CELLULOSE CHEMISTRY AND TECHNOLOGY

MICROCRYSTALLINE CELLULOSE AS A GREEN WAY FOR SUBSTITUTING $BaTiO_3$ IN DIELECTRIC COMPOSITES AND IMPROVING THEIR DIELECTRIC PROPERTIES

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Barium titanate (BT) and microcrystalline cellulose (MCC) were used to improve the dielectric properties of a commercial vinylic resin. Using a green method, two binary composites (vinylic resin/$BaTiO_3$, vinylic resin/MCC) and one ternary composite (vinylic resin/$BaTiO_3$/MCC) were prepared. The results obtained for the MCC containing composite show an identical evolution of the relative permittivity compared to $BaTiO_3$ composites with weak dielectric losses. In consequence, the feasibility of the substitution of $BaTiO_3$ with MCC, an economical and biosourced material is demonstrated.

Keywords: polymer composites, biocomposites, dielectrics, barium titanate, microcrystalline cellulose

INTRODUCTION

The actual trend toward miniaturization in the electronics industry has opened a wide research field for dielectric composites because they exhibit properties associated to both organic and inorganic materials.[1] The main advantage of these composites comes from the possibility to obtain various properties according to the characteristics of the constituting materials. Among these characteristics, nature, inclusion shape, volume fraction, dispersion in the matrix and orientation under external constraints have a significant influence on the physical properties of the final material.[2,3] For example, several studies have been published about the dispersion of polar particles in weakly polar polymeric matrices. In one of them, X. Zhao *et al.*[4] have compared polydiacrylate-$BaTiO_3$ composites prepared by thermal treatments and electron beam. The second method gave the best particle dispersion and permittivity. Environment protection has oriented research efforts toward natural molecules. In the last decade, the use of polysaccharide-based products such as starch and cellulose derivatives has rapidly spread.[5] In this context, Bouthegourd *et al.*[6] have elaborated a composite containing rubber and potato starch nanocrystals. The correlation between dielectric properties and conductivity was used to determine the agglomeration threshold of nanoparticles (15 wt%). More recently, the addition of a third element (i.e. fiber glass, multi-walled carbon nanotubes, vapor-grown carbon fibers) to the binary mixture was shown to improve dielectric properties. This addition promoted the interconnection between dipoles thus helping the formation of micro-capacitors and the improvement of the dielectric permittivity of the material while minimizing dielectric losses.[7,8,9]

In this paper, we describe the realization of three types of polymer/ferroelectric oxide composites: vinylic resin/barium titanate (VR/BT), vinylic resin/microcrystalline cellulose

(VR/MCC) and vinylic resin/barium titanate/microcrystalline cellulose (VR/BT/MCC). Room temperature dielectric responses at different frequencies were measured for various concentrations of ferroelectric oxide, microcrystalline cellulose and combinations of both materials. Using the same preparation method for all binary and ternary composites allowed comparing the effect of BT and MCC on dielectric properties.

EXPERIMENTAL

Materials

The vinylic resin emulsion (W301) was supplied by the Société Marocaine des Polymères (SMP) and consisted in an Ethylene Vinyl Acetate/VeoVa terpolymer (VeoVa is the vinyl ester of versatic acid). The solid content of the resin was 51.7 wt% with a viscosity of 7600 mPa.s and a glass transition temperature of 34 °C as indicated by the supplier. The microcrystalline cellulose (Avicel PH-105) was received from FMC Europe NV (Brussels, Belgium). The average particle size was ~20 µm. Barium titanate (BT) was custom-made by reacting stoichiometric amounts of solid TiO_2 and $BaCO_3$ (both from Sigma Aldrich) at 1100 °C for 2 hours in a laboratory oven. The average particle size of the obtained solid was ~600 nm as determined by a laser particle size analyzer (HORIBA Partica LA-950V2).

Composite preparation

Binary composites were prepared by adding predefined weight percentages (10, 20, 30, 40 and 50 wt%) of BT or MCC to the vinylic resin. The dispersion was kept under mechanical mixing at room temperature for 30 minutes. For ternary composites, the 80/20 VR/BT blend was used as the base material to which an additional amount of 1 to 4 wt% MCC was added.[10] The mixtures were left under mechanical mixing for 30 minutes at room temperature. The obtained dispersions were deposited on Teflon paper under a saturated atmosphere. After coalescence and water evaporation, composites were dried in a vacuum oven at 70 °C until a constant weight was reached (at least 24 h).[11]

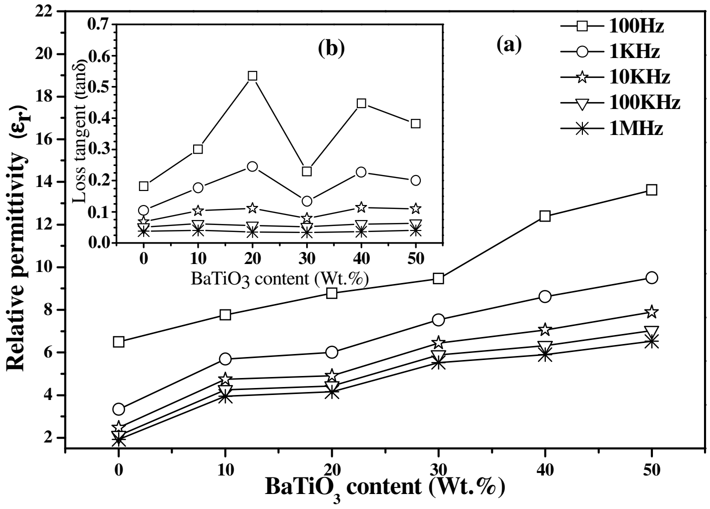
Dielectric measurements

Dielectric measurements were carried out at room temperature (27 °C) with an impedancemeter (Agilent 4294A) using a cell (Agilent 16451B) allowing direct measurements without any electroding of the samples. The frequency sweep was from 100 Hz to 1 MHz.

RESULTS AND DISCUSSION

Vinylic resin/$BaTiO_3$ (VR/BT) and vinylic resin/MCC (VR/MCC) composites

Figure 1 shows the variation of the relative permittivity (ε_r) and the loss factor (tan(δ)) with BT and MCC loadings. The relative permittivity increases with the percentage of added particles and decreases with frequency. For a 50 wt% BT loading, the ε_r value reaches 13.60 at 100 Hz, which is 2.1 times the value obtained for the vinylic resin alone. A similar result was obtained for the 50 wt% MCC loading with a value of 13.20. The results for VR/BT are in accordance with those obtained with resins having a similar permittivity.



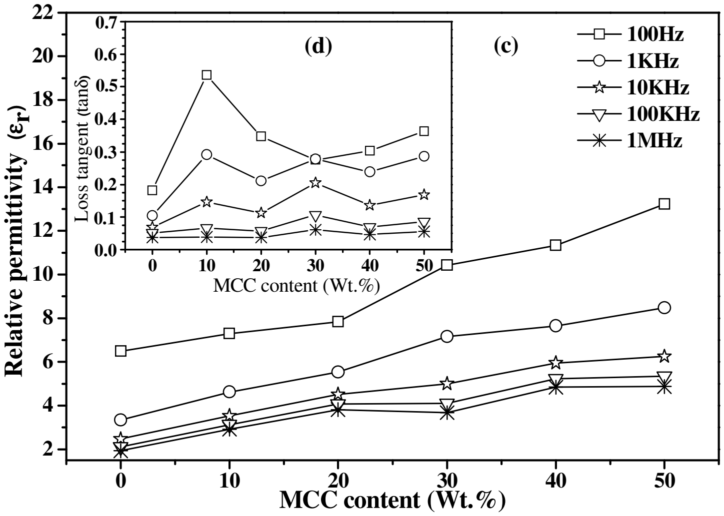


Figure 1: Dielectric constants (a) and (c) and loss factors (b) and (d) for VR/BT and VR/MCC composites

For example, F.J. Wang *et al.*[12] found permittivity values in the range of 4 (pure resin) to 12.5 for a polyethersulfone-BT (50 wt%) composite at 100 kHz. For both BT and MCC composites, dielectric losses are almost constant at high frequencies. In the low frequency range, very high values are obtained due to the polarization mechanism: the contribution of added particles (BT and MCC) to the increase of the dielectric permittivity is due to the appearance of space charges (or interfacial polarization) in the polymeric matrix. The combination of space charges and orientation polarization give a high relative permittivity with a unique relaxation. The same effect was observed by N.J.S. Sohi *et al.*[13] by adding carbon black, short carbon fibers or carbon nanotubes to an Ethylene Vinyl Acetate resin. In our case, the contribution of MCC is caused by local movements of polysaccharide chains[11] and by the increase in the dipolar moment of the composites due to the hydroxyl groups present on MCC particles.[14] Also, strong MCC-VR interactions are responsible for the high permittivity at 50 wt% MCC (13.20). This value is higher than those reported by M. Beztout *et al.*[14] for the addition of 30 wt% MCC in PVC-MCC (ε_r=3.76 to 4.19). D. M. Panaitescu *et al.*[15] also studied the addition of MCC to PE, but the effect of MCC on the permittivity was marginal: 3.3 for PE alone and 3.8 for a 20 wt% loading of MCC.

Other recent studies have used nanoparticles, with or without modification or coupling, to insure an improvement of the dielectric permittivity of composites.[16,17] It has been shown that this improvement is observed only when large amounts of particles are added, generally over 40 wt%. This high loading adversely affects the mechanical properties of the film. To overcome this drawback, a third constituent is necessary.[8,10,18] This third constituent improves the connectivity between dipoles and makes it possible to decrease the amount of incorporated particles. In our case, and considering previous results, MCC was chosen as the third constituent to improve the relative permittivity by creating bridges between polymeric chain dipoles.

Vinylic resin/BaTiO$_3$/MCC (VR/BT/MCC) hybrid composites

Figure 2 shows the effect of the MCC loading (from 1 to 4 wt%) on ε_r and tan(δ) for the hybrid composite (VR/BT/MCC). The relative permittivity (Figure 2.a) increases with the mass fraction of MCC. It reaches a value of 13.24 at 100 Hz at the maximum MCC loading (4 wt%). This value is 1.5 times higher than the one obtained for the base composite VR/BT 80/20 (~8.75). Y.C. Li *et al.*[10] have found a similar effect by adding nanographite (GN) particles to a polyvinylidene fluoride (PVDF)/BT composite. Dielectric losses (Figure 2.b) exhibit a remarkable decrease with increasing MCC loading. For a 100Hz frequency, the base composite has a tan(δ) of 0.53 compared to 0.17 for the 4 wt% MCC hybrid composite. Both RV/BT/MCC 80/20/4 and RV/BT 50/50 composites have similar relative permittivities (~13.60), but different dielectric losses (0.17 vs. 0.38). In consequence, we can conclude that by adding 4 wt% MCC to the composite, the $BaTiO_3$ loading can be reduced from 50 wt% to 20 wt% while keeping the same relative permittivity and reducing the losses. The high permittivity obtained with MCC is generally associated to the charge spacing polarization between MCC-VR and MCC-BT.[8] This leads to interfacial polarization, which adds to other types of polarization: polymer chain orientation and VR-BT interface. According to the percolation theory, this increase of polarization can be attributed to the existence of several micro-capacitors formed by the separation of charges in the neighborhood of a polymer/ceramic insulating layer, as it is the case for ternary composites, PVDF/BT/GN and PS/BT/GNs(Graphite Nanosheets).[10,18]

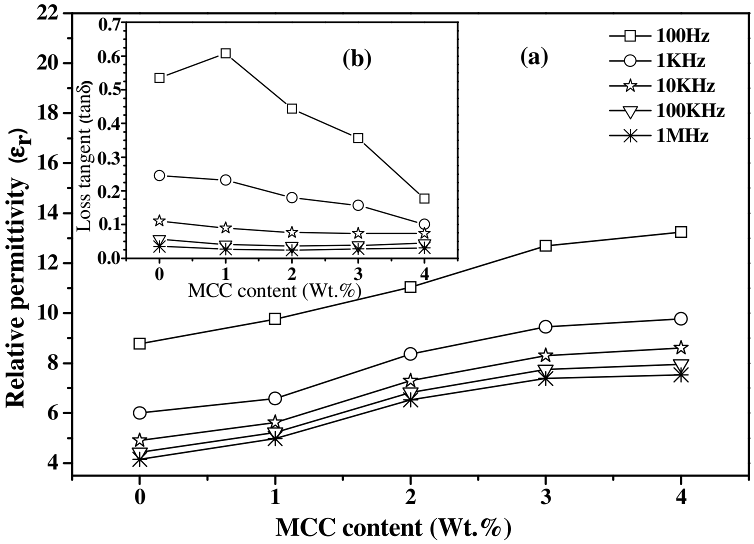


Figure 2: Dielectric constants (a) and loss tangents (b) with MCC content for VR/BT/MCC (80/20/x wt%) hybrids

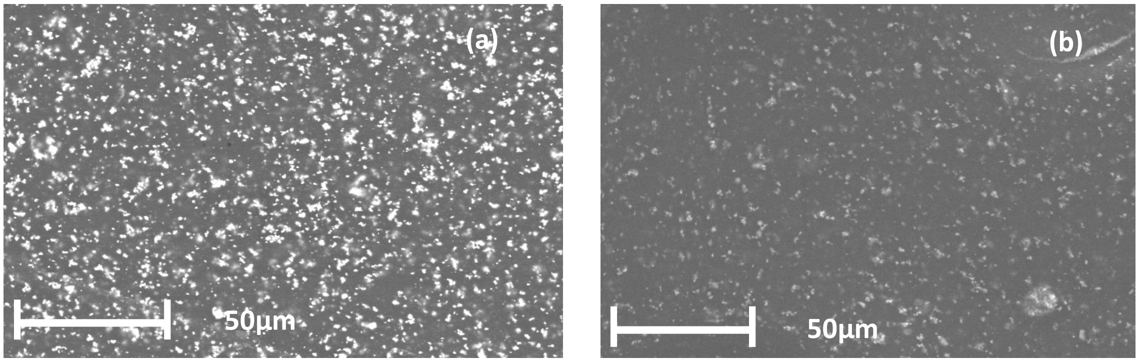


Figure 3: SEM micrographs of (a) binary composite VR/BT 80/20, and (b) ternary composite VR/BT/MCC 80/20/4 (white: $BaTiO_3$; black: Polymer and MCC)

The introduction of MCC with the resin alone or containing BT has promoted the improvement of dielectric properties of the composite compared to BT alone. 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 (Figure 3). In consequence, it is possible to imagine the formation of micro-capacitors, in which the crystalline area of MCC acts as electrodes and BT together with the VR matrix serve as medium, in the same manner as in the case PI/BT/graphene.[19] In consequence, charges accumulate in the micro-capacitors, and the dielectric permittivity subsequently increases.[19] As dielectric losses are linked to charge movements (radical or chain segment relaxations), the steadiness, or reduction, of losses can be explained by the immobilization of charges caused by the presence of strong hydrogen bonds in the system. This would confirm the formation of macro-dipoles by the introduction of MCC.

CONCLUSION

In conclusion, on the one hand, MCC proved to be a very good replacement for $BaTiO_3$ to improve dielectric properties (ε_r and tanδ) of polymeric materials. On the other hand, using MCC instead of graphite nanosheets, as the third phase of a RV/BT 80/20 composite, illustrated the potentiality of this biosourced compound in polymeric dielectric materials. These first results open the way for new possibilities in composite green chemistry for applications in the electronic industry.

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