A.C Conductivity and Dielectric Properties of Epoxy - TiO_2 Nanocomposites

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Abstract

In this paper, A.C conductivity of micro and nano grain size-TiO_2 filled epoxy composites is measured. The dielectric material used is epoxy resin, while micro and nano-sized titanium dioxide (TiO_2) of grain size (1.5μm, and 50nm) was used as filler at low filler concentrations by weight (3%, and 5%). Additionally the effect of annealing temperature range (293-373)º K and at a frequency range of 10^2-10^6 Hz on the A.C conductivity of the various specimens was studied.

The result of real permittivity for micro and nanocomposite show that the real permittivity increases with decreasing frequency at range of 10^2-10^6Hz. The micron-filled material has a higher real relative permittivity than the nano-filled this is true at all the temperatures measured.

The variation of the A.C conductivity with frequency for micro and nanocomposites shows that A.C conductivity for all samples increase with increasing frequency and the temperature dependence on the A.C conductivity increases as the frequency decrease.

Keywords
Epoxy, Fillers, Fiber fabric, Nanocomposites, Electrical conductivity

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الخصائص العزلية والتوصيلية المتناوبة لمتراكبات الايبوكسي- TiO_2 النانوية

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الخلاصة

في هذا البحث تم قياس التوصيلية المتناوبة لمتراكبات الايبوكسي مع ثاني اوكسيد التيتانيوم ذو الحجم الحبيبي مايكروونانو. المادة العزلية المستخدمة هي راتنج الايبوكسي بينما ثاني اوكسيد التيتانيوم ذو الحجم الحبيبي (1.5μm, and 50nm) تم استخدامه بتراكيز قليلة (3% and 5%) . إضافة لذلك تم دراسة تأثير الحرارة لمدى (293-373)º K ولمدى من الترددات (10^2-10^6 Hz) على التوصيلية المتناوبة لمختلف العينات .

تظهرنتائج ثابت العزل الحقيقي للمتراكبات المايكروية ولمتراكبات النانوية الزيادة مع نقصان التردد. كما ان العزلية لمتراكبات الميكرو اعلى مما لمتراكبات النانو وهذا واضح عند كل درجات الحرارة.
يوضح تغير التوصيلية المتناوبة مع التردد لمتراكبات الميكروية والنانوية ان التوصيلية المتناوبة تزداد مع زيادة التردد وان التوصيلية المعتمدة على درجات الحرارة تزداد مع نقصان التردد.

Introduction

Filling the polymer matrix is the cheapest and most used method to change the basic properties of reinforced composites. The effects of fillers on the electrical properties of the formed composites were investigated. Epoxy and epoxy based composites are preferred insulating materials for several electrical applications, especially printed circuit boards, bushings, generator ground wall insulation system and cast resin transformers. Recently, epoxy based nanodielectric systems are being increasingly investigated for their electrical properties, since the introduction of nanofillers demonstrate several advantages in their properties when compared with the similar properties obtained for epoxy systems with micrometer sized fillers [1,2].
Several dielectric properties in epoxy. Epoxy, one of the most widely used insulating materials in the electrical industry is used as the base polymer material in the present study The resin was selected because it was benign (i.e. without other fillers or diluents), had a low initial viscosity, and a glass transition below 100 ºC [3,4].
TiO_2 has been the subject of many studies due to its remarkable optical electronic properties [5]. Epoxy resin was chosen as a matrix due to its good adhesion with the fillers, having enhanced thermal stability resistance to chemical attack and resistance to the degradation [6]. New fields of dielectric with high dielectric constants appeared in recent years with the preparation of ceramic nanoparticles such as nano TiO_2, Al_2O_3, MgO, and ZnO for polymer composites [7,8 and 9].

1.Electrical and dielectric measurements

The empirical relation for the frequency dependence of a.c conductivity is given by[10] :

$$\sigma_{a.c}(\omega) = A_1 \omega^s \quad \ldots.(2)$$

where:

A_1 is proportional factor, ω is the angular frequency ,and**(s)** is the exponent factor and is determined from the slope of a plot Ln $\sigma_{a.c}(\omega)$ versus Ln ω, then **(s)** is not constant but decreases with increasing temperature, usually $0<s<1$ it approach as unity at low temperatures and decrease to (0.5) or less at high temperatures [11].

The total conductivity was calculated from the equation:

$$\sigma_{total(\omega)} = (d/A)G \quad \ldots.(3)$$

Where **d** is the thickness of the sample, **G** is the sample conductance, and **A** it's the cross sectional area of parallel plate capacitor with area.
The dielectric constant **ε** indicates the ability of the material to store energy from the applied electric field was calculated from the equation:-

$$\varepsilon_r = C/C_\circ \quad \ldots. (4)$$

where **C** the capacitance of the electrodes with dielectric**,** $C_\circ$ is the geometrical capacitance of the sample without dielectric ($C_\circ = \varepsilon_\circ A/d$,where $\varepsilon_\circ$ is the permittivity of free space and equal to 8.85×10^{-12} **F/m).**

The dielectric loss **έ** was calculated from the equation**:-**

$$\varepsilon_i = G/\omega C_\circ \quad \ldots. (5)$$

Then dissipation factor (tanδ) the degree of dielectric loss can be calculated from the equation:-

$$\tan\delta = \varepsilon_i/\varepsilon_r \quad \ldots. (6)$$

2. Sample preparation method

In this paper, using transmission electron microscope (TEM), the formation process of TiO_2 nano powder as shown in fig.(1). Epoxy (EP10) and hardener type (HY-956) were used in this study in ratio of 3:1 for curing with nanoTiO_2 (50nm) and micro TiO_2 (1.5μm) to form nano and micro composites with two different concentration of TiO_2 (3%, and 5%) weight percentage. Careful mixing of EP with TiO_2 and composites were then further mixed in an ultrasonic processor at 20 kHz for typically 20 minutes, was needed to minimize voids and clustering of the particles, and finally, they were cast in moulds The specimen were cut dimensions (250mm*250mm*3mm). Detailed sample for many electrical characterizations, the cast film was provided with evaporated 100 nm aluminum electrodes.

For a.c measurements, samples were sandwiched between two gold electrodes and a programmable automatic LRC bridge was used (PM60304 Philips) to measure the sample conductance G and the capacitance C , directly. The measurements were carried out through the temperature range (293-373) º K and at a frequency range of 10^2-10^6 Hz.

Figure 1 TEM images of nano Raw TiO_2

3. Results and Discussion

3.1Real and imaginary components of relative permittivity dependence temperature and frequency

Figure (2-5) shows the variation of the real and imaginary components of relative permittivity as a function of temperature and frequency obtained for the 3 and 5 wt% micro- and nano-composites through the temperature range (293-373) º K and at a frequency range of 10^2-10^6 Hz . At higher frequencies, the micron-filled material of 5Wt% has a higher real relative permittivity; this is presumably due to the high relative permittivity of the filler (99). This compares with the measured value of 24.28 under the same circumstances, perhaps indicating some interfacial effects. However, in marked contrast, the nanocomposite at 1 kHz, 393 K exhibits a measured value of 22.69, which is significantly less than that of the microcomposite. The permittivity associated with the epoxy component in the nanocomposite will still exist in spite of the polymer chain immobilizations. This is because the nanocomposite will have several dipolar groups which are not interacting with the nanoparticles and so they would be free to orient with the applied electric field. This is true at all the temperatures measured. That the interaction zone surrounding the nanoparticles is having a profound effect on the dielectric behavior of the nanocomposite. The nanoparticles appear to restrict end-chain or side-chain movement of the epoxy molecules [12].

The micro and nanocomposite real permittivity however shows a marked increase with decreasing frequency. This clearly associated with the micro and nanoparticles and is possibly a Maxwell-Wagner interfacial polarization

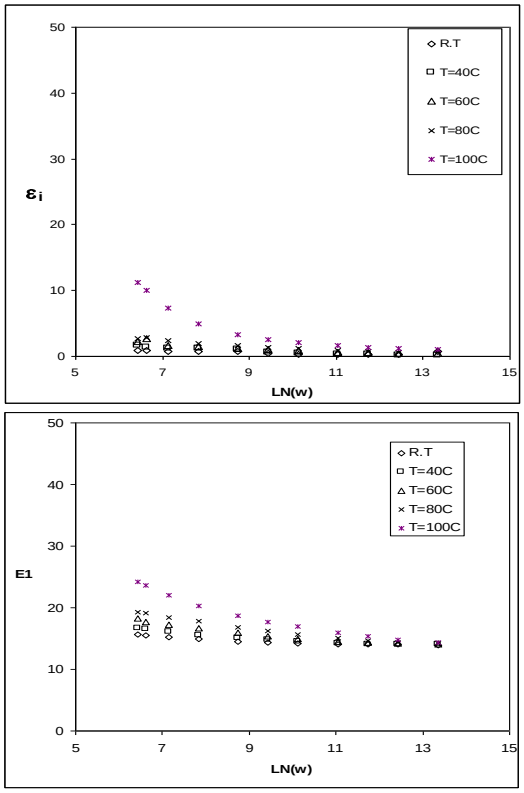


Figure 2: Real and imaginary relative permittivity of 3%micro-composite

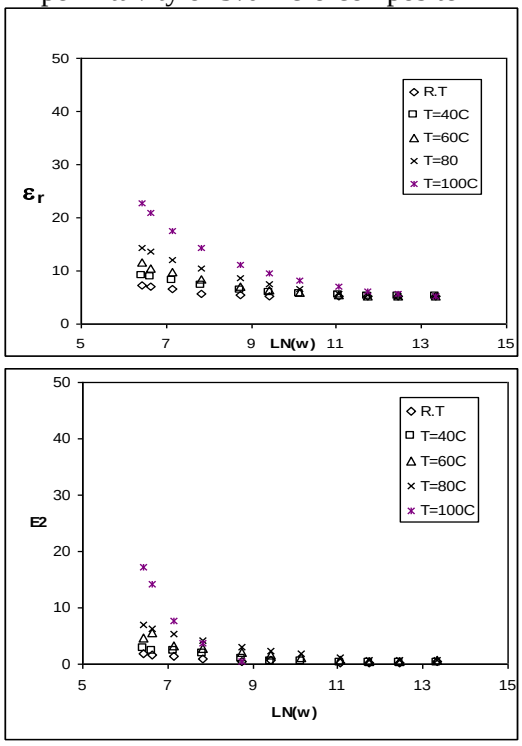


Figure 3: Real and imaginary relative permittivity of 3% nano-composite materials

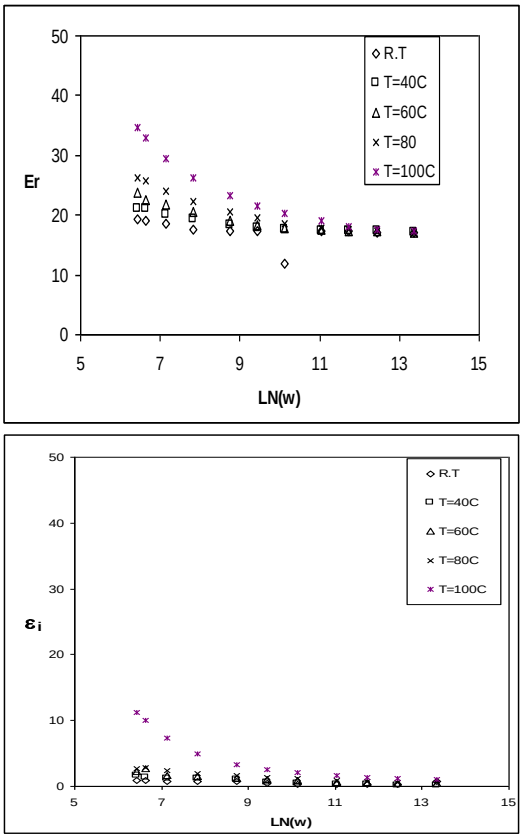


Figure 4: real and imaginary relative permittivity of 5% microcomposit materials

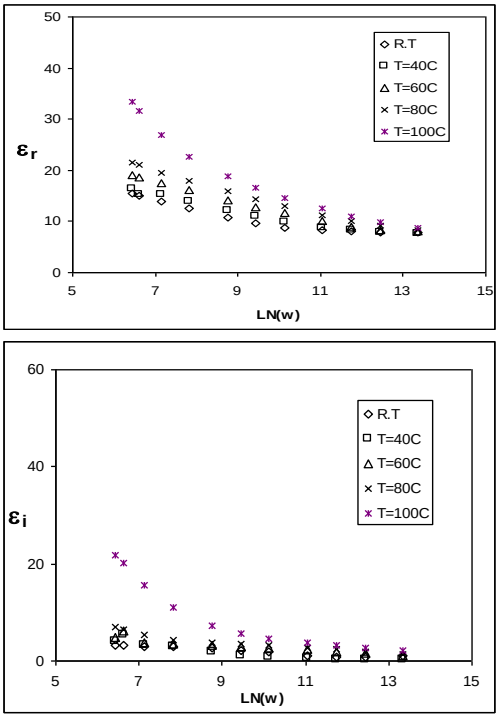


Figure 5: Real and imaginary relative permittivity of 5% nano-composite materials

3.2 Frequency Dependence of $\sigma_{ac}(w)$

Fig (6) shows the relation between ln $\sigma_{a.c}(\omega)$ and ln(ω) for epoxy TiO2(nano and micro composites) at room temperature (293) ̊K .It is clear from the figures that $\sigma_{a.c}(\omega)$ increases with the increase of frequency(according to eq.(2)) at room temperature. The highest conductivity for EP/TiO_2 composites (nano and micro) at 100 KHz is shown in Table (1).

Table (1): The conductivity values for EP/TiO_2 composites (nano and micro)

Samples	**Ln σ at 100 KHz**
EP+3% micro T iO_2	**-17.48**
EP+5% micro T iO_2	**-16.66**
EP+3% nano T iO_2	**-16.44**
EP+5% nano T iO_2	**-16.11**

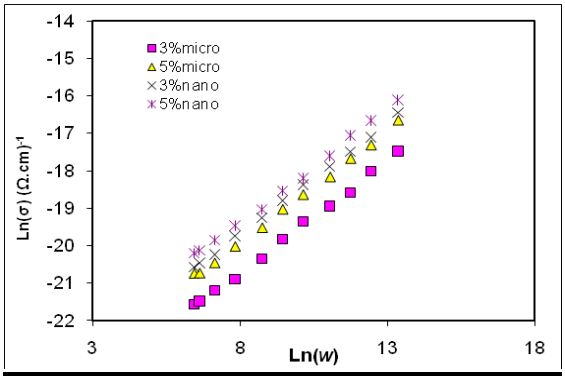


Fig. 6 conductivity as a function of frequency of all composites at R.T.

Hence, it is proposed that two factors influence σ_t (ω), which are ions motions and polymer backbone (main chain) motion. Furthermore ions motion is contributed at high frequency [7, 13]. The increasing of σ_t (ω), at low frequencies over (100-400) Hz is the attributed to the interfacial polarization, since the direct conductivity (σ_d.c) is significant at this region [10]. The rapidly increasing of σ_t (ω) with increasing frequency at the frequency greater than 10^3 Hz referred to the electronic polarization effect, and the conductivity is pure a.c conductivity $\sigma_{a.c}(\omega)$ in this region .

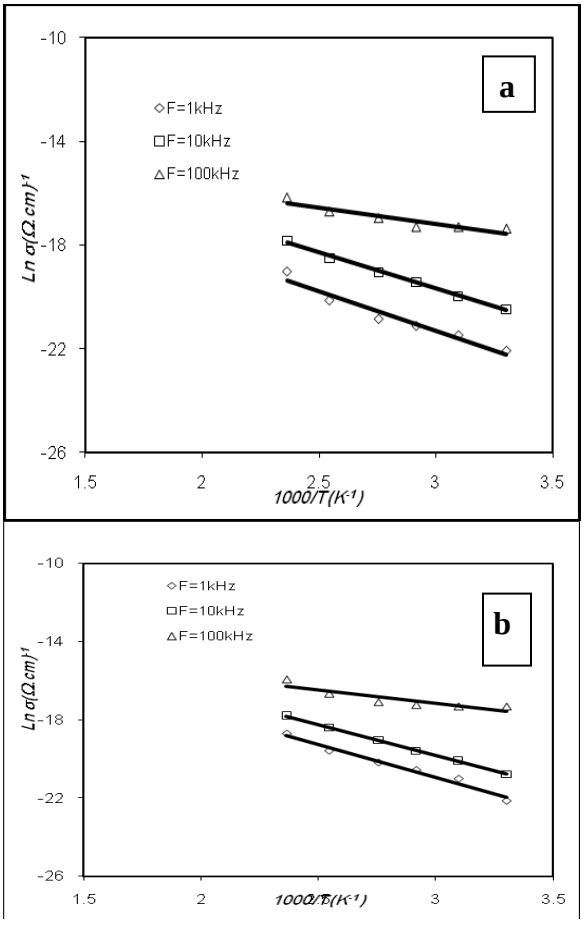
3.3 Temperature Dependence of $\sigma_{ac}(\omega)$

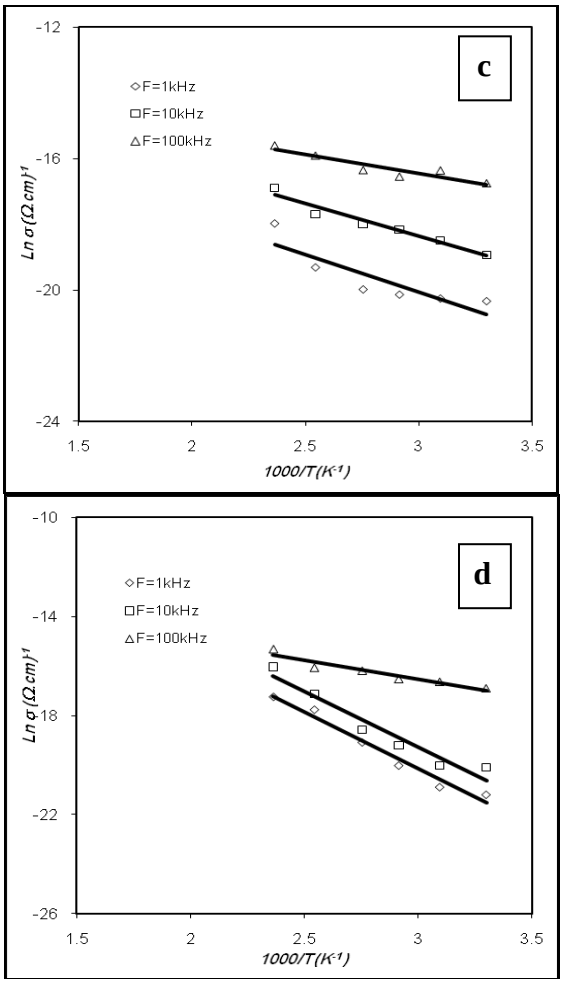
The variation of $\sigma_{ac}(\omega)$ with increase temperature (1/T) for the samples and annealed at temperatures ((293-373) º K for three fixed frequencies (1kHz,10kHz and 100kHz) are shown in Figs.(7a-d) for 3 and 5 wt% micro- and nano-composites .It is evident from the figures, a linear behavior of $\sigma_{ac}(w)$ of one stage is observed over the entire temperature range indicating a thermal activated conduction mechanism.

It was emphasized that the only model which appears to be the most charge/carriers to percolate through overlapping shells for composites sheets[14]. The temperature dependence of σ_{ac} (ω) increases as the frequency decreases. The decreasing activation energies (E_w) for frequencies (1kHz, 10kH+z and 100kHz) are listed in Table (2), which is consistent with the hopping mechanism. On the other hand that the exponent factor (s) was decreased with increasing TiO_2 in epoxy. It is observed that the values are less than unity (0.734-0.443), another indication for correlated barrier hopping (CBH) mechanism.

Table (2) A.C activation energy for micro and nanocomposite of TiO_2/epoxy at different TiO_2 wt. % contents

TiO_2 wt.%	E_w(eV) at		
	1kHz	10kHz	100kHz
3micro	0.174	0.166	0.087
3nano	0.15	0.132	0.054
5micro	0.198047	0.17037	0.098575
5nano	0.143	0.122	0.043





Fig(5-a,b,c and d) ln σ (ω) versus 1000/T for 3 and 5 wt% micro- and nano-composites at different annealing

4. Conclusions

1-The real and imaginary components of relative permittivity values for all composites decrease with increasing frequency this is true at all the temperatures measured.

2- The temperature dependence of σ_{ac} (ω) increases as the frequency decreases

3- Activation energy decreases with increase of TiO_2 concentration.

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