt% (50:50)  $10^{-3}$ 49 ABS GO 3.8 wt%  $10^{-7}$ 50 PBT  $10^1$ CNT 3.5 vol% 51 PLA CNT  $10^{0}$ 3 vol% 52 PLA r-GO  $10^{2}$ 6 wt% 18 TPU MWCNT  $10^{-1}$ 3 wt%  $10^{-4}$ 9 TPU CNT 3 wt%

TABLE 10 Comparison of electrical conductivity of nanocomposites produced via fused filament fabrication

filaments for 3D printing by FFF technique. According to the mechanical properties, the addition of TPU increased the flexibility aimed for the final parts. SEM images showed the achievement of a co-continuous blend where CB-PPy was preferable localized in the PVDF phase when the composition of the blend was 50/50 vol% of PVDF/TPU. Moreover, the electrical conductivity of all composites increased with the increasing of filler content. However, PVDF/TPU composites comprised of the blend containing 50/50 vol% of each polymer as matrix showed a lower percolation threshold (1.3 vol%) when compared with the blends comprising 38/62 vol% (3.12 vol%), confirming that the presence of a co-continuous phase assists in the reduction of the percolation threshold while improves the flexibility and printability of PVDF composites. As expected, 3D printed parts showed a lower electrical conductivity when compared to compression molded composites with same composition. Although the PVDF/ TPU 38/62 vol% composite containing 3.74 vol% of CB-PPy prepared by melting mixing presented an electrical conductivity of  $1.94 \times 10^{-1}$  S m<sup>-1</sup>, after the printing process the composite showed an electrical conductivity lower than  $10^{-7}$  S m<sup>-1</sup>. On the other hand, the composite PVDF/TPU/CB-PPy 6.77 vol% (50/50 vol%) prepared by melting mixing displayed an electrical conductivity of  $1.70 \times 10^{1}$  S m<sup>-1</sup>, while the 3D printed specimens with same composition showed an electrical conductivity of  $4.14 \times 10^{0}$  S m<sup>-1</sup>, indicating that after the printing process the material can still be potentially used for electrical conductive applications. Overall, the results demonstrate that the investigated PVDF/TPU/CB-PPy composites are promising materials for technological applications, such as electrostatic, electromagnetic shielding or flexible sensors.

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