The Role of PU Ratio on the Dielectric Properties of EP /PU Blends

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Abstract. Electrical A.C conductivity Epoxy/polyurethane EP/PU blends with different blend ratio were synthesized and characterized. A.C conductivity measurements of EP/PU blends were studied in the frequency and temperature ranges (4x10^4Hz) and (293-373K) respectively. Effect of PU loading levels and temperature on dielectric properties was investigated. The EP/PU blends were diagnosed using FTIR. The results showed that AC conductivity $\sigma_{A.C}$ to be proportionate to $\omega$. The behavior of the exponent s explained in terms of the correlated barrier hopping and small polaron models. The value of dielectric constant 29723 and dielectric loss 705 of neat epoxy were exhibit to decrease with frequency and increase with temperature. The dependence of activation energy and conduction behavior on the blend ratio also studied. The results showed that the estimated activation energy varied with PU content. The polarizability ($\alpha$) decreases with increase of PU content and temperature which refer to weaken the intermolecular forces. The addition of PU to EP was responsible about the increase of charge carriers.

Keywords: A.C conductivity, Dielectric properties, EP/PU Polymer blends, Universal power law, Dielectric loss.

1. Introduction
There is progressive increase of tendency to combine physical properties of molecular materials science, such as magnetism and electrical conductivity in a synergistic way in order to produce materials of high technical interest [1,2]. In recent years, the DC electrical properties of different organic and inorganic materials were extensively investigated, but relatively little work done on their AC electrical properties [3-6]. Information on the conduction process involved in the material can be provided from D.C measurements [7]. By varying the type of the electrode metal, the applied electric field strength, and the operating temperature it is possible to estimate whether the process is electrode or bulk limited. Measurements of AC conductivity, however, provide information which can be used to determine which of the three main conduction models applicable to organic and inorganic materials, namely the hopping model, the variable hopping model, and band theory [5], is operative in the system under study. The present study, we have therefore studied the AC conductivity and dielectric properties of epoxy/polyurethane (EP/PU) blends in order to determine the effect of blend ratio on mechanism responsible for the conductivity of this system.

2. Samples Preparation and Procedure
Epoxy resin (EP), type (Thortex) with hardener Isophorone diamine(IPD), supplied by (Thortex Division of E.Wood Ltd.) ,and thermoset Polyurethane resin( PU), type (Swiss Chem.) with hardener
Isocyanate (HYG), supplied by (Swiss Chem. Company Ltd.) were used to prepare the samples of this work. An proper amount of special hardener was added to the epoxy resin with weight ratio of resin to hardener (2:1) by using a sensitive electronic balance of sensitivity (0.01 gm). The epoxy/polyurethane blends were prepared with (weight%/weight%) ratios for both polymers. Blends were synthesized by simultaneous mixing of both constituents with suitable mixing ratios of resin to hardener for both polymers (for epoxy 2:1 and for polyurethane 7:1). The content was mixed by a fan type stirrer before casting it as a sheets (of dimensions 25x20cm²) 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 353°K. The blend samples were prepared with the following ratios: 100%EP, 95%EP+5%PU, 90%EP+10%PU, 85%EP+15%PU, 80%EP+20%PU, 75%EP+25%PU and 70%EP+30%PU.

Fourier transform infrared spectroscopy (FTIR) was measured in the wavenumber range (4000-400) cm⁻¹ on a Perkin-Elmer 1710 spectrophotometer using KBr pellets at room temperature.

A.C measurements were performed under certain conditions as follows:

1. The frequency range concerned in this work was 10⁻² - 4x10⁴ 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.

Aluminum electrodes with thickness 2000°A were deposited on each adjacent surfaces of samples using thermal evaporation method under pressure of 10⁻⁵ mbar using coating unit type Edward. 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 (R), total capacitance (C) and dissipation factor tanδ with an accuracy of 0.1%. A. C. conductivity has been evaluated from dielectric data in accordance with the relation, σAC is the A.C conductivity given by the relation:

\[ \sigma_{AC} = \frac{I}{R \cdot A} \] (1)

Where: t is thickness of film, R is resistance of film, A is effective area for capacitance.

The dielectric constants (\(\varepsilon_1, \varepsilon_2\)) can be calculated using the following relations:

\[ \varepsilon_1 = \frac{C \cdot t}{\varepsilon_0 \cdot A} \] (2)

where: C is capacitance, \(\varepsilon_0\) is the permittivity of free space =8.854x10⁻¹⁴ (F/cm).

\[ \varepsilon_2 = \frac{\sigma_{AC}}{\omega \varepsilon_0} \] (3),

where \(\omega\) is angular frequency.

3. Results and discussion

3.1 FTIR Spectroscopy

The FTIR spectra of neat epoxy and epoxy / polyurethane blends were shown in Fig. 1. The spectrum of neat epoxy A, 3487cm⁻¹ (-OH) is one of the characteristic absorption peaks of epoxy resin, while the peak at 1296cm⁻¹ is the absorption band of the quaternary carbon atom in the epoxy. On the other hand peaks at 829cm⁻¹ and 916cm⁻¹ represent epoxy group. As PU introduced to the epoxy matrix, the typical absorption peaks of at 3286cm⁻¹ (N-H), 2875cm⁻¹ (CH₂ and CH₃), 1716cm⁻¹ (C=O), 1539cm⁻¹ (N-H), and 1107cm⁻¹ (C-O-C), of urethane polymer will come to appear in the blends curves. Additionally, the other typical absorption bands at 1668cm⁻¹ (C=O), 1454cm⁻¹ (=CH) referred that C=O bonds incorporated in the polyurethane chains. It evidence that the intensity of absorption peak at 2300cm⁻¹ (-NCO) will be decreases, and it confirms the good degree of reaction of the -NCO group. Compared with pure epoxy spectra, the absence of the absorption peaks at 3487cm⁻¹, 829cm⁻¹ and 916cm⁻¹ implied that the -OH group and the epoxy groups of epoxy resin had already been reacted with -NCO group. The existence of the peak of the quaternary carbon atom at 1300cm⁻¹ confirms that epoxy group had been grafted in polyurethane chain. As it is shown in Figure 6, the intensity of the characteristic band of C=O stretching vibration at 1736 cm⁻¹ increases with the
increase of PU content. This explained the enhancement of conductivity as PU content will be raised in the blends samples. It was pointed out that the viscosity of PU increased with the increasing of -COOH content. Since as -COOH content increased, the content of carboxylate anions in the polyurethane chains raised, and intermolecular interaction increased accordingly. The movement of polyurethane chains will be hindered. Hence, the viscosity of PU increased. The previous researchers showed that there is direct relation between the viscosity and epoxy content. It can be observed the intermolecular interaction force of polyurethane chains decreases obviously with reducing epoxy content, since little rigid benzene rings which were introduced into polyurethane chains, which caused the reducing steric hindrance effects. As a result of viscosity will be reduced and hence, the movement of polyurethane molecule chains was accelerated. On the other hand the previous results showed there is relationship between hardness and epoxy content, such as with increasing of PU content, the opaque of epoxy turned to be transparent. As a result, crosslinking structure may beworsted with the increase of PU content [8].

![Figure 1](Image)

**Figure.1** FTIR transmittance spectra for EP/PU Blends with different blend ratios.

### 3.2 A.C Conductivity

Dielectric properties of EP/PU blends with different blends ratio were investigated on samples with parallel plate capacitor configuration. Fig. 2 shows the variation of $\sigma_{AC}$ with angular frequency for EP/PU blends with different blends ratio and temperatures. The AC conductivity patterns for neat
Epoxy show frequency dependence in the hole frequency range. This behavior obeys the universal power law, \( \sigma(\omega) = \sigma_{d.c} + A\omega^s \), where \( \sigma_{d.c} \) is the dc conductivity (frequency independent plateau in the low frequency region). This behavior get to vanish with the introduction of PU to the EP matrix and the AC conductivity become frequency independent i.e. the frequency independent plateau of A.C conductivity become the dominated behavior in the hole frequency range. The A.C electrical conductivity \( \sigma_{A.C} \) increases with the increase of frequency and temperatures for neat epoxy. Indeed \( \sigma_{A.C} \) at \( F=100\text{Hz} \) for EP and 95/5 EP/PU samples increases from \( 7.5 \times 10^{-11} \) to \( 3.17 \times 10^{-9} \) and to \( 9.21 \times 10^{-10} \) (ohm.cm)\(^{-1} \) with the increase of frequency from \( 100 \) to \( 4 \times 10^4 \) Hz and temperature from 293 to 373K respectively. A.C electrical conductivity \( \sigma_{A.C} \) showed significant increase with temperatures for 90/10, 85/15 EP/PU blends samples where \( \sigma_{A.C} \) increases three and two ordered of magnitude while residual blends samples showed temperature independent relation and remain nearly constant with the increase of temperatures. Moreover \( \sigma_{A.C} \) of the mentioned samples increases from \( 1.47 \times 10^{-8} \) (ohm.cm)\(^{-1} \) to \( 5.05 \times 10^{-5} \) (ohm.cm)\(^{-1} \) and from \( 2.58 \times 10^{-9}(\text{ohm. cm})^{-1} \) to \( 1.38 \times 10^{-6} \) (ohm.cm)\(^{-1} \). The exponent \( s \) was calculated from the equation \( s = \frac{d}{d\ln\omega} \) and illustrate in Tables.1. It obvious that \( s \) decreases with the increase of blend ratio, indeed \( s \) decreases from 0.85 to 0.13 when PU increase from 0 to 30%. While \( s \) exhibits to change in nonsystematic manner with the increase of temperature i.e. increases in the first stage and then decreases with further increases of temperature, indeed \( s \) for 85/15 EP/PU increases from 0.13 to 0.36 when \( T \) increase from 293 to 313 K and then return to decrease to 0.047. The most suitable models to explain our results are small polaron S.P and correlated barrier hopping(CBH)models.

The activation energy for conduction \( E_{ac} \) in the temperature range (293-373K) obtained from the plot of \( \ln\sigma_{A.C} \) with reciprocal temperature at definite frequency fitting different regions with the equation \( \sigma = \sigma_{d.c} e^{-E_{ac}/k_BT} \). The activation energy is found to reduce with increase of PU content in the blend samples in the first stage and then get to increase with further increase of PU content in the blends samples, the calculated activation energy are illustrated in table(2). Indeed \( E_{ac} \) decreases from 0.201 to 0.175eV when PU content increases from 0 to 10%. This can be possible due to the increase of charge carriers and enhances the electrical conductivity.
Figure 2. Relation between $\ln \sigma_A$ and $\ln (\omega)$ for EP/PU Blends with different blend ratios and different temperatures.
Table 1. The values of exponent $s$ and $\alpha$ for EP/PU blends

| The Blend ratio % | Temperature (K) | $s$   | $\alpha$ |
|-------------------|----------------|-------|----------|
| 100EP             | 293            | 0.85  | -        |
|                   | 313            | 0.58  | -        |
|                   | 333            | 0.81  | -        |
|                   | 353            | 0.73  | -        |
|                   | 373            | 0.59  | -        |
| 95EP+5PU          | 293            | 0.48  | -        |
|                   | 313            | 0.54  | -        |
|                   | 333            | 0.87  | -        |
|                   | 353            | 0.48  | -        |
|                   | 373            | 0.43  | -        |
| 90EP+10PU         | 293            | 0.065 | -        |
|                   | 313            | 0.16  | -        |
|                   | 333            | 0.10  | -        |
|                   | 353            | 0.04  | -        |
|                   | 373            | 0.43  | -        |
| 85EP+15PU         | 293            | 0.13  | 0.1555   |
|                   | 313            | 0.36  | 0.1555   |
|                   | 333            | 0.0028| 0.1333   |
|                   | 353            | 0.038 | 0.1333   |
|                   | 373            | 0.047 | 0.1111   |
| 80EP+20PU         | 293            | 0.025 | 0.1111   |
|                   | 313            | 0.15  | 0.1111   |
|                   | 333            | 0.041 | 0.2222   |
|                   | 353            | 0.35  | 0.0666   |
|                   | 373            | 0.15  | 0.0222   |
| 75EP+25PU         | 293            | 0.10  | 0.0222   |
|                   | 313            | 0.17  | 0.1111   |
|                   | 333            | 0.10  | 0.1333   |
|                   | 353            | 0.13  | 0.0666   |
|                   | 373            | 0.12  | 0.1111   |
| 70EP+30PU         | 293            | 0.13  | 0.3333   |
|                   | 313            | 0.36  | 0.3333   |
|                   | 333            | 0.0028| 0.0222   |
|                   | 353            | 0.38  | 0.2222   |
|                   | 373            | 0.047 | 0.2222   |
3.3 The Dielectric Constants

The angular frequency dependence of \((\varepsilon_1)\) for EP/PU blends at different PU content in the temperature range (293-373K) is plotted in Fig.3. The frequency dependence of permittivity which obvious in the low frequency region and followed by a nearly frequency independent behavior above 1 kHz is clearly observed in the spectra of neat epoxy but is found to vanish in the spectra of 95/5, 90/10 and 85/15 EP/PU blends samples and then return to appear for residual blends samples. The reduction of \((\varepsilon_1)\) with increase in frequency ascribed 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. The data showed that \((\varepsilon_1)\) exhibit to increase with the increase of PU content in the first and then decreases with continues addition of PU, indeed \((\varepsilon_1)\) increases from 539 to 15759 when PU increases from 0 to 10%.

The loading of PU may lead in more localization of charge carriers along with mobile ions causing higher conductivity. This may be the reason for higher \((\varepsilon_1)\) and strong low frequency dispersion samples with high PU content which show temperature independent behavior. On the other side the dielectric constant exhibit to change in different manner with temperature, i.e. decreases or increases with temperature, indeed \(\varepsilon_1\) for 90/10 EP/PU increases from 15759 to 991628 when temperature increases from 293 to 333 K and then decreases to 519540 when temperature increases 373 K. Fig.4 show the frequency dependence of \((\varepsilon_2)\) for EP/PU blends with different blend ratios and temperatures in the range (293-373K) respectively. The spectra of some samples characterizes by peak appearing at a definite frequency proposed the presence of relaxing in all the samples. The strength and frequency of relaxation depend on relaxation type. The relaxation peaks get to vanish at high temperature and especially for samples rich with PU. The addition of PU is believed that there is an increase in the free charge carriers in the materials. The small mobile elements PU speed up the segmental motion. Better transport properties on composites can be achived by the relatively fast segmental motion, but with further increase of PU content results in the reduction of the mobility of free charge which in turns reducing \(\sigma_{AC}\) and \(\varepsilon_2\).

More addition of PU to EP results in overall increase of \((\varepsilon_1)\) and \((\varepsilon_2)\) due to free charge contributions. So the increase of the molecular mobility is reflected both by increasing of free charge mobility. The enhancement of conductivity take place with increase of loading with PU up to 10% , but then the opposite case take place.

### Table 2. The values \(E_{ac}\) EP/PU blends.

| Blend ratio                  | \(E_{ac}\) (eV) | Temp. Range K |
|------------------------------|-----------------|---------------|
| 100 EP                       | 0.201816        | 293-373       |
| 95% EP + 5% PU               | 0.194942        | 293-373       |
| 90% EP + 10% PU              | 0.175588        | 293-373       |
| 85% EP + 15% PU              | 0.193536        | 293-373       |
| 80% EP + 20% PU              | 0.17946         | 293-373       |
| 75% EP + 25% PU              | 0.180064        | 293-373       |
| 70% EP + 30% PU              | 0.18737         | 293-373       |
Figure 3. Variation of $\varepsilon_1$ with $\text{Ln}(\omega)$ for EP/PU Blends with different blend ratios and different temperatures.
Figure 4. Variation of $\varepsilon_2$ with Ln($\omega$) for EP/PU Blends with different blend ratios and different temperatures.

3.4 Cole-Cole diagrams
The existence of multi-relaxation time in EP/PU blends is obtained by plotting Cole-Cole diagrams as shown in Fig.5 for different blends ratio. It is clearly obvious from arc of circles having their centers lying below the absicca axis for all samples. This proves the existence of distribution of ($\tau$) in
the samples, polarizability (α) had been determined by determining the angles (απ/2) the values of the polarizability and are listed in Table 1. The values of (α) shows non regular variation with the increase of PU content (i.e. increases and decreases with loading of PU), indeed α decreases with the addition of PU and then increases, moreover (α) decreases from 0.155 to 0.022 when PU content increases from 15 to 25% and then increase to 0.333 when PU ratio increases to 30%, the reduction of (α) with the increase of PU content results from strength of the forces of the intermolecular while the increase of(α) is related with the weaken of intermolecular forces[11,12], on the other side (α) tends to increase with the increase of temperature which results from the weaken the forces.

Figure 5. Cole – Cole diagrams for EP/PU Blends with different blend ratios and different temperatures.
4. Conclusions
A.C conductivity of EP/PU blends with different blend ratios was studied and the following results can be deduced:

The A.C conductivity for EP/PU blends changed with blends ratio and accordingly with frequency, the dielectric properties of the blends can be modified by the loading level of PU. The values of $(\varepsilon_1)$ and $(\varepsilon_2)$ changed with the EP/PU blend ratios. The exponents increase with the increasing of loading level of PU but decrease with temperature. Loading EP with PU enhanced the conductivity (EP/PU) blends. The enhancement of stretching band of the epoxy matrix lead to enhanced dielectric properties of the blends.

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