

## STUDIES ON ELECTRICAL CONDUCTIVITY AND THERMAL BEHAVIOUR OF PVAc/PVdF-HFP/Al<sub>2</sub>O<sub>3</sub> POLYMER BLEND ELECTROLYTES

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### Introduction

In the recent years, there has been a tremendous interest in the preparation of polymer electrolytes with high ionic conductivity, good mechanical strength and thermal stabilities because these polymer electrolytes play a major role in solid-state batteries, electrochromic windows, sensors, fuel cells *etc.*<sup>[1]</sup>. Polymer electrolytes are known to exhibit several advantages like flexibility, ease of thin film formation and good mechanical stability over liquid electrolytes which are deemed to be hazardous as they may leak, produce undesirable gases on overcharging and even explode. Poly (vinyl acetate) (PVAc) is a petroleum-derived polymer usually obtained by emulsion polymerization. It has low TG and acts as a plasticizer. It features excellent adhesion to various substrates. Thus large quantities of PVAc are produced for use as a binder in emulsion paints, adhesives, and various textile finishing operations. PVAc is rather brittle and rigid but compounding it with other polymers frequently improves physical properties<sup>[2]</sup>. Poly (vinyl acetate) (PVAc) based emulsions have been used widely in conservation in Spain since their introduction in the 1950's, and are still used today in many conservation treatments (Robson 1993; Quandt 2002). Many researches were carried out on Poly (vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP)<sup>[3-5]</sup> due to

various interesting properties such as high dielectric constant ( $\epsilon=8.4$ ) which support for dissociation of salt, low crystallinity which can improve the ionic conductivity and low glass transition temperature ( $T_g$ ) of (PVdF-HFP) considered as a suitable polymer host<sup>[4-6]</sup>. PVdF-HFP has excellent chemical stability due to the crystalline vinylidene (Vdf) phase and plasticity, mainly supported by amorphous hexafluoropropylene (HFP) part<sup>[5,7]</sup>. In addition, adding an appropriate amount of lithium salt into the polymer matrix is significantly enhanced the ionic conductivity of the polymer electrolyte by increasing the number of charge carrier which provides free ions for conduction. Polymer electrolytes with a variety of ceramic particles such as TiO<sub>2</sub>, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and BaTiO<sub>3</sub><sup>[8,9]</sup> incorporated were prepared and they showed remarkable conductivity at room temperature with good mechanical stability.

In order to develop and improve the performance of the polymer electrolyte, an attempt was made in the preparation of PVAc/PVdF-co-HFP/PC/LiClO<sub>4</sub> based electrolytes with varying concentrations of Al<sub>2</sub>O<sub>3</sub>. The ionic conductivities of blend complexes are studied by means of ac impedance technique. X-ray Diffractometry (XRD), Thermo-Gravimetric (TG) and Differential Thermo Gravimetric (DTG) analyses are

employed in this study to improve the properties of polymer electrolyte.

## **Experimental**

### **Materials And Methods**

PVAc, PVdF-co-HFP, salt LiClO<sub>4</sub>, and the Al<sub>2</sub>O<sub>3</sub> (Aldrich chemicals, USA) were dried under vacuum at 100°C for 6 hours. Propylene carbonate (PC) (Aldrich, USA, 99%) was used as received. Commercial grade acetone was used as co-solvent. All the composite polymer electrolytes were prepared using a simple solvent casting technique. The salt LiClO<sub>4</sub> and the polymers were first dissolved in acetone separately and then mixed together. The given amounts of plasticizers were also added into the above polymer-salt mixtures. Finally, the nanofiller Al<sub>2</sub>O<sub>3</sub> was incorporated into the complex mixture and was stirred continuously about 24 hours for avoiding the fillers aggregation and to ensure the fine mixing. The obtained homogenous viscous slurry was degassed to remove air bubbles and was poured into the Petri dish. The films were further dried for 5 hours in vacuum at 60°C to remove any trace of solvent, which provided mechanically stable, free standing and flexible films. The composite polymer electrolyte films were harvested and stored in an evacuated desiccators.

### **Characterization**

Ionic conductivity of the polymer composite electrolytes was estimated with the help of stainless steel blocking electrodes using a computer controlled micro-Auto lab Type III Potentiostat/Galvanostat electrochemical work station of frequency range 1 Hz–

300 kHz. The ionic conductivity ( $\sigma$ ) of the composite electrolytes was calculated using the following equation:  $\sigma=l/R_bA$ , where  $l$ ,  $R_b$  and  $A$  are the thickness (cm), the bulk resistance ( $\Omega$ ) and the surface area (cm<sup>2</sup>) of the membrane respectively. The conductivity values were found at different temperature.

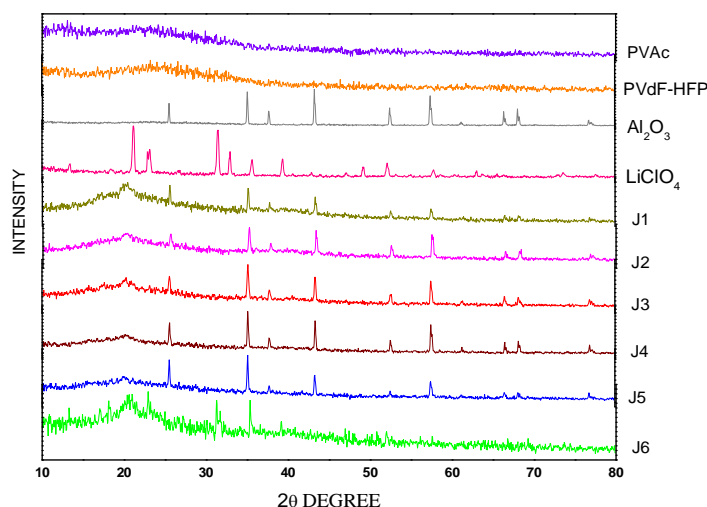
The XRD equipment used in this study is X'pert PROPANalytical diffractometer using Cu-K<sub>α</sub> radiation as source and operated at 40 KV. The sample was scanned from 10 to 80° for 2 sec in the 2θ step scan mode. TG/DTA thermal analysis study of the membrane having maximum ionic conductivity was performed using Perkin Elmer Pyris-6 TG/DTA in an atmosphere containing nitrogen from ambient temperature to 86 °C with the heating rate of 10 °C min<sup>-1</sup>.

## **Results and Discussion**

### **X-ray Diffraction Analysis**

X-ray diffraction (XRD) studies can provide a wide range of information on crystal structure, crystal orientation, crystallinity, crystal size and phase changes of materials which are characterized by the presence of sharp diffraction peaks. In amorphous materials, there is no long-range order present; however, the non-crystalline samples are characterized by 1 or 2 broad “Halos” for the present case. The XRD method has been used only in a limited perspective to identify the following:

- Amorphous, crystalline or semi crystalline nature of material
- Complex formation
- Relative amorphousity of the composite film.



**Fig. 1. XRD patterns of pure and prepared electrolyte membranes**

The XRD patterns are pure PVAc, PVdF-HFP, LiClO<sub>4</sub>, Al<sub>2</sub>O<sub>3</sub> and the complexes are shown in Fig. 1. It is evident from the Fig. 1 (PVAc, PVdF-HFP) that PVAc and PVdF-HFP exhibit an amorphous phase. The presence of sharp peaks pertaining to LiClO<sub>4</sub> in the polymer complexes shows that the complexation has taken place in the amorphous phase. The XRD patterns obtained for the electrolyte films PVAc/PVdF-HFP/PC/LiClO<sub>4</sub>, with different concentration of Al<sub>2</sub>O<sub>3</sub> indicate the

presence of undissolved Al<sub>2</sub>O<sub>3</sub> in the polymer matrix. Some of the crystalline peaks are found to be absent and some shifted in the complex indicating the interaction between the constituents of the complex. It is evident from the Fig.1 (J5) the crystalline peaks are few and amorphous nature is maintained till 10% of Al<sub>2</sub>O<sub>3</sub> and further addition of Al<sub>2</sub>O<sub>3</sub> the crystallinity of the complex is found to increase, which could be the reason for the lower conductivity of the film.

### AC Impedance Analysis

Figure 2 shows the complex impedance plot of PVAc (6.25) - PVdF-HFP (18.75) - PC (67) - LiClO<sub>4</sub> (8) with X wt% of Al<sub>2</sub>O<sub>3</sub> of the total polymer weight at room temperatures. This plot shows linear spikes. The disappearance of the high frequency semicircular portion in the polymer complex impedance plot indicates that the current carriers are ions

and the total conductivity is the result of ionic conduction. The bulk resistance of the electrolyte was measured by extrapolating the intercept of this plot on the real axis. The electrical conductivity of the electrolyte was calculated for the known values of bulk resistance ( $R_b$ ), area (A) and the thickness (l) of the film using the formula  $\sigma = l/R_b A$ .

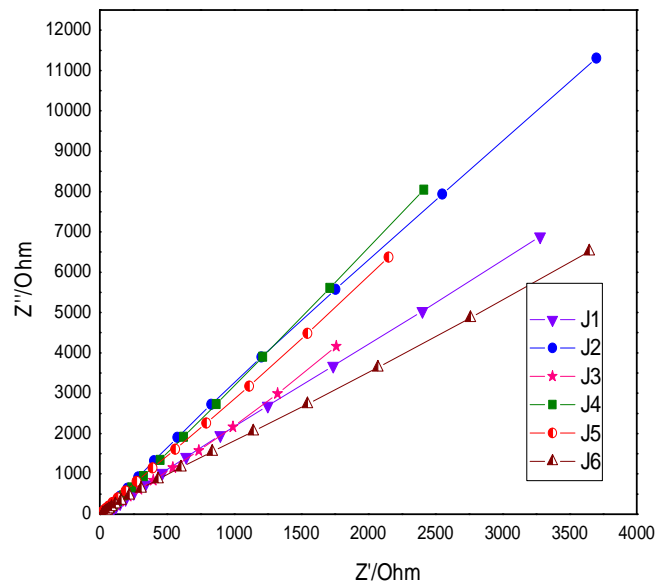


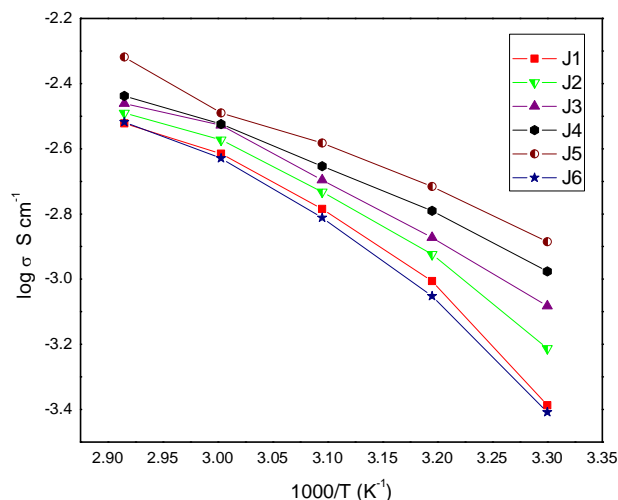
Fig. 2. Room temperature complex impedance plot of the prepared samples

Table 1: Ionic conductivity values of PVAc (6.25)/PVdF-co-HFP (18.75)/PC (67)/LiClO<sub>4</sub> (8)/ Al<sub>2</sub>O<sub>3</sub> X wt% of in the total polymer weight

Sample coding	PVAc(6.25)/PVdF-co- HFP(18.75)/PC(67)/LiClO <sub>4</sub> (8)/ Al <sub>2</sub> O <sub>3</sub> (X) Wt.%	Ionic conductivity values ( $\sigma$ ) $\times 10^{-3}$ Scm <sup>-1</sup> at different temperatures (K)				
		303	313	323	333	343
J1	X=2	0.410	0.986	1.643	2.426	3.006
J2	X=4	0.613	1.190	1.851	2.676	3.236
J3	X=6	0.826	1.341	2.014	2.968	3.456
J4	X=8	1.056	1.621	2.221	2.988	3.650
J5	X=10	1.301	1.923	2.616	3.235	4.801
J6	X=0	0.390	0.865	1.543	2.348	3.033

From the Table 1, it is seen that the addition of inorganic fillers leads to an increase in the ambient temperature conductivity up to 10 wt% of Al<sub>2</sub>O<sub>3</sub> in the total polymer weight and then the ionic conductivity decreases due to higher concentration of ceramic fillers. The result reveals that the addition of small particle size ceramic powders enhances the degree of amorphicity of the polymer electrolyte. Indeed, one may

summarize that the presence of high dispersed particles in the polymer matrix may affect the crystallization rate by preventing the agglomeration of the polymer chains. Further, the particle size and content of the ceramic additive appear to be a critical factor. It is also seen that a reasonably high concentration of the filler is also necessary to affect the re-crystallization rate of the polymer host.

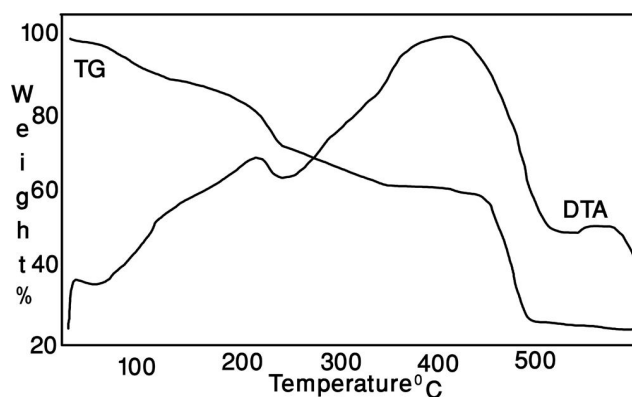


**Fig. 3. Temperature dependent ionic conductivity plots of the prepared samples**

The temperature dependence of the ionic conductivity of PVAc(6.25)- PVdF-HFP(18.75)- PC(67)- LiClO<sub>4</sub>(8)- X% of Al<sub>2</sub>O<sub>3</sub> (where X = 0,2,4,6,8,10) in the total polymer electrolyte is shown in the Figure 3. From the plot it has been observed that as temperature increases the conductivity increases for all the compositions. The non-linearity in Arrhenius plots indicates that ion

transport in polymer electrolytes is dependent on polymer segmental motion. The curvature behaviour of the plots suggests that the data can be better described by the Vogel–Tamman–Fulcher (VTF) relation, which describes the transport properties in a viscous matrix. It supports the idea that the ion moves through the plasticizer-rich phase.

### 3.4 TG/DTA Analysis



**Fig. 4: TG/DTA analysis of PVAc (6.25)-PVdF-HFP (18.75)-PC (67)-LiClO<sub>4</sub> (8) - Al<sub>2</sub>O<sub>3</sub> (10 wt. %)**

Figure 4 shows the TG/DTA traces of PVAc (6.25)-PVdF-HFP (18.75)-PC (67)-LiClO<sub>4</sub> (8) - Al<sub>2</sub>O<sub>3</sub> (10 wt%) polymer composite which shows maximum conductivity value. An endothermic peak was observed at 100°C and corresponding (about 5%) weight loss is attributed to the presence of moisture in the samples. The film starts decomposing at 200°C followed by an endothermic peak, which indicates that the film is stable up to 200°C. The DTA trace shows an endothermic peak around 288°C, which corresponds to the melting point of PVAc polymer host.

It is clear from these observations that the PVAc based composite polymer electrolytes with Al<sub>2</sub>O<sub>3</sub> as filler can be operated up to 200°C.

### Conclusions

PVAc, PVdF-co-HFP based polymer composites have been successfully prepared for different filler concentrations. The complex formation was confirmed by XRD analysis. Thermal stability of the film ascertained from TG/DTA studies. The composite membrane containing 10 wt% of Al<sub>2</sub>O<sub>3</sub> nanofiller showed better ionic conductivity ( $1.301 \times 10^{-3} \text{ S cm}^{-1}$ ) and the membrane is found to be thermally stable up to a temperature of 200°C. The nano-sized filler particle such as Al<sub>2</sub>O<sub>3</sub> that intergraded into the solid polymer electrolyte increase the mechanical strength and enhanced the ionic conductivity.

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