Study of the effect of the CuO inthe dielectric properties of the nanocomposites Epoxy resin /$BaTiO_3$

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***Abstract*—In the development of dielectric composite,it is interesting to know the structure-property relationship at nanoscale level and the effect of each phase in the global properties of the material. In this context, we present an experimental analysisin the case of a ternary composite material. Several homogeneous microstructures samples with copper (II) oxide (CuO) and barium titanate ($BaTiO_3$) particles in powder form with various amounts dispersed in a host matrix of Epoxy Resin are prepared. Their dielectric permittivity spectra are measured using time domain Reflectometry (TDR) technique.Theexperimental data isanalyzed by means of electric modulus formalisms.In high frequency, the electrical modulus confirms the presence of two relaxations process.The real part of such composite presents a stability before the frequency where the relaxation phenomena appeared.The addition of the CuO does not affect the real part of permittivity significantly, but its effect is clear in the imaginary part and hence the AC conductivity.The conductivity indicates that the conduction is ionic and due to the ion of CuO primarily. According to results obtained from this study, we can made composite materials with desired characteristics using these two phases in the limits of their dielectric intrinsic permittivity.The manufacturing process of such composite is simple andcan be used in manufacture.In addition, the reproducibility of such composite ischecked in this study.**

Index terms—Ternary Composite, Copper (II) oxide, Barium titanate, Relaxation phenomena,electrical modulus,Conductivity.

I. INTRODUCTION

Recently, there has been a great interest in a new generation of composite materials exhibiting high dielectric performance with lower cost, size, weight, and easy processability [1–3]. Low dielectric losses and moderate dielectric constants are required for use in microelectronic packaging and in RF component [4, 5]. These requirements demand significant efforts in research and development; nevertheless, it is possible to combine different materials in order to obtain optimum properties [1-5].

One of the most advantageous solutions involves using integral passive technology, in which resistors, inductors and capacitors embedded directly into printed wiring board's substrate. Composite materials have been extensively used such technologies. The fact that they are often made up of at least two constituents or phases enables us to tailor materials for special purposes. The electrical properties of a composite system are determined by the properties of the constituents, interaction between them, and geometrical configuration. In designing composite materials with specified properties for electrical applications, one should take these parameters in consideration.To explain, predict the effect of each phase and investigate the behavior of the permittivity, relaxation phenomenon on the composite dielectric properties, various laws and formalisms have been proposed and used.Hence provides information of the structure-properties relationship of the materials. [3, 18].

In our study, we will investigate the effect of CuO, the volume ratio of loads, the geometrical structures and the interaction microscopic between phases (grain and grain boundary) on the dielectric properties.The presence of the relaxation process in this study will be investigated also by means of the electric modulus spectra formalism.

II. EXPERIMENTAL

1. System of measurement

The experimental values of the complex permittivity are obtained from measures made with a time domain reflectometry system (TDR) [5] composed of a very fast pulse generator HP 54121 (amplitude of 200 mV, rise-time of 35 ps), associated with a sampling oscilloscope (HP 84120B). The tension it propagated in a coaxial line APC-7mm with a characteristic impedance of 50 Ω. The composite sample with a thickness d placed in a measuring cell used like part of this coaxial line and finished by a final load Z_0. The reflection coefficient in the air-sample interface allows the evaluation of the dielectric permittivity [1, 4-7]. All Dielectric measurements were performed in the frequency range DC - 5GHz and at room temperature about(300K).

2. Preparation of samples

The preparation of samples can influence the obtained results [5, 7-12]. It is necessary to take into account that samples must have the same orders of dimension in order to facilitate their machining, sintering, treatment of the results and to obtain a very good correlation between the ideal models and the experimental results. Both components (copper (II) oxide CuO purchased from FLUKA CHEMEKA and the barium titanate $BaTiO_3$ (TBa) purchased from SIGMA ALDRICH and were used as delivered. which are in the form of powder in high purity (99.98% and 99.99% respectively) are mixed withresin (Re). The increase of the volume fraction of the load results difficulties to maintain the grains by the resin matrix, which becomes saturated. The viscosity of the mixture increases, and one then encounters another difficulty in the flow of the mixture in the sample recipient. It is the principally reason of limitation of ratio load to 30%. The average delay of mixing using the shear technique between 5 to 10 minutes is necessary to obtaining a microscopically homogeneous mixture.All samples dried atroom temperature roughly 300K during 72 hours.

III. Results and Discussions

The contamination of the samples in pores of airs and the effect of the rate of load in the density it studied by the measurement of the density of each sample. We noted that the density did not change appreciably vs. the amount of load, and therefore, the theoretical density given by equation (1) can give us help on the contamination of the samples in pores of airs. The theoretical density it given by the relation

$$\rho_C = f_{Re}\rho_{Re} + f_{TBa}\rho_{TBa} + f_{CuO}\rho_{CuO} \quad (1)$$

$$f_{Re} + f_{TBa} + f_{CuO} = 1 \quad (2)$$

wheref_{Re},f_{TBa}et $f_{CuO}$the volume fraction of Re, TBa et CuO andρ_C ,ρ_{Re}, $\rho_{TBa}$and$\rho_{CuO}$are the individualdensities ofcomposite, Re, TBa and CuO respectively .

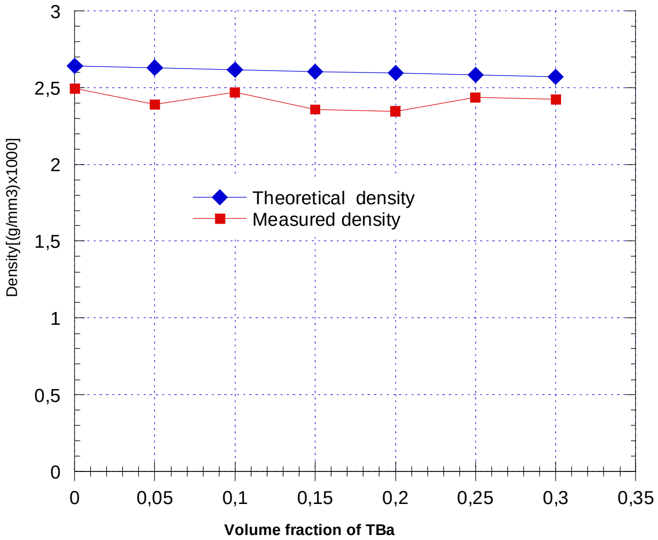

Fig. 1.The variation of theoretical and the measured density vs. the volume fraction of TBa, Re it fixed at 70%.

The difference between these densities due primarily to the presence of pores of airs in the composite, which produced during the process of mixing caused by the high viscosity of the system. This variation is nearly constant and can explained by the constant of solubility of air in the resin. The same remarks for the other samples with 75% and 80% of Re respectively prepared for this study.

1. Dielectric study

For measurement in broadband we carried out several samples in toric form, the results obtained of permittivity spectra are represented on Figs.2 and 3. In this section, we had the results obtained by temporal Reflectometry (TDR) at room temperature. The permittivity ($\varepsilon'$and ε'') of the ternary composite are depicted in order to see the behaviour of the later according to the volume fraction of load and of the frequency.

Following the measurements taken on the several samples worked out as function of the volume fraction, we should represent the variation of the permittivity of the pure resin Fig.2in addition, of the other samples as function of the volume fraction of TBaFig.3.

The Fig.2. Depict the variation of dielectric parameters or the pure resin, which used as a reference.The permittivity diminishes with frequency, because of the inertia of the permanent and induced dipoles to follow the alternation of the applied field, reflecting the reduction of polarization. Values of (ε') increase with filler content, since the composites become more conductive, their heterogeneity raises, charges accumulate at the interfaces of the system and thus interfacial polarization enhances. In polymer composite systems, dielectric relaxation effects arise from both the polymer matrix and the interaction with the reinforcing phase. This relaxation process is usually labelled α and is referred as the primary relaxation [11-15]. In our case the relaxation phenomena arise in the limit of our range of frequency, were the measurement are performed (around 4GHz).

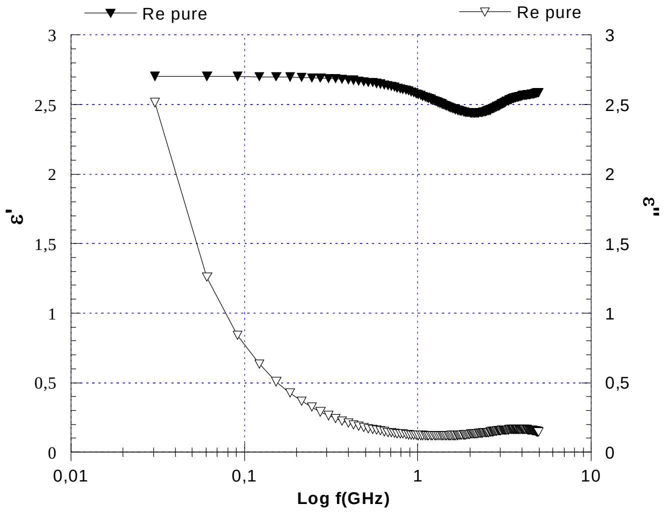

Fig. 2.Variation of the real and the imaginary part of the permittivity of the pure resin.

Fig.3. shows the variation of the spectra of the permittivity of the nanocomposite. The low value of the real parts of the permittivity of the ternary composite due to the low content in ceramics with high permittivity dispersed in Re. In this case, the dielectric response results mainly from the continuous matrix with weak permittivity. From Fig.3.the imaginary part of the permittivity presents peaks at high volume ratio in CuO;this is may duefirstly to the ion of the CuO and to the charges accumulated at the interface of the system.

The real part of the permittivity as function of the volume fraction of TBa and the frequency is shown in Fig.3it can be seen that the (ε′) is influenced by the load of fillers; the latter increases with the increases in TBa, such the ceramics have very high permittivity according to its crystallographic states.

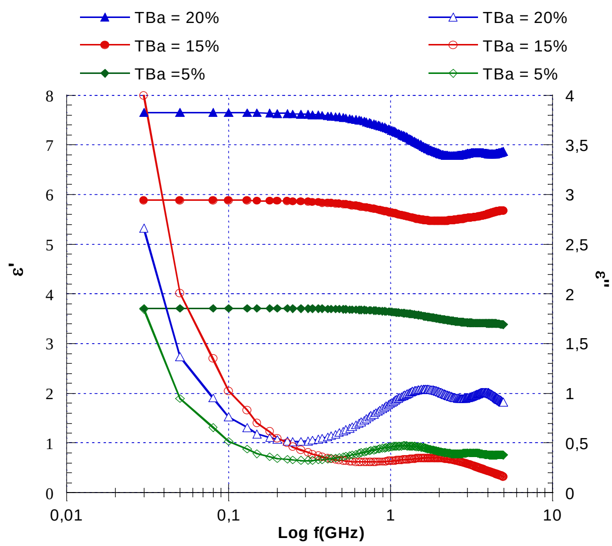

Fig. 3.Variation of the real and the imaginary part of the permittivity of the ternary composite as function of the frequency,Re it fixed at 75%.

The frequency dependence of the real (ε′) and the imaginary (ε′′) part respectively it can be expected, the real parts of the permittivity rose as the ceramic volume fraction increases in all cases. Values as high as 8.15 were obtained with addition of 75 % of Re and 25% of TBa. Moreover, it was observed that the imaginary part decreases as function the volume fraction of TBa and the frequency to obey to the Debye law. The peak in (ε′′) appeared in high frequency indicate the existence of a relaxation process. The high amount in CuO (Low in TBa)let us see another peak or a second relaxation. This phenomenon it observed in other composites with metallic oxide [14]. From Fig.4 we can note that the peak of the first relaxations shift to the low frequency as function of the rate of load but the second relaxations (relaxation of the host matrix) are fixed at the same frequency around 4GHz. The CuO rise the magnitude of the peak of the relaxation due to the latter. When the rate of load (both TBa and CuO) diminishes the real and imaginary part of the permittivity (ε′ and ε′′) diminishesthesetwo characteristics can be used to tailor the composite dielectric properties.

2. Electrical modulus spectra

In order to understand the frequency relaxation process and electrical behavior of the ternary composite systems electrical modulus and conductivity are used. These formalisms are able to describe the electrical phenomena, which are present in the heterogeneous complex systems (in our case a ternary composite). In the present study, dielectric relaxation processes are studied in terms of electrical modulus, which is defined according to Equation (3), Electric modulus, is defined as the inverse quantity of complex permittivity [11-15]:

$$M^{*} = \frac{1}{\varepsilon^{*}} = \frac{1}{\varepsilon' - j\varepsilon''} = \frac{\varepsilon'}{\varepsilon'^{2} + j\varepsilon''^{2}} + j\frac{\varepsilon''}{\varepsilon'^{2} + j\varepsilon''^{2}} = M' + jM'' \quad (3)$$

Where (M′) and (M′′) are the real and the imaginary parts of the electric modulus respectively.

Fig.4 presents the frequency dependence of real and imaginary part of electric modulus, as function of the frequency of the pure resin. The presence of relaxation processes becomes evident via the step like transitions from low to high ε′ values in the spectra of M′, and the formation of loss peaks in the corresponding plots of M".

Fig.5 shows clearly two relaxations process rise with the increase in the volume fraction of CuO. It is interesting to note that in the frequency range 1.4GHz and 5.5 GHz a relaxation process detected for all the composites that include copper oxide particles. In the Fig.5two peaksappeared in M" at the volume fraction of 15% and 20% of TBacan show the effect of the particle of the copper (II) oxide in the imaginary part (magnitude and process of relaxation) of the electrical modulus of the composite and no effect in the real part. In all studied cases it is evident the occurrence of a relaxation process in high frequency range. This an interest characteristic for this ternary systems which can be noted in this case.

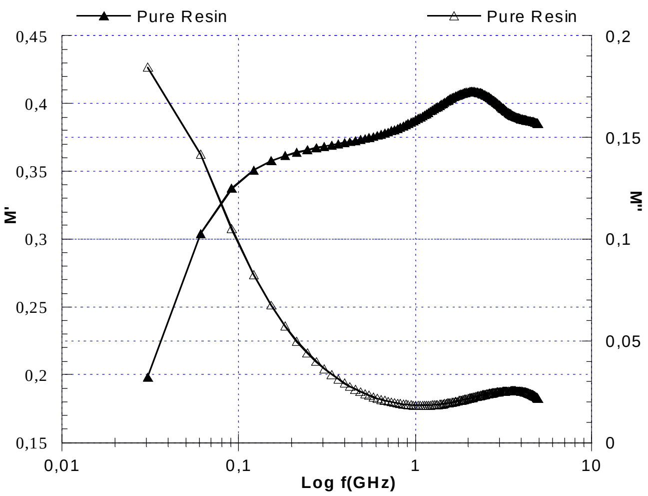

Fig. 4.Real and imaginary part of electric modulus versus frequency for the resin pure

After this study in this section, we can conclude the same remarks and confirm the results obtained in the section1 about relaxation and the effect of both TBa and CuO in the global properties of ternary composite carried out.

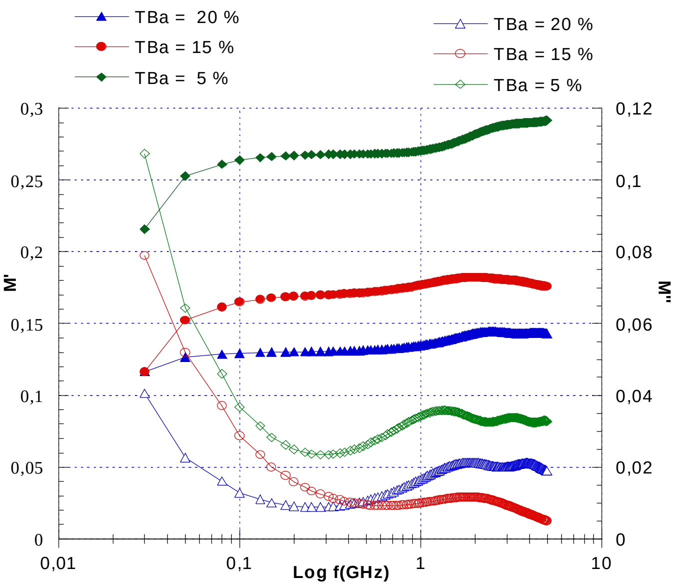

Fig. 5.Real and imaginary part of electric modulus versus frequency for the composite,Re it fixed at 75%.

3. Behavior of the conductivity

The study of the conductivity is useful to understand the frequency dependence of electrical transport of the material; the frequency dependence of the conductivity provides some information on the nature of the charge carriers. The electrical conductivity σ_{AC} calculated using the dielectric measurement in an empirical relation [9-14] such the complex permittivity given by the expression

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon - \varepsilon_\infty}{1 + j\tau\omega} - j\frac{\sigma_{AC}}{\omega\varepsilon_0} \qquad (4)$$

τ,
ε, σ_{AC} and ε_∞ are the Relaxation time,Thestaticpermittivity, Static conductivityand the permittivity in very high frequency respectively.Where the influence of the third term is decisive in low frequencies

$$\varepsilon'' = \frac{\sigma_{AC}}{\omega\varepsilon_0} \quad (5)$$

The last relation shows that the dielectric mixture has a conducting behaviorin high frequencies.The dispersion of ac conductivity with frequency for the systems it depicted in Figs 6. and 7. Alternating current conductivity has been calculated from the dielectric loss, according to Equation (6):

$$\sigma_{AC} = \varepsilon''\varepsilon_0.2\pi f(6)$$

With ε_0 and ε'' the Permittivity of the vacuum and the Imaginary part of the measured permittivity respectively.

Results obtained of conductivity as vs. the volume fraction of each component are represented by Fig.6 for the pure resin and Figs.7for the ternary composite.According to Fig.7 we can see that the static conductivity of the ternary composite increases with the rate of load in TBa. Conductivity present inflections points for the volume fraction 0.1 and 0.2 of TBa; concavity in bottom for the volume fraction (10%) of TBa and in top for the two other volume fraction of TBa i.e. (20%).

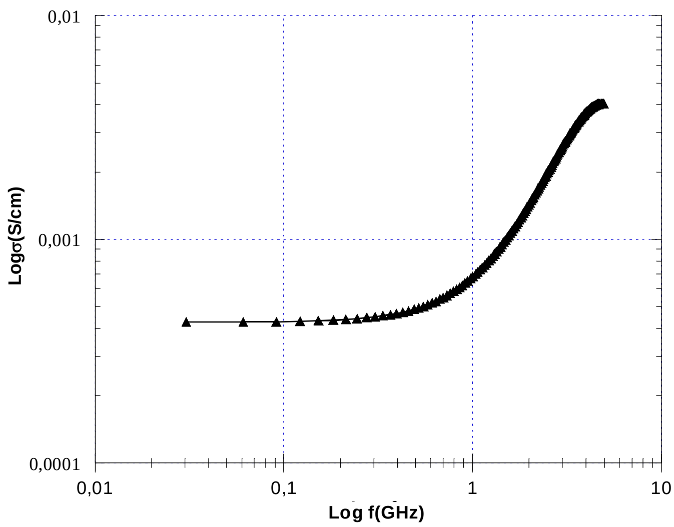

Fig. 6.Variation of the AC conductivity as function as the frequency of the pure resin

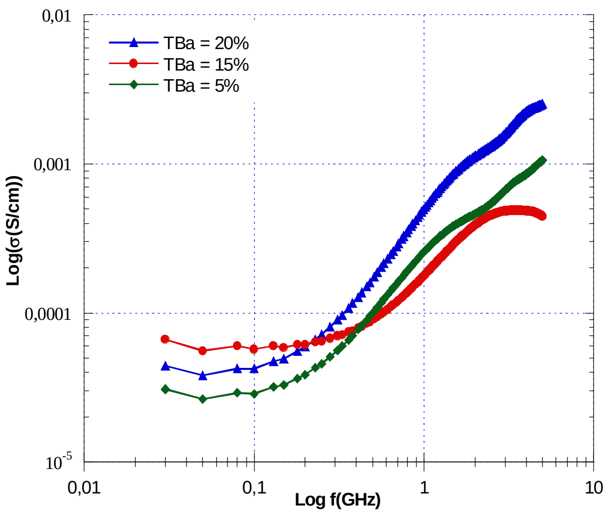

Fig. 7.Variation of the AC conductivity as function of the frequencyand the volume fraction of TBa, Re it fixed at 75%.

The fig.6. Present the conductivity of the pure resin, this last is very weak and present a stability around 4.10-5 S / Cm in the range of frequency DC -1GHz. then it increases a very stiff manner in the range 1GHz-4GHz.

In fig.7, the conductivity is due to the three phases. Knowing that the rate of load in TBa and in CuO reaches 35%. In low-frequency f < 200MHz, the conductivity increases with a light slope in the band DC-20MHz then it stabilizes until 200MHz. From this frequency, the conductivity increases with a less fast slope than the one of the pure resin. In this band and in this case the curves of the conductivity are superposed. In low frequency, it is clear that the CuO increase the magnitude of the conductivity.

More decrease of the rate of load in the host matrix, the contrast between the conductivities increases (case of the fig.7). However, the effect of the CuO on the conductivity of the nanocomposites remains obvious. It confirms that the peak of the first relaxation is essentially due to the ions of the CuO.

IV. Conclusion

The functionality of the composite systems is related to the abrupt variation of the real part of permittivity and to the relaxation process due to the different phases and conditions of preparation.

The increase in the volume fraction of TBa significantly increases the permittivity of the composite as well as the difference between the permittivity's and on the other hand the increase in the volume fraction of CuO slightly increases (almost null) the permittivity of the composite. The presence of relaxation processes becomes evident via the step like transitions from low to high values of (ε′) and (M′) in their spectra and the formation of loss peaks in the corresponding plots of (ε′) and (M′). In all studied cases it is evident the occurrence of a relaxation process in high frequency range 1.4 - 3.5 GHz.The manufacturing process of such composite is simple and can be used in manufacture of the antennas, resonatorscavity, electronic components and moreapplications.

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