Structural and electrical studies of PMMA and PVdF based blend polymer electrolyte

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Abstract

PMMA-Poly Methyl Methacrylate, PVdF-Poly Vinylidene Fluoride and Silver Nitrate (AgNO_3) based blend polymer electrolytes have been prepared by solution cast method. DMF (Dimethyl Farmamide) was used as a common solvent. These systems have been characterized by Scanning Electron Microscopy, Fourier Transform IR Spectroscopy and X-ray Diffraction for various ratios of prepared solid polymer electrolytes. DC ion conductivity has been studied for prepared electrolyte systems and the ionic conductivity of these systems showed Arrhenius behavior. It has been found that the electrolyte membrane's ionic conductivity rises with temperature. AC conductivity, electric modulus and dielectric studies have been investigated. The enhancement of conductivity was observed to be maximum for PMMA(70%):PVdF(30%): AgNO_3 (5%) ($9.13 \times 10^{-6} \text{ S/cm}$) and is attributed to decrease in crystallinity.

Keywords Solution casting · XRD · FTIR · SEM · Ionic conductivity · Solid polymer electrolyte · Dielectric studies · Impedance analysis

1 Introduction

Solid polymer electrolytes (SPEs) have attracted significant attention due to their high energy density, and their applications are growing up at a quicker rate than that of any other compound electrolyte materials. SPEs provide certain unique advantages over electrolytes dissolved in organic solvents. These materials exhibit high mechanical strength and high ionic conductivity in the ambient environment, which resulted in remarkable interest for many researchers [1–3]. Polymer electrolytes are suitable for applications from a small-scale generation of sophisticated high energy density electrochemical devices, along with portable electronic devices like mobile phones, notebook computers, etc., to hybrid electric vehicles. Researchers have worked on several polymers like polyethylene

oxide (PEO), polyvinyl pyrrolidone (PVP), polyvinyl chloride (PVC), etc., with salts like LiClO_4 , NaI, LiCF_3SO_3 , NaClO_4 , etc., to optimize electrical conductivity [4–6] and other properties. The maximum studies of polymer electrolytes have been performed on PEO matrix. Various approaches, such as co-polymerization, blending [7, 8], plasticization [9], and inorganic nanofillers [10] have been added to enhance the conductivity due to ions in the polymer electrolyte and its performance. By blending the chains of two or more polymers to form a network polymer, the electrical and structural properties can be improved [11–13]. Many researchers exemplified the ionic conductivity of blend polymer electrolyte systems by varying polymer ratios.

Among the polymers, PMMA has attracted good attention due to transparent, colorless, good life period, high mechanical, chemical stability and considerable

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wettability and also has some drawbacks such as thermally low stability, low electrochemical stability and low cyclic rate performance. To overcome the disadvantages of electrolyte systems based on PMMA polymer, in the current work, the PMMA was blended with PVdF to achieve better performance of the electrolyte with improved electrochemical stability. There are two possible types of intermolecular interactions between PVdF and PMMA. One is hydrogen bonding between carbonyl groups of PMMA and methylene groups of PVdF. The other is a dipole–dipole interaction between methylene groups of PMMA and difluoromethylene groups of PVdF [14].

Therefore, it is appropriate to blend PMMA with PVdF. In the current research, blended polymer electrolyte systems with PMMA, PVdF and AgNO_3 were prepared using solution casting technique. This study aims to investigate the ionic conductivity and dielectric properties of the prepared solid blend polymer electrolytes.

2 Experimental procedure

2.1 Base materials

Commercially available polymers, PVdF (avg $M_w = 2,75,000$), PMMA (avg $M_w = 1,20,000$), and Silver Nitrate (AgNO_3 99.0%) have been procured from Sigma Aldrich, India. The solvent N–N Dimethylformamide (DMF, 99.5%) was obtained from MERCK. Before being used in the preparation of SPE films, they were dried in hot air.

2.2 Preparation

Solution cast method is the easiest way to render the samples with wide surface area. PMMA and PVdF host polymers were dissolved in 50 ml DMF in a suitable ratio. The solution was stirred at 350 rpm on a hot plate magnetic stirrer at 50 °C for 4 h. Silver nitrate was slowly transferred into the polymer solution and continued the stirring for 24 h until it formed a homogeneous solution. The resulting suspension has been poured on a petri dish and dried in a vacuum oven for 36 h at 50 °C. A thick brownish colored SPE films were formed in accordance with [(1-x) % PMMA + (x)% PVdF] (equivalent to 1 g weight) and

5 wt% of AgNO_3 (where x = 10, 20, 30 and 40). Finally, the prepared films were coded as shown in Table 1 and stored in desiccators.

2.3 Characterization

XRD was carried out for pure AgNO_3 and blend polymer electrolyte systems by XRD-700 X-Ray Diffractometer (SHIMADZU) with Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$) in the range $2\theta = 15 - 60^\circ$ at ambient environment. FTIR investigation was carried out for blended polymer electrolytes between 400 and 4000 cm^{-1} by FTIR-8400S (SHIMADZU). SEM analysis for the samples carried out by S-3700 N (HITACHI) up to optical magnification 50.0 K X. The impedance analysis was carried out for the prepared films at various temperatures in the frequency range of 100 Hz–30 MHz by Impedance Analyzer PSM-1735 (N4L).

3 Results and discussion

3.1 X-ray diffraction (XRD)

XRD patterns of pure AgNO_3 , pure PMMA, pure PVdF, different wt% ratios of PMMA and PVdF with constant AgNO_3 (5 wt%) are shown in Fig. 1. A very high intense and sharp peak was observed at 40.20° indicating a highly crystalline form of pure AgNO_3 and several other low-intensity salt peaks at 19.5° , 21.8° , 24.2° , 29.6° , 32.7° , 35.6° and 38.9° affirm its extremely crystalline nature as notified in the literature [15]. The β phase of PVdF crystal peak at 20.22° and α phase peak at 38.8° was observed in accord with the earlier results [16]. From figure, it was clearly noticed that no characteristic peaks were observed for pure PMMA which confirms the amorphous nature. Except a very low intense peak around 38° , all other peaks could not be recorded in the polymer blend electrolytes. The peak corresponding to β phase of PVdF was drastically depressed and the position slightly shifted [17, 18] as PVdF wt% increased. The peak broadening increased and shifted slightly towards lower angles, indicating that the association among the polymer chains contributes to a decline in the inter-molecular interaction between polymer chains. This resulting in

Table 1 Sample composition, codes, parameters obtained by XRD and crystallite sizes of samples

Sample composition (with weight %)	Sample code	2θ (Degree)	FWHM (Degree)	Crystallite size ($\text{\AA}$)
90% PMMA + 10% PVdF + 5% AgNO_3	PPA1	38.254	0.4723	178.062
80% PMMA + 20% PVdF + 5% AgNO_3	PPA2	38.346	0.5323	158.035
70% PMMA + 30% PVdF + 5% AgNO_3	PPA3	38.1697	0.6298	133.498
60% PMMA + 40% PVdF + 5% AgNO_3	PPA4	38.3466	0.5372	156.594

Fig. 1 XRD patterns of pure AgNO_3 , PMMA, PVdF and blend polymer electrolyte systems

an improvement in the amorphous nature of the blend polymer electrolyte systems. Such quantitative differences in the crystal process support ion–dipole interactions in the $(1-x)\%$ PMMA + $(x)\%$ PVdF + 5% AgNO_3 membranes are heavily affected by the compositional weight ratios of the polymers in their blends for the preparation of various solid blend polymer electrolyte systems. This promotes the significant movement of polymer chains in the amorphous phase and the blended polymer electrolytes have undergone a systematic structural reorganization. The diffraction peak intensity decreased gradually and the least was observed for PPA3. The crystallite size of different polymer ratios was calculated using Sherrer's formula [19], $d = \frac{0.89\lambda}{\beta \cos\theta}$, where " λ " is the wavelength of monochromatic X-ray beam (Cu-K α radiation = 1.5418 Å), β is the full-width half maxima (FWHM) and 2θ is the angle of diffraction. The calculated values of the crystallite size of different samples were recorded in Table 1. The size of crystallite decreases with the decrease in PMMA percentage and the least was observed for PPA3 sample, which infers the increase in amorphous nature due to structural reorganization [20].

Fig. 2 FT-IR analysis of PPA1, PPA2, PPA3 and PPA4 samples

3.2 Fourier transform IR Spectroscopic analysis

Fourier Transform IR spectra of blend polymer electrolyte systems are shown in Fig. 2. The vibrational bands related to the α (1441 cm^{-1} and 1383 cm^{-1}) and β (841 cm^{-1} and 510 cm^{-1}) phase crystals of the innate PVDF are exhibited and assigned in the literature [21–23]. The absorption bands observed at 1726 cm^{-1} [24] are associated with C=O stretching of carbonyl group belonging to PMMA polymer. Another absorption band at 2953 cm^{-1} compared to that of symmetric oscillations of PVdF [25, 26] and 3439 cm^{-1} corresponds to N–H stretching (medium). The absorption peaks at 1665 cm^{-1} , 1441 cm^{-1} , 2999 cm^{-1} and 1065 cm^{-1} are related to C=C stretching, C–H bending (medium), strong N–H stretching and C–O stretching bonds respectively [27]. All the peaks have been shifted slightly [28] with loading of PVdF and a significant shift was observed for PPA3, which indicate the complexation of blend polymer with AgNO_3 . These observations in the FTIR spectra specifically indicates the variations in the polymer–polymer associations as well as conjugated PMMA and PVDF chain frameworks developed by coordination among ion and dipole in these electrolyte films.

3.3 Scanning electron microscopy (SEM)

Figure 3 demonstrates the SEM morphological images of PPA1, PPA2, PPA3 and PPA4 samples. The white spots seen in PPA1 (Fig. 3a) could be due to presence of AgNO_3 crystallites. The film's morphology changed substantially after PVDF was added with different weight percentages. The surface of PPA2 (Fig. 3b) appear to be non-uniform

Fig. 3 SEM morphological images of (a) PPA1, (b) PPA2, (c) PPA3, (d) PPA4 at 10 KX magnification and (e) PPA3, (f) PPA3 at 50 KX magnification

with increasing number of white spots due to the semi-crystalline phase of PVdF [29–31] and AgNO_3 . The further addition of PVdF resulted in the homogeneous distribution of white spots [26] indicating a smooth and porous structure for PPA3 (Fig. 3c) compared to other samples. Figure 3e and f shows the magnified view at 50 KX resolution. Finally, in PPA4 (Fig. 3d), agglomeration of these white spots can be observed.

3.4 Complex impedance analysis

The impedance spectra of blend polymer electrolyte systems were presented in the Nyquist plots as given in Fig. 4. Impedance spectroscopy is an effective method for analyzing the process of conduction, transport and involvement of chains of polymer in the charge carrier development phenomenon [32]. The semicircle of high-frequency suggests the electrolyte properties includes bulk resistance and bulk capacitance that arises from the migration of

silver ions and polarization of electrolyte respectively. Figure 4b depicts the impedance plot of the PPA3 sample at various temperatures. When the temperature increases, the arc intercept of the impedance spectrum will shift towards the center on the x-axis(real), i.e., for the rise in temperature, the bulk resistance (R_b) reduces.

3.4.1 DC ionic conductivity

The DC ionic conductivity of the blend polymer electrolyte systems was calculated using the formula $\sigma_{dc} = \frac{t}{AR_b}$ [33] where A is the area of cross-section, t is the thickness and R_b is the bulk resistance of the electrolyte. The values of R_b reduced as the temperature increased. Figure 5 shows Log σ vs. $1000/T$ for various blend polymer electrolytes. With the temperature rise, the conductivity increases with the temperature dependence of Arrhenius [34] type. The increase of DC conductivity with

Fig. 4 Cole–Cole plots of (a) PPA1, PPA2, PPA3 and PPA4 at 373 K (b) PPA3 at various temperatures

Fig. 5 Log σ Vs. $1000/T$ of PPA1, PPA2, PPA3 and PPA4

temperature can be ascribed to be the dissociation of ions and thus increase the number of charge carriers. The activation energy (E_a) has been calculated for all the samples. The conductivity increases as the host polymer PVdF wt% increases [35] and maximum conductivity was observed for PPA3, which could be attributed to the hopping phenomenon [36, 37] among the coordination sites and polymer segmentation. The conductivity of PPA3

(PMMA/PVdF/AgNO₃:70/30/5) is 9.13×10^{-6} S/cm at 373 K.

3.4.2 AC Conductivity

The logarithmic conductivity plots as a variable of frequency displayed in Fig. 6 for different polymer ratio compositions of PMMA and PVdF with AgNO₃ salt. This conductivity in polymer electrolytes is a typical phenomenon and this is because of a sudden rise of charge carrier mobility in the complex polymer film. In general, the frequency-dependent conductivity could exhibit in three types of dispersion regions with frequency, (1) low-frequency region, which demonstrates the space charge polarization, (2) dc saturation zone in mid-frequency region and (3) dc-to-ac switching at high frequency-zone, which due to the coulombic interaction of charge carrier and disruption within the framework [38, 39]. Figure 6a demonstrates explicitly that the conductivity is almost unchanged in the low-frequency area, which correlates to conductivity which is independent of frequency. This could be due to the transport of charges through infinite paths [40]. At high frequency, the mobility of charge carriers is greater, so the conductivity increases with frequency. As the PVdF wt% increases, the conductivity increases due to the availability of mobile species and reaches to the maximum value for

Fig. 6 Frequency dependent conductivity of (a) PPA1, PPA2, PPA3 and PPA4 (b) PPA3 at various temperatures

certain concentration, i.e., 30 wt% of PVdF + 70 wt% PMMA (PPA3). Higher wt% of PVdF in the electrolyte membrane helps to increase the viscosity, which in effect, reduces the mobility of charge carriers thus decreases the conductivity [41]. The frequency-dependent conductivity for PPA3 sample at various temperatures was shown in Fig. 6b. As the temperature rises, the frequency scattering gradually moves to the higher frequency zone. At higher frequencies, the transport is controlled by hopping-infinite group contributions. The conductivity increases exponentially and follows Jonscher's power law [42].

$$\sigma_{ac}(\omega) = \sigma(\omega_0) + A\omega^n$$

where $\omega = 2\pi f$ is the angular frequency, A is the constant and n is frequency exponent.

3.4.3 Electric modulus

The standardized electric modulus can be used to analyze the strategies of relaxation in a broad variety of materials. This relaxation mechanism is attributed to the dispersal of relaxation times, which could be attributed to unevenness, domains of conduction and phase conjunction, etc. The complex electric modulus, $M^* = M'(\omega) + jM''(\omega)$, where M' and M'' are the real and imaginary elements of electric

modulus [43]. The following equations can be used to obtain M' and M'' .

$$M'(\omega) = \frac{\epsilon'}{\epsilon'^2 + \epsilon''^2} \quad \text{and} \quad M''(\omega) = \frac{\epsilon''}{\epsilon'^2 + \epsilon''^2}$$

where ϵ' and ϵ'' are the real and imaginary parts of dielectric constants. The modulus spectra of blend polymer electrolyte systems have been reported in Fig. 7. A constant value of M' at very low frequency is identified to increase with frequency rapidly and reaches saturation at very high frequency which could be noticed from the Fig. 7a. As the PVdF percentage increases, the M' plateau increased in the low-frequency region and decline in peak shifted towards the high-frequency zone, which attributed the interaction between the polymer chains which leads to decrease in relaxation time. The variation of M' with frequency at various temperatures of the PPA3 sample was examined and shown in Fig. 7b. The M' values declined with rise in temperature at high frequency and the relaxation frequency shifts into high-frequency zone [44]. This may be attributed to rise in the movement of the polymer segmentation due to blending the polymers and charge carriers with the temperature [35]. Figure 8 represents the variation of M'' with the frequency of the blended polymer electrolyte systems. The broadening and shifting of the peaks were noticed in the blended polymer membranes. The existence

Fig. 7 Variation of Real Electric modulus of (a) PPA1, PPA2, PPA3 and PPA4 (b) PPA3 at various temperatures

Fig. 8 Variation of imaginary Electric modulus of (a) PPA1, PPA2, PPA3 and PPA4 samples (b) PPA3 at various temperatures

of relaxation peaks in M'' infers that the films are the great promise of ionic conductors [45]. The investigation of M'' with frequency at various temperatures was carried out for PPA3 sample and shown in Fig. 8b. The curves of M'' shows the broad peaks with noticeable asymmetry. It was observed that there is a shift in $M''_{\max}$ towards the high-frequency area with an increase in temperature suggests that the increased movement of the charge carriers leading to decrease in relaxation time, which attributes to the fast movement of Ag^+ ions [46].

3.4.4 Dielectric studies

The complex dielectric permittivity (ϵ^*) of a material as frequency dependence is given as, $\epsilon^* = \epsilon'(\omega) + j\epsilon''(\omega)$, where ϵ' is the standard dielectric constant of the sample that determines the quantity of electric energy retained in the substance over every period of the applied alternating field. Figure 9a demonstrates the variation of ϵ' of the polymer blend electrolyte samples with different wt% ratio of PMMA and PVdF. From the figure, it is noticed that the dielectric constant is large at low frequency, which attributes to the tendency of dipoles to align along the field direction [47, 48]. And also observed that, as the PVdF wt% increases, PVdF enables to disperse the ions more and reached to the maximum for PPA3. Figure 9b depicts the dielectric constant

variation of PPA3 sample at dissimilar temperatures. Due to space charge polarization and electrode polarization, the dielectric constant increases with temperature. It can be clearly shown that there was a high distortion of the permittivity noticed in the low-frequency zone accompanied by an almost frequency independent activity beyond 100 kHz. Permittivity values increased with an increase in temperature. Significant improvements in permittivity at the low-frequency area are attributable to space charge and electrode polarization impacts which are responsible for the non-Debye action [40]. Figure 10a represents the imaginary dielectric constant (ϵ'') of the blend polymer electrolyte systems with frequency at 373 K. The rise in dielectric constant with temperature [49] corresponds to the rise in density of Ag^+ -ions and was shown for PPA3 sample in Fig. 10b. The polarization of space charge induces a high dielectric constant at low frequency. It is attributed to the deposition of charges at electrodes and confirms the non-Debye dependence. The higher values of ϵ'' at lower frequency region is due to the movement of free charges within the material, and the prime charge carriers are Ag^+ -ions in these polymer electrolytes. The disparity of loss tangent with frequency could be used in ionic conductors to illustrate the mechanism of relaxation and for the blended polymer electrolyte systems under the study are shown in Fig. 11a. The loss tangent ($\tan \delta$) is expressed as $\tan \delta = \frac{\epsilon''}{\epsilon'}$ where δ is the loss

Fig. 9 (a) Variation of real permittivity of PPA1, PPA2, PPA3 and PPA4 (b) at different temperatures of PPA3 sample

Fig. 10 (a) Variation of imaginary permittivity of PPA1, PPA2, PPA3 and PPA4 (b) at different temperatures PPA3 sample

Fig. 11 (a) Frequency dependent dielectric loss tangent of PPA1, PPA2, PPA3 and PPA4 (b) at various temperatures of PPA3

Fig. 12 Variation of Z'' and M'' of PPA3 sample with frequency at 373 K

angle [37]. Figure 11b exemplifies the dielectric loss tangent with frequency at various temperatures. From the figure, the maximum loss shifts to the high-frequency area when the temperature rises [50] which results in an increase of conductivity due to decreasing relaxation time. The non-Debye behavior of the sample PPA3 could be understood with the electric impedance and modulus spectrum conveyed in Fig. 12. This could be shown that $Z''_{\max}$ and $M''_{\max}$ do not coincide at the same frequency [51]. Z'' widened in lower frequency while M'' spectrum widened in higher frequency, which indicates the dispersion of relaxation times, i.e., non-Debye activity of electrolyte film.

4 Conclusions

PMMA and PVdF based blend polymer electrolytes with 5 wt% of AgNO₃ were prepared by solution cast method by varying the polymers wt% ratio. The effect of polymer ratio variation on morphology, structural and electrical

studies investigated systematically. On the integration of PVdF, the solid polymer electrolyte exhibits improved electrical properties. In specific, 70 wt% PMMA: 30 wt% PVdF with 5 wt% of AgNO₃ has uniform surface and highly amorphous compared with other samples, which has been proven in XRD, SEM and FT-IR analysis. A large plateau region in frequency-dependent conductivity suggests that conductivity is mostly due to ions migration and the sudden rise of ionic conductivity in the high-frequency region is due to the hopping mechanism. Analysis of electric modulus reveals the distribution of relaxation time. Dielectric studies reveal that energy storage (ϵ') at the low-frequency area is higher because of polarization and higher value of energy loss (ϵ'') is due to non-Debye type relaxation.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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