Investigations on lithium ion complexed polyvinyl chloride (PVC) solid polymer electrolyte films

P. CHANDRA SEKHAR*, P. NAVEEN KUMAR, U. SASIKALA, V.V.R.N. RAO AND A. K. SHARMA

Department of Physics, S.V. University
Tirupati – 517502, A.P., India

Abstract— **This paper reports on solid polymer electrolyte films based on PVC complexed with different concentrations of LiClO$_4$ salt using solution cast technique. The films were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and impedance spectroscopy studies. Optical absorption studies were made in the wavelength range 200-600 nm. Optical constants like absorption edge and band gap were estimated for pure and LiClO$_4$ doped films. It was observed that the optical constants shifted to lower energies with the increase in dopant concentration. The electrical conductivity was evaluated from impedance spectroscopy studies in the temperature range 303-363 K and the conductivity was found to increase with increasing dopant concentration. The polymer complexes exhibited Arrhenius type dependence of conductivity with temperature.**

Keywords- Polymer electrolyte films; morphology; XRD; electrical conductivity

I. INTRODUCTION

Solid polymer electrolyte materials are attracting growing interest in recent years because of their potential applications in ionic devices such as rechargeable batteries, super capacitors, fuel cells, gas sensors and electrochromic display devices/smart windows [1-3]. The electrical and optical properties of polymers have attracted much attention in view of their applications in optical devices with remarkable reflection, antireflection, interference and polarization properties [4]. Polyethylene oxide (PEO) complexes have received much interest due to their high ionic conductivity and ability to effectively coordinate with salt cations and form homogeneous solutions [5-6]. PEO, doped with various lithium salts such as LiCF$_3$SO$_3$ (lithium triflate) [7], LiClO$_4$ (lithium perchlorate) [8] etc., has been particularly explored. However, there are several disadvantages as PEO tends to form crystalline complexes and high ionic conductivities can be achieved only above its melting temperature.

In recent times, polyvinyl chloride (PVC) has also received much attention and is being exploited as a polymer host [9-11]. PVC is a commercially available, inexpensive polymer and is compatible with plasticizers such as dibutyl phthalate (DBP), dioctyladipate (DOA), dioctyl phthalate (DOP), polycarbonate (PC) and ethylene carbonate (EC). Various PVC based systems have been found to form electrolytes with conductivities ranging from 10^{-8} to 10^{-3} Scm^{-1} at room temperature [12]. The electrical and optical properties of polymers can be suitably modified by the addition of

dopants depending on their reactivity with the host matrix. LiClO$_4$ is a fast-ion conducting salt in a number of crystalline and amorphous materials, its incorporation in a polymeric system may be expected to enhance the electrical and optical performance.

This paper reports the results of investigations on the structural, optical and electrical properties of LiClO$_4$ complexed PVC solid polymer electrolyte films.

II. EXPERIMENTAL

A. Preparation of Polymer electrolytes

Polymer electrolyte films (thickness 100-150 μm) of LiClO$_4$ complexed PVC were prepared using solution-cast technique. Tetrahydrofuran (THF) was used as a solvent. The compositions of the polymer complexes were (100-X) PVC+X LiClO$_4$, where X (%) = 5,10 and 15. The mixtures of salt solutions were stirred for 12 h to get uniform homogeneous mixture and cast into polypropylene dishes. The films were annealed in a vacuum of 10^{-3} m bar to remove any traces of solvent.

B. Characterization techniques

X-ray diffraction (XRD) studies were performed using SEIFERT X- ray diffractometer. The morphology of the samples was studied using JOEL JSM 840A Scanning electron microscope (SEM). The electrical conductivity of polymer complexes was measured using Hioki 3532-50 LCR Hi- tester interfaced to a computer in the frequency range 1Hz-1MHz. The optical absorption profiles of these films were recorded at room temperature in the wavelength range 200-600 nm using UV-VIS-NIR (model 3100) spectrophotometer.

III. RESULTS AND DISCUSSION

A. XRD data

In order to investigate the influence of Lithium salt on PVC structure, XRD studies were performed. Figure 1(a–e) shows the XRD patterns of pure PVC, LiClO$_4$ salt, and PVC complexed with LiClO$_4$ salt. Comparison of the XRD patterns of complexed PVC films with those of pure PVC and LiClO$_4$ reveals the following differences. Peaks observed for 2θ values around 22° for pure PVC disappear in complexed polymer films. This indicates that the addition of LiClO$_4$ salt causes a decrease in the degree of crystallinity and a simultaneous increase in the amorphicity of the complexed
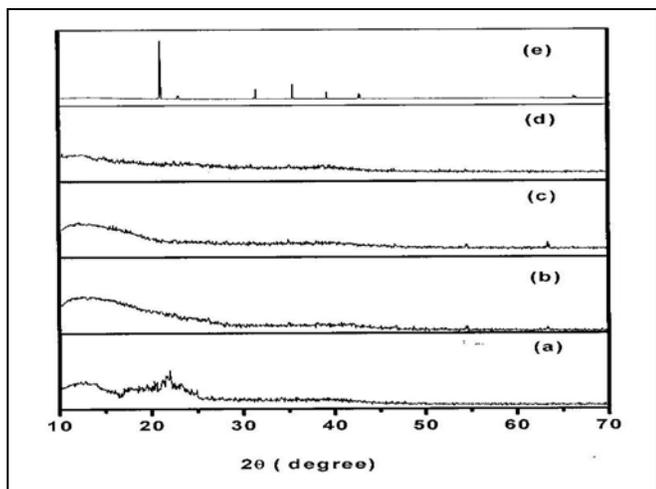
Figure 1. XRD plots of (a) Pure PVC (b) PVC+LiClO$_4$ (95:5) (C) PVC+LiClO$_4$ (90:10) (d) PVC+LiClO$_4$ (85:15) and (e) LiClO$_4$ Salt.

films. This is in agreement with the results reported by Rajendran et al. [13] and indicates that the polymeric films are composed of a combination of semicrystalline and amorphous phases [14]. The crystalline peaks for 2θ values at 21, 31.3, 35.3 and 39.2° corresponding to LiClO$_4$ (Fig. 1e) are absent in complexed PVC. This indicates the absence of any excess (uncomplexed) salt in the complexed polymer electrolyte films. Therefore, it may be confirmed that complexation has taken place in the amorphous phase.

B. SEM analysis

The morphology of pure PVC and LiClO$_4$ complexed PVC based composite polymer electrolytes with different weight ratios was studied using SEM technique. The film surface was of uniform type but with different degrees of roughness as shown in Fig. 2(a-d). Several holes were observed for films which had LiClO$_4$ concentration of 10% (fig 2(c)). The formation of holes on the surface is due to rapid penetration of Li+ ions into the polymer matrix or the rapid evaporation of THF during the preparation of film. The surface of the composite sample with 15% LiClO$_4$ has morphology of increasing roughness Fig 2(d). The increase of degree of roughness with increased LiClO$_4$ salt concentration indicates segregation of the dopant in the host matrix. The difference in morphology of the LiClO$_4$ doped films consistent with the significant differences in the ionic conductivity of these films.
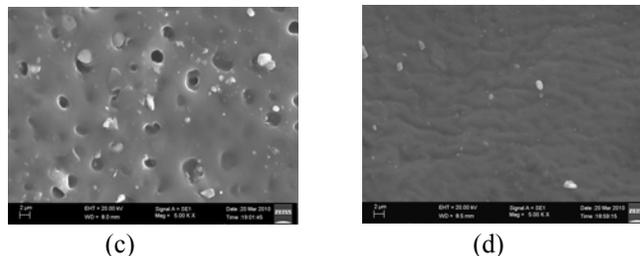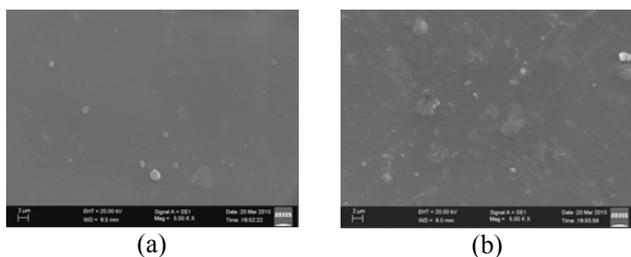

(a)   (b)

(c)   (d)

Figure 2. SEM Photographs of (a) Pure PVC (b) PVC+LiClO$_4$ (95:5) (C) PVC+LiClO$_4$ (90:10) and (d) PVC+LiClO$_4$ (85:15).

C. Optical absorption

The study of optical absorption gives information about the band structure of solids. Insulators semiconductors are generally classified into two types: (1) direct band gap and (2) indirect band gap. In direct band gap semiconductors, the top of the valence band and the bottom of the conduction band both lie at 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.

Optical absorption studies on pure and doped films were carried out to determine the optical constants such as optical band gap E$_g$ and the position of the fundamental band edge. The absorption coefficient was determined from the spectra using the formula

$$\alpha = A/d$$

where A is the absorbance and d is the thickness of the film.

When a direct band gap exists, the absorption coefficient has the following dependence on the energy of the incident photon [15, 16]

$$\alpha h\nu = C\,(h\nu - E_g)^{1/2}$$

where E$_g$ is the band gap, C, a constant dependent on specimen structure, υ, the frequency of incident light, and h, the Planck's constant.

Plots of $(\alpha h\nu)^2$ vs hν (photon energy), as shown in Fig. 3, are linear. The intercept on the energy axis on extrapolating the linear portion of the curves to zero absorption value may be interpreted as the value of the band gap.

For pure PVC electrolytes, the direct band gap lies at 4.24 eV while for doped films, the values are found to decrease from 4.23 to 4.14 eV (Table 1).

For indirect transitions, which requires phonon assistance, the absorption coefficient has following dependence on the photon [15, 16]

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

where E_p is the energy of the phonon associated with the transition, and A, B are constants depending on the band structure.

The indirect band gaps were obtained from the plots of $(\alpha h v)^{1/2}$ vs hv (photon energy) as shown in Fig. 4. For pure PVC, the indirect band gap lies at 4.13 eV, while for doped films, the values are found to decrease from 4.13 eV to 3.96 eV. The position of the absorption edge was estimated by extrapolating the linear portions of the α vs hv plots (Fig. 5) to zero absorption value. For pure films, the absorption edge lies at 4.21 eV and for doped films, the values are found to decrease from 4.21 to 4.08 eV.

The direct band gap, indirect band gap and absorption edge values showed a decrease with increasing $LiClO_4$ concentration as is seen in Table. 1. This kind of behavior has been reported earlier in different polymers [17-19]. The magnitude of the activation energies obtained from conductivity data is small in comparison with optical band gap energies. This is due to the fact their nature is different. While the activation energy corresponds to the energy required for conduction from one site to another, the optical band gap corresponds to interband transition [20].

D. Conductivity studies

Impedance spectroscopy has become a powerful tool for the investigation of ionic conductivity of solid electrolyte films. Typical impedance plot of $(PVC+ LiClO_4)$ (85:15) at ambient temperature in the frequency range 1 Hz-I MHz is shown in fig.6. It has been found that the idealized impedance plot of Z" as a function of Z', i.e. Cole-Cole plot of the film ($Z^{''}$ and $Z^{'}$ denote the real and imaginary parts of the complex impedance Z^{*}), contain a disappearance of semicircular portion in the high frequency region of complexed electrolyte impedance plot indicates that the conduction is mainly due to the ions [21] in complexed films.

The ionic conductivity of the samples has been calculated by the following equation:

$$\sigma = L/R_b\, A$$

where σ is the conductivity, L the thickness of the sample, A the area of the sample and R_b the bulk resistance.

The bulk conductivity has been calculated from the impedance plot, and logarithms of conductivity were plotted against the inverse of temperature to observe the temperature dependence of conductivity. Fig.7 shows the linear dependence of log σ on inverse temperature (1000/T) for pure and complexed films. The linear variation in log σ vs. 1000/T plot suggests an Arrhenius-type thermally activated process represented by

$$\sigma_{dc} = \sigma_0 \exp(-E_a/kT)$$

where σ_0 is the pre-exponential factor, E_a the activation energy, k the Boltzmann constant and T the absolute temperature .The magnitude of ionic conductivity was found to increase with increase in temperature in all compositions of the polymer electrolyte system including pure film. This may be explained on the basis of an increase in either ionic mobility or the concentration of carrier ions [22]. The

observed Arrhenius behavior of log σ vs.1000/T plots is in agreement with the theory established by Tareev [23]. This is rationalized by considering the free volume model [24].
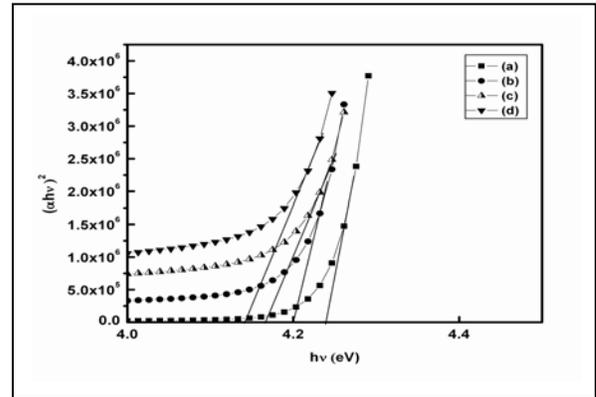

Figure 3. $(\alpha h v)^2$ vs hv (photon energy) of (a) Pure PVC (b) PVC+$LiClO_4$ (95:5) (C) PVC+$LiClO_4$ (90:10) and (d) PVC+$LiClO_4$ (85:15).
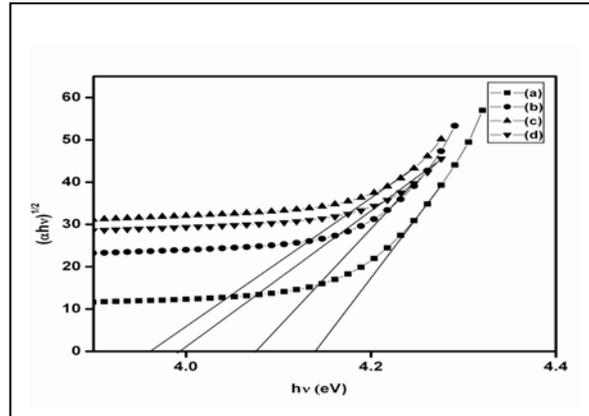

Figure 4. $(\alpha h v)^{1/2}$ vs hv (photon energy) of (a) Pure PVC (b) PVC+$LiClO_4$ (95:5) (C) PVC+$LiClO_4$ (90:10) and (d) PVC+$LiClO_4$ (85:15).
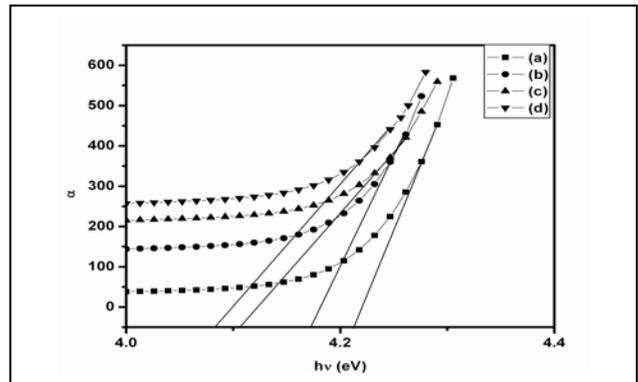

Figure 5. α vs hv (photon energy) of (a) Pure PVC (b) PVC+$LiClO_4$ (95:5) (C) PVC+$LiClO_4$ (90:10) and (d) PVC+$LiClO_4$ (85:15).

TABLE 1. Absorption edge, optical band gap, activation energy of (PVC+LiClO$_4$) polymer electrolyte system

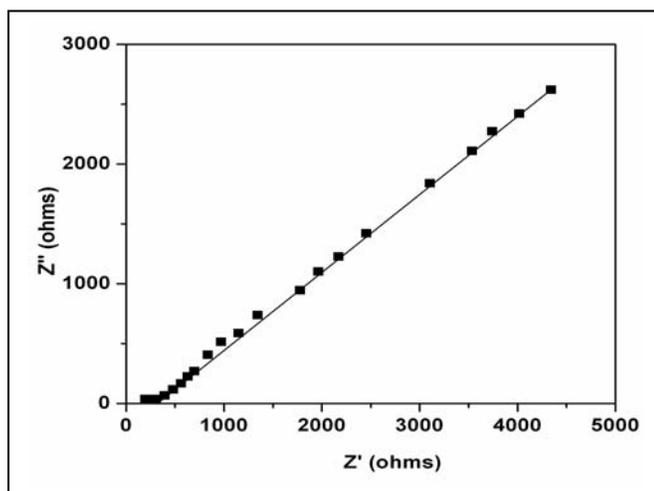| Polymer electrolyte system (Wt%) (PVC+LiClO$_4$)	Absorption edge (eV)	Direct band gap (eV)	Indirect band gap (eV)	Activation energy (eV)	Conductivity at ambient temperature (S/cm)x10^{-6}
100:00	4.21	4.23	4.13	0.25	1.86
95:05	4.17	4.20	4.07	0.18	3.47
90:10	4.10	4.16	3.99	0.11	5.88
85:15	4.08	4.14	3.96	0.06	9.54

Figure 6. Impedence plots of PVC+LiClO$_4$ (85:15) polymer electrolyte at ambient temperature.
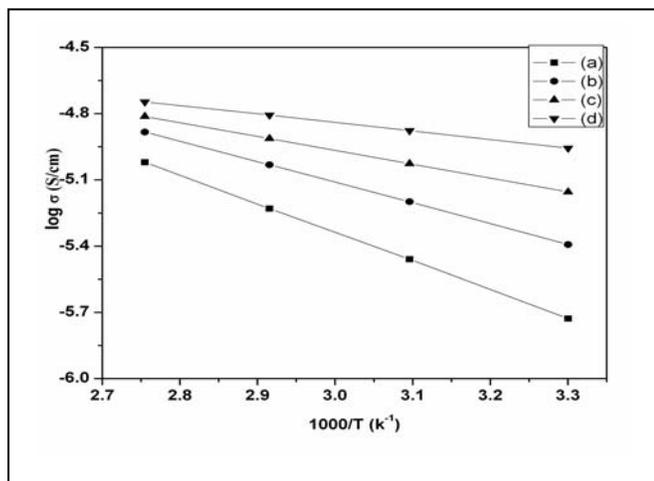

Figure 7. Plots of Log of AC conductivity vs 1000/T for (a) Pure PVC (b) PVC+LiClO$_4$ (95:5) (C) PVC+LiClO$_4$ (90:10) and (d) PVC+LiClO$_4$ (85:15).

The enhancement in ionic mobility can be interpreted by ionic transport mechanism involving coordinating sites, local structural relaxations and segmental motion of the polymer chain in free volume model. When the temperature increases the vibration energy of a segment of polymer chain becomes sufficient to push against the hydrostatic pressure imposed by its neighboring atoms and create a small amount of space surrounding it sown volume in which vibrational motion can occur [25]. Therefore, the free volume around the polymer chain causes the mobility of the ions to increase and the segmental motion of polymer chain causes the conductivity to increase. The amorphous nature also provides a bigger free volume in the polymer electrolyte system on increasing temperature [26].

E. Activation energies

The activation energy values of different polymer electrolytes were calculated from the slopes of linear fit of Arrhenius plots of different polymer electrolytes and are listed in Table 1. The activation energy is a combination of energy of charge carrier creation (defect formation) and the energy of ion migration that can be evaluated by linear fitting to the log σ vs. 1000/T plots [27]. Therefore, it can be suggested that the value of Ea is due to the energy that is required to provide a conductive condition for the migration of ions. Fig. 7 reveals that conductivity does not show any abrupt change with the temperature, indicating that the electrolyte exhibits amorphous nature. The activation energy is found to decrease gradually with increase in LiClO$_4$ salt concentration, confirming the increase in amorphous nature of polymer electrolyte.

IV. CONCLUSIONS

In summary, it could be concluded that the structure, morphology, optical and electrical properties of PVC polymer electrolyte films can be influenced by complexing it with LiClO$_4$ salt. The complex formation in PVC-LiClO$_4$ system has been confirmed from XRD studies. The conductivity values were seen to increase with increased LiClO$_4$ concentration and temparature. The activation energy values obtained from conductivity data decreased with increasing dopant concentration. Optical absorption edge and optical energy gaps (both direct and indirect) showed a shift towards lower energies with increased dopant concentration.

REFERENCES

[1] A. L. Gopalan, P. Santhosh, K. M. Mahesh, J. H. Nho, S. Chul-Gyun Hwang and K. P. Lee, "Development of electrospun PVdF–PAN membrane-based polymer electrolytes for lithium batteries", J. Membr. Sci., 325, pp.683-690, 2008.

[2] B. P. Tripati and V. K. Shahi, "Organic–inorganic nanocomposite polymer electrolyte membranes for fuel cell applications", Polym.Sci., 36, pp. 945-979, 2011.

[3] A. Bhide and K. Hariharan, "Ionic transport studies on $(PEO)_6$:$NaPO_3$ polymer electrolyte plasticized with PEG_{400}" Eur.Polym.j., 43, pp. 4253-4270, 2007.

[4] S. Proneanu, R. Torcu, M. Brie and G. Mihilesan, "Electrochemical and Optical Studies of Metallic Ion Insertion in Polypyrrole Films", Mater. Sci. Forum, 191, pp. 241-246 , 1995.

[5] V. Madhu Mohan, V. Raja, A. K. Sharma and V. V. R. Narasimha Rao, "Ionic conductivity and discharge characteristics of solid-state battery based on novel polymer electrolyte $(PEO+NaBiF_4)$" Materials Chemistry Physics, 94, pp.177-181, 2005.

[6] N. K. Kiran, D. K. Pradhan, R. Thomas, B. Natesan and R. S. Katiyar, "Solid Polymer electrolytes based on polyethylene oxide and lithium trifluoro- methane sulfonate $(PEO–LiCF_3SO_3)$: Ionic conductivity and dielectric relaxation", Solid State Ionics, 179, pp. 689-696, 2008.

[7] A. Vallee, S. Besner and J. Prud home, "Comparative study of poly(ethylene oxide) electrolytes made with $LiN(CF_3SO_2)_2$, $LiCF_3SO_3$ and $LiClO_4$: Thermal properties and conductivity behaviour", Electrochim Acta , 37 (9), pp.1579-1583, 1992.

[8] Ch. V. Subba Reddy, G. P. Wu, C. X. Zaho, C. Y. Zhu, W. Chen and R. Kalluru, "Characterization of SBA-15 doped $(PEO+LiClO_4)$ polymer electrolytes for electrochemical applications", Journal of Non- Crystalline Solids, 353, pp. 440-445, 2007.

[9] T. J. R. Reddy, V. B. S. Achari, A. K. Sharma and V. V. R. N Rao "Preparation and electrical characterization of ($PVC+KBrO_3$) electrolytes for solid state battery applications", Ionics, 13, pp.435-439, 2007.

[10] S. Ramesh, Geok Bee Teh, Rong –Fuh Louh, Young Kong Hou, Pung Yen Sin and Lim Jing Yi , "Preparation and characterization of plasticized high molecular weight PVC based polymer electrolytes", Indian Academy Sciences, 35, pp. 87-95, 2010.

[11] Nira Mishra, H. S. Panda, Govinda Kapusetti, Shilpa Jaiswal and Subhratanu Bhattacharya, "Physical and conductivity properties of poly (vinyl chloride) ionomers", Indian J. Phys., 85 (2), pp. 271-279, 2011.

[12] A. M. Sukeshini, A. Nishimoto and M. Watanabe, "Transport and electrochemical characterization of plasticized poly(vinyl chloride) solid electrolytes", Solid State Ionics, 86-88 , pp.385-393, 1996.

[13] S. Rajendran, Ravi Shanker Babu and P. Sivakumar, "Investigations on PVC/PAN composite polymer electrolytes", Journal of Membrane Science, 315, pp.67-73, 2008.

[14] J. Li, X. Huang and L. Chen, "X-ray diffraction and vibrational spectroscopic studies on PAN-LITFSI polymer electrolytes" J Electrochem Soc ,147(7), pp. 2653 -2657, 2000.

[15] P. W. Davis and T. S. Shilliday, "Some optical Properties of Cadmium Telluride", Phys Rev, 118, pp. 1020,1960.

[16] G. M. Thutupalli and S. G. Tomlin, "The optical properties of thin films of cadmium and zinc selenides and tellurides" J Phys D: Appl Phys, 9, pp. 1639-1647, 1976.

[17] N. Reddeppa, T. J. R. Reddy, V. B. S. Achari, V. V. R. N. Rao and AK Sharma, "Electrical and optical characterization of (PEO+PVAc) polyblend films", Ionics, 15, pp. 255-259, 2009.

[18] V. B. S Achari, T. J. R Reddy, A. K. Sharma, V. V. R. N. Rao, "Electrical, optical, and structural characterization of polymer blend (PVC/PMMA) electrolyte films", Ionics, 13, pp. 349-354 , 2007.

[19] K. Kiran Kumar, M. Ravi, Y. Pavani, S. Bhavani, A. K. Sharma and V. V. R. N. Rao, "Investigation on the effect of complexation of NaF salt with polymer blend (PEO/PVP) electrolytes on ionic conductivity and optical energy band gaps", Physica B, 406, pp.1706 -1712, 2011.

[20] K. Rama Mohan, V. B. S. Achari, V. V. R. N. Rao and A. K. Sharma, "Electrical and optical properties of (PEMA/PVC) polymer blend electrolyte doped with $NaClO_4$", Polymer Testing, 30, pp. 881-886, 2011.

[21] M. Watanabe, K. Sanui, N. Ogata, T. Kobayashi and Z. Ohbaki, "Ionic conductivity and mobility in network polymers from poly(propylene oxide) containing lithium perchlorate" J Appl. Phys, 57, pp. 123-128, 1985.

[22] J. M. G. Cowie, in: J. R. Mac Callum, C. A. Vincent (Eds.), "Polymer Elecrtolyte Reviews", vol.1, Elsevier Applied Science, London, pp.92, 1987.

[23] B. Tareev, "Physics of the Dielectric Materials", MIR Publications, Moscow ,1979.

[24] S. Ramesh, A. H. Yahana and A. K. Arof, "Dielectric behaviour of PVC-based polymer electrolytes", Solid State Ionics, 152, pp. 291-294, 2002.

[25] P. C. K. Pillai, P. Khurana and A. Tripathi, "Dielectric studies of poly(methyl methacrylate)/polystyrene double layer system", Mater. Sci. Lett., 5, pp. 629-632, 1986.

[26] A. A. Mohamad, N. S. Mohamad M. Z. A. Yahna, R. Othman, S. Ramesh, Y. Alias and A. K. Aroof, "Ionic conductivity studies of poly(vinyl alcohol) alkaline solid polymer electrolyte and its use in nickel–zinc cells", Solid State Ionics, 156, pp. 171-177, 2003.

[27] L. Famiza, A. Madzlan, K. Nasir, A. M. M Ali and Z. Y. Muhd, "The role and impact of rubber in poly(methyl methacrylate)/ lithium triflate electrolyte", Journal of Power Sources, 159, pp. 1401-1404, 2006.