

## **CONDUCTIVITY AND DIELECTRIC STUDIES ON FILLER-DOPED HEXANOYL CHITOSAN BASED POLYMER ELECTROLYTES**

F.H.Muhammad<sup>a</sup>, N.R.A.Razak<sup>a</sup>, R.H.Y Subban<sup>a</sup>, Tan Winie<sup>a</sup>, A.K.Arof<sup>b</sup>

*<sup>a</sup>Faculty of Applied Sciences, Universiti Teknologi MARA,  
40450 Shah Alam, Selangor, Malaysia*

*<sup>b</sup>Physics Department, Faculty of Science, University of Malaya,  
50603 Kuala Lumpur, Malaysia*

### **ABSTRACT**

Solid polymer electrolytes based on hexanoyl chitosan complexed with lithium trifluoromethanesulfonate (LiCF<sub>3</sub>SO<sub>3</sub>) were prepared using solution casting technique. The effect of addition of Al<sub>2</sub>O<sub>3</sub> on the conductivity behaviour of hexanoyl chitosan-based polymer electrolyte system was investigated by impedance spectroscopy for temperature ranging from 273 to 343 K. The conductivity for filler-free polymer electrolyte is  $2.75 \times 10^{-5} \text{ S cm}^{-1}$  whereas with addition of 6 wt % Al<sub>2</sub>O<sub>3</sub> the conductivity increased by 1 order of magnitude to  $1.01 \times 10^{-4} \text{ S cm}^{-1}$ . Within the temperature range investigated, the conductivity of the polymer electrolytes are thermally assisted and can be described by Arrhenius law. Dielectric studies were analyzed using complex permittivity  $\epsilon^*$  and complex electrical modulus  $M^*$  for the sample with the highest ionic conductivity.

### **INTRODUCTION**

Polymer based electrolytes are increasingly popular in advanced application especially in electrochemical system as it offers good mechanical properties, fair filmability and good contact with electrode materials. Generally, the polymer electrolytes could be classified into three categories: dry solid polymer electrolytes, plasticized polymer electrolytes and composite polymer electrolytes. The early stage of work with dry solid polymer electrolytes began with linear polyethylene oxide (PEO) complexes with lithium salt. Although PEO-based electrolytes possess good mechanical properties, they are generally poor conductors ( $\sigma \approx 10^{-8} \text{ S cm}^{-1}$ ) at room temperature which limits their practical applications [1].

To overcome some drawbacks of the dry solid polymer electrolytes, the incorporation of plasticizer such as ethylene carbonate (EC) and propylene carbonate (PC) to polymer host was introduced [2]. The plasticizers aid in the dissolution and dissociation of salts thus increasing the number of mobile charges. The plasticizer also reduces the medium viscosity and hence eases the movement of the charge carriers which resulted in higher rate of conductivity. However the problems associated with plasticized polymer electrolytes are poor mechanical properties, solvent volatility and reactivity of the polar

plasticizer with lithium electrode [3].

The addition of ceramic filler such as  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ , and  $\text{TiO}_2$  is one of the approaches to increase the mechanical properties and the ionic conductivity of the polymer system. The addition of filler to the polymer-salt complexes helps in lowering the glass transition temperature  $T_g$  of the polymer, by increasing the volume fraction of the amorphous phase [4-5]. In general, the decrease of glass transition temperature of filler-added polymer electrolyte samples will improve the segmental flexibility of polymer chains which leads to the increase in mobility of conducting ions [5].

This paper discusses the effect of alumina ( $\text{Al}_2\text{O}_3$ ) addition on the conductivity behaviour of hexanoyl chitosan:  $\text{LiCF}_3\text{SO}_3$ : EC electrolyte system. For the sample that exhibited high ionic conductivity value, dielectric and electrical modulus formalism were studied over a selected temperature and frequency range.

## EXPERIMENTAL

Hexanoyl chitosan, lithium trifluoromethanesulfonate ( $\text{LiCF}_3\text{SO}_3$ ) with purity > 96 % from Aldrich, EC with purity > 99 % purchased from Fluka,  $\text{Al}_2\text{O}_3$  with particle size (20-30 nm) were used as the starting materials. Prior to use,  $\text{LiCF}_3\text{SO}_3$  was dried for 24 hrs at  $120^\circ\text{C}$  in vacuum oven. Tetrahydrofuran (THF) with purity > 99 % from J.T Baker was used as received. Films of hexanoyl chitosan-based polymer electrolyte were prepared by the solution casting method. The required amount of  $\text{Al}_2\text{O}_3$  (0-10 wt. %) was added to hexanoyl chitosan and  $\text{LiCF}_3\text{SO}_3$  dissolved in THF. The solution was stirred at room temperature until complete dissolution. The solutions thus obtained were cast in glass Petri dishes and allowed to evaporate slowly at room temperature to form films.

The impedance measurement of the films was carried out using HIOKI 3532-50 LCR Hi Tester in the frequency range of 100 Hz to 1 MHz over the temperature range 273 K to 343 K. The prepared electrolyte film was sandwiched between two stainless steel electrodes with diameter 1 cm under spring pressure. The ionic conductivity,  $\sigma$  of the samples was calculated using the equation,

$$\sigma = \frac{t}{R_b A} \quad (1)$$

where  $t$  is the thickness of the film and  $A$  is the film-electrode contact area. The bulk resistance,  $R_b$  is determined from the complex impedance plot. Impedance analysis provides simple method to interpret the dielectric spectra with different formalisms such as complex impedance  $Z^*$ , complex permittivity  $\epsilon^*$  and complex electrical modulus  $M^*$ .

Complex impedance  $Z^*$  was represented by its real,  $Z_r$  and imaginary,  $Z_i$  component through the relation:

$$Z^* = Z_r - jZ_i \quad (2)$$

Both the real,  $\epsilon_r$  and imaginary part,  $\epsilon_i$  of complex dielectric constant can be defined as follows:

$$\epsilon_r = \frac{Z_i}{\omega C_o (Z_i^2 + Z_r^2)} \quad (3)$$

$$\epsilon_i = \frac{Z_r}{\omega C_o (Z_i^2 + Z_r^2)} \quad (4)$$

where  $C_o = \frac{\epsilon_o A}{t}$ ,  $\epsilon_o$  is the permittivity of the free space,  $A$  is the sample electrode contact area and  $t$  is the thickness of the samples.  $\omega = 2\pi f$ , where,  $f$  being the frequency in Hz.

Complex electrical modulus,  $M^*$  is defined as the inverse quantity of complex dielectric constant by the following equation:

$$M^* = \left( \frac{\epsilon_r}{\epsilon_r^2 + \epsilon_i^2} \right) - j \left( \frac{\epsilon_i}{\epsilon_r^2 + \epsilon_i^2} \right) \quad (5)$$

where the real,  $M_r$  and the imaginary parts,  $M_i$  of the electrical modulus can be calculated from  $\epsilon_r$  and  $\epsilon_i$ .

Loss tangent,  $\tan \delta$  can be expressed as:

$$\tan \delta = \frac{\epsilon_i}{\epsilon_r} \quad (6)$$

## RESULTS AND DISCUSSION

The temperature dependence of conductivity for hexanoyl chitosan-based polymer electrolytes containing different amount of  $Al_2O_3$  were carried out to analyze the mechanism of ionic conduction in polymer electrolytes. The conductivity was measured over several temperatures ranging from 273 K to 343 K. The conductivity is found to increase with increasing temperature as presented in Figure1. The regression value,  $R^2$  are in the range 0.97-0.99 indicating that all points lie in an almost straight line, implying that the conductivity mechanism is thermally assisted and can be described by Arrhenius law. The activation energy of the polymer electrolytes is depicted using the equation:

$$\sigma = \sigma_o \exp\left(-\frac{E_a}{KT}\right) \quad (7)$$

where  $\sigma_o$  is the conductivity pre-exponential factor,  $E_a$  is the activation energy,  $K$  is the Boltzman constant and  $T$  is the absolute temperature in Kelvin.

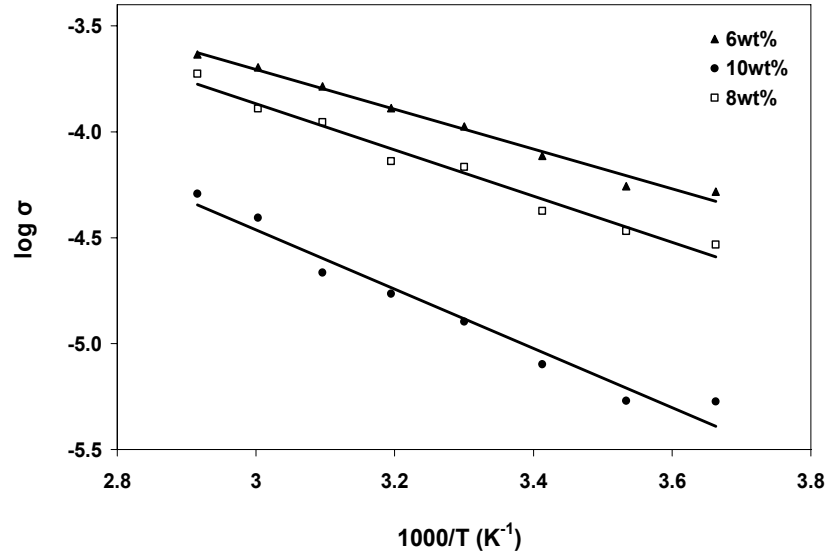


Figure 1: Temperature dependence of conductivity for hexanoyl chitosan LiCF<sub>3</sub>SO<sub>3</sub>-EC-Al<sub>2</sub>O<sub>3</sub> complexes

The variation of room temperature conductivity and  $E_a$  for hexanoyl chitosan-based polymer electrolytes with the incorporation of nano-size Al<sub>2</sub>O<sub>3</sub> (0-10 wt %) are presented in Figure 2. With addition of 2 wt% Al<sub>2</sub>O<sub>3</sub>, the conductivity of the prepared electrolyte increases from  $2.75 \times 10^{-5} \text{ S cm}^{-1}$  to  $3.01 \times 10^{-5} \text{ S cm}^{-1}$  and reaches a maximum at  $1 \times 10^{-4} \text{ S cm}^{-1}$  with addition of 6 wt% of Al<sub>2</sub>O<sub>3</sub>. However, the conductivity decreases with further addition of Al<sub>2</sub>O<sub>3</sub> beyond 6 wt%.

The conductivity enhancement with addition of Al<sub>2</sub>O<sub>3</sub> could be attributed to the increase in the amorphicity of the electrolytes. This is consistent with works reported by Pitawala et al. [5]. In the amorphous region, rapid segmental motions of polymeric chain increases the mobility of lithium ions leading to higher ionic conduction [6-7].

Further addition of Al<sub>2</sub>O<sub>3</sub> beyond 6 wt% resulted in a decrease in conductivity. This may be attributed to ion association which decreases the number of charge carriers available for ionic conductivity. Also, the decrease in conductivity with addition of Al<sub>2</sub>O<sub>3</sub> up to an optimal amount could be attributed to the blocking effects of conducting

pathways due to the presence of a large number of ion aggregate [6]. This in turn results in the reduction of the mobility of ions which in turn leads to the decline in the conductivity value.

Figure 2 also clearly shows that the value of activation energy,  $E_a$  decreases as increasing the conductivity of the system. This is attributed to the completely amorphous nature of the polymer electrolyte that facilitates the fast Li-ion motion in the polymer network and it further provides a higher free volume in the polymer electrolyte system upon increasing the temperature [8].

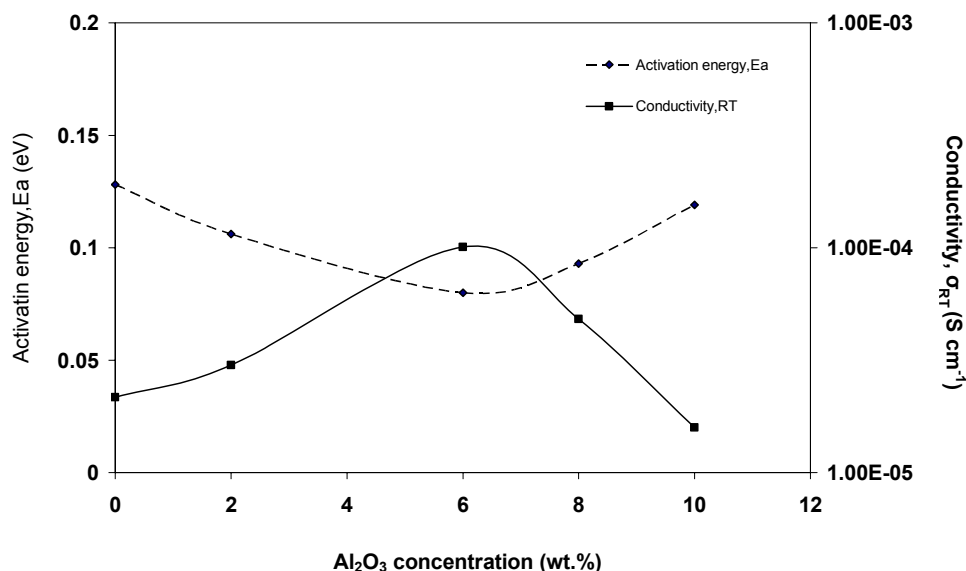


Figure 2: Ionic conductivity of hexanoyl chitosan-based polymer electrolytes as a function of Al<sub>2</sub>O<sub>3</sub> concentration at room temperature.

Dielectric relaxation behaviour of the polymer electrolyte brings about insights into ionic transport phenomena. The dielectric constant is a measured of storage charge. Since the charge is made up of Li<sup>+</sup> ions, the increase in dielectric constant represents the increase in the number of Li<sup>+</sup> ions [9]. In the present study, the dielectric behaviour of the polymeric system has been studied over a range of frequency and temperature. Figure 3 (a) and (b) shows the plot of dielectric constant and dielectric loss as a function of frequency at different selected temperatures for the high conducting sample that containing 6 wt. % Al<sub>2</sub>O<sub>3</sub>.

From Figure 3 (a) and (b), it is observed that both of the dielectric constant and dielectric loss decrease with increasing frequency. At high frequencies, due to high periodic reversal of the applied field, there is practically insufficient time for the ionic charge carries to follow the imposing direction of the applied field. This is turn decrease

their contribution to the polarization, resulting to a decrease of the dielectric constant and dielectric loss [10-12].

On the other hand, in the low frequency region, the values of dielectric constant and dielectric loss are found to increase with increasing temperature. The effect of temperature on the value of dielectric constant can be summarized as follows. The value of dielectric constant increases with temperature indicating an increase in the number of  $\text{Li}^+$  ions with temperature. This shows that the salt undergoes greater dissociation as the temperature increases. This implies that conductivity is thermally assisted which is in good agreement with the results shown in Figure 1.

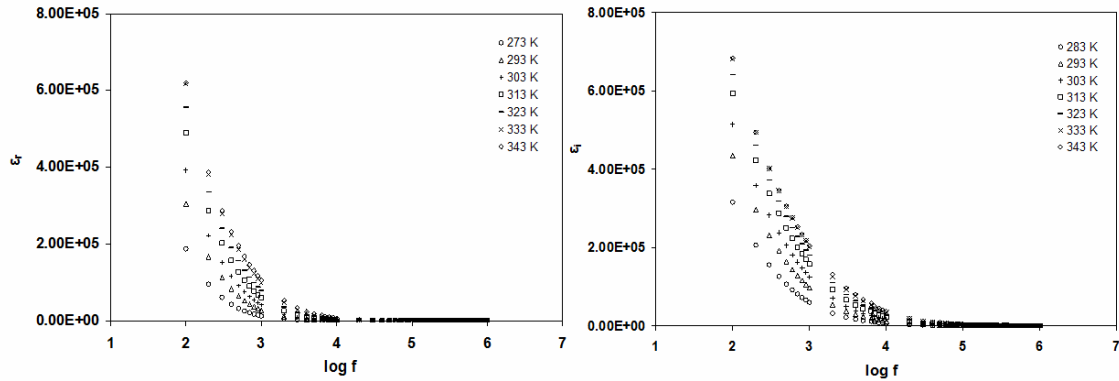


Figure 3: Frequency dependence of (a) dielectric constant,  $\epsilon_r$  (b) dielectric loss,  $\epsilon_i$  for hexanoyl chitosan –  $\text{LiCF}_3\text{SO}_3$ -EC-6 wt. %  $\text{Al}_2\text{O}_3$  complexes

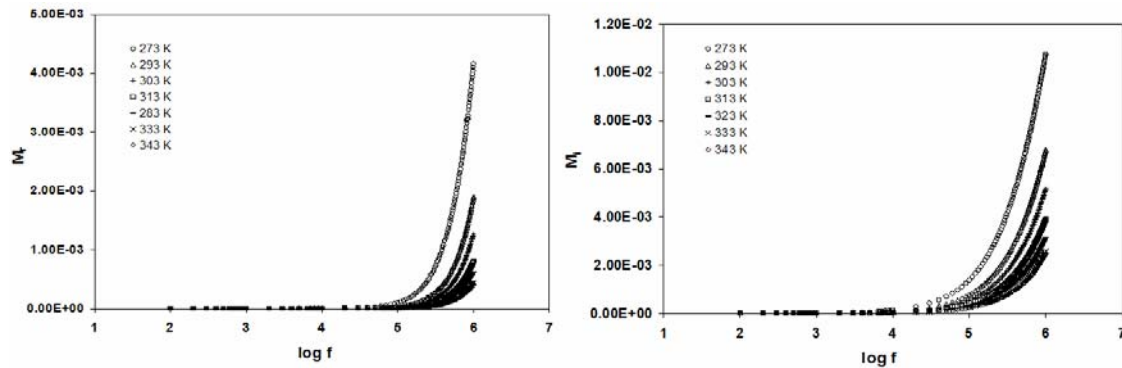


Figure 4: Frequency dependence of (a) real part,  $\epsilon_r$  (b) imaginary part,  $\epsilon_i$  of dielectric modulus for complexes of hexanoyl chitosan –  $\text{LiCF}_3\text{SO}_3$ -EC-6 wt. %  $\text{Al}_2\text{O}_3$  complexes

A further analysis of the dielectric behavior could be successfully achieved using dielectric modulus, which suppresses the effects of electrode polarization [13]. The variations of real  $M_r$  and imaginary  $M_i$  parts of electric modulus as a function of frequency over a range of temperature are depicted in Figure 4 (a) and (b). From Figure 4 (a), at low frequency region, the value for both  $M_r$  and  $M_i$  are approaching zero indicating that the contribution of electrode polarization is negligible [14]. This type of behavior supports the conduction phenomena is due to long-range mobility of charge carriers [15]. As frequency increases, the value of  $M_r$  increases with increasing

temperature due to the lack of restoring force governing the mobility of charge carriers under the action of an induced electric field [16].

The variation of loss tangent,  $\tan \delta$  as a function of frequency at selected temperatures for sample containing 6wt. %  $\text{Al}_2\text{O}_3$  was plotted as shown in Figure 5. From the figure 5, it is clearly observed that  $\tan \delta$  increases with frequency at different temperature, reached a maximum value and thereafter decreases. As temperature increases, the maximum of  $\tan \delta$  shift towards higher frequency due to the increment in the number of charge carriers available for the ionic conduction [9].

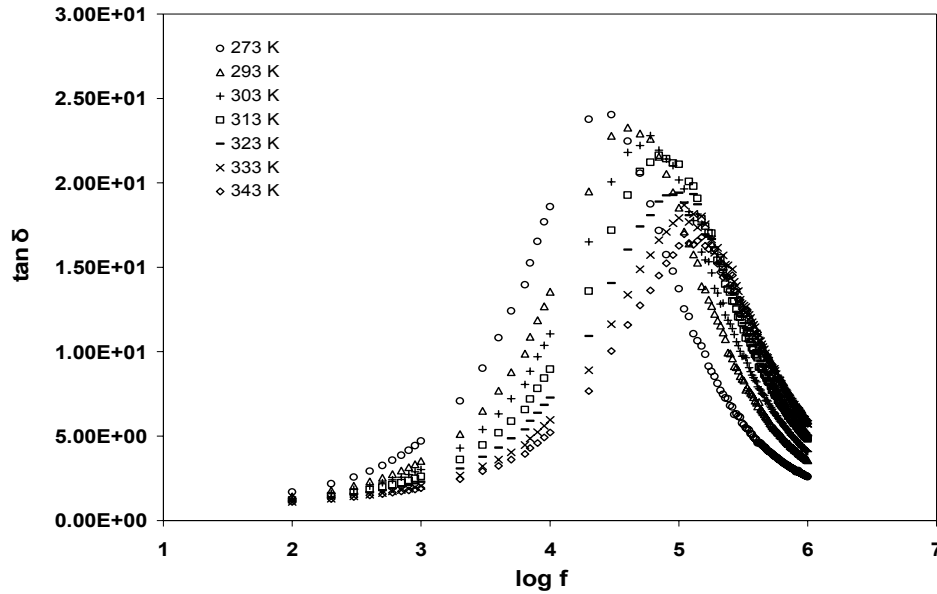


Figure 5: Variation of loss tangent with frequency for hexanoyl chitosan –  $\text{LiCF}_3\text{SO}_3$ -EC-6 wt. %  $\text{Al}_2\text{O}_3$  complexes

From Figure 5, the shifting of the  $(\tan \delta)_{\max}$  towards higher frequency with increasing temperature indicates that relaxation time decreases with increasing temperature due to the increased mobility of the ionic charge carriers. This may be clearly seen in a plot of relaxation time with temperature as shown in Figure 6. According to the previous study [9, 17], the occurrence of relaxation times can be obtained from the peak of  $\tan \delta$  using the relation:

$$\tau\omega \approx 1 \quad (8)$$

At this point, it may be necessary to define relaxation time as the time which occurs as a result of the ionic charge carriers within the polymer material obeying the change in the direction of the applied field. From Figure 6, it suggests that the temperature dependence of relaxation time appears to be thermally activated and may be described by the Arrhenius law as given in equation (7) [18].

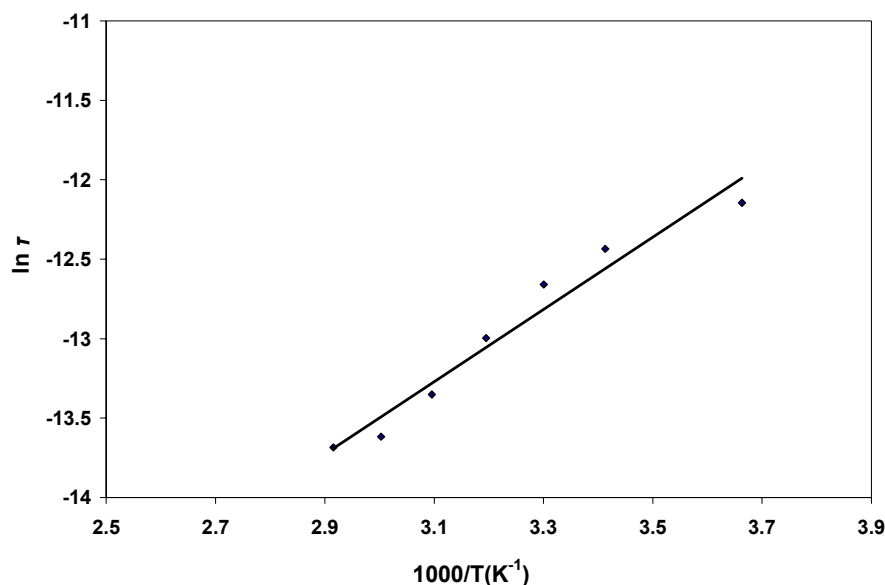


Figure 6: Variation of  $\ln \tau$  with temperature for sample containing 6 wt. %  $\text{Al}_2\text{O}_3$ .

## CONCLUSIONS

The ionic conductivity and dielectric behaviour of hexanoyl chitosan:  $\text{LiCF}_3\text{SO}_3$ : EC:  $\text{Al}_2\text{O}_3$  polymer electrolytes were studied with different weight ratio of  $\text{Al}_2\text{O}_3$  as a function of frequency (100 Hz to 1 MHz) and in temperature range (273 – 343 K). The addition of nano-size  $\text{Al}_2\text{O}_3$  to hexanoyl chitosan– $\text{LiCF}_3\text{SO}_3$ –EC–polymer electrolytes has been found to result in an increase in conductivity. The dielectric constant was found to increase with the temperature as well as the conductivity of the samples and decrease with the increasing of frequency. The plot of relaxation time for the ionic charge carriers were extracted from the loss tangent maximum peak at various temperatures shows Arrhenius type behaviour.

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