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Conductivity and Dielectric Behavior Studies on Solid Polymer Electrolyte Based Poly(methyl methacrylate) (PMMA) Grafted Natural Rubber (MG49) Polymer Blends

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ABSTRACT

A series of solid polymer electrolyte films, employing 49% poly(methyl methacrylate)(PMMA)-grafted natural rubber (MG49) as polymer host and lithium tertrafluoroborate ($LiBF_4$) as conducting material were prepared by solution casting technique. The films of MG49-$LiBF_4$, MG49-PMMA and MG49-Poly(vinylidene fluoride-co-hexafluoropropylene)(PVDF-HFP) at the optimum weight percentage of $LiBF_4$ (25 wt.%, 25 wt.% and 30 wt.%) respectively, were characterized using potentiostatic electrochemical impedance spectroscopy (EIS) technique to measure their impedans. The measurements were conducted at the temperature range from 303 K to 403 K. The values of dielectric constant, ε_r increases with the increase of ionic conductivity. The dielectric constant, ε_r and dielectric loss, ε_i decrease with increase in frequency at the low frequency region attributed to the electrode polarization effects, but almost negligible in the high frequency region due to frequency independent. The imaginary part, M_i of electrical modulus are observed increases with frequency. The systems are concluded as ionic conductors by the present of M_i peak in the plot M_i versus frequency. The presence of peaks at certain frequency in the tan δ versus frequency plots of the polymer electrolytes indicate the existence of relaxation of charge in all samples contributed by the ions and polar functional groups.

Keywords: Battery; energy storage; impedance spectroscopy; modified natural rubber; solid polymer electrolytes

INTRODUCTION

Battery is an electrochemical device that convert chemical energy into electrical energy by electrochemical oxidation and reduction reactions, which occur at the electrodes. Battery can be classified into two types, primary and secondary batteries. Secondary batteries can be recharged electrically after discharge, while primary batteries not capable to recharge after discharging. Almost all of commercialized secondary batteries or well known as rechargeable batteries such as lithium batteries used liquid electrolytes. The problem on the vitality of liquid electrolytes have encouraged researchers to encounter by implementing solid polymer electrolytes (SPE) into lithium polymer-ion batteries. Comparable conductivity value and stability of SPE over liquid electrolytes counterparts had shown many other advantages such as, possessing good mechanical strength and flexibility, as well as being leak free (Dias, Plomp and Veldhuis, 2000). Moreover, the dependency on petrochemical materials-based electrolyte can be reduced and will contribute to green technology in development of energy storage devices.

Solid polymer electrolyte can be defined as a membrane that has ability for transporting ions. The discovery of ionic conducting properties in polymer complexes with salts by Fenton et al. (1973) has driven to the utilization of polymer electrolytes in electrochemical devices. These solid polymer electrolytes have several advantages compared to conventional liquid electrolytes. The advantages including no internal shorting, leakage of electrolytes and non-combustible reaction products at electrode surface (Stephan, 2006). Apart from that, the preliminary studies on modified rubber as bio-based polymer electrolytes showed some appealing of physical properties such as flexible and good elasticity. Therefore, a good contact is predicted between the electrolytic layer and electrodes in energy storage device system such as battery. Ali et al. (2013) has proved that modified rubber based SPE providing ionic transport at par with liquid electrolytes in lithium ion battery. TianKhoon et al. (2015) has fabricated lithium ion battery using methyl grafted natural rubber polymer (MG49) blended with PVdF-HFP and hybrid nano oxides of ZrO_2-TiO_2 using in-*situ* sol-gel method. They obtained the highest conductivity at S cm^{-1} and battery capacity of 301 $mAhg^{-1}$, which is on par with theoretical value of lithium metal capacity. Therefore, the utilization of modified rubber as solid polymer electrolytes in lithium-ion batteries not only can replace liquid electrolyte and also may contribute to the advancements of green technology applications. based polymer electrolytes.

Some of natural rubber-based polymer, epoxidized natural rubber (ENR) and poly (methyl methacrylate)-grafted natural rubber (MG) possess good in ionic conductivity (Ahmad et al. 2012). Ataollahi et al. (2013) reported that 49% poly(methyl methacrylate)-grafted natural rubber (MG49) complexes with salts showed high conductivity around 10^{-4} S cm^{-1}. Kamisan et al. (2009) reported that modified natural rubber has distinctive characteristics such as low glass transition temperature, soft elastomeric characteristics at room temperature, good elasticity and adhesion. These characteristics make it a suitable candidate as a polymer host for polymeric system. Figure 1 shown the structure of MG49 with the existence of a polar group in their carbonyl functional group that will provide coordination sites for lithium ion conduction (Su'ait et al. 2012). Ahmad et al. (2011) reported through infrared analysis showed that the interaction between oxygen atoms and lithium ion occurred at ether (C-O-C) and carbonyl (C=O) group in the methyl methacrylate (MMA) host.

Previous studies on MG49 complexes with salts such as lithium tetrafluoroborate ($LiBF_4$), solid polymer electrolyte was prepared by solution casting technique showed significant value of ionic conductivity. Ahmad, Lien and Su'ait (2010) reported the highest ionic conductivity for MG49-$LiBF_4$ is S cm^{-1} with 25 wt.% of $LiBF_4$ salt. Then, the study made by Su'ait et al. (2011) showed the highest ionic conductivity of MG49-PMMA-$LiBF_4$ obtained at S cm^{-1} with 25 wt.% of $LiBF_4$. Ataollahi et al. (2012) successfully conducted study on MG49-PVDF-HFP-$LiBF_4$ by getting highest ionic conductivity at S cm^{-1} with 30 wt.% of $LiBF_4$. Besides that, Ahmad et al. (2011) found the highest ionic conductivity of MG49-TiO_2-$LiBF_4$ at S cm^{-1} with 25 wt.% $LiBF_4$.

Therefore, this study will involve the further analyze on ionic conductivity data of poly (methyl methacrylate)-grafted natural rubber (MG49) based solid polymer electrolyte.

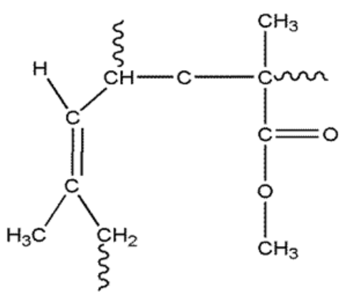


FIGURE 1. Structure of MG49 monomer
Source: Su'ait et al. (2012)

MATERIALS AND METHODS

MATERIALS

49% poly (methyl methacrylate) grafted natural rubber (MG49) also known as "MEGAPOLY" was purchased from Green HPSP (M) Sdn. Bhd. (Petaling Jaya, Malaysia). Lithium tetrafluoroborate ($LiBF_4$), poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVdF-HFP), poly (methyl methacrylate) (PMMA) were supplied by Sigma-Aldrich (St. Louis, Mo, USA). Organic solvents such acetonitrile (ACN) was supplied by Systerm ChemAR (Poland) while tetrahydrofuran (THF) ACS reagent type was purchased from J.T. Baker (USA) and acetone was provided by Sigma-Aldrich (St. Louis, Mo, USA). All of the materials were used without further purification.

PREPARATION OF SOLID POLYMER ELECTROLYTE

Three types of solid polymer electrolytes are chosen to be prepared based on their reasonable value of ionic conductivities from the previous studies (Ahmad et al. 2010, Su'ait, Ahmad & Rahman, 2009, Su'ait et al. 2012 and Ataollahi et al. 2012). All of the electrolytes are prepared by using solution casting technique as below:

1. MG49-$LiBF_4$ at 25 wt.% of $LiBF_4$ salt

1 g of MG49 in grain size was dissolved in stopped flask containing 20 mL tetrahydrofuran (THF) solvent. After 24 hours of stirring using magnetic stirrer, the solution kept on stirring for the next 24 hours until the MG49 was completely dissolved and turned into clear viscous solution. Besides that, 0.25 g of $LiBF_4$ salt was dissolved in 3 mL of acetonitrile (ACN) solution and stirred for 12 hours. Then, these two solutions was mixed together and stirred for 24 hours to obtain a homogenous solution. The electrolyte solution were then poured in Teflon petri dish and was put in fume hood at room temperature. It is to allow the solvent evaporated slowly and become a free standing film. Then, the film was further dried in vacuum oven at 50 °C for 24 hours to remove the residual solvent. The sample was stored in a desiccator before further testing.

2. MG49-PMMA- 25 wt.% of $LiBF_4$ salt

MG49 (0.3 g) was dissolved in stopped flask containing 6 mL of THF for 24 hours. Meanwhile, PMMA (0.7 g) in 14 mL of THF was stirred for 24 hours in another stopped flask. These two solutions were then mixed together for 24 hours until homogenous solution was obtained. Then, 0.25 g of $LiBF_4$ salt was dissolved in 3 mL of ACN solution and stirred for 12 hours. The salt solution was then added with polymer solution and continuously stirred for 24 hours until it become a homogeneous solution. Next, the electrolyte solution was cast in Teflon petri dish and slowly evaporated in fume hood at room temperature. After free standing film was obtained, it was further dried in vacuum oven for 24 hours at 50 °C to remove the residual solvent. The sample was stored in a desiccator before undergoes any characterization.

3. MG49-PVDF-HFP- 30 wt.% of $LiBF_4$ salt

6 mL of THF used to dissolve 0.3 g of MG49 and stirred in stopped flask for 24 hours. 0.7 g of PVDF-HFP will be

dissolved in 14 mL of acetone solvent and stirred for 24 hours. A homogeneous solution was obtained by mixing between these two solution. $LiBF_4$ salt solution was prepared by dissolving 0.3 g of $LiBF_4$ in ACN and stirred for 12 hours. Then, $LiBF_4$ solution will be added to the blend solution and further stirred for 24 hours. The blend in solid state will be obtained by casting the solution onto the Teflon petri dish, and the solvent will be allowed to slowly evaporate in a fume hood at room temperature solution. Finally, a free standing electrolyte film will be obtained after drying process in vacuum oven at 50 °C for 24 hours. The sample will be stored in desiccator until further analyzing.

ELECTRICAL ANALYSIS

Potentiostatic electrochemical impedance spectroscopy (EIS) technique was used to determine the ionic conductivity value. It was measured using VersaSTAT 4 potentiostat galvanostat by Princeton Applied Research with the frequency range of 1 MHz to 0.1 Hz at 500 mV perturbation amplitude. The measurements were conducted within temperature range from 303 K to 403 K. The disc-shaped SPE film with 2 cm diameter was sandwiched between two stainless steel as blocking electrodes. The bulk resistance (R_b) was obtained from the intercept of the real impedance (Z') axis. From the R_b value, the ionic conductivity (σ) was then calculated using the following equation:

$$\sigma = [l/(A.R_b)] \quad (1)$$

where l is the film's thickness and A is the contact area between the film and electrodes (A = 1.767 cm^2). Then, the data from the impedance measurements was used for further analysis which is dielectric studies. It is to study the dielectric behavior for the three different types of solid polymer electrolytes.

RESULTS AND DISCUSSION

TEMPERATURE DEPENDENCE ANALYSIS

Depicted in Figure 1 is the conductivity-temperature relationship for all three types of polymer electrolytes. It can be seen that, the conductivity increased with the temperature. Overall, the conductivity of MG49-PVdF-HFP-$LiBF_4$ (30 % wt.) sample took the led as the highest conductivity, followed by MG49-PMMA-$LiBF_4$ (25 % wt.) and MG49-$LiBF_4$ (25 % wt.). The differences are contributed by the percentage of salts concentration and numbers of electron lone pairs presences in each polymer segment/backbone. As understood, fluoride atom in PVdF-HFP carried three electron lone pairs, in comparison to two electron lone pairs presence at oxygen atom in methacrylate functional groups. In addition, fluoride is the most electronegative atoms and thus, act as Lewis base to interacts strongly with lithium ions as Lewis acid. In contrary, the presence of PMMA blend in MG49, has increase the dissolution ability of polymeric system towards $LiBF_4$ salts due to the additional number of methacrylate functional groups. However, at certain temperature, the conductivity. started to decrease. This is due to the removal of the trapped solvent residues in the polymer electrolytes systems hence, concentrated the electrolyte systems by reducing the mobility of charge carrier *via* ion-pairing in the solid polymer electrolytes. Sekhon, Deepa and Agnihotry (2000) observed a small decrease in conductivity at higher concentration due to the ion-pair formation. We also found out that the transport mechanism of all systems do not obey either Arrhenius or VTF behaviors.

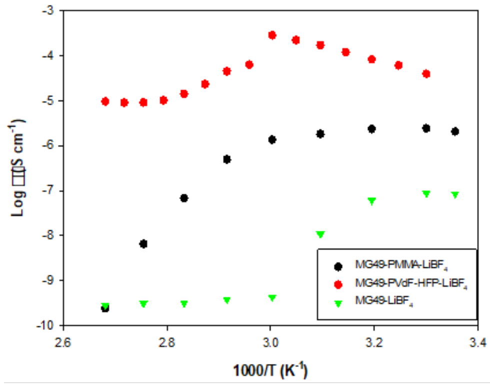


FIGURE 2. Temperature dependence on electrochemical impedance spectroscopy of MG49-$LiBF_4$ (25 % wt.), MG49-PMMA-$LiBF_4$ (25 % wt.) and MG49-PVdF-HFP (30 % wt.)

DIELECTRIC ANALYSIS

Dielectric analysis of solid polymer electrolyte is helpful to better understanding on the ion dynamics by analyzing the real and imaginary parts of complex permittivity (Das and Ghosh, 2015). Studies on relative permittivity or dielectric constant, ε^* in solid polymer electrolytes helps to understand the polarization effects at the electrode/electrolyte interface and the capability of polymer electrolyte to dissolve salts. The relative permittivity, ε^* described in complex form in a function of angular frequency that contain a real and imaginary part which are 90º out of phase. The real and imaginary components of relative permittivity was calculated as follow:

$$\varepsilon^* = 1 / j\omega C_o Z^* \quad (2)$$

$$\varepsilon^* = \varepsilon_r - j\varepsilon_i \quad (3)$$

$$\varepsilon_r = Z_i / \omega C_o (Z_r^2 + Z_i^2) \quad (4)$$

$$\varepsilon_i = Z_r / \omega C_o (Z_r^2 + Z_i^2) \quad (5)$$

where ω is angular frequency (ω = 2π*f*), C_o is vacuum capacitance ($C_o = \varepsilon_o A/l$), A is the surface contact area, (ε_o = 8.85 x 10^{-12}) is the permittivity of vacuum, l is the thickness of solid polymer electrolyte and Z^* is complex impedance where plotted in the complex plane depicted by real part of impedance (Z_r) versus imaginary part of impedance (Z_i)

plots (Nobre and Lanfredi, 2003)in the frequency range from 5 Hz to 13 MHz. Electric measurements were performed from 100 to 700 °C. Pyrochlore type phase was synthesized by the polymeric precursor method. Dense ceramic with 97% of the theoretical density was prepared by sintering via constant heating rate. The dielectric permittivity dependence as a function of frequency and temperature showed a strong dispersion at frequency lower than 10 kHz. The losses (tanδ.

Figure 2 shows the dielectric constant versus log *f* at various temperatures for all the three types of solid polymer electrolytes. The highest values of dielectric constant are observed at the highest ionic conductivity and optimum temperature of the polymer electrolytes. In the low frequency region, high values of ε_r dispersion are attributed to the dielectric polarization. At the same time, this phenomenon may be caused by electrical relaxation processes. Usually, as these solid polymer electrolytes are ionic conductor, there are two sources of dipoles which are mobile cation-anion pairs from the dissociation of salts and localized molecular polar groups caused imbalance of charges. The ions diffuse and mobile along the electric field but unable to cross the electrode-electrolyte interface due to blocking electrodes. Then, the finite trapped ions form a hetero-charge layer at the interface which will drive towards electrode polarization by increasing of the charge density. The rotation of carbonyl and ether of the polymer chain that trying to align towards the ions also contribute to the polarization effect. The high value of ε_r is also may be because the presence of ion pairs which are facilitated to do long-range movement and behave like localized dipoles in the immobilized state. These localized dipoles react to the externally applied electric field due to sufficient time and caused the increases in dielectric constant and bulk capacitance (Tripathi et al. 2018).

Dielectric constant, ε_r decreases significantly and becoming frequency independent in the high frequency region. There is almost no excess ion diffusion in the direction of electric field due to the periodic reversal of electric fields happens extremely fast. Therefore, the translation of charge carriers and orientation of dipoles in the polymer chain difficult to occur (Woo, Majid and Arof 2012)the frequency dependence of dielectric and electric modulus as well as morphological characteristics of poly (??-caprolactone.

DIELECTRIC LOSS ANALYSIS

The studies on dielectric loss is crucial for determining the compatibility of polymer electrolyte for energy storage applications. Figure 3 shows the dielectric loss versus log *f* of the solid polymer electrolytes. The plot shows that it follows the same trend as the conductivity and dielectric constant studies at various temperature. The translational of ions and dipole orientation present in the electrolyte systems shows the effect of inertia as it contains mass. The phenomenon is caused by the motion processes under the stimulation of AC polarity. cause the effect of inertial as both have mass. As expected, the electrolyte systems show the effect of inertia as it has mass. The amount of energy loss caused by internal friction during the translation and dipole orientation demonstrate in dielectric loss (Basri and Mohamed, 2009). It has been proved by the highest energy loss with the highest ionic conductivity at optimum temperature. The energy loss determined during the conduction process at low frequency.

ELECTRIC MODULUS ANALYSIS

The electric modulus analysis used to study the ionic transport dynamic and analyze the electrical relaxation processes. The electric modulus equations are given by the relationship of relative permittivity and impedance as follow:

$$M^* = M_r + jM_i \tag{6}$$

$$M^* = j\omega C_o Z^* = j\omega C_o Z_i + j\omega C_o Z_r \tag{7}$$

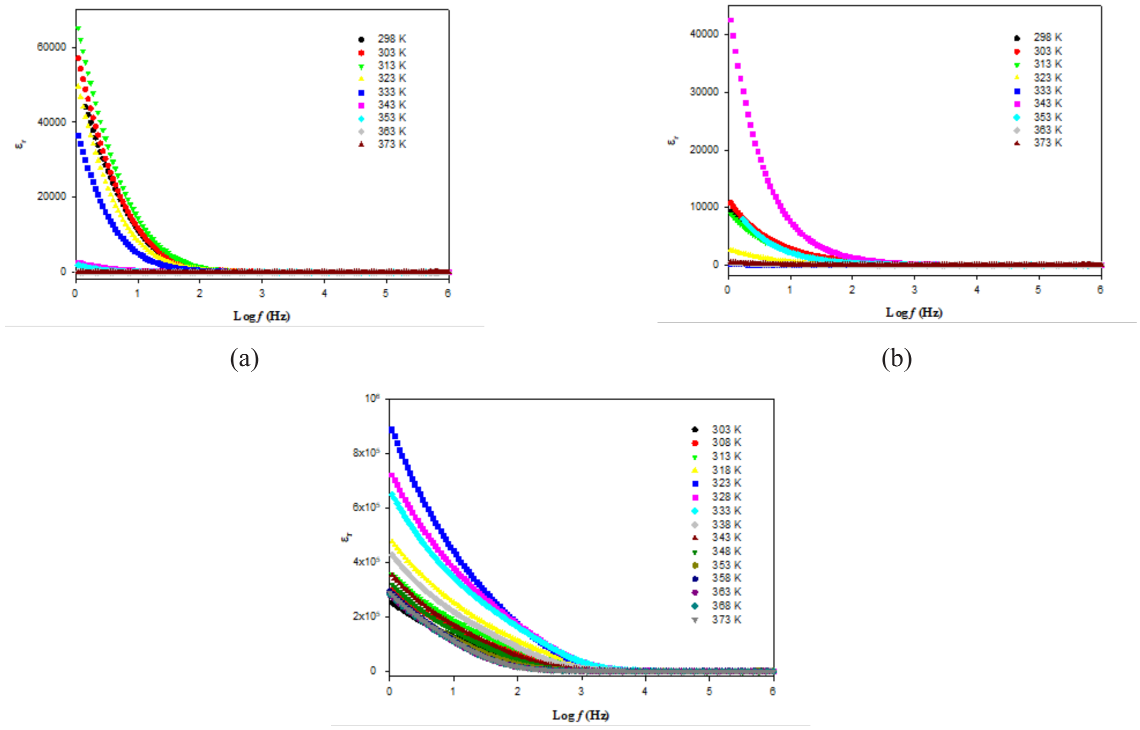
Figure 4 shows the plot M_i versus Log *f* at various temperature. It can be observed, M_i approach zero at low frequency. It is contributed by the large capacitance due to the electrode polarization (Govindaraj et al. 1995). The value of M_i also can be seen that it is increase with frequency at high frequency region and form sigmoidal shape. It indicates that the polymer electrolytes systems are ionic conductors. However, the peak of M_i in Figure 4(c) cannot be seen and are expected to clearly presence at higher frequency.

TANGENT LOSS ANALYSIS

Figure 5 shows the variation of tangent loss with frequency at different temperatures. The loss tangent, tan δ can be determined from equation (9).

$$\tan \delta = \varepsilon_i / \varepsilon_r \tag{8}$$

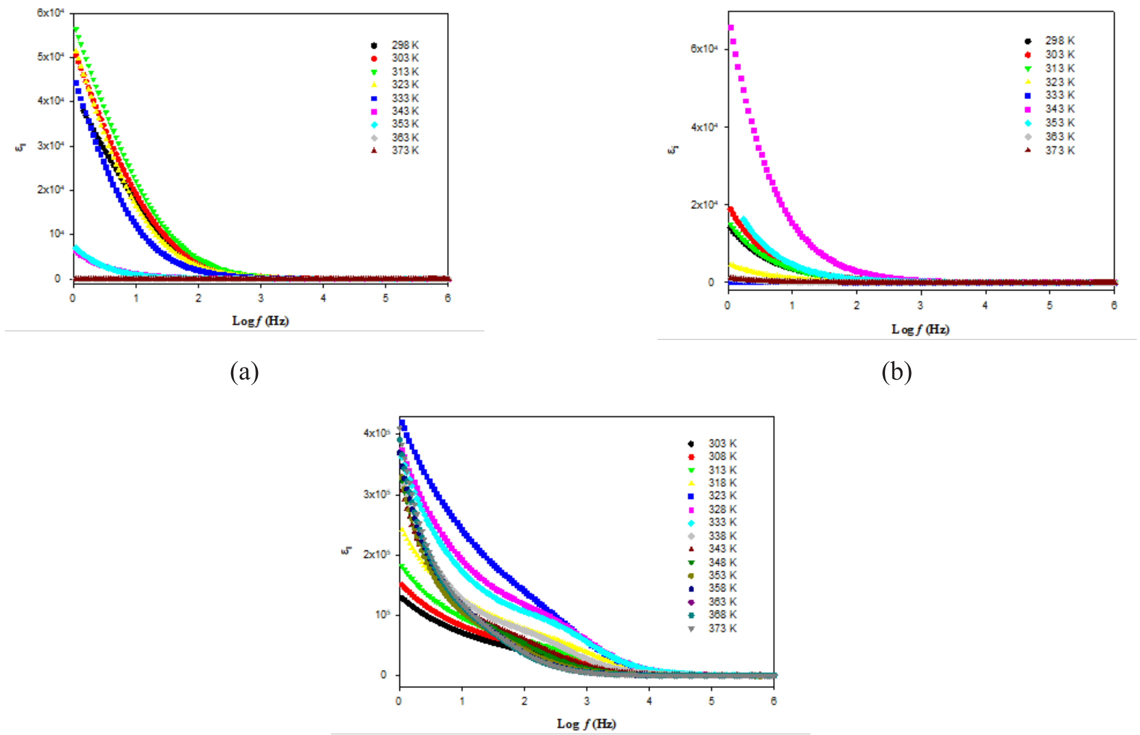
The presence of peaks at certain frequency of the polymer electrolytes indicate the existence of relaxing poles in all samples. The increasing of tan δ with frequency at low frequency region due to the predominant of active component (ohmic) than the reactive component (capacitive). At higher frequency, tan δ behavior become vice versa because of the independence ohmic portion toward frequency and the reactive component get bigger with the frequency (Chopra et al. 2003). The shifting of relaxation peaks towards high frequency indicates the decrease of relaxation time and thus, increase the charge transfer dynamics. From the Figure 5, as the temperature increases, the relaxation time will be shifted to the high frequency side until optimum temperature which most efficient charge transport. After the optimum temperature, the relaxation peaks shifted towards low frequency and increase relaxation time caused by the decrease of space charge. This phenomenon will restrict the movement of charge and segmental motion of the polymer (Arya and Sharma 2018)we have studied the structural, microstructural, electrical, dielectric properties



(a) (b)

(c)

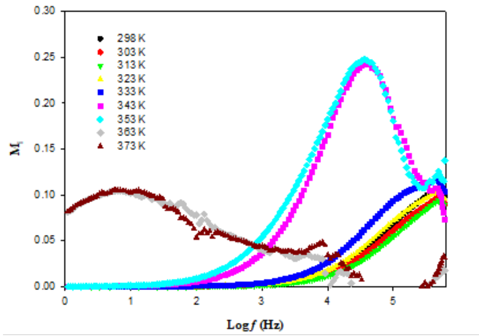
FIGURE 3. Frequency dependence of dielectric constant, ε_r of (a) MG49-LiBF$_4$ (25 % wt.) (b) MG49-PMMA-LiBF$_4$ (25 % wt.) (c) MG49-PVdF-HFP (30 % wt.)



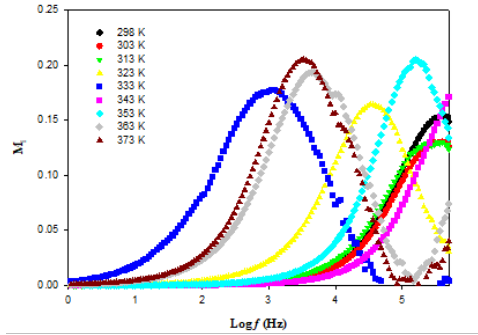
(a) (b)

(c)

FIGURE 4. Frequency dependence of dielectric loss, ε_i of (a) MG49-LiBF$_4$ (25 % wt.) (b) MG49-PMMA-LiBF$_4$ (25 % wt.) (c) MG49-PVdF-HFP (30 % wt.)



(a)



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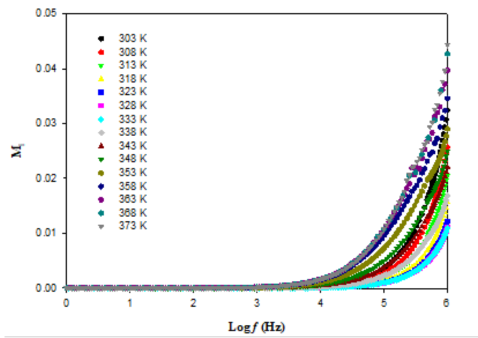
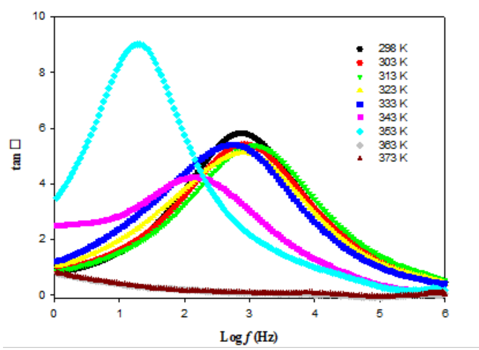
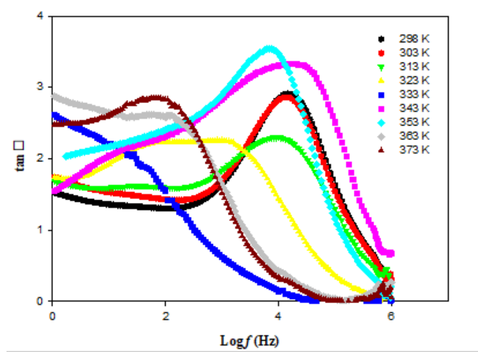


(c)

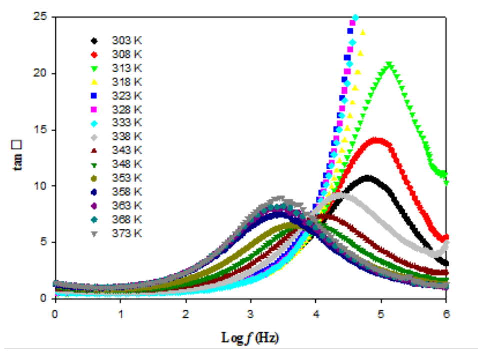
FIGURE 4. Frequency dependence of electric modulus of (a) MG49-$LiBF_4$ (25 % wt.) (b) MG49-PMMA-$LiBF_4$ (25 % wt.) (c) MG49-PVdF-HFP (30 % wt.)



(a)



(b)



(c)

FIGURE 5. Frequency dependence of tangent loss of (a) MG49-$LiBF_4$ (25 % wt.) (b) MG49-PMMA-$LiBF_4$ (25 % wt.) (c) MG49-PVdF-HFP (30 % wt.)

and ion dynamics of a sodium-ion-conducting solid polymer electrolyte film comprising PEO8-NaPF6+ x wt. % succinonitrile. The structural and surface morphology properties have been investigated, respectively using x-ray diffraction and field emission scanning electron microscopy. The complex formation was examined using Fourier transform infrared spectroscopy, and the fraction of free anions/ion pairs obtained via deconvolution. The complex dielectric permittivity and loss tangent has been analyzed across the whole frequency window, and enables us to estimate the DC conductivity, dielectric strength, double layer capacitance and relaxation time. The presence of relaxing dipoles was determined by the addition of succinonitrile (wt./wt..

CONCLUSION

The decrease of ionic conductivity at certain temperature is because of the solvent residue in polymer electrolytes systems begin to evaporate. The values of dielectric constant, ε_r were found to increase with the increase of ionic conductivity. The optimum temperature with the highest charge transport indicated the highest values of dielectric constant and dielectric loss. The temperature with the optimum charge transfer showed the lowest relaxation time. The systems are concluded as ionic conductors by the present of M_i peak.

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DECLARATION OF COMPETING INTEREST

None.

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