Toward green three-phase composites with enhanced dielectric permittivity

Adel Zyane, François Brouillette, Ahmed Belfkira, Romain Lucas, Pascal Marchet

Towards green three-phase composites with enhanced dielectric permittivity

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ABSTRACT

This work aims to investigate the dielectric potential of Microcrystalline Cellulose (MCC), a green biosourced material, as a third constituent in the three-phase composites based on Ethylene Vinyl Acetate-Vinyl Ester of Versatic Acid (EVA-VeoVa) Terpolymer and $BaTiO_3$. For that, new green three-phase composites were prepared using an economic and green process, with simple implementation at room temperature and using water as a solvent. Compared with the binary composite EVA-VeoVa/$BaTiO_3$, the three-phase composite EVA-VeoVa/$BaTiO_3$/MCC showed an improvement of the $BaTiO_3$ particles dispersion, enhanced relative permittivity and reduced dielectric loss, which explains the significance of this study.

KEYWORDS: Polymer composites, microcrystalline cellulose (MCC), barium titanate ($BaTiO_3$), environmentally friendly composite, dielectric properties.

INTRODUCTION

Recently, substantial efforts have been dedicated to find new ways to improve the performance and reduce the weight and volume of dielectric components [1]. In this regard, inorganic–organic systems (such as polymer/$BaTiO_3$ composites) have received an increasing amount of attention because of their many characteristics, in particular the effect of inorganic phases on polymeric relaxation dynamics [2]. The improvement of the dielectric properties of the polymeric composite depends on the type of fillers added, the nature of the interface between the filler and the polymer, the manufacturing process and the homogeneity of the dispersion of the particles in the matrix [3,4]. However, this improvement is observed only when large amounts of inorganic particles are added (generally over to 40 wt.%). Such high filler levels are detrimental to the mechanical properties of the film [5]. To counter this drawback, the introduction of a third constituent into the polymer/$BaTiO_3$ system was proposed [6]. Therefore, the third constituent is generally a conductive material (i.e. vapor-grown carbon fibers [7], multi-walled carbon nanotubes [8,9], nanographite [10], graphite nanosheets [11], grapheme [12], ZnO [13]). The total amount of the third component is much lower than $BaTiO_3$, but it is necessary to achieve a critical concentration of conductive fillers (i.e., the percolation threshold) [14,15]. This is required to provide a significant increase in dielectric permittivity while minimizing dielectric losses. According to the literature, the third constituent promotes the interconnection between dipoles, and causes the formation of micro-capacitor networks by separating the neighboring conductive fillers with a thin insulating polymer/ceramic layer [9,11].

Recent studies have shown that the presence of ethylene vinyl acetate (EVA) as a matrix of composite materials improves the dielectric, barrier and fire retardant properties [16–22]. The success of EVA polymers is due to its ease of fabrication, flexibility, transparency, heat sealability, high adhesivity, processablity and environmentally friendly character [19,20,23]. Several studies were conducted to evaluate the dielectric properties of EVA/BaTiO$_3$ composites. They report a good interaction between EVA and BaTiO$_3$ particles, that exhibit a good dispersion and enhanced dielectric properties [24–28]. More recently, environmentally protection has steered research efforts toward natural molecules such as cellulosic fiber and cellulose derivatives. This is due to the advantageous properties of these materials, such as low weight, high strength, free formability and substantial resistance to corrosion and fatigue [29]. Some work focusing on the dielectric properties of hybrid composites based on cellulose was reported, such as rubber/potato starch nanocrystals [30], rubber/nanofibrillated cellulose [31], natural rubber/cellulose II nanocomposites [32]. However, the application of polymer composites with cellulosic fibers in electronics is restrained by their low dielectric properties and the lack of information about morpho-structural aspects and the behavior of such materials when electrical stresses are applied [33].

Microcrystalline cellulose (MCC) is one of the most widely used cellulose derivatives in diverse applications such as medical, pharmaceutical, food, cosmetics and light chemicals [34,35]. MCC is abundant, inexpensive, environmentally friendly and renewable [34]. More importantly, the crystalline structure of this material allows the MCC to perform much better as a reinforcing filler than natural cellulose [36], also this structure has advantages in the formation of a

parallel-board micro-capacitor network with low filler loading in the ternary composite, in the same manner as conductive fillers [7–13].

In this study, MCC was chosen as the third constituent in the three phase composite based on EVA-VeoVa terpolymer and $BaTiO_3$. Up to now, there has been no report on the preparation of green three-phase composites based on EVA-VeoVa, $BaTiO_3$ and MCC. In addition to the environmentally friendly character of raw materials, we present an economic and green process to produce new dielectric composite materials. The process is simple to implement. It is carried out at room temperature and uses water as a dispersion medium. The addition of MCC should improve the dispersion of $BaTiO_3$ particles and the relative permittivity of the material. The resulting properties of the composite materials will be investigated in comparison with the EVA-VeoVa/$BaTiO_3$ system.

EXPERIMENTAL

Materials

MCC (Avicel PH-105) was received from FMC Europe NV (Brussels, Belgium). The average particle size was ~20μm. The latex W301® based on EVA-VeoVa terpolymer (referred as VR), was supplied by Société Marocaine des Polymères (SMP). The solid content of the aqueous emulsion was 51,7 wt.% with a viscosity of 7600 mPa.s and a glass transition temperature of 34°C as indicated by the supplier. Barium titanate $BaTiO_3$ (BT) was synthesized according to our previous work. It has a diameter of ~600nm [37].

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Preparation of the ternary composite

The base material used to prepare ternary composites consisted in a 80/20 blend of EVA-VeoVa terpolymer (VR) and barium titanate (BT). The preparation technique of the VR/BT binary composite was described previously [37]. The ternary composite was obtained by adding 1 to 4 wt.% MCC to the VR/BT (80/20) blend. The mixtures were left under mechanical mixing for 30 minutes at room temperature. The obtained dispersions were deposited on Teflon paper under a water-saturated atmosphere. After coalescence and water evaporation, composites were dried for at least 24h in a vacuum oven at 70°C until a constant weight was reached.

Characterization of the ternary composite

Scanning Electron Microscope/Energy Dispersive X-Ray Spectrometer (SEM/EDS) images of the composites films were obtained on a JEOL JSM-5500 and OXFORD Instruments, X-Max 20mm^2, respectively. Gold/Palladium electrodes were deposited on both sides of all samples to ensure a good electrical contact. The dielectric properties of all films were measured in the frequency range from 10^2 Hz to 10^6 Hz using a precision impedance analyzer (Agilent 4294A). Measurements were taken at different temperatures between 30°C and 120°C.

RESULTS AND DISCUSSION

Morphology of VR/BT/MCC composite films

The MCC used in polymer composites has a diameter of ~20 µm as shown by the SEM image presented in figure 1a. The chemical structure of the surface of MCC particles promotes interfacial interactions with the VR by creating bridges between hydroxyl groups of MCC and

EVA-VeoVa polymeric chain dipoles [20,38]. Also, MCC has a much lower specific gravity and a better dispersibility than BT in the initial emulsion and in the dried film. This contributes to the good dispersion of BT in the case of the ternary composite. This effect is shown in Figure 1b-d, which presents SEM images of the binary composite with 20 wt.% of BT and the ternary composites with 1 and 4 wt.% of MCC, respectively. The element mapping of different composites (Figure 2) confirms the enhanced dispersion of the BT particles in the matrix obtained by the addition of a small amount of MCC powder. Figure 2a presents some aggregation of BT particles in the VR/BT composite due to the high affinity between filler particles. The addition of 1 wt.% of MCC contributes to the decrease of these aggregations leading to a more uniform ternary composite as shown in Figure 2b. The introduction of 4 wt.% of MCC in the VR/BT composite further improves the dispersion of BT in the matrix (Figure 2c) that confirms the contribution of MCC to the enhancement of BT dispersion. This phenomenon could be explained by the effective interfacial interaction between the three phases, in addition to the hydrophilic character and the high viscosity of the medium (Latex) described in our previous work [37]. In consequence, it is possible to propose the formation of micro-capacitor networks, in which the crystalline areas of MCC act as electrodes and the VR/BT serves as the medium, in the same manner as in the case of PI/graphene/BT [12].
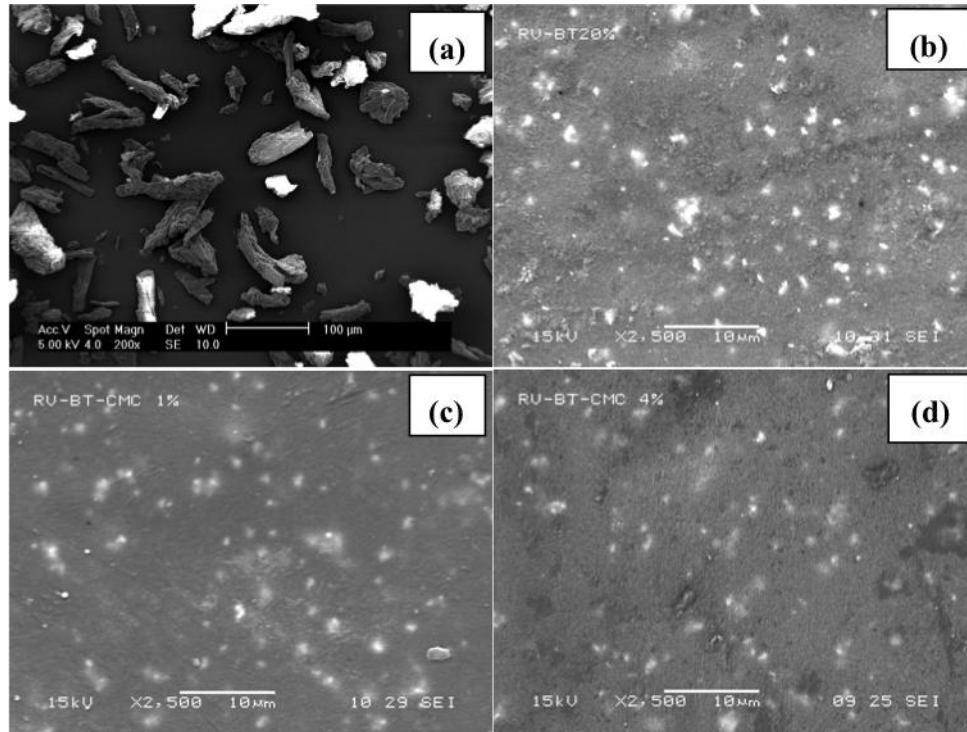
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Figure 1: SEM images of (a) MCC powder, (b) VR/BT binary composite with 20 wt.% of BaTiO$_3$, (c) and (d) VR/BT/MCC ternary composites with 1 and 4 wt.% of MCC, respectively.
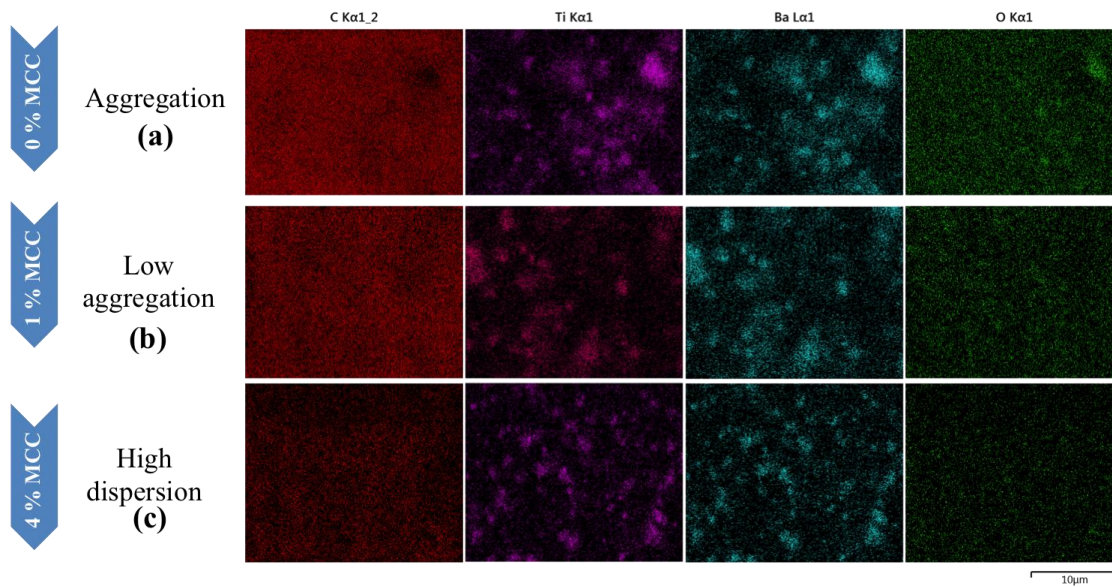

Figure 2: Elements mapping (carbon, titanium, barium and oxygen) of (a) binary composite VR/BT with 20 wt.% of BT, (b) and (c) ternary composites VR/BT/MCC with 1 wt.% and 4 wt.% of MCC, respectively.

Dielectric properties

Figure 3 presents the temperature dependence of the dielectric permittivity and loss factor of the pure resin and different composites at 1 kHz. In the present study, the BT content of the composite films was 20 wt.%, to which an additional amount of 1 to 4 wt.% MCC was added. Figure 3a illustrates that the relative permittivity increases as a function of temperature, due to the orientation polarization of the polar groups of the polymer, as explained in our previous work [37]. Also, the dielectric permittivity of the composites increased with MCC concentration for the whole temperature range. VR/BT/MCC composites achieved a dielectric permittivity of 19.15 when the MCC content reached 4 wt.%, which is 1.8 and 1.5 times higher than that of pure VR and VR/BT 80/20 composite, respectively. These results are also higher than those previously reported for VR/BT composites. In other words, the BT content of the composite can be relatively reduced from 50 to 20 wt.% by adding only 4 wt.% of MCC [37].

Dielectric applications require another important parameter, which is the dielectric loss (tanδ). The temperature dependence of the dielectric loss of the composites, with different amounts of MCC, is shown in Figure 3b. Composites with both BT and MCC show much smaller dielectric losses than the pure VR and the VR/BT composite, which establishes the significance of this study. VR/BT/MCC composites had a tanδ of 0.012 at low temperature and 0.15 at the maximum of relaxation when the MCC content reached 4 wt.%. These results are 5.5 and 1.7 times smaller than that of pure VR and VR/BT 80/20 composite, respectively. The reduced dielectric loss is due to the progressive formation of strong bridges between MCC and VR, BT and VR and BT/MCC interfaces. In parallel, the slight leakage of conducive current and the third

constituent are not connected [12]. Instead of the result reported by Fu-An He et al. for

sPS/BaTiO$_3$-GNs composites [11], VR/BT/MCC composites do not present conductive paths,

which give rise to the leakage of conducive current, responsible for the increase of the

dielectric loss. In our case, the incorporation of MCC leads to the formation of successive thin

dielectric layers that effectively blocked the leakage current and contributed to the reduction of
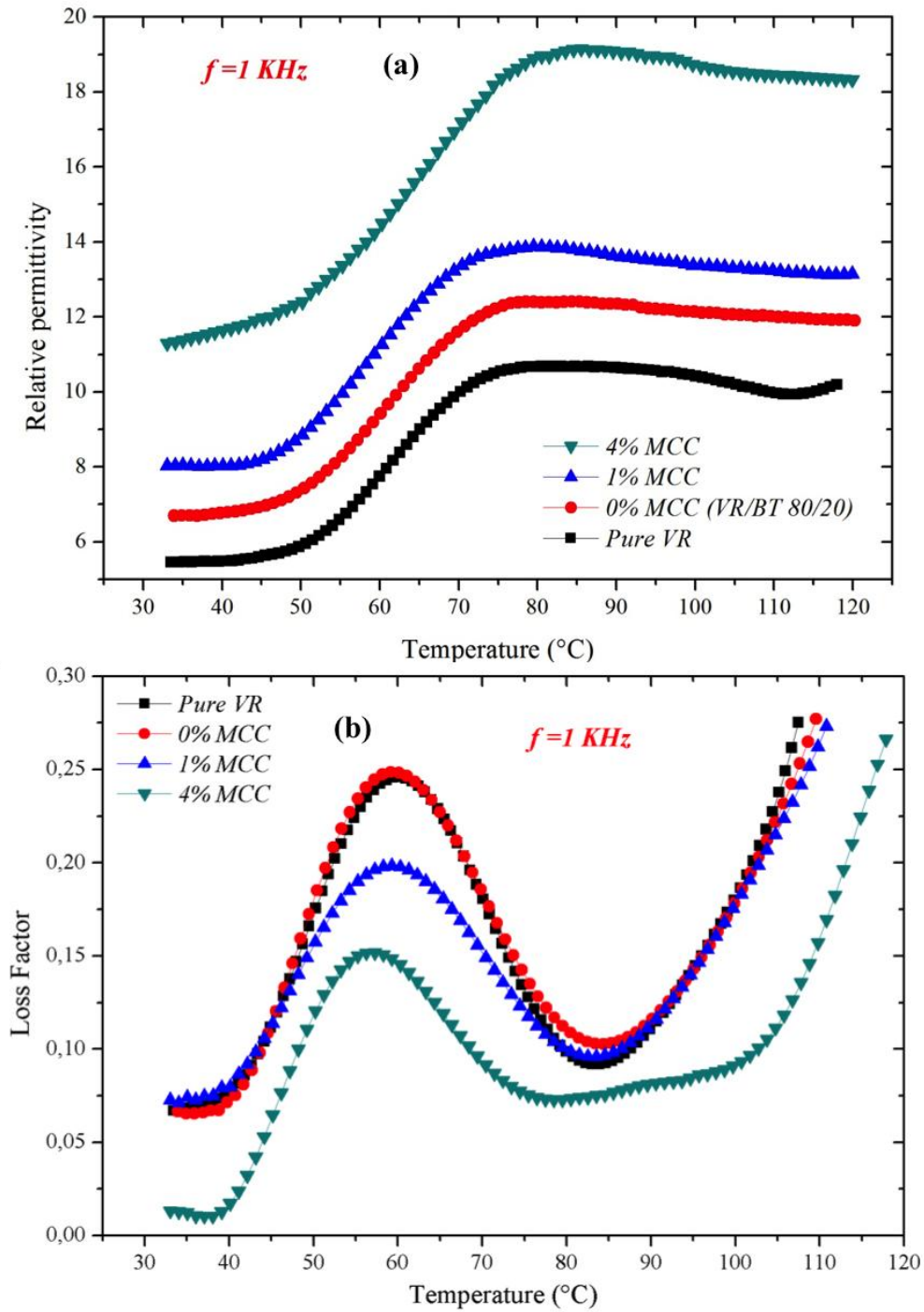
the dielectric loss.

Figure 3: Temperature dependence of (a) dielectric permittivity and (b) loss factor of pure VR and VR/BT/MCC composites with different amounts of MCC at 1 kHz.

Figure 4 represents the dielectric permittivity of the maximum transition (Figure 3) as a function

of MCC loading at different frequencies. It can be observed that the dielectric permittivity

decreases with increasing frequency. This inverse dependence can be explained experimentally.

When the frequency is raised, the dipoles get much less time to orient themselves in the

direction of the applied field [37,39]. Also, Figure 4 shows that the dielectric permittivity

increases similarly with the increase in MCC loading for all frequencies. This increase can be

ascribed to the interfacial polarization (Maxwell-Wagnar effect) originating from the VR/MCC,

VR/BT, and BT/MCC interfaces [40]. However, according to the percolation theory, this increase

in polarization can be attributed to the existence of several micro-capacitors resulting from the

separation of neighboring conductive fillers with a thin insulating polymer/ceramic layer as it

was shown for other ternary composites: PVDF/BT/GN and PS/BT/GNs (Graphite Nanosheets)

[10,11]. In our case, it is possible to imagine the formation of micro-capacitor networks, in

which the crystalline zones of MCC act as electrodes and the VR/BT serves as medium. For

visual understanding of the dimensional structure of the different constituents in the ternary

composite, Figure 5 shows the schematic microstructure evolution processes of VR/BT (0 wt.%

of MCC) and VR/BT/MCC (1 and 4 wt.% of MCC). Figure 5a shows that BT particles can be

distributed uniformly in the VR matrix with some aggregation in accordance with element

mappings (Figure 2). These aggregations decrease when 1 wt.% of MCC is incorporated in the

VR/BT composite, as it can be observed in figure 5b. The introduction of 4 wt.% of MCC in the

VR/BT composite improves the BT dispersion in the matrix as shown in Figure 5c. However,

MCC particles can effectively inhibit the connection of BT particles to increase dispersion of

fillers on the one hand and on the others to reduce the leakage current in the BT network and

endow the film with reduced dielectric loss. Moreover, MCC particles lead to the formation of a

micro-capacitor network, which structure is represented with red dash circles in Figure 5c.

Therefore, high charges are generated and accumulated in the micro-capacitors when an

electric field is applied to the film. This induces the abrupt increase of capacitance and the

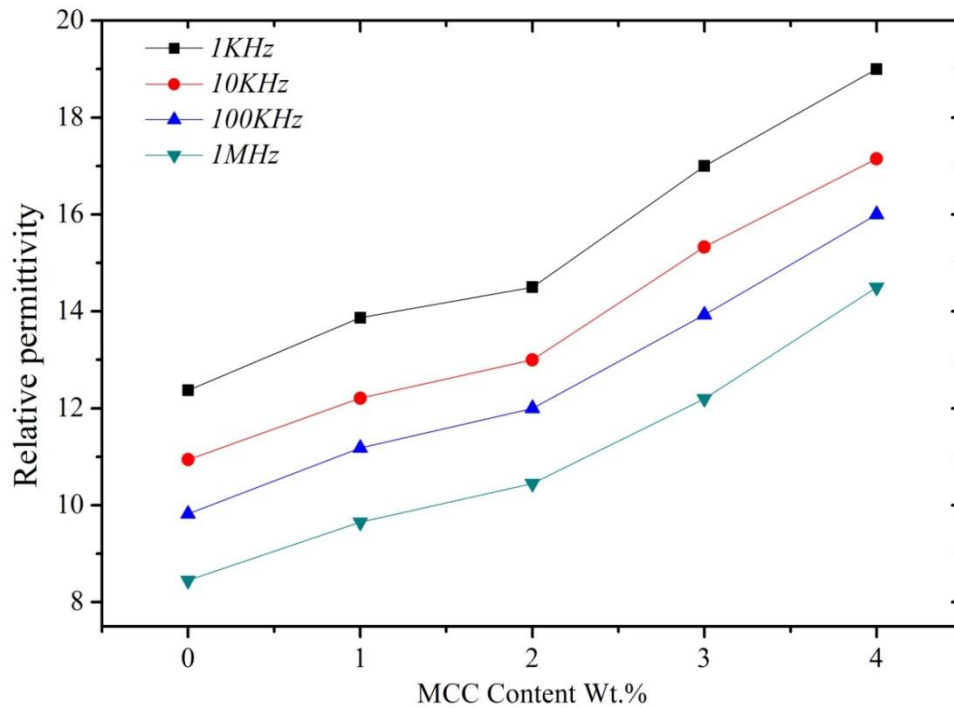dielectric permittivity subsequently increases.

Figure 4: Dielectric permittivity of VR/BT/MCC composites as a function of MCC loading at different frequencies.
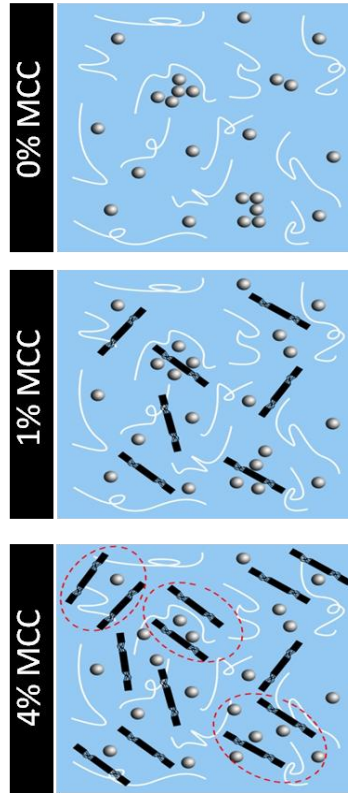
Figure 5: Schematic microstructure of VR/BT (0 wt.% of MCC) and the three-phase composites VR/BT/MCC (1 and 4 wt.% of MCC).

CONCLUSIONS

Microcrystalline Cellulose (MCC) was chosen as the third constituent in the three-phase composites based on EVA-VeoVa terpolymer (VR) and $BaTiO_3$ (BT) to prepare new green three-phase dielectric composites. The addition of MCC to the VR/BT composites leads to a significant enhancement of properties: (i) MCC particles can effectively inhibit the connection of BT particles to increase the dispersion of fillers in the matrix by creating bridges with the composite constituents; (ii) MCC particles promote the formation of a micro-capacitors network that can generate and accumulate high charges when an electric field is applied to the film. This induces an abrupt increase of capacitance and a subsequent increase of the dielectric

permittivity; (iii) MCC particles lead to the formation of successive thin dielectric layers that effectively blocked the leakage current and contributed to the reduction of the dielectric loss.
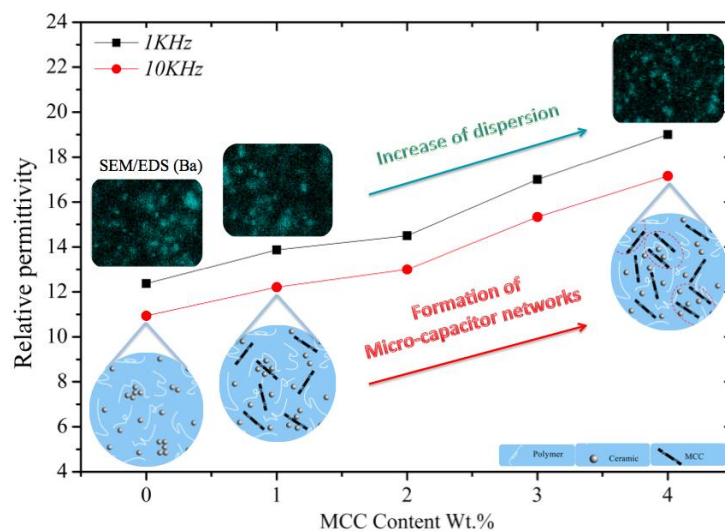
ACKNOWLEDGEMENTS

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GRAPHICAL ABSTRACT

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