Dielectric Study of Polymer Nanocomposite Films for Energy Storage Applications

M. Sadiq, Anil Arya and A.L. Sharma

Abstract In the present study we have a novel report on the types of dielectric studies of the two blend polymer consisting of polyacrylonitrile (PAN) as the host polymer-polyethylene oxide (PEO) as a copolymer, $LiPF_6$ as lithium salts and clay containing different weight percent of DMMT as modified montmorillonite. The polymer nanocomposite (PNC) films were prepared by using solution cast technique. However the pure PAN-PEO+$LiPF_6$ film was prepared as a reference. Keeping in view of characterization of PNCs films were study by impedance spectroscopy technique. The high frequency range of dielectric measurement is 1 Hz–1 MHz. This technique is shown to be a viable and straight forward means of obtaining dielectric data on polymer electrolytes. Permittivity ($\in'$), dielectric loss ($\in''$) and a.c. conductivity variation with frequency was studied to estimate the relaxation times for PAN-PEO polymer electrolyte.

1 Introduction

Energy storage has become more important in the 21st century due to increasing demand of renewable energy for everyone. Solid Polymer Electrolyte batteries having Li as mobile cation are playing an important role as energy storage/conversion devices in particular, consumer electronics, electric or hybrid cars, fuel cell, super capacitors, solar cells and electro chromic display devices. However, safety issues of batteries must be addressed before their use at commercial level, since aprotic organic solvents are prone to under the abuse

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condition [1]. As electrolyte is a crucial part of the battery system, therefore, the research on electrolyte become important for the research community. Polymer electrolytes (PEs) are a suitable candidate in this context. SPEs that exhibit high ionic transport, high energy density, long cycle life, flexible characteristics, and safety are important for the application. Solid polymer electrolytes (SPEs) are gaining more interest worldwide since the first report was given by Peter V. Wright and a major focus on technological potential observed by Michel Armand in 1978. The SPEs are solid solutions of monovalent ($LiClO_4$, $NaClO_4$, $LiCF_3SO_3$, $LiBF_4$, etc.) or divalent ($Ca(ClO_4)_2$, $MgCl_2$, $Mg\ (CF_3SO_3)_2$) metal salts in host polymer. From all host matrices so far the best polymer which is used as host is having –CH_2–CH_2–O– repeat unit (PEO), also it have lower glass transition temperature which provides film flexibility and faster ionic transport [2]. Especially, free standing thin polymeric membrane would be suitable to be used as electrolyte due to advantage of good contact with electrodes. Polymer plays a dual role as a separator and electrolyte. Currently growing interest for lithium-ion storage devices based on nano filler such as SiO_2, Al_2O_3, TiO_2, ZrO_2, and $BaTiO_3$ because of their high surface area, porosity, etc. The addition of nano filler leads to improved ionic conductivity as well as enhanced mechanical strength and stability of the prepared free standing polymeric films. These SPNCs, generally formed by integrating the ion for mobile ionic species into a solid polymer matrix. However, ionic conductivity is one of the key parameters that need to be optimized for the better performance of the devices [3]. Also the dielectric properties and dielectric relaxation in these PNC films are studied. When the dielectric material is exposed to an alternating electric field that is generated by applying a sinusoidal voltage the displacement polarization leads to electric oscillations in the materials. The response of the orientation polarization to a change of the electric field is therefore always opposite in direction of the field. This process is known as dielectric relaxation. The characteristic time constant of such a relaxation process is the time for reaching a new equilibrium after changing the excitation is called the relaxation time ($\omega\tau = 1$) and is obtained from the graph of tangent loss vs. frequency [4, 5]. The response of dielectric has been shown to be a function of the salt complex. Few examples of polymer electrolytes have been performed for improving the dielectric properties of polymer electrolytes using various combinations,

PEO/$LiClO_4$ [6], PAN/LiTFSI [7], PEO/NH_4I [8], PEO/PMMA/$LiClO_4$ [9], PEO-PMMA-$AgNO_3$/Al_2O_3 [10], PAN-$LiCF_3SO_3$+DMMT [11], PVA-PEOAg NO_3, PEG/Al_2O_3 [12], (PVP coVAc) and (PMMA)/Tetrapropyl ammonium iodide (TPAI) and Potassium iodide (KI) [13], PEO-$LiClO_4$+MMT [14], PEO/PVP+MMT [15], PEO/NaI+DMMT [16], PEO/$LiPF_6$+CNT [17], PEO-PDMS-$LiPF_6$ [18] has been found report in the literature.

The Present report is done to study the effect of different clay concentration on the dielectric properties in terms of dielectric permittivity, ac conductivity and relaxation time in prepared polymer salt complex films comprised of $(PAN\text{-}PEO)_6$–$LiPF_6$+ wt% DMMT clay. The variation of dielectric parameters Permittivity ($\in'$), dielectric loss ($\in'$) and ac conductivity with the frequency and concentration at room temperature are presented and studied.

2 Experimental Section

Free standing polymer electrolyte-cum separator films have been prepared by solution cast technique reported elsewhere [19]. This is one of the traditional procedures for casting films of Solid Polymer Electrolyte (SPE) as well as Composite Polymer Electrolyte (CPE). In this technique, appropriate amount of polyacrylonitrile [PAN; M/S Aldrich, average molecular weight 1.5×10^5, (USA); 0.7 gm] and polyethylene oxide [PEO; M/S Aldrich, average molecular weight 6×10^5, (USA); 0.3 gm], *N,N*-dimethylformamide (10 ml), (E-Merck Germany) was used as organic solvent, lithium hexaflourophosphate ($LiPF_6$; Sigma Aldrich) as the salt and modified montmorillonite (SWy-2 variety) procured from Clay Minerals Society (USA). The modification process of montmorillonite clay is reported elsewhere [20]. Although the addition of an appropriate amount salt by stoichiometric ratio has been calculated considering nitrogen of PAN. The formula for the stoichiometry ratio ae shown below:

For Poly(acrylonitrile) (PAN);

$$\frac{\ddot{N}}{\mathrm{Li}^{+}} = \frac{\text{No. of monomer unit in half gram of PAN}}{\text{No. of LiPF}_6\text{ molecular inhalf gram of salt}} \times \frac{\text{wt.of PAN taken}}{\text{wt.of salt taken}}$$

The detail of stoichiometric calculation has been reported by [17]. On the basis of the above stoichiometric ratio in the blend polymer host (PAN-PEO) matrix be maintained at an optimized proportion of ($\ddot{N}/Li = 6$) is obtained. Preparation sample was approved in the three stages via solution casting technique using the subsequent stage as shown in the Fig. 1.

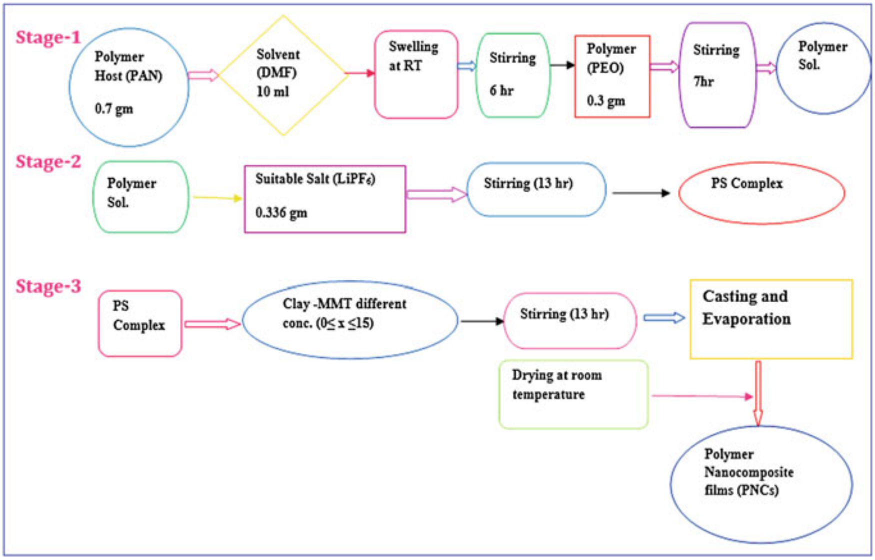


Fig. 1 Flow chart of solution cast technique method

2.1 Material Characterization

Dielectric properties of PNCs films were measured using computer interfaced CHI 760—impedance analyzer over the frequency range 1 Hz–1 MHz at room temperature. The sampled are placed in cell configuration SS/PNC/SS with an ac input signal of 10 mV.

3 Results and Discussion

3.1 Study of Electrical Property

The dielectric constant of material is represented by $\varepsilon^* = \varepsilon' - j\varepsilon''$, ε' is related to the stored energy within the medium and ε' is related to the dielectric energy loss of energy within the medium. The frequency dependent real part of dielectric constant (ε') can be calculated by using the relation $\varepsilon' = \frac{-Z''}{\omega c_o (Z'^2 + Z''^2)}$, $\varepsilon'' = \frac{Z'}{\omega c_o (Z'^2 + Z''^2)}$ where ω is angular frequency, where $C_o = \frac{\varepsilon_o A}{d}$ is vacuum capacitance of sample, A is the contact area of the electrode and d is the thickness of the composite films. It is observed from the Fig. 2 that decreases with increase in frequency and attains an independent value at a higher frequency. The initial value of permittivity is high, and decreases with increase in the frequency, which could be due to the polarization

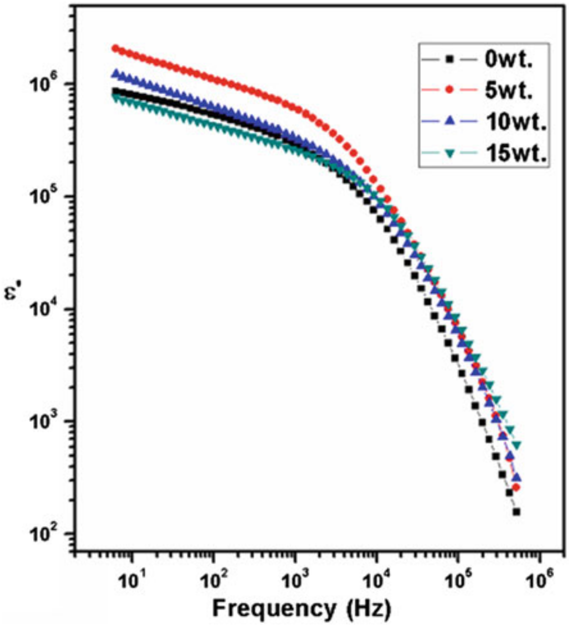


Fig. 2 The variation of real part of permittivity versus frequency at room temperature of the sample (PAN-PEO) $_6$ − LiPF$_6$ + wt% DMMT

effects led to the disability of dipole to follow the field at higher frequencies. The low frequency region appears due to the contribution of charge accumulation at the electrode-electrolyte interface or space polarization effect. At higher frequencies, the periodic reversal of the electric field leads to a reduction of charge carriers in the system so that there is no diffusion of ions in the direction of the field and is related to hoping process in host polymer matrix PAN-PEO [21].

It has been observed that same trend is observed of dielectric permittivity with frequency in all the samples. With the increase in clay concentration from 0 to 10 % there is higher dielectric constant at lower frequencies which clearly shows the faster ion dynamics. The polarization reduction takes place with an increase in frequency which leads to a corresponding decrease in the value of ε' at high frequency. The high frequency region attributed to hopping process (forward backward motion) of charge carriers from one available site to another in the host polymer matrix PAN. These moving charge carriers behave as dipoles depending on the frequency applied [22].

The dielectric constant increases initially with increasing clay concentration up to 5 %. This increase in dielectric constant represents the increase in a number of free ions provided by interaction of clay with polymer host which enhances more conductivity. At high frequency, charge accumulation is eliminated and the periodic flipping reversal of the electric field due to alternating current, which results in back and forth motion of the charge carriers and limits the ion diffusion along the direction of alternating electric field.

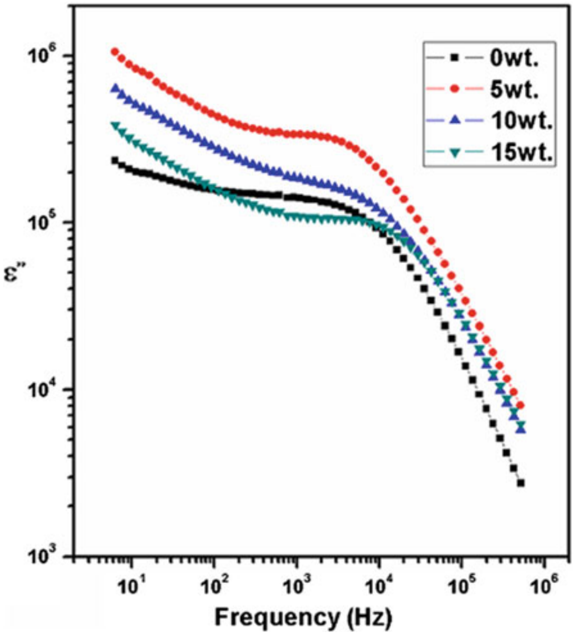
The low frequency dispersion for ε' and absence of loss peak for ε' are characteristics of purely ionic transport systems. Initially ε' increases sharply at low frequency and is independent of frequency at a higher frequency as shown in Fig. 3. The higher the value of dielectric loss at lower frequency shows presence of electrode polarization and confirming the non-Debye dependence [23]. At higher frequency the periodic reversible of the field prevents charges from the orientation in the direction of electric field, results in the decrease in ε' and hence reduction in the ε' [24]. The higher value of ε' in the PNC films is due to the presence of more number of charge carriers.

The conductivity spectrum for the sample with low salt concentration consists of two frequency regions: (i) a frequency-independent zone at high frequency and (ii) an increase in conductivity at higher frequencies as shown in Fig. 4. The ac conductivity of the PNC films is obtained from dielectric loss using the relation

$$\sigma_{ac}=\varepsilon_o\omega\varepsilon''=\varepsilon_o\omega\varepsilon'\tan\delta.$$

Where ϵ_0 is the dielectric permittivity of free space and ω. angular frequency. The similar results of frequency-dependent conductivity are obtained for ionically conducting ceramic glasses and polymers. At lower frequencies, ions transport is faster and easily jumps from one available site $(C\equiv\ddot{N})$ to another in the host polymer PAN matrix. A hoping is said to be successful hopping if ion goes to neighboring site easily having long relaxation time and contributes to electronic conductivity [25]. This observation evidences the complex ion transport process

Fig. 3 The variation of imaginary part of permittivity with frequency at 30 °C of the sample (PAN-PEO) $_6$ −LiPF$_6$ + wt% DMMT



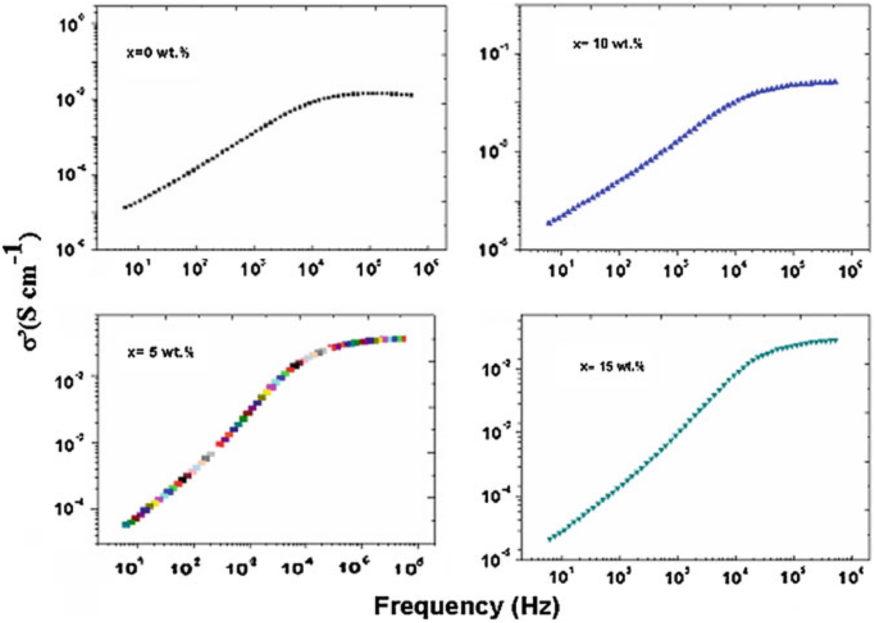


Fig. 4 Variation of ac conductivity versus frequency at RT of the sample (PAN-PEO) $_6$ + LiPF$_6$ + wt% DMMT

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due to both electrode polarizations at low frequency followed by long range ion migration at higher frequencies. At low frequency ionic charges drift for a long range on the application of the field. In the high frequency region, both ε' and ε'' increase with increasing frequency and may be attributed to the dielectric contribution [26]. At higher frequency there is frequency independent region where electrode polarization is steady and a new mechanism of ion migration is supported by ions.

From this Fig. 4 it is observed that the conductivity of x = 0 wt% of pure PAN-PEO+LiPF$_6$ at 30 °C. But when we addition the varying amount of clay then it is obtained that the conductivity is increased. But at higher concentration x = 15 wt% the conductivity is a decrease of the order of magnitude. As the concentration of clay increases there is a decrease in mobile cation concentration due to clustering of free ions ac conductivity decreases as shown in the Fig. 4. There are two mechanisms that ac conductivity follows one is long range conduction and other is hopping of ions through the electron lone pair site. The first effect is due to transport of free anions or cation in polymeric films and later one is due to a reduction in mean charge carrier displacement which makes conductivity dependent on frequency [27, 28]. In polymer Nanocomposites films active role is played by clay and is clearly visible in results. The clustering of filler leads to slow ion dynamics, commonly expressed as rates of hopping/mobility [4, 25].

3.2 Summary and Conclusion

Intercalated PNC films based on (PAN-PEO)$_6$ +LiPF$_6$+x wt% DMMT has been prepared using solution cast technique. Variation of ac conductivity versus frequency shows three regions low-frequency region, intermediate saturation, followed by high-frequency dispersion region. Ion transport in PNC films is contributed by the effect of clay concentration in increasing free carriers and hopping process in amorphous phase and concentration of DMMT plays a crucial role in the transport of ions. In future we may expect that the hopeful ways to improve the electrochemical performance and surface morphology of polymer electrolytes are by fabricating a nanocomposite electrolyte and addition of modified montmorillonite clays to such an electrolyte, retaining an ionic conductivity of 10^{-3} S cm^{-1} and negligible electronic conductivity is 10^{-7} S cm^{-1}. These polymer nanocomposite electrolytes are associated with considerably better capacity and high cycle efficiency in lithium polymer secondary batteries while inhibiting the formation of dendrite growth in films between the electrolyte and the electrodes.

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References

1. H. Aydın, A. Bozkurt, J. Mater. Res. **29**(05), 625–632 (2014)
2. F.M. Gray (1997), Polym. Electrolytes. Ayman Salim Ayes Polym. J. **41**(8), 616–621 (2009)
3. A. Ahmad, S. Saqa'an, Y. Ramadin, A. Zihlif, J. Thermoplast. Compos. Mater **19**, 531 (2006)
4. N. Shukla, A.K. Thakur, S. Archana, Marx T. David, Int. J. Electrochem. Sci. **9**, 644–7659 (2014)
5. F.M. Gray, C.A. Vincent, M. Kent, State Ionics **28**, 936–940 (1988)
6. P.A.R.D. Jayathilaka, M.A.K.L. Dissanayake, I. Albinsson, B.E. Mellander, Solid State Ionics **156**(1), 179–195 (2003)
7. A.S. Ayesh, Polym. J. **41**(8), 616–621 (2009)
8. S. Farheen, R.D. Mathad, Int. J. Innovative Res. Sci. Eng. Technol. (An ISO 3297: 2007 Certified Organization) **3**(11), (2014)
9. S. Poonam, K. Dinesh Kumar, G. Nirali, Open J. Org. Polym. Mater. (2012)
10. A.L. Sharma, A.K. Thakur, Ionics **17**(2), 135–143 (2011)
11. P. Joge, D.K. Kanchan, P. Sharma, N. Gondaliya, A comparative study
12. M.K. Jawad, S.R. Majid, E.A. Al-Ajaj, M.H. Suhail, Adv. Phys. Theor. Appl. **29**, 14–22 (2014)
13. R.J. Sengwa, S. Choudhary, S. Sankhla, Compos. Sci. Technol. **70**(11), 1621–1627 (2010)
14. S. Choudhary, R. Sengwa, Indian J. Phys. **86**, 335–340 (2012)
15. D.K. Pradhan, R.N.P. Choudhary, B.K. Samantaray, Express Polym. Lett. **2**(9), 630–638 (2008)
16. S. Ibrahim, S.M.M. Yasin, N.M. Nee, R. Ahmad, M.R. Johan, Solid State Commun. **152**(5), 426–434 (2012)
17. A. Das, A.K. Thakur, K. Kumar, Solid State Ionics **262**, 815–820 (2014)
18. S.K. Tripathi, A. Gupta, M. Kumari, Bull. Mater. Sci. **35**(6), 969–975 (2012)
19. A. Arya, A.L. Sharma, Appl. Sci. Lett. **2**(2), 72–75 (2016)
20. X. Qian, N. Gu, Z. Cheng, X. Yang, E. Wang, S. Dong, Electrochim. Acta **46**(12), 1829–1836 (2001)
21. S. Ramesh, A.H. Yahaya, A.K. Arof, Solid State Ionics **152**, 291–294 (2002)
22. A.S. Nowick, A.V. Vaysleyb, I. Kuskovsky, Phys. Rev. B **58**(13), 8398 (1998)
23. N. Shukla, A.K. Thakur, A. Shukla, D.T. Marx, An applicability of almond-west formalism. Int. J. Electrochem. Sci. **9**, 7644–7659 (2014)
24. T. Furukawa, M. Imura, H. Yuruzume, Jpn. J. Appl. Phys. **36**(3R), 1119 (1997)
25. A.L. Sharma, A.K. Thakur, Ionics **21**(6), 1561–1575 (2014)
26. A.L. Sharma, N. Shukla, A.K. Thakur, J. Polym. Sci. Part B Polym. Phys. **46**(23), 2577–2592 (2008)
27. N. Shukla, A.K. Thakur, A. Shukla, R. Chatterjee, J. Mater. Sci. Mater. Electron. **25**(6), 2759–2770 (2014)
28. C. Bhatt, R. Swaroop, A. Arya, A.L. Sharma, J. Mater. Sci. Eng. **5**(11–12), 418–434 (2015)