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# Dielectric Behaviour of $CaCu_3Ti_4O_{12}$-Epoxy Composites

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The dielectric behavior of composite materials (epoxy resin – barium titanate and epoxy – CCTO) was analysed as a function of ceramic amount. Composites were prepared by mixing the components and pouring them into suitable moulds. In some compositions, the matrix was reduced by tetrahydrofuran (THF) incorporation. Samples containing various amounts of ceramic filler were examined by TG/DTA and scanning electron microscopy analysis. Dielectric measurements were performed from 20 Hz to 1 MHz and 30 to 120 °C. It was demonstrated that the epoxy – CCTO composites possessed higher permittivity than classic epoxy – $BaTiO_3$ composites. However, the low resin permittivity prevailed in the composite dielectric performance.

**Keywords:** *polymer-matrix composites (PMCs), electrical properties, composites*

## 1. Introduction

In recent years, there has been an increasing interest on high dielectric constant flexible particulate composites made up of a ferroelectric ceramic and a polymer for high density energy storage and capacitor applications[1]. However, the dielectric constant of such polymer based composites is rather low (about 50) because of the lower dielectric constant of the matrix (usually below 10)[1-5]. For instance, in $BaTiO_3$/epoxy composites, though $BaTiO_3$ has relatively high dielectric constant (>1000), the effective dielectric constant ($\varepsilon_{eff}$) of the composite was as low as 50, even when the highest possible volume fraction of ceramics was incorporated[2]. As the volume fraction of ceramics increased, the composite, unfortunately, lost its flexibility.

A new generation of ultrahigh dielectric materials such as $CaCu_3Ti_4O_{12}$ (CCTO) can be used in order to obtain composites with better performance[6]. A number of theoretical studies and experimental observations has attempted to elucidate the remarkable (ultra high) dielectric properties of CCTO perovskite-like material. These materials have demonstrated to have a dielectric constant as high as 50,000.

In this work, the dielectric performance of epoxy – CCTO composites was studied. Systems were prepared mixing components with a solvent (tetrahydrofuran, THF) in order to reduce the polymer viscosity and to pour them into suitable moulds. Relaxation phenomena as a function of frequency, temperature, and filler volume fraction were analysed.

## 2. Experimental

Epoxy DER 325 (Dow Chemical) was chosen because of its good dielectric properties ($\varepsilon = 4.5$, $\tan\delta = 0.0082$). DEH 324 (Dow Chemical) was the curing agent (12.5 phr) and THF (Dorwil Chemical) was used as solvent (9 phr).

$CaCu_3Ti_4O_{12}$ (CCTO) polycrystalline ceramics were prepared by solid-state reaction. All the starting materials used were of analytical grade: $CaCO_3$ (Aldrich, 99.99%), $TiO_2$ (Aldrich, 99.8%), and CuO (Riedel, 99%). These materials were ball milled in an alcohol medium for 24 hours in a polyethylene bottle, using zirconium balls. After this, the slurry was dried and thermally treated at 900 °C in air atmosphere for 12 hours. In order to compare the influence of CCTO addition on the epoxy resin, $BaTiO_3$ composites were prepared. In this way, commercial barium titanate, $BaTiO_3$ (TAM Ceramics Inc.) was used as filler. It was doped with 0.6 mol (%) of $Nb_2O_5$ to modify its dielectric properties. Powders were mixed in isopropilic alcohol by agitation at 6000 rpm during 5 minutes. Afterwards, alcohol was eliminated by heating at 65 °C until constant weight was achieved. The powder was thermally treated at 1350 °C for 180 minutes using a heating and a cooling rate of 3 °C/min. The powder was milled using a planetary mill with $ZrO_2$ balls (Fritsch, Pulverisette 7) for 90 minutes in isopropilic medium.

The ceramic powders were added to the epoxy resin at different volume fractions and then suitably blended using an ultrasonic mixer (Sonic vibra-cell 150 W) for 4 minutes. THF was introduced to reduce the viscosity of the mixture with filler fractions between 5 and 15 vol (%). Each mixture was poured into glass moulds and cured at 100 °C for 2 hours. Afterwards, samples were analysed by thermal gravimetric technique (TGA, Shimadzu TGA-50) in a nitrogen atmosphere and at a heating rate of 10 °C/min from room temperature to 800 °C. Density ($\rho$) was measured by Archimedes' method and theoretical density ($\rho_T$) was calculated using Equation 1.

$$\rho_T = (1 - V).\rho_p + V.\rho_m \qquad (1)$$

where $\rho_p$ is the filler density, $\rho_m$ is the matrix density, and V is the volume fraction of filler.

Finally, for dielectric measurements, samples were painted with a silver paste. Dielectric measurements were performed using a Hewlett Packard 4284A Impedance Analyser from 20 Hz to 1 MHz between 20 and 120 °C.

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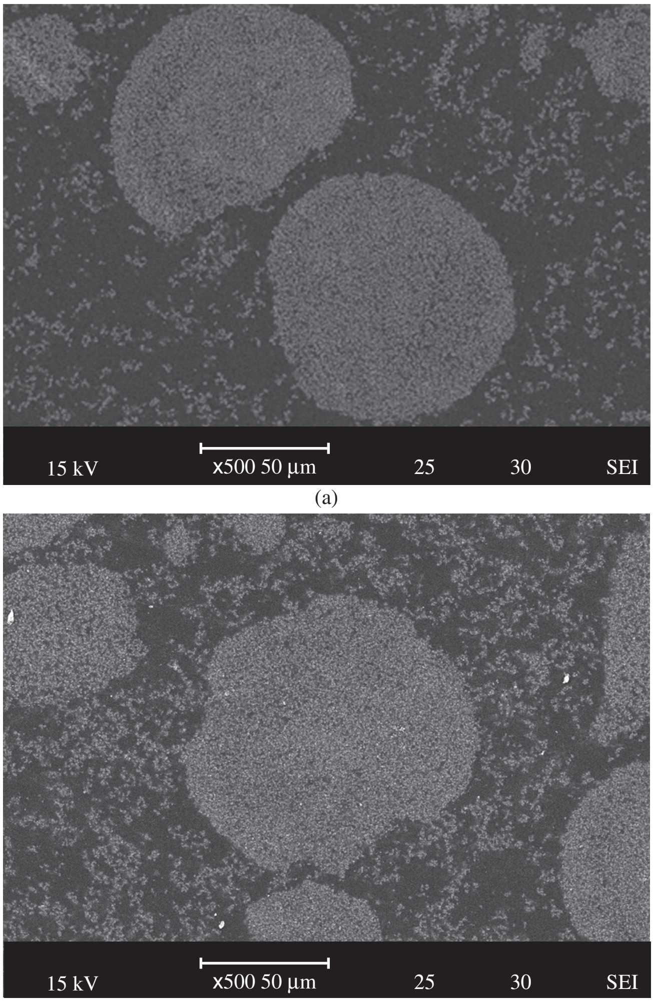
## 3. Results and Discussion

The experimental and theoretical densities of CCTO composites for different filler amounts are shown in Table 1. The difference between the experimental ($\rho_E$) and theoretical ($\rho_T$) density values is fundamentally due to the presence of pores into the composite, which are produced during the mixing process when air flow is restricted due to the high viscosity of the system.

Micrographs obtained by scanning electron microscopy of composites are shown in Figure 1. Regions without filler or trails of microporosity are observed. Moreover, particles with low size and relative fine distribution size can be seen. In both samples, particle distribution is not homogeneous and there is a lot of particle agglomeration due to a bad dispersion of particles during the mixing step.

**Table 1.** Theoretical ($\rho_T$) and experimental ($\rho_E$) density and calculated porosity of composites with different CCTO volume fraction (determined through $^x$TGA).

| Volume fraction (%)$^x$ | $\rho_T$ (g.cm$^{-3}$) | $\rho_E$ (g.cm$^{-3}$) | Porosity (%) |
|---|---|---|---|
| 4.90 | 1.336 | 1.336 | 0.00 |
| 9.84 | 1.526 | 1.514 | 0.83 |
| 14.63 | 1.711 | 1.686 | 1.51 |



(a)

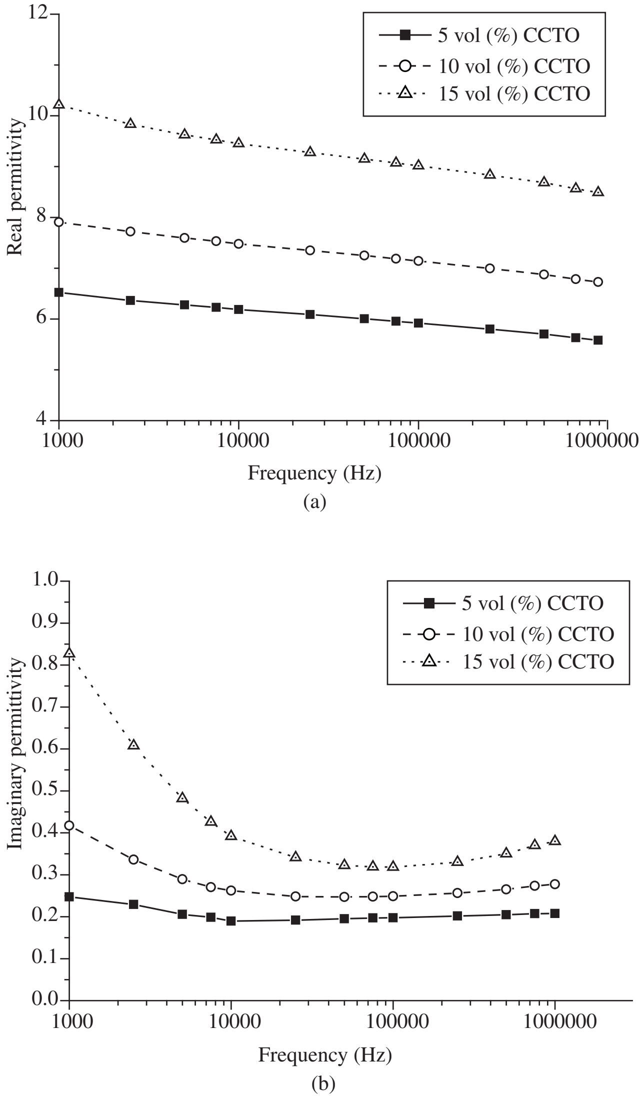
(b)

**Figure 1.** SEM of composites with a) 10 and b) 15 vol (%). Bar 50 μm.

Figures 2 and 3 show real and imaginary permittivity parts as a function of frequency and temperature, respectively. As it can be expected, real permittivity rose as the ceramic volume fraction increases. Values as high as $10\varepsilon_0$ were obtained with the addition of only 15 vol (%) of particles. Besides, the real permittivity increased as the temperature did (Figure 3) due to the higher mobility of polymer chains. Moreover, it was observed that imaginary permittivity decreased at low frequencies (Figure 3b), because of a relaxation process[7-8].

Changes in the permittivity values as a function of frequency are attributed to dielectric relaxations. These are more pronounced at low frequencies and high temperatures due to micro-Brownian motion of the whole chain (segmental movement). Nevertheless, these changes are also affected by the interfacial polarization process known as Maxwell-Wagner-Sillar, which exists in heterogeneous dielectric materials and is produced by the traveling of charge carriers[9].

In order to study the frequency and temperature dependence of relaxation processes, electrical modulus was used. Figure 4 shows the real and imaginary parts of the electrical modulus obtained



(a)

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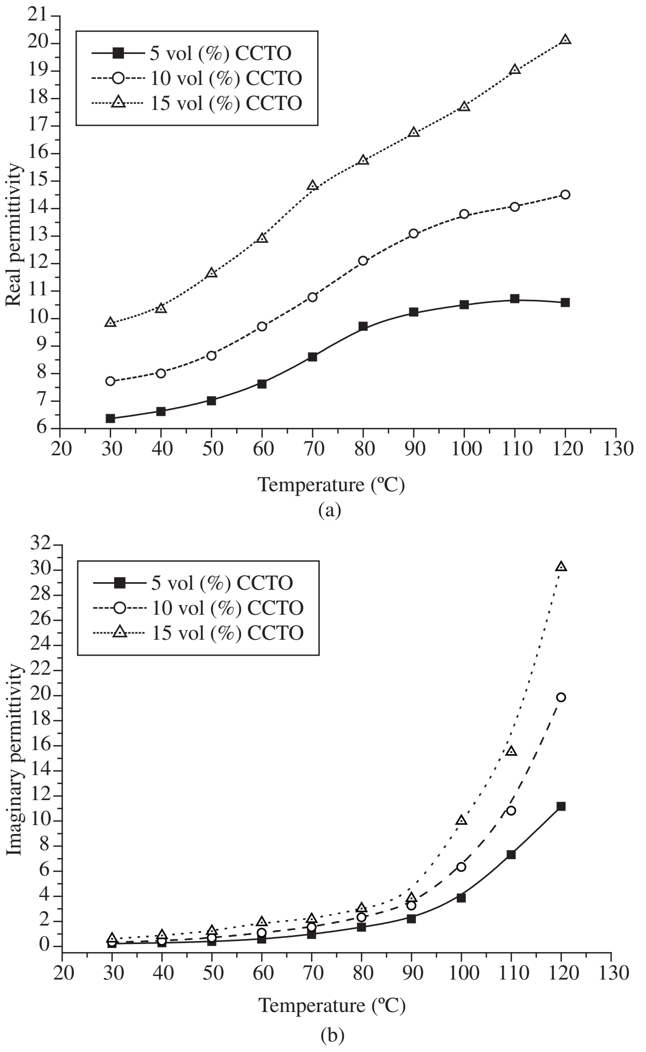
**Figure 2.** a) Real and b) imaginary permittivity vs. frequency for composites with different CCTO volume fraction (Temp. 30 °C).



(a)

(b)

**Figure 3.** a) Real and b) imaginary permittivity vs. temperature for composites with different CCTO volume fraction (Freq. 2500 Hz).

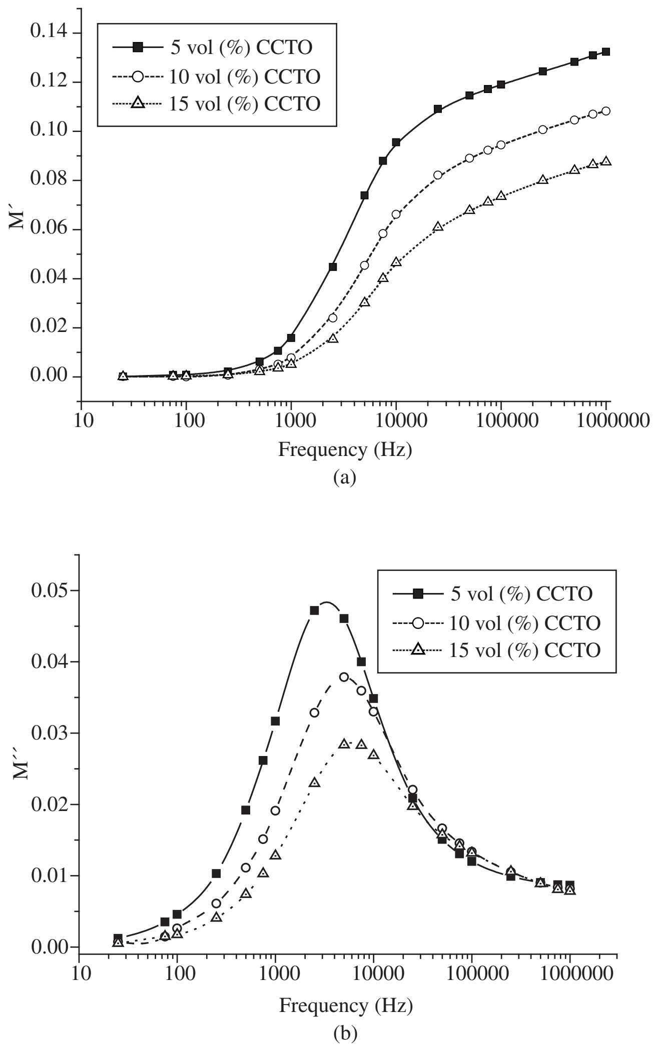
through Equation 2[7] as a function of frequency and temperature, respectively.

$$M^* = \frac{1}{\varepsilon^*} = \frac{1}{\varepsilon' - j\varepsilon''} = \frac{\varepsilon'}{\varepsilon'^2 + \varepsilon''^2} + j\frac{\varepsilon''}{\varepsilon'^2 + \varepsilon''^2} = M' + j'.M'' \quad (2)$$

In Figure 4 it can be seen that M´ values increased with frequency. Nevertheless, peaks in M´´ values were developed at this same frequency range, indicating the appearance of a relaxation process (α relaxation). The maximum of M´´ decreased when filler amount increased. Relaxations peaks were displaced to higher frequencies, since relaxation processes were influenced by the interfacial polarization effect which generated electric charge accumulation around the ceramic particles and the displacement of peak[8] as the particle content increased.

Real permittivity values were fitted through the Lichtenecker model (Equation 3). In Figure 5 the experimental data of real permittivity values at 30 °C and 2500 Hz, as a function of the filler volume fraction, are plotted. From the fitting, it was obtained that real permittivity of $BaTiO_3$, CCTO, and the pure resin were of 2280, 9000, and 4.5, respectively[7, 10].

$$\log(\varepsilon_c) = V_m.\log(\varepsilon_m) + (0.7).V_f.\log(\varepsilon_f) \quad (3)$$



(a)

(b)

**Figure 4.** a) Real part (M´) and b) imaginary part (M´´) of electrical modulus vs. frequency and volume CCTO fraction (at 120 °C).

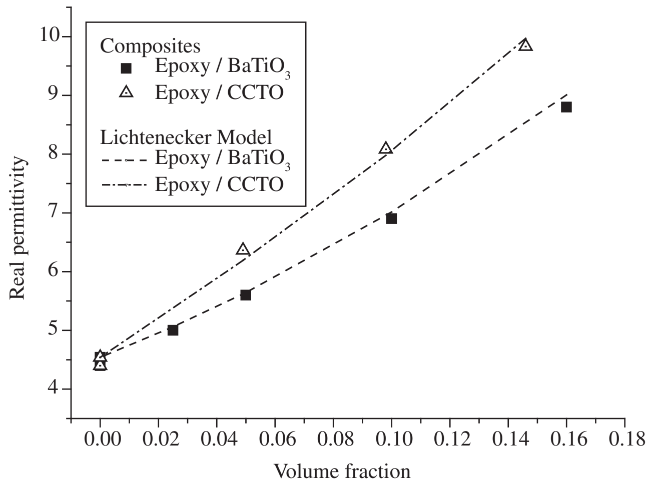


**Figure 5.** Real Permittivity as a function of volume fraction of CCTO and $BaTiO_3$ systems.

It can be seen that the real permittivity of both systems is appropriately fitted by the model. The real permittivity of CCTO systems was higher than $BaTiO_3$ composites, throughout the volume fraction range. Nevertheless, considering that dielectric permittivity of CCTO is 9000 $\varepsilon_0$[10] against 2500 $\varepsilon_0$ of $BaTiO_3$[7], composites permittivities did not show great differences at the same volume fraction due to the resin influence ($4.5\varepsilon_0$) on the composite permittivity[7]. Moreover, heterogeneous particle distribution could have affected composite permittivity values.

## 4. Conclusions

On the one hand, real permittivity was influenced by filler volume fraction. Ceramic particles produced a rise in permittivity and had more influence on samples with high volume fraction. On the other hand, porosity was very low even though in the composites with higher amount of filler.

Resin had influence on the imaginary part of permittivity and generated relaxation processes near their $T_g$ on all composites, while ceramic content only influenced the real part of permittivity. Interfacial polarization processes known as Maxwell-Wagner-Sillar were generated by particles. These processes produced an accumulation of charges on the interface which displaced peaks to higher frequencies.

Dielectric constants of CCTO composites were higher than the ones of $BaTiO_3$ / epoxy composites. However, the low resin permittivity prevailed in the composite dielectric performance.

The real permittivity variation with the filler content could be fitted by the Lichtenecker model.

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