

A.C Conductivity of (PS-PC) Blends Films **التوصيلية الكهربائية المتناوبة لأغشية الخلطات** **(PS-PC)**

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Abstract:

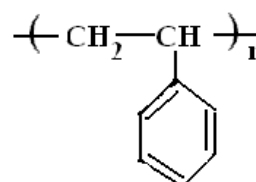
Measurements of A.C conductivity of Polystyrene and Polycarbonate (PS-PC) blends over frequency range (10^2 - 10^6 Hz) and temperature range (293-473K) shows that the A.C conductivity follows the empirical formula $\sigma_{a.c}(w)=Aw^s$, where (s) lies between (0.45880-0.6317), the $\sigma_{a.c}(w)$ declared exponentially dependence on the reciprocal of absolute temperature for all samples. The activation energies (E_{ac}) of blends samples were lower than those of pure PS and PC samples. The results were interpreted that the resistivity difference accompanied the PC addition to PS.

ملخص

أظهرت قياسات التوصيلية الكهربائية المتناوبة $\sigma_{a.c}(w)$ لأغشية الخلطات (PS-PC) في مدى درجات الحرارة (293-473)K وفي مدى التردد (10^2 - 10^6 Hz) إن التوصيلية المتناوبة تخضع للعلاقة $\sigma_{a.c}(w)=Aw^s$, حيث الثابت الأسّي يقع ضمن المدى (0.4588-0.6317) إذ إن التوصيلية الكهربائية المتناوبة أظهرت اعتماداً أسّي على مقلوب درجة الحرارة لجميع العينات وأن طاقات التنشيط (E_{ac}) لخلطات الأغشية للنماذج المحضرة كانت أقل من تلك للنماذج النقية من PS و PC. فسرت النتائج على الأختلاف في قيم المقاومة والذي يرافق إضافة PC إلى PS.

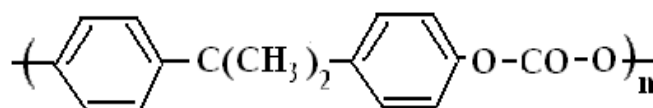
Introduction:

Polystyrene with molecular structure :



Where n is the degree of polymerization and can be as high as 6000 , while the molecular mass of styrene is approximately equal 104 ,the molecular weight of polystyrene amount to 624000 . the melting point is (-33°C) and the softening temperature varies between 70 and 85°C .

Polycarbonate with molecular structure:



is a transparent material with high impact resistance , high stiffness , good dimension stability and good electrical properties [1].

Thermosets like PS and PC are network polymers that are heavily cross- linked to give a dense three –dimensional network. They are normally rigid .They cannot melt on heating and they decompose if the temperature is high enough. The term is now used to describe this type of material even when heat is not required for the cross-linking to take place [2,3,4].

Two or more existing polymers may be blended for various reasons . One reason is a combination of the properties of the constituents , e.g. a blend of two polymers , one of which is chemically resistant and the other tough , or to save costs by blending a high – performance polymer with a cheaper material. A very important use of blending is the combination of an elastomer with a rigid polymer in order to reduce the brittleness of the rigid polymer. Therefore, the blending of polymers are excellent methods for modification and improvement of polymer properties. If the molecules have similar sizes , each type of molecule is then surrounded , on average , by molecules of the two types in proportion to the component ratio of the two polymers in the mixture [5].

Polymers can be divided into two broad classes , amorphous and semi crystalline. If observation are made at a fixed frequency . Crystalline polymers often exhibit three major transitions as the temperature is reduced usually α , β , and γ in decreasing order of temperature, whereas amorphous polymers generally exhibit two major transitions labelled α and β in decreasing order of temperature. If the relaxation are seen at lower temperatures , they are labeled γ and δ respectively. For an amorphous polymer the transition at high temperature labeled α always corresponds to glass transition temperature , whereas for polymers of low crystallinity it is often the transition labeled β that corresponds to the glass transition .

A real amorphous polymer usually exhibits more than one transition .As indicated above , there is a high temperature transition , usually labeled α or α_a (i.e. at amorphous state) , which is the glass transition and corresponds to the onset of main chain segmental motion , and secondary transitions at lower temperatures, these are assigned to various types of motion , such as motion of side groups , restricted, motion of the main chain or motions of end groups . The secondary relaxation often show up more clearly in the loss modulus or $\tan \delta$. The behavior of shear modulus (G_1) and $\tan \delta$ of PS can be distinguishes four transitions labeled α , β , γ , and δ , the stronger α transition , the glass transition, while β transition is due to co-operative restricted oscillation involving both the main chain and the phenyl ring , γ transition is associated with 180° ring flips.

Rotational jumps not involving translations are observed in many polymers including amorphous polymers such as polycarbonate PC .Ring flips have been seen in polystyrene PS[3].

This research come from point of view that the ac conductivity measurements are complementary to the d.c measurements since the last is not able to detect the presence of internal barrier nor the probe the bulk material behind them thus the a.c measurements provide information on the polarization behavior under the influence of the electric field. In this paper the real (ϵ_1) and imaginary part (ϵ_2) of dielectric constant for(PS-PC) blends films with various polycarbonate content were measured ,the relation between them were discussed .An attempt had also made to interpret the results in terms of Maxwell- Wagner model. Cole-Cole diagrams were plotted and used to estimate the values of polaizability (α)or distribution parameter and the relaxation time(τ).

Basic Considerations

Information about the nature of the conduction mechanism in a material can be obtained from a.c conductivity. In these experiments the electrical conductivity is measured as a function of the frequency (ω) where $\omega = 2\pi f$ is the angular frequency and f is the frequency of an alternating electric field The total conductivity σ_{tot} at a certain frequency and temperature is defined as:

$$\sigma_{tot} = \sigma_{a.c}(\omega) + \sigma_{d.c} \quad (1)$$

where $\sigma_{d.c}$ is the D.C conductivity which depends strongly on temperature and dominate at low frequencies, while $\sigma_{a.c}$ is the A.C. conductivity which is weaker temperature dependence than $\sigma_{d.c}$ and dominate at high frequency and nondependent temperature then, the empirical relation of frequency dependence on a.c conductivity ($\sigma_{a.s}(w)$)has been observed in many amorphous semiconductors and insulators both inorganic and polymeric material has the form:

$$\sigma_{a.c}(\omega) \propto \omega^s \quad (2)$$

$$\sigma_{a.c}(\omega) = A_1 \omega^s \quad (3)$$

where: A_1 is constant ,then we can re-write the eq. (1) as follows:

$$\sigma_{tot}(\omega) = A_1 \omega^s + \sigma_{d.c} \quad (4)$$

and (s) is a function of frequency and is determined from the slope of a plot $\ln \sigma_{a.c}(\omega)$ versus $\ln(\omega)$ then [6] :

$$s = \frac{d[\ln \sigma_{a.c}(\omega)]}{d[\ln(\omega)]} \quad \text{-----} \quad (5)$$

And because of the presence of logarithmic term then s is not constant, usually $0 < s < 1$ and approaching unity at low temperature and decreasing to 0.5 or less at high temperature .

For non metallic materials the A.C. electrical conductivity depends on the temperature (T) according to the Arrhenius equation [7]-

$$\sigma_{a.c}(\omega) = \sigma_0 \exp(-E_{a.c}/k_B T). \quad (5)$$

The mechanisms of a.c conductivity ($\sigma_{ac}(\omega)$) gives information about the nature of the polarization mechanisms in dielectric also provide information about the electrodes capacitance interface and amount electronic conductivity present

Indeed, so wide spread is this phenomenon that appears to be a common feature of the amorphous non metallic state. This phenomenon has variously been ascribed to relaxation processes caused by the motion of electrons or ions, hopping or tunneling between equilibrium states. Measurements over the wide frequency range the a.c conductivity generally followed from the equation(3) , for rather wide range of frequency.

The a.c conductivity (σ_{ac}) can be calculated using the following relation:

$$\sigma = \frac{t}{R.A} \quad (6)$$

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

The dielectric constants (ϵ_1, ϵ_2) can be calculated using the following relations:

$$\epsilon_1 = C.t / \epsilon_0 .A \quad (7)$$

where C is Capacitance, ϵ_0 is the Permittivity of free space $= 8.854 \times 10^{-14}$ (F/cm).

$$\epsilon_2 = t/w \epsilon_0 R A = \sigma_{ac} / w \epsilon_0 \quad (8)$$

There are three mechanisms of charge transport can contribute the frequency dependent a.c conductivity ($\sigma_{a.c}(\omega)$) as follows:

a- Transport by excited carriers to the extended state near conduction or valence bands, $\sigma_{a.c}(\omega)$ are given by

$$\sigma_{a.c}(\omega) = \sigma_0 / (1 + \omega^2 \tau) \quad (9)$$

where $\sigma_0 = ne^2 \tau / m^*$

m^* is the electron effective mass, n is the carrier density and e is the electron charge.

b- Transport by carriers excited into localized states at the edges of the valence or conduction bands. A $\sigma_{a.c}(\omega)$ follows the formula.

$$\sigma_{ac} = \text{const} \omega [\ln\{\frac{1}{\omega \tau}\}]^4 \quad (10)$$

where $\omega < 1/\tau$.

c- Hopping transport by carriers with energies near the Fermi level, according to this mechanism the $\sigma_{a.c}(\omega)$ given by:

$$\sigma_{a.c}(\omega) = 1/3 \pi e^2 k_B T [N(E_F)]^2 \bar{\alpha}^{-5} \omega [1n(1/\omega \tau)]^4 \quad (11)$$

where, $N(E_F)$ is the density of state near Fermi level and $\bar{\alpha}$ is the decay factor $\bar{\alpha}^{-1} = r_p$ is polaron radius.

Many different theories for a.c conduction have been proposed in the past. It is commonly assumed that the dielectric loss occurs because the carrier motion is considered to be localized within pairs of sets. Two distinct processes have been proposed for interpretation these relaxation mechanisms, namely quantum mechanical tunneling (QMT), in this process the a.c conductivity is linearly dependent on temperature and the exponent s is frequency dependent, which it is independent on temperature.

The second process is called correlated barrier hopping (CBH) when the electrons hop over the potential barrier between two sites, the a.c conductivity is due to hopping between defect states or dangling bonds ($D^+ D^-$). In CBH the $\sigma_{a.c}(\omega)$ is exponentially dependent on temperature, and exponent s approaches unity when the temperature approaches zero[8].

Experiment Procedure:

Samples Preparation:

Polystyrene PS and polycarbonate PC were supplied from Alamo polymer Corp. and Saudi basic Indust. Corp. respectively. Casting method was achieved to obtain blends films of PS and PC with different ratios:

(100%PS, 75%PS+ 25 %PC, 50%PS+50%PC, 25%PS+75%PC, and 100%PC) The mixing of polymers grains according to the weight ratios were dissolved in (10ml) of hexane to give solutions of 6% wt/vol.. The solution were shaken to achieve a homogenous content, (3ml) of this solution was transferred into clean Petri dish of 20 cm in diameter and put in an oven of temperature (50°C) for 2 hours and left to cool slowly to room temperature. The average thickness of the prepared films was measured in the range (0.4-0.49)mm using digital micrometer. The prepared films were kept in a desiccators in order to be moisture free.

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 $2000^\circ\text{\AA}$ 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). 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_T), total capacitance (C_T) and dissipation factor $\tan\delta$ with an accuracy of 0.1%. All measurements were performed in the frequency range $10^2 - 10^6$ Hz and temperature range (293- 363)K, the temperature was changed by constant rate of 2K/min, A constant voltage of (1V) was applied in all frequency range and temperature.

Results and Discussion:

The exponential factor (s) were obtained from the plotting of $\ln(\sigma(\omega))$ versus $\ln(\omega)$ for (PS-PC) blends as shown in Fig.(1), the values of (s) were listed in Table (1). It is clear that (s) values less than unity which confirmed the hopping mechanism. It is evident that addition of PC to PS increases the conductivity of the later i.e. increases the charge carriers, on the other hand Table (2) declares the values of exponents as function of temperatures for pure PS and PC and blends (PS-PC) with different compositions. It is obvious that s value for pure PS and PC decreases with temperature while s increases with temperature for blends samples. To explain our results we

suggests Correlated Barrier Hopping(CBH)model for pure samples, while small polaron (SP) model is convenient for blends samples , Small Polaron Tunneling (SP)is the most suitable when the exponent s get to rise with increasing of temperature, this occurs when addition of charge carrier to the covalent solid causes a large degree of local lattice distortion, which form small polaron ,.

The variation of $\sigma_t(w)$ versus temperature (T)for (PS-PC) blends with different PC ratios at (10^3 Hz) was shown in Fig. (2). All specimens shows that $\sigma_t(w)$ increases exponentially with increase (T) which is constituent Arrhenius equation ,this is explained by the increase of charge carriers, The values of A.C activation energy E_{ac} for(PS-PC) blends with different PC ratios were determined from the plot of $\ln\sigma_t(w)$ against the reciprocal absolute temperature which is shown if Fig.(3),it is clear that pure sample revealed one conduction mechanism i.e. one activation energy E_{ac} , in contrast to that of blends samples which declare two conduction mechanisms or two activation energies E_{ac1} and E_{ac2} .It is obvious that E_{ac} values of blends samples were less than these of pure one , although E_{ac} values of pure PS exceeded that of PC, this attributed to the fact that resistivity of PS is higher than that of PC. The most significant result was the activation energy value showed a drastic decrease with the addition of PC to PS ,moreover the values of (E_{ac1}) decreased from (1.061 to 0.083) eV when PC content increased from (0 to 25%) as shown in Table (3).

Fig.(4 and 5) show plotting the curves of ($\log \epsilon_1$) versus ($\log w$) and ($\log \epsilon_2$)versus ($\log w$) .Deby's of intrinsic relaxation equations predict that these curves must be symmetrical around w_D ,where the angular frequency w_D corresponds to maximum absorption (according to the equation $w_D=1/\tau$ where (τ) represent the most probable value of a spread of relaxation times . The two components of the dielectric constant ϵ_1, ϵ_2 give the physical meaning of the dissipation factor $\tan\delta$ which is the (energy dissipated per cycle /energy stored per cycle .

The dielectric constant ϵ_1 of (PS-PC) with different ratios (0,25,50,75, and 100 wt.%) were measured within the employed frequency range(10^2 - 10^6 Hz),from the spectrum of ($\log \epsilon_1$) versus ($\log w$) it is obvious that ϵ_1 tends to increase with increase PC content in the blend samples while it decreased with increase frequency to reach lower values this ascribed to the fact that electrode blocking layer is dominated thus the dielectric behavior is affected by the electrode polarization, while at high frequency the dielectric signal is not affected by electrode polarization ,moreover (at frequency = 10^2 Hz) ϵ_1 increased from (8.935 to 60.338) when PC content increased from (0 to 25 wt.%), however ϵ_1 decreased from 60.338 to 44.908 with further addition of PC. The increase of ϵ_1 with PC content ascribed to the increase of capacitance(direct relation according to equation (7)). Fig.(5)shows the variation of (ϵ_2) with frequency for blends samples with different PP content, one can be seen the dielectric loss absorption bands appear within the frequency range employed for pure PS and blends with low ratios of PC ,thus the relaxation time were calculated as usual from frequencies corresponding to the loss maxima using equation $w_D=1/\tau$ and the values of τ were listed in Table (1). The w_{max} which is corresponding the peak is approximately equal the reciprocal macroscopic relaxation time ,moreover it is clear that the (ϵ_2) spectrums of PS and blends with low ratios of PC (i.e. from 0 to 25 wt.%) declared two relaxation peaks located at definite and different frequencies ranges ,but the relaxation peak belonged to the lower frequency range will disappear for blends samples with PC content increases from 50 to 100 wt.% while the another relaxation peak belonged to the high frequency range remains.

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 80°C , (2) a well pronounced. a β -peak at approximately 0°C , γ -peak in the temperature range -50 and -100°C . 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.

The reason of declaring more than one peak in the spectrum of ϵ_2 versus frequency is the foundation of multiphase in our blends samples (i.e. amorphous and crystalline phase of PS and PC respectively) and the disappearing of relaxation peak in the low frequency range confirms the dominating of one phase.

The most significant result is the location of the relaxation peaks did not affect strongly by the addition of PC which means that (τ) values independent upon the PC content (see Table(1)).

A direct evidence of the existence of multi-relaxation time in (PS-PC) films blends is obtaining by plotting Cole-Cole diagrams as shown in Figs(6 A,B,C, D and E). It has been observed that for all films reported here (ϵ_1) versus (ϵ_2) curves represent the arc of circles having their centers lying below the abscissa axis. This confirms the existence of distribution of (τ) in all films. By measuring the angles ($\alpha\pi/2$) the values of the polarizability (α) had been determined and were listed in Table(1). We can notice that the values of (α) shows a non systematic variation with the increase PC content, the decrease of (α) with the increase in PC results from rise of the forces of the intermolecular [9,10], while the increase of (α) value came from the weakened forces..

Conclusions:

A.C conductivity of (PS-PC) blends with different PC content have been conducted and several significant results have emerged from this study:-

- 1- A.C conductivity of (PS-PC) blends varied with PC contents and frequency.
- 2- The resistivity of pure samples exceeds the blends, i.e. blended PS with PC decrease the resistivity of the constituents
- 3- The values of (ϵ_1) and (ϵ_2) clearly affected by the increasing of PC content.
- 4- The relaxation peaks of the blends samples with low PC content (i.e. from 0 to 25 wt.%) distributed in the low and high frequency range while blends samples with high PC content (i.e. from 25 to 100 wt.%) declared relaxation peak in the high frequency range only.
- 5- PS and PC presents in different phases in the blends samples and the domination of any phase upon the other depend strongly on the content ratio of the constituents.

Table (1) Illustrates the values s , τ and α for (PS-PC) blends films.

The blends ratio %	(s)	τ (sec)	(α)
100PS	0.4588	5.031×10^{-4} 0.243×10^{-4}	0.3340
75PS+25PC	0.4847	9.951×10^{-4} 1.041×10^{-4}	0.1334
50PS+50PC	0.6317	5.140×10^{-3}	0.2445
25PS+75PC	0.4486	2.658×10^{-4}	0.1500
100PC	0.4927	2.478×10^{-4}	0.1112

Table (2) Illustrates the s values at different temperatures for (PS-PC) blends films.

The blends ratio%	T=293K	T=303K	T=313K	T=323K
100%PS	0.7706	1.1055	0.5351	0.4925
75%PS+25%PC	0.4847	0.4143	0.7143	0.7511
50%PS+50%PC	0.6317	0.6038	0.7599	1.2636
25%PS+75%PC	0.4486	0.5853	1.4454	1.0482
100%PC	0.4927	1.0355	0.8322	0.8385

Table (3) Illustrates the values E_{ac1} and E_{ac2} for (PS-PC) blends films.

The blends ratio %	E_{ac1}(eV)	Temp.Range(K)	E_{ac2}(eV)	Temp.Range(K)
100PS	1.0610	333-363	0.3788	293-333
75PS+25PC	0.0839	363-293	-	-
50PS+50PC	0.2497	363-293	-	-
25PS+75PC	0.2010	363-293	-	-
100PC	0.8080	333-363	0.1021	293-333

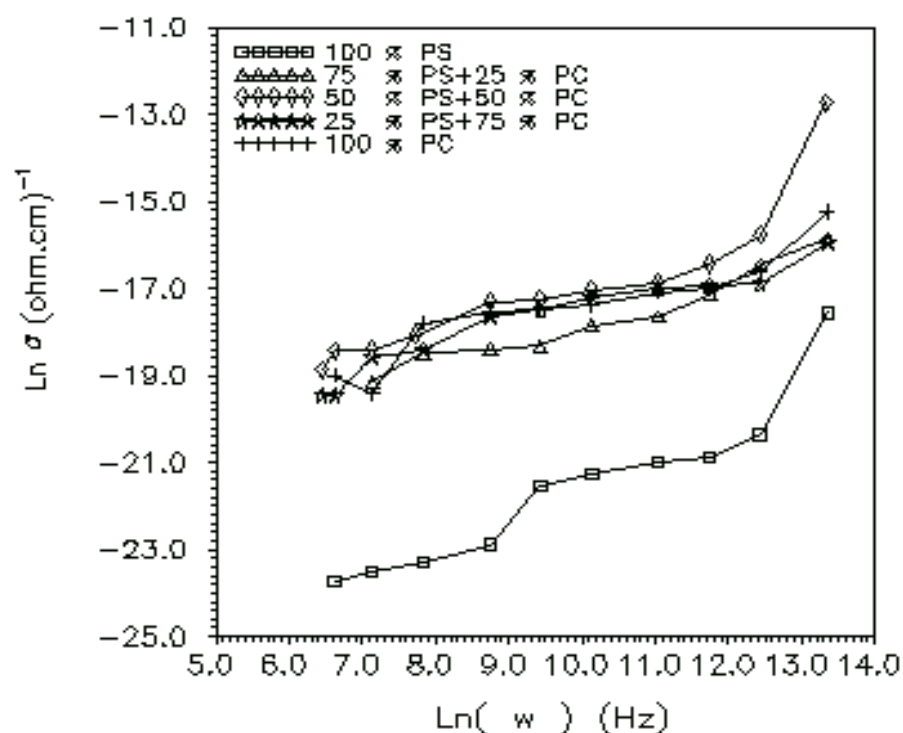


Fig.(1)The variation of $\ln \sigma_{a.c}(\omega)$ with $\ln(\omega)$ for (PS-PC) blends films.

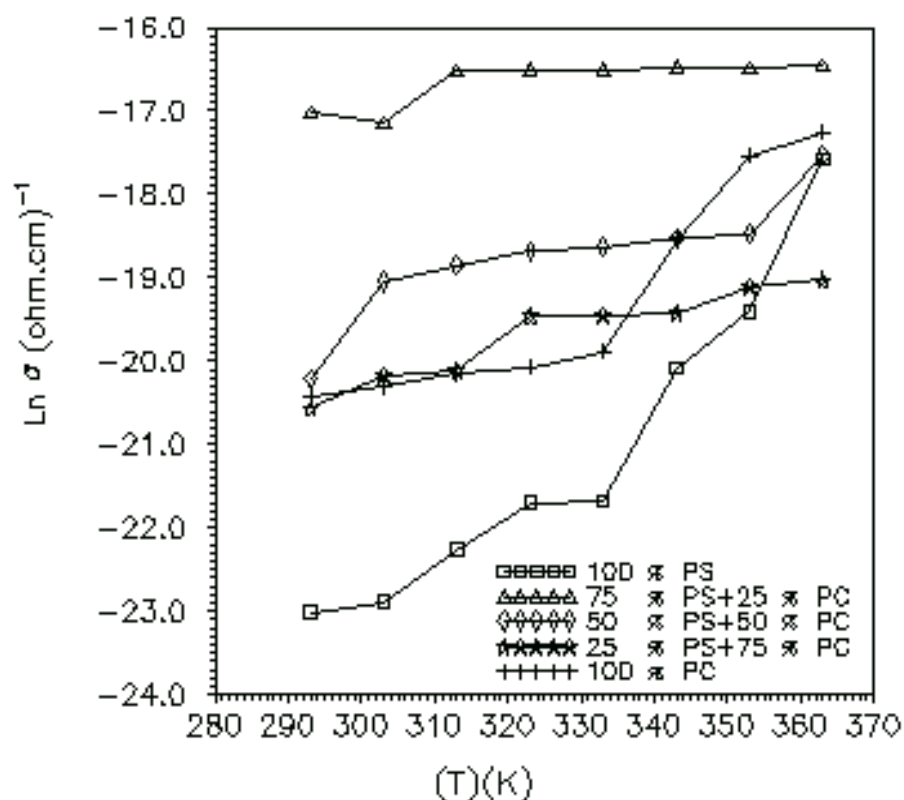


Fig.(2) (T) for (PS-PC) blends The variation of $\ln \sigma_{a.c}(\omega)$ with temperature films.

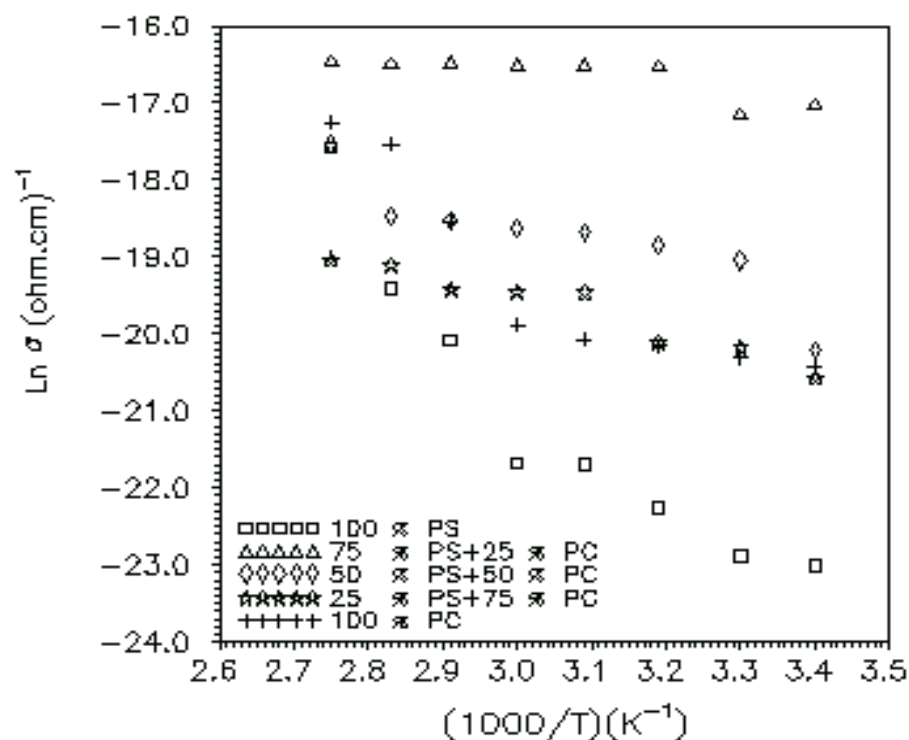


Fig.(3)The variation of $\ln \sigma_{a.c}(w)$ with reciprocal temperature($1/T$) for (PS- PC) blends films.

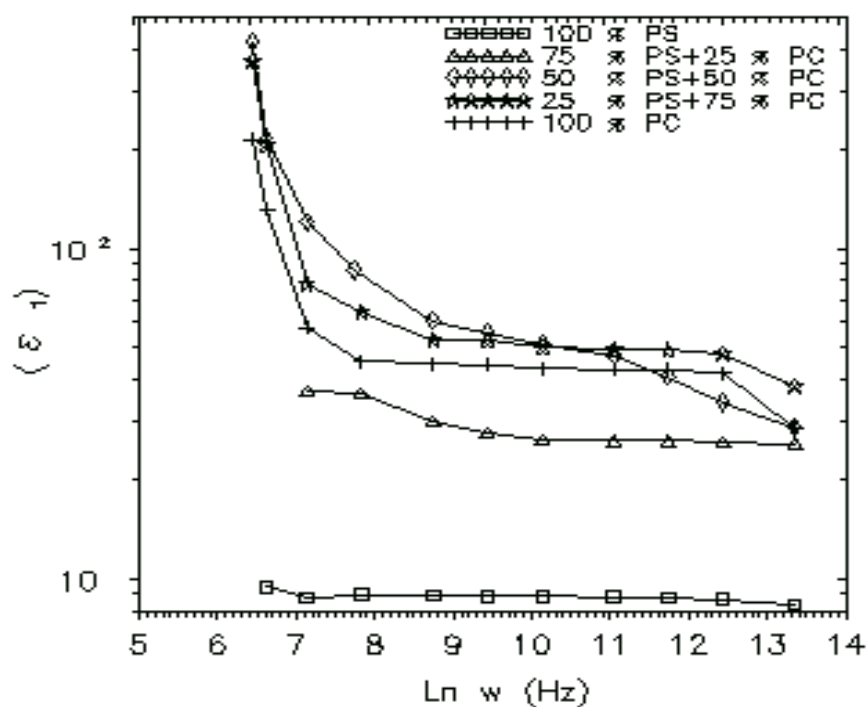


Fig.(4) The variation of $\log (\epsilon_1)$ with $\ln (w)$ for (PS-PC) blends films.

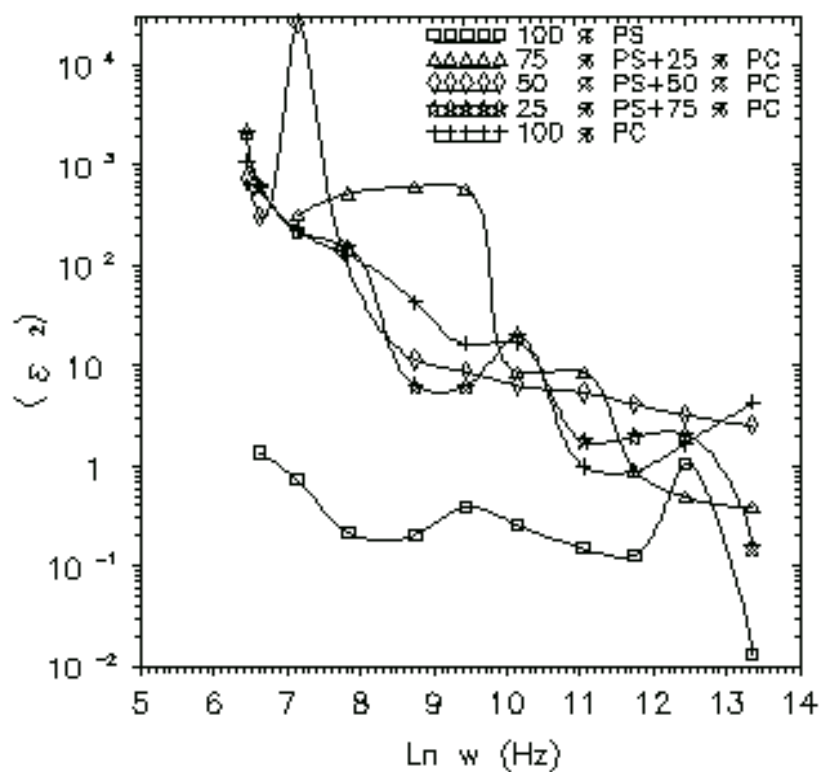
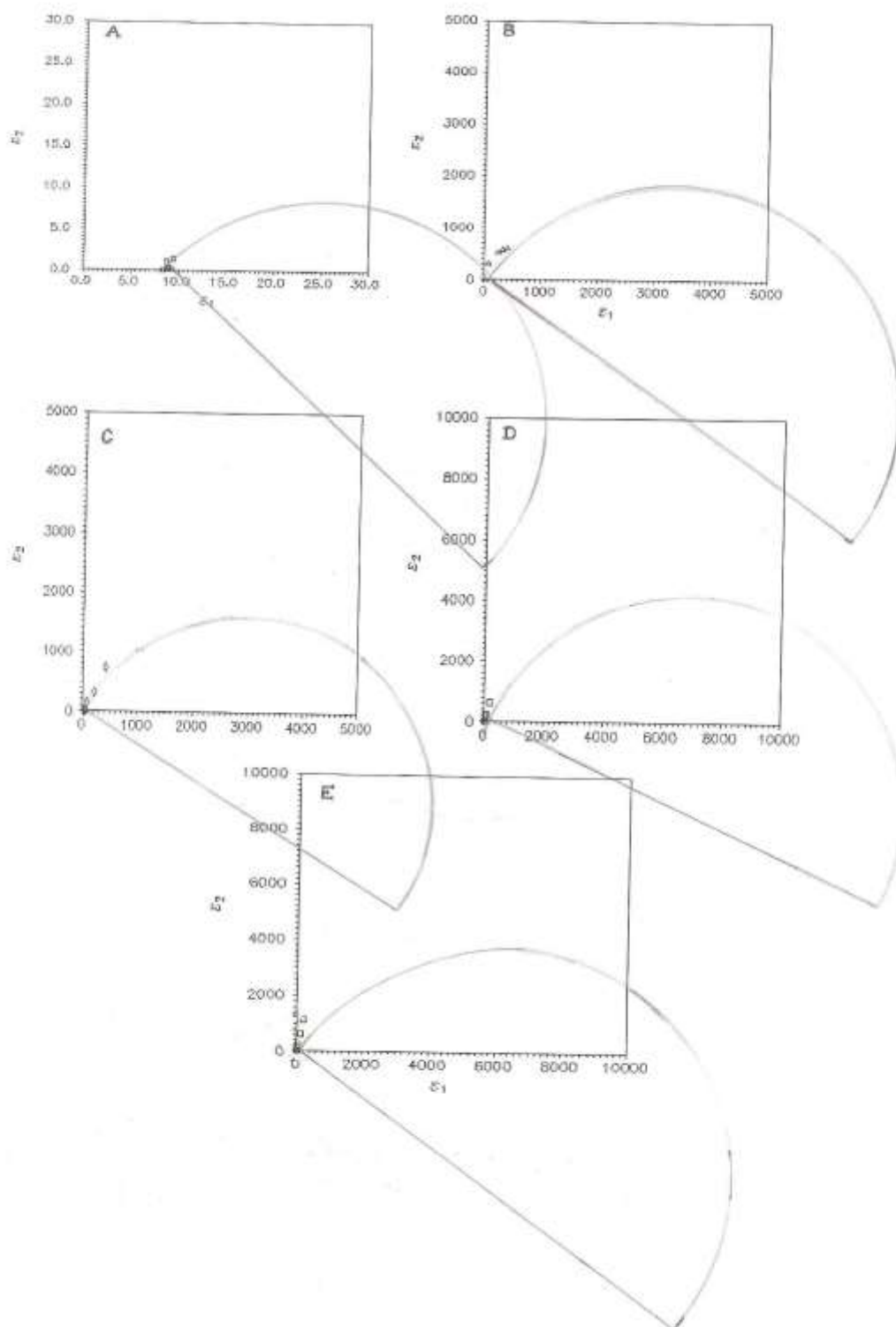


Fig. (5) The variation of $\log (\varepsilon_2)$ with $\ln (w)$ for (PS-PC) blends films.



**Fig.(6) Cole- Cole diagrams of (PS-PC) blends films,
(A)100%PS (B)75%PS+25%PC
,(C)50%PS+50%PC,(D)25%PS+75%PC, and (E)100%PC.**

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