Effect of plasticizers on ionic conductivity and dielectric relaxation of PEO-LiClO$_4$ polymer electrolyte

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A B S T R A C T  
In this paper, we report the effect of different plasticizers, such as polyethylene glycol, propylene carbonate, ethylene carbonate and dimethyl carbonate on the ionic conductivity and dielectric relaxation of PEO-LiClO$_4$ solid polymer electrolytes. The highest ionic conductivity is obtained for polymer electrolyte plasticized with polyethylene glycol. The temperature dependence of ionic conductivity follows the well known Vogel–Tamman–Fulcher relation which indicates a strong coupling of ionic and segmental motions for all compositions. The experimental data for the complex dielectric permittivity and electric modulus have been studied using Havriliak–Negami function for the understanding of ion dynamics. Maximum dielectric strength is obtained for polymer electrolyte plasticized with polyethylene glycol. The modulus data have been analyzed using non-exponential Kohlrausch–Williams–Watts (KWW) function. It is observed that the non-exponential parameter $\beta$ is quite lower than unity, suggesting highly a non-exponential relaxation exists in these materials. The temperature dependence of relaxation times obtained from dielectric and modulus formalisms also follow Vogel–Tamman–Fulcher relation for all plasticizers in the compositions.

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1. Introduction

Solid polymer electrolytes are technologically important materials for electrochemical devices [1–3]. Basically, a polymer electrolyte consists of a host polymer (such as polyethylene oxide) doped with an alkali salt (such as LiClO$_4$). The mechanical and electrical properties of the polymer electrolytes are controlled by both the host polymers and dopant salts. At room temperature, the host polymers are generally biphasic consisting of both amorphous and crystalline phases [4]. It is well known that ionic conduction occurs mainly in the amorphous phase. There are many techniques, such as inclusion of nanoparticles, doping of ionic liquid, etc. for enhancement of the amorphous phase and hence for the improvement of the ionic conductivity of polymer electrolytes [5–8]. Plasticization is also an important way to improve ionic conductivity. Plasticization occurs when organic compounds with low molecular weight and high dielectric constant are added to polymer matrix [9–13]. Recently, there is a great attention for the study of ion transport in these polymer electrolytes. Ion transport in these polymer electrolytes is not only controlled by ionic motion, but also coupled with segmental motion of host polymers [14]. A study of ion transport mechanism in polymer electrolytes is a great challenge from scientific viewpoint due to the intrinsic complexity of coupled motion. The impedance spectroscopy has been widely used to get insight into ion transport in ion-conducting materials. Impedance spectroscopy data can be expressed as different representations such as ac conductivity, dielectric permittivity, electric modulus, etc.

In this work, we have studied ionic conductivity and dielectric properties of PEO-LiClO$_4$ polymer electrolytes containing different plasticizers such as polyethylene glycol (PEG), propylene carbonate (PC), ethylene carbonate (EC) and dimethyl carbonate (DMC).

2. Experimental technique

2.1. Materials

PEO (MW = 400000), LiClO$_4$, PEG, EC, PC and DMC were purchased from Sigma-Aldrich. PEO and LiClO$_4$ were dried in vacuum prior to use. Acetonitrile, also purchased from Sigma-Aldrich, was used as a solvent.

2.2. Preparation of solid polymer electrolytes

For preparation of solid polymer electrolytes, the molar ratio of ethylene oxide segments to lithium ions was kept at EO/Li = 18.
Appropriate amounts of PEO and LiClO₄ were dissolved in acetonitrile and stirred in a magnetic stirrer. The solution became thick after 24 hours due to evaporation of the solvent. The solution was then cast in a PTFE container and kept for 24 hours for normal evaporation. At last it was dried for 36 hours at 50 °C in vacuum to form free standing homogeneous film. For the preparation of plasticized polymer electrolytes, a fixed amount (30 wt.%) of PEG, PC, EC and DMC was added separately to the solution of PEO and LiClO₄ in acetonitrile under stirring condition. The same technique as stated above was followed to get films of thickness in the range from 0.2 mm to 0.4 mm.

2.3. Impedance spectroscopy

The measurements of capacitance and conductance of the dried films were carried out in a RLC meter (Quad Tech, model 7600) in the frequency range 10Hz–2 MHz in vacuum and in a wide temperature range with a temperature stability of ±0.10 K. For the electrical impedance measurement the samples were sandwiched between two stainless steel blocking electrodes of a conductivity cell and kept under vacuum (0.01 mbar) condition to avoid moisture. The ionic conductivity of the films was obtained from the complex impedance plots. The conductivity (σ) of the films was calculated using the relation \( \sigma = L/(R_bA) \), where L is the thickness of films, A is the effective contact area of the electrodes and \( R_b \) is the bulk resistance obtained from the complex impedance plots.

2.4. Field emission scanning electron microscopy (FE-SEM)

The surface morphology of the platinum-coated polymer films was studied using a field emission scanning electron microscope (JEOL, model JSM-6700F).

3. Results and discussion

3.1. Surface morphology

Fig. 1 shows FE-SEM images for different plasticized polymer electrolytes at different magnifications. The SEM images show the existence of crystalline and amorphous regions. The images with micro-pores are commonly observed due to fast evaporation of acetonitrile during solution cast method. Reduction of crystalline phase in PEO is associated with the smooth surface morphology of the polymer electrolyte through the interaction between ether oxygen of PEO and Li⁺ ions. It is observed that surface morphology becomes smooth for polymer electrolyte plasticized with PEG compared to other plasticized electrolytes.

3.2. Ionic conductivity

The variation of ionic conductivity (σ) for PEO-LiClO₄-30 wt.% (PC, EC, DMC, PEG) polymer electrolytes with the reciprocal temperature is shown in Fig. 2(a). It is noted that the plots in

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**Fig. 1.** FE-SEM images of (a) PEO-LiClO₄ (b) PEO-LiClO₄-30 wt.% EC (c) PEO-LiClO₄-30 wt.% DMC (d) PEO-LiClO₄-30 wt.% PEG polymer electrolytes.
3.3. Ac conductivity spectra

The frequency dependence of the ac conductivity at different temperatures for PEO-LiClO₄-30 wt.% PEG electrolyte is shown in Fig. 3. It is observed that in the low frequency region the conductivity is independent of frequency and corresponds to the dc ionic conductivity for all compositions and temperatures. However, the dispersion of the conductivity starts at higher frequencies, indicating that a crossover from the dc ionic to the dispersive conductivity occurs at a particular frequency called crossover frequency. It is further noted that the crossover frequency shifts towards higher frequencies as the temperature is increased. Other plasticized polymer electrolytes also showed similar frequency dependence.

The ac conductivity data for different electrolytes has been analyzed in the framework of the power law formalism [18,19]. In this formalism, the frequency dependent conductivity is given by

$$\sigma'(\omega) = \sigma[1+(\omega/\omega_c)^n]$$

(2)

where $\sigma$ is the ionic conductivity, $\omega_c$ is the crossover frequency, and $n$ is the power law exponent. The value of $n$ is usually in the range, $0 < n < 1$. We have fitted the frequency dependent conductivity data to Eq. (2) using $\sigma$, $\omega_c$ and $n$ as variable parameters. The values of the parameters $\sigma$, $\omega_c$ and $n$ obtained at 298 K from the best fits are listed in Table 1. It is observed that higher dc conductivity is associated to higher crossover frequency which is maximum for polymer electrolyte plasticized with PEG. The charge transport mechanism is related to the hopping of Li⁺ ions from one site to another favourable site. It is also noted that the value of $n$ is less than unity.

### Table 1

<table>
<thead>
<tr>
<th>Plasticizer</th>
<th>$E_a$ (eV) ($\pm0.002$)</th>
<th>$T_0$ (K) ($\pm2$)</th>
<th>$\log_{10}(\sigma)$ ($\Omega^{-1} \text{cm}^{-1}$) at $T = 298$ K ($\pm0.04$)</th>
<th>$\log_{10}(\omega_c)$ (rad s$^{-1}$) at $T = 298$ K ($\pm0.04$)</th>
<th>$n$ ($\pm0.01$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO-LiClO₄</td>
<td>0.094</td>
<td>174</td>
<td>-5.82</td>
<td>6.56</td>
<td>0.58</td>
</tr>
<tr>
<td>EC</td>
<td>0.140</td>
<td>151</td>
<td>-5.54</td>
<td>7.06</td>
<td>0.64</td>
</tr>
<tr>
<td>PC</td>
<td>0.074</td>
<td>171</td>
<td>-4.84</td>
<td>7.25</td>
<td>0.54</td>
</tr>
<tr>
<td>PEG</td>
<td>0.063</td>
<td>174</td>
<td>-4.71</td>
<td>8.63</td>
<td>0.65</td>
</tr>
<tr>
<td>DMC</td>
<td>0.163</td>
<td>156</td>
<td>-6.32</td>
<td>6.53</td>
<td>0.64</td>
</tr>
</tbody>
</table>

Fig. 2(a) for all plasticizers follow Vogel-Tamman-Fulcher (VTF) empirical formula given by [15–17]

$$\sigma = \sigma_0 T^{-\frac{1}{2}} \exp \left[\frac{-E_a}{k_B (T-T_0)}\right]$$

(1)

where $\sigma_0$ is a pre-exponential factor, $k_B$ is the Boltzmann scaling temperature, $E_a$ is the pseudo activation barrier related to the critical free volume for ion transport, $T_0$ is the Vogel scaling temperature, where the configuration entropy or the critical volume becomes zero and $T$ is the absolute temperature. The excellent fits of the conductivity data presented in Fig. 2(a) to VTF formula are obtained in the entire temperature range, indicating clearly that the motion of Li⁺ ions is coupled with the polymer segmental motion in all polymer electrolytes. The values of the ionic conductivity at 298 K and the parameters obtained from VTF fits are shown in Table 1. It is noted in Table 1 that the activation energy $E_a$ exhibits a minimum and the ionic conductivity a maximum for polymer electrolytes plasticized with PEG. The addition of DMAC, which has lower dielectric constant ($\varepsilon = 3.1$) than PEO ($\varepsilon = 5$), has no effect on the enhancement of the conductivity for PEO-LiClO₄ electrolyte. But the plasticizers EC, PC and PEG have dielectric constants of 89.78, 66.14 and 12.4 respectively, which are higher than that of PEO and their ionic conductivity is higher than that of PEO-LiClO₄ electrolyte. Thus, it can be concluded that value of dielectric constant of a plasticizer should be higher than that of the polymer used, otherwise it shows anti-plasticization effect. The higher value of dielectric constant dissociates ion aggregates and thus helps in increasing the ionic conductivity.
The dielectric relaxation is often studied in terms of a frequency dependent complex dielectric permittivity given by

$$\epsilon^{\prime}(\omega) = \epsilon^{\prime \infty} - j\epsilon''(\omega)$$  \hspace{1cm} (3)$$

where $\epsilon^{\prime}$ and $\epsilon''$ are the real and imaginary parts of the dielectric permittivity, known as dielectric constant and dielectric loss respectively. Figs. 4(a) and 4(b) show frequency dependent dielectric constant and loss respectively at several temperatures for the polymer electrolyte plasticized with EC. It is observed in Fig. 4(a) that at lower frequencies the high dielectric constant value corresponds to space charge polarisation near electrode-electrolyte interface and at higher frequencies shows a labelling-off denoted as $\epsilon^{\prime \infty}$, which arises from the rapid polarization of atoms and electrons when a time dependent electric field is applied.

An extra term $\frac{1}{\omega^p}$ is added to Eq. (6) to account for the contribution of electrode polarization as the dielectric relaxation peaks due to permanent dipoles are concealed by polarization of mobile ions in polymer material. The value of $p$ is between 0 and 1 and the unity value of $p$ corresponds to ideal Ohmic behaviour. The solid lines in Figs. 4(a) and 4(b) are the best fits for $\epsilon^{\prime}(\omega)$ and $\epsilon''(\omega)$ given by Eqs. (5) and (6) respectively to the experimental data. The parameters such as $\Delta \epsilon = \epsilon^{\prime \infty} - \epsilon_0$, $\alpha_{HN}$, $\gamma_{HN}$ and exponent $p$ obtained from the best fits are given in Table 2 for different compositions. The value of $p$ is less than unity, indicating a divergence from ideal Ohmic behaviour in the polymer electrolytes. In the inset of Fig. 4(b) the contribution of the ionic conductivity is shown by solid lines, while that of relaxation by the dotted lines. Similar behaviour is also observed for all other compositions. It is observed in Table 2 that the dielectric strength obtained for PEG plasticized polymer electrolyte is higher than those composition containing other plasticizers.

<table>
<thead>
<tr>
<th>Plasticizer (30 wt.%)</th>
<th>$\Delta \epsilon = \epsilon^{\prime \infty} - \epsilon_0$</th>
<th>$\alpha_{HN}$</th>
<th>$\gamma_{HN}$</th>
<th>$p$</th>
<th>$E_0$ (eV)</th>
<th>$T_0$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO-LiClO$_4$</td>
<td>19</td>
<td>0.86</td>
<td>0.52</td>
<td>0.89</td>
<td>0.040</td>
<td>192</td>
</tr>
<tr>
<td>EC</td>
<td>27</td>
<td>0.81</td>
<td>0.55</td>
<td>0.84</td>
<td>0.043</td>
<td>207</td>
</tr>
<tr>
<td>PC</td>
<td>21</td>
<td>0.76</td>
<td>0.54</td>
<td>0.95</td>
<td>0.016</td>
<td>211</td>
</tr>
<tr>
<td>PEG</td>
<td>40</td>
<td>0.79</td>
<td>0.61</td>
<td>0.90</td>
<td>0.072</td>
<td>173</td>
</tr>
<tr>
<td>DMC</td>
<td>14</td>
<td>0.65</td>
<td>0.62</td>
<td>0.96</td>
<td>0.061</td>
<td>189</td>
</tr>
</tbody>
</table>

**Fig. 4.** Frequency dependence of (a) dielectric constant $\epsilon^{\prime}(\omega)$ and (b) dielectric loss $\epsilon''(\omega)$ at several temperatures for PEO-LiClO$_4$-30 wt.% EC respectively. Frequency dependence of $\epsilon^{\prime}(\omega)$ for different plasticized polymer electrolytes at 298 K is shown in the inset of Fig. 4(a). The contributions of the conductivity and dielectric relaxation at 258 K are shown by solid and dotted lines respectively in the inset of 4(b).

3.4. Dielectric relaxation

The dielectric relaxation is often studied in terms of a frequency dependent complex dielectric permittivity given by

$$\epsilon^{\prime}(\omega) = \epsilon^{\prime \infty} + \frac{1}{1 + (\omega \tau_{HN})^\gamma_{HN}}$$  \hspace{1cm} (4)$$

where $\epsilon_0$ and $\epsilon^{\prime \infty}$ are the static and high frequency dielectric constants respectively, $\tau_{HN}$ is the relaxation time and $\alpha_{HN}$ and $\gamma_{HN}$ are the shape parameters with condition $0 < \alpha_{HN} < 1$ and $0 < \gamma_{HN} < 1$. Ideal Debye relaxation is obtained, when shape parameters are unity and the non-zero value corresponds to a distribution of relaxation time.

The real and imaginary parts of $\epsilon^{\prime}(\omega)$ are respectively expressed as,

$$\epsilon^{\prime}(\omega) = \epsilon_0 + \frac{1 + 2(\omega\tau_{HN})^{\alpha_{HN}} \cos(\alpha_{HN}\pi/2) + (\omega\tau_{HN})^{2\alpha_{HN}}}{\sin(\alpha_{HN}\pi/2) + \cos(\alpha_{HN}\pi/2)}$$  \hspace{1cm} (5)$$

and

$$\epsilon''(\omega) = (\epsilon_0 - \epsilon^{\prime \infty}) \left[ \frac{1 + 2(\omega\tau_{HN})^{\alpha_{HN}} \cos(\alpha_{HN}\pi/2) + (\omega\tau_{HN})^{2\alpha_{HN}}}{\sin(\alpha_{HN}\pi/2) + \cos(\alpha_{HN}\pi/2)} \right]^{\gamma_{HN}/2}$$  \hspace{1cm} (6)$$

An extra term $\frac{1}{\omega^p}$ is added to Eq. (6) to account for the contribution of electrode polarization as the dielectric relaxation peaks due to permanent dipoles are concealed by polarization of mobile ions in polymer material. The value of $p$ is between 0 and 1 and the unity value of $p$ corresponds to ideal Ohmic behaviour. The solid lines in Figs. 4(a) and 4(b) are the best fits for $\epsilon^{\prime}(\omega)$ and $\epsilon''(\omega)$ given by Eqs. (5) and (6) respectively to the experimental data. The parameters such as $\Delta \epsilon = \epsilon^{\prime \infty} - \epsilon_0$, $\alpha_{HN}$, $\gamma_{HN}$ and exponent $p$ obtained from the best fits are given in Table 2 for different compositions. The value of $p$ is less than unity, indicating a divergence from ideal Ohmic behaviour in the polymer electrolytes. In the inset of Fig. 4(b) the contribution of the ionic conductivity is shown by solid lines, while that of relaxation by the dotted lines. Similar behaviour is also observed for all other compositions. It is observed in Table 2 that the dielectric strength obtained for PEG plasticized polymer electrolyte is higher than those composition containing other plasticizers.

**Table 2** Dielectric strength ($\epsilon_0$, $\epsilon^{\prime \infty}$, $\alpha_{HN}$ and $\gamma_{HN}$, $p$, $E_0$ and $T_0$ obtained from VTF fits for relaxation time for PEO-LiClO$_4$ electrolytes with 30 wt.% plasticizers.

<table>
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<th>Plasticizer (30 wt.%)</th>
<th>$\Delta \epsilon = \epsilon^{\prime \infty} - \epsilon_0$</th>
<th>$\alpha_{HN}$</th>
<th>$\gamma_{HN}$</th>
<th>$p$</th>
<th>$E_0$ (eV)</th>
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<td>0.62</td>
<td>0.96</td>
<td>0.061</td>
<td>189</td>
</tr>
</tbody>
</table>
that variation of dielectric strength is in the order \((\Delta \varepsilon)_{\text{PEG}} > (\Delta \varepsilon)_{\text{PC}} > (\Delta \varepsilon)_{\text{EC}} > (\Delta \varepsilon)_{\text{DMC}} \) \( [(\Delta \varepsilon)_{\text{D}}\) is the dielectric strength without plasticizers]. The inverse of dielectric relaxation time \(\tau_{\text{HN}}\) is plotted with reciprocal temperature in Fig. 5. It is observed that the temperature dependent relaxation time \(\tau_{\text{HN}}\) is well fitted to VTF function and parameters obtained from the best fits are listed in Table 2. The relaxation time decreases due to faster segmental motion coupled with mobile ions for polymer electrolyte plasticized with PEG compared to other plasticizers.

### 3.5. Electric modulus

Ion transport in the polymer electrolytes has been further studied using electric modulus formalism. Interfacial polarization which is masked by the conductivity arises from the additive in conducting polymers and the dielectric permittivity is also high at low frequencies. To overcome this difficulty, the electric modulus has been used to investigate and understand conductivity relaxation mechanism. In the modulus formalism [22], an electric modulus \(M^*\) is defined as the inverse of the complex dielectric permittivity \(\varepsilon^*\)

\[
M^*(\omega) = \frac{1}{\varepsilon^*(\omega)} = M' + iM'' = \frac{\varepsilon' - \varepsilon''}{\varepsilon'^2 + \varepsilon''^2} + \frac{i\varepsilon''}{\varepsilon'^2 + \varepsilon''^2}
\]

where \(M'\) and \(M''\) are the real and imaginary parts of the complex modulus \(M^*\). The frequency dependence of \(M'\) and \(M''\) spectra at different temperatures for PEO- LiClO₄-30 wt.% EC electrolyte is depicted in Figs. 6(a) and 6(b) respectively. It is observed that the real modulus \(M'\) shows dispersion as the frequency is increased and tends to saturate at \(M'_s\) for higher frequencies. The imaginary modulus \(M''\) exhibits a single relaxation peak which shifts towards higher frequencies with increasing temperature. At higher frequencies \((10^4\text{ Hz})\), the peak shifts because increase in temperature results in faster ionic motion, leading to decrease in relaxation time. Thus, the charge carriers are thermally activated. The frequency of the peak of \(M'\) spectra corresponds to the conductivity relaxation frequency \(\omega_m\). The conductivity relaxation time \(\tau_{\omega_m}\) is obtained from the relation \(\omega_m \tau_{\omega_m} = 1\) [22]. We also observe in Fig. 6(b) that \(M''\) spectra are much broader than what is expected for the ideal Debye peak and show asymmetric and skewed towards the high frequency sides of the maxima. Such a broad nature of the peak may be taken as a consequence of the distribution of relaxation times and is an indication of the non-Debye type relaxation. The temperature and frequency dependence of \(M'\) and \(M''\) for other samples also shows similar nature.

To study the non-Debye relaxation, we have used the empirical Havriliak - Negami equation [20,23,24] given by

\[
M^*(\omega) = M_\infty + (M_s - M_\infty) \left[ \frac{1}{1 + (i\omega \tau_{\text{HN}})^{\alpha_{\text{HN}}}} \right] ^\beta
\]

where \(M_s\) and \(M_\infty\) are respectively the high frequency and low frequency limiting values of electric modulus, \(\tau_{\text{HN}}\) is the relaxation time, \(\alpha_{\text{HN}}\) and \(\gamma_{\text{HN}}\) are the shape parameters which describe the symmetric and asymmetric broadening respectively of the

### Table 3

<table>
<thead>
<tr>
<th>Plasticizer (30 wt.%)</th>
<th>(\log_{10} (\tau_{\text{HN}})) (s)</th>
<th>(\alpha_{\text{HN}})</th>
<th>(\gamma_{\text{HN}})</th>
<th>(\beta)</th>
<th>(E_a) (eV)</th>
<th>(T_0) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO-LiClO₄</td>
<td>-4.44</td>
<td>0.74</td>
<td>0.43</td>
<td>0.39</td>
<td>0.029</td>
<td>207</td>
</tr>
<tr>
<td>EC</td>
<td>-4.58</td>
<td>0.80</td>
<td>0.37</td>
<td>0.39</td>
<td>0.051</td>
<td>188</td>
</tr>
<tr>
<td>PC</td>
<td>-5.82</td>
<td>0.88</td>
<td>0.35</td>
<td>0.41</td>
<td>0.040</td>
<td>188</td>
</tr>
<tr>
<td>PEG</td>
<td>-3.68</td>
<td>0.86</td>
<td>0.38</td>
<td>0.42</td>
<td>0.098</td>
<td>179</td>
</tr>
<tr>
<td>DMC</td>
<td>-5.91</td>
<td>0.81</td>
<td>0.19</td>
<td>0.27</td>
<td>0.027</td>
<td>194</td>
</tr>
</tbody>
</table>

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Fig. 5. Reciprocal temperature dependence of the relaxation time \(\tau_{\text{HN}}\) obtained from dielectric relaxation for different plasticized PEO-LiClO₄ electrolytes. Solid lines are fits of experimental data to VTF formalism given in Eq. (1).

Fig. 6. Frequency dependence of (a) real part \((M')\) and (b) imaginary part \((M'')\) of complex electric modulus \(M^*\) for PEO-LiClO₄-30 wt.% EC electrolytes. The solid lines are fits of the experimental data to Eq. (8).
isothermal modulus peak, such that $0 < \alpha_{hn} \leq 1$ and $0 < \gamma_{hn} \leq 1$. In Figs. 6(a) and 6(b) we have shown fits of the experimental data for $M'$ and $M''$ to the real and imaginary parts of Eq. (8). The parameters obtained from the best fits are shown in Table 3. The inverse of relaxation time $\tau_{0M}$ is plotted with reciprocal temperature in Fig. 7(a). It is noted that the VTF function similar to Eq. (1) has been fitted well to the temperature dependence of the relaxation time $\tau_{0M}$. The variation of $\alpha_{hn}$ and $\gamma_{hn}$ with temperature is shown in Fig. 7(b) for EC plasticized polymer electrolytes. It may be noted that the values of $\alpha_{hn}$ and $\gamma_{hn}$ are almost independent of temperature and composition except at higher temperatures.

The complex modulus $M^*(\omega)$ can be expressed in terms of Fourier transform of a decay function $\Phi(t)$ as given below [23]

$$M^*(\omega) = M_\infty [1 - \int_0^\infty e^{-i\omega t} \frac{d\Phi(t)}{dt} dt]$$  \(\text{(9)}\)

where $\Phi(t)$ is the relaxation function giving the time evolution of the electric field in time domain given by, $E(t) = E(0)\Phi(t)$ within the materials. For ideal Debye case, $\Phi(t)$ shows an exponential nature. But in the case of non-Debye type behaviour, $\Phi(t)$ is approximated by a stretched exponential Kohlrausch–Williams–Watts (KWW) function [25,26] given by

$$\Phi(t) \approx \exp \left[-\left(\frac{t}{\tau_{\text{KWW}}}\right)^n\right]$$  \(\text{(10)}\)

where $\beta$ is the stretched exponent lying between 0 to 1 and its value is unity for the ideal Debye relaxation. Smaller is the value of $\beta$, greater is the deviation from the Debye type relaxation. The function $\Phi(t)$ in the time domain can be calculated using the inverse transform of Eq. (9) given by

$$\Phi(t) = \frac{2}{\pi} \int_0^\infty \frac{M'}{\omega M_\infty} \cos(\omega t) d\omega$$  \(\text{(11)}\)

We have shown in Fig. 8 (a) the experimental decay curve obtained from Eq. (10) for the PEO-LiClO$_4$-30 wt.% PC polymer electrolyte. The decay curves are fitted with KWW function and the values of exponent $\beta$ obtained from the fits are listed in Table 3 for different compositions. In Fig. 8(b), it may be noted that the values of $\beta$ do not vary significantly with temperature and composition. The small values of $\beta$ are an indication for highly non-exponential relaxation. The lower values of $\beta$ also suggest co-operative motion resulting from strong ion-ion interaction in these electrolytes [27]. Ngai [28] has proposed a relation between the power law exponent $n$ and the stretched exponent $\beta$ as, $n = 1 - \beta$. Though exponent $n$ and $\beta$ are obtained from two different methods, they are well valid for smaller range of ac conductivity data [29,30]. We note that this relationship between $n$ and $\beta$ is almost satisfied for the present plasticized polymer electrolytes.

4. Conclusions

The enhancement of the ionic conductivity depends on the value of dielectric constant of plasticizers. The plasticizers having dielectric constants higher than PEO help to increase the ionic conductivity of PEO-LiClO$_4$ electrolyte. Addition of DMC in polymer
matrix acts as an anti-plasticization effect due to low dielectric constant than that of the base polymer (PEO). The temperature dependent ionic conductivity for all plasticized polymer electrolytes follows well known VTF relation, confirming coupled motion of Li$^+$ ions and segment of polymer chain. The dielectric strength is observed to be high for PEG based polymer electrolyte. The inverse temperature dependence of the relaxation time obtained from dielectric and modulus spectra follows the VTF nature. The small values of stretched exponent $\beta$ indicate non-exponential relaxation.

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REFERENCES