VISCOSE-BARIUM TITANATE COMPOSITES FOR ELECTROMAGNETIC SHIELDING

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The paper proposed an ultrasound assisted method for the preparation of a material appropriate for uses in the manufacturing of electromagnetic shields. Thus, viscose fiber-barium titanate polymeric composites of different compositions were obtained by heating the precursors and homogenizing the mixture via ultrasonication. As proved by FTIR and scanning electronic microscopy, the composites consist of perovskite-type barium titanate particles of 400-600 μm, uniformly disposed around the viscose fibers. The composites possess high dielectric constants, the values being dependent on the content of barium titanate and on the preparation procedure. The materials were found to be useful as electromagnetic shields in the range of industrial frequency (50-55 Hz). The best results were obtained for a sample prepared under high electric field, which was characterized by a penetration depth of 240 μm and a total shielding effectiveness of -9 dB.

Keywords: viscose, barium titanate, composites, ultrasonication and microwave assisted process

INTRODUCTION

Composites are materials of great applicative value and have been the subject of many researches over the last decades. They represent a group of heterogeneous materials with at least two components of different physical properties and with major structural barriers. The components complete each other and the result is a new material with superior properties. The properties of composites depend on the properties of the constituent phases, their relative amounts and the geometry of the dispersed phase, as well as on the method of preparation.

For polymeric composites, the combination of a non-polymer material with a polymer matrix is very attractive, not only to reinforce the polymer, but also to introduce new properties based on the morphological modification or electronic interaction between the two components. Polymeric composites have been prepared by various methods, such as colloidal dispersions,[1] electrochemical encapsulation,[2] coating of inorganic polymers, and *in situ* polymerization in the presence of nanoparticles.[3]

The barium titanate, BaTiO₃, is a ferroelectric material from the perovskite family, largely used in electronic and energetic industry for manufac-

turing passive and active electronic components (ceramic condensers, multi-layer condensers and piezoelectric devices), sensors (by using the pyroelectric effect), electro-optical devices, thermistors, electromagnetic shields with electric field absorption.[4] All these applications are connected to the high dielectric constant of barium titanate.

Cellulose is a major part of plant biomass. This abundant and renewable natural resource is characterized by a low dielectric constant, but it also has other advantages, such as low processing temperature. Cellulose-based composites received great attention due to their interesting properties and availability of the precursor materials at convenient prices. The dispersion of ferroelectric phases into the organic polymer is an issue of both scientific and technological interest and, quite often, nano- or micro-sized perovskite-type ceramics (usually BaTiO₃) have been used as "high-k" fillers.[5] Cellulose/barium titanate composites combine the advantages of high dielectric performance of perovskite with relatively low-cost and easily processed organic polymers. This combination offers a class of high-k materials having superior properties and

additional functionalities to be used in compact capacitors. Composites of cellulose or cellulose derivates (ethyl cellulose, viscose, etc.) with barium titanate have been studied for various applications. A. F. Ali *et al.* explored the use of environmentally friendly polymers as dispersion media for high-k ceramic fillers by using cellulose and barium titanate.[6] Y. Hamzeh *et al.* synthesized and studied ferroelectric composites of cellulose acetate-butyrate and cellulose acetate-propionate with various amounts of barium-strontium titanate nanoparticles in order to increase the dielectric constant.[7]

To get higher dielectric constants, a heat treatment of composites under intense electric field was applied. By applying the electric field during the heat treatment or immediately after, the molecules can be oriented more effectively due to their higher mobility. Subsequent heat treatment locks the molecules in the preferred orientation, the orientation along the external electric field. This thermally stimulated discharge technique has been applied by U. Kubon *et al.* for amorphous poly(methyl methacrylate)-based composites, by heating to well above the glass transition temperature of the polymer and by subjecting it to an electric field of 20 kV/cm.[8] This treatment gave rise to the orientation of dipoles and also to the injection of charges into the sample. The same treatment made for vinylidene-fluoride polymer and its copolymer-based composites resulted in increasing the dielectric constant from 8 to 16.[9,10]

Composites with high dielectric constants were also used as electrical insulation for medium voltage electrical currents (electromagnetic shields). Electromagnetic shielding refers to the reflection and/or adsorption of electromagnetic radiation by a material, which acts as a shield against the penetration of the radiation through the shield. Three different mechanisms, namely reflection loss (R), absorbance (absorption-A) and internal reflections (or multiple internal reflection-MR), may contribute to overall attenuation of the electromagnetic field (Fig. 1).[11,12]

To reflect radiation, a shield should contain carriers (electrons or holes) that will react with the electric component (electric field) of the electromagnetic field. The shield material is electrically conductive with a conductivity of 1 Ω/cm. The material of an absorbent shield is a dielectric with high electric and/or magnetic dipoles (ferroelectric and/or ferromagnetic materials). The absorption loss occurs because the electromagnetic waves induced in the medium produce ohmic losses and heating of the material (heat loss). Multiple reflective shields involve the presence of large specific surfaces (porous foam materials) or of a large interface (nanofibers, nanotubes, nanometric pyramidal structures).

Mathematically, shielding effectiveness can be expressed as a logarithmic scale:[13-16]

$$SE\ [dB] = SE_R + SE_A + SE_{MR} = 10\ \lg\ (P_t/P_i) = 20\ \lg\ (E_t/E_i) = 20\ \lg\ (H_t/H_i) \qquad (1)$$

where SE, SE_R, SE_A and SE_{MR} are total, reflection, absorption and shielding multiple reflection effectiveness; P_i, P_t: power of waves (i: incident, t: transmitted waves), $E_{i\ or\ t}$ and $H_{i\ or\ t}$: intensities of incident or transmitted electric and magnetic fields, respectively.

Abbas *et al.* prepared polyaniline-barium titanate-carbon based composites with maximum loss of -25 dB (for a 2.5 mm thick sample) at 11.2 GHz and band width of 2.7 GHz.[17] Phang *et al.* produced polyaniline-TiO_2 and polyaniline-TiO_2-carbon nanotube composites possessing moderate conductivity and dielectric properties, with a maximum loss of -31 dB at 10 GHz and -21.7 dB at 6 GHz, respectively.[18,19]

In this paper, we are interested in obtaining viscose fiber/$BaTiO_3$ composite materials with high dielectric constants, as well as high dielectric loss provided by a small amount of ferroelectric precursor, for applications as felt absorbent materials in electromagnetic fields.

EXPERIMENTAL
Materials
All reagents – barium carbonate (Sigma-Aldrich, 99% purity), titanium dioxide (Chemical Company; 99%), viscose fibers (V), (Lenzing AG, Austria; linear density, 1.3 dtex; fiber length, 39 mm) and distilled water (Milli-Q) – were used as received.

Preparation of barium titanate particles (BT)
The appliances and devices involved in the processes of preparation were as follows: ultrasound generator Sonics Vibracell (750W nominal electric power, 20 kHz ultrasound frequencies, display for information on the energy delivered to the end of the probe, temperature sensor), microwave heating facility (800 W electric power, 2.5 GHz microwave frequency), Vulcan A 130 laboratory oven, Specac laboratory press, home made high voltage installation (30-40 kV).

Barium titanate was prepared through a multistep procedure, where the classical mixing/grinding and drying steps were replaced by ultrasonication and microwave assisted processes, respectively. Thus, a

mixture of 1/2 w/w titanium dioxide (TiO$_2$)/barium carbonate (BaCO$_3$) precursors were ultrasonicated in a Milli-Q ultrapure water bath. The ultrasound time-span process was established after several attempts at 60 minutes, while an amount of 119 kJ of energy has been dissipated into the mixture. The mixture was then dried in the microwave oven for 10 min. The last step was the thermal treatment performed in a laboratory oven at 500 °C for 3 h. The BT sample was obtained as a white powder.

Preparation of viscose-barium titanate composites (V-BT)

V-BT composites were prepared by ultrasonication (conditions: ultrasonic frequency, 20 kHz; time, 10 minutes, energy dissipated, 19, 83 kJ; ultrasonic environment, Milli-Q ultrapure water) of the precursors in different ratios (V/BT = 9/1 or 8/2 w/w)

and drying under microwave for 10 min. Another sample noted V-BT1$_{el}$ and having a V/BT ratio of 9/1 was heated after drying at 50 ºC for 20 min and left to cool under high electric field induced by a potential difference of 30 kV. For dielectric spectrometry measurements, tablets of 3 mm thickness were made with a laboratory press by applying a force of 10 tons on a diameter of 13 mm.

Characterization

The structure of barium titanate and of the composites was investigated by FTIR spectroscopy on potassium bromide pellets by using a Bruker Vertex 70 Spectrometer. The surface morphologies of barium titanate and of the composites were visualized by SEM microscopy on an ESEM Quanta 200 Electronic Deflection Microscope.
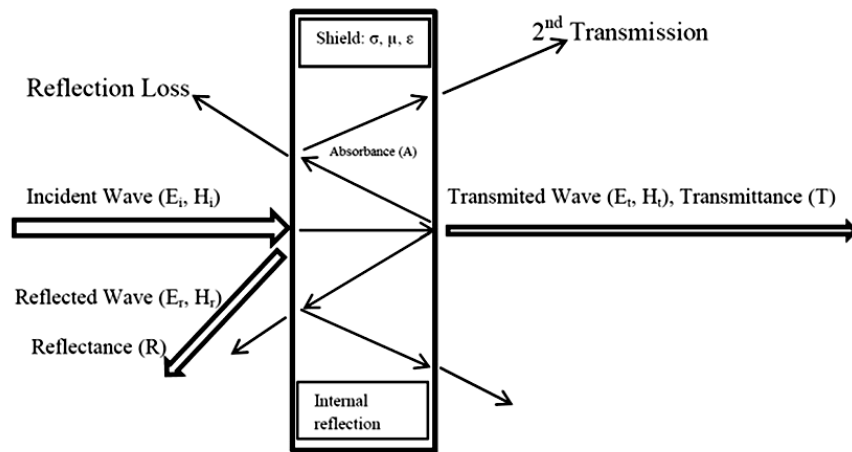

Figure 1: Schematic representation of shielding mechanism (i: incident, r: reflected, t: transmitted waves); E and H represent the intensities of electromagnetic field, σ, μ, ε represent constants of the shield material (electric conductivity, magnetic permeability and electric permittivity, respectively)

The dielectric properties of the composite pellets were measured on a Concept 40 Novocontrol Dielectric Spectrometer in a frequency range of 10^6-10^{-2} Hz, at room temperature, with silver electrodes by using cylindrical tablets with the thickness of 3 mm.

The penetration depth (the distance required by the wave to be attenuated to 37% of its original strength), the reflection and absorption shielding effectiveness were calculated using the following formulae (2-4):[11,12]

$$\delta = (2/\omega\mu_r\sigma)^{1/2} \tag{2}$$
$$SE_R \text{ (dB)} = -10 \log_{10} (\sigma/16\omega\epsilon_0\mu_r) \tag{3}$$
$$SE_A \text{ (dB)} = 20 \log_{10} (H_t/H_i) = -20(d/\delta)\log_{10}e =$$
$$= -8.68 (d/\delta) = -8.68(d\sigma\omega\mu_r/2)^{1/2} \tag{4}$$

where ω is the angular frequency of the electric field (2πν); μ is electric field frequency, μ$_r$ is the relative magnetic permeability of the shield material (equal to 1, for a non-magnetic material); σ is the electrical

conductivity of the shield material calculated with Equation (5):

$$\sigma = \omega \cdot \epsilon_0 \cdot \epsilon'' \tag{5}$$

where ε$_0$ is free space (vacuum) permittivity: 8.854·10^{-12} F/m; ε'' – absorption permittivity; d – shield thickness.

As the studied composites are composed of fibers and particles of micron dimensions, the multiple reflection term (SE$_{MR}$) was ignored in the calculation of the total shielding effectiveness (SE). Thus, SE was calculated as:

$$SE \text{ (dB)} = S_{ER} + SE_A \tag{6}$$

The graphs were processed with the Origin Pro 8 program based on the data obtained from the analysis of dielectric spectroscopy.

RESULTS AND DISCUSSION
Preparation and structural characterization of composites

BT particles were prepared by a novel method, where the ball grinding and mixing of the barium carbonate and titanium dioxide precursors, and the oven drying were replaced by ultrasonication and microwave treatment, respectively. The procedure allowed milder preparation conditions, as compared to the traditional processes. Thus, the duration of the mixing/grinding and of the drying steps was reduced from several hours to 60 min and from around 2 h at 100-120 °C to 10 min, respectively. Moreover, probably as a result of the well-known effects of ultrasonication on the intimate mixing of the powder components and on their surface activation, the thermal treatment step requested only 500 °C for 3 h, to obtain the desired perovskite-like structure, as compared to other reported procedures,[4] which required higher heating durations and temperatures (650 °C for a hydrothermal process; 5-6 h at 1200 or 1350 °C for a solid process).

Composites with different V/BT ratios were prepared by mixing and drying procedures similar to those used for BT particles. As expected and proved later, the high electric field applied in the preparation of V-BT1$_{el}$ sample resulted in improved dielectric properties. The composition and properties of the as-prepared composites are indicated in Table 1.

The precursors and the composites were first assessed through infrared spectrometry. Fig. 2 shows the FTIR spectra for barium titanate (BT), viscose fibers (V) and V-BT1 (the characteristic bands of V-BT2 and V-BT1$_{el}$ samples are similar to those of V-BT1). The attribution of the vibration bands for BT[20-22] and for V samples[23-26] was made based on the available literature (Table 2).

Table 1
Composition and properties of composites

Sample	V/BT (w/w)	Electromagnetic shielding properties at 50-55 Hz	
		D^b (μm)	SE^c (dB)
V	-	3800	-
V-BT1	9/1	300	- 4
V-BT2	8/2	275	- 5
V-BT1$_{el}$^{a}	9/1	240	- 9

[a] Sample thermally treated under electric field; [b] Depth of penetration; [c] Total shielding effectiveness

Table 2
Interpretation of FTIR characteristic bands for BT, V and V-BT1

| Sample	Band position (cm^{-1})	Vibration mode
BT	438, 559	O_6 octahedra deformation mode (bending and stretching vibrations, respectively)
V	611	Vibration specific to S-O
	667	C-OH (out of plane bending)]
	731	C-H out of plane
	895	γ (COC) in plane, symmetric stretching
	997, 1018, 1155	C-OH, C-H (ring and side group vibrations); C-O-C (asymmetrical stretching)
	1315, 1367, 2891	C-H (rocking, in plane bending, symmetrical stretching, respectively)
	3350	OH stretching
V-BT1	443, 553	O_6 octahedra deformation mode (bending and stretching vibrations, respectively)
	894	γ (COC) in plane, symmetric stretching
	991, 1018, 1162	C-OH, C-H (ring and side group vibrations); C-O-C (asymmetrical stretching)
	1375, 1425, 2890	CH
	1644	OH (absorbed water)
	3437	OH stretching
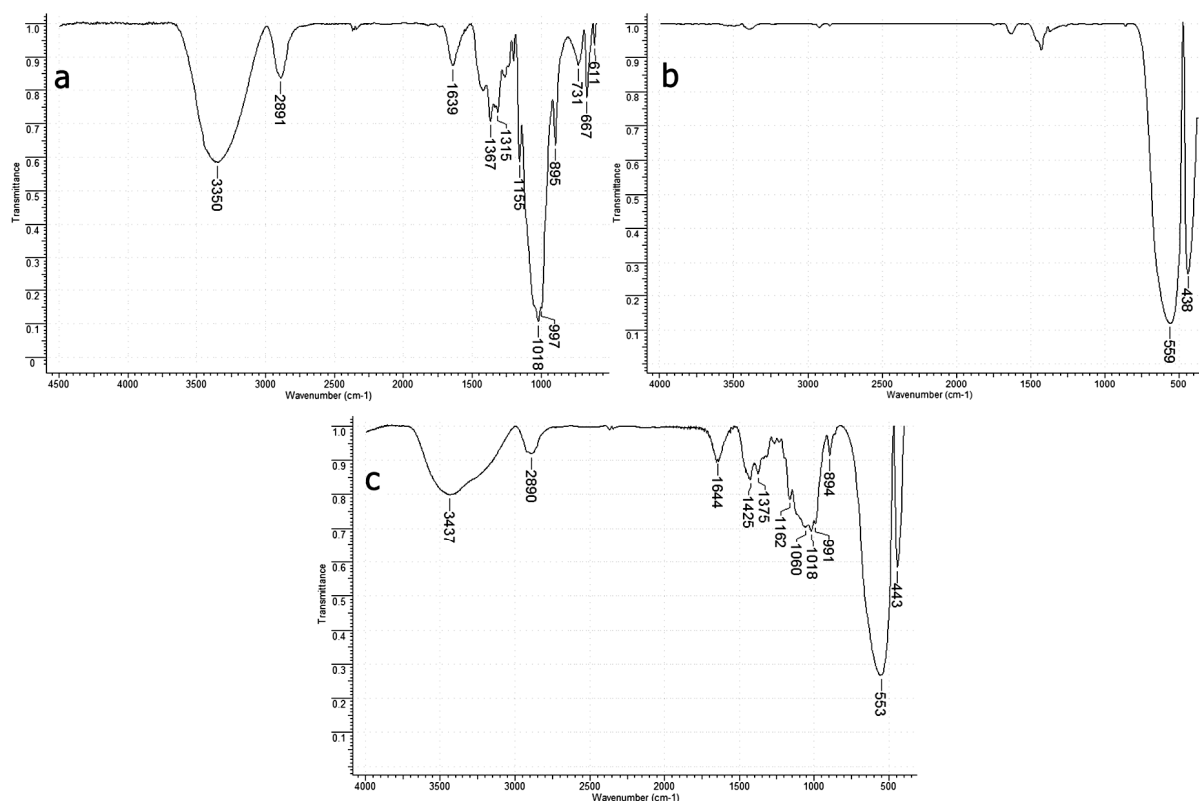
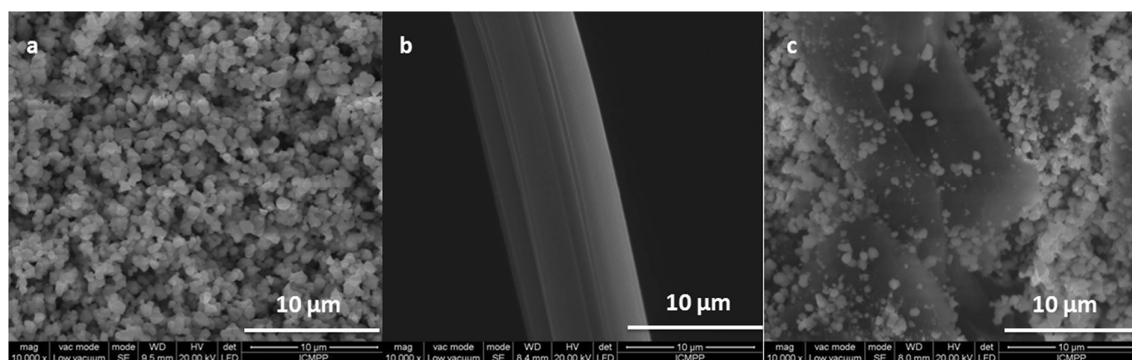Figure 2: Infrared spectra of V (a), BT (b) and V-BT1 composite (c)

Figure 3: SEM micrographs for BT (a), V (b) and V-BT1 (c)

As one may see from Fig. 2 and Table 2, the vibration bands of both V and BT are visible in the spectrum of the V-TB1 composite. The small shifting of the characteristic bands of BT from 438 and 559 cm^{-1} to 443 and 553 cm^{-1} in the spectrum of V-BT1 does not change the cell of barium titanate and can be attributed to the ultrasonic process made for homogenization of the composite.

As for the comparison between the spectra of viscose and those of the composite sample, the most important difference consists in the enlargement of the C-O-C and OH characteristic bands at around 1000 and 3500 cm^{-1} in the composite sample, probably due to the interaction of the polymer chain with the BT particles.

The surface morphologies of the composites and their precursors are compared in Fig. 3.

As observed in Fig. 3a, the powder of BT consists of agglomerated particles characterized by a quite uniform shape. The dimensions of the BT particles range between 400 and 600 nm. Pristine viscose fibers with a smooth surface and diameter of 5-10 μm may be seen in Fig. 3b. In the composite SEM image (Fig. 3c), clusters of barium titanate particles relatively homogenously dispersed around the fibers of viscose are visible. The polymer fibers, on their turn, have suffered deformation and fragmentation during the ultrasonic process.

Dielectric properties

The components of the complex dielectric permittivity (dielectric constant, ε', and absorption permittivity, ε'') were measured in the frequency range of 10^{-2}-10^{6} Hz. The variation of these material parameters as a function of frequency for composites and their precursors is depicted in Figs. 4 and 5. For all samples, as the frequency increases, the real (ε') and imaginary (ε'') permittivity decrease and remain constant at higher frequencies, indicating the occurrence of dielectric dispersion (ionic and orientation polarizabilities).[27,28] This may be attributed to the dipoles resulting from changes in valence states of cations and space-charge polarization.[28,29] Electronic polarization is always higher than ionic and orientation polarization, i.e., $\varepsilon' > \varepsilon''$. The analyzed specimens did not present the phenomenon of dielectric perforation at high values of the frequency.

For the barium titanate, the real part of the complex dielectric permittivity, ε', ranges from 14 to 176000 (which reveals a high ferroelectric character)[29] (Fig. 4a), while the coefficient of the complex part, ε'', (Fig. 5a) registers values from 0.04 up to 35290. ε' values between 4.9 and 5.4 were measured for the viscose dielectric constant (Fig. 4b), while its absorption permittivity varies from 0.1 to 0.4 (Fig. 5b). An important increase is noticed in the dielectric constant of all the composites. Thus, for industrial frequency (50, 55 Hz), ε' is 6.8 for V-BT1, 7.8 for V-BT2 and 9.1 for V-BT1$_{el}$ compared with 5.3 for viscose. It is obvious that both the higher proportion of BT and the heat treatment under electric field determined the increase of the dielectric constant.

The penetration depth (δ) and the total effectiveness (SE) were calculated by using Equations (2-6) (Experimental) and their variation as a function of frequency is presented in Fig. 6.

For viscose, the maximum penetration depth is about 3800 μm, and for the composites, this value drops below 1000 μm (Fig. 6a). For industrial frequency (50-55 Hz), the penetration depth for the composites is situated around 250 μm, making them appropriate candidates for shielding electric fields emitted by currents on these frequencies.

In terms of shielding effectiveness (Fig. 6b), viscose has no shielding properties (SE V > 0 dB), while for the composites, maximum shielding is obtained for frequencies between 10^{4}-10^{5} Hz (-18 dB for V-BT 1, -20 dB for V-BT 2 and -22 dB for V-BT 1$_{el}$). In the range of industrial frequency, SE is -4 dB for V-BT1, -5 dB for V-BT2 and -9 dB for V-BT1$_{el}$.
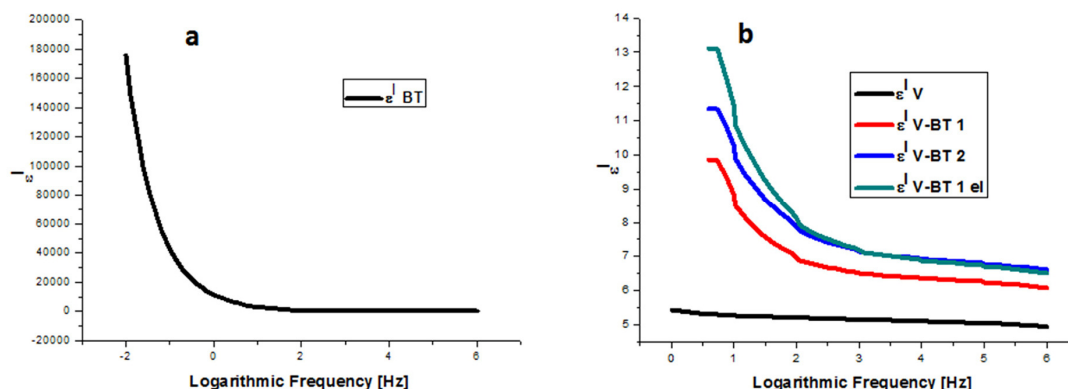

Figure 4: Dispersion spectra ($\varepsilon'=\varepsilon'(\nu)$) for BT (a), V and composite samples (V-BT1, V-BT2, V-BT1$_{el}$) (b)
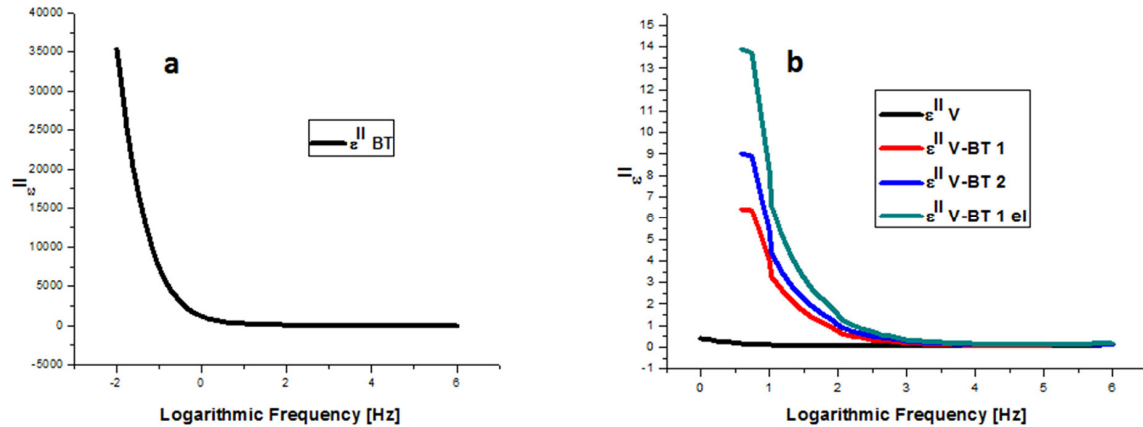
Figure 5: Absorption spectra ($\varepsilon''=\varepsilon''(\nu)$) for BT (a), V composite samples (V-BT1, V-BT2, V-BT$_{el}$) (b)
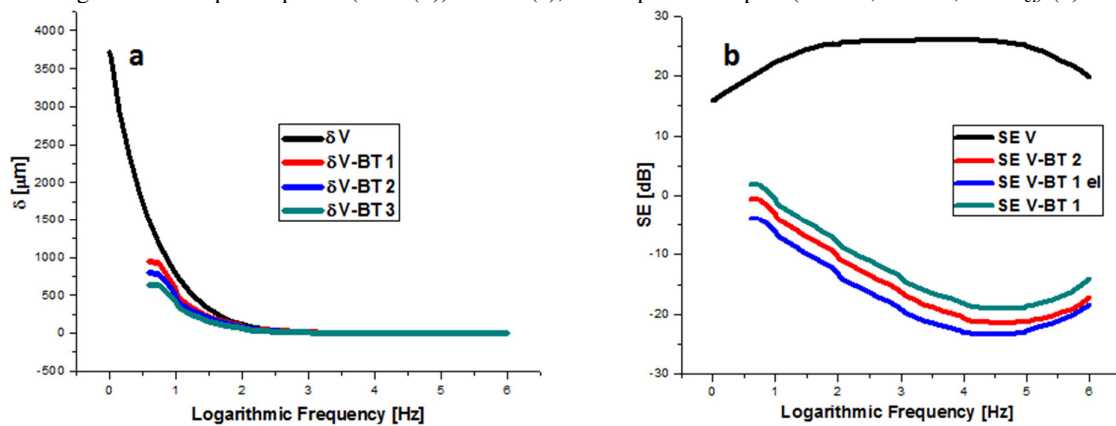

Figure 6: Penetration depth ($\delta(\nu)$) (a) and shielding effectiveness (SE (ν)) for V and composite samples
(V-BT1, V-BT2, V-BT$_{el}$) (b)

CONCLUSION

Viscose-barium titanate composites were successfully prepared in various compositions through an ultrasound/microwave assisted procedure, in the presence or in the absence of a thermal treatment under high electric field. Analyses of infrared spectrometry (FTIR), electronic microscopy (SEM) and dielectric spectrometry showed that relatively homogenous materials have been obtained. Viscose/BaTiO$_3$ composites possess a lower dielectric constant compared to that of the ferroelectric precursor, but a higher one compared to that of the polymer precursor. The composites have a great potential to be used as textile materials with insulating properties and as electromagnetic interference shielding materials, as proved by the values of the penetration depth and of the total shielding effectiveness.

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