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CONDUCTIVITY AND FTIR STUDIES ON PVA/CHITOSAN-LiCF$_3$SO$_3$

N.A.A. Razak, T. Winie, F.S.A. Ghani and A.H. Ahmad

Institute of Sciences, Faculty of Applied Sciences, University Teknologi MARA,
40450 Shah Alam, Selangor, Malaysia

ABSTRACT

New polymer electrolytes using Chitosan and Poly(vinyl alcohol)[PVA] with different weight percent (wt%) have been prepared using solution cast technique. The low conductivity of this system (S/cm) was enhanced due to the dissociation of lithium trifluoromethanesulfonate (LiCF$_3$SO$_3$) added to the blend. The ac conductivity of the polymer electrolytes has been investigated by using impedance spectroscopy method in the frequency range of 100 kHz to 5 MHz at room temperature. Result for conductivity studies has shown that the sample with 45% lithium trifluoromethanesulfonate exhibits the highest conductivity of 1.241 x 10^{-4} S/cm at room temperature. The enhanced conductivity observed was due to complexation occurred between the Li^+ cation and the lone pair electron of the nitrogen (N) and oxygen (O) atoms present in the polymer blend. Infrared spectroscopy was employed to confirm the polymer-salt complexation.

INTRODUCTION

Studies on polymer electrolytes have attracted great interest in the effort to clarify the mechanism of conductivity enhancement in such systems. Solid polymer electrolytes in the formed of thin film has the ability to accommodate a wide range of doping compositions which enables the control of properties such as good electrode-electrolyte contact due to their flexibility and relatively high ionic conductivity. Synthetic polymer such as PEO, PVA, PMMA [1-3] and natural polymer such as cellulose and chitosan [4-5] have been used as the host polymer in polymer electrolyte. Polymer blend is one of the methods that have provided new desirable polymeric materials.

Blending chitosan with poly(vinyl alcohol) [PVA] has shown to enhance the mechanical properties as the amount of intermolecular interactions between chitosan and PVA in the blends [6-7]. Polymer-salt complexes are normally formed by dissolving an amount of salt with the host polymer in the appropriate solvent to influence the ionic conductivity based on the host polymer. The chosen salts for polymer electrolyte are those with polarizing cations and large anions of delocalized charge such as alkali metal salts, LiX with X such as BF$_4$, ClO$_4$, CF$_3$SO$_3$, Cl and etc [8-9]. In this study, the main objective is to produce and investigate a new type lithium-salt solvating polymer that is PVA/Chitosan as polymer blend doped with LiCF$_3$SO$_3$.

Corresponding Author: azizhanom@salam.uitm.edu.my

EXPERIMENTAL METHOD

PVA [Sigma Aldrich] and Chitosan [Fluka] were blended at different weight percent (wt %) and dissolved in 100 ml of 1% acetic acid solution using solution cast techniques. The mixtures were stirred with a magnetic stirrer for a day at room temperature. Different weight percent of lithium trifluoromethanesulfonate ($LiCF_3SO_3$) from Fluka was added to the polymer blends and stirred continuously until the mixture formed a homogeneous viscous liquid.

The salted polymer blend mixture was then poured into different plastic petri dishes and left to dry at room temperature. Finally, the films were left for further drying in a desiccator before any analysis was carried out. The samples were characterized by impedance spectroscopy (HIOKI 3532-50 LCR Hi Tester) in the frequency range 100 kHz to 5 MHz at room temperature. The films were sandwiched between stainless steel electrodes and held with spring-loaded contact. The electrical conductivity was calculated using the following expression:

$$\sigma = \frac{t}{R_b A}$$

where t is thickness for the sample, R_b is the bulk resistance and A is the cross-sectional area of the sample [1,10]. The bulk resistance R_b was determined from the complex impedance plot (Cole-Cole plot). FTIR spectra of the samples were obtained using Perkin Elmer FT-IR Spectrometer SPECTRUM 2000. The IR spectra were recorded in the range of 450-4500cm^{-1} with resolution of 2 cm^{-1}.

RESULTS AND DISCUSSION

Electrical Impedance Spectroscopy Analysis

Figure 1 shows the variation of conductivity as a function of wt% of salt in a PVA/Chi-$LiCF_3SO_3$ system at room temperature. The compositions of PVA/Chi-$LiCF_3SO_3$ with their weight percent and conductivity values are listed in Table 1. The conductivity of the polymer PVA/Chitosan blends was 9.87x 10^{-8} S/cm. The conductivity of the system increased to 1.280×10^{-7} S/cm when added with 5wt% of $LiCF_3SO_3$ to the polymer blend PVA/Chitosan. It can be seen from Figure 1 that the conductivity increases as the weight percent (wt %) of $LiCF_3SO_3$ increased until a maximum conductivity of 1.24×10^{-4} S/cm was achieved with 45wt% of $LiCF_3SO_3$. Further addition of the salt resulted in lower conductivity. Improvement in conductivity could be due to the occurrence of complexation and the formation of a new polymeric system.

Corresponding Author: azizhanom@salam.uitm.edu.my

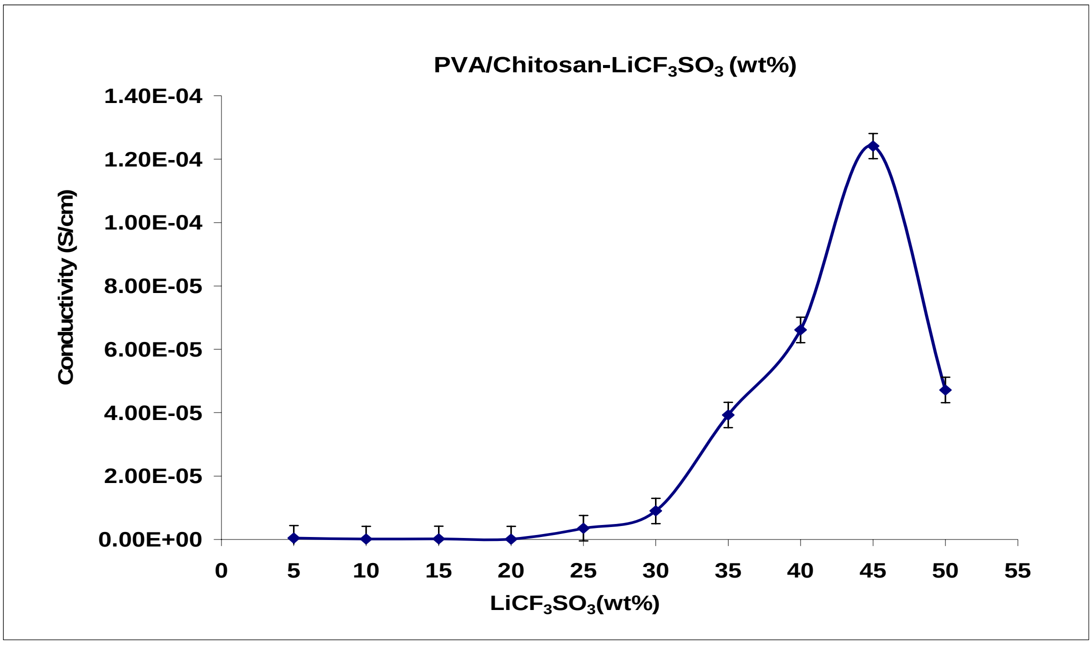

Figure 1: Variation of conductivity of PVA/Chi-$LiCF_3SO_3$ polymer electrolytes with weight percentage of $LiCF_3SO_3$ (wt %).

Table 1: Average conductivity values of PVA/Chitosan blends at room temperature

Sample	Weight percent (wt %)	Average conductivity (S/cm)
PVA/Chi-$LiCF_3SO_3$	95:5	1.280×10^{-7}
PVA/Chi-$LiCF_3SO_3$	90:10	1.452×10^{-7}
PVA/Chi-$LiCF_3SO_3$	85:15	1.913×10^{-7}
PVA/Chi-$LiCF_3SO_3$	80:20	2.583×10^{-7}
PVA/Chi-$LiCF_3SO_3$	75:25	3.527×10^{-6}
PVA/Chi-$LiCF_3SO_3$	70:30	8.996×10^{-6}
PVA/Chi-$LiCF_3SO_3$	65:35	3.928×10^{-5}
PVA/Chi-$LiCF_3SO_3$	60:40	6.614×10^{-5}
PVA/Chi-$LiCF_3SO_3$	55:45	1.241×10^{-4}
PVA/Chi-$LiCF_3SO_3$	50:50	4.716×10^{-5}

Some lithium ions (Li^+) that have enough energy provided by ac current to attach with nitrogen or oxygen atom from the chain of polymer until all the segments of the polymer are fully occupied because of the complexation process [11-12]. Here, it can be notified that the increase in the salt leads to the increase of the charge carrier and hence the ionic conductivity of the system increases until 45wt% of $LiCF_3SO_3$ [13]. However, the value of conductivity decreases to 4.716×10^{-5} S/cm when 50wt% of $LiCF_3SO_3$ was added to the blend. The aggregation phenomena occurred when more and more ionic clusters replace the charge carrier in the systems. The density of mobile ions is reduced and hence decreased the conductivity. As the amount of salt is increased to more than

Corresponding Author: azizhanom@salam.uitm.edu.my

50wt%, the mechanical stability of the film decreases and difficult to peel off from the petri dish. Therefore the sample was discarded [14-15].

Fourier Transform Infra-Red (FT-IR) Analysis

FT-IR spectroscopy has been used to identify and analyse the presence of the functional group and determine whether any interactions or complexation among the components in polymer mixtures has occurred. In order to understand the phenomena of conductivity as measured using impedance spectroscopy, further characterization of the sample using FTIR has been carried out. Figure 2 shows the spectra of the samples in the region 2500-1700 cm^{-1}. From the spectra, it can be seen that there are new peaks appeared at the wave numbers of 2460 cm^{-1}, 2340 cm^{-1}, 2220 cm^{-1} and 1940 cm^{-1}. This implies that some complexation has occurred and new phase has formed either between the salt and the nitrogen atom or oxygen atom of the amine and hydroxyl group, respectively. The broad bands between 2230 cm^{-1} to 1970 cm^{-1} in the PVA/Chitosan become shallow when the salt content added to the polymer blends was increased.

As the salt content in the sample increased, the band at 1736 cm^{-1} has shifted towards lower wave numbers. The mechanism formation in Figure 3 and Table 2 have shown that the ionic molecules could be the permanent or temporary site for lithium ion to hop at other side of molecules with low energy that gave conductivity enhancement for the system. From Figure 3, when the dissociation process happens to salt ($LiCF_3SO_3$) that provides the lithium ions (Li^+) and trifluoromethanesulfonate ions ($CF_3SO_3^-$), the formation or complexation can occurr when the lithium ion (Li^+) interacted with the oxygen from the PVA. From the literature, the chelation of cation or proton ion takes place at the amine site in chitosan [16]. This is due to the nitrogen that is more likely to donate lone pair of electrons as compared to the oxygen in the O-H bond [17-18]. The association or aggregation between ions will take place for the next process and decreased the ionic conductivity value of the system.

Table 2: Functional group and types of bonds that expected to appear from the system.

Functional of group	Types of bonds
-OH (PVA) + $-NH_2$ (Chitosan)	$C\text{-}N^{\oplus}$, $C\text{-}O^-$

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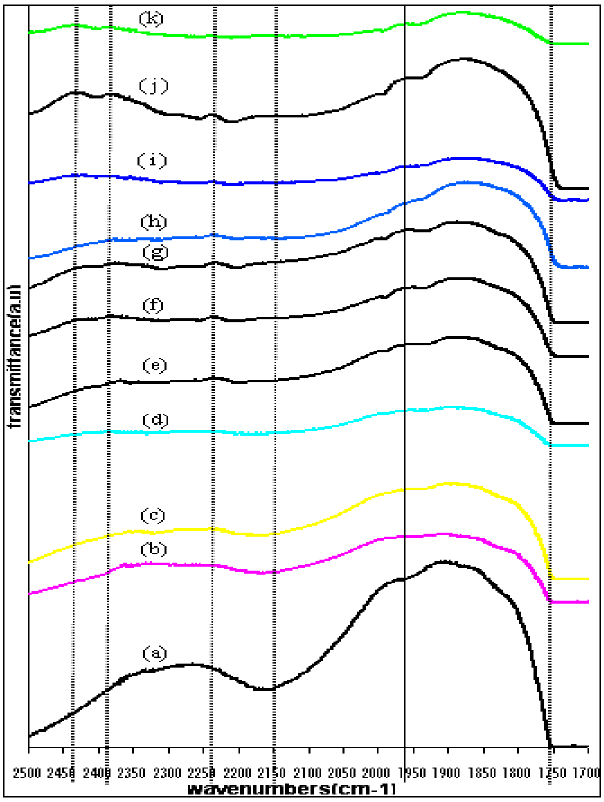

Figure 2: FTIR spectra with region from 2500-1700 cm^{-1} (a)PVA/Chi, (b)PVA/Chi-5wt%LiCF$_3$SO$_3$, (c) 10wt%, (d) 15wt%, (e) 20wt% (f) 25wt%, (g) 30wt%, (h) 35wt%, (i) 40wt%, (j) 45wt% and (k) 50wt%

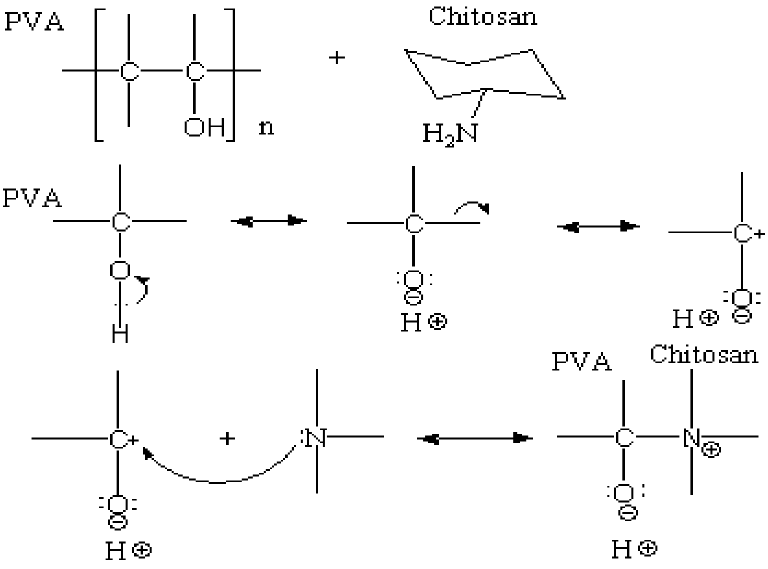

Figure 3: Mechanism formation between PVA and Chitosan blend.

Corresponding Author: azizhanom@salam.uitm.edu.my

CONCLUSION

Maximum conductivity value obtained for PVA/Chi-$LiCF_3SO_3$ polymer electrolyte system was 1.241×10^{-4} S/cm for the sample of 45wt% $LiCF_3SO_3$. Results from fourier transform infrared (FTIR) show the band at wave number 1736 cm^{-1} has shifted which implies that the complexation has occurred and a new phase has formed.

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