

Effect of Nano-Filler on the Properties of Polymer Nanocomposite Films of PEO/PAN Complexed with NaPF_6

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Abstract: Free standing transparent PNC (Polymer nanocomposite) films based on PEO/PAN + NaPF_6 with different concentration (wt./wt.) filler of nano sized (TiO_2) is synthesized by using standard solution cast technique. HRXRD (High resolution X-ray diffraction) and FESEM (Field emission scanning electron microscopy) have been performed to see the structural and microstructural behavior of the PNC films. The microscopic interaction among polymer, salt and nano-ceramic filler has been analyzed by FTIR (Fourier transformed infra-red) spectroscopy. The reduction of ion pair formation in polymeric separator is clearly observed on addition of nano-filler in the polymer salt complex film. Electrical (ionic/electronic) conductivity has been estimated ($\sim 10^{-4}$ S/cm) optimized PNC films concentration of nanofiller (15 Wt.%). The estimated value of electrical conductivity is well corroborated by FTIR study. Thermal analysis has been done with thermo gravimetry analysis to find out thermal stability of PNC films. Transport properties associated due to majority mobile carriers ions and only negligible participation from electrons was observed through transport number analysis. The band gap (i.e. direct as well as indirect) decreases on the addition of nano-filler observed from the optical analysis. The estimated result of the prepared PNC films are at par with desired value for the device application.

Key words: Sodium ion battery, polymer electrolyte, PEO, dielectric property, optical property.

1. Introduction

Basically electronic and ionic two types of conduction occurs in material. Solid state ionics is the branch of physics which deals with the material having high ionic transport properties. From tremendous application of these material one is for the sake of energy storage devices. As portable electronics is becoming more and more common in our society, and many aspects of our lives are now dependent on the performance of electronics equipment's, also the demand for safe, reliable and efficient mean to store electrical energy for energy storage devices has increased. Also, recent advances in processing power, screen size and urge for thinner and lighter devices, have increased the demand for lighter batteries with higher energy density [1].

Polymer electrolyte desired for energy storage

purposes like high energy density solid polymer batteries due to the reason solid electrode/solid electrolyte contact. Flexible material like organic polymer can produce excellent solid /solid interface between solid electrode and solid electrolyte [2]. The main role of polymer electrolyte is to act as separator between anode and cathode material in batteries [3]. It also act as ions transport medium for the conduction of ions during the electrochemical process such as charging and discharging, the ions in the electrolyte get adsorbed and desorbed on the porous electrode, which cause rapid charging and discharging of the polymer so that the high energy density battery has been obtained [4, 5].

In order to achieve high ionic conductivity at room temperature, various method to be employed such as conventional dry solid polymer electrolyte, plasticized solid polymer electrolyte, rubbery electrolyte, polyelectrolyte and gel polymer electrolyte. But after

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the evaluation of these material for device application these exhibits some kind of limitation. These limitation arises because of low ionic conduction at room temperature, concentration polarization, and poor mechanical stability. If the host polymer matrix is more crystalline then it lead to poor segmental mobility and low ionic conductivity. And it may be due to strong attraction between oppositely charged ions, they lead to formation of ion pairing also called concentration polarization [6].

To overcome above limitations faced in the polymer electrolyte film an effective approach is polymer nanocomposite formation by addition of nano-filler such as TiO₂, SiO₂, BaTiO₃, ZrO₂, and Al₂O₃ etc. in polymer salt complexes [7]. Due to the large surface area of nano-sized filler we obtain enhanced properties such as electrical, optical, thermal and mechanical properties of free standing polymer nanocomposite electrolyte film can be achieved. PEO shows excellent chemical and high surface resistance and offers high optical transparency. PEO complexed with salt consist of gross morphological structure which consist of feature that is helpful in determining ion transport properties of material [8, 9]. Poly (acrylonitrile) (PAN) can enhance mechanical properties such as small thermal resistance and flame retardant property stiffener in the electrolyte due to its immiscibility with the plasticizer [10]. Sodium salts are more environmentally friendly, less expensive, more abundant, easily distributed, easier to extract, and fourth most abundant element in earth crust and easy to recycle, it is used for sodium ion batteries [11, 12].

In the present study, investigation of solid state polymer electrolyte cum separator is done by adding various composition of TiO₂ nano-filler in PEO/PAN polymer blend complexed with an atomic ratio of (Ö/Na = 20) NaPF₆ salt. Addition of nano-filler with different composition increases interaction between polymer and nano-filler. All important result need to be added with fact figure.

2. Experimental Setup

Following polymer, salt and nano-filler is to be used for the synthesis of free standing polymer electrolyte film are PEO Poly (ethylene oxide), and PAN Poly (acrylonitrile) purchased from Sigma Aldrich. PEO has been used as host polymer and it contain crystallinity about 70-85%. It has linear chain formed with the repeating (CH₂-CH₂-O)_n unit. The melting temperature of crystalline phase and the glass transition temperature of amorphous phase is 65 °C and -60 °C respectively. PAN has melting point 319 °C and glass transition (T_g) temperature is 85 °C and formed by repeating of (C₃H₃N)_n unit. PAN gave mechanical support to polymer electrolyte film due to its unique properties. NaPF₆ (sodium hexafluorophosphate) used as a salt having melting point 200 °C molar mass 167.95 and density 2.369 g/cm³. To see effect of nanofiller on the polymer electrolyte film TiO₂ was chosen as a nano-filler.

In experiment the pure polymer blend of composition (PEO/PAN) films complexed with NaPF₆ salt prepared by solution cast technique. The weight percent ratio such as 50 weight percent of PEO, PAN, and salt of Ö /Na ratio 20 are mixed by a solution casting technique using DMF (dimethylformamide) as solvent.

Then in same blend polymersalt complex addition of nano-filler (TiO₂) with different composition was done in different proportion such as 1, 2, 7, 10, 15, and 20 weight percent. The above composition of TiO₂ is added as a dopant, and stirred for about 10 h. These solutions were cast and left for evaporation with a similar manner. Finally we got free standing film of pure and doped polymer electrolyte. Fig. 1 shows flow chart for the preparation of free standing film. The solution of above composition mixed for several hours by means of stirrer, until the solution mixed properly, and then casted onto polypropylene dishes and left for evaporation at room temperature, dried under vacuum at 10⁻³ mbar pressure for 2-3 days.

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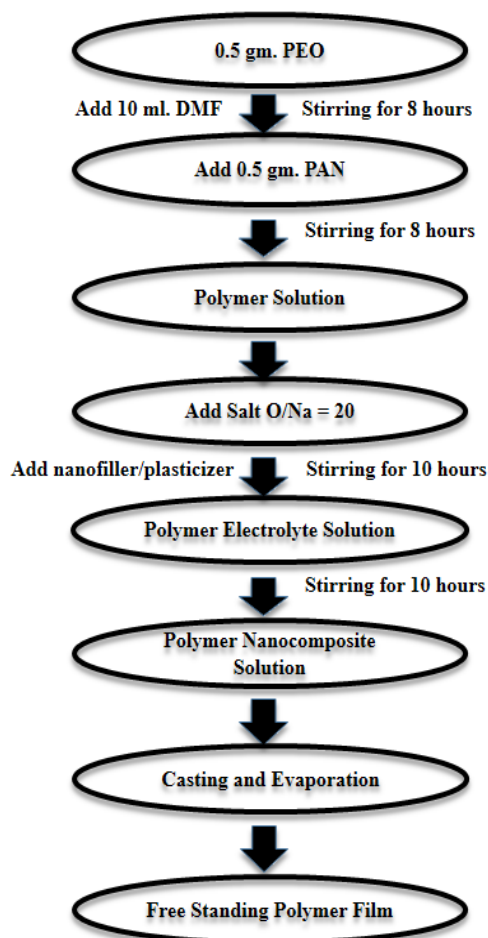


Fig. 1. Flow Chart for preparation of free standing polymer film by solution cast method.

2.1 Material Characterization

XRD (X-ray diffraction) patterns analysis was done by using X'PT PRO X-ray diffractometer machine equipped with X-ray beam K-alpha irradiation as the photon source 1.54060 Å. Samples were analysed in the 2θ range from 10° to 80° scanning at a room temperature. To investigate the influence of salt on polymer structure XRD is performed. X-ray diffraction provides the most definitive structure information interatomic distances and bond angles. To understand the properties of any material it is very necessary to understand the structural morphology of ions in the solid polymer electrolyte film, as the properties of material are closely related to its structure. Structural characterization of solid was done by field emission scanning electron microscopy

(FESEM (Card Ziess Merlin Compact)) to investigate the influence of salt on polymer structure. Impedance spectroscopy was carried out for conductivity measurement with CHI 760 instrument electrochemical workstation over the frequency range from 1 Hz to 1MHz with sample sandwiched between stainless steel electrodes. From the impedance analysis dielectric properties of prepared film were also studied. FTIR (Fourier transform infrared) spectroscopy was done by Bruker Tensor-27, and spectrum was observed in the range of $600\text{--}4,000\text{ cm}^{-1}$ to detect the presence of various functional groups. In infrared spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. TGA has been done to analyze thermal stability of prepared film.

3. Experimental Results

3.1 High Resolution X-Ray Diffraction (HRXRD)

HRXRD patterns of PEO/PAN polymer blend complexed with NaPF₆ and 15 weight percent TiO₂ nano-filler was shown in Fig. 2. The polymer and nano-filler peaks have been identified and indexed to

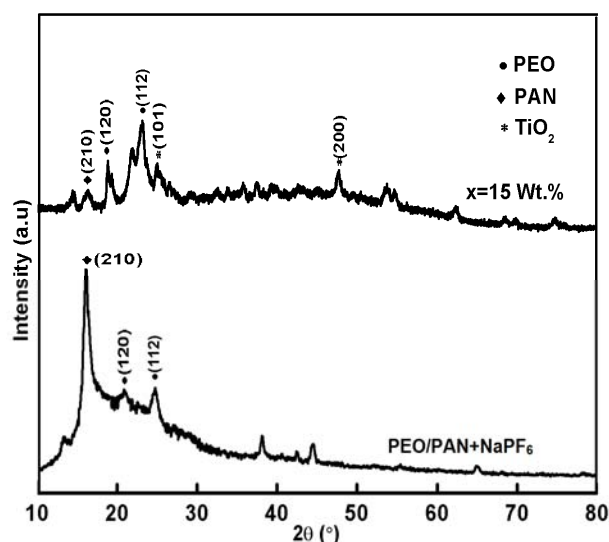


Fig. 2. XRD pattern of PEO/PAN + NaPF₆ with x weight percent of TiO₂.

confirm the interaction of polymer, salt, and nano-filler at the microscopic level. PEO/PAN complexed with NaPF₆ film exhibits two strong peaks at 2θ equal to 19.2° , and 23.6° for PEO [13]. Characteristic peak for PAN exist at 2θ equal to 17.0° respectively [14]. Peaks of NaPF₆ salt was not present in the polymer blend complexed with NaPF₆ sample. This means that our salt is properly complexed with the polymer blend. There are some extra peak appearing around the main peak of PEO and PAN polymer which are not the peak of PEO/PAN, TiO₂ and salt. These extra peak indicate the coordination of Na⁺ of the salt with the ether group of PEO. The low intensity of the HRXRD pattern observed for polymer blend complexed with NaPF₆ and 15 weight percent TiO₂ nano-filler shows the presence of amorphous phase. This phase was proved to be useful for improving polymer chain segmental motion. So HRXRD confirms the coordination or complexation of polymer blend with salt. Some changes occur in general profile of polymer main peak as a function of nano-filler concentration. Such as shifting of host polymer PEO characteristic peak at 19.2° , and 23.6° toward low angle with the addition of nano-filler, increasing d-spacing and lowering in the peak intensity. These changes observed among components of PNC films during XRD analysis may be due to microscopic interaction and these provide supportive evidence at microscopic level [15].

3.2 Field Emission Scanning Electron Microscopy (FESEM)

The morphological and structural analysis of nanocomposites is often done with FESEM. The properties associated with polymer nanocomposites are a function of the filler size, shape, dispersion, and of the polymer matrix - filler interaction. Phase separation in polymer electrolyte due to rapid evaporation of solvent DMF are shown by various pores in micrograph image Fig. 3a. The difference in pores is due to the difference in driving force for

phase separation. The polymer with the nano-filler (TiO₂) lessen the difference in driving force for phase separation and produce homogeneous film of better quality.

Rough surfaces as observed in Fig. 3 may be due to uneven distribution of crystallite component in predominately amorphous polymer matrix. Agglomerations in Fig. 3b results due to weaker polymer/nano-filler interfacial interactions and higher stress concentration regions. As the dispersed particle size becomes smaller and the particle dispersion is more uniform then homogeneous film was produced which have better electrical as well as mechanical properties [16].

3.3 Fourier Transform Infrared (FTIR) Spectroscopy

FTIR microscopy analysis of the sample was done to detect the presence of various functional groups. FTIR spectrum was observed in the range of 600-4000 cm⁻¹ as shown in Fig. 4. The peak in the wavenumber range 800 cm⁻¹ to 900 cm⁻¹ corresponds to salt which causes due to the vibrational mode of PF₆⁻ anion. The characteristic absorption peak of PEO polymer observed in the spectral pattern of polymer salt complex and PNC films at the wavenumbers ~ 834-830-827, ~ 1,104-1,096, ~ 1,350, and 2,865 cm⁻¹ are attributed to rock(CH₂), ν (C-O-C), wag(CH₂), and ν (CH₂) respectively. Peak near 1356 cm⁻¹ which, corresponds to CH₂ wagging (wag(CH₂)) [17]. The characteristic peak of PAN polymer observed in the spectral pattern of polymer salt complex and PNC films at the wavenumbers 1,250 cm⁻¹, 1,450 cm⁻¹, 1,665 cm⁻¹ and 2,243 cm⁻¹ are assigned to wagging mode of CH₂, bending mode of CH₂, symmetric stretching of C=C group, and symmetric stretching of nitrile group in PAN respectively. The C $\equiv$ N stretching band in the IR spectrum appearing at 2,243 cm⁻¹ is the most characteristic feature of nitrile group in pure PAN [5].

The FTIR analysis gives us the information of role of salt in the polymer and salt interaction in the

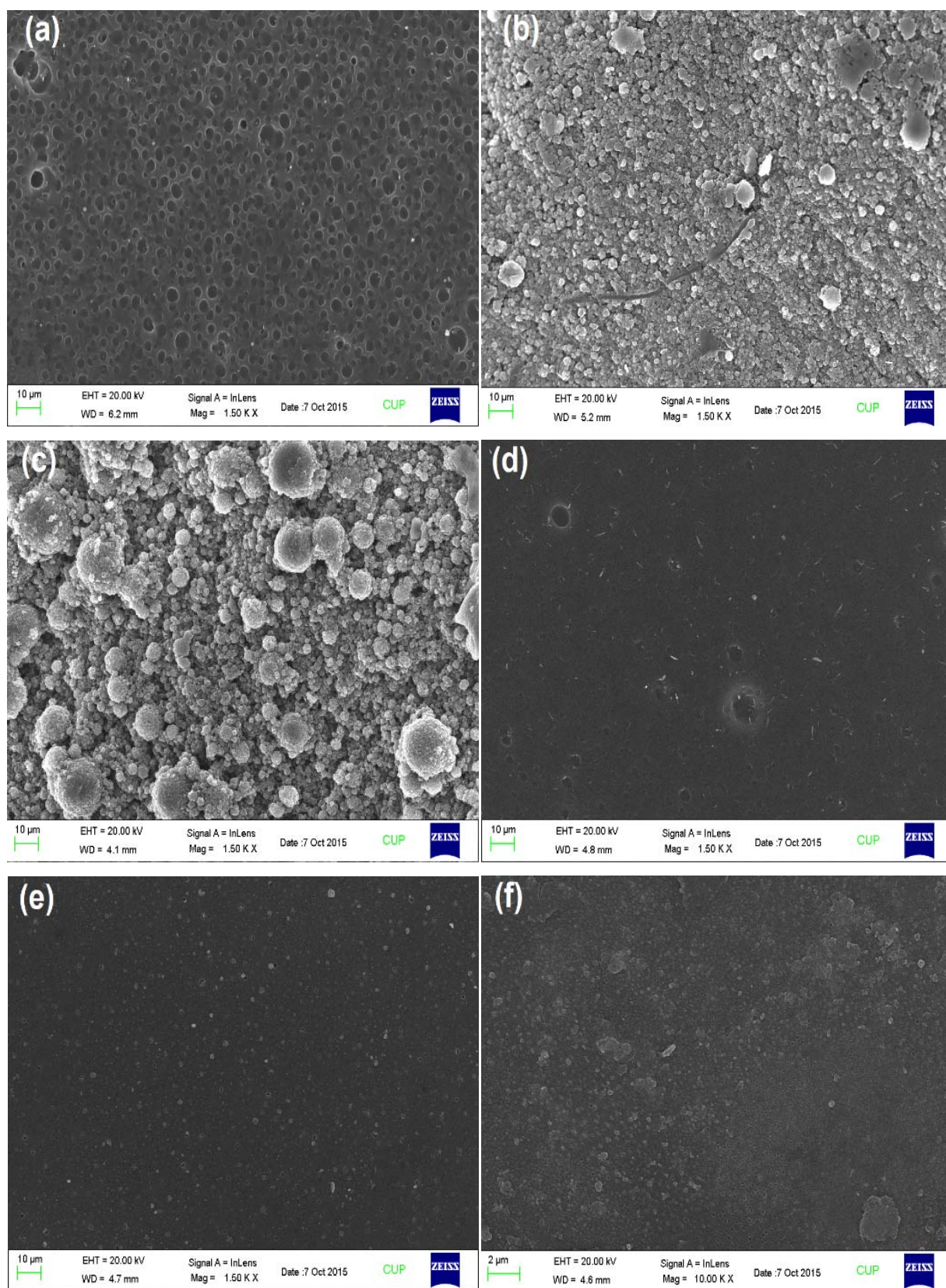


Fig. 3. FESEM micrograph of polymer electrolyte film based on $(\text{PEO/PAN})_{20}\text{NaPF}_6 + x \text{ wt.\% TiO}_2$ (a) $x = 0$ (b) $x = 1$ (c) $x = 2$ (d) $x = 10$ (e) $x = 15$ (f) $x = 20$.

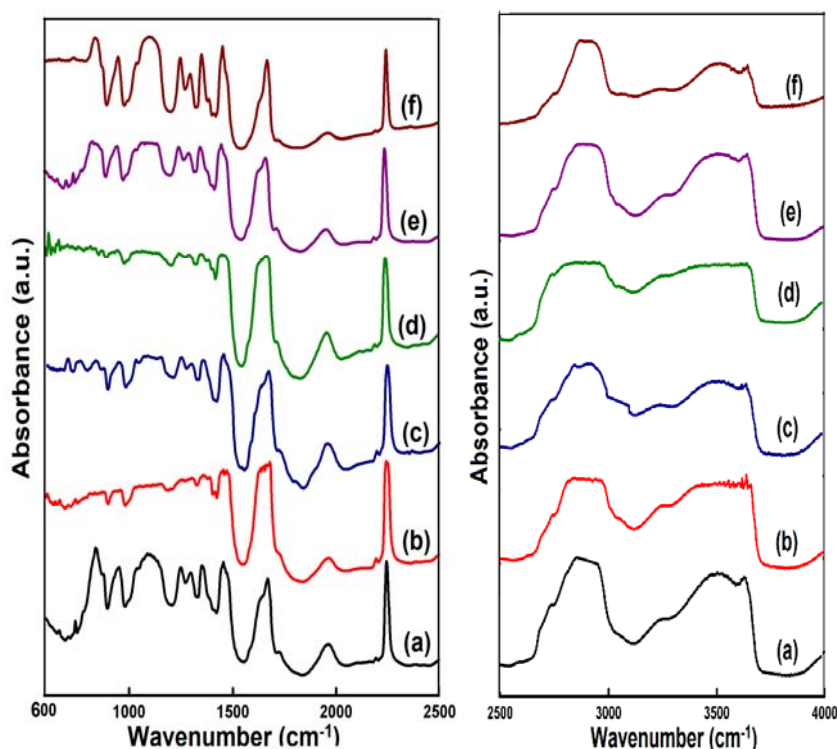


Fig. 4 FTIR spectra for polymer nanocomposite electrolyte film based on (PEO/PAN)₂₀-(NaPF₆) + x wt.% TiO₂ showing (a) x = 0 (b) x = 1 (c) x = 2 (d) x = 10 (e) x = 15 (f) x = 20.

Table 1 FTIR band assignment of polymer nanocomposite films based on (PEMA/PVC)₈NaPF₆ + x wt. % TiO₂ nano-filler.

(PEO/PAN) ₂₀ NaPF ₆ x = 0	(PEO/PAN) ₂₀ NaPF ₆ +xwt% TiO ₂					Assignment mode	Source
	x = 1	x = 2	x = 10	x = 15	x = 20		
834	827	827	827	830	834	rock(C-H ₂)	PEO
950	957	950	957	951	942	v (F ₂ P)	Salt
1096	1042	1050	1042	1071	1104	v(C-O-C)	PEO
1250	1250	1250	1250	1249	1250	wag(CH ₂)	PEO
1350	1357	1350	1357	1351	1357	wag(CH ₂)	PEO
1450	1457	1442	1457	1454	1457	bend(CH ₂)	PAN
1665	1665	1650	1673	1668	1673	v(C=C)	PAN
1958	1965	1965	1965	1966	1965	v(C=C)	PEO
2243	2243	2243	2243	2255	2243	v(C≡N)	PAN
2865	2850	2889	2889	2897	2896	v(CH ₂)	PEO

polymer film. Characteristic absorption peak observed in the spectral pattern in the wavenumber 600-4,000 cm⁻¹ was shown with the help of band assignment in Table 1.

Peak due to the vibrational modes of PF₆⁻ anion has been observed at 950 cm⁻¹. Asymmetric stretching observed on peak keeps on changing with change in the nanofiller concentration in the composite phase [18]. This asymmetry in the anion stretching vibrational mode is an outcome of the degeneracy

arising out of more than one contribution possibly due to the presence of free anion and ion pairs.

3.3.1 Polymer Ion Interaction

Nano-filler effect substantial spectral change in the profile of FTIR spectrum of PEO host polymer by addition of nano-filler concentration in the wavenumber. Shift in carbonyl stretching (v (C-O-C)) of PEO peak in the range of 1000-1200 cm⁻¹ with addition of salt was clearly seen in Fig. 5. Because Na⁺ ion from NaPF₆ was attracted toward the negative

charge lone pair on oxygen atoms of carbonyl (C=O) group in PEO, which confirms the coordination of Na⁺ ions of NaPF₆ on the oxygen atom of carbonyl group of PEO. Upshift occurring in the peak for the concentration of 10, 15, 20 wt.% addition of TiO₂.

Minor shifting of peak for the wagging mode of CH₂ (wagg(CH₂)) observed in the range 1330-1390 cm⁻¹. Shift in this peak with the addition of salt and nanofiller shown in Fig. 6. Shifting in the peak correspond to bending mode of CH₂ (bend(CH₂)) in the wavenumber 1,420-1,520 cm⁻¹ shown in Fig. 7.

As filler concentration increases, there is shift in peak of symmetric (ν_s(CH₂)) and asymmetric ν_a(CH₂))

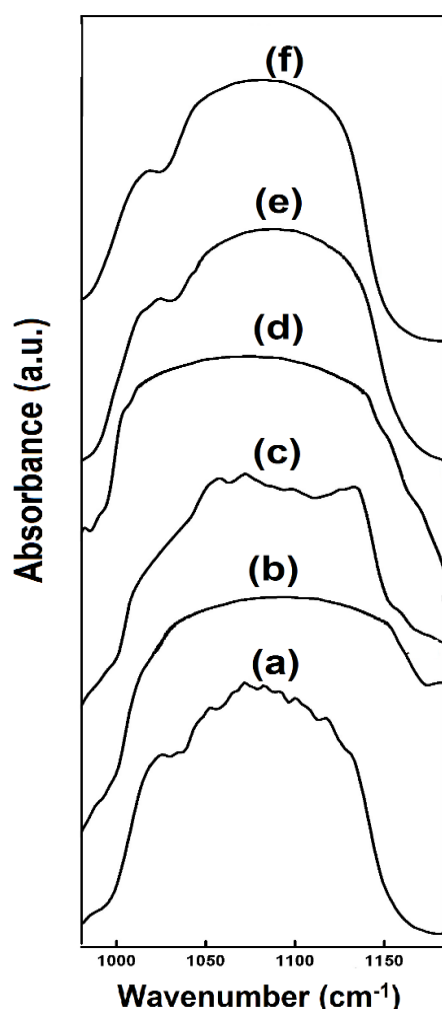


Fig. 5. FTIR spectra for polymer nanocomposite(PEO/PAN)₂₀(NaPF₆) + x wt.% TiO₂ (a) x = 0 (b) x = 1 (c) x = 2 (d) x = 10(e) x = 15 (f) x = 20 polymer nanocomposite solid state polymer electrolyte in

wavenumber 1,000-1,200 cm⁻¹.

stretching CH₂ mode at region 2800 to 3000 cm⁻¹ for PS film as compared to PNC film as shown in Fig. 8.

The shifting in peak can be attributed to Lewis acid base interaction occurring between the surface group of filler and Na⁺. Peaks in this region upshifted after addition of nano-filler and also get split into two contribution in PNC films. This splitting and asymmetric FTIR band may get affected due to strong interaction between host polymer and nanofiller.

3.3.2 Ion-Ion Interaction

To estimate free anion and ion pair area the band pattern in the wavenumber 880-1,000 cm⁻¹ has been deconvoluted using Voigt profile with a commercial software peak fit analyser. Two distinct contribution observed at 925 and 851 cm⁻¹ in the deconvoluted pattern as shown in Fig. 9. The peak appearing at 850

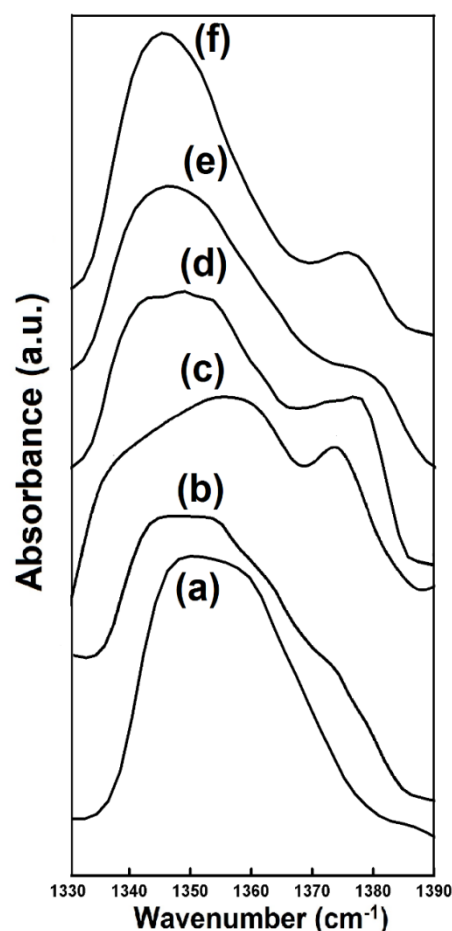


Fig. 6. FTIR spectra for polymer nanocomposite electrolyte film based on (PEO/PAN)₂₀(NaPF₆) + x wt.% TiO₂ (a) x = 0

(b) x = 1 (c) x = 2 (d) x = 10 (e) x = 15 (f).

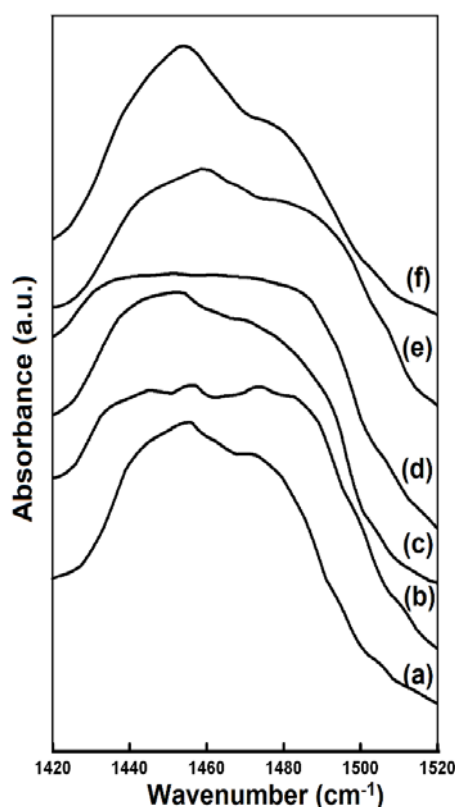


Fig. 7. FTIR spectra for polymer nanocomposite (PEO/PAN)₂₀(NaPF₆) + x wt.% TiO₂ (a) x = 0 (b) x = 1 (c) x = 2 (d) x = 10 (e) x = 15 (f) x = 20 in wavenumber 1,420-1,520 cm⁻¹.

cm⁻¹ has been attributed to free anions and peak appearing at 872 cm⁻¹ has been attributed to presence of ion pairs in the solid polymer electrolyte film [5].

Free anion area increases whereas ion pair area decreases with the addition of nano-filler up to certain limit of nano-filler that is x = 15 wt. % TiO₂ here, further addition of nano-filler at x = 20 wt. % TiO₂ nano-filler it decreases. Also Table 2 shows Peak position of deconvoluted free anion peak of polymer nanocomposite films based on (PEO/PAN)₂₀NaPF₆ + x wt.% TiO₂ nano-filler. The presence of two distinct degenerate FTIR band in the deconvoluted pattern for experimental spectrum provides an evidences of strong ion-ion interaction in the prepared polymer nanocomposite film.

3.4 Electrochemical Properties

From transport number analysis it was observed

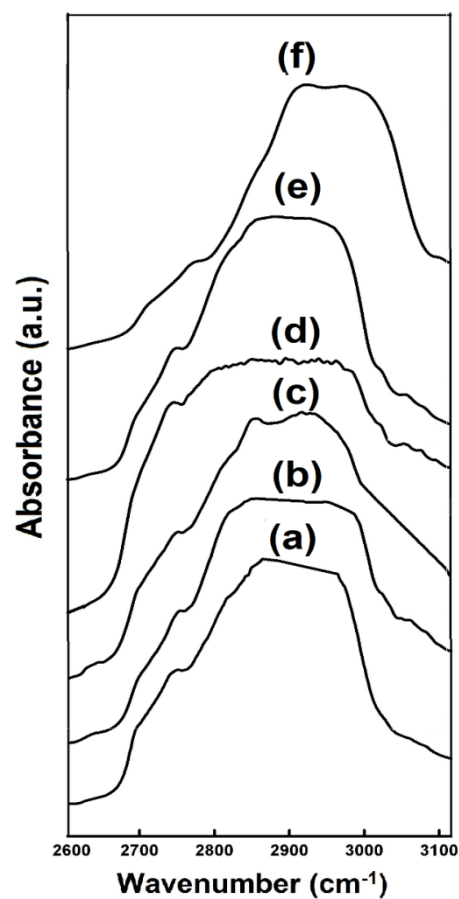


Fig. 8 FTIR spectra for polymer nanocomposite (PEO/PAN)₂₀(NaPF₆) + x wt.% TiO₂ (a) x = 0 (b) x = 1 (c) x = 2 (d) x = 10 (e) x = 15 (f) x = 20 in wavenumber 2,600-3,000 cm⁻¹.

with the addition of nano-filler there is increase in ionic conductivity and electronic conductivity reduces or say that electronic conductivity reaches to negligible value. The ionic and electronic conductivity value calculated from the following Eq. (1):

$$\sigma_{ion} = \sigma_{dc} T_{ion}$$

$$\sigma = 1 - \sigma_{ion} \quad (1)$$

where, T_{ion} is the ionic transport number which is equal to 0.88 for (PEO/PAN)₂₀(NaPF₆) + 15 wt.% TiO₂ concentration shown in Fig. 10. As the electrical conductivity w.r.t. nanofiller concentration is shown in Fig. 11. The percentage of ionic conductivity and electronic conductivity can be measured very easily using these two data. σ_{dc} is the dc conductivity obtained from the impedance data, it was analyzed from the impedance data that with the addition of

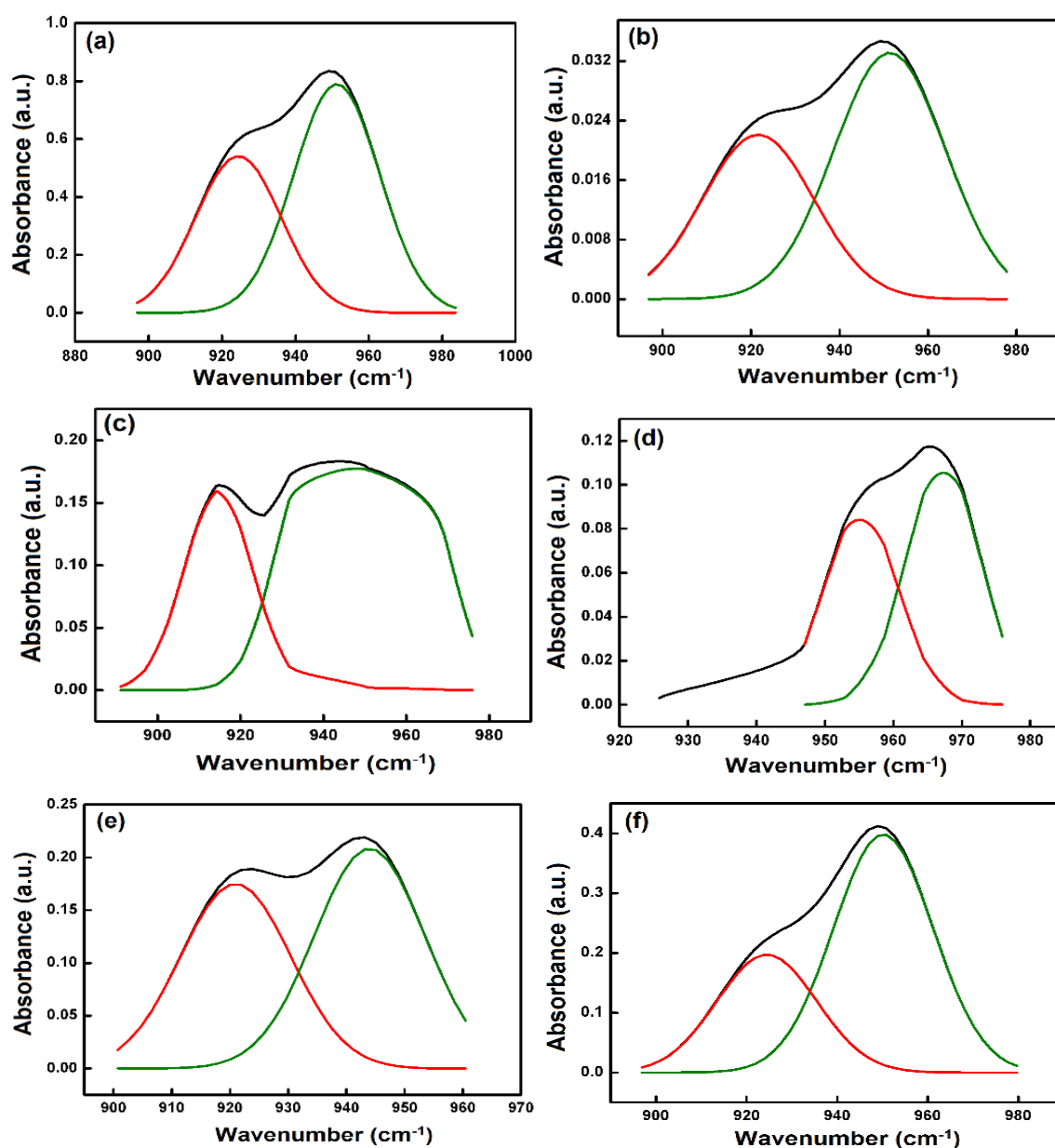


Fig. 9. Deconvolution pattern of $\nu(\text{PF}_6^-)$ in nanocomposite $(\text{PEO/PAN})_{20}(\text{NaPF}_6) + x \text{ wt.}\% \text{ TiO}_2$ (a) $x = 0$ (b) $x = 1$ (c) $x = 2$ (d) $x = 10$ (e) $x = 15$ (f) $x = 20$.

Table 2. Peak position of deconvoluted free anion peak of polymer nanocomposite films based on $(\text{PEO/PAN})_{20}\text{NaPF}_6 + x \text{ wt.}\% \text{ TiO}_2$ nano-filler.

Nano-filler TiO ₂ (in wt. percent)	Deconvoluted anion peak data				Correlation coefficient (r ²)
	Free anion peak		Ion pair peak		
	Position (cm ⁻¹)	Area (%)	Position (cm ⁻¹)	Area (%)	
0	924	40.47	951	59.52	0.9875
1	924	40.70	951	59.29	0.9625
2	921	44.68	958	55.31	0.9563
10	937	44.57	957	55.42	0.9664
15	921	46.25	943	53.74	0.9190
20	924	33.03	950	66.96	0.9933

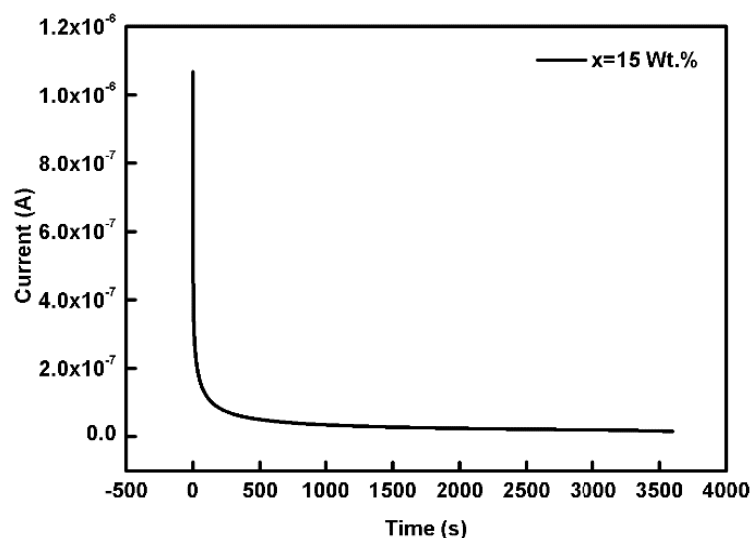


Fig. 10 Current versus time plot of (PEO/PAN)₂₀NaPF₆ + x wt. % TiO₂ nano-filler.

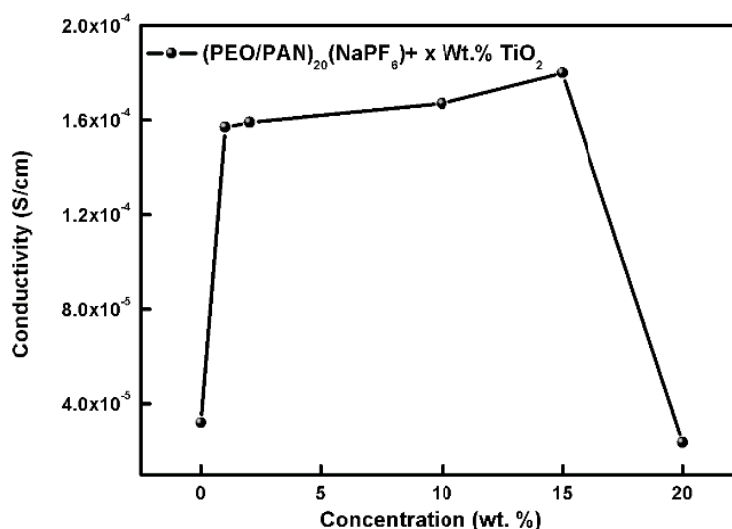


Fig. 11 Variation of conductivity with the concentration of TiO₂ nano-filler.

nano-filler, there is continuous increase in conductivity such as for our prepared sample without addition of nano-filler conductivity initially is in the range of 3.2×10^{-5} , but with the addition of micro range inorganic nano-filler it increases continuously and reaches to $1.8 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$ for $x = 15 \text{ wt.}\%$ concentration of TiO₂ because addition of nano-filler improves the host polymer us region and provides free volume polymer matrix. Also filler helps in faster dissociation of salt by interacting with it and more free ions are formed which increase the amorphous region and provides free volume polymer matrix. Also filler helps in faster dissociation of salt by interacting with it

and more free ions are formed which increase the conductivity. But there is further decrease in the value of ionic conductivity with further addition of nano-filler. This is may be due to gradual formation of neutral aggregates of nano-filler, which creates blockages in the conducting path, reduces free volume, and increase crystallinity of the polymer blend film [19]. These factor may be responsible to resist the movement of mobile ions and polymer segmental motion in the polymer matrix [20]. We observe this type behavior of prepared polymer nanocomposite film at $x = 20 \text{ wt.}\%$ concentration of doped TiO₂.

By substituting these values we get ionic conductivity values is 10^{-4} S/cm for $x = 15$ weight percent TiO₂ doped polymer electrolyte film, 10^{-5} S/cm for without nano-filler added sample. Electronic conductivity is in the range 10^{-6} and 10^{-7} S/cm which is negligible as compared to ionic conductivity. Hence transport properties mainly dominated by ions to that of electrons, only negligible amount of current has been obtained due to electrons. This limit show good suitability of prepared film for the device application [21].

3.5 Dielectric Analysis

The complex permittivity or dielectric constant is the sum of two components known as real part (ϵ') measure the storage ability of charge carriers and imaginary part (ϵ'') of dielectric constant also called dielectric loss measure loss of transport charge in the solid polymer films as shown by Eq. (2).

$$\epsilon^* = \epsilon' - j\epsilon'' \quad (2)$$

where,

$$\epsilon' = \frac{-Z''}{\omega c_0(Z'^2 + Z''^2)}$$

and

$$\epsilon'' = \frac{-Z'}{\omega c_0(Z'^2 + Z''^2)}$$

Similarly real and imaginary part of conductivity was observed with the help of following Eq. (3).

$$\sigma' = \omega \epsilon_0 \epsilon'' \text{ and } \sigma'' = \omega \epsilon_0 \epsilon' \quad (3)$$

where, ϵ_0 is known as permittivity of free space and ω is the frequency. They are obtained from real (ϵ') and imaginary part (ϵ'') dielectric constant. The real part of conductivity is directly proportional to complex part of dielectric constant. The real part of conductivity σ_1 referred as ac conductivity. Which is defined by following Eq. (4) for conducting medium.

$$\sigma_{ac} = \omega \epsilon_0 \epsilon'' = \omega \epsilon_0 \left(\frac{\sigma_{dc}}{\omega \epsilon_0} + \epsilon''_{corrected} \right) \quad (4)$$

where first part is dc conductivity and second part is fully dependent upon frequency [22]. From Fig. 12, it was observed that as frequency increases dielectric constant (ϵ') continuously decreases with the increasing of frequency and approaches to a constant value at particular frequency region. But dielectric loss (ϵ'') gain very large value ($\sim 6 \times 10^7$) at the low

Table 3. Ionic transport number, ionic conductivity, electronic conductivity for (PEO/PAN)₂₀NaPF₆ + x wt. % concentration TiO₂.

Nano-filler (TiO ₂) x wt.(%)	Transport number (T _{ionic})	DC conductivity (S/cm)	Ionic conductivity (S/cm)	Electronic conductivity (S/cm)
x = 15	0.98	1.8×10^{-4}	1.76×10^{-4}	5×10^{-6}
x = 20	0.98	2.37×10^{-5}	2.32×10^{-5}	6×10^{-7}

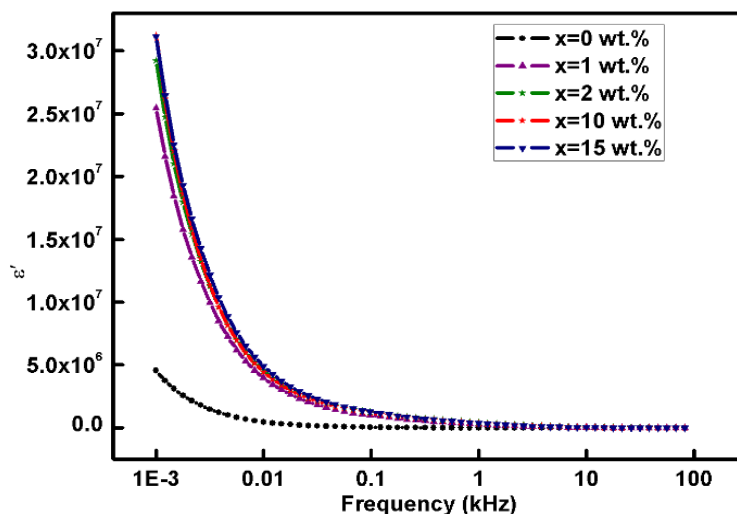
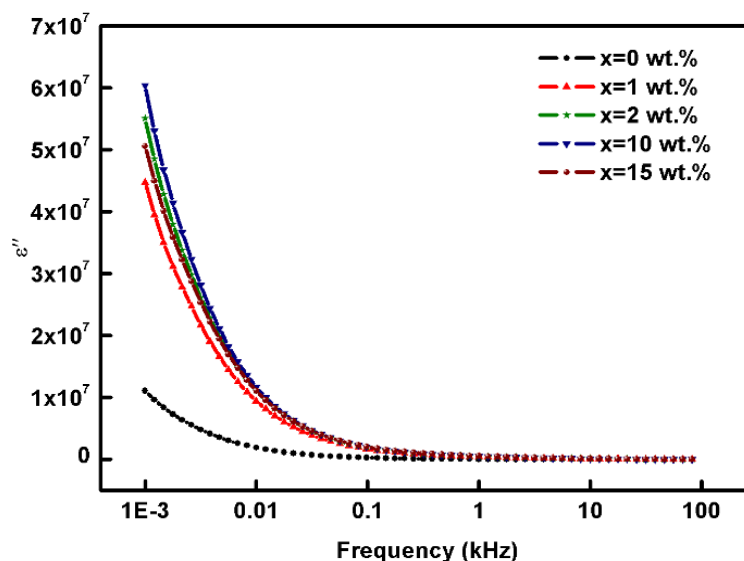
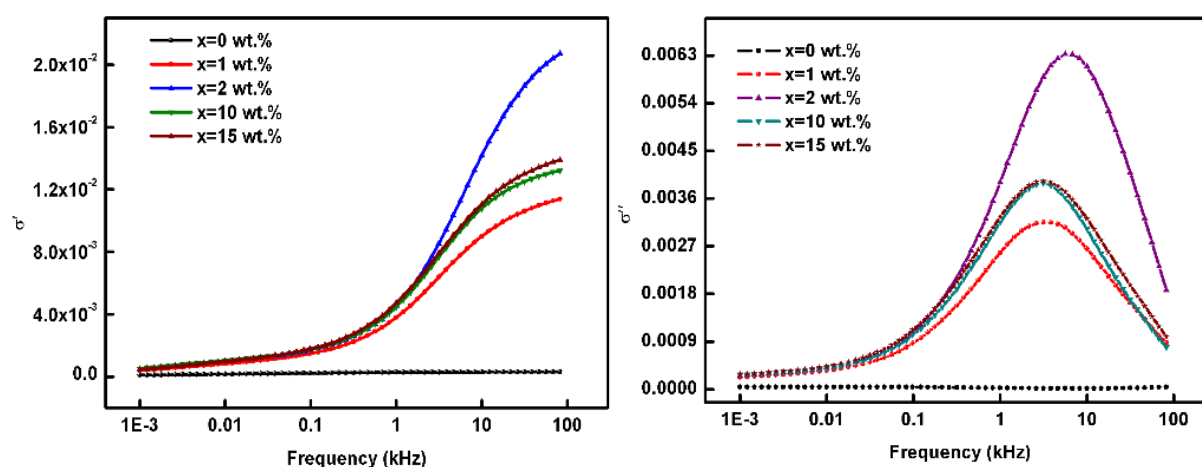


Fig. 12 Dielectric constant (ϵ') versus frequency plot of (PEO/PAN)₂₀NaPF₆ + x wt. % TiO₂ nano-filler.

 Fig. 13 Dielectric loss (ϵ'') versus frequency plot of (PEO/PAN)₂₀NaPF₆ + x wt. % TiO₂ nano-filler.

 Fig. 14 σ' and σ'' versus frequency images of (PEO/PAN)₂₀NaPF₆ + x wt.% TiO₂ nano-filler.

frequency region shown in the Fig. 13. This is due to the motion of free charge motion within the material.

The large value of electric field at the high frequency region and at that frequency region dipole find difficult to orient in the direction of applied electric field. Hence less orientation of dipole at the high frequency region results decrease in the value of dielectric constant at that region. Whereas at low frequency region tendency of dipoles to orient themselves in the direction of electric field in the macromolecules region [23]. At the electrode-electrolyte interface there is accumulation of large number of charge carrier. If the large number of

charge carrier accumulate at the electrode-electrolyte interface which results in to polarization. Due to polarization of charge carrier there is formation of space charge region at the electrode-electrolyte interface Debye type of behavior is obtained.

In the high frequency region increase in the values of σ' and σ'' due to the dielectric contribution occurs. It refers to the region in the conductivity spectrum which have strong frequency dependence. Both σ' and σ'' increase with increasing frequency, this is the region of high frequency shown in Fig. 14.

The frequency, at which the conductivity starts following this type of behavior is called critical

frequency or hopping frequency (ω_p). It is that frequency in which ions start oscillate in small distance due to flipping or reversal order of electric field. With increasing frequency, increasing conductivity indicates that ionic transport occurs at time scales shorter than $1/\omega_p$. So, ionic transport in the prepared polymer electrolyte film causes by ionic diffusion i.e. forward backward motions of ions which is non-random. These transport mainly depends upon the critical frequency which can vary with temperature and how much filler concentration used [24].

Tangent loss tells about the energy dissipation occurs during ionic transport and polarization of a charge dipole. Loss tangent variation with the frequency consist of peak, presence of peak in the tangent loss results represent relaxing dipoles in the prepared samples. With the addition of nano-filler this peak shifts toward higher frequency region as shown in Fig.15 correspond to the decrease in the value of relaxation time.

Relaxation time decrease directly means polymer chain segmental motion speed up, which happen when there is increase in amorphous region[25]. Hence transport properties increases with the addition of nano-filler up to certain limit.

3.6 Optical Analysis

To study the information about the optical properties of solid we have to study for the band

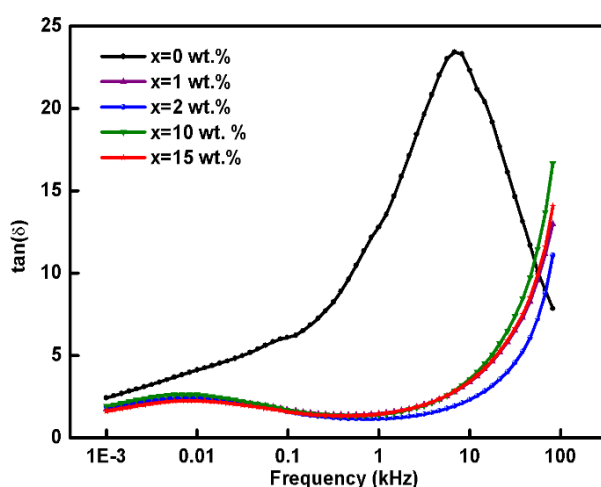


Fig. 15. $\tan \delta$ vs. frequency plot for ((PEO/PAN)₂₀NaPF₆) + x wt.% TiO₂ nano-filler.

structure of solids which describe which type of solid material exist. Insulator or semiconductor have two types of band gap that is direct band gap or indirect bad gap. For direct band gap semiconductors the top of valence band and bottom of conduction band both lie at the same crystal momentum space (wave vector) whereas not in the indirect band gap. Direct band gap have dependence upon the incident photon energy. As we observe from Fig. 16 that direct band gap decrease with the addition of nanofiller and it reaches to the value 4.82 eV for 15 weight percent doped TiO₂ concentration of nano-filler from 5.47 for pure PEO/PAN complexed with NaPF₆ sample it means direct band gap decreases with the addition of nanofiller. At 15 wt. % band gap is lower, means in this there will be faster ionic transport and higher ionic conductivity. This decrease in band gap is in good agreement with electrochemical studies [26, 27].

With the addition of nano-filler and salt there may be increase in the defects which can lead to disordered arrangement in the film. Also these defects creates energy states in the optical band gap. Hence increase in the amorphicity with the addition of filler in PS matrix lead to enhancement in the conductivity.

In indirect band gap both of valence as well as conduction band do not correspond to same crystal momentum space. $\alpha h\nu$ value has been shown by following Eq. (5):

$$\alpha h\nu = A(h\nu - E_g + E_p)^2 + B(h\nu - E_g - E_p)^2 \quad (5)$$

Where E_p is energy of photon, E_g band gap, A and B are some constant depend on the band structure [28]. Indirect band gap also decrease with the addition of nanofiller and it reaches to the value 4.74 for 15 weight percent doped TiO₂ concentration of nano-filler from 5.44 for without doped PEO/PAN complexed with NaPF₆ as we observe from Fig. 17.

The absorption edge obtained by plotting absorption coefficient (α) versus energy ($h\nu$) and to obtain value, linear portion of curve extrapolated to

zero absorption value. Absorption coefficient can be obtained from the following Eq. (6).

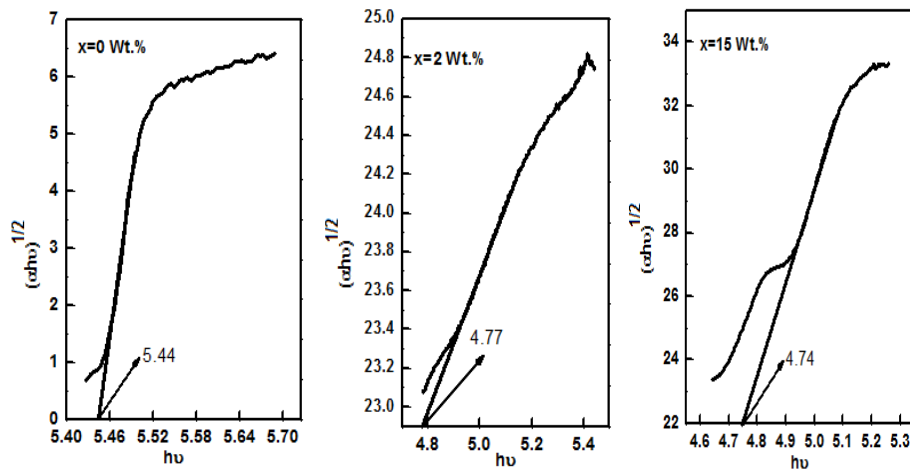


Fig. 16. $(\alpha h\nu)^{1/2}$ vs. $h\nu$ (photon energy) images of $(\text{PEO/PAN})_{20}\text{NaPF}_6 + x \text{ wt.}\% \text{ TiO}_2$ nano-filler.

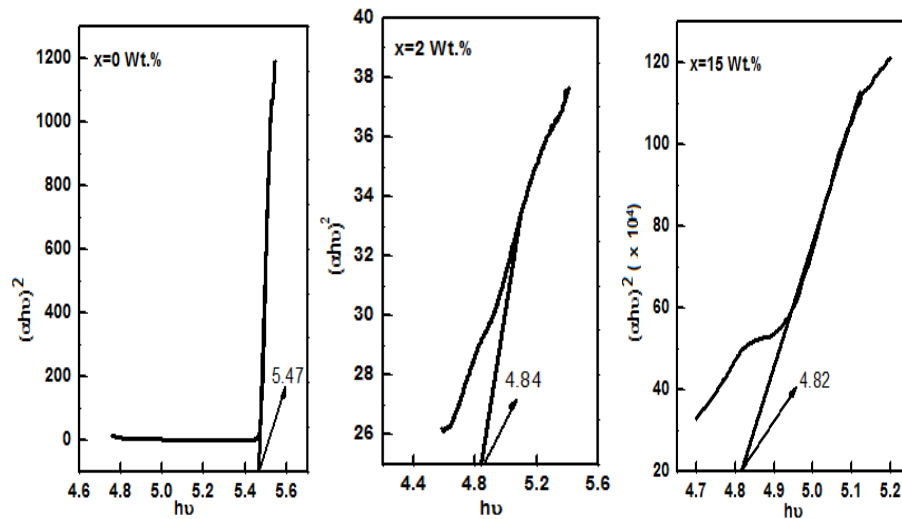


Fig. 17. $(\alpha h\nu)^2$ vs. $h\nu$ (photon energy) images of $(\text{PEO/PAN})_{20}\text{NaPF}_6 + x \text{ wt.}\% \text{ TiO}_2$ nano-filler.

$$\alpha = \frac{(2.303) \times A}{t} \quad (6)$$

where, A is the absorbance, t is thickness of sample. Absorption edge also decrease with the addition of nanofiller and it reaches to the value 4.67 for 15 weight percent doped TiO_2 concentration of nano-filler from 5.44 for without doped PEO/PAN complexed with NaPF_6 as we observe from Fig. 18.

All band gap values such as direct, indirect band gap, and absorption edge decreases with the addition of nano-filler as shown in Table 4. These was obtained from the extrapolating of graph plotted between $(\alpha h\nu)^2$, $(\alpha h\nu)^{1/2}$, (α) versus energy ($h\nu$) in the x-axis

which is energy axis. Electron from the conduction band fill the hole in the valence band if they are in the same crystal momentum. With the doping this transition of the charge carrier becomes easy. Because with the addition of nano-filler impurity generated which cause shift in the energy level corresponding to Fermi level. Also creates allowed energy states within the band gap. With happening this kind of phenomenon cause increase in the conductivity. Similarly trend for optical properties was observed as for previous series sample.

3.7 Thermo Gravimetry Analysis (TGA)

TGA confirms thermal properties of polymer as a function of temperature. Changes in three different electrolyte film in the form of weight loss

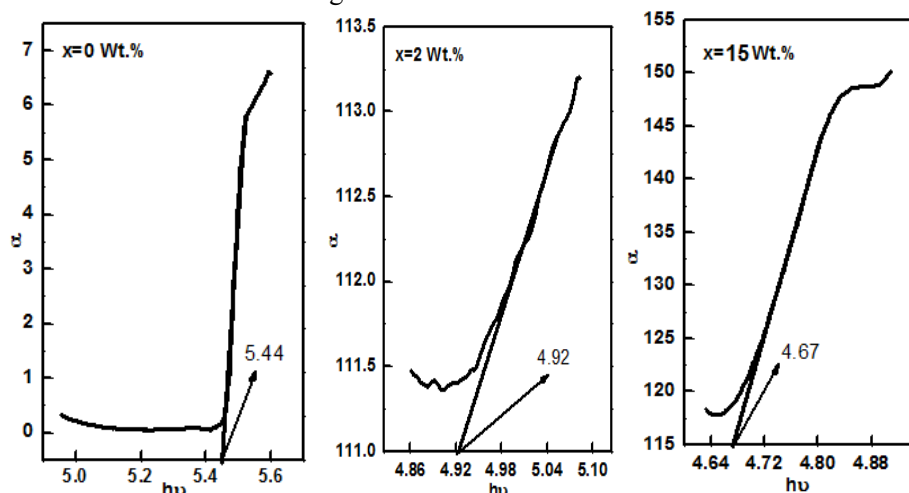


Fig. 18 α vs. $h\nu$ (photon energy) images of (PEO/PAN)₂₀NaPF₆ + x wt.% TiO₂ nano-filler.

Table 4. Absorption edge, direct and indirect band gap values for polymer nanocomposite films based on (PEO/PAN)₂₀NaPF₆ + x wt.% TiO₂ nano-filler.

Polymer electrolyte	Doping TiO ₂ (wt. %)	Absorption edge (eV)	Band gap (eV)	
			Direct	Indirect
(PEO/PAN) + NaPF ₆	0	5.44	5.47	5.44
(PEO/PAN) + NaPF ₆	2	4.92	4.84	4.77
(PEO/PAN) + NaPF ₆	15	4.67	4.82	4.74

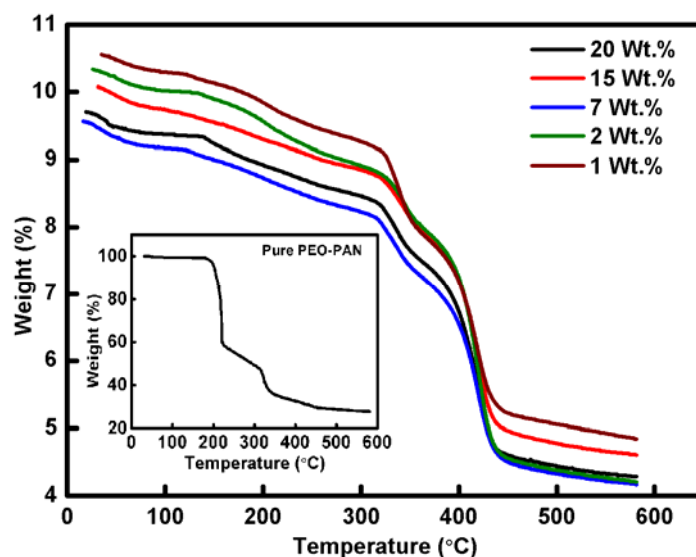


Fig. 19 Thermo gravimetry analysis (TGA) images of (PEO/PAN)₂₀NaPF₆ + x wt.% TiO₂ nano-filler.

region in a different manner. In region 1 lies from 0 to 320°C there is weight loss rate is slow that is gradual loss of weight as a function of temperature. This is due to the presence of moisture in the film at the time of loading the sample.

In region 2 there is rapid loss of weight as a function of temperature due to the region that in host polymer structural decomposition take place. For pure PEO-PAN there is rapid drop in temperature at 200 °C, but addition of filler broadens this region and film

is stable up to 300 °C. The decomposition of the films start completely at temperature 320 °C which means that the prepared film is stable up to 320 °C shown in Fig. 19.

and in the third region no weight loss with the change in temperature observed in the range approximately in the range 420 °C. This flatness in the curve was due to the inorganic residue after decomposition in the polymer nanocomposite film [29, 30].

4. Conclusions

Free standing electrolyte film of PEO/PAN complexed with NaPF₆ with the varying composition of TiO₂ was prepared. The structural/microstructural verification of film was done with XRD and FESEM analysis. The polymer with the nano-filler (TiO₂) lessen the difference in driving force for phase separation and produce homogeneous film at x = 15 wt.% of nano-filler, and produce polymer film of better quality which can enhance the electrical as well as mechanical properties of prepared polymer films.

There is decrease in the value of absorption edge, direct and indirect band gap with the addition of nano-filler hence enhancement in conductivity. Without addition of nano-filler absorption edge, direct and indirect band gap has values 5.44, 5.47, 5.44 eV, but with the addition of micro range inorganic nano-filler it becomes 4.67, 4.82, 4.74 eV. Addition of nano-filler improves the host polymer amorphous region by slowing the recrystallization rate. FTIR confirms ion-polymer, polymer-polymer interaction and the presence of various functional groups present in prepared polymer electrolyte film by observing the spectra in the wavenumber 600-4,000 cm⁻¹. Shift in the peak position for various wavenumber either upshift or downshift proves complexation of polymer-polymer, polymer-ion, and polymer-ion-nanofiller interaction. The presence of two distinct degenerate FTIR band in the experimental spectrum provides an evidences of strong ion-ion

interaction in the prepared polymer nanocomposite films.

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References

- [1] Zhang, R., Chen, Y. and Montazami, R. 2015. "Ionic Liquid-Doped Gel Polymer Electrolyte for Flexible Lithium-Ion Polymer Batteries." *Materials* 8 (May): 2735-48.
- [2] Pradhan, D. K., Samantaray, B. K., Choudhary, R. N. P., Karan, N. K., Thomas, R. and Katiyar, R. S. 2011. "Effect of Plasticizer on Structural and Electrical Properties of Nanocomposite Solid Polymer Electrolytes." *Ionics* 17 (Dec): 127-34.
- [3] Yang, M. and Hou, J. 2012. "Membranes in Lithium Ion Batteries." *Membranes* 2 (July): 367-83.
- [4] Verma, M. L., Minakshi, M. and Singh, N. K. 2014. "Structural and Electrochemical Properties of Nanocomposite Polymer Electrolyte for Electrochemical Devices." *Industrial and Engineering Chemistry Research* 53 (Sep.): 14993-5001.
- [5] Sharma, A. L. and Thakur, A. K. 2013. "Plastic Separators with Improved Properties for Portable Power Device Applications." *Ionics* 19 (May): 795-809.
- [6] Sharma, A. L. and Thakur, A. K. 2011. "Polymer Matrix-Clay Interaction Mediated Mechanism of Electrical Transport in Exfoliated and Intercalated Polymer Nanocomposites." *Journal of Materials Science* 46 (Nov): 1916-31.
- [7] Pitawala, H. M. J. C., Dissanayake, M. A. K. L. and Seneviratne, V. A. 2007. "Combined Effect of Al₂O₃ Nano-Fillers and EC Plasticizer on Ionic Conductivity Enhancement in the Solid Polymer Electrolyte (PEO)₉LiTF." *Solid State Ionics* 178 (May): 885-8.
- [8] Amir, S., Mohamed, N. S. and Subban, R. H. Y. 2013. "Ionic Conductivity Studies on PEMA/PVC-NH₄I Polymer Electrolytes." *International Journal of Materials Engineering Innovation* 2 4 (Jan): 281-90.
- [9] Arya, A. and Sharma, A. L. 2016. "Conductivity and Stability Properties of Solid Polymer Electrolyte Based on PEO-PAN + LiPF₆ for Energy Storage." *Applied Science Letters* 2 (April): 72-5.
- [10] Genova, F. K. M., Selvasekarapandian, S., Karthikeyan, S., Vijaya, N., Sivadevi, S. and Sanjeeviraja, C. 2015. "Lithium Ion-Conducting Blend Polymer Electrolyte

- Based on PVA-PAN Doped with Lithium Nitrate.” *Polymer-Plastics Technology and Engineering* 55 (June): 25-35.
- [11] Hieu, H. K. 2015. “Volume and Pressure-Dependent Thermodynamic Properties of Sodium.” *Vacuum* 120 (Oct.): 13-6.
- [12] Moreno, J. S., Armand, M., Berman, M. B., Greenbaum, S. G., Scrosati, B. and Panero, S. 2014. “Composite PEO_n: NaTfI Polymer Electrolyte: Preparation, Thermal and Electrochemical Characterization.” *Journal of Power Sources* 248 (Feb.): 695-702.
- [13] Kesavan, K., Mathew, C. M., Rajendran, S., Subbu, C. and Ulaganathan, M. 2015. “Solid Polymer Blend Electrolyte Based on Poly (ethylene oxide) and Poly (vinyl pyrrolidone) for Lithium Secondary Batteries.” *Brazilian Journal of Physics* 45 (Oct.): 19-27.
- [14] Sikkantar, S., Karthikeyan, S., Selvasekarapandian, S., Pandi, D. V., Nithya, S. and Sanjeeviraja, C. 2015. “Electrical Conductivity Characterization of Polyacrylonitrile-Ammonium Bromide Polymer Electrolyte System.” *Journal of Solid State Electrochemistry* 19 (Dec.): 987-99.
- [15] Sharma, A. L., Shukla, N. and Thakur, A. K. 2008. “Studies on Structure Property Relationship in a Polymer-Clay Nanocomposite Film Based on (PAN)₈LiClO₄.” *Journal of Polymer Science Part B: Polymer Physics* 46 (Oct.): 2577-92.
- [16] Rajendran, S., Prabhu, M. R. and Rani, M. U. 2008. “Characterization of PVC/PEMA Based Polymer Blend Electrolytes.” *International Journal of Electrochemical Science* 3 (Jan): 282-90.
- [17] Suthanthiraraj, S. A. and Sheeba, D. J. 2007. “Structural Investigation on PEO-Based Polymer Electrolytes Dispersed with Al₂O₃ Nanoparticles.” *Ionics* 13 (Dec.): 447-50.
- [18] Pradeepa, P., Edwinraj, S. and Prabhu, M. R. 2015. “Effects of Ceramic Filler in Poly (Vinyl Chloride)/Poly (Ethyl Methacrylate) Based Polymer Blend Electrolytes.” *Chinese Chemical Letters* 26 (Sep.): 1191-6.
- [19] Arya, A., Sharma, A. L., Sharma, S. and Sadiq, M. 2016. “Role of Low Salt Concentration on Electrical Conductivity in Blend Polymeric Films.” *Journal of Integrated Science and Technology* 4 (May): 17-20.
- [20] Abdullah, O. G., Saber, D. R. and Hamasalih, L. O. 2015. “Complexion Formation in PVA/PEO/CuCl₂ Solid Polymer Electrolyte.” *Universal Journal of Materials Science* 31-5.
- [21] Sharma, A. L. and Thakur, A. K. 2010. “Improvement in Voltage, Thermal, Mechanical Stability and Ion Transport Properties in Polymer-Clay Nanocomposites.” *Journal of Applied Polymer Science* 118 (June): 2743-53.
- [22] Sharma, A. L. and Thakur, A. K. 2015. “Relaxation Behavior in Clay-Reinforced Polymer Nanocomposites.” *Ionics* 21 (Dec): 1561-75.
- [23] Manjunath, A., Deepa, T., Supreetha, N. K. and Irfan, M. 2015. “Studies on AC Electrical Conductivity and Dielectric Properties of PVA/NH₄NO₃ Solid Polymer Electrolyte Films.” *Advances in Materials Physics and Chemistry* 5(Aug): 295-301.
- [24] Shukla, N., Thakur, A. K., Shukla, A. and Chatterjee, R. 2014. “Dielectric Relaxation and Thermal Studies on Dispersed Phase Polymer Nanocomposite Films.” *Journal of Materials Science: Materials in Electronics* 25 (April): 2759-70.
- [25] Sharma, A. L. and Thakur, A. K. 2015. “Relaxation Behavior in Clay-Reinforced Polymer Nanocomposites.” *Ionics* 21 (Dec.): 1561-75.
- [26] Patil, S. U., Yawale, S. S. and Yawale, S. P. 2014. “Optical Properties of SiO₂ Nanoparticles Doped PEO-LiClO₄ Nanocomposite Polymer Electrolyte Films.” *Research and Reviews: Journal of Physics* 3: 8-12.
- [27] Tsutsumi, H., Matsuo, A., Onimura, K. and Oishi, T. 1998. “Conductivity Enhancement of a Polyacrylonitrile-Based Polymer Electrolyte Containing Cascade Nitrile as a Plasticizer.” *Electrochemical and solid-state letters* 1 (Sep.): 244-5.
- [28] Rao, S. L. S., Ramadevudu, G., Shareefuddin, M., Hameed, A., Chary, M. N. and Rao, M. L. 2013. “Optical Properties of Alkaline Earth Borate Glasses.” *International Journal of Engineering, Science and Technology* 4 (Dec.): 25-35.
- [29] Lee, L., Park, S. J. and Kim, S. 2013. “Effect of Nano-Sized Barium Titanate Addition on PEO/PVDF Blend-Based Composite Polymer Electrolytes.” *Solid State Ionics* 234 (March): 19-24.
- [30] Xu, J., Xu, W., Shen, X., Bai, Z. and Yao, M. 2012. “Thermal, Mechanical and Electrical Properties of the PEO-Based Solid Polymer Electrolytes Filled by Yttrium Oxide Nanoparticles.” *Journal of Wuhan University of Technology-Material Science Ed.* 27 (June): 495-500.