Dielectric behavior and Ac conductivity measurements of bulk (TiO_2, ZnO/Epoxy) composites.

دراسة السلوك العازل الكهربائي والتوصيلية الكهربائية المتناوبة لتمراكبات (راتنج الايبوكسي ـ اوكسيد التيتانيوم) و(راتنج الايبوكسي ـ اوكسيد الزنك)

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ABSTRACT:

Dielectric behavior and ac conductivity measurements on epoxy resin filled with (5, 10, 15, 20, 25 wt.%.) micro sized particles of TiO_2 and ZnO have been studied.. The measurements were carried out in the frequency range (120Hz - 2MHz) and over a wide temperature 30 °C and 110°C. Different dielectric behavior was observed depending on filler type, filler contact, frequency and temperature.

Results show that dielectric permittivity (ε') and dielectric loss(ε") increases with the addition of epoxy resin, which has been attributed to interfacial polarization. The value of (ε') increased with increasing temperature, due to the greater freedom for movement of the dipole molecular chains within the epoxy at high temperature. The value of (ε') decreases with increasing frequency, which indicates that the major contribution to the polarization comes from orientation polarization. Interfacial relaxation is found to be strongly dependent on the presence of micro-filler particles. The Alternating Current (AC) conductivity increases as the temperature and frequency, because of the segmental mobility and electrical conduction.

Key word: dielectric spectroscopy, ac conductivity, epoxy resin, TiO_2, ZnO.

الخلاصة

تمت دراسة السلوك العازل الكهربائي والتوصيلية الكهربائية المتناوبة لراتنج الايبوكسي المضاف إليه حشوات اوكسيد التيتانيوم و اوكسيد الزنك بنسب وزنية(5, 10, 15, 20, 25 wt.%). أجريت القياسات العملية لسلوك العزل الكهربائي عند مدى الترددات (120Hz - 2MHz) ودرجة حرارة ^oC (30 – 110) . ان اختلاف السلوك العازل للمتراكبات المحضرة يعتمد على نوع ومحتوى الحشوة والتردد ودرجة الحرارة. أظهرت النتائج المختبرية بان سماحية العزل و فقد العازل تزداد بزيادة محتوى الحشوة والذي قد تعزى إلى ظهور الاستقطاب البيني، كذلك تزداد السماحية بزيادة درجة الحرارة نتيجة لزيادة حرية الحركة للسلاسل الجزيئية لثنائيات الأقطاب داخل الايبوكسي عند درجة حرارة عالية، وتقل السماحية بزيادة التردد بسبب الاستقطاب ألاتجاهي. كذلك تم الاستنتاج على إن الاسترخاء البيني يعتمد على الحجم ألدقائقي للحشوة. التوصيلية الكهربائية المتناوبة تزداد بزيادة درجة الحرارة والتردد بسبب حركة الشحنات الحرة و تيار التوصيل.

INTRODUCTION:-

In the last decade many research teams from all over the world have focused their energies toward studies on polymer composites as effective materials for electrical insulation [1].The increasing interest in the behavior of these newly born dielectrics is mainly due to the fact that these materials possess a huge filler – polymer matrix interface which has a major influence on the electrical, thermal and mechanical properties [2].

Epoxy and epoxy based composites are preferred insulating materials for several electrical applications, especially printed circuit boards, bushings, GIS spacers, motors, generator ground wall insulation system and cast resin transformers. This is because epoxy resins are excellent electrical insulators and protect electrical components from moisture, dust and short circuiting. Recently,

epoxy based dielectric systems are being increasingly investigated for their electrical properties, since the introduction of fillers demonstrate several advantages in their properties when compared with the similar properties obtained for epoxy systems with micrometer sized fillers [3,4]. For some interesting applications we need to improve the electrical conductivity of such adhesives. So the dispersion within the epoxy matrix of conductive powder particles with sufficient quantity allows reaching high electrical conductivity values and consequently conductive or semi-conductive composite is then formed. These composite polymeric materials have found a variety of applications because they constitute excellent models for studying the interactions between condensed matter and electromagnetic radiation such as microwaves. They are also used for spatial applications [5].

Titanium dioxide and zinc oxide are extensively studied because of their interesting chemical, electrical and optical properties used as semiconductor, catalytic, dielectric materials, high-density dynamic-memory devices, capacitors in microelectronics, insulator gate in MIS structures, etc [6, 7].

Polymers such as polyethylene, polypropylene, epoxy resins and silicone rubbers are combined with fillers such as layered silicate (LS), silica (SiO_2), Titanium dioxide (TiO_2), zinc oxide (ZnO) and alumina (Al_2O_3) [8]. The properties of composites certainly depend on the kind of particle materials, physical and chemical conditions of their surfaces, the kind of coupling agents to bridge inorganic and organic substances chemically and physically, the kind and content of compatibilizers and/or dispersants, and the kind of polymer matrices. [9-11].

EXPERIMENTAL:

Materials:

The materials tested in this study were (epoxy resin- TiO_2) and (epoxy resin- ZnO) composites, as well as epoxy polymer. The polymer matrix was a Bisphenol-A based epoxy resin of type diglycidylether of bisphenol-A (DGEBA-368WG) Mw = 624 gm / mole, density =1.27 gm /cm^3, and a Triethylenetetramine (TETA) , supplied by United Chemical Company Ltd. (UNICHEM, JORDEN) was used as hardener. The content of fillers of the tested formulations was (5, 10, 15, 20 and 25 wt.%.). As for the fillers, highly pure grades of commercially available uncoated particles [filler size ≈ 0.25 μm for TiO_2 and ZnO] are procured from Sigma Aldrich .

Sample preparation :

The (TiO2, ZnO) powders were added to the epoxy resin (as received) at weight contact and then mixed at about 70^0C for 5 minutes, then curing agent triethylene tetra amine (TETA), TETA was added as hardener in the percent epoxy (1:4) and mixed for 5 minutes also. The mixture, then cast on clean aluminum substrates.

The initial curing was carried at room temperature for 24 hours, followed by post curing at 120^oC for 2 hours, Circular aluminum electrodes in diameter (6mm) were vacuum deposited on the upper side of the composite sample, and thermosetting sheets of epoxy composites were made.

Characterization and measurements :

Dielectric properties of (TiO_2, ZnO /Epoxy) composites were investigated using Digital RCL bridge type (MEGGER B131), on a frequency range of 120 Hz and 1kHz. At the 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 impedance Z at different frequency up to 500 kHz was measured by RCL bridge type (Hewlett-Packard A 4800).

The real and imaginary parts of the complex dielectric permittivity ($\varepsilon^* = \varepsilon' - j\,\varepsilon''$) were obtained with the assumption that studied cell is equivalent to a circuit consisting of an ideal capacitance Cp in parallel with a pure (ohmic) resistance Rp. The capacitance of a parallel-plate capacitor is, for the real case, when the losses are present [12]:

$$C = \varepsilon^* C_o = \varepsilon o\,(\varepsilon' - j\,\varepsilon'')\,A / d \quad \ldots\ldots\ldots (1)$$

where ε_o is the absolute permittivity of the vacuum (8.854×10^{-12}F/m), ε' is the dielectric permittivity (the real part of the complex dielectric constant), ε'' is the imaginary part of the complex

permittivity, d is the distance between the plates, A is the area of a plate and C_o is the capacitance of the empty cell

$C_o = \varepsilon_o A / d.$

The dielectric permittivity is given by [13, 14]:

$\varepsilon' = Cp/ C_o$ …… (2)

The imaginary part of the complex permittivity can be expressed as:

$\varepsilon'' = 1/(C_o Rp2\pi f)$ …… (3)

The dielectric loss for the real capacitor is given by:

$\tan \delta = G / (2 \pi f C_p) = 1/ (2 \pi f C_p R_p)$ …… (4)

where G is the electrical conductance, C_p capacity of parallel, resistance of parallel and f is the signal frequency.

By measuring Cp and Rp, eqs. (2), (3) and (4) permit to determine the values of ε', ε" and tan **δ**.

The as conductivity σ_{ac} for an ionic electrolyte material of all samples has been calculated from the dielectric losses according to the relation

$\sigma_{a.c} = \varepsilon_o.\varepsilon''.2 \pi f$ …**.....** (5)

Result and Discussion:

The determination of the dielectric relaxations and a.c conductivity behavior of (TiO_2,ZnO-epoxy) composites is necessary to find its appropriate application[15] .The (TiO_2, ZnO) powder was mixed with epoxy to form composite with (5, 10, 15, 20and 25) wt.% filler. The dielectric permittivity (ε′) of (TiO_2,ZnO-epoxy) composites as a function of filler content in two fixed frequencies 120Hz and 1kHz at room temperature is shown in figure1 (a&b). The addition of filler to the polymer increases the dielectric permittivity of the prepared composite as the filler content increases. That could be caused by relaxation process between the filler particles and the polymer matrix [16, 17].

Figure 2 (a&b) shows curves the variation of dielectric permittivity behavior for (TiO_2 /Epoxy) and (ZnO /Epoxy) composites as a function temperature in the range (30 – 110) ^oC at constant electric field frequency of 1kHz. It can be seen that, the values of (ε') of the composites lay between the values for the polymer and the values for the ceramics as expected. The value of (ε') increases with temperature at fixed frequency, this is true for all the samples at all frequencies. At lower frequencies this effect is more prominent. The increase in (ε') with temperature is due to greater freedom of movement of dipole molecular chain of polymer at high temperature. At lower temperature, as the dipoles are rigidly fixed in the dielectric, the field can not change the condition of dipoles. As the temperature increases, the dipoles comparatively become free and they respond to the applied electric field, thus polarization increases and hence dielectric constant is also increases with the increasing of temperature [18].

The variations of effective dielectric permittivity (ε') with respect to frequency for the epoxy composites with TiO_2 and ZnO fillers and at different filler contents are shown in Figure 3 (a&b) respectively. It is obvious that the dielectric permittivity decreases with the frequency for all of the TiO_2 and ZnO fillers concentration. The measurement temperature is maintained constant in this study; hence, its influence on the permittivity behavior can be neglected. The effective permittivity of composites is determined by dielectric polarization and relaxation mechanisms in the bulk of the composite material. Permittivity is a frequency dependent parameter in polymer systems. The epoxy component of permittivity is governed by the number of orient able dipoles present in the system and their ability to orient under an applied electric field [19,20]. Usually, the molecular groups which are attached perpendicular to the longitudinal polymer chain contribute to the dielectric relaxation mechanisms. At lower frequencies of applied voltage, all the free dipolar functional groups in the epoxy chain can orient themselves resulting in a higher permittivity value at these frequencies. As the electric field frequency increases, the bigger dipolar groups find it difficult to orient at the same pace as the alternating field, so the contributions of these dipolar groups to the

permittivity goes on reducing resulting in a continuously decreasing permittivity of the epoxy system at higher frequencies. Similarly, the inherent permittivity in TiO_2 and ZnO particles also decrease with increasing frequencies of the applied field [21,22]. This combined decreasing effect of the permittivity for both epoxy and the filler particles result a decrease in the effective permittivity of the epoxy composites also when the frequency of the applied field increases. In general, the dielectric permittivity for (TiO_2, -epoxy) composites is higher than dielectric permittivity for (ZnO-epoxy) composites. That is probably because of its higher inherent permittivity, TiO_2 filled systems display a higher permittivity at all filler contents as compared to ZnO based composites.

Figure 4 (a&b) shows variation of dielectric loss (ε") as a function of filler content and temperature, at a constant frequency (1 kHz) applied field for (TiO_2 /Epoxy) and (ZnO /Epoxy) composites. The dielectric loss increases in is general as the filler contents and temperature increase. The increase in (ε") with the increase of filler contents are related to the interfacial polarization. The increase of (ε") with temperature can be explained by dividing the relaxation phenomenon into three parts: (i) conduction losses, (ii) dipole losses, and (iii) vibration losses [23,24]. At low temperature condition, losses are minimum as they depend on the product of ac resistivity and frequency. As the temperature increases, the ac resistivity increases and so the conduction losses increase. [25].

Figure 5 (a&b) shows the frequency dependence of dielectric loss (ε") at a constant temperature for (TiO_2 /Epoxy) and (ZnO /Epoxy) composites. It was observed that (ε") increases as the frequency increases and reaches a maximum and thereafter decreases for composites. As the temperature increases the frequency at which (ε") reaches a maximum shifted towards higher frequencies. The increase in ε" is attributed to interfacial relaxation process known as Maxwell-Wagner Sillars (MWS) effect. In fact, epoxy resin networks present a lacunar structure with micro spherical voids produced during mixing process when air liberation is restricted due to the system viscosity [26]. Frequency in figure 5 (a&b) are called dielectric relaxation, being characterized by a relaxation time τ or relaxation frequency f_o corresponding to Δε/2. The relaxations shift to lower frequencies with the increasing of (TiO_2, ZnO) contents. The plots of relaxation time against the filler content for (TiO_2 /Epoxy) and (ZnO /Epoxy) composites are shown in figures 6 (a&b). It can be seen that the relaxation time increases with the increasing of filler content. The increase in relaxation time for all composite related to interfacial polarization. The values of τ vary from 6.98×10^{-4}sec. to 20.93×10^{-4}sec. As a consequence it is supposed that the set up of electrical polarization in the interface of fillers and polymer phases is a slow process. From a dielectric point of view, in order to examine the relaxation process, a numerical calculation is carried out using the Cole-Cole type distribution relation [27]:-

$$\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{(1+\omega^2\tau^2)} \qquad \ldots\ldots\ldots (6)$$

Where $\omega = 0$ $\quad \varepsilon(0) = \varepsilon_s$

$\omega = \infty$ $\quad \varepsilon(\infty) = \varepsilon_\infty$

Where (ε_s) and (ε_∞) are the limiting values at low and high frequencies, $\omega=2\pi f$ is the angular frequency. The Cloe-Cloe diagrams can be drawn as shown in Figure 7 (a&b). It can be concluded that the relation between ε' and ε" are a symmetrical circle arc [26,27]. This suggests that the relaxation is a single relaxation process and is caused by the Maxwell-Wagner effect, being attributed to the interfacial polarization mechanism [28].

Table (1): The relaxation time of (TiO_2 ,ZnO /Epoxy) composites.

wt.%	Ti02 (Sec.) τ $\times 10^{-4}$	ZnO (Sec.) τ $\times 10^{-4}$
0	6.98	6.98
5	7.85	7.85
10	8.97	8.97
15	10.47	12.56
20	15.7	12.56
25	20.93	15.7

The effect of adding TiO_2 and ZnO fillers to the epoxy resin on ac conductivity as a function of temperature are shown in figure 8(a&b). It was noticed that the ac conductivity increases with the increasing of filler content for the same temperature circumstances. The observed increase in ac conductivity with temperature is due to the mobility of the charge carriers which is responsible for hopping. As the temperature increases the mobility of hopping ions also increases thereby increasing the conductivity. The electrons which are involved in hopping are responsible for electronic polarization in these composites [29].

AC conductivity as a function of frequency for TiO_2 and ZnO filled epoxy composites and unfilled epoxy is presented in figure 9(a&b). It was obvious that the ac conductivity increases for all cases in which filler were added. This increase in ac conductivity may relate to the interfacial polarization and electrical conduction [30].

Conclusions:

Frequency and temperature dependence of dielectric permittivity and dielectric loss in (TiO_2, ZnO /Epoxy) composites are studied in the frequency range (120Hz - 2MHz) and in the temperature range (30 -110 $^{\circ}$C). Dielectric relaxations of an epoxy resin matrix and epoxy composites made by dispersing conductive micro particles (TiO_2 and ZnO) in the epoxy matrix were investigated. Interfacial or Maxwell-Wagner-Sillars effect (MWS) is evident in the dielectric spectrum of the pure epoxy resin matrix. Compared to (TiO_2, ZnO /Epoxy) composite, the permittivity of (TiO_2 /Epoxy) composite is higher than (ZnO /Epoxy) composite for all filler content due to electrical conductivity of TiO_2 filler particle

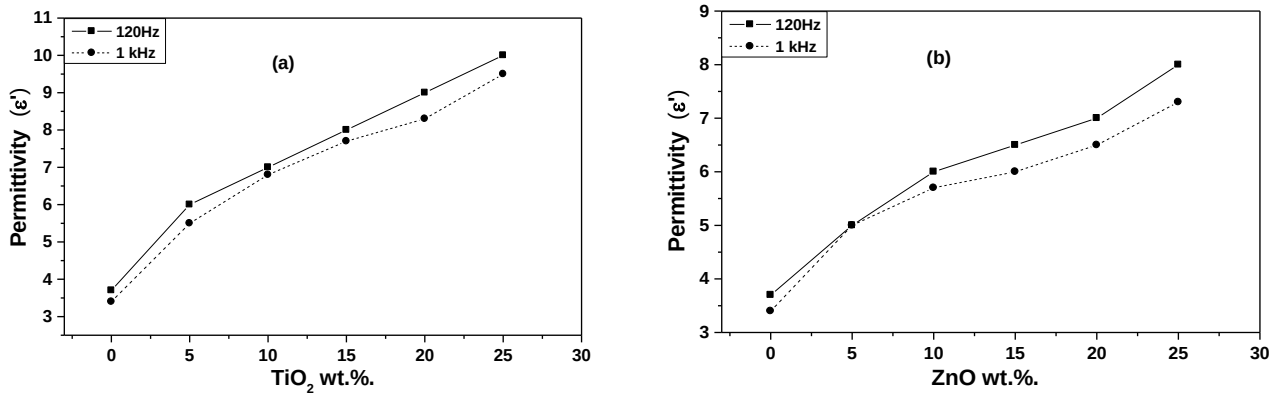

Fig. (1).Variation of permittivity with two different frequencies (a) TiO_2 and (b) ZnO

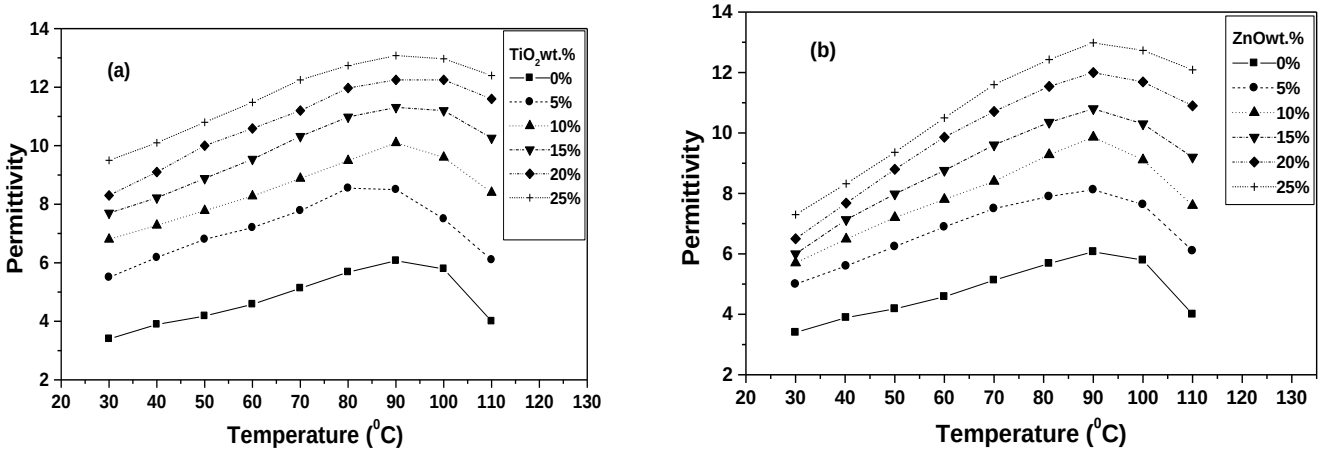

Fig. (2) Permittivity as a function of temperature for different content of (a) TiO_2 and (b) ZnO- epoxy composite.

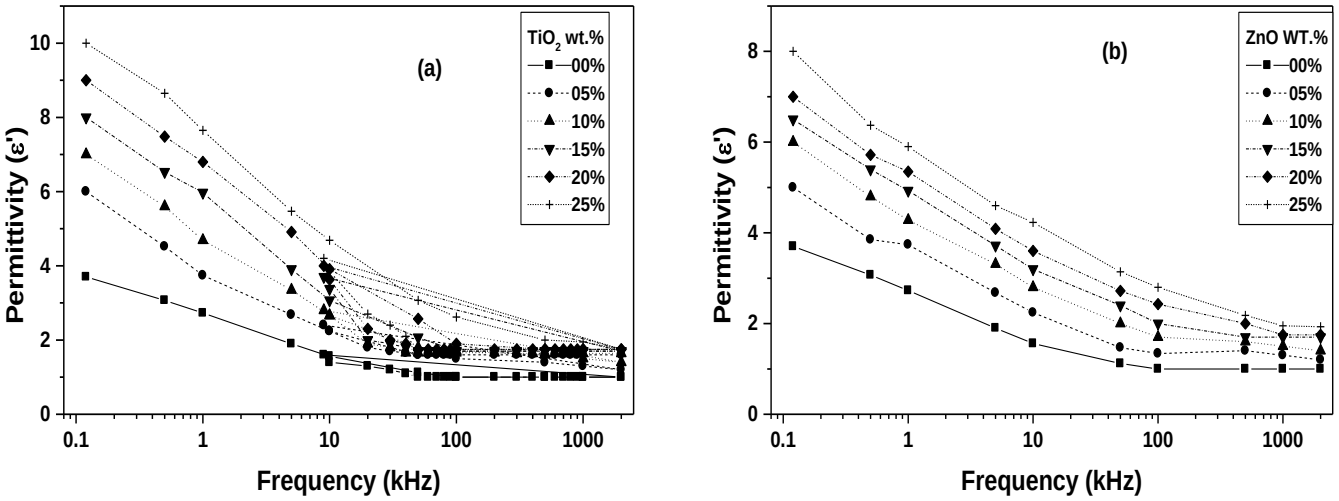

Fig. (3) The permittivity as a function frequency for different content of (a) TiO_2 and (b) ZnO- epoxy composite.

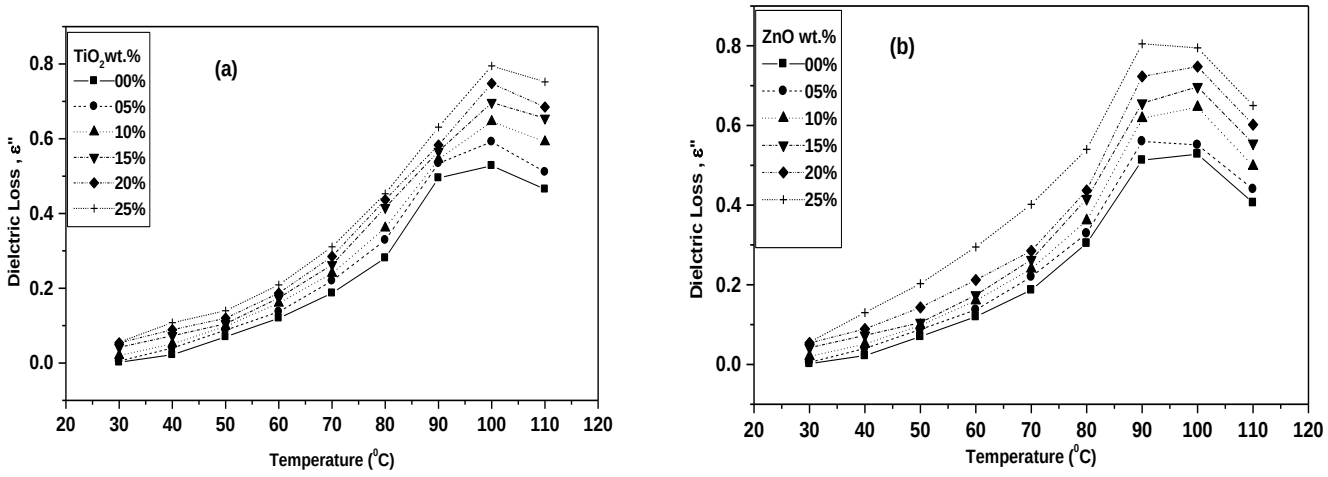

Fig. **(3) Dielectric loss as a function of temperature for different content of (a) TiO_2 and (b) ZnO- epoxy composite**.

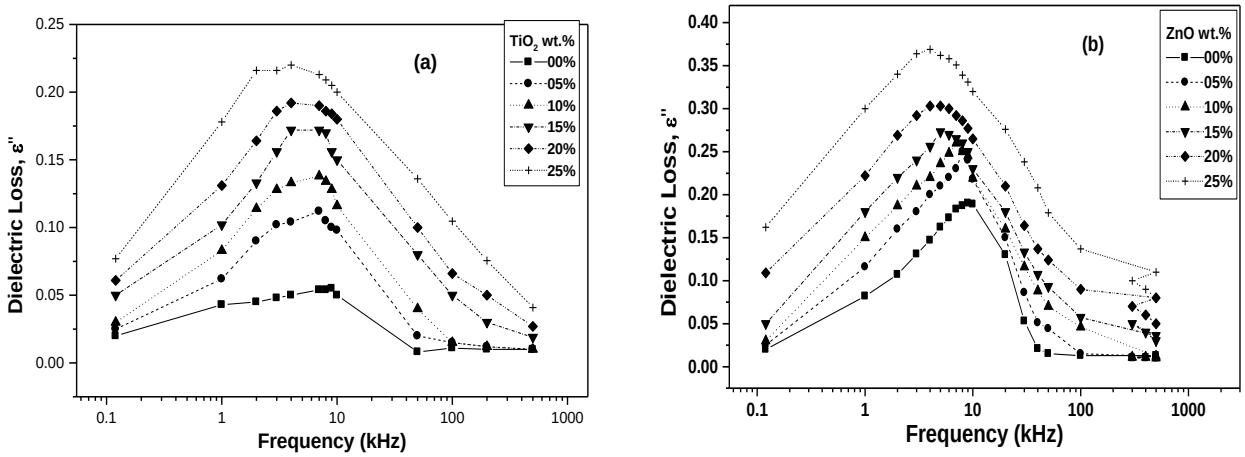

Fig. **(5) Dielectric Loss as a function of filler content and frequency for different content of (a) TiO_2 and (b) ZnO- epoxy composite.**

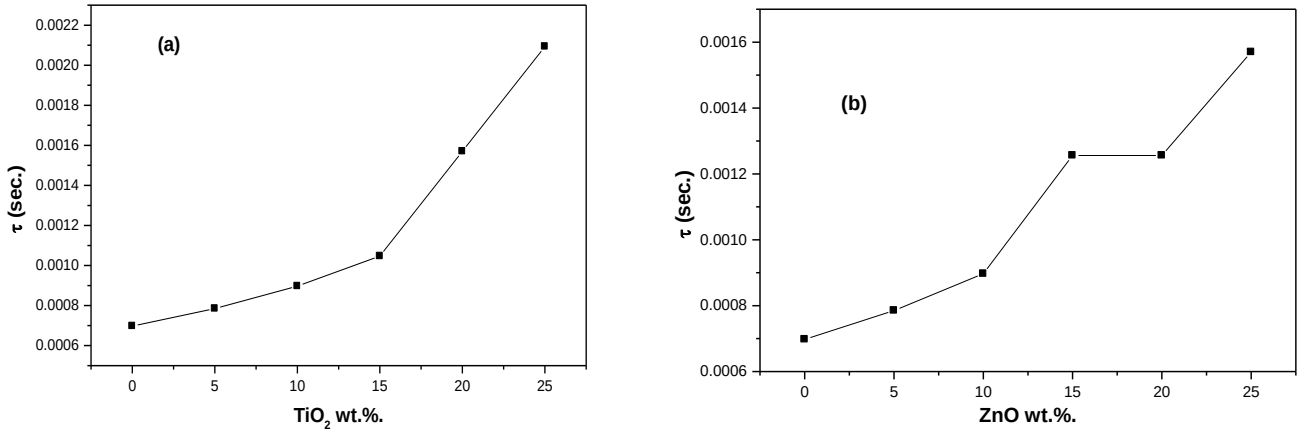

Fig. (6) Relaxation time as a function of filler content for (a) TiO_2 and (b) ZnO- epoxy composite.

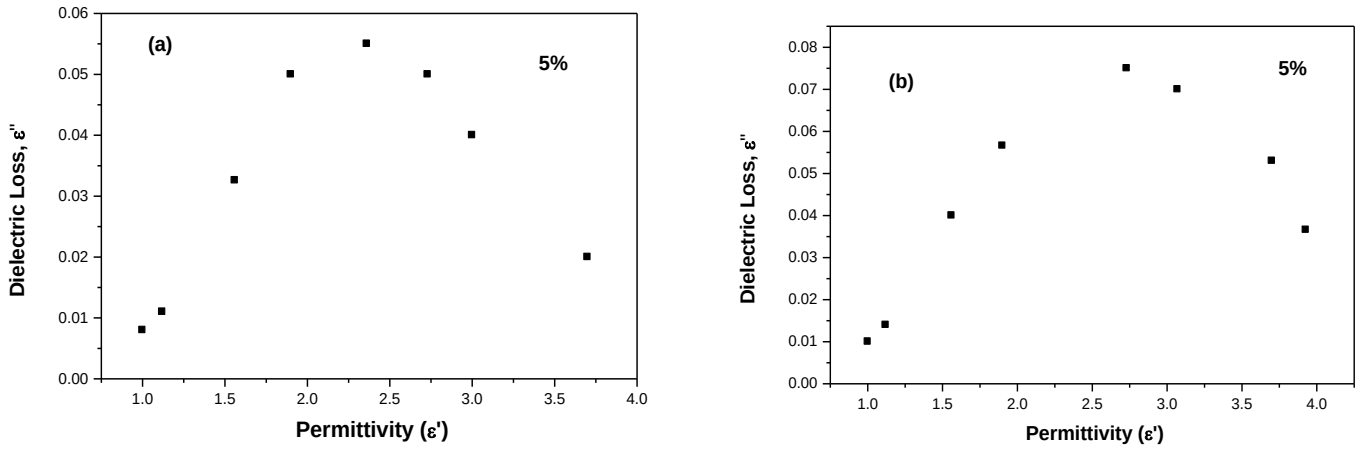

Fig. (7) Cole-Cole diagram for (a) TiO_2- epoxy composite and (b) ZnO- epoxy composite.

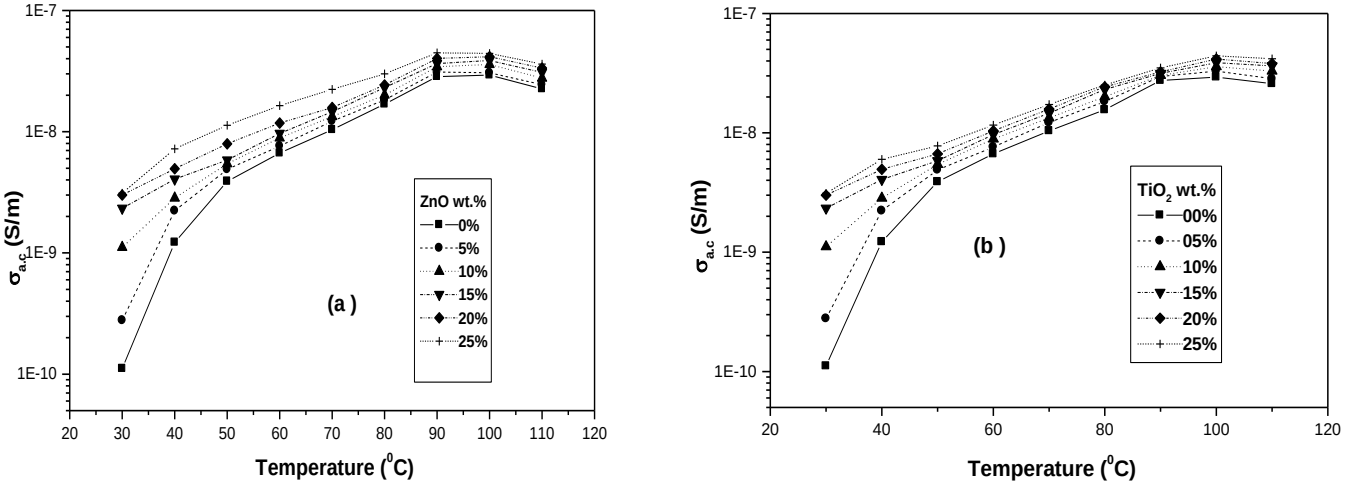

Fig**. (8) Ac conductivity as a function of temperature for different content of (a) TiO_2 and (b) ZnO- epoxy composite.**

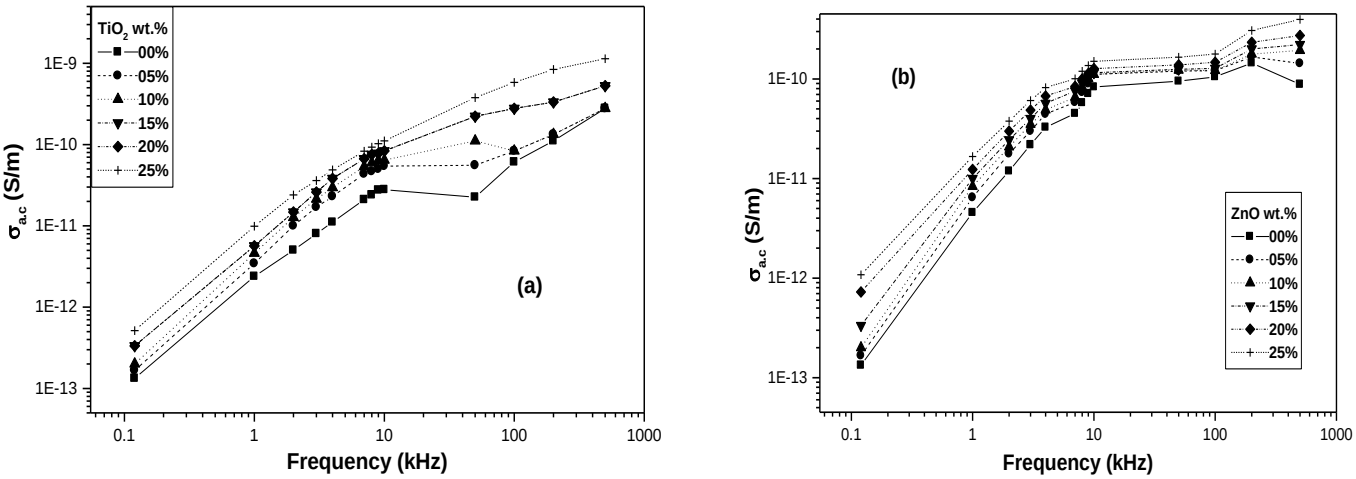

Fig.(9) AC conductivity as a function of frequency for different content of (a) TiO_2 and (b) ZnO- epoxy composite.

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