OPTICAL AND ELECTRIC MODULUS STUDIES OF PMMA: CH$_3$COOLi COMPLEXES WITH THE ADDITION OF EMIMTFSI

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ABSTRACT
Using solution casting technique PMMA with Lithium acetate of polymer electrolytes like PMMA (60 wt. %): CH$_3$COOLi (40 wt. %): EMIMTFSI (0 wt. %, 0.5 wt. %, 1 wt. %) by incorporating ionic liquid are prepared. From UV-Visible studies maximum band gap (eV) is 2.8 eV for PMMA: CH$_3$COOLi: EMIMTFSI (60:40:1 wt.%). Tangent dielectric loss revealed the behavior of the ion charge carrier’s polymer electrolyte system. Electric modulus studies revealed the information about charge carrier’s relaxation behavior. From the results, prepared polymer electrolyte films are the best candidates for energy storage devices.

Keywords: Polymer Electrolytes, PMMA, Lithium Salts, Ionic Liquid, UV-Visible Spectroscopy, Electric Modulus.

INTRODUCTION
The ever-increasing worldwide thirst for energy storage devices due to their great electrochemical performances and environmentally friendly nature, several of those energy storage sources are solar cells, fuel cells, lithium-ion batteries, super capacitors etc. Primarily liquid electrolytes were introduced in many technologies and there are several disadvantages like dendrites formation that resulting in considerable capacity loss aside from basic issues involved in portable devices like minimum operating temperature, dispelling of electrolyte, lower electrochemical stability window, certain drawbacks of conventional liquid electrolytes encountered in achieving an appreciably good electrochemical performance tend to limit their wider use. Unlike liquid electrolytes, solid polymer electrolytes are reliable and stable, and which has wide range tolerance of chemical stability, thermal stability, and electrochemical stability. Because of their numerous inherent advantages, “solid polymer electrolytes” (SPE’s) are promising routes for energy storage devices. As a result, enormous development in the fabrication of (SPE’s) has been conducted in order to generate highly conducting electrolyte systems used in several applications. In order to enhance the huge ionic conductivity polymer electrolytes (gel/blends/Nanocomposite) are redeemed in the place of liquid electrolytes. The research begins to be deep-rooted by conducting with the addition of suitable plasticizers, polymers and nanocrystalline inorganic ceramic fillers to these polymer electrolytes. PMMA is one of the widely used host polymers with the best results mostly in lithium-based polymer electrolyte systems because of its lithium electrode durability. Pure PMMA films result as brittle films that do not adhere well to the electrode, due to some air gap it also holds against the ionic conduction.

Due to poor mechanical qualities produced by the larger amount of plasticizer, agglomeration caused by the filler, and poor film homogeneity when combined with other polymers, these attempts were mainly unsuccessful. Only when PMMA is manufactured as a thin film can it be stable towards lithium electrodes. Due to the adjacent methyl group (CH$_3$) in the polymer structure, PMMA is determined to be an amorphous thermoplastic. The cations from the IL or the doping salt will interact with the oxygen atoms in PMMA (C=O and –OCH$_3$ groups). As a result, PMMA satisfies the criteria for a suitable polymer host in an electrolyte system. The addition of salt to the polymer is necessary to supply ions as charge carriers.
Ionic transport is more common in amorphous or non-crystalline regions, where it is associated with polymer segmental motion. The addition of salt to a polymer can diminish the polymer's crystalline concentration. Lithium salts are preferred in polymer electrolyte research because lithium is the lightest metal and can give a large potential window. A positively charged cation and a negatively charged anion make up an organic salt. Li\(^+\), Mg\(^{2+}\), and Na\(^+\) are the most regularly utilized cations in PE systems, while anions such as CF\(_3\)SO\(_3^-\), CH\(_3\)COO-, BF\(_4^-\), and I\(^-\) are widely employed ions. The lithium-ion-based salt is preferred because lithium ions are smaller (0.76) than sodium ions (1.06), so this leads to ion mobilization in the polymer electrolyte system. The salts dissociate easily if the lattice energy is too low. Salts of massive anions like ClO\(_4^-\), BF\(_4^-\), CF\(_3\)SO\(_3^-\), and CH\(_3\)COO- are so formed. Both the polymer and doping salt influence ionic conductivity, chemical stability, and mechanical strength. PEs shows excellent conductivity where it depends on the least value of lattice energy of complexing salt. Polymers dielectric constant value and salts lattice energy is more, it facilitates solvating the salts in polymer chains. In salt solvation, the acetate ion (CH\(_3\)COO-) is favoured due to hydrogen bonding.

“Room temperature ionic liquids” are also called RTILs because they remain in the molten state at room temperature. These RTILs are mixed bulky combinations of asymmetric organic cations as well as inorganic anions. Basically, these RTILs’ are categorized into protic and aprotic ionic liquids, these are introduced into Polymer electrolytes because of their inherent properties like low melting point, inflammable, non-toxic, non-volatility, high ionic conductivity, excellent electrochemical window, no vapour pressure, Non-volatility, thermally, mechanically and chemically stable. RTIL also has inherent advantages, such as being a versatile solvent that can dissolve extensive varieties of organic, organometallic, and inorganic compounds. They don't work well with enzymes, metal complexes, and a variety of inorganic and organic substrates. Because of their exceptional properties, RTILs can replace plasticizers as an alternative component in PEs, where it improves ionic conductivity.

**EXPERIMENTAL**

**Materials**

(PMMA) Poly (methyl methacrylate) with a molecular weight of 12× 10\(^5\) g/mol was used as host polymer, (CH\(_3\)COOLi) Lithium acetate used as dopant salt, (EMIMTFSI) (1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide) were purchased from Sigma Aldrich. (DMF) dimethyl form amide can be used as the solvent.

**Process of Polymer Electrolyte Preparation**

(PMMA) Poly (methyl methacrylate) (60 wt. %) used as host polymer, (CH\(_3\)COOLi) Lithium acetate (40 wt. %) used as dopant salt were properly mixed using DMF solvent. Additionally incorporated ionic liquid to this polymer electrolyte solution is (EMIMTFSI) (1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide) (0 wt. %, 0.5 wt. %, 1 wt. %) for further enhancement of properties. Polymer electrolyte solution along with ionic liquid is stirred for 48 hours to get complexation in order to obtain flexible polymer electrolyte films.

**Characterization Studies**

The prepared PEs of PMMA (60 wt. %):CH\(_3\)COOLi (40 wt. %): EMIMTFSI (0 wt. %, 0.5 wt. % and 1 wt. %) studied using different characterization techniques. Optical properties were studied through UV-visible spectroscopy using a JASCO V-670 spectrophotometer of wavelength 200-900 nm. Electrical properties were studied through Tangent loss and electric modulus using HIOKI 3532-50 LCR HITESTER with a frequency range of 500HZ to 3MHZ.

**RESULTS AND DISCUSSION**

**UV-Visible Spectroscopic Studies**

Optical properties of PMMA (60 wt. %):CH\(_3\)COOLi (40 wt. %): EMIMTFSI (0 wt. %, 0.5 wt. % and 1 wt. %) were studied. From Fig.-2, UV-Visible absorption studies with wavelengths in between 200-900 nm. In polymers, According to molecular orbital theory, electronic transitions occur in \(\pi\), \(\pi^*\), and n-orbitals, where absorption of light occurs in the UV region and visible region. In both UV-Visible regions for
different wavelength regions the transitions occur as $n \rightarrow \pi^*$ transition takes place in between 400-700 nm, from 200-400 nm region, $\pi \rightarrow \pi^*$ the electronic transition takes place, the electronic transition $n \rightarrow \sigma^*$ takes place from 150-250 nm wavelength region.

Figure-2 represents, there is the possibility for $\pi \rightarrow \pi^*$ transition takes place between the wavelength region from 230 - 240 nm due to absorption. Figure-2 represents there is longer absorption for PMMA (60 wt. %): CH$_3$COOLi (40 wt. %): EMIMTFSI (1 wt. %), because increasing CH$_3$COOLi and EMIMTFSI ratios, due to $\pi$ – delocalization, Li$^+$ trapped into polar groups of polymer chains which enhances amorphous phase. As a result, because of polymer-salt interaction, there will be longer absorption. UV-visible spectroscopy is a method that details the optical absorption process, where the energy band gap $(E_g)$ deals with maximum transitions by an electron when it absorbs energy and it makes transitions from fundamental energy state to higher energy state called as absorption edge. While increasing salt ratio there is an electronic energy loss processes leads to several factors like cross-linkage between polymer and Li$^+$, free radical formation and conjugated system of bonds. Due to the increase of lithium salt concentrations, optical density increases, and peaks get broadened and shift towards longer wavelength regions. Generally based on the material absorption edge can be of two categories. In the case of overlapping of conduction and valence band, the crystalline moment is zero, in the indirect band gap conduction, and valence band is not equal here crystalline moment is non-zero. From Fig.-2 to 5 represents absorption graphs for $(\alpha)$, $(\alpha h \nu)^{1/2}$and $(\alpha h \nu)^2$ of PMMA (60 wt. %):CH$_3$COOLi (40 wt. %): EMIMTFSI (0 wt. %, 0.5 wt. %, 1 wt. %). The absorption coefficient value is derived from Fig.-3 and tauc’s plots plotted from the equation:

$$\alpha(h\nu) = K(h\nu - E_g)^n$$  \hspace{1cm} (1)

Here ‘$\alpha$’ is the absorption coefficient which can be derived from the photon energy function is

$$\alpha = 2.303 \left( \frac{a}{d} \right)$$  \hspace{1cm} (2)

Above equations, ‘$E_g$’ represents energy band gap, ‘$a$’ is the specimen area and ‘$d$’ is the sample thickness, planks constant ‘$h$’, ‘$\nu$’ is the frequency of incident light. Table-1 indicates of $(\alpha)$, $(\alpha h \nu)^{1/2}$and $(\alpha h \nu)^2$ of PMMA (60 wt. %): CH$_3$COOLi (40 wt. %): EMIMTFSI (0 wt. %, 0.5 wt. %, 1 wt. %). The “$(E_g)$” value for PMMA : CH$_3$COOLi : EMIMTFSI (60:40:00 wt.%) is 4.5 eV, it is decreased to 2.8 eV as salt concentration and ionic liquid concentration increased as follows PMMA : CH$_3$COOLi : EMIMTFSI (60:40:1 wt.%). By incorporating salt ratio there is the development
of local crosslinking between polymer and salt resulting in an amorphous phase such that it affects the lower activation energy. From Fig.-2, in the UV region between 200-400 nm wavelength region, the maximum absorption takes place. Here the maximum absorption can be represented as ‘λₘₐₓ’ at a particular wavelength. From Fig.-2 we can observe that the shifting of ‘λₘₐₓ’ towards the higher wavelength region is considered as a ‘Red shift’.20

Table-1: (α), (αhυ)¹⁄₂ and (αhυ)² for PMMA (60 wt. %):CH₃COO Li (40 wt. %): EMIMTFSI (0 wt. %, 0.5 wt. %, 1 wt. %) Based Polymer Electrolytes

| Polymer electrolyte system | Energy band gap values | Eₙ (eV) |
|---------------------------|------------------------|--------|
|                           | Direct band gap (eV) | Indirect band gap (eV) |
| PMMA : CH₃COO Li : EMIMTFSI (60:40:00 wt. %) | 4.7 | 4.7 | 4.5 |
| PMMA : CH₃COO Li : EMIMTFSI (60:40:0.5 wt. %) | 3.5 | 3.7 | 3.6 |
| PMMA : CH₃COO Li : EMIMTFSI (60:40:1 wt. %) | 2.7 | 2.7 | 2.8 |

Fig.-2: UV-Visible Spectra for Different Ratios of of PMMA : CH₃COO Li : EMIMTFSI (60:40:00 wt. %, 60:40:0.5 wt. %, 60:40:1 wt. %)

Fig.-3: Absorption Edge Graph For Different Ratios of PMMA : CH₃COO Li : EMIMTFSI (60:40:00 wt. %, 60:40:0.5 wt. %, 60:40:1 wt. %)

Fig.-4: Indirect Energy Band Gap Values For Different Ratios of PMMA : CH₃COO Li : EMIMTFSI (60:40:00 wt. %, 60:40:0.5 wt. %, 60:40:1 wt. %)
Tangent Loss

Tangent dielectric loss (tanδ) is to obtain information of polymer electrolyte dielectric characteristics where to study the distribution of relaxation time, which is charge carrier jumping probability per unit time. The dielectric properties of the electrolyte may also be studied by tan with altering temperature and frequency, according to a previous study.\textsuperscript{21} Due to the long-range electric conductivity, this permits resolving spatial relaxation processes such as dipole reorientation.\textsuperscript{22} Fig.-6 depicts variations for PMMA : CH$_3$COOLi : EMIMTFSI (60:40:00 wt. %, 60:40:0.5 wt. %, 60:40:1 wt. %) at various salt concentrations in relation to the logarithm of the frequency. The results demonstrate that as CH$_3$COOLi : EMIMTFSI was increased, the peaks of tanδ in the high-frequency area climbed to a maximum value, which corresponds to the relaxation peak. From the CH$_3$COOLi, due to existence of Li$^+$ ions helped the relaxation process which was assigned to an increase in the tanδ peak. Furthermore, the increase in tanδ with increasing CH$_3$COOLi concentration is associated with an increase in charge carrier concentration, which reduced the electrolytes resistance.\textsuperscript{23} However, as the conducting salt concentration was increased to 40 wt.%, the value of tanδ decreased, which ascribes to accumulation and agglomeration of carrier charges in for PMMA: CH$_3$COOLi: EMIMTFSI composites. Similarly, it has been observed that a significant amount of ions in GPE causes ions pairs to congregate, which blocks conducting pathways and prevents ions from being transported, resulting in a drop in the concentration of mobile ions causing loss in stored energy or tanδ. The drop in tanδ at greater wt. % salt concentrations assigned as the creation of ion-ion pairing, which results in a reduction in free ions.\textsuperscript{24}
Electric Modulus Studies

According to the earlier study, Macedo was the first to apply electric modulus to explore the space charge carrier’s relaxation phenomena of electrolyte material. The study of $M^*$ is significant in electrolytes because it is used to analyse conductivity relaxation processes of materials. Similarly, charge accumulation at an electrode, known as electrode polarisation, causes a large permittivity. The relaxation process of ions during polarization and observing the electrical property of the polymer electrolytes can be studied using $M^*$ which is the inverse of $\varepsilon'$. Hence $M^*$ is the sum of $M'$ (real modulus) and $M''$ (Imaginary modulus). While noticing both $M'$ and $M''$ increase in frequency as they go closer to high frequencies, which is consistent with recent research. The synthesized GPEs are effective ionic conductors due to the resemblance of the peak curve near the high-frequency values in the $M'$. From both $M'$ and $M''$ decrease with prolonged extension at lower frequencies, indicating that the electrode polarisation phenomenon has only a minor impact. Based on the electrode material’s highest capacitance achieved, it has been claimed that the extended train can occur at lower frequencies. At some frequencies, $M'$ achieved a constant value. $M'$ was shown to approach zero at lower frequencies, confirming the presence of significant electrode or ionic polarisation in the system. The elimination of electrode polarisation is shown by the modest value of $M'$ at lower frequencies, which corresponds to the amount of capacitance associated to the effect of electrode polarisation leading to the accumulation of ions near the electrolyte-electrode medium. Further movement of the polymer segments and carrier charges causes the decrease in $M'$ as the temperature rises. It has been claimed that at high temperatures, aligning carrier charges with molecule dipoles is easier.

\[
M^* = \frac{1}{\varepsilon'} = M' + jM'' = \frac{1}{\varepsilon'} - j \frac{\varepsilon''}{[\varepsilon'^2 + \varepsilon''^2]} + \frac{j \varepsilon''}{[\varepsilon'^2 + \varepsilon''^2]} \tag{3}
\]
\[
M^* = j\omega c_0 Z^* = \omega c_0 Z' + j\omega c_0 Z'' \tag{4}
\]

Here, further these two modulus ($M'$ and $M''$) can also be expressed as
\[
M' = \frac{\varepsilon'}{\varepsilon'^2 + \varepsilon''^2} \\
M'' = \frac{\varepsilon''}{\varepsilon'^2 + \varepsilon''^2}
\]  

(5)  
(6)

\(M''\) represents one of the segments of the electric modulus that abbreviates behaviour of ions and their momentum in polymer electrolyte systems with respect to frequency. The hopping mechanism ions detailed from Fig.-8 Imaginary modulus (\(M''\)) vs logf. At the low-frequency side, the ions cannot take back their position due to less relaxation time, so there is a shortage of accumulation of ions at the electrolyte-electrode medium. As a result, \(M''\) decreases as the logf decreases.\(^{31}\) In the case of higher frequency side the orientation of charge carriers is possible because of high relaxation time, so, the accumulation of charge carriers is more at the electrode and electrolyte interface. Such that at higher frequency side \(M''\) increases within the potential. From Fig.-8 using the formula \(2\pi f_{\text{max}}\tau = 1\) where we can calculate relaxation time ‘\(\tau\)’. Here, the ‘\(f_{\text{max}}\)’ value is also known as \(M''\) max.\(^{32}\)

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CONCLUSION

PMMA based polymer electrolytes were prepared as PMMA (60 wt. %): \(\text{CH}_3\text{COOLi} \) (40 wt. %): EMIMTFSI (0, 0.5, 1 wt. %) along with ionic liquid using the solution casting method. From the UV-Visible spectroscopic studies, the maximum energy band gap is from 4.5 eV to 2.8 eV for PMMA: \(\text{CH}_3\text{COOLi}: \text{EMIMTFSI} \) (60:40:1 wt.%). For PE’s the tangent dielectric loss (tan\(\delta\)) revealed the dissipation of charge carriers with respect to frequency. The nature of ions at the electrode and electrolyte interface with respect to frequency is revealed from the modulus analysis. From all the studies it revealed that the polymer electrolyte films with different ratios PMMA (60 wt. %): \(\text{CH}_3\text{COOLi} \) (40 wt. %): EMIMTFSI (0, 0.5, 1 wt. %) are prominent candidates for energy storage devices.

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