BaTiO$_3$ incorporation effect on the dielectric properties of polymer from aqueous emulsion: An enhanced dispersion technique

Adel Zyane,[1,2] Ahmed Belfkira,[2] François Brouillette,[1] Pascal Marchet,[3] Romain Lucas[3]

[1]Centre de recherche sur les matériaux lignocellulosiques (CRML), Université du Québec à Trois-Rivières, 3351 boul. des Forges C.P. 500, Trois-Rivières, Canada
[2]Laboratoire de Chimie Bioorganique et Macromoléculaire (LCBM), Faculté des Sciences et Techniques, Avenue Abdelkrim Khattabi BP 549, Marrakech, Maroc
[3]Université de Limoges, SPCTS, UMR 7315, F-87000, Limoges, France
Correspondence to: A. Zyane (E-mail: adel.zyane@uqtr.ca)

ABSTRACT: An economic and environment friendly process was adapted to synthesize new dielectric composite materials. Using ethylene vinyl acetate (EVA)/vinyl ester of versatic acid (VeoVa) terpolymer as an aqueous emulsion provides a homogenous dispersion of BaTiO$_3$ (BT) particles, due to the high viscosity and polarity of the vinyl resin (VR). Composites films were obtained from these dispersions by water evaporation. The evolution of the dielectric properties as a function of the BaTiO$_3$ content, was correctly fitted by a Maxwell-Garnett model. This fitting of the experimental curve shows a good dispersion of filler in the vinyl resin and the particles separation by a layer of resin as expected for the preparation method used in this study. The VR/BT composites show good synergy between the dielectric properties of the different phases of the composites due to the formation of macrodipoles and to the strong interactions between polar EVA/VeoVa groups and the BaTiO$_3$ particles surface. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 44333.

INTRODUCTION

The high demand in the microelectronic field for materials exhibiting excellent dielectric properties and processability had led to the vast development of organic–inorganic composite systems, which combine advantages: firstly of performance polymers, like flexibility, ease of implementation as an organic material from one side; and secondly of inorganic materials such as ferroelectric oxide (BaTiO$_3$), that present high dielectric properties.[1–4] The success of these composites comes from the possibility to obtain various properties according to the characteristics of the constituent phases, which are defined as fillers (size, shape, aspect ratio, etc.), their distributions in the matrix (use or non-use of coupling agent), and their volume fractions.[5–7] Consequently, several polymer/BaTiO$_3$ composite systems were studied, while treating the effect of each parameter separately. These studies show that a homogenous dispersion of these particles is highly required for optimizing the dielectric properties (high relative permittivity and low loss factor).[4,8] A comparative study had been made by Zhao *et al*[9] between polydiacrylate/BaTiO$_3$ composites prepared by spray deposition using either electron beam polymerization or thermal polymerization. This study shows that electron beam polymerization provides a good dispersion, which improves the relative permittivity of this composite. Furthermore, some studies showed better dispersion interest by adding a coupling agent which leads to good dielectric properties insuring great polymer-particle interactions.[10] The existence of this interfacial interaction possibly gives rise to more interfacial polarization of the composite system, which can lead to the Maxwell–Wagner–Sillars (MWS) effect.[5] Polymer matrices play a critical role in the performance of dielectric composites.[11] The matrix polarity joins the parameters listed previously, that govern the dielectric properties of polymer-ceramic composites. However, the polarity of the polymers can lead to composites with either high or low dielectric permittivity. Various polymers were studied, and most of them exhibit a very small dielectric constant. Among these studied polymers, PVDF and its copolymer P(VDF-TrFE) are ferroelectric and give a polymer-ceramic composite with dielectric constants as high as 100, but they exhibit an unfavorable high loss factor.[11]

Recently, ethylene vinyl acetate (EVA) has attracted more interest in the composite systems as a result of its wide applications
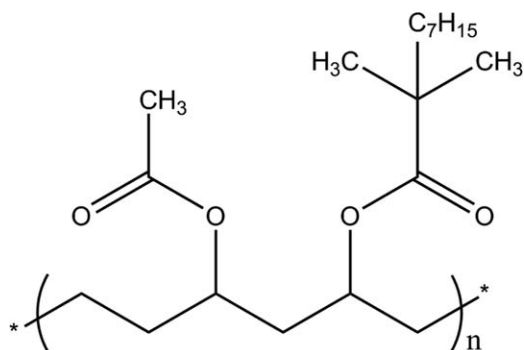
Figure 1. Chemical structure of a proposed repetitive unit of the EVA/VeoVa terpolymer.

in different fields such as petroleum industry, packaging of components, cable jacketing, food packaging, barrier (low permeability to gases, solvents, and organic vapors), dielectric sensor, and fire retardant.[12–18] The success of EVA is due to its ease of fabrication, flexibility, transparency, heat sealability, high adhesivity, and processablity.[15,16] Many authors have reported on different dielectric composites of EVA. Hui et al.[19] studied the effect of nanosilica on the dielectric properties of EVA/LDPE TPE system (low-density polyethylene–ethylene vinyl acetate thermoplastic elastomers). Sohi et al.[20] investigated the effect of different types of carbon particles (carbon black (CB), short carbon fiber (SCF), and multiwall carbon nanotube (MWNT)) on the dielectric properties of EVA-based composites, concluding that relative permittivity and loss factor depend on the filler type and loading. Rahaman et al.[18] revealed the possibility of using EVA/Polyaniline composite as a dielectric sensor and demonstrated that the addition of polyaniline into EVA improves the dielectric properties of the system.

Several studies reported for the dielectric properties of EVA/BaTiO₃. Nagata et al.[21] showed that the dispersibility of BaTiO₃ particles and dielectric properties were clearly improved by the augmentation of the vinyl acetate groups in the LDPE matrix. Agoudjil et al.[22,23] used a Rheomix mixer (at $100\,^\circ C$) followed by compression molding (at $130\,^\circ C$) to elaborate EVA/BaTiO₃ composite. The method shows that dispersion of the particles took place only with a few regions of particle aggregation. The dispersion obtained by a previous method was improved via Huang et al.[24–26] by adding a silane coupling agent to create a strong interaction between the surface of BaTiO₃ particles and the EVA matrix, which provides good dielectric properties. Moreover, many other elaboration techniques of EVA composites were reported. Ramesan[12] suggests a mill mixing technique to prepare EVA/IONPs (iron oxide nanoparticles) composite. This technique is highly efficient without using any organic solvent. This method is also relatively quick and easier to handle, besides avoiding the drawback of "solution blending" and "melt blending." The first one used organic or common solvents to disperse particles, which are hazardous to our health and environment. The second technique affects the mechanical properties of the composite.[12]

Compared to other elaboration methods, the results presented in this study have the characteristic of being economic and ecological. Indeed, our method uses ethylene vinyl acetate (EVA)/vinyl ester of versatic acid (VeoVa) terpolymer, considered as an environmental friendly polymer.[16,27] In addition, the EVA/VeoVa latex, with high viscosity, is an aqueous and stable emulsion, allowing for the elaboration of composites using water as solvent. As a consequence and contrary to previous studies, a good dispersion is provided by the viscosity and the polarity of the matrix without coupling agent. Thus the aim of this study is to evaluate the contribution of BaTiO₃ loading on the dielectric properties of EVA/VeoVa with simple implementation at room temperature.

EXPERIMENTAL

The vinyl resin emulsion (W301) containing the terpolymer EVA/VeoVa (Figure 1) in the aqueous emulsion form (Latex) was supplied by the "Société Marocaine des Polymères (SMP)." The solid contents of the resin was 51,7 wt % with a viscosity of 7600 mPa s and a glass transition temperature of $34\,^\circ C$ as indicated by the supplier. Titanium dioxide (TiO₂) and Calcium carbonate (BaCO₃) were used for BaTiO₃ synthesis (Sigma-Aldrich, Cat 1402 and Cat 329436, respectively). BaTiO₃, hereafter designed as BT, was prepared by classical solid-solid reaction, at $1100\,^\circ C$ for 2 h in a laboratory oven.[28] The vinyl resin/BT (VR/BT) composites were prepared by a clean, economical, and environmentally friendly method, described in Figure 2, using water as a solvent, with a simple mechanical stirring at room temperature.

Structures and morphologies of BaTiO₃ particles and composites films were characterized by scanning electron microscope and energy dispersive X-ray spectrometer SEM/EDS (JEOL,
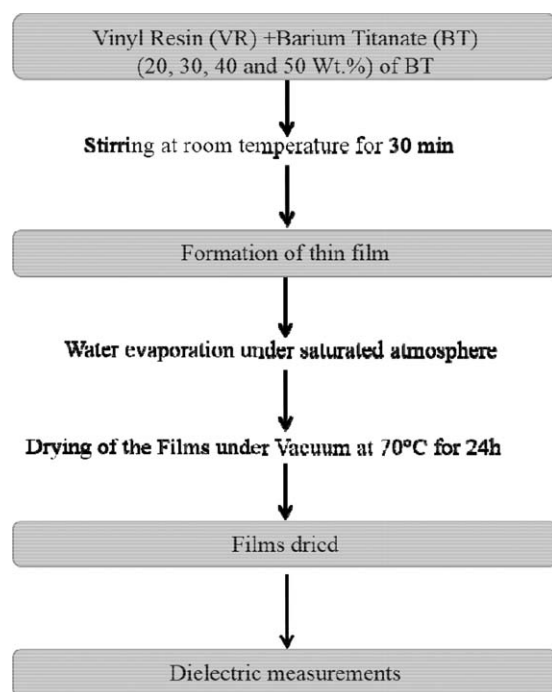
Figure 2. Schematic representation of the VR/BT film preparation.

JSM-5500 and OXFORD Instruments, X-Max 20 mm^2), X-ray diffraction (D8 ADVANCE Bruker), and laser particle size analyzer (HORIBA ParticaLA-950V2). For the measurement of dielectric behavior, gold electrodes were deposited by DC-sputtering on both sides of the samples in order to obtain planar capacitors with known geometries. The dielectric properties of all films were measured between 30 °C and 120 °C in the 10^2 Hz to 10^6 Hz frequency range using a precision impedance analyzer (Agilent 4294A).

RESULTS AND DISCUSSION

Morphology of the BT Nanoparticles

XRD patterns [Figure 3(c)] confirmed the formation of tetragonal BT phase: most of the peaks of synthesized BT particles correspond well with the standard pattern of BT (JPCDS#5-626). The calculated lattice parameters are $a = b = 0.3993$ nm and $c = 0.4036$ nm, in agreement with the reported values for tetragonal BT ($a = b = 0.3994$ nm and $c = 0.4038$ nm, JCPDS 5-626). The SEM image [Figure 3(a)] gives the size and shape of BT particles. It clearly shows that BT particles are polydispersed. The average size of the BT particles obtained by laser particle size analyzer is around 600 nm, as shown by Figure 3(a). The curve of particle size distribution shows some agglomerations, due to sonication during measurement. The EDS analysis [Figure 3(b)] reveals that the BT powders resulting from the synthesis consists of the chemical elements: Ba, Ti and O, with a minor impurity (traces of carbon) due either to unreacted $BaCO_3$ remaining after the solid-solid reaction or to adsorption of CO_2 after reaction.

Morphologies of the Polymer/BT Composite Films

The uniform dispersion of the particles inside the polymer matrix is one of the most important challenges in the field of dielectric composite. In order to achieve high quality properties, compatibility between polymer and ceramic particles is highly required, generally provided by dispersing agent, thus limiting aggregation and/or agglomeration of fillers.[29–31] The EVA/$BaTiO_3$ composites are generally prepared by compression molding, with or without silane coupling agent,[22–26] which aims to increase the dispersion of the particles in the matrix. In the same sequence, recently a study was carried out using high-energy ball milling (HEBM) under the temperature of the liquid nitrogen (cryomilling). The dispersion results were interesting but the process remains less economic.[32,33]

In this experiment, a simple mechanical stirring at room temperature was used. While, the emulsion used is for the formulation of waterborne paints, with a high ability to disperse and maintain in the dispersed state several kinds of additives, such as, titanium dioxide and calcium carbonate particles. Combination between hydrophilicity effect and high viscosity of the medium (emulsion) will allow inorganic particles wetting, and help with their dispersion. Medium stability will be achieved by creating a network formed by Van Der Waals interactions between carbonyl groups of the chain segments (Figure 1) and surface of barium titanate particles. SEM images in Figure 4(a,b) give surface morphology of the pure vinyl resin and the composite containing 50 wt % of $BaTiO_3$ particles. The chemical elements mapping [Figure 4($a1_2,b_{1-4}$)] confirmed the
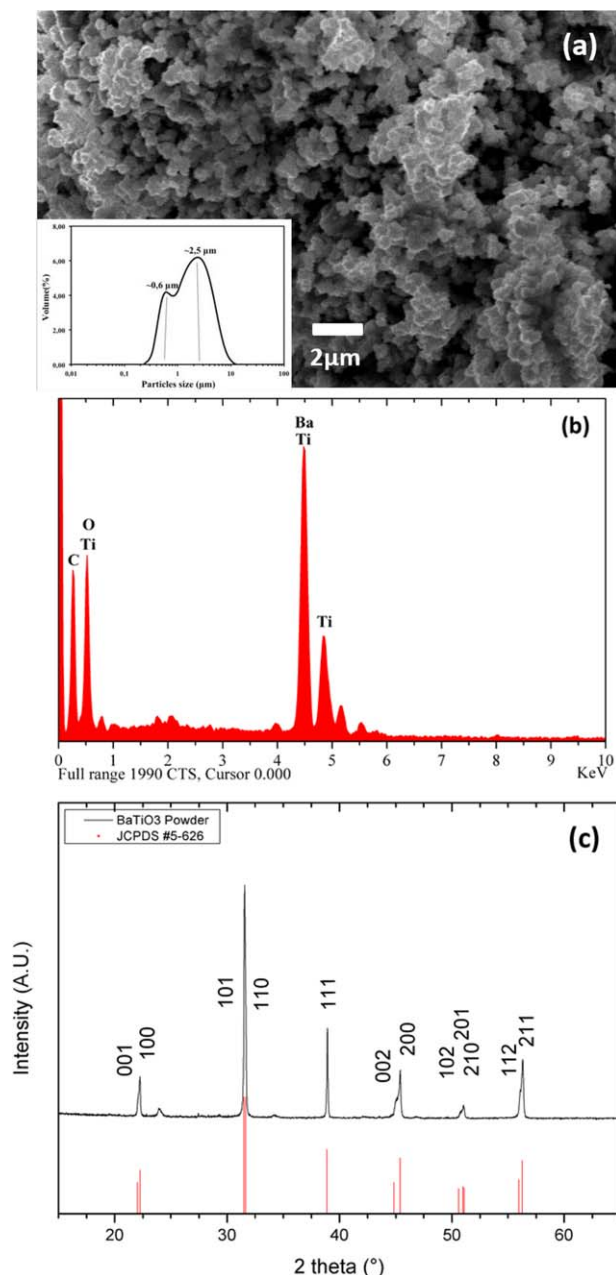
Figure 3. (a) SEM pictures and particle size distribution, (b) EDS characterization, and (c) XRD patterns of $BaTiO_3$ powders (Miller indices correspond to the tetragonal variety of $BaTiO_3$, JPCDS#5-626). [Color figure can be viewed at wileyonlinelibrary.com.]

impregnation of $BaTiO_3$ particles by the polymeric chains, as well as a good dispersion of these particles in the matrix, without $BaTiO_3$ aggregate formation, proved by the absence of black holes or element concentration in some map areas of 50 wt % composites. Indeed, the resin viscosity, with 7600 mPa s, keeps the suspension for $BaTiO_3$ grains inside polymeric chains while minimizing agglomeration and sedimentation during the composite preparation and film formation, by coating each particle with a layer of polymer as shown in Figure 4(b). Also, the high polymer polarity is one of the factors governing the degree of
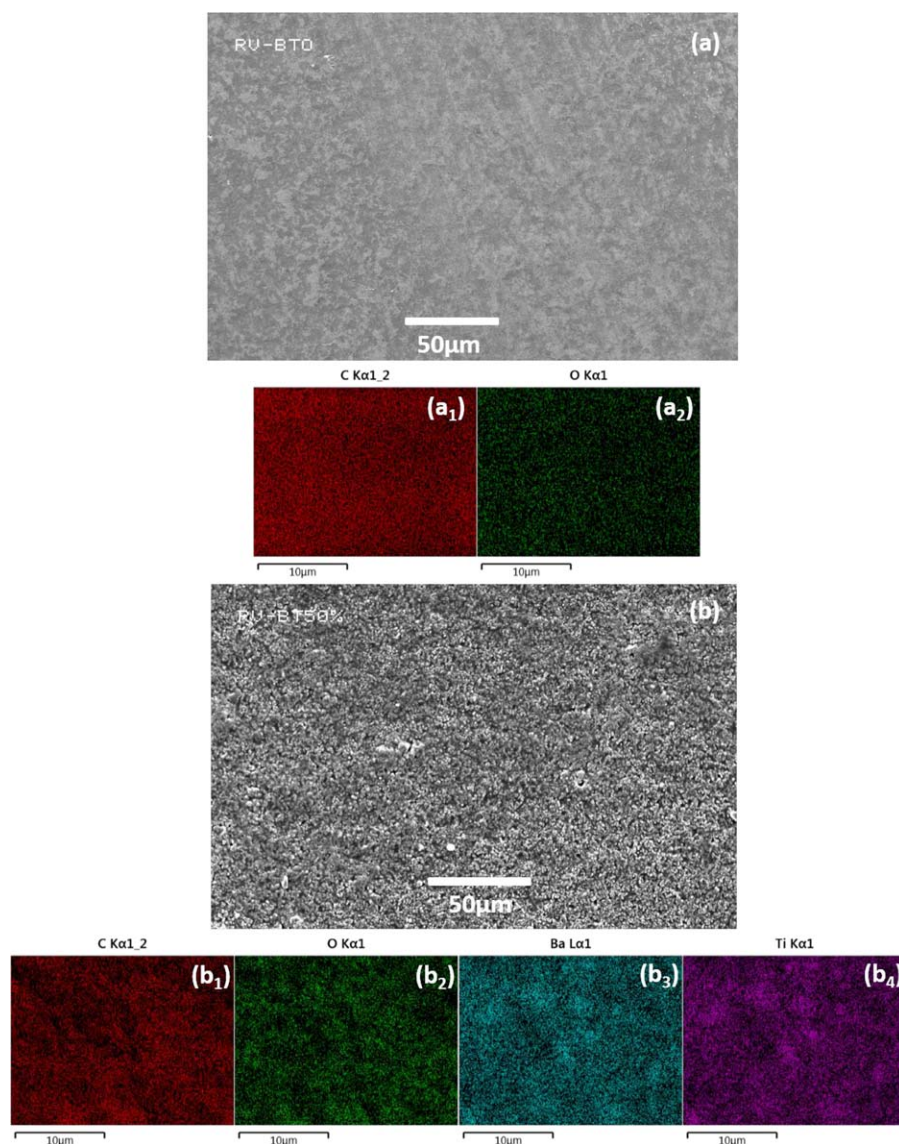
Figure 4. (a,b) SEM and ($a_{1,2}$,b_{1-4}) EDS images of the surfaces of pure terpolymer and composite 50 wt % film, respectively. [Color figure can be viewed at wileyonlinelibrary.com.]

$BaTiO_3$ dispersion in EVA.[21] The polar groups of vinyl acetate and VeoVa interact effectively with the surface of the $BaTiO_3$ particles, reducing particles agglomeration and providing a good dispersion. These results indicate for the excellent compatibility between EVA/VeoVa and $BaTiO_3$ particles.

Dielectric Properties

Dielectric permittivity ε_r and loss factor (tan δ) of pure EVA/VeoVa resin were studied as a function of the temperature, for four frequencies (Figure 5). At 25 °C and 1 kHz, the EVA/VeoVa terpolymer has a permittivity about ~5.5 and ~0.06 as a loss factor. These values are relatively higher than those of the pure EVA, i.e., ~3.5 and ~0.01 as a permittivity and loss factor, respectively.[20,26] This difference is explained by the high polarity of EVA/VeoVa resin, conferred by the carbonyl groups of VeoVa monomer (Figure 1). At the same time VeoVa represents a large steric hindrance for providing significant flexibility to polymeric

chains. The flexibility and high polarity chains allow for the increasing the orientation polarization, which is the most important part of the permittivity for polar polymers such as EVA.[19] The polarization effect in this material is detected [Figure 5(a)] through the maximum of the dielectric permittivity, which is about 10.7 at a frequency of 1 kHz and then decreases to 7.40 (1 MHz) while the frequency of the maximum is increased (relaxation effect). In addition, the dielectric loss of EVA/VeoVa [Figure 5(b)] shows a tendency to the relaxation peak attenuation at the highest frequencies. Generally, the peaks observed at the temperature dependence of the loss factor correspond to polymer relaxations, mostly designated by the letters α, β, and γ.[34] These relaxations represent the movement of chains and segments in the polymer. However, the type of relaxation can be determined by the activation energy (E_a) via the Arrhenius law. In our case, EVA/VeoVa represents α-relaxation at 60 °C for 1 kHz [Figure 5(b)], confirmed by the value of
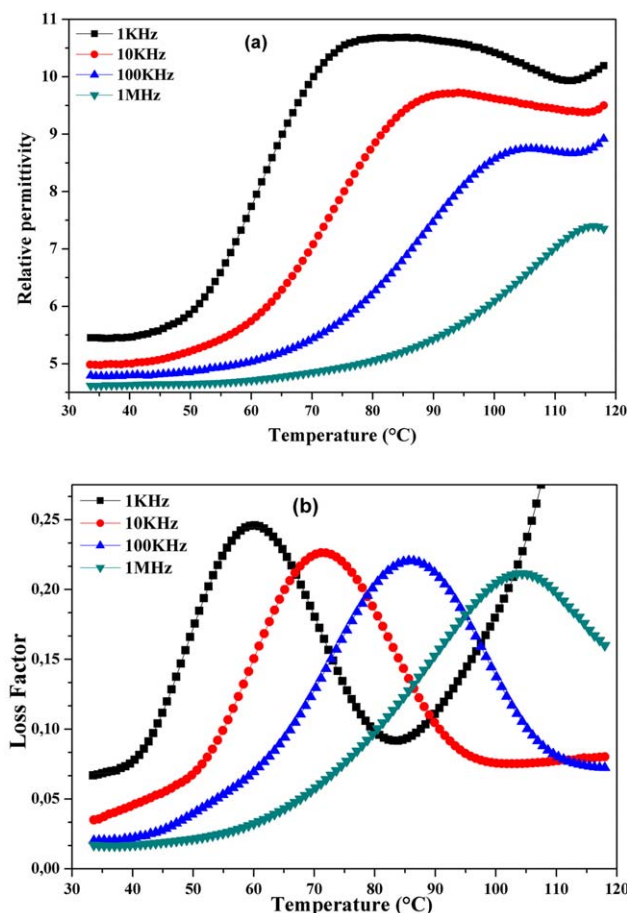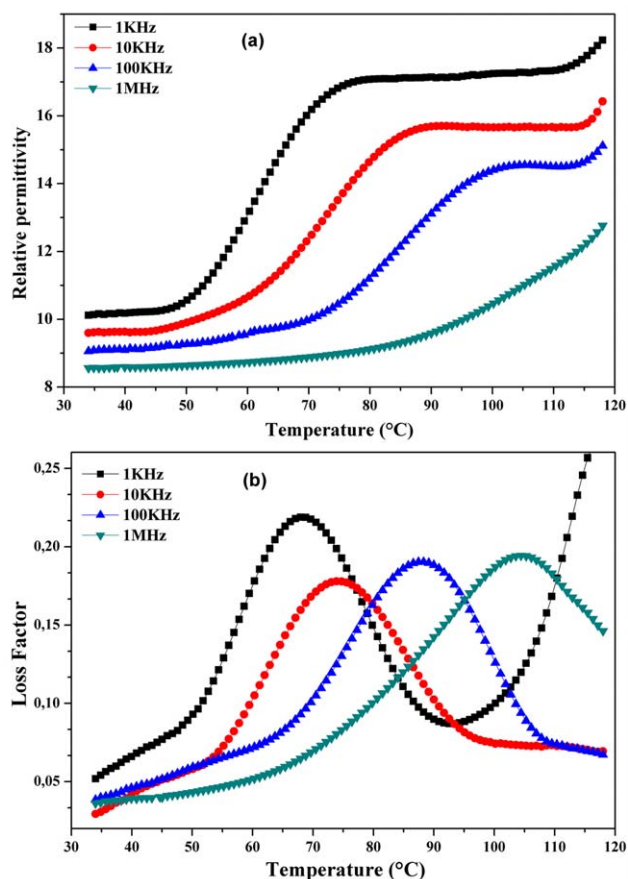
Figure 5. (a) Relative permittivity and (b) loss factor of pure terpolymer as a function of temperature for four selected frequencies. [Color figure can be viewed at wileyonlinelibrary.com.]

Figure 6. (a) Relative permittivity and (b) loss factor of the composite based on 50 wt % of $BaTiO_3$ as a function of temperature for four selected frequencies. [Color figure can be viewed at wileyonlinelibrary.com.]

activation energy (156 kJ/mol) calculated from peaks of Figure 5(b) and represented in Table I. This relaxation associated to glass transition temperature is attributed to the segmental motion of the terpolymer amorphous part. Also, this transition reflects both relaxation of flexible chains of "vinyl acetate groups" and "VeoVa side chain."[12,35]

Four composites were prepared using the same conditions and different BT content: 20, 30, 40, and 50 wt % of $BaTiO_3$. Figure 6 shows the evolution of permittivity and loss factor of the composite based on 50 wt % of $BaTiO_3$, as a function of the temperature, for four frequencies. It can be observed that permittivity evolution of composite is identical to the one in the pure resin (Figure 5), i.e., a relaxation phenomenon: the permittivity decreases with increasing frequency. This inverse

Table I. The Activation Energy Values Obtained from Arrhenius Law of Different Composites

Composites (BT wt %)	0	20	30	40	50
E_a (kJ/mol)	156	157,61	166,91	175,79	195,34

relationship can be explained experimentally: while the frequency is raised, the dipoles get very less time to orient themselves in the direction of the applied field.[20] The comparison of composites with different $BaTiO_3$ filler loadings presented in Figure 7, shows an increase in the dielectric permittivity at 1 kHz frequency from 10.7 (Pure VR) to ~17.1 for the 50 wt % composite [Figure 7(a)]. Also, the Figure 7(b) present a decrease of dielectric loss, which can be explained by the absence of leakage current induced generally by the percolating paths and structural imperfections.[3] The increase of permittivity indicates that the interfacial polarization becomes more and more predominant and adds to the dipolar orientation phenomenon.[12,20] In the same manner as in the case of PI/BT composites.[5] The interfacial polarization between BT particles and matrix play an important role in improving the dielectric properties of the composite films.[5] Furthermore, the increase of activation energy with the BT loading (Table I) confirms also the interfacial interaction between matrix and particles responsible of interfacial polarisation and the increase of permittivity. Thus, this polarization leads to the apparition of a "microcapacitor network" at the interface particles/polymer, which increases with the amount of particles loading.[4] The effect of microcapacitors is ensured by the polydispersities of shape and size of BT powder, which
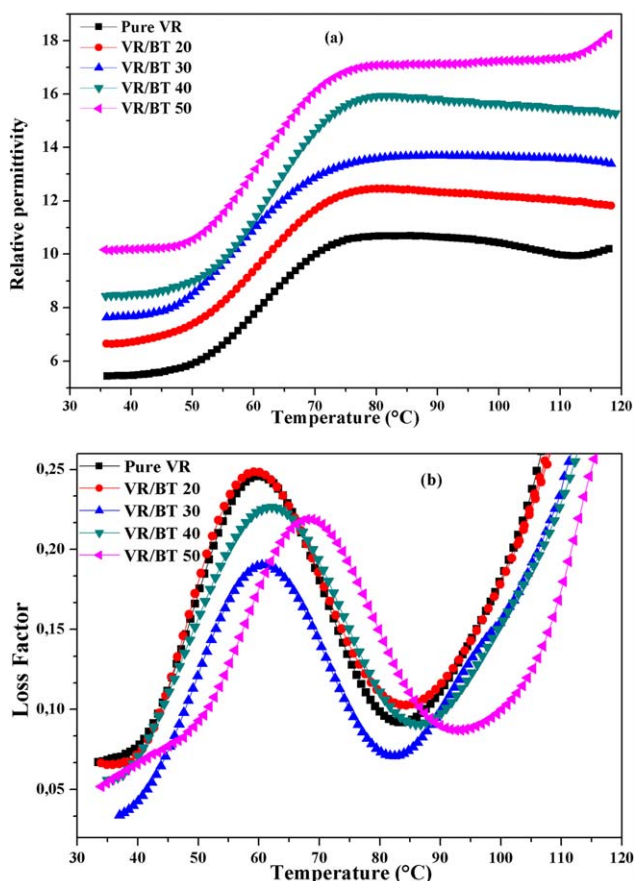
Figure 7. (a) Relative permittivity and (b) loss factor of all composites as a function of temperature at 1 kHz. [Color figure can be viewed at wileyonlinelibrary.com.]

by a continuous matrix.[2] Two rules are mostly used, logarithmic mixing rule and effective medium theory (EMT),[2,9,37] and specially two models: (i) Linchtencker logarithmic mixing law [eq. (1)] and (ii) Maxwell–Garnett theory [eq. (2)].[38,39]
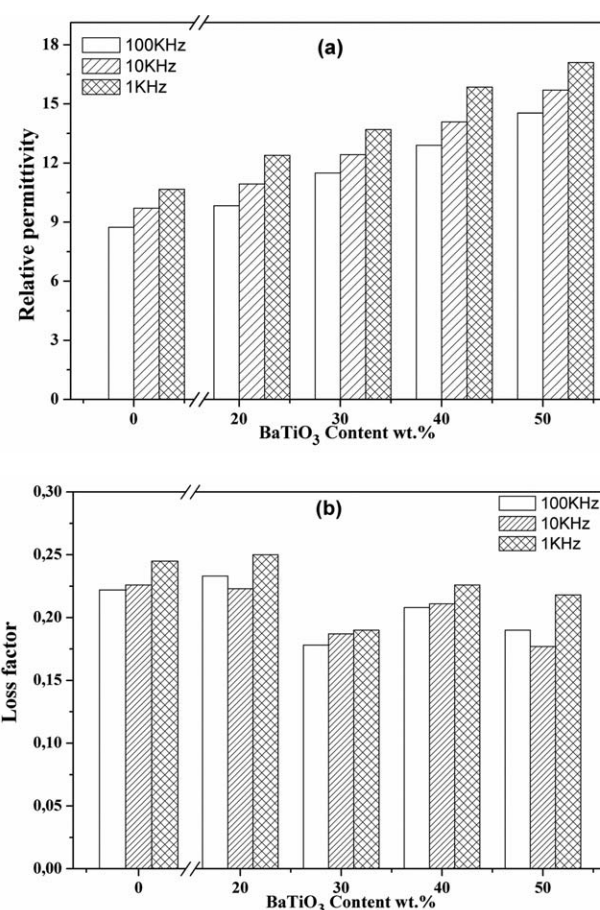
Lichtenecker logarithmic mixing law:

$$\log \varepsilon_{eff} = V_P \log \varepsilon_P + V_C \log \varepsilon_C \tag{1}$$

Maxwell-Garnett theory:

$$\varepsilon_{eff} = \varepsilon_P \frac{2\varepsilon_P + \varepsilon_C + 2V_C(\varepsilon_C - \varepsilon_P)}{2\varepsilon_P + \varepsilon_C - V_C(\varepsilon_C - \varepsilon_P)} \tag{2}$$

where ε_{eff} represents the effective dielectric constants of polymer composite systems. (V_c, ε_c) and (V_P, ε_p) represent the volume fraction and relative permittivity of ceramic and polymer, respectively. The volumes fractions V_c and V_P are linked by the relation $V_P = 1 - V_c$. Each fraction represents a mixture constituent's volume divided by the total composite's volume.

The results of calculations performed by using eqs. (1) and (2) are plotted in Figure 9(a) to hold a comparison with experimental results of composites as a function of volume fraction. The numerical values of relative permittivity of polymer and BaTiO$_3$ used for this simulation (at 1 kHz and 25°C) are 5.4 and 1000, respectively. It suggests that experimental data points

allows for the creation of compact particles network during the films formation. This means the good dispersion of grains in the matrix [as shown by Figure 4(b)] and a synergy between dielectric properties of constituents. This effect is more visible on Figure 8, which represents the permittivity and loss factor at the maximum associated to the relaxation phenomenon for three frequencies as a function of BaTiO$_3$ filler loading. It can be observed that dielectric constant increase and losses decreases with the increasing filler loading. This behavior can be explained by the increase of hydrogen bonds and/or dipole-dipole interaction between the surface of the "BaTiO$_3$ particles" and "polar groups of the vinyl acetate and VeoVa" that would lead to a cooperative polarization.[21,36] The occurrence of a quite high loss factor [Figure 8(b)] is unavoidable due to the apparition of space charges between polymer and particles interface,[36] accompanied by decreasing in loss values while increasing filler loading. This observation indicates that, as the loadings increase, the contribution of reorientable dipoles and polar entities are lowered due to the hindrance effects of the nanopaticles.[24,25]

The literature shows that there are several theoretical approaches, which describe the dielectric behavior of biphasic composite similar to the one used in this study. Generally, they take into account ceramic particles surrounded homogeneously

Figure 8. (a) Relative permittivity and (b) loss factor for three selected frequencies at the maximum associated to relaxation phenomenon, as a function of BaTiO$_3$ filler loading.
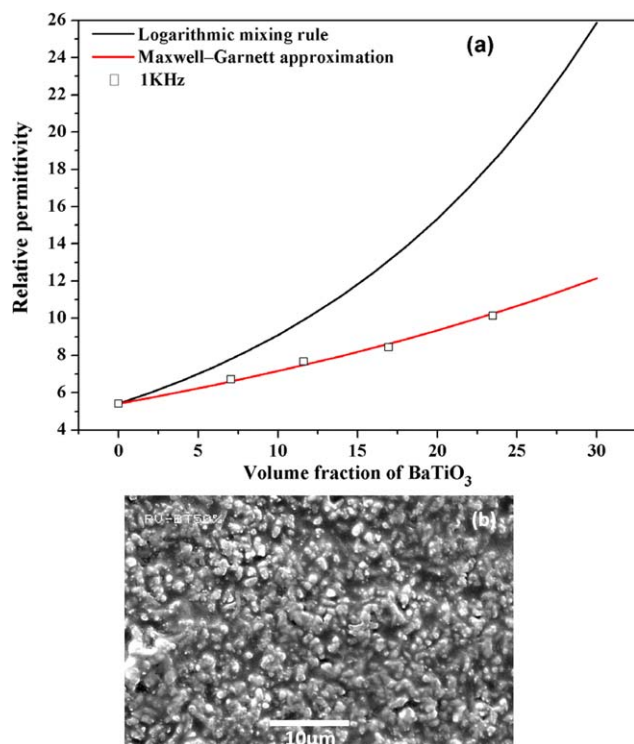
Figure 9. (a) Comparison between numerical models (1 kHz, 25 °C, relative permittivity are 5.4 for polymer and 1000 for BaTiO$_3$) and experimental results of composites as a function of volume fraction and (b) SEM image of composite based on 50 wt % of BaTiO$_3$. [Color figure can be viewed at wileyonlinelibrary.com.]

obey the Maxwell-Garnett theory for all filler contents. This supports previous results for a good dispersion of filler in the vinyl resin and the particles separation by a layer of resin, approved by Figure 9(b), which are the most important conditions of the Maxwell-Garnett theory.[11,38] These results are in conformity with those obtained by Nagata et al.[21] which reported that EVA/BaTiO$_3$ composites show a good relationship between the experimental results and the Maxwell's theoretical values. This is due to the introduction of polar vinyl acetate groups in the LDPE matrix, which presents an appreciable interaction between the surface of the BaTiO$_3$ particles and the vinyl acetate groups of EVA, involving the good dispersion of the particles in the copolymer.

CONCLUSIONS

Homogeneous EVA/VeoVa/BaTiO$_3$ composites were obtained by a clean, economical, and environmentally friendly method, using water as a solvent, with a simple mechanical stirring at room temperature. Using this process, a good dispersion was successfully obtained as demonstrated by the SEM/EDS observations. The evolution of the dielectric properties as a function of the BaTiO$_3$ content was correctly fitted by a Maxwell-Garnett model. This fitting of the experimental curve proves a good dispersion of filler in the vinyl resin and the particles separation by a layer of resin as expected for the preparation method used in this study. The homogeneous dispersion of the dielectric filler in the matrix improves the synergy between dielectric properties

of the different phases inside the composite. On one hand, it can be found that high viscosity of resin keeps BaTiO$_3$ grains suspended between polymeric chains. On the other hand, the chain structure and polarity of EVA/VeoVa terpolymer also play an essential role in particles dispersion. Therefore, the strong interactions between polar groups of terpolymer and BaTiO$_3$ particles interface would create the interfacial polarization, side by side with orientation polarization, which explains the significant improvement in the dielectric properties as a function of BaTiO$_3$ filler content.

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