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Dielectric Properties of Epoxy /Cu, Al Composites

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Abstract: Epoxy/ Cu,Al composites with different Cu,Al contents were prepared and fully characterized. Measurements of A.C conductivity of EP/Cu,Al composites films over frequency range (102-107Hz)and temperature range (293-373K)have been performed. The influence of Cu and Al loading levels on various properties was also explored. Dielectric and electrical properties of Cu,Al /epoxy composites were studied for samples in parallel plate configuration Cu,Al /epoxy composites prepared in this fashion reached a high dielectric constant close to 208 at Cu =15% at T= 353K , a dielectric loss tangent less than 1.07at room temperature and 100 Hz. The variation of activation energy and conduction behavior has been studied. The calculated activation energy varied with Cu and Al content, temperature, and applied frequency. Conductivity plots against frequency suggested the response obeying the universal power law concerning the AC conductivity and dielectric behavior of polymer. The polarizability α increases with increase of Cu and Al content and temperature indicating weekends and of intermolecular forces.The results were interpreted according to the increase of charge carriers accompanied the addition of both elements to EP.

Keywords: Polymer composites Dielectric properties, Universal power law, Dielectric loss spectra

1. Introduction

The growing demand for the miniaturization and performance in electronic devices has been driving research and development activities for embedded passives (such as resistors, capacitors and inductors). By eliminating surface mount components and embedding into the substrate boards, embedded passive components offer various advantages over traditional discrete ones, including higher component density, increased functionality, improved electrical performance, increased design flexibility, improved reliability and reduced unit cost[1,2]. For embedded capacitor applications, study on ferroelectric ceramic/polymer composites with high dielectric constant (k) has been actively explored, since polymers meet the requirements for the low cost organic substrate process such as low temperature processibility and mechanical flexibility [3,4]. However, some challenging issues in these polymer composites for high k applications have been addressed, such as limited dielectric constants, low adhesion strength and poor processibility. Dramatic increase of dielectric constant close to the percolation threshold observed in the conductor insulator percolative system arouses interest of developing conductive metal/polymer composites as candidate materials for embedded capacitor applications. Various metal fillers, such as silver, aluminum, nickel, have been used to prepare the metal/polymer composite or three-phase percolative composite system [5 to11]. This material option represents advantageous characteristics over the conventional ceramic/polymer composites, specifically, ultra-high ε with balanced mechanical properties including the adhesion strength. The influence of Cu and Al loading levels on dielectric properties of Cu,Al/epoxy composites was discussed. Frequency dependency of dielectric properties for Cu,Al /epoxy composites was also presented in the range of 100 Hz to10 MHz. The correlation of the microstructure with the corresponding dielectric properties was discussed.

2. Samples Preparation and Procedure

The materials were used to prepare the samples of this work are: Epoxy resin (EP), type (Thortex) with hardener Isophorone diamine (IPD),supplied by (Thortex Division of E.Wood Ltd.), Al and Cu with high purity 99.999 ٪ supplied from Bulzer. An exact amount of special hardener was added to the epoxy resin with weight ratio of hardener to resin (1:2) Appropriate weights ratio of Cu cupper and aluminum by using a sensitive electrical balance type (Metter H35) by using a sensitive electronic balance of sensitivity (0.01 gm).The content was mixed thoroughly by a fan type stirrer before casting it as a sheets (of dimensions 25x20cm2) by using glass mould. The sheets were stored at room temperature for 72 hours, and then for post-curing, the sheets were left for 4 hours in an oven at temperature 800C.

The composites samples were prepared with the following ratios:

EP wt.%	100	95	85	75
Cu,Alwt .%	0	5	15	25

The specimen was fixed in specimen holder and placed into temperature controlled oven type (Heresies electronic). High and low holder terminals are connected to dielectric analyzer type Hewlett Packard model (HP4274A & HP4275A), the third holder terminal was connected to the earth. Three dielectric parameters were measured directly from above setup total resistance (RT), total capacitance (CT) and dissipation factor tanδ with an accuracy of 0.1%. All measurements were performed under certain conditions as follows:

The frequency range concerned in this work was 10 2- 10 7 Hz

2- Temperature range between (293- 373) K, the temperature was changed by constant rate of 2K/min

3-A constant voltage of (1V) was applied in all frequency range and temperature those are indicated in this work.

Because of our study mainly deals with dielectric properties: since these properties is very sensitive to impurities. A pre preparation requires obtaining reliable and stable properties. Every sample was grinded perfectly to obtain smooth surface and perfect electrodes adhesive. The samples were washed by absolute alcohol and subsequently dried by an air jet and placed in an oven at 343K for 20min to minimize the influence of moisture. Aluminum electrodes with thickness 2000°A were deposited on each adjacent surfaces of specimen by thermal evaporation technique under pressure of (10-5 mbar) using coating unit type Edward model E306A. The specimen was fixed in specimen holder and placed into temperature controlled oven type (Heresies electronic). A. C. conductivity has been evaluated from dielectric data in accordance with the relation: The dielectric constants (εr,εi) can be calculated using the following relations:

$$\varepsilon r = C.t / \varepsilon 0 .A \qquad (1)$$

where C is Capacitance, ε0 is the Permittivity of free space =8.854x10-14 (F/cm).

$$\varepsilon i = \sigma AC / \omega \varepsilon o \qquad (2)$$

Where t is thickness of film R is Resistance of film, A is Effective area for capacitance.

3. Result and discussion

3.1. The Dielectric Constants

Fig.1-4 show that the variations of εr, with frequency for the Ep/ Cu, Al composites having different Cu, Al content and at different temperatures respectively. In all the cases, a strong frequency dispersion of permittivity is observed in the low frequency region followed by a nearly frequency independent behavior above 1 kHz. The decrease of (εr) with increase in frequency may be attributed to the electrical relaxation processes, but at the same time the material electrode polarization cannot be ignored. The material electrode interface polarization superimposed with other relaxation processes at low frequencies. It is seen that with increase of Cu and Al content increases (εr) value up to content of 15% of both elements but further loading causes decrease of it. The loading of Cu and Al may result in more localization of charge carriers along with mobile ions causing higher conductivity. This may be the reason for higher (εr) and strong low frequency dispersion .On the other hand the dielectric constant exhibit to decrease with temperature (Figs.3and 4) in low temperature range but then increases. Indeed εr increases from 3.68 to75.66 and 8.4 respectively when Cu and Al content increase from 0 to 15% but then decrease to37.52 and 4.8 with further loading of both elements.

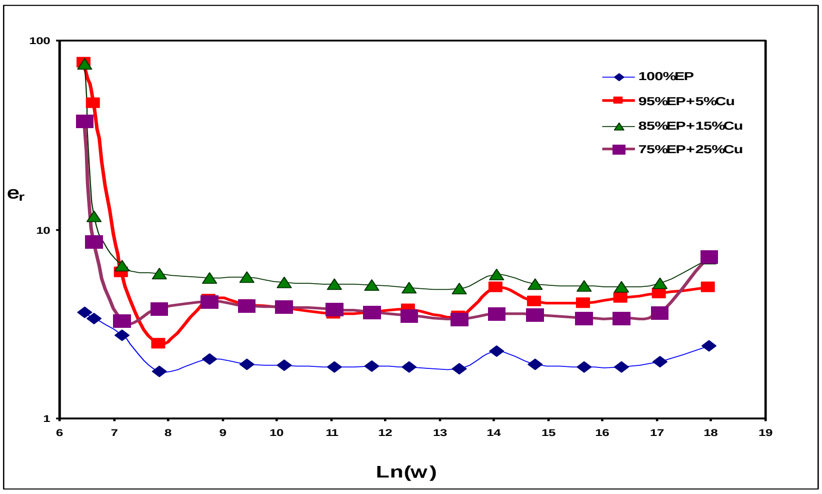

Figure 1: Variation of real part of permittivity (εr) with frequency of EP/Cu composites of different Cu content at room temperature

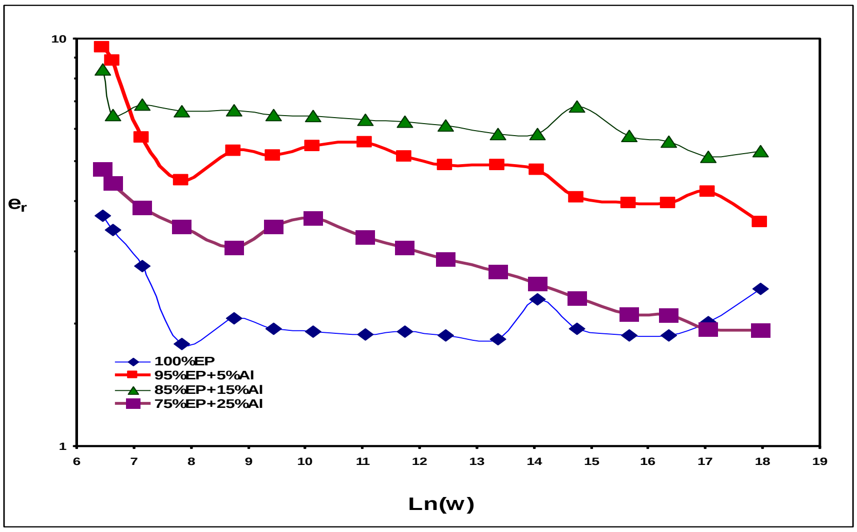

Figure 2: Variation of real part of permittivity (εr) with frequency of EP/Al composites of different Al content at room temperature.

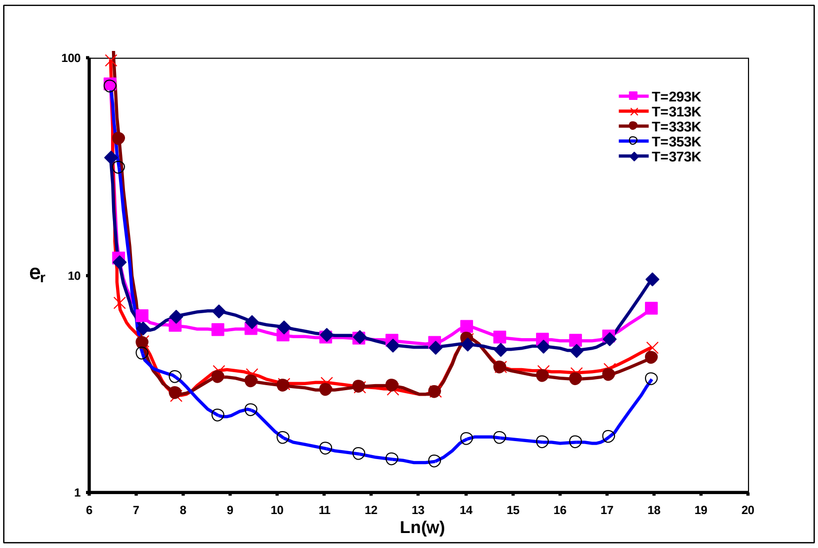

Figure 3: Variation of real part of permittivity (εr) with frequency85% EP+15%Cu composites at different temperatures.

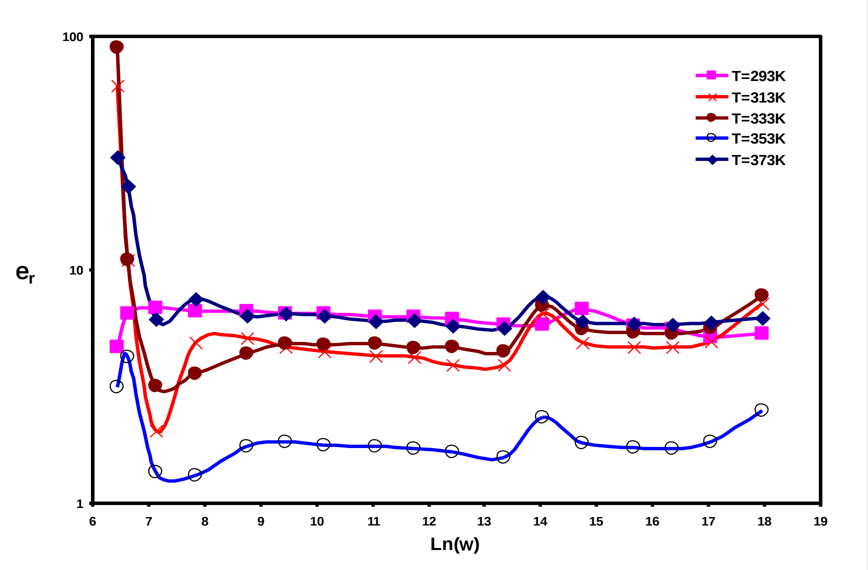

Figure 4: Variation of real part of permittivity (εr) with frequency85% EP+15%Al composites at different temperatures.

Figs.5 - 8 show the εi spectra with frequency for Cu, Al/ Ep composites samples for different Cu and Al content and temperatures respectively. The spectra characterizes by peak appearing at a characteristic frequency suggest the presence of relaxing in all the samples. The strength and frequency of relaxation depend on characteristic property of relaxation. The relaxation peaks shift towards the higher frequency side with the increase of Cu and Al content for low content values (0,5,15%) but then shifts to lower frequency side. With the increase of Cu and Al content it is believed that there is an increase in the free charge carriers in the materials. The small mobile elements of Cu and Al and speed up the segmental motion. It is evidenced by the peak shifting toward higher frequency side, thereby reducing the relaxation time, The relatively fast segmental motion enhances the transport properties on composites, but with further increase of Cu and Al content leads to decrease the mobility of free charge in turns reducing σA.C and εi .

Dielectric relaxation is a result of the reorientation process of dipoles in the polymer chains, which show a peak in εi spectra. For polymer with higher ion concentration, the movement of ions from one site to another will perturb the electric potential of the surroundings. Motion of the other ions in this region will be affected by perturb potential. Such a cooperative motion of ions will lead to non-exponential decay, or a conduction processes with distribution of relaxation time.

It is generally believed that dielectric data is characterized by superposition of two processes: a conductivity contribution that produces an increase of both real part εr and the imaginary part εi of the dielectric function on decreasing frequency and a relaxation process exhibiting a maximum in εi that shifts lower frequency side with increase in temperature.

The reason of declaring more than one peak in the spectrum of εi versus frequency is the foundation of multiphase, in our composites samples phase of Cu, Al and Ep composites, the disappearing of relaxation peak confirms the dominating of one phase.

Increase of Cu and Al content results in overall increase of εr and εi due to free charge contributions. So the increase of the molecular mobility is reflected both by increase of free charge mobility and the shift of the peak towards the higher frequency side with simultaneous increase of its magnitude. The overall result is enhancement of conductivity with increase of loading with Cu and Al up to 15%, but then the opposite case take place.

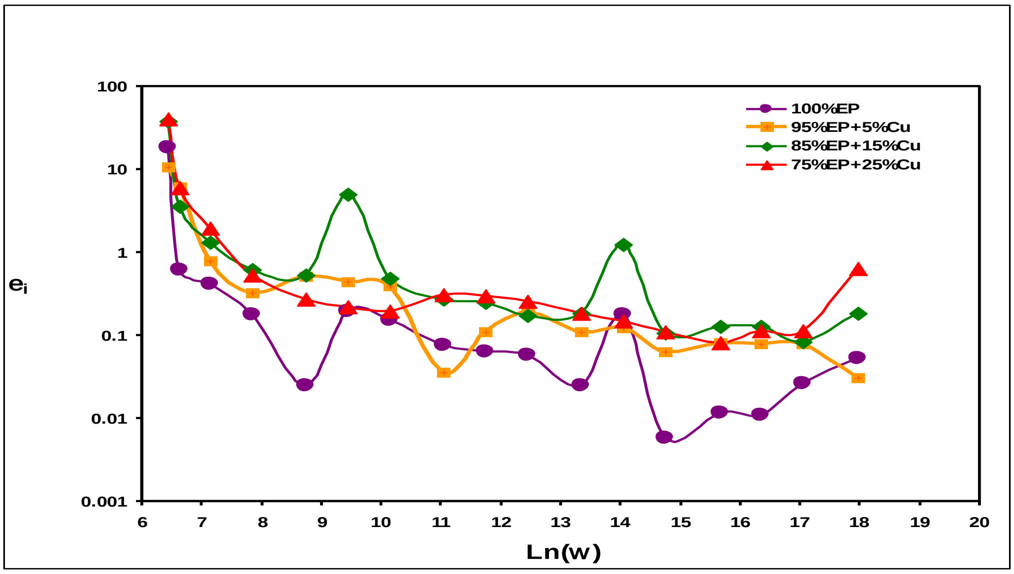

Figure 5: Variation of imaginary part of permittivity (εi) with frequency of EP/Cu composites of different Cu content at room temperature

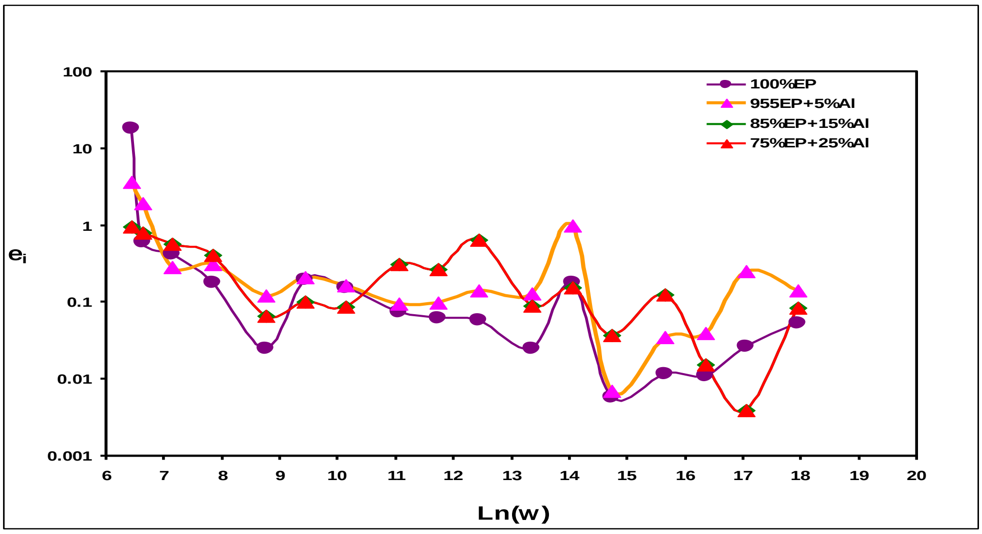

Figure 6: Variation of imaginary part of permittivity (εi) with frequency of EP/Al composites of different Cu content at room temperature

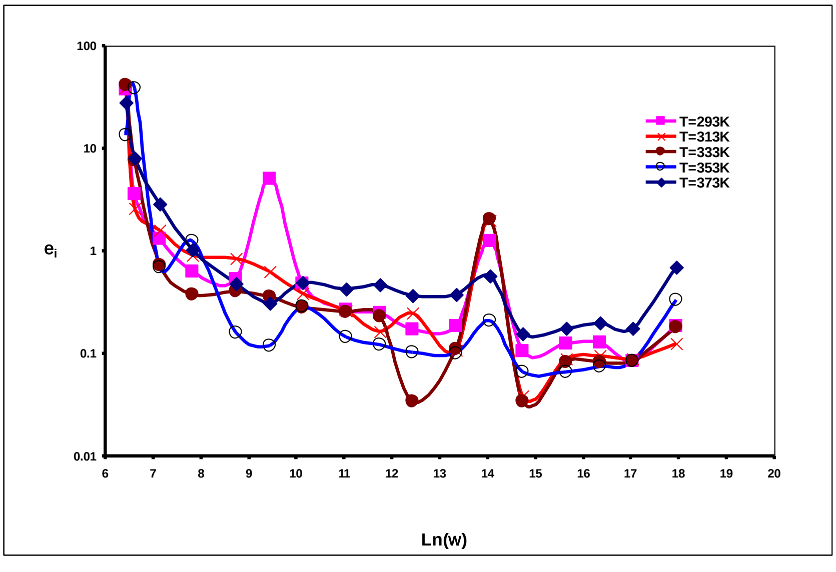

Figure 7: Variation of imaginary part of permittivity (εi) with frequency85% EP+15%Cu composites at different temperatures.

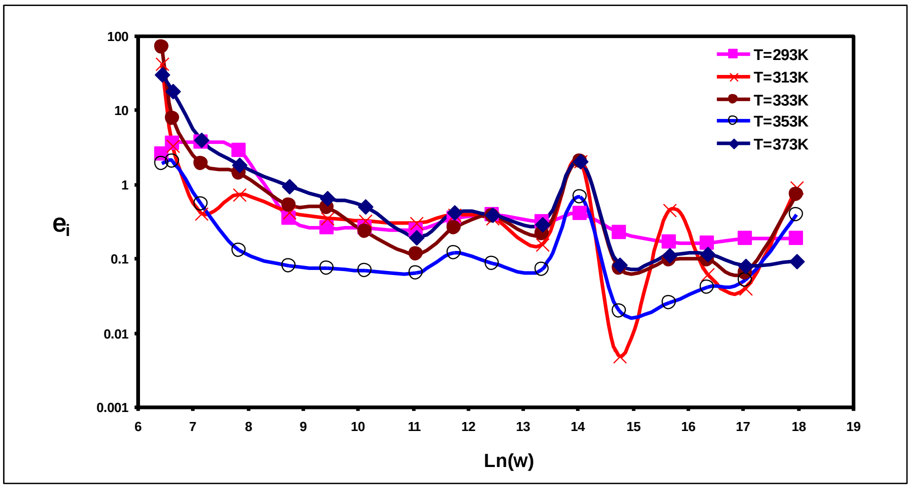

Figure 8.Variation of imaginary part of permittivity (εi) with frequency85% EP+15%Au composites at different temperatures.

3.2 A.C Conductivity

Electrical properties of Cu, Al/epoxy composites with different Cu and Al contents were studied on samples with parallel plate capacitor configuration.

The AC conductivity σA.C is directly related to the imaginary part of dielectric constant εi as σA.C = ε0ω εi where ε0 and ω is the permittivity of the free space and angular frequency respectively. Figs. 9 to 12 show the variation of σA.C with frequency for different Cu and Al content and temperatures of EP/Cu, Al composites respectively. The AC conductivity patterns exhibits dispersion at hole frequency range. This behavior obeys the universal power law, σ(ω) = σ0+ Aωs, where σ0is the dc conductivity (frequency independent plateau in the low frequency region). The electrical conductivity σA.C at F=10kHz of neat epoxy is 1.37 x 10-10 S cm-1while σA.C of composite containing 15 % Cu and Al were 2.93 x 10-9 S cm-1and 1.92 x10-9 respectively. The value of the exponent s at different temperatures and Cu and Al content are calculated by fitting the curves of Fig. 9 and 10 and listed in Tables.1 .It found that s changes in different manner with temperature and Cu and Al content, i.e. s increases with Cu content, indeed s increases from 0.63 to 0.70 when Cu increase from 0 to 25% while s for Ep /Al composites change in different manner since s increase in the former but decrease with further addition of Al, indeed s increase from 0.63 to 0.82 when Al increase from 0 to 5% but then decreases to 0.72, while s decreases with temperature for all composites samples. To explain our results we suggests Correlated Barrier Hopping (CBH) model.

The activation energy for conduction (Eac) in the entire region estimated from the plot of σAC with reciprocal temperature for various frequencies as shown in Figs. 13 and 14 for EP/Cu, Al composites, then (Eac) are calculated by fitting different regions with the equation $\sigma = \sigma_0 e^{-E_a/k_B T}$. The activation energy is found to decrease with increasing frequency which is given in Table 3 and 4.This can be possible due to the increase of applied field frequency and enhances the electronic jumps between the localized states, also (Eac) decreases with the addition of Cu and Al content.

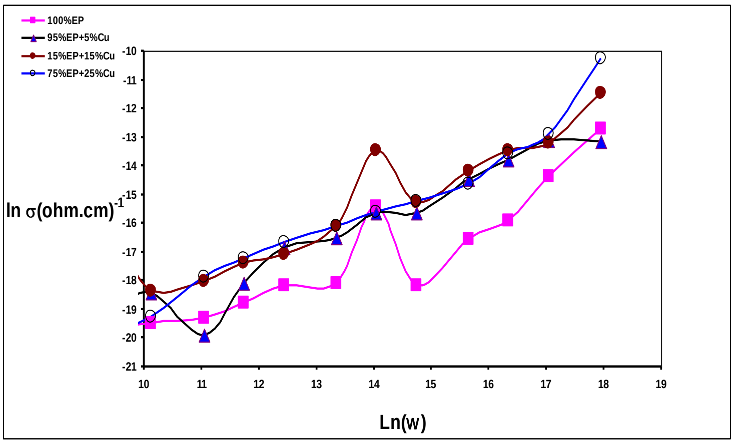

Figure 9: Variation of σ A.C with frequency of EP/Cu composites of different Cu content at room temperature.

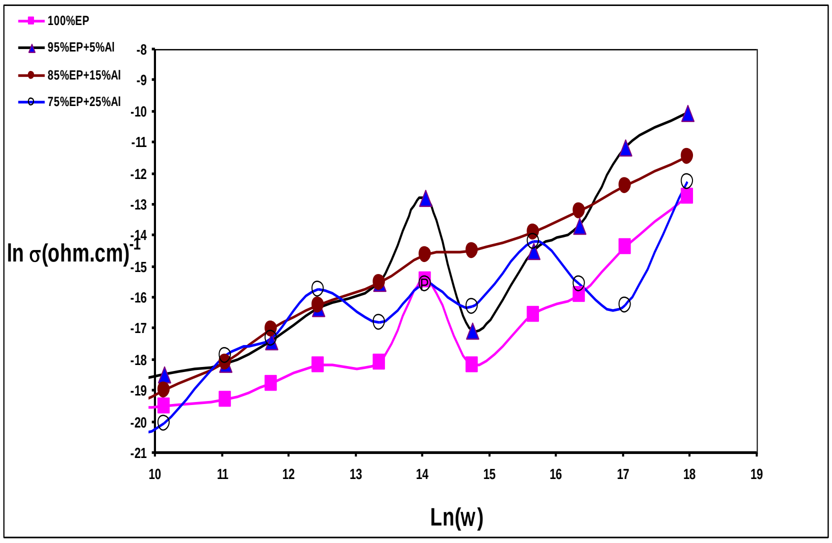

Figure 10: Variation of σ A.C with frequency of EP/Al composites of different Al content at room temperature.

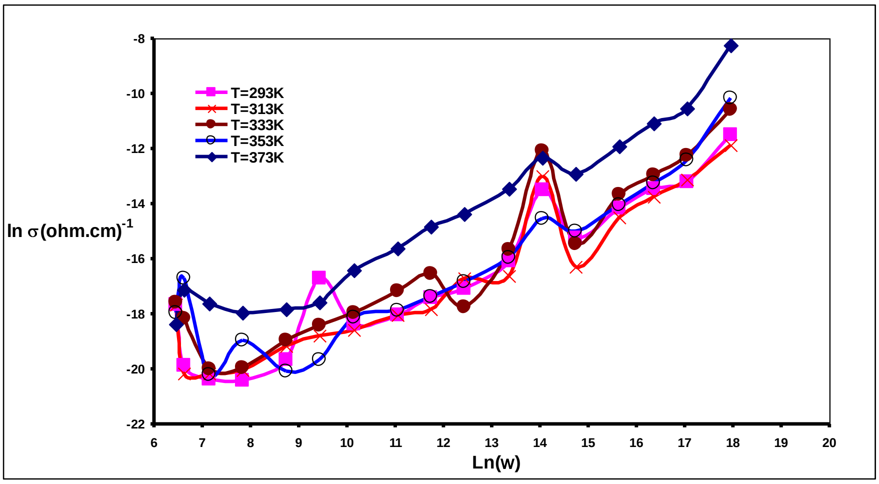

Figure 11: Variation of σ A.C with frequency of 85% EP+15%Cu composites at different temperatures.

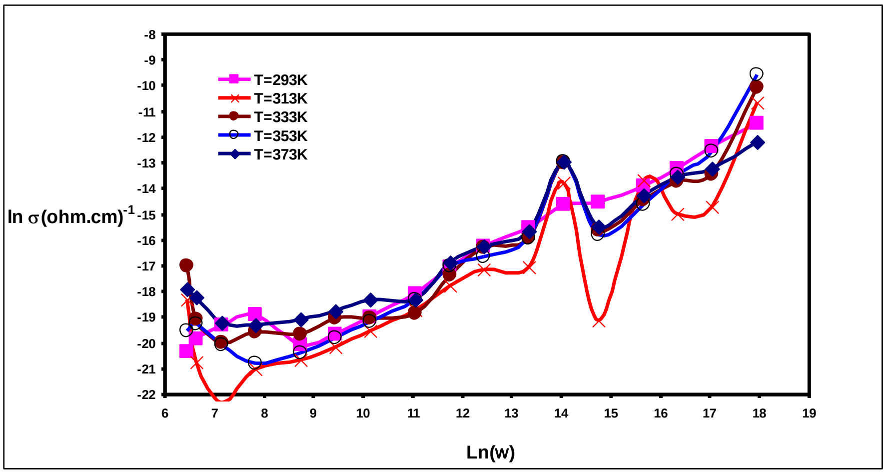

Figure 12: Variation of σ A.C with frequency of 85% EP+15%Al composites at different temperatures.

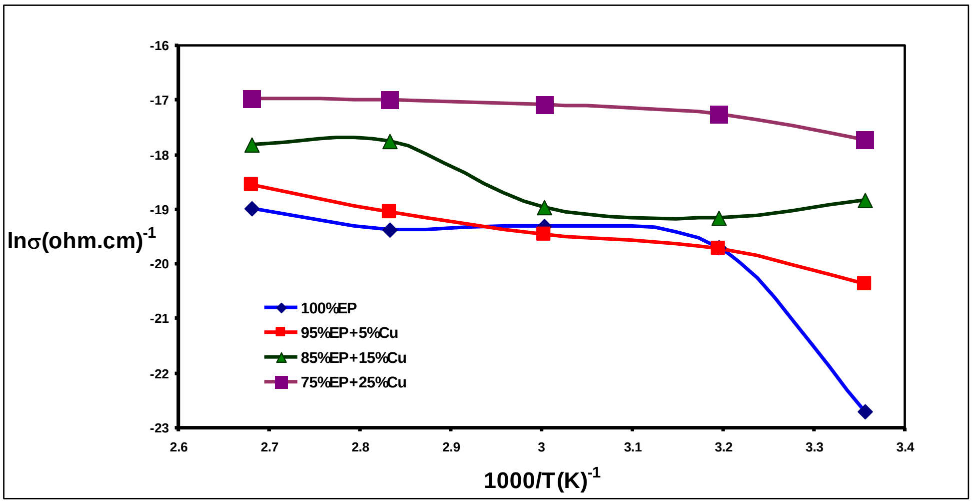

Figure 13: Temperature dependence of AC conductivity for EP/Cu composites.

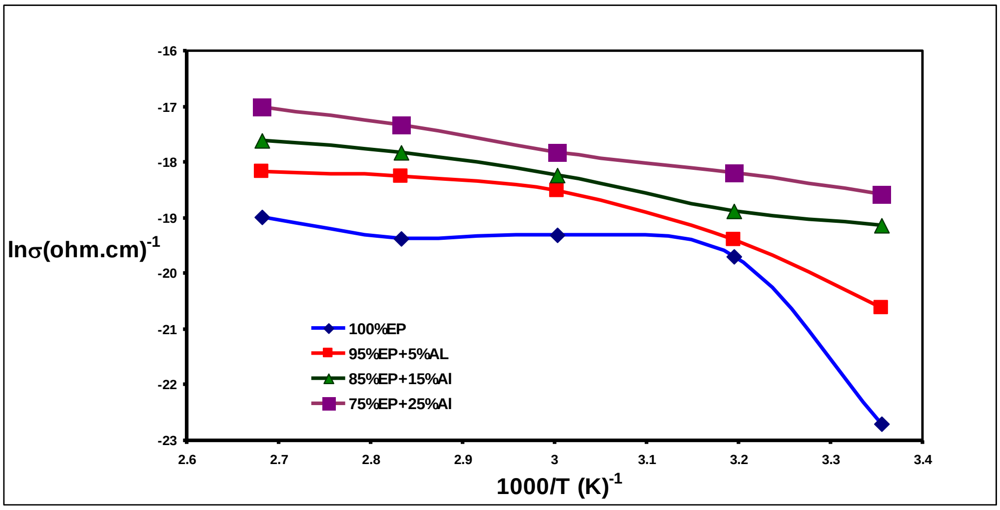

Figure 14: Temperature dependence of AC conductivity for EP/Al composites.

Table.1 Illustrates the values of s and α for EP/ Cu,Al composites.

The Composites ratio %	Oven Temperature (K)	s	α
100EP	293	0.63	0.0448
	313	0.48	0.0336
	333	0.60	0.168
	353	0.61	0.168
	373	0.60	0.168
95EP+5Cu	293	0.64	0.0896
	313	0.48	0.2016
	333	0.36	0.0336
	353	0.49	0.056
	373	050	0.1344
85EP+15Cu	293	0.67	-------
	313	0.65	0.0112
	333	0.69	0.0224
	353	0.66	0.0224
	373	0.78	0.112
75EP+25Cu	293	0.70	0.168
	313	0.57	0.28
	333	0.57	0.0112

	353	0.68	0.0112
	373	0.61	0.0672
95EP+5Al	293	0.82	0.1456
	313	0.50	0.2912
	333	0.68	0.056
	353	0.49	0.112
	373	0.51	0.2352
85EP+15Al	293	0.75	0.056
	313	0.72	0.1344
	333	0.67	0.112
	353	0.80	0.1344
	373	0.59	0.168
75EP+25Al	293	0.72	0.224
	313	0.55	0.2352
	333	0.79	0.2016
	353	0.60	0.2016
	373	0.40	0.28

Table.2 Illustrates the values Eac (EP/ Cu) composites.

The Composites ratio %	Eac(eV)	Temp.Range K
100EP	0.3617	298-373
95EP+5Cu	0.1914	298-373
85EP+15Cu	0.1539	298-373
75EP+25Cu	0.0791	298-373

Table.3 Illustrates the values Eac, for (EP/ Al) composites.

The Composites ratio %	Eac(eV)	Temp.Range K
100EP	0.3617	298-373
95 EP+5Al	0.3052	298-373
85 EP+15Al	0.2076	298-373
75 EP+25Al	0.2003	298-373

3.3 Cole-Cole diagrams

The polymer material exhibits three dispersion peaks which are (α ,β , and γ) each of which represents an individual relaxation process, (1) weak α-peak observed at temperature range 30 and 800C,(2) a well pronounced. a β-peak at approximately 00C,γ-peak in the temperature range -50 and -1000C. The γ-dispersion is probably due to torsional motion of the chain units, the origin of α-dispersion is the relaxation process in the crystalline phase, the β- dispersion produced by far the largest peak and is due to the motion of comparatively long chain segments in the amorphous phase the intensity of β-peak depends on the relative concentration of noncrystalline phase, thus the measurements of dielectric loss of polymer lead to analogous results regarding the molecular motion responsible for the relaxation processes.

A direct evidence of the existence of multi-relaxation time in Ep/ Cu, Al composites is obtaining by plotting Cole-Cole diagrams as shown in Fig.15 and 16 for different Cu, Al content. It has been observed that for all films reported here (εr) versus(εi) curves represent the arc of circles having their centers lying below the absicca axis. This confirms the existence of distribution of (τ) in all films. By measuring the angles (απ/2) the vales of the polarizability (α) had been determined and are listed in Table.1.

We can notice that the values of (α) shows different variation with the increase of Cu,Al content(i.e. increases and decreases with loading with Cu and Al), indeed α increase with Cu addition from 0 to 5% but then decreases follows by another increase when Cu/ Al = 25%, , the increase of(α) is related to weaken of intermolecular forces while the decrease of (α) with the increase of loading results from rise of the forces of the intermolecular [12,13],on the other hand(α) exhibit to increase with the increase of temperature which came from the weaken the forces.

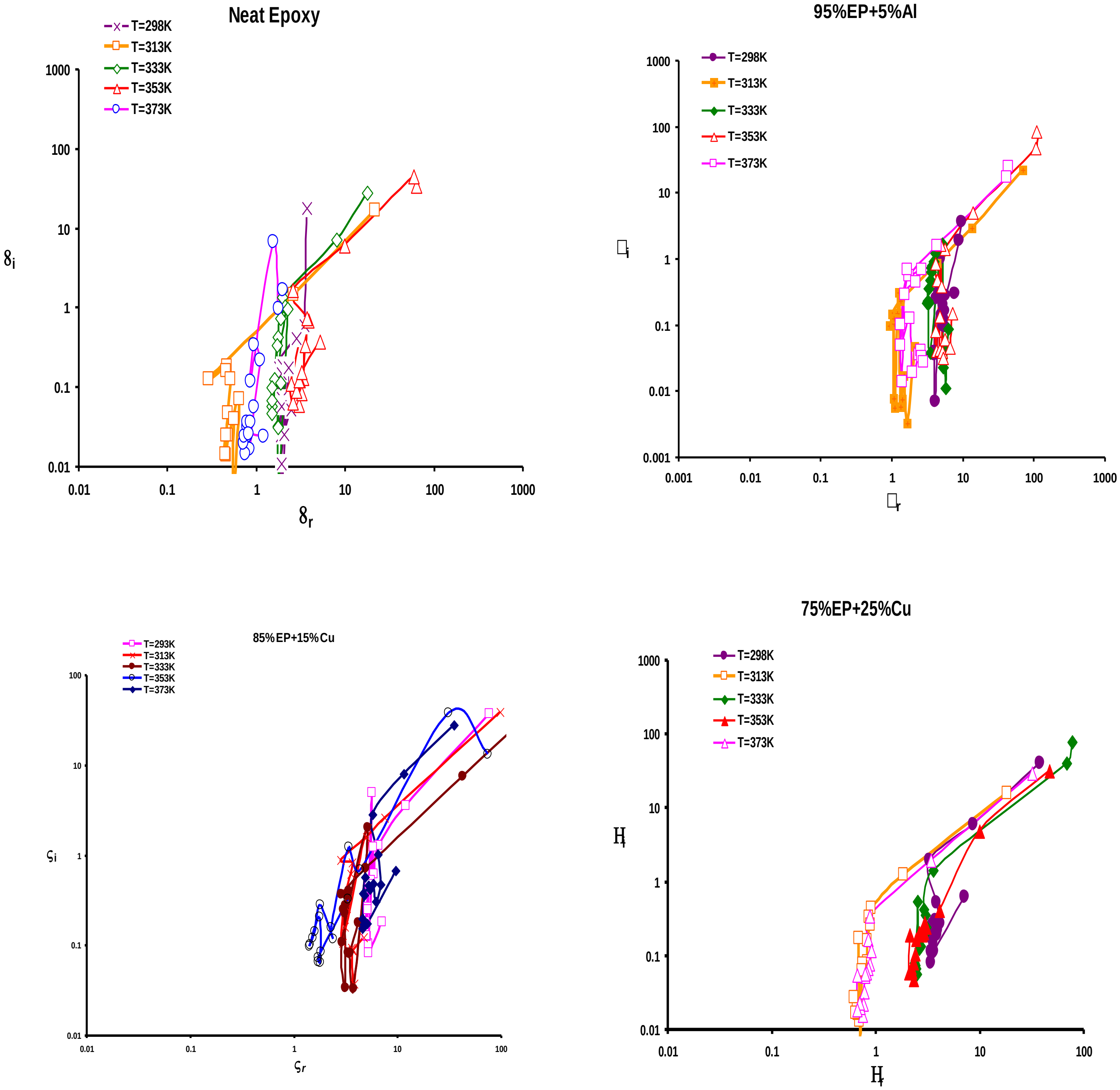

Figure 15. Cole – Cole diagrams of Ep/ Cu composites with different Cu content at different temperatures

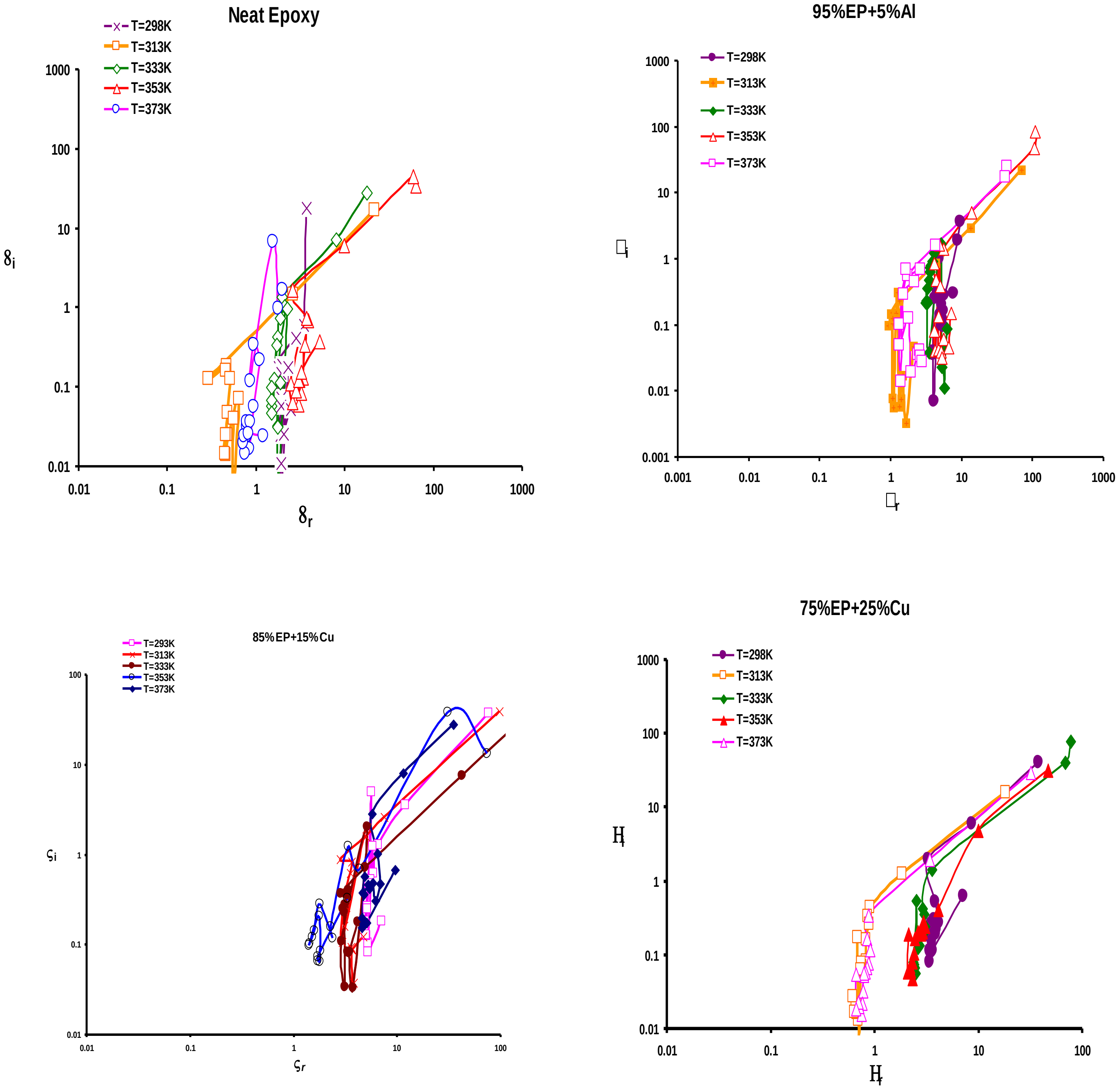

Figure 15: Cole – Cole diagrams of Ep/ Cu composites with different Cu content at different temperatures

4. Conclusions

A.C conductivity of (EP/Cu, Al) composites with different content have been conducted and several significant results have emerged from this study:-

1-The elimination of agglomerates surrounded by insulating matrix and the formation of a fine network led to enhanced dielectric properties of the composites.

2- A.C conductivity of (EP/Cu, Al) composites varied with Cu and Al contents and frequency accordingly, the dielectric properties of the composites could be tailored by the loading level.

3-The values of (εr) and (εi) clearly affected by the increasing of Cu and Al content.

4-s factor increases with the increasing of Cu and Al ratio in the composites samples but decrease with temperature.

5-The conductivity of (EP/Cu)composites exceed that of(EP/Al)composites samples consequently the activation energies of the former are lower than the later.

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