Obtaining and Characterizing 3D Printable Polymer Based Composites with BaTiO₃ Filler

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Abstract: By the extrusion and injection technique, polymer-based composite samples (polypropylene and thermoplastic polyurethane) were obtained with BaTiO₃ filler in concentrations between 0 and 35 %. Following the preliminary characterizations performed by coupled thermal analysis techniques, it was found that the composite samples obtained have thermal stability up to a temperature of about 250 ºC and can be processed by extrusion at temperatures between 180 and 240ºC. Above this temperature, a series of degradation processes take place by successive thermooxidation with the formation of volatile products.The electrical characterization of the composite samples was performed by the dielectric spectroscopy technique, which showed that the Δtgδ dielectric losses increase as the BaTiO₃ content of the composite increases. The maximum increase being recorded at 50 Hz (the slope Δtgδ /% BaTiO₃ about 0.003 /% BaTiO₃). It was also found, that the electrical conductivity (σ) of the composite increases with the increase of content in BaTiO₃ so that σ at 100 kHz for the composite with 35 % BaTiO₃ is about 50 times higher than for the reference sample M 0 (without filler).

Keywords: composite, thermoplastic polyurethane, polypropylene, BaTiO₃, dielectric loss, conductivity

1. Introduction

The In the perspective of sustainable development, the rational use of natural resources, respectively, the development of environmentally friendly advanced materials and technologies is a priority issue [1, 2]. In this context, the development of the composite materials with specific characteristics for the most diverse applications is in the continuous attention of the scientific community and industrial developers [3]. Thus, developments of ceramic composites [4] for various medical applications [5, 6], electrodes for electrochemical synthesis [7], thin layers for photocatalysis [8], polymer-based composites with various fillers [9 - 16] are reported with uses including the electrical engineering field [17-20], etc.

The composite materials development is intended to meet the specific requirements of the target application such as biocompatibility [5, 6], flammability [21], electrical, dielectric, and/or magnetic performance [17-20], ablation [9], mechanical characteristics [14, 20], resistance to the action of microorganisms/biodegradability [11, 22, 23], etc. The development of 3D printers has opened new research directions in the field of advanced materials, respectively the performed of 3D printable materials. In this context, the purpose of the work is the realization and preliminary characterization of composites based on the thermoplastic polymer with filler BaTiO₃ for 3D printing applications.

2. Materials and methods

By the technique of extrusion and injection, composite samples based on thermoplastic polyurethane and polypropylene with BaTiO₃ filler were obtained.

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After weighing, the components (polyurethane and polypropylene pellets with $BaTiO_3$ powder) were mixed (for 30 min at speed 40 rpm) in a TURBULA T2F type cylindrical mixer.

The main characteristics of the polypropylene used (TIPPLEN H 318) [24] are shown in Table 1.

Table 1. Characteristics of TIPPLEN H 318 polypropylene [24]

Properties	Thest method	Unit	Typical value
MFR (230 ^{O}/2.16 KG)	ISO 1133	g/10min.	12
Tensile strength at yield	ISO 527-1,2	MPa	29
Tensile elongation at yield	ISO 527-1,2	%	12
Modulus of elasticity tension	ISO 527-1,2	MPa	1050
Flexural modulus	ISO 178	MPa	1000
Izod impact strengts (notched 23 ºC)	ISO 180/1A	kJ/m^2	6
HDT (0.46 N/mm^2)	ISO 75-1,2	ºC	87
Rockwell hardness	ISO 2039/2	R scale	82

The main characteristics of the polyurethane used (***Estane 58887 TPU*** supplied by Lubrizol Advanced Materials, Inc. [25]) are shown in Table 2.

Table 2. Thermoplastic polyurethane characteristics used [25]

Properties	Value	Unit	Test method
Hardness (5 sec)	87+/-3	Shore A	ASTM D-2240
Specific gravity	1.12		ASTM D-792
Tensile strength	7500	psi (MPa)	ASTM D-412
Ultimate Elongation	500	%	
Tensile strength at			ASTM D-412
-100 % Elongation	1000	psi (MPa)	
-300 % Elongation	1800	psi (MPa)	

The $BaTiO_3$ powder (<2 μm, 99.5 % trace metals basis) used was supplied by MERCK.

The composite was obtained by extruding and granulating the polyurethane/polypropylene/$BaTiO_3$ mixture on a KETSE Brabender laboratory extruder.

The size of the composite granules obtained was about 3 mm.

The working parameters on the extruder were:

- rotation speed (counter-rotation) of the extruder screws 95 rpm;

- feed speed from the feed hopper 450 rpm.

The temperatures on the heating areas of the Brabender KETSE extruder are in Table 3.

Table 3. Temperatures on the heating areas of the extruder

Area	1	2	3	4	5	6
Temperature [ºC]	180	190	200	215	230	220

For the dielectric characterization of the composite, the granules obtained by extrusion were injected (with an injection machine type Dr. Boy A35 - Germany) obtaining samples (specimens) in the form of a disc with a diameter of 30 mm and a thickness of 2.5 mm.

The working parameters on the injection machine (Boy A35 - Germany) were:

- closing force of the mold in the range: 302-317kN;

- injection pressure 550 bar;

- back pressure: 90 bar.

The temperatures of the heating areas of the injection molding machine were shown in Table 4.

Table 4. Temperatures on the heating areas of the injection molding machine

Area	5	4	3	2	1
Temperature [ºC]	220	210	200	190	180

Thus, samples with different compositions were performed. The sample coding obtained according to the composition is presented in Table 5.

Table 5. Composite samples obtained

Sample cod	Content [mass %]		
	BaTiO₃ powder	PP	TPU
M 0	0	6	94
M1	12	5.1	82.9
M2	15	5	80
M3	20	4.7	75.3
M4	25	4.5	70.5
M5	28	4.3	67.7
M6	35	4	61

The thermal characterization of both the polymeric raw materials (polyurethane and polypropylene) and of the composite obtained was performed by thermal analysis techniques on a specialized equipment type STA 449 F3 Jupiter (NETZSCH, Germany). The thermal diagrams were drawn in 50 mL/min synthetic air at a heating rate of 10°C/min. Dielectric behavior - determination of dielectric loss and conductivity vs. frequency - of the composite samples obtained was investigated at a temperature of 20 ± 2°C by dielectric spectroscopy technique with 1296 Dielectric interface / AMTEK - Solartron Analytical.

3. Results and discussions

The thermal diagrams TG + DSC + DTG recorded on the polyurethane (TPU) used to make the composite are shown in Figure 1.
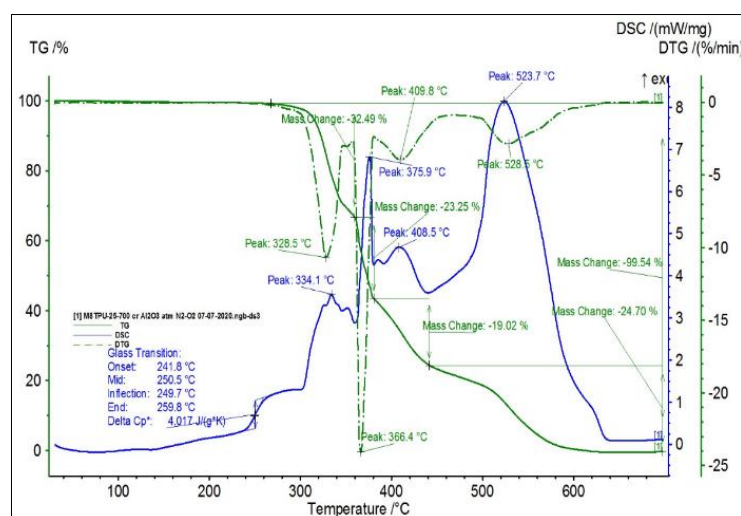

Figure 1. TG + DSC + DTG thermal diagrams
recorded on TPU

Analyzing Figure 1, from the DSC curve, it is found that at the progressive heating of TPU, the material undergoes a glass transition that starts at 241.8°C and ends at 259.8°C.

From the comparative analysis of the TG, DSC, and DTG diagrams, it is found that up to the temperature of about 280°C the material is stable after which several processes of thermooxidation take place (the first with the formation of solid peroxide products with a peak at 334.1°C) and of decomposition with the formation of volatile products, a process that ends that end at a temperature of about 600°C (when the mass loss of the sample is 100 %).

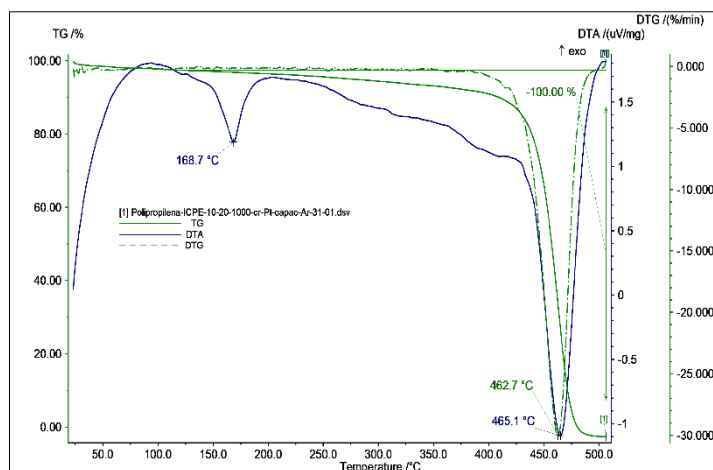The thermal diagrams TG + DSC + DTG recorded on polypropylene (PP) used to make the composite are shown in Figure 2.

Figure 2. Thermal diagrams TG + DSC + DTG recorded on PP

Analyzing the thermal diagrams in Figure 2 it is found that the PP used for obtaining the composite is a product with an ordered structure with a melting temperature of 168.7°C and stable (without processes of thermooxidation and/or decomposition) up to about 425°C.

At the temperature of 425°C, a decomposition process begins with the formation of volatile products, a process which ends at 460°C when the mass loss of the sample is 100%.

The BaTiO₃ component is a particularly stable product at temperatures below 800°C, as shown in Figure 1 and Figure 2, which indicates that the maximum temperature during processing to obtain the composite is limited by the TPU component and is up to 270°C.

The thermal TG + DSC + DTG diagrams obtained, recorded on the *M 5* sample (28 % $BaTiO_3$, 4.3 % PP and 67.7 % TPU) are presented in Figure 3.
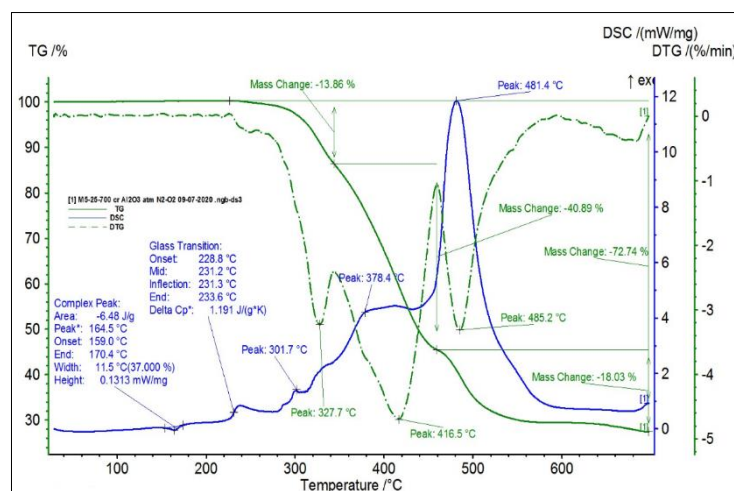

Figure 3. TG + DSC + DTG thermal diagrams recorded
on *M 5* (28 % $BaTiO_3$, 4.3 % PP and 67.7 % TPU)

From the analysis of Figure 3 it is found that at the progressive heating of the *M 5* composite obtained, at about 165°C a slightly pronounced melting endotherm process occurs, after which at 228.8°C a glass transition process begins, which indicates a biphasic structure respectively, a component with ordered structure (with crystallinity, with definite melting point) and a component with disordered structure (glass transition). The composite is stable up to about 250°C when the decomposition begins by the formation of volatile products (in a first stage, up to temperature of 360°C, the mass loss is 13.86 %) and successive exothermic thermooxidation processes (first peak at 301.7°C). Decomposition by formation of volatile products is completed at about 550°C when the total mass loss is 72.24 %, the residue of 27.76 % being

the weight in the BaTiO$_3$ composite. Based on this experimental data, it is considered that the maximum temperature at which the composite obtained can be processed and / or used is about 240°C. By comparing the Figure 3 with Figure 1 and Figure 2 it is observed that in the composite are found both the component with the ordered structure of PP (with defined doping point) and the component with the disordered structure of TPU with modified thermal parameters (glass transition at 228.8°C instead of 241.8°C, first peak of thermooxidation occurs at 301.7°C instead of 334.1°C etc.).

These changes of the thermal parameters of the phase with disordered structure TPU from Figure 3 (compared to Figure 1) suggest that the initial structure of TPU changed following contact with molten PP during applied heat treatments (extrusion and injection). The thermal diagrams recorded on the other composite samples (*M 1, M 2, M 3, M 4* and *M 6*) were practically identical to those recorded on *M 5*, the only differences being recorded at the total mass loss that changes according to the BaTiO$_3$ content of the respective samples. This finding indicates that the polymeric component formed during the composite processing (mixing, extrusion and injection) has a homogeneous structure. By processing the experimental data obtained by dielectric spectroscopy (real and imaginary components of complex permittivity vs. frequency), the dielectric loss *tgδ* of the investigated material samples was determined.

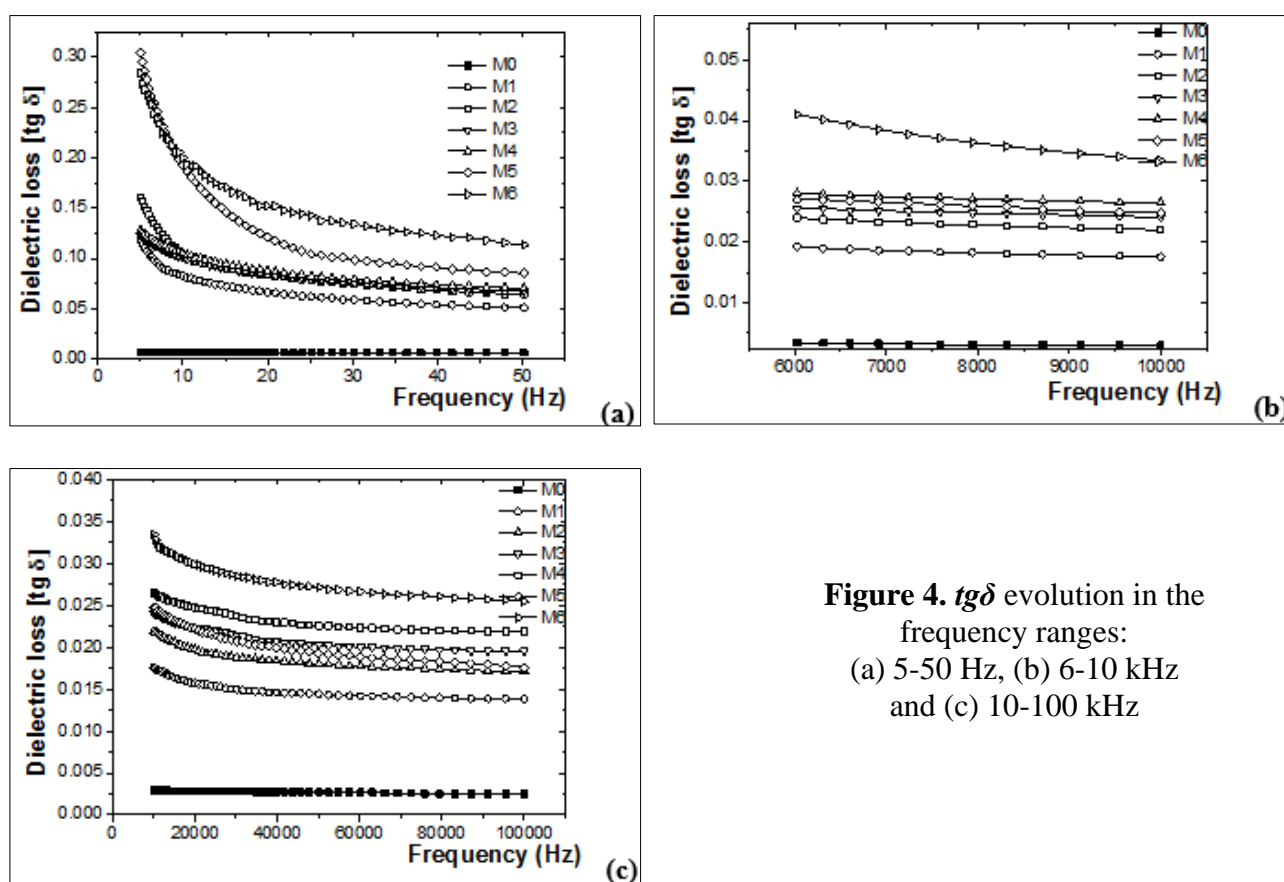The values obtained in different frequency ranges are shown in Figure 4.

Figure 4. *tgδ* evolution in the frequency ranges:
(a) 5-50 Hz, (b) 6-10 kHz and (c) 10-100 kHz

From the analysis of Figure 4 it is found that the dielectric loss value is determined by the content in BaTiO$_3$ of the composite, respectively increases with increasing the content in BaTiO$_3$. The evolution of dielectric loss depending on the BaTiO$_3$ content of the composite for the several frequencies is shown in Figure 5.
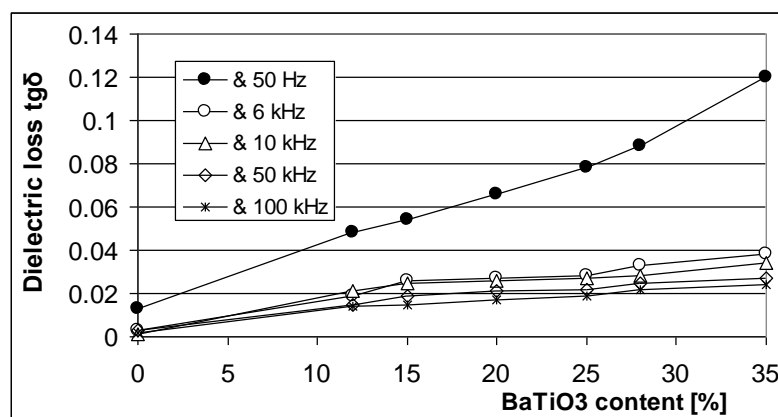
Figure 5. Dielectric loss vs. the BaTiO$_3$ content of the composite

Analysing Figure 5 it is observed that the dielectric evolution of the composite based on PP and TPU polymers with BaTiO$_3$ filler increases approximately linearly as the BaTiO$_3$ content increases, the most pronounced increases being registered at the frequency of 50 Hz (the slope *Δtgδ* /% BaTiO$_3$ about 0.003 / % BaTiO$_3$). Evolution of electrical conductivity σ depending on the frequency of composite samples in the investigated frequency ranges are shown in Figure 6.
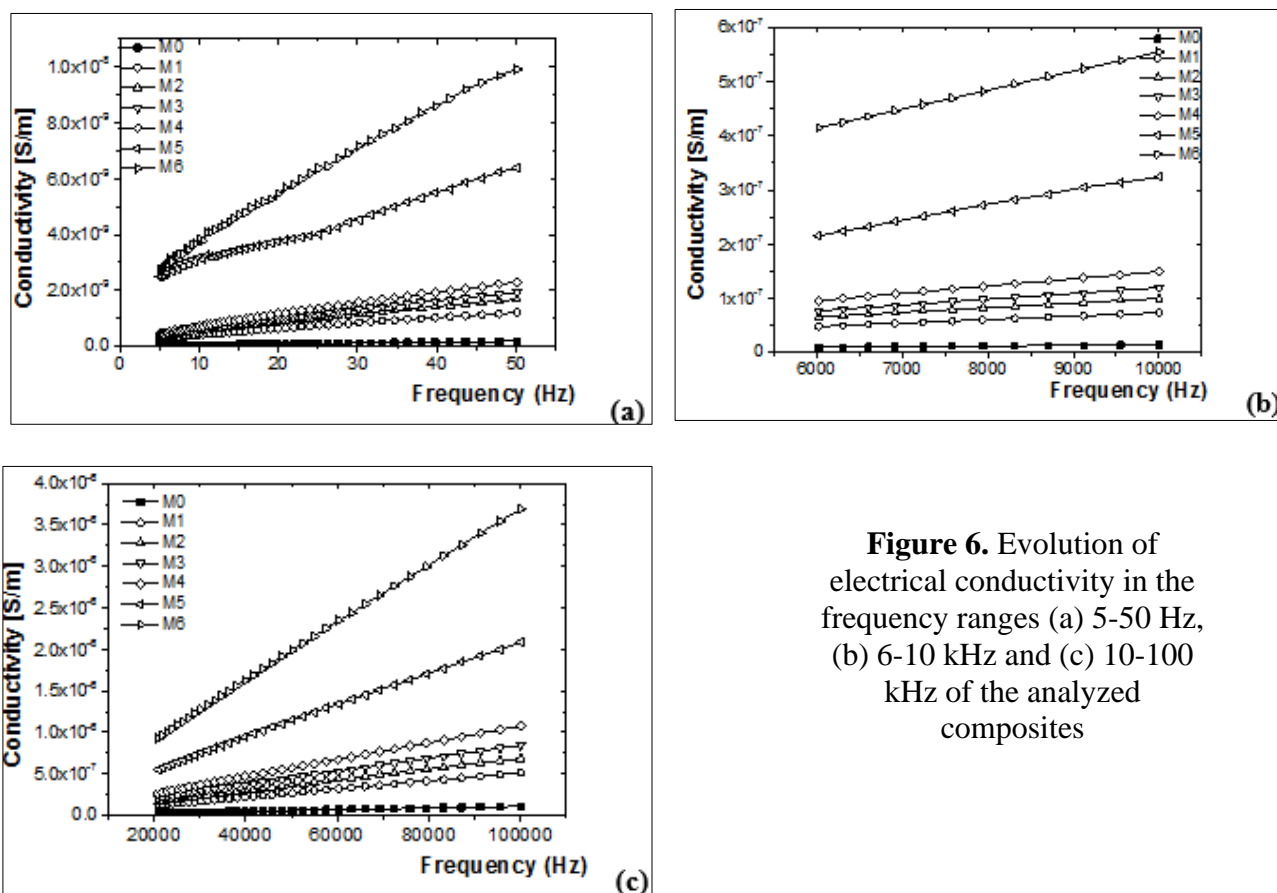

Figure 6. Evolution of electrical conductivity in the frequency ranges (a) 5-50 Hz, (b) 6-10 kHz and (c) 10-100 kHz of the analyzed composites

From the analysis of Figure 6 it can be noted that as the BaTiO$_3$ content increases, the electrical conductivity of the composite samples performed increases (for example: up to 50 times at 100 kHz for a 35 % BaTiO$_3$ content).

From these preliminary characterizations, it is found that the composite material based on polymers (polypropylene and thermoplastic polyurethane) with 35% BaTiO$_3$ filler has adequate electrical and

thermal characteristics for obtaining wires for 3D printers.

4. Conclusions

By the technique of extrusion and injection, samples of polymer-based composite material (polypropylene and thermoplastic polyurethane) with $BaTiO_3$ filler in various concentrations were obtained.

Following the preliminary characterizations performed by coupled techniques of thermal analysis and dielectric spectroscopy of the composite samples obtained, the following were found:

- can be processed by extrusion at temperatures between 180 and 240°C;

- has a thermal stability up to a temperature of about 250°C above which a series of degradation processes begin by successive thermooxidation processes with the formation of volatile products;

- at 600°C the decomposition of the polymeric support is complete, the calcination residues consisting only in the $BaTiO_3$ filler from the composite composition;

- $\Delta tg\delta$ dielectric losses increase with the increasing of $BaTiO_3$ content of the composite, being recorded a maximum increase at 50 Hz (the slope $\Delta tg\delta$ /% $BaTiO_3$ about 0.003 /% $BaTiO_3$);

- the electrical conductivity (σ) of the composite increases as the $BaTiO_3$ content increases, so that the σ at 100 kHz of the composite with 35% $BaTiO_3$ is about 50 times higher than the reference sample M0 (without filler).

Taking in consideration these results, it is found that the composite material based on polymers (polypropylene and thermoplastic polyurethane) with 35% $BaTiO_3$ filler obtained has adequate electrical and thermal characteristics to obtain the wires for 3D printers.

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