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Dielectric Properties of Epoxy / $BaTiO_3$ Composites

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ABSTRACT:

Dielectric properties such as relative permittivity (dielectric constant) (ε′) and dielectric loss (ε") of (epoxy resin – barium titanate) composites behaviour as a function of barium titanate volume fractions (5, 10, 15, 20, 25, 30, 35, 40) vol.%, temperature in the range (30 - 110) ˚C and frequency in the range (120Hz - 2MHz), were investigated and given a qualitative explanation. The permittivity was found to increase with the increase of $BaTiO_3$ filler content, and was high in the low frequency range, but diminishes as the frequency increases. The permittivity was found to increase with the increase of temperature up to the transition temperature (Tg). Ac. conductivity and impedance of the composites behaviours as function of frequency and temperature have also been investigated.

Key words: composite, Dielectric properties, permittivity**,** Barium Titanate, ac. Conductivity, interfacial polarization.

INTRODUCTION:-

Polymeric composites which are polymers filled to a specified volume fraction / weight fractions with filler have aroused much attention for uses in electronic industry. Recently there is an increasing demand for high permittivity (dielectric constant) flexible particulate composite made up of a ferroelectric ceramic and a polymer for high density energy storage and capacitor applications [1-4].

Barium titanate ($BaTiO_3$) is one of the most widely used ferroelectric ceramic materials in modern technology applications due to its excellent dielectric properties (high permittivity). The dielectric constant of bulk $BaTiO_3$ is affected by its grain size at room temperature. It increases to its maximum (6000) with the decreasing the grain size up to (~ 0.9μm), a further decrease leads to a decrease in the dielectric constant (1500) [5-7]. $BaTiO_3$ has provskite structure and its compounds are desired in electroceramic industry since the discovery of its versatility in multilayer ceramic capacitor, positive temperature coefficient of resistance thermistors, piezoelectric sensor, transducers, actuators ferroelectric random access memories and electro-optical device [8].

Epoxy resins are widely used as suitable matrices, besides their other applications in modern technology, because they offer versatility, low shrinking, chemical resistance, relatively low dielectric constant and outstanding adhesion[9]. Epoxy composites are very popular insulators in high voltage engineering, such as epoxy mica composites which is used for the insulation of power transformers, station and line posts, insulation of coils in rotating machines, etc. [10]. Predication of the dielectric permittivity of composite materials can be very important in many relevant technological applications [11].

Ceramic-Polymer composite has the high permittivity of ceramic and the good processability of the epoxy resin.

In this study, (epoxy resin as a matrix and $BaTiO_3$ powder as filler) composites were prepared and dielectric properties were measured as function of filler volume fraction (5, 10, 15, 20, 25, 30, 35, 40) vol.%, temperature in the range (30 - 120) ˚C and frequency in the range

(120Hz - 2MHz). Ac. conductivity and impedance were studied too. All result were given a qualitative explanation [7].

EXPERIMENTAL:

Materials:

In this work a commercially available epoxy (DGEBA-368WG), molecular weight M_w=624 gm/mol and density = 1.27gm /cm^3 supplied by United Chemical Company Ltd. (UNICHEM) **,** with curing agent triethylene tetra amine (TETA) supplied by the same company were used as polymer matrices for the composites .

The barium titanate ($BaTiO_3$) ceramic powder with 99.9975%, grain size of 25 µm and density = 5.91 gm /cm^3. supplied by (ALFA PRODUCTS - Germany.) was used as a filler.

Sample preparation :

The $BaTiO_3$ powders (as received) were added to the epoxy resin in different volume fraction (5, 10, 15, 20, 25, 30, 35, 40) vol.% and then suitably mixed at about 70^0C for 5 minutes, after then the curing agent (TETA) as hardener was added and mixed also. The mixture, then casted as a thick film on clean Al substrates.

The initial curing was carried at room temperature for 24 hours, followed by post curing at 120^oC for 2 hours.

Circular disk shaped thin film Aluminum electrodes (6mm) in diameter were vacuum deposited on the upper side of the casted composites. A sandwich of Al/thermosetting sheets of composites/Al were made finally.

Characterization and measurements :

The samples capacitance and the loss tangent (tanδ) or (D) of composites were measured by digital RCL bridge type (MEGGER B131), at the frequencies 120 Hz and 1kHz. At continuous frequencies in the range (120Hz - 2MHz) RCL bridge type (METRAPOINT-RLC2 and ME 1634 FUNCTION GENERATOR) were used to measure the capacitance of the samples.

The dielectric permittivity ε' were calculated in conformity with the relation, $C = \varepsilon_o \varepsilon' A / d$ [12, 13], where ε_o is the permittivity of the free space, d, is the separation between the capacitor electrodes, A, is the area of the electrodes. The dielectric loss ε'' are given by the relation, $\varepsilon'' = \varepsilon' \tan \delta$ [13, 14].A.C. conductivity($\sigma_{a.c}$) was calculated according to the relation $\sigma_{a.c} = \varepsilon_o \omega \varepsilon''$[15, 16]. The impedance Z at different frequency up to 500kHz. was measured by RLC bridge type (Hewelt pacard A4800) .

Result and Discussion:

The dielectric constant (ε′) of $BaTiO_3$ filled composites and unfilled epoxy as a function of filler content in the room temperature and two fixed frequencies 120Hz and 1kHz is shown in fig.(1). It is obvious that ε′ increases as filler content increase and is high when the frequency is lower (120Hz). The increase in ε′ with both the increase in filler content and lower frequency is an expected increase and is attributed to Maxwell-Wagner Sillars (MWS)/ or interfacial effect appears in complex system exhipting electrical heterogeneity, due to the accumulation of charges at the interfacial of the system [9-17]. The effect of temperature on ε′ of $BaTiO_3$ filled epoxy composite and unfilled epoxy versus temperature in the ran (30 – 110) ^{o}C is depicted in fig.(2). It can be seen that in all cases ε′ increases to a maximum value as the temperature increases, a further increase in temperature leads to a decrease in ε′ value. This may be attributed to:1st the increased mobility of segments of polymer molecules at elevated temperature below transition temperature which facilitates the orientation of dipoles, thereby leading to an increase in ε′,2nd the differential thermal expansion of the resin and filler at elevated temperature can disrupt interfacial polarization, which result in a decrease in ε′ [18]. The two mechanisms compensate at maximum value, while the 1st mechanisms dominated at temperature below transition temperature.

Fig. (3) Shows the variation of ε′ as a function of frequency in the rang (120Hz - 2MHz) for $BaTiO_3$ filled epoxy composites and unfilled epoxy. At room temperature it is clear that ε′ decrease as the frequency increases. High values ε′ in the low frequency rang, are attributed to the process of interfacial polarization and the polarization induced by segmental mobility in the polymer which appears more effective at low frequency and high temperature respectively [19].

The dipoles responsible of these two polarizations have less time to orient themselves in the direction of the alternating field at high frequencies.

Fig. (4) Shows ε'' dependence of $BaTiO_3$ filled epoxy composites and unfilled epoxy on temperature in the rang (30 – 110) ^oC and constant frequency of 1 kHz. It is obvious that, ε'' increases with increasing filler content and temperature. The increase in ε'' for all composite related to the increased segmental mobility and ionic conductivity. Since the rise in temperature and the consequence drop in viscosity exerts an effect on the amount of the losses due to the friction of the rotating dipoles; so that the degree of dipole orientation increases and ionic conduction increases, due to the thermal dissociation of molecules.

The variation of dielectric loss (ε'') of $BaTiO_3$ filled epoxy composites and unfilled epoxy as a function of frequency in the rang (120Hz - 2MHz) at room temperature is shown in fig. (5). It is obvious that, ε'' increases as filler content increases for all frequency rang studied, and that ε'' shows a maximum for each filler content. These maximum relaxation peaks shift towards lower frequencies as the filler content increases, because relaxation processes were influenced by the interfacial polarization effect.

The effect of adding $BaTiO_3$ filler to the epoxy resin on a.c conductivity as a function of temperature is shown in Fig. (6). It can be seen that the ac conductivity increases with the increasing of filler content for the same temperature circumstances, and that, the σ_{ac} for all cases increases as the temperature increases. The influence of temperature on σ_{ac} can be explained by considering the mobility of the charge carriers responsible for hopping. As the temperature increases the mobility of hopping ions (weakly bound ions (T^{++++} and O^{--}) in $BaTiO_3$, (Cl^-) ions in epoxy resin which arises as a causal inevitably product during the synthesis processes.) also increases thereby increasing the conductivity. The electrons which are involved in hopping are responsible for electronic polarization in these composites [20]. A.C conductivity is also related to the polymer segmental mobility and increase dramatically with increasing temperature.

Fig. (7) Shows the variation of impedance Z with frequency for BaTiO3 filled epoxy composites and unfilled epoxy. It was noticed that the phase angle was always negative, indicating that the composites were capacitive and could be represented by parallel RC net- works (lumped circuit) connected in series. Impedance values decrease with increasing frequency and increasing BaTiO3 concentration. The observed decrease in impedance with $BaTiO_3$ content is due to the protonic migration transporting the oxygen, Ba, Ti elements and impurities existing in the $BaTiO_3$ filler. This motion leads to higher electrical conduction in the filled composites [21]. As can be seen, there is an exponential decrease in the impedance with the increase in frequency for all filler volume fraction, and the decrease is greater for high filler contents composites [22].

Fig. (8) Shows the temperature dependency of impedance Z of $BaTiO_3$ filled epoxy composites. There is an obvious decrease in Z, with the increasing of filler volume fraction due to the increased interfacial polarization, and with the rise in temperature. The impedance Z decreases with the temperature rise which is accompanied by clear dips near (90-100 ^oC) temperature for all cases in which filler were added. This decrease in Z may relate to the increased mobility of segmental molecules as the temperature increased. The dips may be related to the glass transition temperature region where the segmental mobility is increased. As a consequence, these dips may refer to the glass transition temperature for all composites.

Conclusions:

It is found that the Permittivity, dielectric loss and a.c conductivity for all composites increase with the increase in of $BaTiO_3$ filler content, and temperature. The Permittivity decreases with the increase of frequency. The impedance Z of the composite decreases with the increase of filler volume content, frequency and temperature.

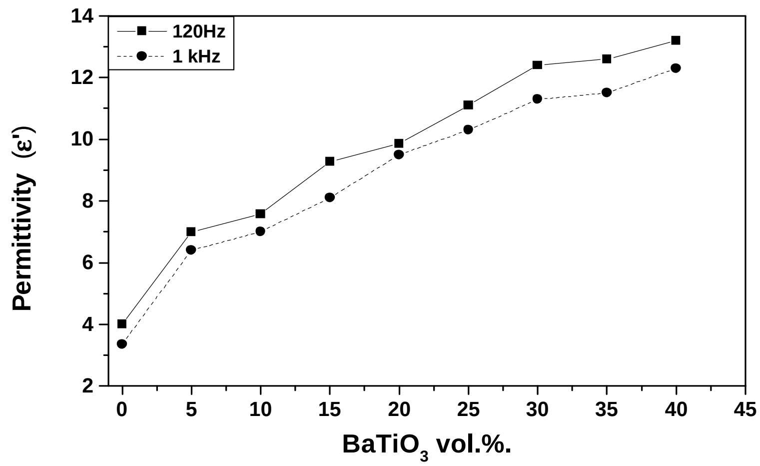

Fig. (1) The permittivity versus filler content at two different frequencies.

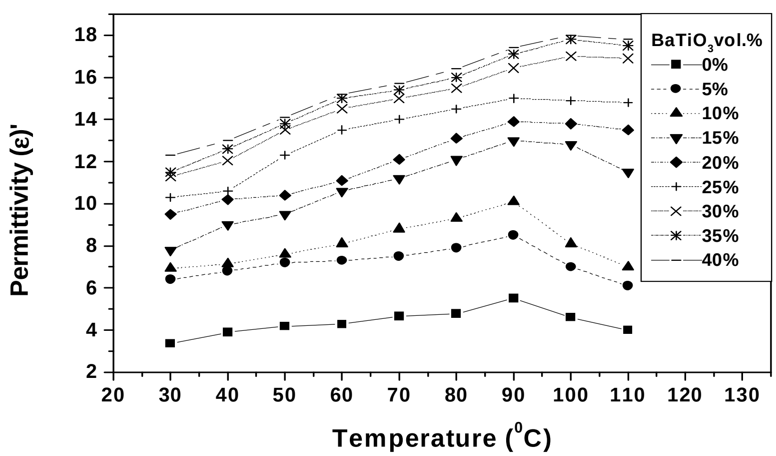

Fig. (2) $BaTiO_3$-epoxy composites permittivity as a function of filler content and temperature.

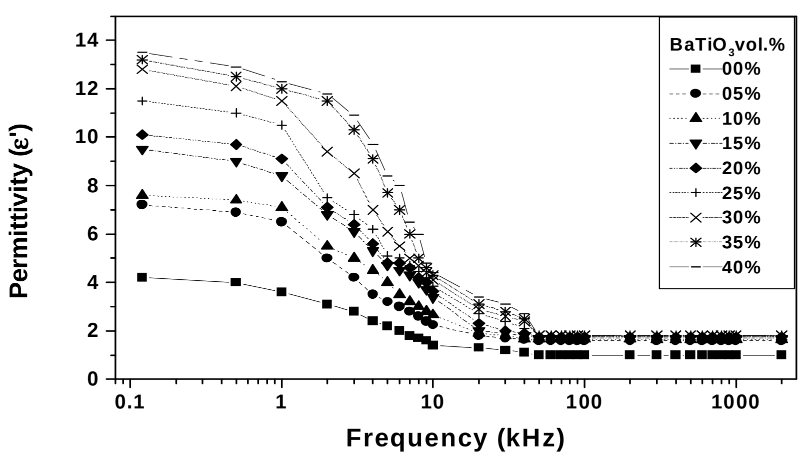

Fig. (3) The permittivity as a function of filler content and frequency for $BaTiO_3$-epoxy composites.

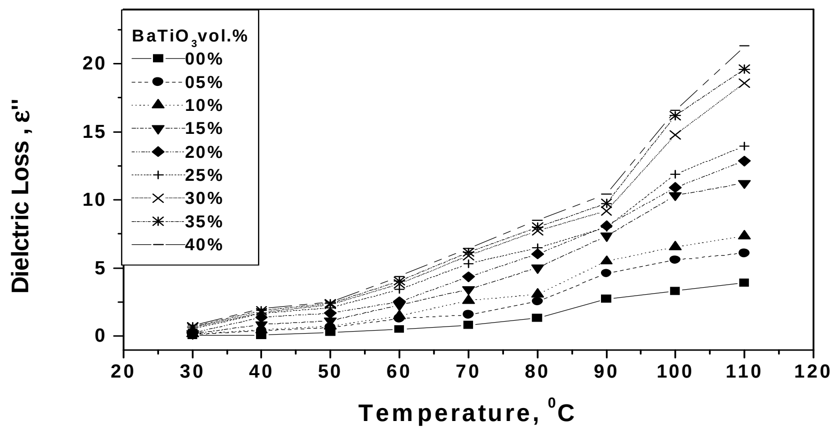

Fig. (4) The loss tangent as a function of filler content and temperature for $BaTiO_3$-epoxy composite .

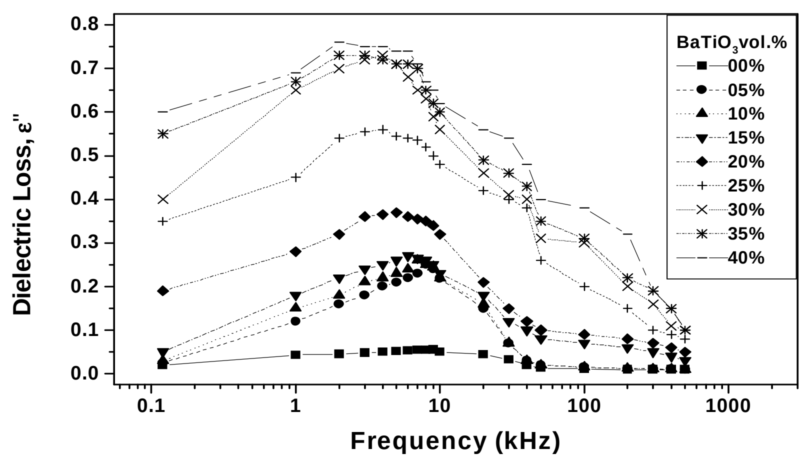

Fig. (5) The dielectric loss as a function of filler content and frequency for $BaTiO_3$-epoxy composite .

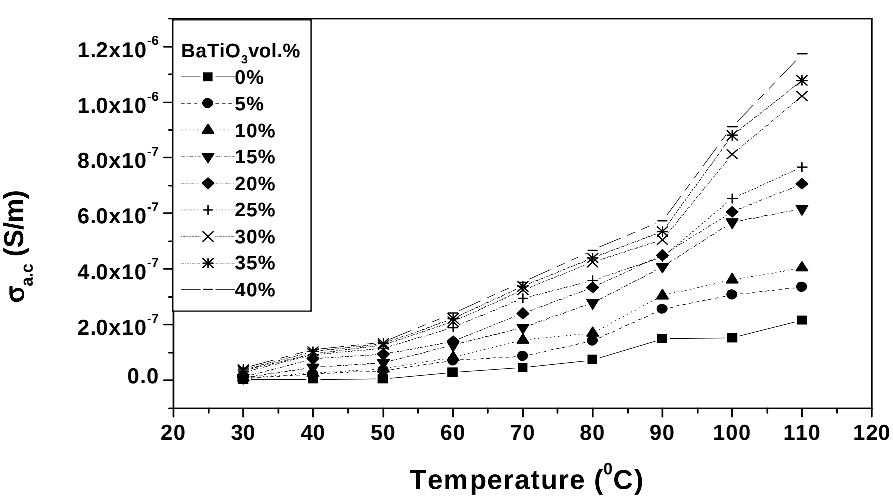

Fig.(6) The σ_{ac} as a function of filler content and temperature ^{0}C for $BaTiO_3$-epoxy composites..

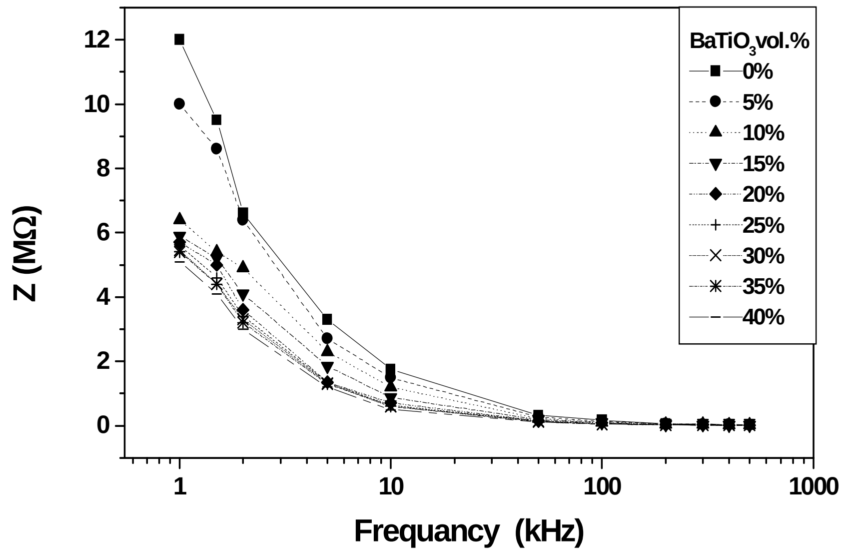

Fig.(7) The impedance of $BaTiO_3$-epoxy composites as a function of filler content and frequency.

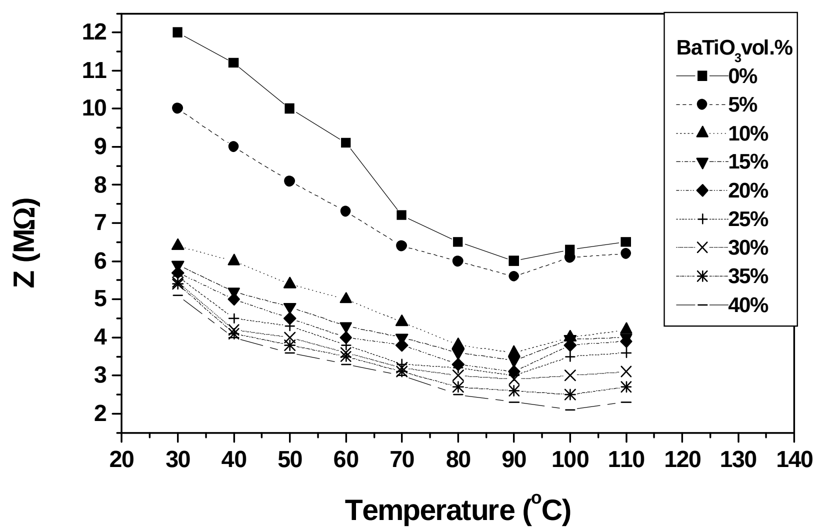

Fig.(8) The impedance of $BaTiO_3$-epoxy composites as a function filler content and temperature.

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دراسة الخواص العازلية لمتراكبات (راتنج الايبوكسي ــ تيتانيت الباريوم)

الخلاصة:

فحصت خواص العزل الكهربائي مثل السماحية (ثابت العزل) وفقد العازل لمتراكبات (راتنج الايبوكسي ــ تيتانيت الباريوم) كدالة للمحتوى الحجمي من تيتانيت الباريوم بالنسب (40%،35،30،25،20،15،10،5)، وكدالة لدرجة الحرارة في المدى – 30) 110) ^oC ، والتردد في المدى(120Hz − 2MHz) ، وتم إعطائها التفسيرات اللازمة. لقد وجد إن السماحية تزداد مع زيـــادة المحتوى من الباريوم تيتانيت ، وتكون أعلى قيمة للسماحية عند مدى الترددات الواطئة وتتلاشى مع زيادة التردد. كما وجدنا إن السماحية تزداد مع ارتفاع درجة الحرارة لغاية درجة حرارة الانتقال الزجاجي. كما تم دراسة سلوك التوصيلية الكهربائية المتناوبة والممانعة لمتراكبات الباريوم تيتانيت كدالة للمحتوى الحجمي والتردد ودرجة الحرارة.