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Electrical Properties of PAN/PMMA Blends Doped with Lithium Salts

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Abstract

Polymer blended electrolytes of various concentrations of undoped PAN/PMMA (80/20, 75/25, 70/30, 65/35 and 60/40 wt%) and doped with lithium salts (LiCl, $Li_2SO_4H_2O$, $LiNO_3$, Li_2CO_3) at 20% wt have been prepared by the solution casting method using dimethylformamide as a solvent. The electrical conductivity has been carried out using an LCR meter. The results showed that the highest ionic conductivity was 2.80×10^{-7} $(\Omega.cm)^{-1}$ and 1.05×10^{-1} $(\Omega.cm)^{-1}$ at 100 kHz frequency at room temperature for undoped (60% PAN + 40% PMMA) and (80% PAN + 20% PMMA) doped with 20%wt Li_2CO_3 composite blends, respectively. It was found from the measurements of the A.C conductivity of undoped (PAN+PMMA) and doped with different lithium salts in the frequency range (1kHz-100kHz) that A.C conductivity follows empirical laws $\sigma_{a.c}(\omega)=A\omega^s$, where (s) is (are) located between (0.501-2.054). The frequency-dependent dielectric constant at room temperature for various composites exhibited that because of interfacial space charge polarization, the dielectric constant has a large value. The fluctuation of dielectric loss with the addition of various kinds of lithium salts and frequency-dependent dielectric loss were shown and discussed.

Article Info.

Keywords:
PAN/PMMA blends, solid electrolyte, Dielectric constant, salts Lithium, ionic conductivity.

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1. Introduction

In the last few years, there has been a great interest in the production of polymer electrolytes because of their potential application in lithium polymer, lithium-ion batteries and electrochemical devices such as supercapacitors [1]. Polymer electrolytes have the following properties: mechanical strength, high ionic conductivity at room temperature, stability, (lighter weight, mechanical flexibility, easy processing, biocompatibility, chemical stability), and conducting materials (electrical properties) which have numerous applications in polymer batteries, supercapacitors, sensors, and electrochromic windows [2]. Polymethyl methacrylate PMMA has an unstructured morphology with a glass transition temperature (T_g) of 120^oC, it has a strong affinity to lithium ions and polymers in organic solvents. As a result of posseting polar functional groups, PMMA shows a plasticizing organic solvent-sloping salt [3]. Polyacrylonitrile (PAN) has a semi-crystalline structure with the formula $(C_3H_3N)_n$, the unit structure is a nitrile (CN) functional group connected to the polyethylene backbone [4]. PAN-based polymer electrolyte demonstrated good ionic conductivity and electrochemical stability [5]. Because conduction in polymer electrolytes occurs through the unstructured domain of the polymer salt system, electrolytes for polymers should have a low degree of crystallinity. Many of the researchers expanded the applicability of PAN-based electrolytes [6]. The advantages of using lithium salts are good conductivity, electrochemical and thermal stability, low cost, safety, and nontoxicity. Kita et al [7] prepared polymer blend electrolytes using the solution casting method for different polymer blend electrolytes with a constant blend of PAN and PMMA polymers for different amounts of $LiClO_4$ salt. XRD and FTIR spectroscopy methods were used to examine the structural and complex forms of the basic components and their complexes. Using A.C. impedance spectroscopy, the influence of salt content on ionic conductivity and the temperature dependence of ionic conductivity in the range 302-373K were investigated. The maximal ionic conductivity value for the film comprising PAN (75 wt%), PMMA (25 wt%), and $LiClO_4$ (8 wt%) was found to be 0.562×10^{-5} $S.cm^{-1}$. Thermo gravimetric analysis and differential scanning calorimetry are used to determine the thermal properties of the films. The ionic conductivity of the sample has increased. Scanning electron microscopy was used to analyze the microstructure of the electrolyte system. Arya and Sharma [8] studied the influence of salt content (LiPF6) on the transport characteristics and ion dynamics of a solution cast mix solid (PEO-PAN) polymer electrolyte. FTIR spectroscopy indicated the presence of microscopic interactions such as polymer-ion and ion-ion interactions as was shown by a change in the peak area of anion stretching mode. The FTIR analysis indicated that the proportion of free anions and ion pairs indicated the fraction of free ions and ion pairs influence the ionic conductivity with different salt concentrations. At ambient temperature, the complex dielectric permittivity, dielectric loss, and complex conductivity have been investigated and fitted throughout the complete frequency range (1Hz to MHz). Salt increased the dielectric constant, and the shift of the relaxation peak in the loss tangent plot toward high frequency implies a reduction in relaxation time. They used Sigma representation (ε_r versus ε_i) for solid lithium-ion conducting films to gain a better understanding of the dispersion area in the Cole-Cole plot (ε_r versus ε_i) at a lower frequency window. The conductivity is inversely proportional to the dielectric strength, relaxation duration, and hopping frequency.

The main goal of this research is to investigate the effect of doping ratio with various lithium salts (LiCl, $Li_2SO_4H_2O$, $LiNO_3$, Li_2CO_3) at 20 wt% on the A.C. conductivity and dielectric properties of (PAN/PMMA) blends with different blends ratios.

2. Experimental work

In this work, (PAN) (Mackun Comp.) with a molecular weight of average 150,000 and PMMA with an average molecular weight of 120,000 was used as polymer electrolyte. Lithium salts used in this work were Li_2CO_3, $Li_2SO_4H_2O$, $LiNO_3$, and LiCl supplied from (Aldrich comp.) The solution cast method created films doped with a lithium salt. Different weight percentage ratios of polymer blend PMMA/PAN (80/20, 75/25, 70/30, 65/35, and 60/40 wt%) were prepared in this work. A constant weight of lithium salt (Li_2CO_3, $Li_2SO_4H_2O$, $LiNO_3$, and LiCl of 20 wt% was dissolved in 25 ml of DMF, (dimethylformamide) as the solvent, and blended using a solution casting method and then stirred with a magnetic stirrer continuously for 6 hrs at 70 °C to obtain a homogenous mixture then the solution was added in a Petri dish glass and then dried in an oven at 50°C for 2 days to get a dried blend sample. All the prepared blend composite samples were characterized using the conductivity, dielectric constant, and dielectric loss values at room temperature 293 K. The A.C conductivity measurement was done at room temperature 293K using an LCR meter (LCR-821) over a frequency range of 1 kHz -200 kHz.

2.1. Basic considerations

A.C. conductivity provides information about the nature of a material's conduction process. Electrical conductivity is determined as a function of angular frequency ω depending on the formula $\omega = 2\pi f$, where f is the frequency of an alternating electric field. At a given frequency and temperature, total conductivity σ_{tot} is defined as:

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

where: $\sigma_{d.c}$ is the D.C conductivity which is temperature dependent and dominates at low frequencies. $\sigma_{a.c}$ is the A.C. conductivity which is frequency dependent and lower temperature dependency. Many amorphous semiconductors and insulators, inorganic and polymeric, have the following form:

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

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

where: A_1 is constant. Eq.(1) can be rewritten as follows:

$$\sigma_{tot}(\omega) = A_I \omega^{s} + \sigma_{d.c} \qquad \textbf{(4)}$$

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

$$s = \frac{d[\ln \sigma_{a.c}(\omega)]}{d[\ln(\omega)]} \qquad \textbf{(5)}$$

And because of the inclusion of a logarithmic factor, s is not always constant; $0 < s < 1$ at low temperatures, approaching unity, and decreasing to 0.5 or less at high temperatures**.** ($\sigma_{ac}(\omega)$) provides information regarding the nature of the polarization processes in dielectrics, as well as the electrode capacitance interface and the degree of electronic conductivity present. This phenomenon appears to be a widespread characteristic of the amorphous nonmetallic state. This behavior has been attributed to relaxation processes generated by electron or ion mobility, hopping, or tunneling between equilibrium states. Measurements of A.C conductivity across a large frequency range are often followed from Eq.(3). Over a rather broad frequency range, the A.C. conductivity may be computed using the formula:

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

where: t is the film thickness, R denotes film resistance, A denotes effective capacitance area. The following relationship may be used to calculate the dielectric constants (ε_1, ε_2):

$$\varepsilon_r = \frac{C.t}{\varepsilon_o.A} \quad \textbf{(7)}$$

where: C is the capacitance, ε_0 is the permittivity of free space =8.854x10^{-14} (F/cm).

$$\varepsilon_i = \frac{t}{\omega\varepsilon_o RA} = \frac{\sigma_{a.c}}{\varepsilon_o\omega} \quad \textbf{(8)}$$

There are three charge transport processes that contribute to frequency-dependent a.c conductivity ($\sigma_{a.c}$ (ω)) which are:

A - Excited carriers' transport to the extended state near conduction or valence bands which is given by $\sigma_{a.c}$ (ω).

$$\sigma_{a.c} = \frac{\sigma_o}{(1+\omega^2\tau)} \quad \textbf{(9)}$$

where: $\sigma_o = \frac{ne_2\tau}{m*}$ where m* is the effective mass of an electron, n is the carrier density, and e is the charge of an electron.

B - Carriers stimulated into localized states near the valence or conduction band's edges transport information. $\sigma_{a.c}$ (ω) conforms to the formula:

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

where $\omega<1/\tau$.

C - The $\sigma_{a.c}$ (ω) given by this mechanism is hopping transport by carriers with energies approaching the Fermi level:

$$\sigma_{ac}(\omega) = \frac{1}{3}\pi e^2 k_B T[N(E_F)^2\alpha^{-5}[\ln(\frac{1}{\omega\tau})]^4 \quad \textbf{(11)}$$

where: N (EF) is the density of state near Fermi level and α is the decay factor where $\bar{\alpha}^{-1}$ = r$_p$ (the polaron radius).

Many theories had postulated to explain A.C conduction. It was supposed that the dielectric loss occurs because the carrier motion is regarded as localized within pairs of sets. Two distinct processes have been proposed for the interpretation of these relaxation mechanisms, quantum mechanical tunneling (QMT), in this mechanism, the A.C. conductivity is linearly dependent on temperature and the exponent is frequency dependent and temperature independent. The second mechanism is called correlated barrier hopping (CBH). The A.C. conductivity resulted from electrons hoping over the potential barrier between two sites i.e., hopping between defect states or dangling bonds (D+ D$^-$). In CBH the $\sigma_{a.c}(\omega)$ is exponentially dependent on temperature, and the exponent s approaches unity when the temperature approaches zero [9].

3. Results and discussion

3.1. Frequency dependence on A.C. conductivity σ_{ac} (ω)

Fig.1(a, b, c, d, and e) shows the total conductivity σ_t (ω) as a function of frequency in the range 1kHz–200kHz at room temperature of (PAN+PMMA) films with different blends ratios undoped and doped with lithium salts (Li_2CO_3, $Li_2SO_4H_2O$, $LiNO_3$ and LiCl. It is clear that $\sigma_{a.c}$(ω) for all blends undoped and doped increases with the increase of frequency, it is suggested that the increase of frequency influences $\sigma_{a.c}$(ω), which are the ions' movements and the polymer spine (main chain). Furthermore, ions move at great speeds at high frequencies. It is obvious that $\sigma_{a.c}$ (ω) for the undoped blends (PAN+PMMA) samples with different weight ratios are lower than that of the polymer blends doped with (Li_2CO_3, $Li_2SO_4H_2O$, $LiNO_3$ and LiCl). It is obvious from Table 1 and Fig.1 that $\sigma_{a.c}$ (ω) increases by increasing the PMMA ratio in blends samples, $\sigma_{a.c}$ (ω) increased from $7.22\ x10^{-10}$ to $2.88\ x10^{-7}$ $(\Omega.cm)^{-1}$, also $\sigma_{a.c}$ (ω) increased by the addition of lithium salts. The conductivity reached maximum value of $1.05932x10^{-1}$ $(\Omega.cm)^{-1}$ at (100 kHz) for the blend sample (80%PAN+20%PMMA) doped with 20% Li_2CO_3. The increase of $\sigma_{a.c}$(ω) by increasing the PMMA ratio is attributed to the large amplitude of vibrating of the blends samples within the polymeric chains; while the increase of $\sigma_{a.c}$ (ω) by the addition of lithium salts is a result of the tremendous increase in the mobility of charge carriers in the composite film. The exponential factor (s) was estimated from the slope of Fig.1, Table 2 shows the values of (s). It is obvious that (s) value of undoped blends (PAN+PMMA) increases by increasing the PMMA ratio but in a non-regular sequence. (s) increased from 0.780 to 2.054 when the PMMA ratio was increased from 20 to 40 wt%, also (s) changed in a non-regular sequence i.e., increasing and decreasing by the addition of different lithium salts. To explain these findings, a small polaron (SP) model for undoped blend samples was proposed. The Correlated Barrier Hopping (CBH) and Small Polaron (SP) models are useful for doped blended samples. Small Polaron Tunneling (SPT) is the best choice when the exponent (s) rises with the increase of the PMMA ratio. This happens when a charge carrier is added to a covalent solid, causing a considerable amount of local lattice deformation and the formation of tiny polarons [10-12]. The A.C. conductivity response of disordered materials across a wide frequency range is of tremendous interest not just for technical applications but also for theoretical one. The Jonscher's power exponent (s) value, as well as its temperature dependency, is a critical parameter in dielectric data analysis and the physical interpretation of conduction pathways in disordered materials. At low frequencies, the power exponent of A.C. conductivity has been found to be larger than (1) in some circumstances. This appears to be in conflict with the universal dynamic reaction. The apparent power exponent (s) has values in the range $0<s<1$ and is closely connected to the properties of mobile charges at shorter time scales, in the case of D.C. conduction and the slowest polarization process caused by charge movements within kind length scales. The appearance of apparent (s) values in the $1\leq s\leq 2$, range over a very small frequency range might be attributed to an extra molecule dipolar relaxation contribution at higher frequencies [13]. The frequency dependent factor (s) can have a value higher than one and there is no physical reason to limit the value of s below one, as in the case of glassy and mixed compounds [14].

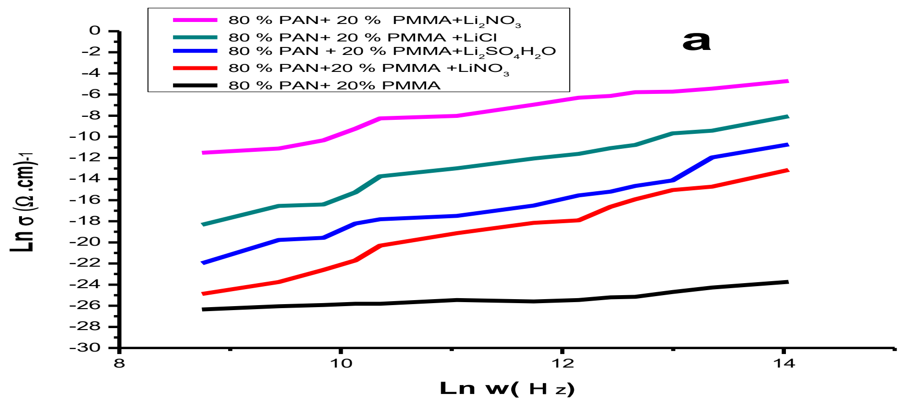

Figure 1 a: Variation of Ln $\sigma_{a.c}$ (ω) with Ln(ω) for (80%PAN/20%PMMA) and doped with 20 % of (Li_2CO_3, $Li_2SO_4H_2O$, $LiNO_3$ and LiCl).

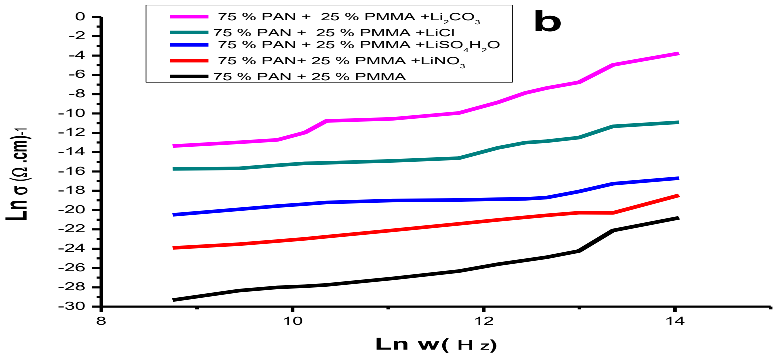

Figure1 b: Variation of Ln $\sigma_{a.c}$ (ω) with Ln(ω) for (75%PAN/25%PMMA) and doped with 20 % of (Li_2CO_3, $Li_2SO_4H_2O$, $LiNO_3$ and LiCl).

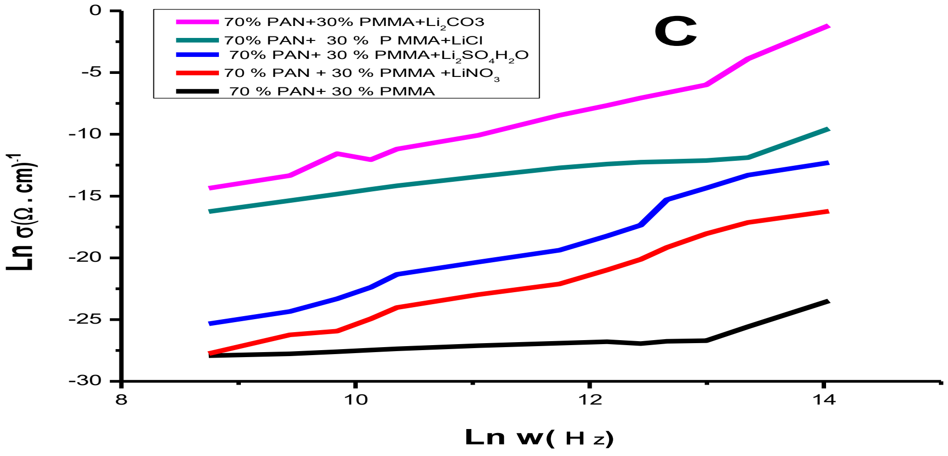

Figure 1 c: Variation of Ln $\sigma_{a.c}$ (ω) with Ln(ω) for (70%PAN/30%PMMA) and doped with 20 % of (Li_2CO_3, $Li_2SO_4H_2O$, $LiNO_3$ and LiCl).

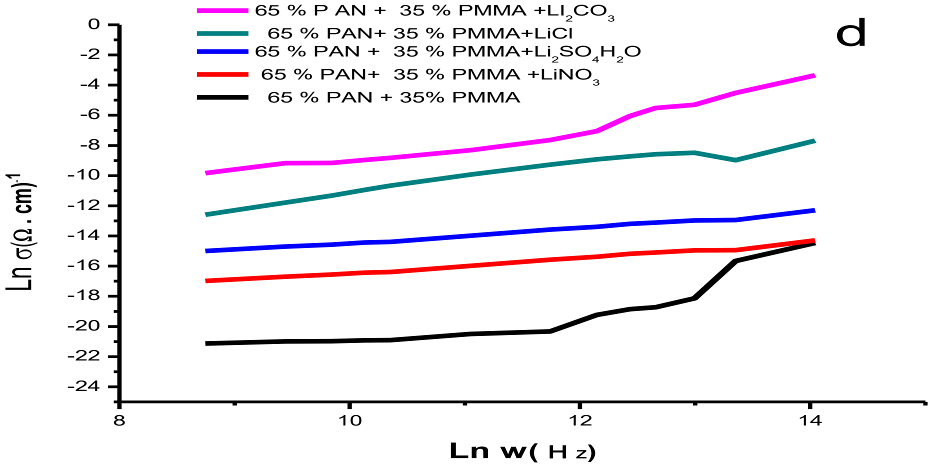

Figure 1 d: Variation of Ln $\sigma_{a.c}$ (ω) with Ln(ω) for (65%PAN/35%PMMA) and doped with 20 % of (Li_2CO_3, $Li_2SO_4H_2O$, $LiNO_3$ and LiCl).

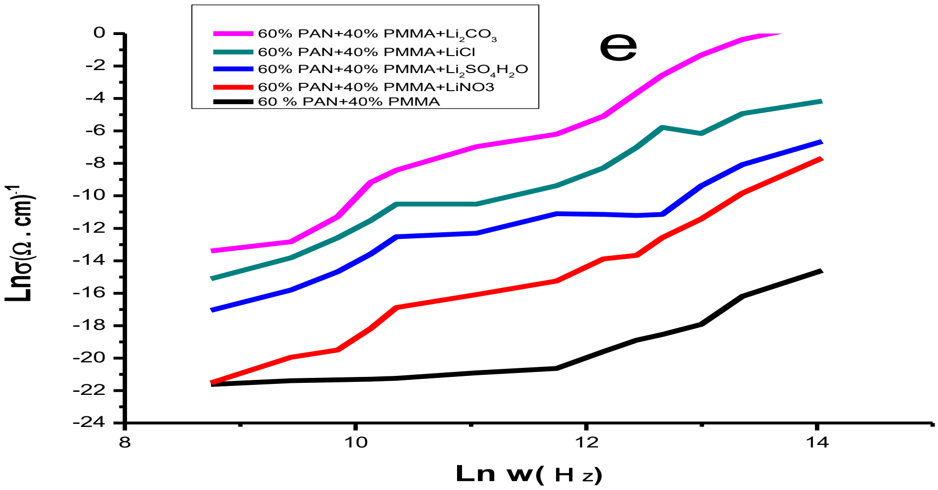

Figure 1 e : Variation of Ln $\sigma_{a.c}$ (ω) with Ln(ω) for (60%PAN/40%PMMA) and doped with 20 % of of (Li_2CO_3, $Li_2SO_4H_2O$, $LiNO_3$ and LiCl).

3.2. Dielectric constant frequency dependence (ε_r)

The quantity of energy stored in the substance at (ε_r) gives the true dielectric constant to expose it to an external electric field, as well as the behaviour of the true dielectric constant in solid materials, which decreases by increasing the frequency of the external electric field [15]. Fig.2 (a, b, c, d and e) shows that the real dielectric constant is a function of frequency for all prepared samples of undoped (PAN+PMMA) films with different blends ratios and doped with (Li_2CO_3, $Li_2SO_4H_2O$, $LiNO_3$ and LiCl) in the range of frequencies (1 kHz -200 kHz). The real value decreased with the increase in the frequency of the applied electric field. Physics has demonstrated that the (ε_r) has a high initial value, but it decreases with increasing frequency; the reason for this is a delay in the reactions of the dipoles to follow the applied electric field at high frequency i.e., the dipoles are unable to follow the change in the electrical field. It is noted that the value of the real dielectric constant is the sum of all types of electrical polarization (ionic, electronic, orientation) at frequencies less than (10 kHz) [13, 16]. Therefore, the value of (ε_r) is high because the dipoles have enough time to rotate towards the external electric field [17]. From the spectrum of ε_r of undoped (PAN+PMMA) films with different blends ratios and doped with (Li_2CO_3, $Li_2SO_4H_2O$, $LiNO_3$ and LiCl) in the frequency range (1 kHz - 200 kHz), it is apparent that ε_r tends to change by the increase of PMMA ratio as well as by addition of lithium salts. Moreover, at frequency = 10^5 Hz, ε_r decreased from 3925 to 389 and then increased to 33084, followed by a drastic reduction to 6.2 when the PMMA ratio changed from 20 to 40 % wt. Also, ε_r increased and reached a maximum value of 516150 with the addition of Li_2CO_3 to (70% PAN +30% PMMA) polymer blends. The formation of a conductor or a nonlinear capacitor with a high-energy barrier is thought to be responsible for the increase in ε_r value. Charge carriers move through one phase in heterogeneous materials, such as Li_2CO_3 doped (70%PAN + 30%PMMA) or multiphase materials. Some charge carriers may be trapped and collected at interfaces and defects; as a consequence, the electric field becomes distorted, and the dielectric constant rises. The Maxwell–Wagner effect is a sort of polarization that is dependent on the conductivity of the present phases [18].

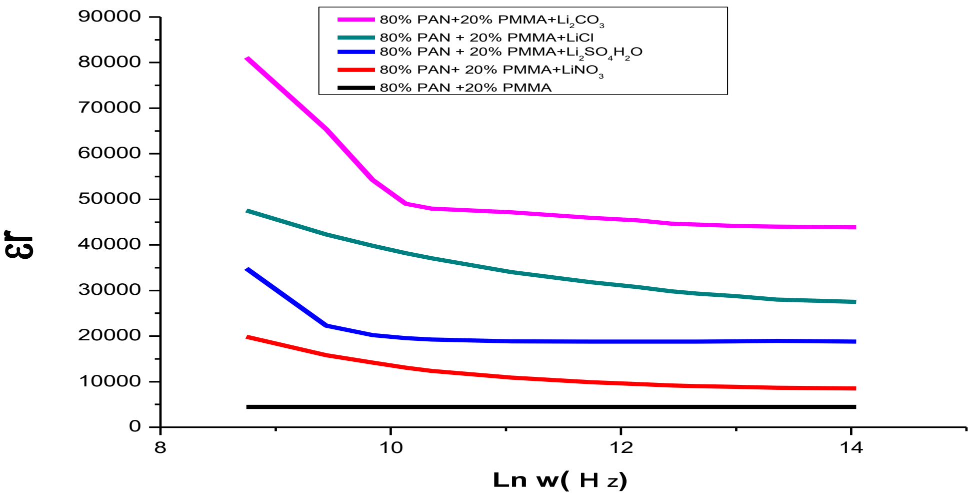

Figure 2a: The real dielectric constant as function of ln (ω) of undoped (80%PAN +20%PMMA) and doped with 20% ($LiNO_3$, LiCl, Li_2CO_3, and $Li_2SO_4H_2O$).

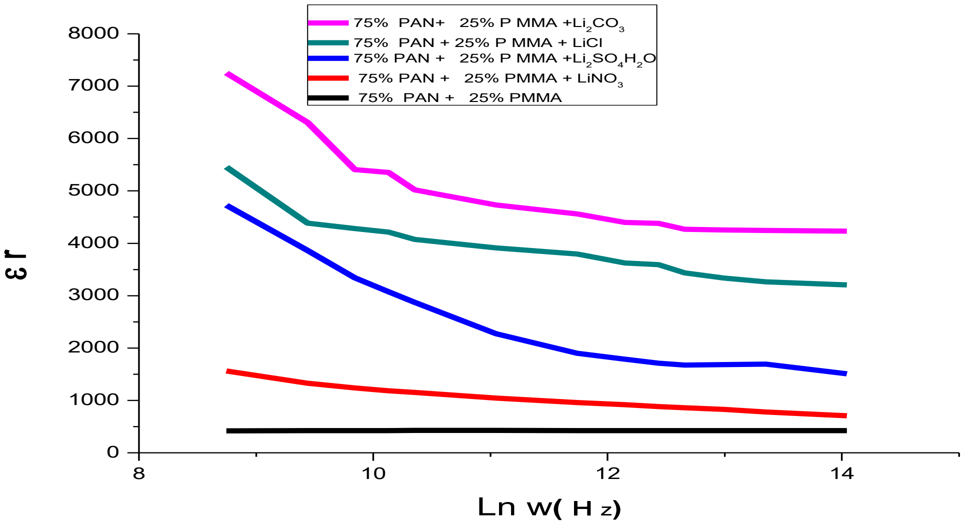

Figure 2b: The real dielectric constant as function of ln (ω) of undoped (75%PAN +25%PMMA) and doped with 20% ($LiNO_3$, LiCl, Li_2CO_3, and $Li_2SO_4H_2O$).

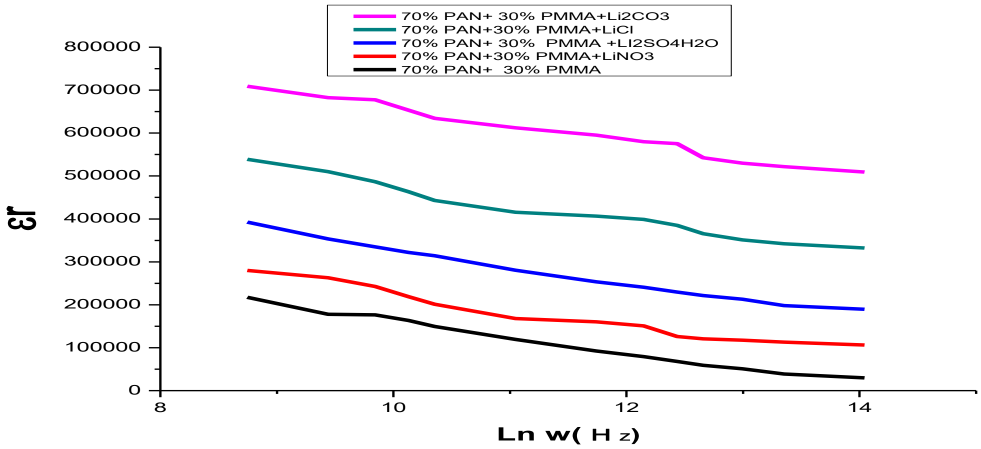

Figure 2c: The real dielectric constant as function of ln (ω) of undoped (70%PAN +30%PMMA) and doped with 20% ($LiNO_3$, LiCl, Li_2CO_3, and $Li_2SO_4H_2O$).

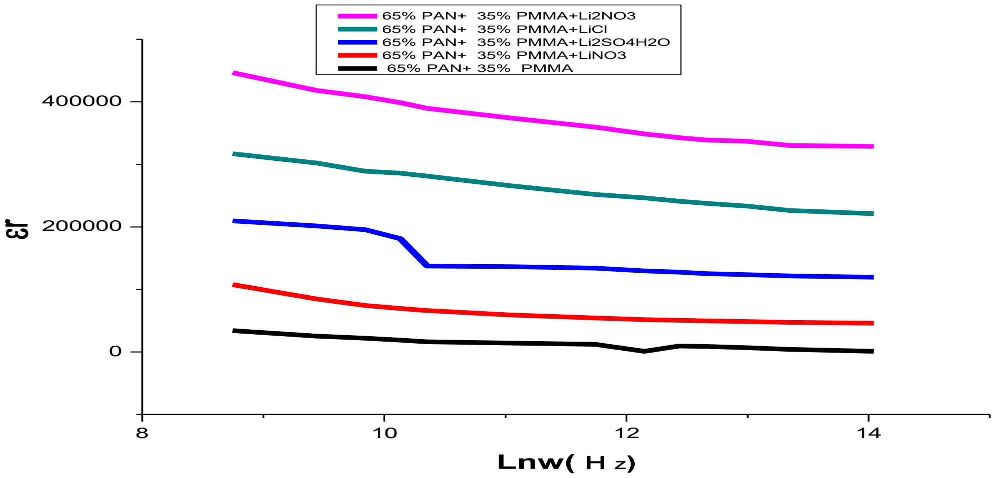

Figure 2d: The real dielectric constant as function of ln (ω) of undoped (65%PAN +35%PMMA) and doped with 20% ($LiNO_3$, LiCl, Li_2CO_3, and $Li_2SO_4H_2O$).

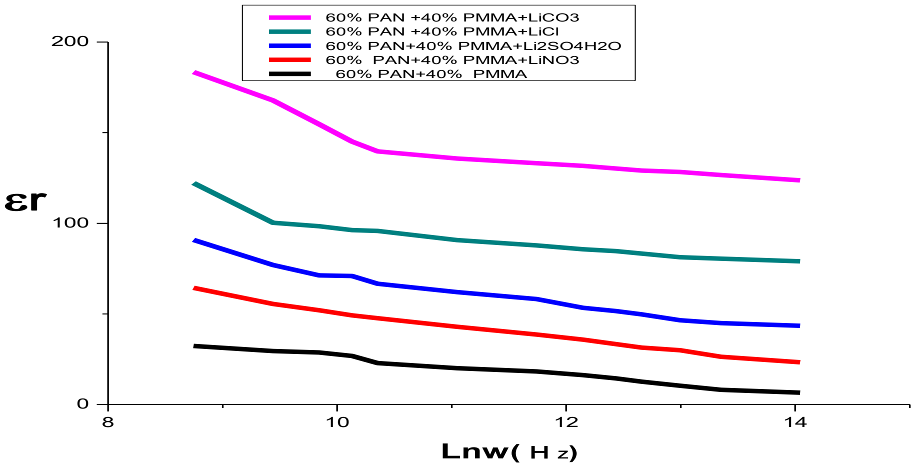

Figure 2e: The real dielectric constant as function of ln (ω) of undoped (60%PAN +40%PMMA) and doped with 20% ($LiNO_3$, LiCl, Li_2CO_3, and $Li_2SO_4H_2O$).

3.3. Imaginary dielectric constant of (PMMA+PAN) polymer blends and doped with 20 % of (Li_2CO_3, $Li_2SO_4H_2O$, $LiNO_3$ and LiCl).

The dielectric constant's imaginary part ε_i means energy absorption and dissipation at the joints. Fig. 3 (a, b, c, d, and e) shows the frequency dependence of ε_i of undoped (PMMA+PAN) polymer blend and doped with 20 % (Li_2CO_3, $Li_2SO_4H_2O$, $LiNO_3$ and LiCl). The local charges are accumulated under the influence of the field alternating electric current and the imaginary dielectric constant decreases with increased frequency, which represent the behaviour of the frequency dependent imaginary dielectric constant of the prepared samples. It is reported that the value of the imaginary dielectric constant decrease is the result of the movement of the charge carriers and also because of its large numbers through the material. It is possible for its movement to decrease when it meets any phase in the material because of the multiple phases, it is possible for the absorbed or dispersed energy to decrease, and a decrease in the value of the imaginary dielectric constant can be observed [19]. It was noted through the results shown in Table 1 that ε_i decreases by increasing the PMMA ratio up to 30% and then it decreased for further increase of PMMA ratio; ε_i increased from 0.84 to 2.8 when the PMMA ratio increased from 20 to 30 wt% and then fell to 1.5 for 40 wt% PMMA ratio. Also, ε_i reached a maximum value of 28.26 for (75%PAN+25%PMMA) doped with Li_2CO_3. At high frequency, the samples showed fluctuations with the frequency change, which may be attributed to the transition of the system to a state of chaos. It is noted that this type of difference is found in insulators, but the case of a decrease in ε_i value with frequency is attributed to polarity electronic and ionic [20]. The imaginary dielectric constant values result from the phase lag from the alternating electric field. It may also be the result of thermal irritation, which may have an effect on polarization material and affects the dielectric constant as a whole [21].

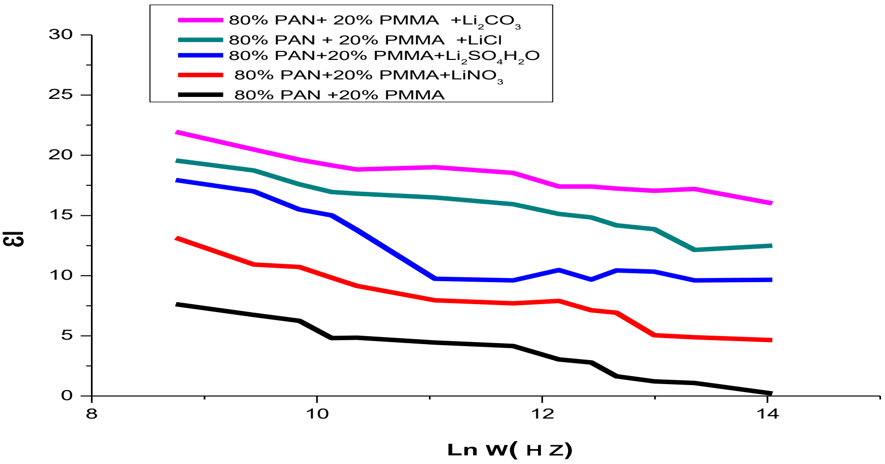

Figure 3a: The Imaginary dielectric constant as function of ln (ω) of undoped (80%PAN+20%PMMA) and doped with 20% ($LiNO_3$, LiCl, Li_2CO_3, and $Li_2SO_4H_2O$).

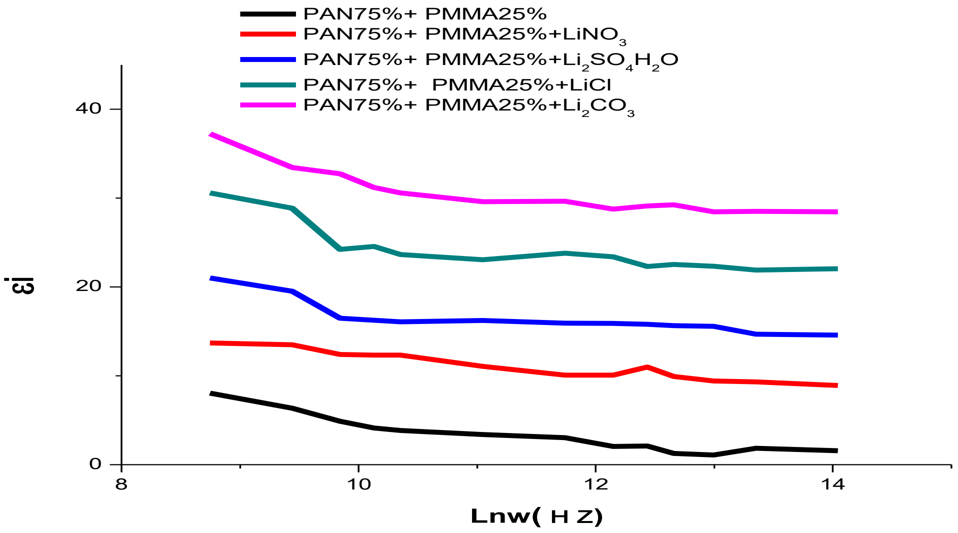

Figure 3b: The imaginary dielectric constant as function of ln (ω) of undoped (75%PAN+25%PMMA) and doped with 20% (Li_2CO_3, $Li_2SO_4H_2O$, $LiNO_3$ and LiCl).

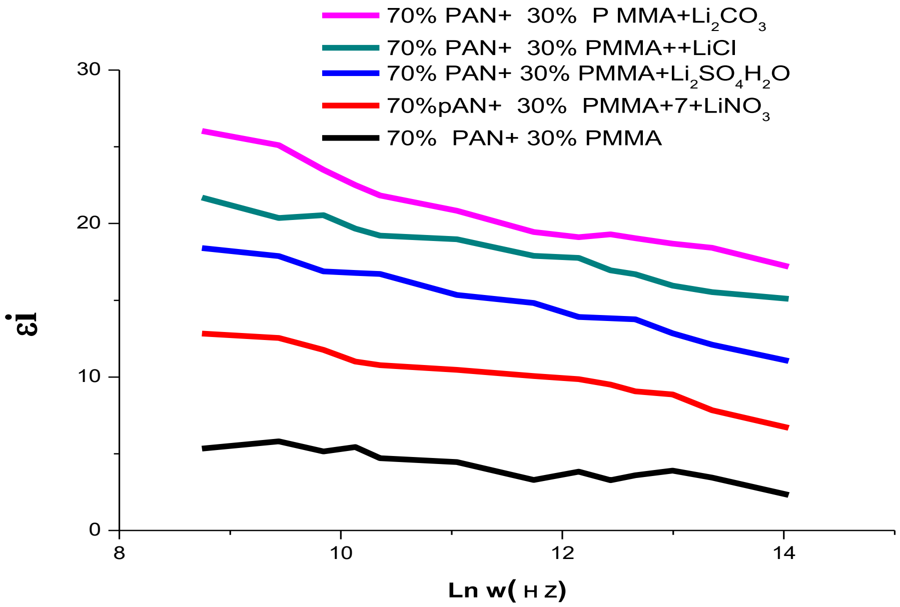

Figure 3c: The imaginary dielectric constant as function of ln (ω) of undoped (70%PAN+30%PMMA) and doped with 20% (Li_2CO_3, $Li_2SO_4H_2O$, $LiNO_3$ and LiCl).

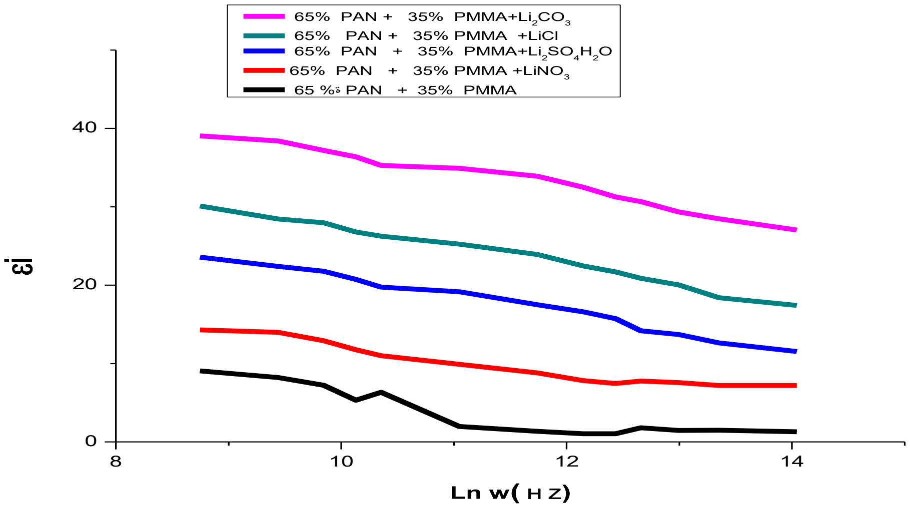

Figure 3d: The imaginary dielectric constant as function of ln (ω) of undoped (65%PAN+35%PMMA) and doped with 20% (Li_2CO_3, $Li_2SO_4H_2O$, $LiNO_3$ and LiCl).

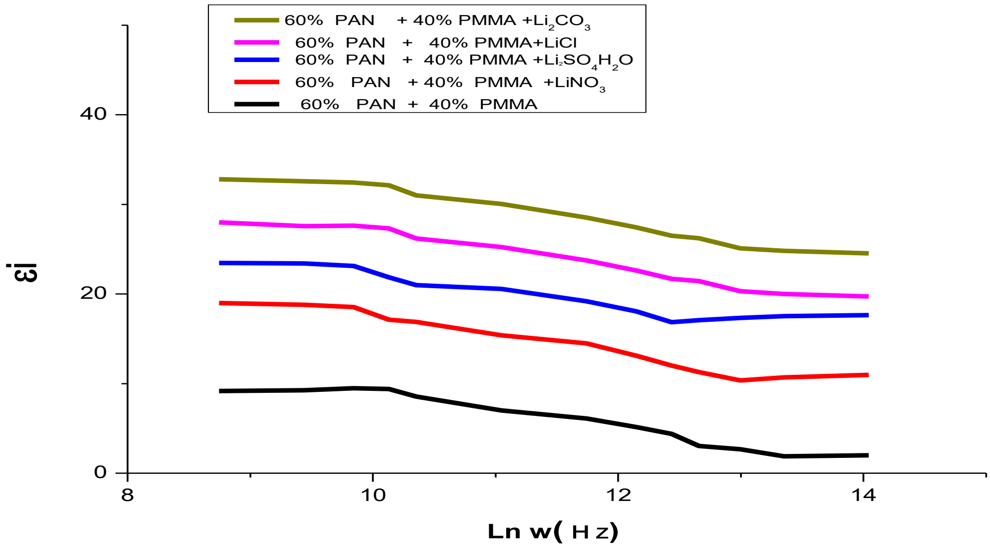

Figure 3e: The imaginary dielectric constant as function of ln (ω) of undoped (60%PAN+40%PMMA) and doped with 20% ($LiNO_3$, LiCl, Li_2CO_3, and $Li_2SO_4H_2O$).

Table 1: The values of electrical conductivity $\sigma_{a.c}$ (ω), the real dielectric constant (ε_r) and imaginary dielectric constant (ε_i) of undoped (PMMA+PAN) at different blends ratios and doped with various lithium salt.

Blend Ratios	**Type of Salts**	**At Frequency=100kHz**		
		σ (Ω cm1$)^{-1}$	**ε_r**	**ε_i**
80%PAN+20%PMMA	Undoped	7.22141E-10	3925	0.84
	Li_2CO_3 20%	1.05932E-01	44189	16.5
	$Li_2SO_4H_2O$ 20%	9.29001E-03	19347	9.4
	LiCl 20%	5.34967E-02	27855	12.1
	$LiNO_3$ 20%	24.719553 E-04	8407	4.7
75%PAN+25%PMMA	Undoped	2.02E-08	389	1.8
	Li_2CO_3 20%	9.04878E-07	4225	28.26
	$Li_2SO_4H_2O$ 20%	3.30331 E-05	1580	14.5
	LiCl 20%	2.3857 E-04	3250	21.8
	$LiNO_3$ 20%	1.88E-05	785	9.34
70%PAN+30%PMMA	Undoped	13,1364E-07	33089	2.8
	Li_2CO_3 20%	5.60376E-07	516150	17.6
	$Li_2SO_4H_2O$ 20%	1.81423E-07	188182	11.5
	LiCl 20%	2.0128126 E-02	337197	15.1
	$LiNO_3$ 20%	2.342829 E-03	108497	7.26
65%PAN+35%PMMA	Undoped	7.37859E-08	3657	1.803
	Li_2CO_3 20%	1.307624 E-03	330163	27.7
	$Li_2SO_4H_2O$ 20%	1.9128E-07	121496	12.2
	LiCl 20%	2.964.8 E-04	221440	17.6
	LiNO3 20%	4.8 E-04	44006	7.1
60%PAN+40%PMMA	Undoped	2.80057E-07	6.2	1.5
	Li_2CO_3 20%	1.03735E-05	124.6	24.5
	$Li_2SO_4H_2O$ 20%	2.15896E-05	45.01	17.2
	LiCl 20%	2.18794 E-06	79.29	19.6
	$LiNO_3$ 20%	1.7901964 E-04	25.6	10.5

Table 2: The values of exponent (s) of undoped (PMMA+PAN) at different blends ratios and doped with various lithium salts.

Sample	**80%PAN+ 20%PMMA**	**75%PAN + PM25% MA**	**70%PAN + PM30% MA**	**65%PAN+ 35%PMMA**	**60%PAN+ 40%PMMA**
Undoped	0.780	1.908	1.389	0.933	2.054
$LiNO_3$ 20%	2.005	1.830	1.887	1.281	2.004
LiCl 20%	1.873	0.955	1.053	0.881	2.005
$Li_2SO_4H_2O$	1.889	0.826	1.972	0.501	1.722
Li_2CO_3 20%	1.354	1.838	2.002	0.939	2.004

4. Conclusions

Poly (acrylonitrile) (PAN) and poly methyl methacrylate (PMMA) electrolytes in a solid polymer blend (PMMA) with different blends ratios doped with various types of lithium salts were successfully prepared using the solution casting technique. The A.C. electrical conductivity was found to increase three order of magnitude by increasing the blend ratios and six order of magnitude for the composite sample (80% PAN + 20% PMMA) doped with (20 %wt) Li_2CO_3. The dielectric constant and dielectric lose were found to be greatly affected by the blend ratios and by doping with different types of lithium salts. Maximum values of dielectric constant and dielectric lose were (516.150 and 28.26) were obtained for (70%PAN+30% PMMA) and (75%PAN+25% PMMA) doped (20 wt. %) Li_2CO_3, respectively.

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Conflict of interest

Authors declare that they have no conflict of interest.

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الخصائص الكهربائية لخلائط البوليمر *PAN/PMMA* المطعمة باملأح الليثيوم

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الخلاصة

تم تحضير خلطات بوليمرية الكترولايتية وبنسب مختلفة من بولي اكريلونايتريل PAN والبولي مثيل ميثا اكريلايت PMMA (80/20,75/25,70/30,65/35 and 60/40wt%) غير المطعمة والمطعمة باملاح الليثوم المختلفة (LiCl, $Li_2SO_4H_2O$,$LiNO_3$,Li_2CO_3) وبنسبة 20 wt% باستخدام تقنية الصب و باستخدام دايمثيل فورمالديهايد DMF كمذيب. تم قياس التوصيلية الكهربائية باستخدام جهاز LCR. أظهرت ألنتائج ان اعلى توصيلية أيونية للعينة $2.80x10^{-7}$ and $(\Omega.cm)^{-1}$ غير المطعمة وللعينة $(\Omega.cm)^{-1}$ $1.05x10^{1-}$ والمطعمة وعند تردد ا كيلو هيرتز وعند درجة حرارة الغرفة للمتراكبات لخلائط على التوالي (60%PAN+40%PMMA) (80% PAN +20%PMMA) مع Li_2CO_3 20%w.t وفي مدى التردد-1kHz)

100kHz) إن التوصيلية المتناوبة تخضع للعلاقة $\sigma_{a.c}(\omega)= A\ \omega^{s}$ حيث الثابت الأسي يقع ضمن المدى,(0.501-2.054). اعتماد
ثابت العزل على التردد وعند درجة حرارة الغرفة ولمختلف المتراكبات اظهر ان استقطاب الشحنات المتكونة عند السطوح البينية ادى
الى قيم عالية لثابت العزل. لقد تم عرض وتفسير اعتماد معامل الفقد على التردد و تغيره مع انواع املاح الليثوم المضافة.