Conductivity and optical studies of plasticized solid polymer electrolytes doped with carbon nanotube

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Abstract

Solid polymer electrolyte films based on Poly(ethylene oxide) (PEO) complexed with lithium hexafluorophosphate (LiPF₆), ethylene carbonate (EC) and amorphous carbon nanotube (aCNTs) were prepared by the solution cast technique. The conductivity increases from 10⁻¹⁶ to 10⁻⁵ S cm⁻¹ upon the addition of salt. The incorporation of EC and aCNTs to the salted polymer enhances the conductivity significantly to 10⁻⁴ and 10⁻³ S cm⁻¹. The complexation of doping materials with polymer were confirmed by X-ray diffraction and infrared studies. Optical properties like direct band gap and indirect band gap were investigated for pure and doped polymer films in the wavelength range 200–400 nm. It was found that the energy gaps and band edge values shifted to lower energies on doping.

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1. Introduction

In recent years, studies on the optical properties of polymers have attracted much attention in view of their application in optical devices [1–3]. The optical properties have been studied aimed at achieving better reflection, antireflection, interference and polarization properties [1]. The optical properties of polymers can be suitably modified by the addition of dopants depending on their reactivity with the host matrix [1]. A change in polymer composition may affect the induced optical absorption due to several reasons, namely the polarization power of network formers, modifiers, their coordination numbers, the concentration of non-bridging oxygen (oxygen ions having dangling bonds), the presence of multivalent network forming and modifying ions [4]. Studying the optical absorption, particularly the shape and shift of the absorption edge, is a very useful technique for understanding the basic mechanism of optically induced transitions in crystalline and non-crystalline materials, as well as providing information about the energy band structure. Although some work has been done on the optical properties of doped polymer electrolyte films [5–15], no report is available on polymer electrolytes doped with carbon nanotubes. The investigation of the optical properties of this system is still limited and much experimental work needs to be done in this direction. Poly(ethylene oxide) is an exceptional polymer; it dissolves in high concentration of a wide variety of salts to form polymer electrolytes. Studies have proved that in PEO–LiPF₆ and PEO–LiCF₃SO₃ systems, conductivity increases with the increase of salt wt%. [16–19]. This paper is concerned with the optical properties of new polymer electrolytes based on a Poly(ethylene oxide) complexed with lithium hexafluorophosphate (LiPF₆), ethylene carbonate (EC) and carbon nanotube. The neural network model has been developed and it was successful to predict the ionic conductivity of nanocomposites polymer electrolyte system [20,21]. The optical properties of the polymer electrolytes are investigated to determine the optical transition characteristics and provide information about the band structure and energy gap.

2. Experimental

Polymer electrolytes were prepared by standard solution-casting techniques. PEO (MW=600,000, Acros Organics) was used as host polymer matrix, lithium hexafluorophosphate (LiPF₆) (Aldrich) as the salt for complexation and ethylene carbonate (EC) (Alfa Aesar) as plasticizer. Amorphous carbon nanotube (aCNT) was prepared by the chemical route at low temperature [22]. Prior to use, PEO was dried at 50 °C for 48 h. Appropriate quantities of PEO, LiPF₆, EC and aCNT were dissolved separately in acetonitrile (Fisher) and stirred well for 24 h at room temperature to form a homogeneous solution. All samples were stored under dry conditions. An electronic digital caliper was used for measuring films thickness and average thickness for films is 0.76 mm. The ionic conductivities of the samples were measured at temperature ranging from 298 to 373 K...
using HIOKI 3531 LCR Hi-Tester with frequency range of 50 Hz to 5 MHz. X-ray diffraction (XRD) patterns of the films were recorded at room temperature using Phillips X-peed MRD X-ray diffractometer. The optical absorption measurements of the samples have been recorded in the range of 200–350 nm using a CARY 50 Scab UV–vis–NIR spectrophotometer. (Photoluminescence) PL measurements were first performed using a Perkin Elmer machine in the range of 200–600 nm. FTIR studies were performed using Perkin Elmer Spectrum 400.

3. Results and discussion

3.1. Ionic conductivity studies

Fig. 1 shows the temperature dependence of conductivity for various electrolytes between 25 and 100 °C. It is evident that the room temperature conductivity increases with different chemical composition. The results are summarized in Table 1. The conductivity increases 5 orders of magnitude with the addition of LiPF₆. The polar and flexible PEO main chain dissociates LiPF₆ to generate carrier ions, and the migration of these ions through interchain and intrachain polymer segments in the amorphous region of the complex [23] is responsible for the increase in conductivity.

As the salt content increases, the conductivity increases because the number density of mobile ions increases and therefore, the polymer segment's motion is promoted [24]. The results agree well with the Rice and Roth model [25,26]

\[
\sigma = \frac{2}{3} \left( \frac{Z e^2}{k_B T} \right) \eta e \exp \left( -\frac{E_A}{k_B T} \right)
\]

where \( \sigma, \eta, Z, E_A \) and \( m \) represent the conductivity, density, valency, activation energy, mass of the conducting ions, respectively. Furthermore, the parameters \( T, k_B, e \) and \( \tau \) represent the absolute temperature, Boltzman constant, electronic charge and time travel of ions between sites, respectively. From Eq. (1), it can be seen that conductivity increases when the density of mobile ions increases. The conductivity increases 4 orders of magnitude with the addition of EC. This reflects that the effects of the physico-chemical properties of the individual plasticizers such as the high dielectric constant of EC (\( \varepsilon_{EC} =85.1 \)) contribute significantly towards improving the conductivity performance [27]. The addition of the plasticizer also decreases the ion pairing. The high dielectric constant of EC effectively reduces the inter-ion Coulomb interactions; hence, more Li⁺ contributed to the conductivity of the complexes. The addition of the plasticizer has been reported to reduce the crystallinity of the complexes that leads to better ionic conductivity [28–30]. Further addition of zCNTs has increased conductivity to 3 orders of magnitude.

The addition of zCNTs increases the conductivity by inhibiting recrystallization of the PEO chains and providing Li⁺ conducting pathway at the filler surface through Lewis Acid base interaction among different species in the electrolytes [31]. The addition of highly flexible zCNTs to PEO networks improved the interaction and cross-linking between zCNTs and PEO molecules, resulting in the increased ionic conductivity [32]. The process of conduction follows the Vogel–Tamman–Fulcher relationship and the conductivity is recorded in Table 1. The conductivity increases due to size of the filler and plasticizer molecule compared to the polymer molecule, which can penetrate easily into the polymer matrix [33].

3.2. X-ray diffraction (XRD) analysis

Fig. 2 shows the XRD pattern of pure PEO and PEO doped with LiPF₆, EC and zCNTs. Sharp and intense diffraction lines occur at 2θ of 20° and 24° indicating the crystalline nature of pure PEO [34]. The intensity of the PEO peaks at that angle were decreased significantly with the addition of salt, plasticizer and zCNTs. This may be due to the further increase of amorphous nature of polymer electrolytes. New peak emerged at 2θ of 43° in the diffractogram for films LiPF₆ (20 wt%) showing the formation of a new crystalline phase [34]. The ordering in PEO is disturbed in the presence of Li salt due to the coordination interactions between Li⁺ ion and ether O atoms [5]. As a result, a marked decrease in the crystallinity of polymer complex is observed compared to the pure PEO as shown in Fig. 2b. Further dilution of the crystalline phase can be noticed in Fig. 2c with the addition of the plasticizer where broad and less intense peaks appeared. The small peaks at 2θ of 26 and 26.1 slowly disappeared when plasticized polymer is added with zCNTs. The absence of sharp peaks pertained to the H⁺ ion and polymer chain atoms [35]. Dispersed phase zCNTs prevented the polymer chain reorganization, resulting in reduction in polymer crystallinity.

3.3. FTIR spectroscopy analysis

Figs. 3 and 4 depict the IR transmittance spectra of various electrolytes recorded at room temperature in the region 4500–500 cm⁻¹. The spectra exhibit bands characteristic of stretching and bending vibrations of the films, which are listed in Table 2. The vibration modes and wave numbers exhibited by PEO are \( \text{CH}_2 \) rocking mode observed at 842 and 963 cm⁻¹, respectively.
The strongest interaction in PEO is the anti-symmetric bridge C–O–C stretching vibration at 1100 cm$^{-1}$ [36], asymmetric CH$_2$ twisting at 1241 and 1280 cm$^{-1}$, and asymmetric CH$_2$ at 1455 cm$^{-1}$. Other absorption bands were observed for symmetric and asymmetric C–H stretching vibrations at 2800–3000 and 2700–3800 cm$^{-1}$, respectively [37].

When LiPF$_6$ was added to the PEO system, CH and C–O–C stretching modes are shifted from 1110 to 1100 cm$^{-1}$ and 2890 to 2880 cm$^{-1}$, respectively. The intensity of this band implies the number of free ions from the addition of salt [38]. This could explain why there is increase in the conductivity value of PEO–LiPF$_6$ samples. This broadening and shifting indicates that there is a possible weak interaction between the polymer and the salt [39]. As shown in Fig. 3c, a small shoulder at 682 cm$^{-1}$ appears for PEO–LiPF$_6$ samples. This is possibly due to weak interaction between PEO and ν(PF$_6^-$) at 651 cm$^{-1}$. The shifted peak and decrease in intensity of CH$_2$ twisting at 961 cm$^{-1}$ proved that interaction occurred between PEO backbone and ν(PF$_6^-$) at 823 cm$^{-1}$. When EC was added to PEO–LiPF$_6$ system, CH and C–O–C stretching modes at 2886 and 1100 cm$^{-1}$ remain unchanged. A small shoulder appeared at 1780 cm$^{-1}$ for the PEO–LiPF$_6$–EC system due to the reaction of salted polymer with ethylene carbonate. The addition of EC leads to the formation of Li$^+$–EC complex [40]. In the EC–LiPF$_6$ complex, there is only one kind of species, namely the ion pair. As a result, there is only one kind of EC–Li$^+$ interaction evident in the C=O bending region [41]. The C=O bending mode appears at 718 cm$^{-1}$ and is shifted to 720 cm$^{-1}$ when EC was added to PEO–LiPF$_6$ sample. The C=O stretching band at 1790 cm$^{-1}$ shifted to 1780 cm$^{-1}$ in salted PEO complexes. This peak again shifted to 1800 cm$^{-1}$ when CNT was added to PEO complexes.

The CH and C–O–C stretching modes remain unchanged. The increase in intensity of the peaks at 2880, 1100 and 842 cm$^{-1}$ indicates the increase in the concentration of free ions. These explain the conductivity trend of the αCNTs–plasticized polymer electrolytes.
3.4. Optical studies

3.4.1. UV–vis analysis

Fig. 5 shows optical absorption spectra recorded for polymer electrolytes in the region 200–300 nm. In the UV region, the band at 200 nm has been observed for pure PEO and PEO doped with LiPF$_6$, EC and a CNTs with different absorption intensity and wavelength. This absorption peak may be attributed to the $n$–$\sigma^+$ transition, which is very sensitive to hydrogen bonding. The absorption band at 250 nm may be assigned as $\pi$–$\pi^*$, which comes from unsaturated bonds mainly C=O and C=C, which are present in the anion (CH$_3$COO$^-$) and tail head of the polymer, respectively. Fig. 5 shows a shift in absorption edge (AE) towards the higher wavelengths. These shifts in the AE indicate the formation of inter/intra molecular hydrogen bonding mainly between lithium ions with that of these adjacent OH groups. These bonds reflect the variation of energy band gap, which arises due to the variation in crystallinity within the polymer matrix [46].

Fig. 6 shows optical transmittance spectra for polymer electrolytes in the region 200–400 nm. As illustrated in Fig. 6, the spectra show interference pattern with a sharp fall of transmittance at the band edge. One can observe for pure and doped polymer electrolytes, nearly zero transmission intensity in the wavelength range 200–220 nm. The transmission intensity starts increasing at 220 nm until it reaches 80% when LiPF$_6$ and EC were added. Then the intensity decreases below 60% when a CNTs are added. The transmission intensity gradually increases up to 330 nm and reaches a constant value.

3.4.2. Photoluminescence (PL) analysis

In order to understand the polymer electrolyte complex films, the photoluminescence spectra of all the samples were recorded and the spectra are shown in Fig. 7. The wavelength of excitation chosen for all samples is 201–250 nm. It can be seen that the emission peaks are at various spectral position (338, 340, 451 and 527 nm). These bands may be assigned to the recombination of free charge carriers at the defects in PEO. It is found that, the fluorescence intensity of the doped films is lower than that of pure PEO. The decrease of the intensity of the emission peak may be due to the weak interaction between the dopant and the polymer and aggregation of dopant molecules [47]. It is also believed that structural modification affected optical properties of polymer electrolytes. LiPF$_6$, EC and a CNT are responsible for the formation of defects in the polymer electrolytes. These defects produce the localized state in the optical properties [48].

### Table 2

<table>
<thead>
<tr>
<th>Material</th>
<th>Vibrational frequency (cm$^{-1}$)</th>
<th>Band assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO</td>
<td>842, 963</td>
<td>CH$_2$ twisting nagging [42]</td>
</tr>
<tr>
<td></td>
<td>1100</td>
<td>Anti-symmetric bridge C–O–C Stretching [42]</td>
</tr>
<tr>
<td></td>
<td>1241, 1280</td>
<td>Asymmetric CH$_2$ twisting [42]</td>
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<tr>
<td></td>
<td>1455</td>
<td>Asymmetric CH$_2$ [42]</td>
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<tr>
<td></td>
<td>2800–3000</td>
<td>Symmetric C–H stretching [42]</td>
</tr>
<tr>
<td></td>
<td>2700–2800</td>
<td>Asymmetric C–H stretching [42]</td>
</tr>
<tr>
<td>LiPF$_6$</td>
<td>651</td>
<td>$\nu$(PF$_6$) [43]</td>
</tr>
<tr>
<td></td>
<td>837</td>
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<td></td>
<td>1164</td>
<td>$\nu$(PF$_6$) [43]</td>
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<tr>
<td>EC</td>
<td>718</td>
<td>C=O bending [44]</td>
</tr>
<tr>
<td></td>
<td>893</td>
<td>Ring breathing [44]</td>
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<td></td>
<td>1774</td>
<td>C=O stretching bands [44]</td>
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<tr>
<td>CNT</td>
<td>1635</td>
<td>H-bonded (C=O stretching) [45]</td>
</tr>
<tr>
<td></td>
<td>1708</td>
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</tr>
<tr>
<td></td>
<td>3437</td>
<td>OH stretching [45]</td>
</tr>
</tbody>
</table>

Fig. 5. Optical absorption spectra for (a) PEO; (b) PEO + LiPF$_6$; (c) PEO + LiPF$_6$ + EC and (d) PEO + LiPF$_6$ + EC + aCNT.

Fig. 6. Transmittance spectra for (a) PEO; (b) PEO + LiPF$_6$; (c) PEO + LiPF$_6$ + EC and (d) PEO + LiPF$_6$ + EC + aCNT.
3.4.3. Determination of optical band gap

From the UV–vis spectra, the optical band gap of polymer electrolytes has been determined. The study of optical absorption gives information about the band structure of solids. Insulators/semiconductors are generally classified into two types: (a) direct band gap and (b) indirect band gap. In indirect band gap semiconductors, the top of valence band and the bottom of the conduction band are both laid at the same zero crystal momentum (wave vector). If the bottom of the conduction band does not correspond to zero crystal momentum, then it is called an indirect band gap semiconductor. In indirect band gap materials transition from valence to conduction band should always be associated with a phonon of the right magnitude of crystal momentum. The fundamental absorption, which corresponds to the transition from valance band to the conduction band, can be used to determine the band gap of the material. The relation between absorption coefficient ($a$) and incident photon energy ($h\nu$) can be written as

$$a = A(h\nu - E_g)^n / h\nu,$$

where $A$ is a constant, $E_g$ is the band gap of the material, the exponent $n$ depends on the type of transition. $n$ may have values 1/2, 2, 3/2 and 3 corresponding to the allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions, respectively.

Figs. 8 and 9 show the variation of $(zh\nu)^{1/2}$ and $(zh\nu)^2$ with $h\nu$. Optical band gap $E_g$ can be determined by the extrapolation of best fit line between $(zh\nu)^{1/2}$ and $(zh\nu)^2$ intercept in the $h\nu$ axis. Variation of optical band gap with different concentrations of LiPF$_6$, EC and αCNT is given in Table 3. By adding different elements to the PEO complexes, optical band decreases from 5.92 to 4.60 eV for direct optical band gap and from 5.70 to 4.42 eV for indirect optical band gap. The decrease in the band gap is caused by an doping elements effect, namely a compositional change in the host material itself [50,51]. The decrease in the optical gap results in an increase in the degree of disorder in the films. Doping elements such as LiPF$_6$, EC and αCNT are

![Fig. 7. Photoluminescence spectra of (a) PEO; (b) PEO + LiPF$_6$; (c) PEO + LiPF$_6$ + EC and (d) PEO + LiPF$_6$ + EC + αCNT.](image)

![Fig. 8. Plots for direct band gap in polymer electrolytes for (a) PEO; (b) PEO + LiPF$_6$; (c) PEO + LiPF$_6$ + EC and (d) PEO + LiPF$_6$ + EC + αCNT.](image)

![Fig. 9. Plots for indirect band gap in polymer electrolytes for (a) PEO; (b) PEO + LiPF$_6$; (c) PEO + LiPF$_6$ + EC and (d) PEO + LiPF$_6$ + EC + αCNT.](image)

### Table 3

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_g$ (direct)</th>
<th>$E_g$ (indirect)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO</td>
<td>5.92</td>
<td>5.70</td>
</tr>
<tr>
<td>PEO–20 wt% LiPF$_6$</td>
<td>5.90</td>
<td>5.74</td>
</tr>
<tr>
<td>PEO–20 wt% LiPF$_6$–15 wt% EC</td>
<td>5.80</td>
<td>5.63</td>
</tr>
<tr>
<td>PEO–20 wt% LiPF$_6$–15 wt% EC–5 wt% αCNT</td>
<td>4.60</td>
<td>4.42</td>
</tr>
</tbody>
</table>
4. Conclusion

Optical properties of the polymer electrolytes appear to be strongly connected to the chemical and structural modifications induced in the polymer. It has been demonstrated in this paper that the addition of various weight percent of salt, plasticizer and filler to the PEO matrix enhances conductivity. The complexation of LiPF$_6$, EC and xCNT with PEO was confirmed by XRD and FTIR studies. The PL intensity decreases as the element was added to polymer complexes. The optical band gap values show the decreasing trend with an increasing dopant concentration. It is also observed that the absorption edge shifted to longer wavelength on doping. Results of the optical measurements indicate the presence of a well-defined $\pi\rightarrow\pi^*$ transition associated with the formation of a conjugated C=O and/or C=O electronic structure.

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