

Accepted Manuscript

Conductivity and dielectric behaviour of PEO-based solid nanocomposite polymer electrolytes

Suriani Ibrahim, Siti Mariah Mohd Yasin, Ng Meng Nee, Roslina Ahmad, Mohd Rafie Johan

PII: S0038-1098(11)00641-7
DOI: [10.1016/j.ssc.2011.11.037](https://doi.org/10.1016/j.ssc.2011.11.037)
Reference: SSC 11411

To appear in: *Solid State Communications*

Received date: 5 March 2011
Accepted date: 27 November 2011

Please cite this article as: S. Ibrahim, S.M. Mohd Yasin, N.M. Nee, R. Ahmad, M.R. Johan, *Solid State Communications* (2011), doi:10.1016/j.ssc.2011.11.037

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.



Conductivity and Dielectric Behaviour of PEO-based Solid Nanocomposite Polymer Electrolytes

Suriani Ibrahim^{*}, Siti Mariah Mohd Yasin, Ng Meng Nee, Roslina Ahmad, Mohd Rafie Johan

Advanced Materials Research Laboratory
Department of Mechanical Engineering
Faculty of Engineering
University of Malaya
50603 Kuala Lumpur
Malaysia

Email^{*}: sue_83@um.edu.my;
Tel^{*}: +60123010248 Fax^{*}: +60379675317

ABSTRACT

In this research, thin films of poly(ethylene oxide) (PEO) blend with lithium hexafluorophosphate (LiPF₆) salt and ethylene carbonate (EC) as plasticiser and carbon nanotube (CNT) as filler, are prepared using solution casting method. The conductivity and dielectric response of the nanocomposite polymer electrolyte systems are studied within the broad frequency range of 5 Hz - 5 MHz and within a temperature range of 298 - 373 K. The conductivity-temperature plots are observed to be of Arrhenius nature. The dielectric behaviour is analysed using the dielectric permittivity (ϵ_r and ϵ_i), loss tangent ($\tan \delta$) and electric modulus (M_i and M_r) of the samples. It is observed that the dielectric permittivity rises sharply towards low frequencies due to electrode polarisation effects. The maxima of the loss tangent ($\tan \delta$) shifts towards higher frequencies and the height of the peak increases with increasing temperature.

Keywords: A. Polymers, A. Thin films, B. Chemical synthesis, D. Dielectric response

INTRODUCTION

The development of polymeric systems with high ionic conductivity is one of the main objectives in polymer research. This is due to their potential applications in solid state batteries [1-4]. Polymer batteries possess advantages such as high ionic conductivity, high energy density, solvent-free condition, leak proof, wide electrochemical stability windows, ease in processability and light weight. Generally, ionic conduction in polymer electrolytes is dominated by the amorphous elastomeric phase [5]. Polymers having the dipole moment aligned parallel to the chain contour exhibit a dielectric relaxation due to the fluctuation of the end-to-end vector of the chains [6, 7]. The study of dielectric relaxation in solid polymer electrolytes is a powerful approach for obtaining information regarding the characteristics of ionic and molecular interactions. The dielectric parameters associated with relaxation processes are of particular significance in ion - conducting polymers where the dielectric constant plays a fundamental role, which shows the ability of a polymer material to dissolve salts [8]. The frequency-dependent conductivity and dielectric relaxation are both sensitive to the motion of charged species and dipoles of the polymer electrolytes [8]. Wintersgill and Fontanella [9] studied low-frequency dielectric parameters of polyethylene oxide (PEO) and polypropylene oxide based polymer electrolytes. It has been shown that the dielectric parameters are strongly influenced by the nature of the additives as well as temperature. Ansari et al. [10] investigated a PEO complex with ammonium trifluoromethane sulfonate $[(\text{PEO})_8\text{NH}_4\text{SO}_3\text{CF}_3]$. Their results showed that the dielectric constant and dielectric loss decrease with increasing frequency and these parameters are also dependent on the phases of the material. In this paper, the effects of salts, plasticiser and filler on the ionic conductivity of PEO polymer electrolytes are reported. The dielectric behaviour of PEO polymer electrolytes are also investigated.

Experimental

PEO films were used as host polymer electrolytes and were prepared by standard solution casting techniques. The materials used in this work were PEO ($MW = 600,000$, Acros), lithium hexafluorophosphate (LiPF_6) (Aldrich), ethylene carbonate (EC) (Alfa Aesar), and acetonitrile (Fisher). Amorphous carbon nanotubes (α -CNTs) were prepared via chemical route at low temperature. Prior to use, PEO was dried at $50\text{ }^\circ\text{C}$ for 48 hours. All components were added and dissolved in acetonitrile. The solutions were stirred for 24 hours at room temperature until homogeneous solutions were obtained. The solutions were cast onto glass Petri dishes and were left to evaporate slowly to form films. All samples were prepared at room temperature and stored under dry conditions. The ionic conductivities of the samples were measured at within a temperature range of 298 to 373 K using HIOKI 3531 LCR Hi-Tester with a frequency range of 50 Hz to 5 MHz. The conductivity (σ) was determined using the equation below:

$$\sigma = t / R_b A \quad (1)$$

From Equation 1, t represents the thickness of sample, A represents the contact area between the electrode and sample and R_b is the bulk impedance of the sample. The dielectric constant ε_r and the dielectric loss ε_i can be defined as:

$$\varepsilon_r(\omega) = \frac{Z_i}{\omega C_0 (Z_r^2 + Z_i^2)}, \quad (2)$$

$$\varepsilon_i(\omega) = \frac{Z_r}{\omega C_0 (Z_r^2 + Z_i^2)}. \quad (3)$$

where Z_i represents the imaginary impedance, Z_r represents the real impedance, ω is the angular frequency, C_0 represents the vacuum capacitance of any configurations of the electrode, ϵ_r is the real permittivity and ϵ_i is the imaginary permittivity.

The real and imaginary parts of the electrical modulus M_r and M_i were calculated from:

$$M_r(\omega) = \frac{\epsilon_r}{(\epsilon_r^2 + \epsilon_i^2)}, \quad (4)$$

$$M_i(\omega) = \frac{\epsilon_i}{(\epsilon_r^2 + \epsilon_i^2)}. \quad (5)$$

The tangent loss can be expressed as

$$\tan \delta = \frac{\epsilon_i}{\epsilon_r} \quad \text{or} \quad \frac{M_i}{M_r}. \quad (6)$$

3.0 Results and Discussion

3.1 Conductivity Studies

[Fig. 1]

Fig. 1 shows the temperature dependence of conductivity for various electrolytes within a temperature range of 25 and 100 °C. It is evident that the room temperature conductivity increases with different chemical compositions. The results are summarised in Table 1. The conductivity increases by 5 orders of magnitude upon the addition of LiPF₆, 4 orders of magnitude upon the addition of EC and 3 orders of magnitude upon the addition of α -CNTs. The sudden increase in conductivities is due to the role of lithium ions in the PEO, the increase in flexibility of the polymer chain due to the EC, and high electrical conductivity properties of α -CNTs on the polymer electrolytes.

It is observed that there is a sudden increase in conductivity for pure PEO electrolyte at 40 – 50 °C, as shown in Fig. 1(a). However, the ionic conductivity increases linearly beyond 50 °C. The thermal effects are clearly observed in Figs. 1 (b) – (d), upon the addition of LiPF₆, EC and α -CNT. More salts were dissociated into ions when EC was added into the system, which have low viscosity in the system and therefore increases the ionic mobility. The addition of α -CNTs increases the conductivity by inhibiting recrystallisation of the PEO chains and providing Li⁺ conducting pathway at the filler surface through Lewis Acid base interactions among different species in the electrolytes [11]. The process of conduction is Arrhenius and the activation energy is recorded in Table 1. The sample which consists of LiPF₆, EC and α -CNTs

shows lower activation energy at an ambient temperature of 298 ~ 373K. A transportation lithium ion requires low energy within the polymer matrix and hence increases the conductivity. This is possibly due to the size of the filler and plasticiser molecules compared to the polymer molecules, which could penetrate easily into the polymer matrix [12].

[Table 1]

3.2 Complex Impedance Analysis

[Fig. 2]

Fig. 2 shows the complex impedance spectra for various electrolytes at lower and higher temperatures. The semicircle in Fig. 2 represents the ionic resistance of the polymer electrolyte in the higher frequency range and an inclined line at lower ones. It shows a typical blocking electrode capacitive behaviour. The slopes of the inclined lines are not strongly dependent on the components' molar ratios at higher temperatures. This indicates that the resistance of the inclined line is mainly against ion passage at the electrolyte/electrode interface. However, it is a different case for lower temperatures, in which the inclined lines are strongly dependent on the components' molar ratios. The semicircle shrinks and decays as a result of shifting to higher frequencies due to a decrease in ionic resistance of the electrolyte at higher temperatures. The arc's intercept on the real axis gives the value of the bulk resistance, which decreases with increasing temperature.

3.3 Dielectric Permittivity Studies

3.3.1 Dielectric Constant (ϵ_r)

[Fig. 3]

3.3.2 Dielectric Loss (ϵ_i)

[Fig. 4]

Figs. 3 and 4 show the frequency dependence of the dielectric constant, ϵ_r and dielectric loss ϵ_i , at various temperatures for polymer nanocomposite electrolytes. Since appreciable relaxation peaks were not observed, ϵ_r and ϵ_i were used to indicate that, the increase in conductivity was primarily due to an increase in the number density of mobile ions [13]. It is clearly observed that the values of ϵ_r and ϵ_i increase upon the addition of salt, plasticizer and filler into the polymer matrix. The dielectric constants decrease continuously with increasing frequency, and reaches a constant value at about 2.5 kHz. A rapid decrease in dielectric constant may be noticed above a frequency range of 4 kHz. This may be attributed to the tendency of dipoles in the macromolecules to orient themselves in the direction of the applied field within the low frequency range.

However, in the high frequency range the dipoles are unable to orient themselves in the direction of the applied field and hence, the values of the dielectric constant decrease [14]. The conductivity in polymer-salt is due to the migration of Li^+ [15]. The dielectric permittivity rises sharply towards low frequencies due to electrode polarisation effects [16, 17]. Thus, the addition of carbon nanotubes is expected to increase the degree of salt dissociation and redissociation,

which increase the number of mobile Li^+ . The enhancement in conductivity is explained based on the assumption that the filler particles act as a supporting matrix. This, in turn, helps to retain an overall solid structure with unchanged volume for Li^+ transport at ambient and elevated temperatures [18]. The observed variations in ϵ_r versus frequency for the two electrolytes could be attributed to the build-up of space charge regions at the electrode-electrolyte interface.

At low-frequency regions, the dielectric constant ϵ_r for both electrolytes is proportional to ω^{n-1} , indicating non-Debye dependence [19]. This implies that the conductivity exhibits relaxation, which is non-exponential in time [20]. This dispersion reflects the existence of space charge polarisation, where there is time for the charges to build up at the interface before the applied field changes direction, giving a large value of ϵ_r [13]. On the other hand, there is no time for charge build-up at the interface with increasing frequencies due to the increasing rate of electric field reversal. The polarisation due to charge accumulation decreases, which leads to a decrease in value of ϵ_r [21, 22].

3.4 Electrical Modulus Studies

3.4.1 Real Electrical Modulus M_r

[Fig. 5]

3.4.2 Imaginary Electrical Modulus M_i

[Fig. 6]

Figs. 5 and 6 depict the variations of real and imaginary electrical modulus (M_r and M_i) for PEO nanocomposite electrolytes. The long tail due to the large capacitance, which is associated with the electrodes at low-frequency regions, confirms the non-Debye behaviour [22-25]. Since definitive peaks were not observed in the M_i plots for both cases, the loss tangent, $\tan \delta$ was plotted with respect to frequency for the PEO nanocomposite. This is shown in Fig. 7.

3.4.3 Loss tangent ($\tan \delta$)

[Fig. 7]

From Fig. 7, it can be seen that $\tan \delta$ increases with increasing frequency, passes through a maximum value and thereafter decreases for pure PEO. The maxima of $\tan \delta$ shifts towards higher frequencies and the height of the peak increases with increasing temperature. This is attributed to the increment in number of charge carriers for conduction, which decreases the resistivity of the samples [25]. When salt, EC and α -CNTs were added into the polymer

complex, a sharp peak is observed at low frequencies for PEO-LiPF₆ complex, and at high frequencies for PEO-LiPF₆-EC and PEO-LiPF₆-EC- α -CNTs. For PEO-LiPF₆ complex, the relaxation peak shifts towards higher frequencies with increasing temperature, which indicates that the charge carrier is thermally activated. The dielectric response caused by ion relaxation was studied using the reciprocal quantity of electric permittivity [26]. For PEO-LiPF₆-EC, the frequency values shift towards higher frequencies compared with the PEO-LiPF₆ complex.

Conclusions

Polymer electrolytes based on PEO, LiPF₆, EC and α -CNTs have been prepared by solution casting technique, with various compositions. The dielectric behaviour of PEO and its complexes has been studied. The dielectric constant, dielectric loss and loss tangent of PEO are found to increase upon the addition of LiPF₆ and these parameters are significantly influenced by the temperature and frequency. The dielectric constant and dielectric loss of PEO-LiPF₆ increase upon the addition of EC and α -CNTs, and these parameters are also significantly influenced by the temperature and frequency. No significant effects are observed, however, for the loss tangent of this complex.

Acknowledgements

The authors gratefully acknowledge the financial support by PPP fund (PS083/2009B) provided by University of Malaya and Science fund (13-02-03-3068) provided by the Ministry of Science, Technology and Environment (MOSTE) Malaysia. The authors thank Ms. Nina from Department of Physics, University of Malaya for her assistance during writing of this paper. The authors specially thank Ms. Nadia for her constructive comments on the manuscript.

REFERENCES

1. Hooper A, North JM, *Solid State Ionics* 1983;9:1161.
2. Mac Callum JR, Vincent CA, *Polymer Electrolytes Reviews 1 and 3*, Elsevier, London, 1987/1989.
3. Acosta JL, Morales E, *Solid State Ionics* 1996;85:85 – 90.
4. Kim JY, Kim SH, *Solid State Ionics*, 1999;124:91 – 99.
5. Whang WT, Lu CL, *Journal of Applied Polymer Science* 1995;56:1635.
6. Adachi K, Kotaka T, *Progress in Polymer Science* 1993;18:585.
7. Hayakawa T, Adachi K, *Journal of Polymer* 2001;42:1725 – 1723.
8. Singh KP, Gupta PN, *Journal of European Polymer* Vol 34, No. 7, pp. 1023-1029.
9. Wintersgill MC and Fontanella JJ, in *Polymer Electrolyte Reviews 2*, ed. MacCullum JR and Vincent CA. Elsevier, London, 1989, p. 45.
10. Ansari SM, Brodwin M, Stainer M, Druger SD, Ratner MA, and Shriver DF, *Solid State Ionics* 1985;17:101.

11. Crose F, Persi L, Scrosati B, Serriano F, Plichta E, Hendrickson MA, *Electrochimica Acta* 2001; 46:2457.
12. Pradhan DK, Samantaray BK, Choudhary RNP, Thakur AK, 11 (2005)95.
13. Majid SR, Arof AK, *Physica B* 2007;390:209 – 215.
14. Reicha FM, El-Hiti M, El-Sonabati AZ, Diab MA, *Journal of Physics D Applied Physics* 1991;24:369.
15. Stevens JR, Wieczorek W, Raducha D, Jeffrey KK, *Solid State Ionics* 1997;97:347.
16. Campbell JA, Goodwin AA, Simon GP, *Journal of Polymer* 2001;42:4731 – 4741.
17. Mishra R, Baskaran N, Ramakrishna PA, Rao KJ, *Solid State Ionics* 1998;112:261 – 273.
18. Park Y, Nagai M, Kim JD, Kobayashi K, *Journal of Power Sources* 2004;137:175.
19. Gondivaraj G, Baskaran N, Shahi K, Monoravi P, *Solid State Ionics* 1995;76:47.
20. Balaya P, Goyal PS, *Journal of Non-Crystalline Solids* 2005;351:1573.
21. Molak A, Ksepko E, Gruszka I, Ratuszna A, Paluch M, Ujma Z, *Solid State Ionics* 2005;176:1439.
22. El Shafee E, *Carbohydrate Polymers* 1996;31:93.
23. Muralidharan P, Venkateswarlu M, Satyanarayana N, *Journal of Non- Crystalline Solids* 2005;351:583.
24. Baskaran R, Selvasekaranpandian S, Kuwata N, Kawamura J, Hattoriac T, *Material Chemistry and Physics*, 2006;98:55.
25. Prabakar K, Narayandass K, Mangalaraj D, *Materials Science and Engineering B* 2003;98:225.
26. Gokulamurali N, Suthanthiraj SA, Maruthamuthu P, *Proceeding Solid State Ionics: Material Applied* 1992: 373.

Table 1 Conductivity and activation energy values for composite polymer electrolytes systems

Polymer electrolytes	Conductivity at 298K, σ (S cm ⁻¹)	Activation energy, E_a (eV)
PEO	3.25×10^{-10}	0.61
PEO+ 20 wt. % LiPF ₆	3.57×10^{-5}	0.19
PEO+ 20 wt. % LiPF ₆ + 15 wt. % EC	2.06×10^{-4}	0.14
PEO+ 20 wt. % LiPF ₆ + 15 wt. % EC + 5 wt. % CNT	1.30×10^{-3}	0.08

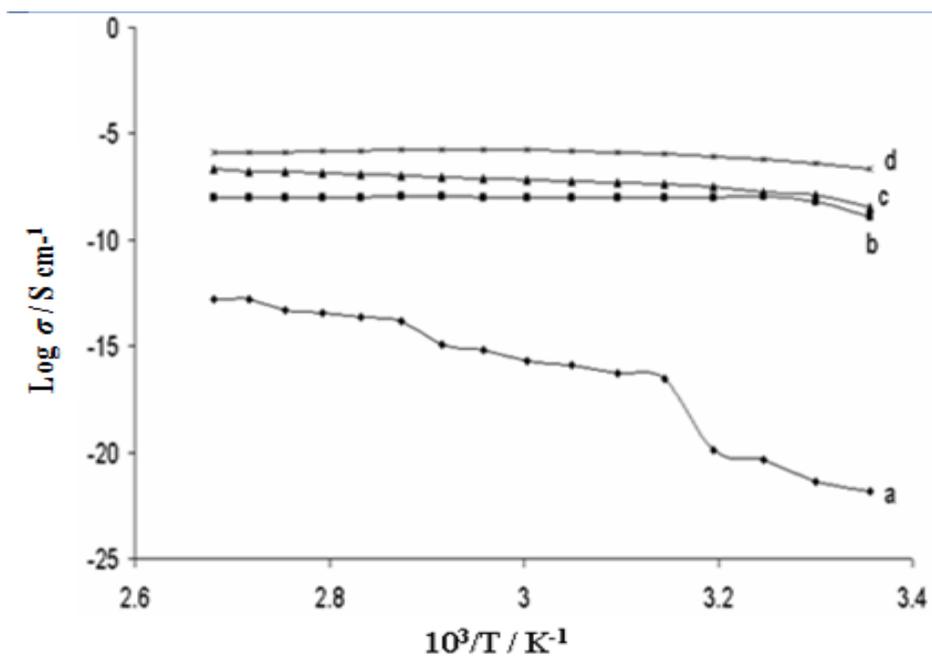


Fig. 1 Conductivity dependence temperature of nanocomposite polymer electrolytes at various compositions (a) PEO (b) PEO + 20 wt%. LiPF₆ (c) PEO + 20 wt%. LiPF₆ + 15 wt%. EC (d) PEO + 20 wt%. LiPF₆ + 15 wt%. EC + 5 wt%. α -CNTs

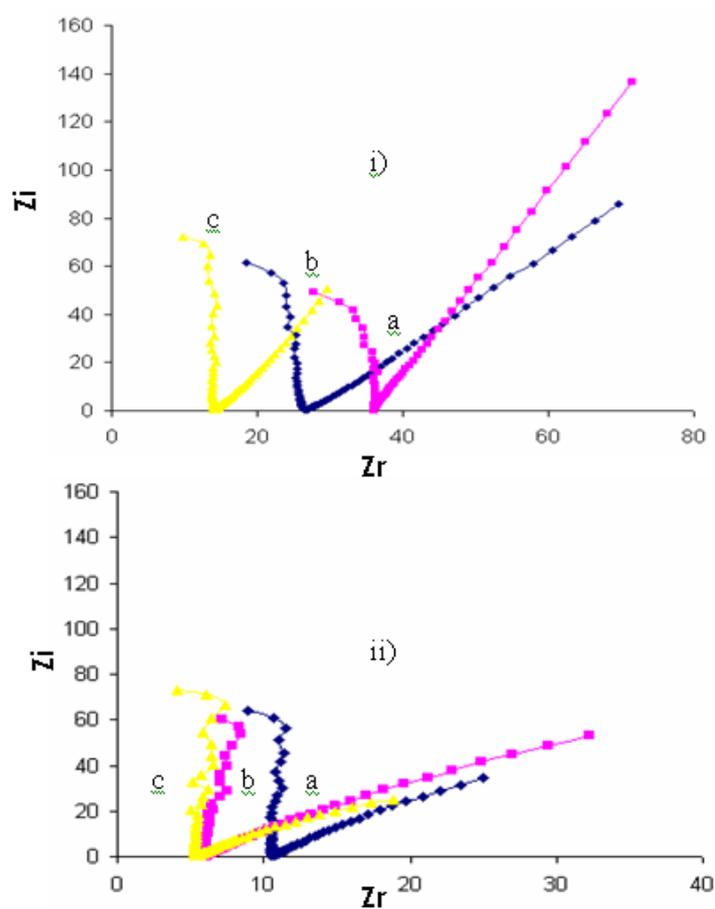


Fig. 2 Complex impedance plot for (a) PEO + 20 wt%. LiPF_6 (b) PEO + 20 wt%. LiPF_6 + 15 wt%. EC (c) PEO + 20 wt%. LiPF_6 + 15 wt%. EC + 5 wt%. α -CNTs at (i) Low temperature (298K) (ii) High temperature (373K)

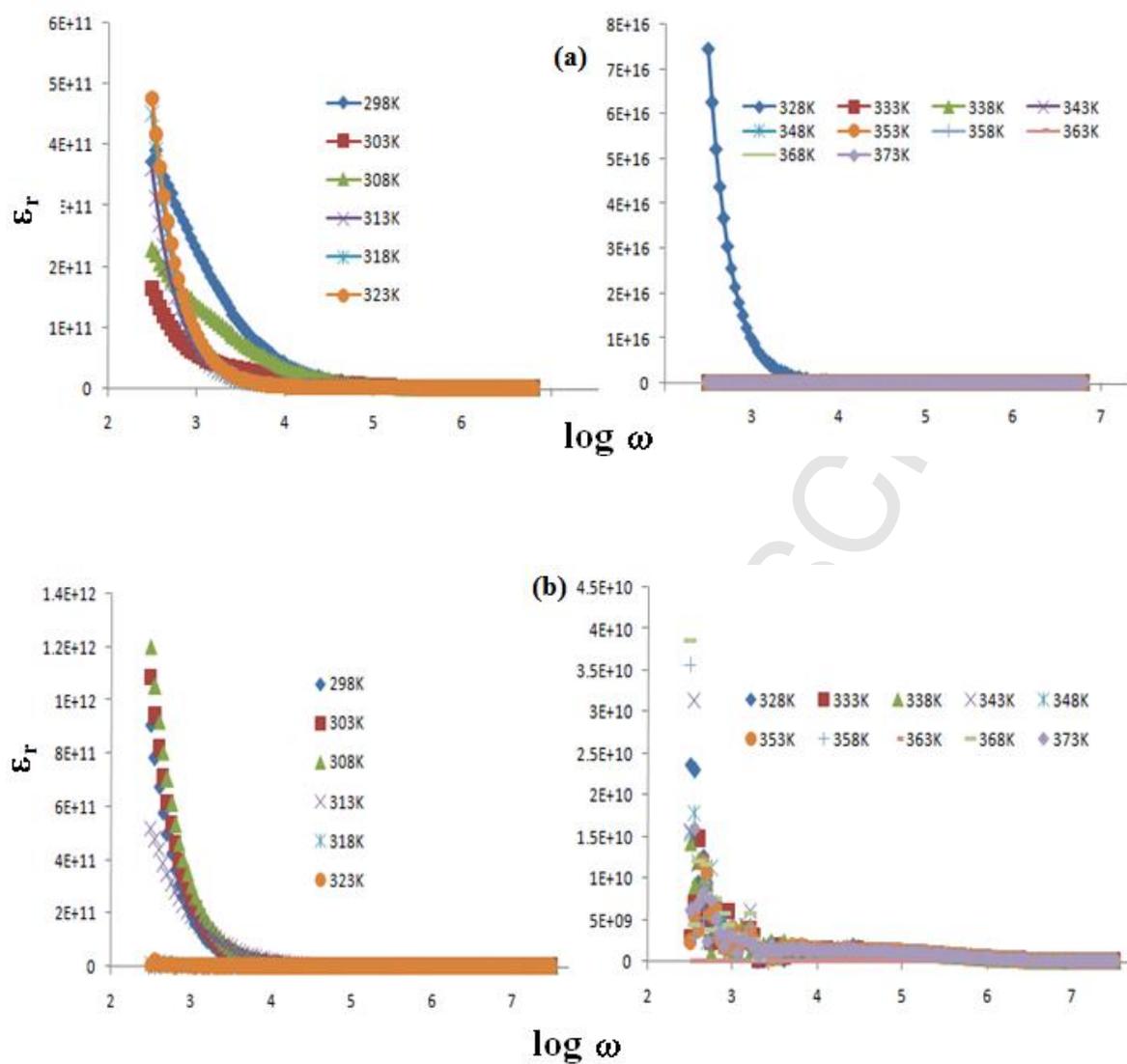


Fig. 3 Variations of dielectric constant (ϵ_r) with frequency for (a) PEO (b) PEO+20wt%. LiPF_6

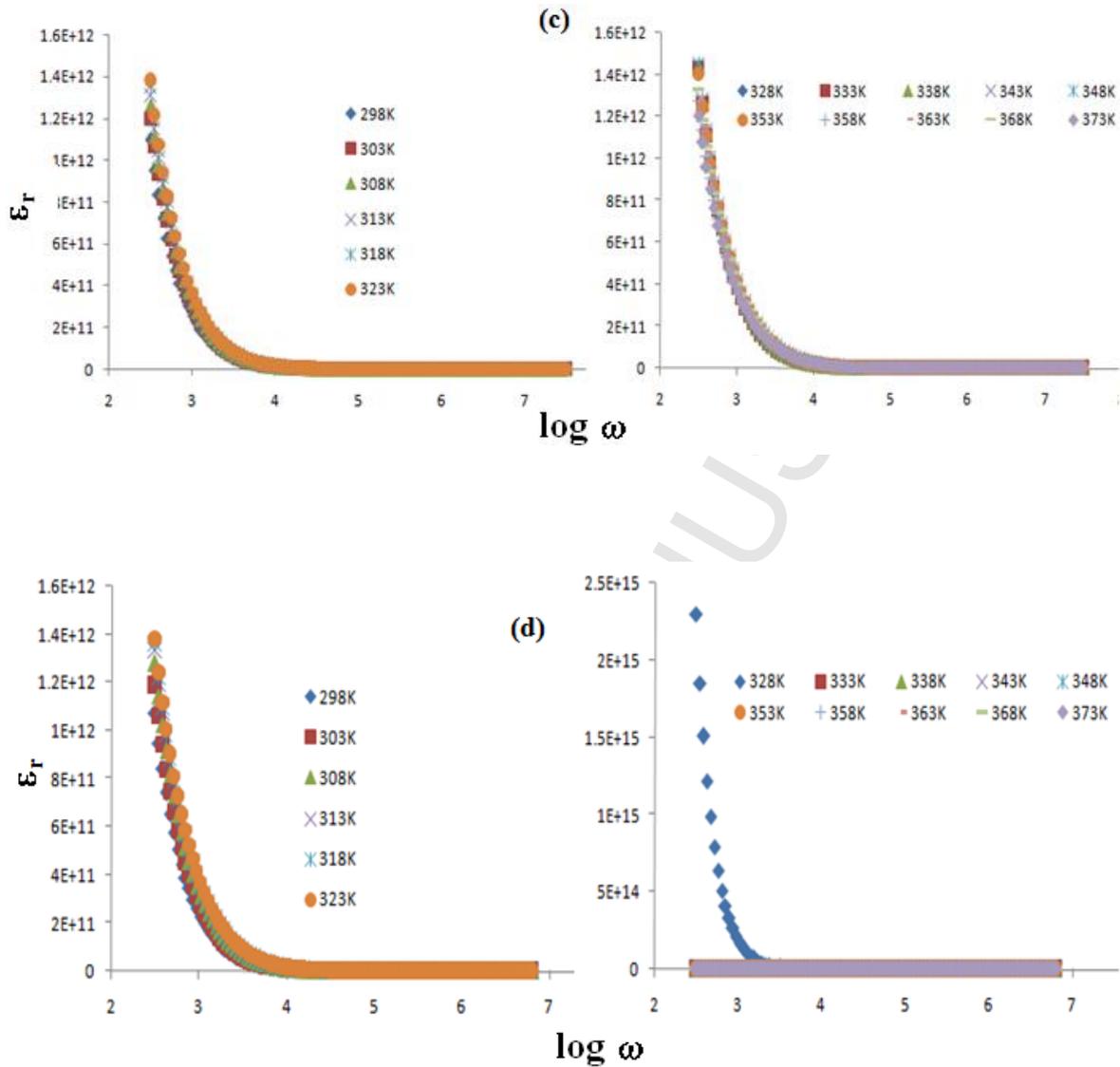


Fig. 3 Variations of dielectric constant (ϵ_r) with frequency (c) PEO+20wt%. LiPF₆+ 15 wt%. EC (d) PEO+20wt%. LiPF₆+15wt%. EC+5wt%. α -CNTs

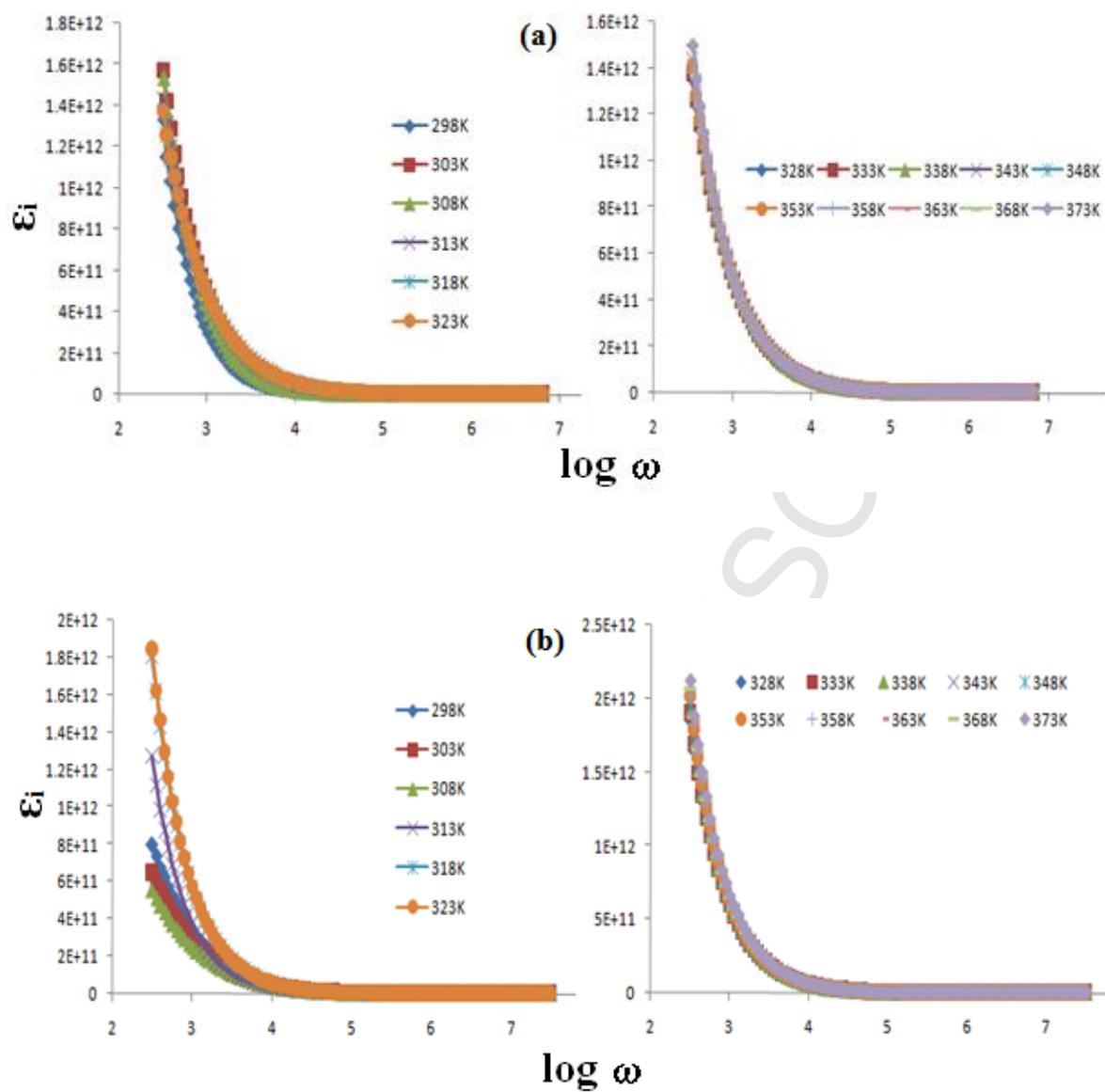


Fig. 4 Variations of dielectric constant (ϵ_i) with frequency for (a) PEO (b) PEO+20wt%. LiPF₆

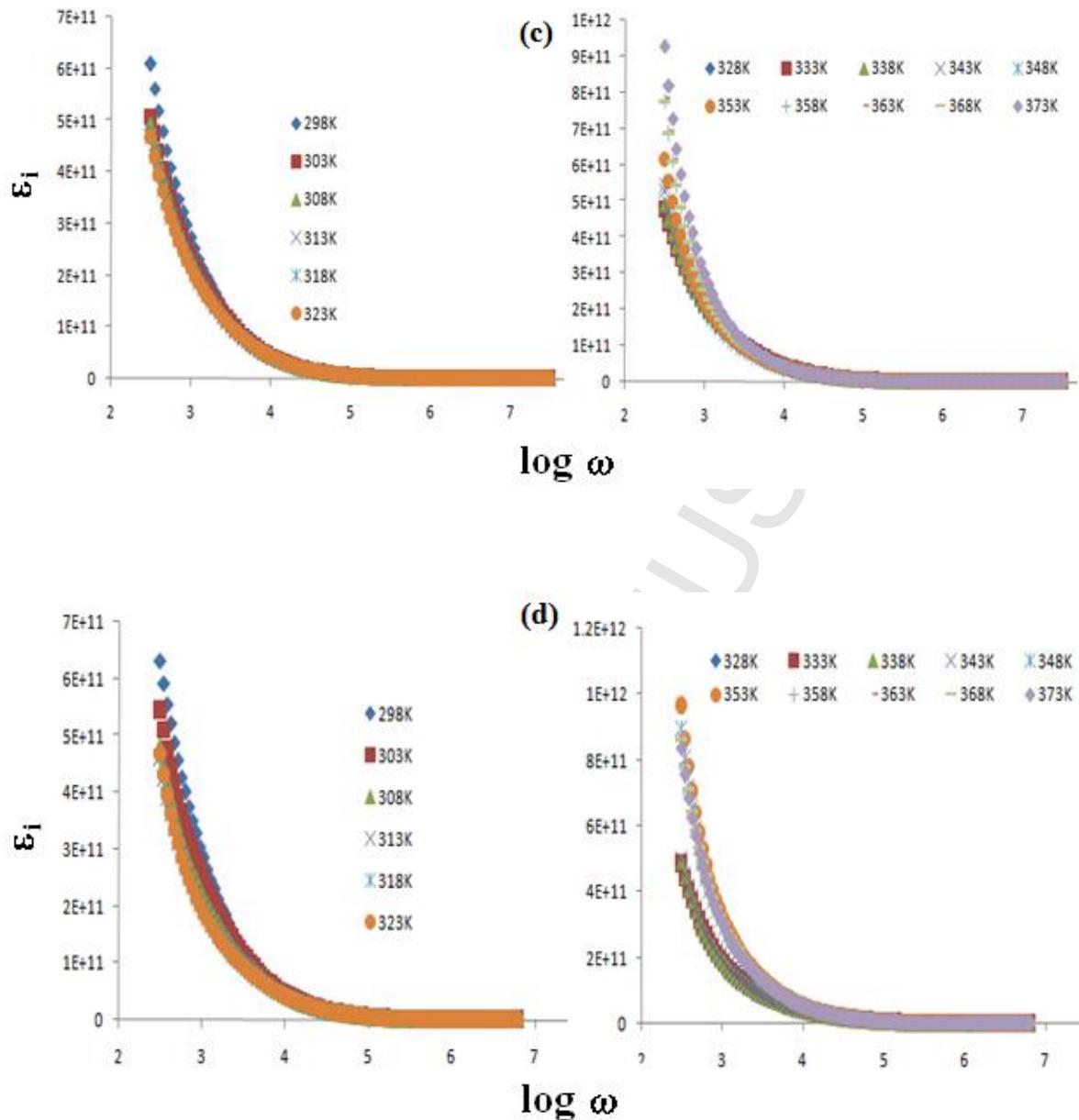


Fig. 4 Variations of dielectric constant (ϵ_i) with frequency for (c) PEO+20wt%. LiPF₆+15 wt%. EC (d) PEO+20wt%. LiPF₆+15wt%. EC+5wt%. α -CNTs

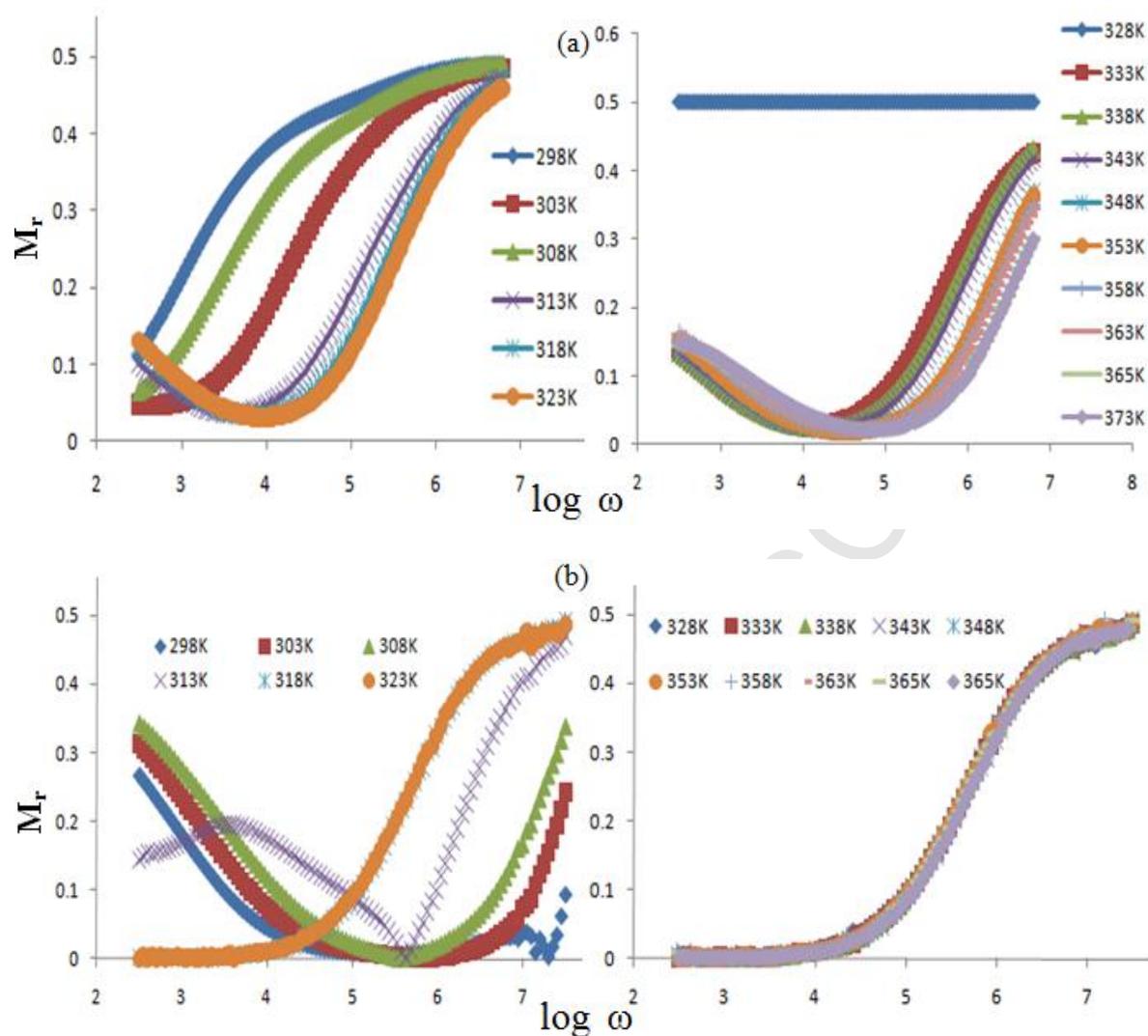


Fig. 5 Variations of the real part of modulus M_r with frequency for (a) PEO (b) PEO+20wt%. LiPF₆.

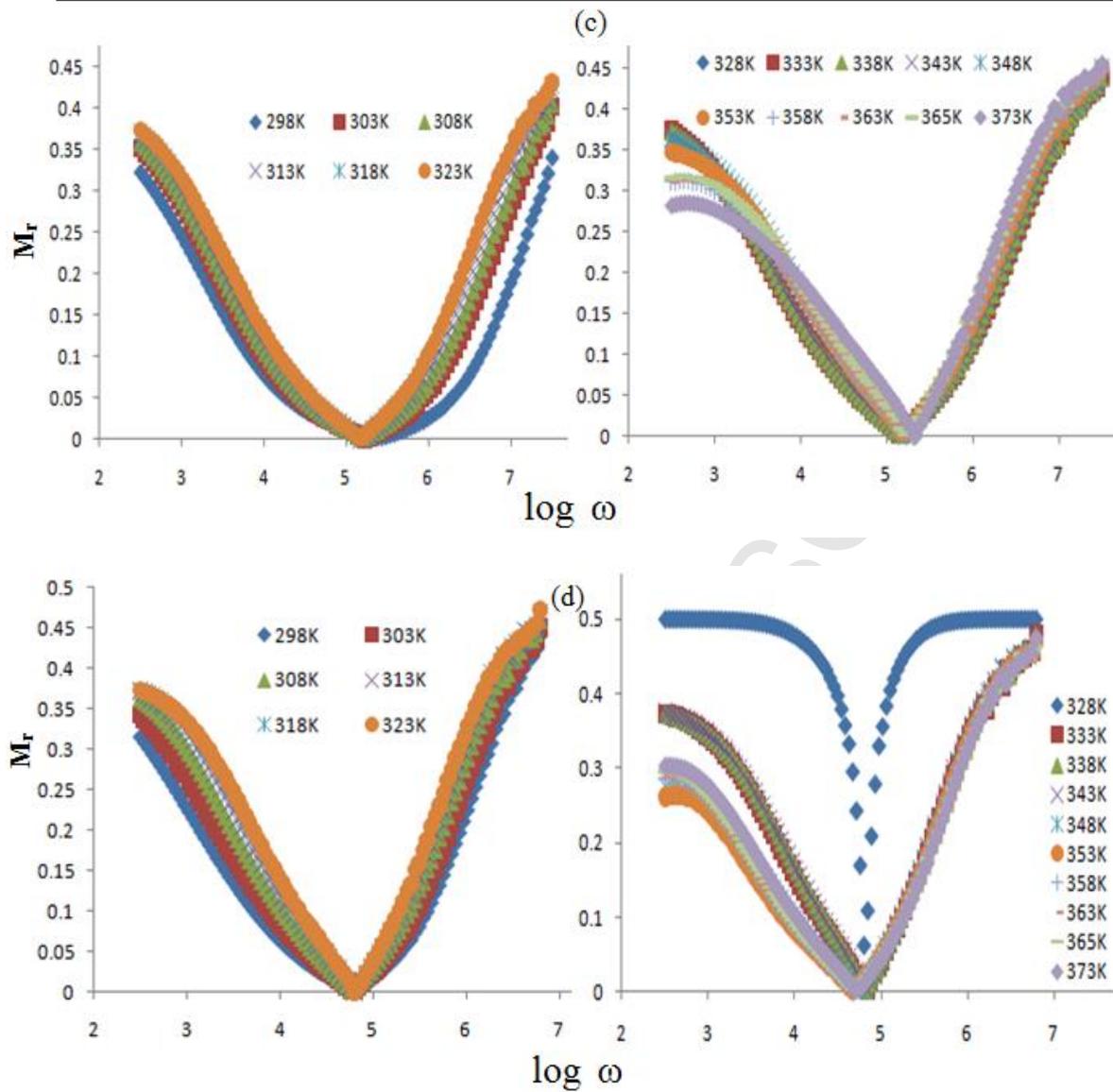
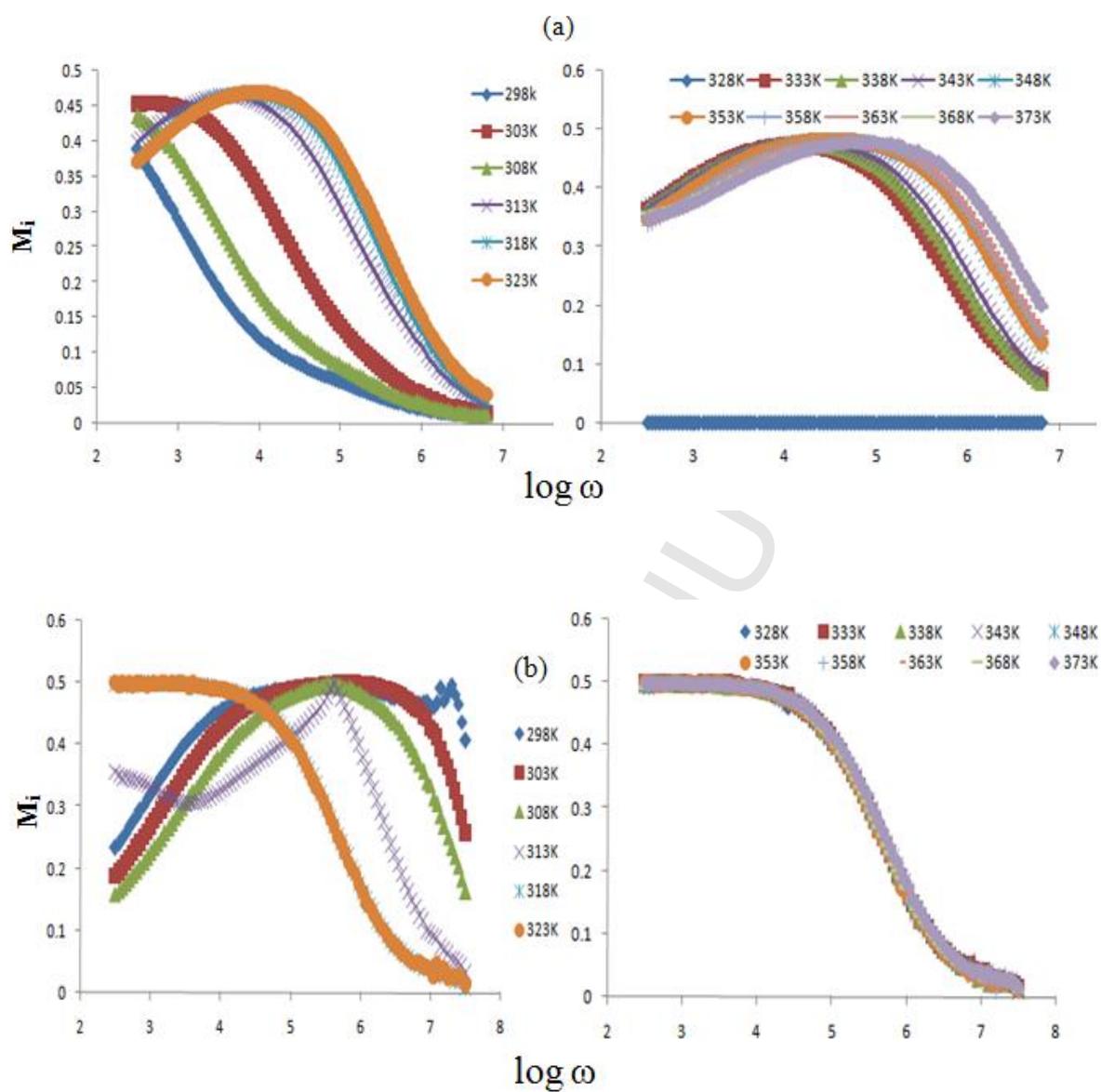


Fig. 5 Variations of the real part of modulus M_r with frequency for (c) PEO+20wt%. LiPF₆+15wt%. EC (d) PEO+20wt%. LiPF₆+15wt%. EC+5wt%. α -CNTs



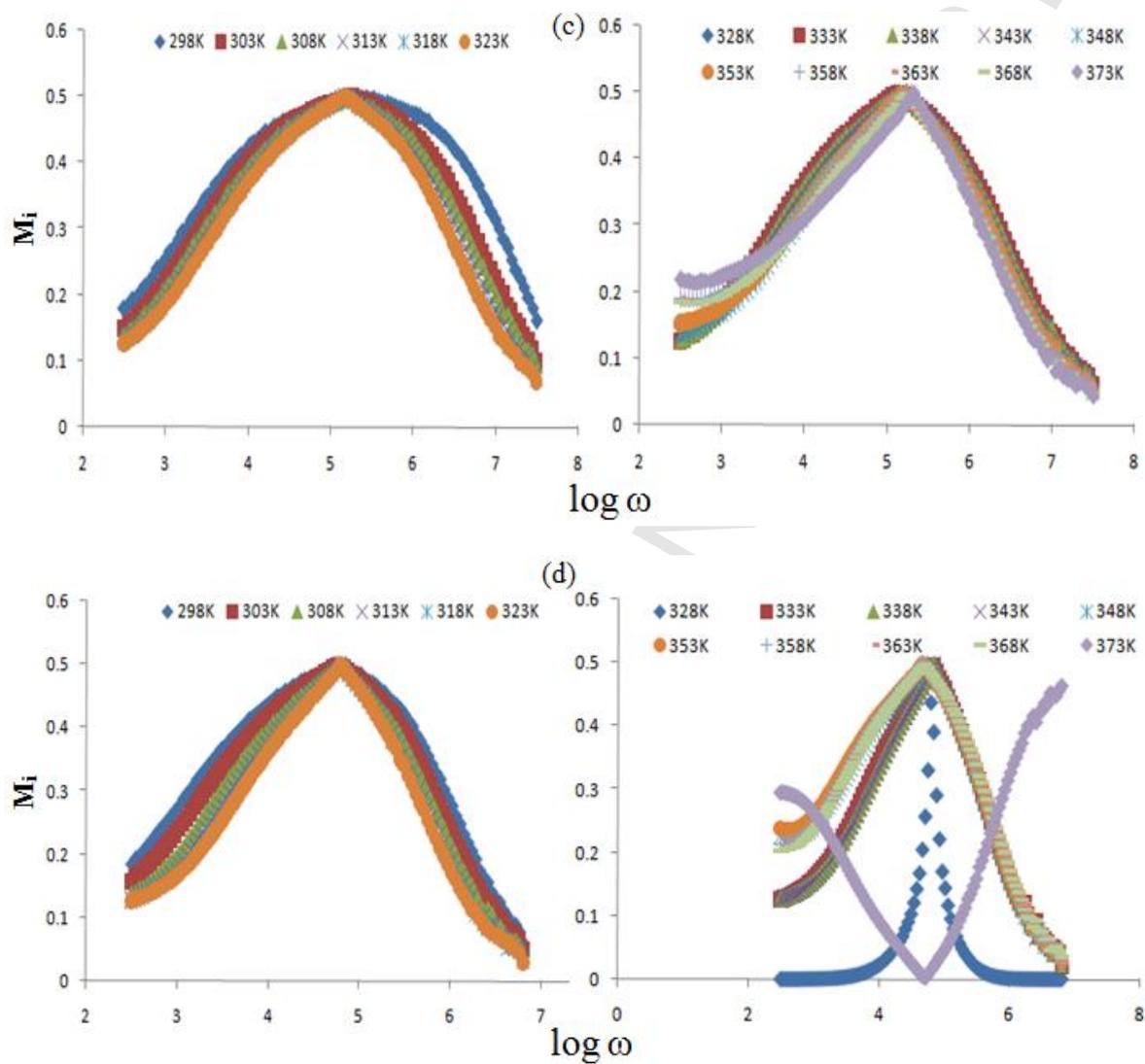


Fig. 6 Variations of the imaginary part of modulus M_i with frequency for (c) PEO+20wt%. LiPF₆+ 15 wt%. EC (d) PEO+20wt%. LiPF₆+15wt%. EC+5wt%. α -CNTs

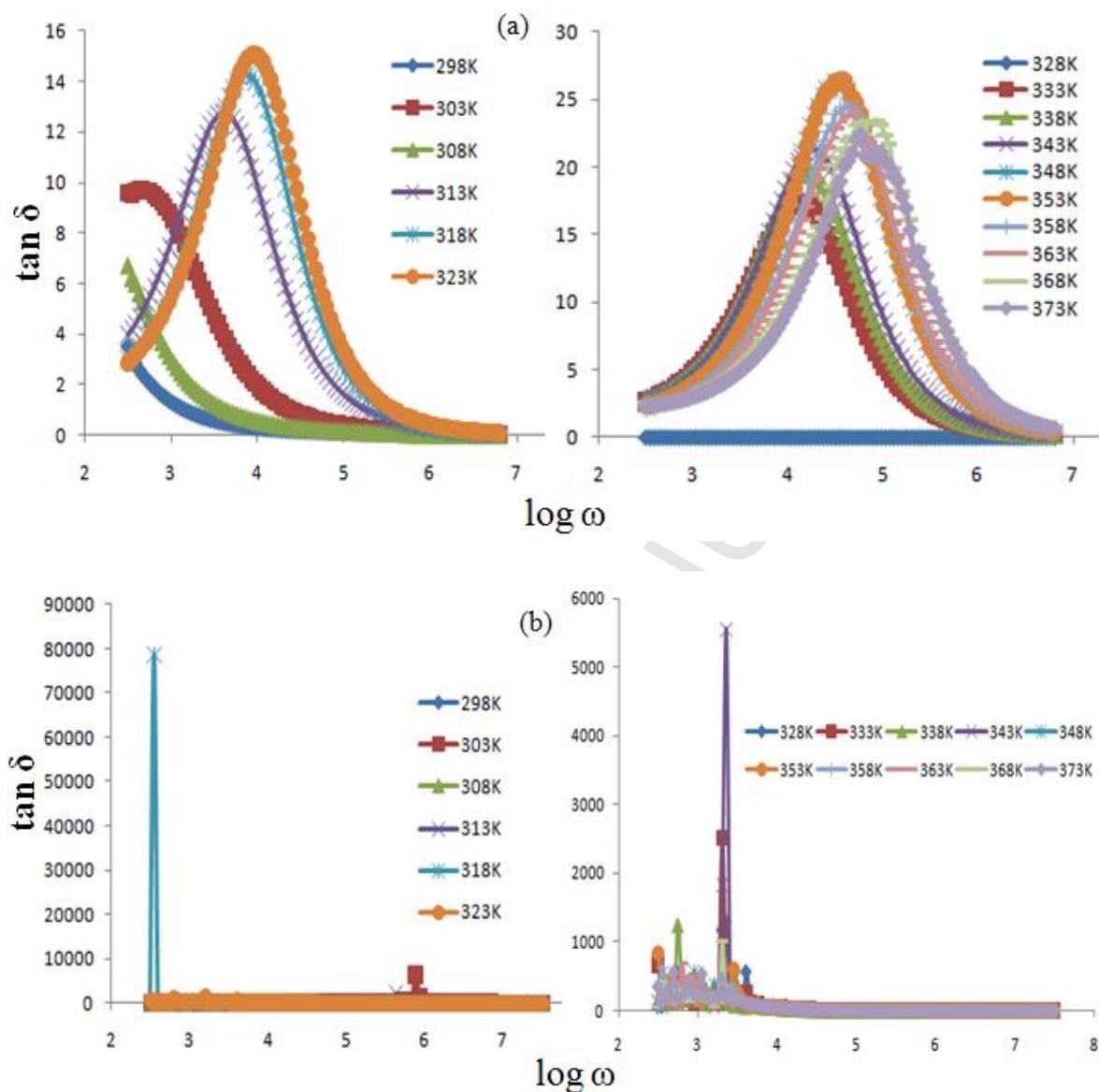


Fig. 7 Variations of loss tangent ($\tan \delta$) with frequency for (a) PEO
(b) PEO+20wt%. LiPF_6

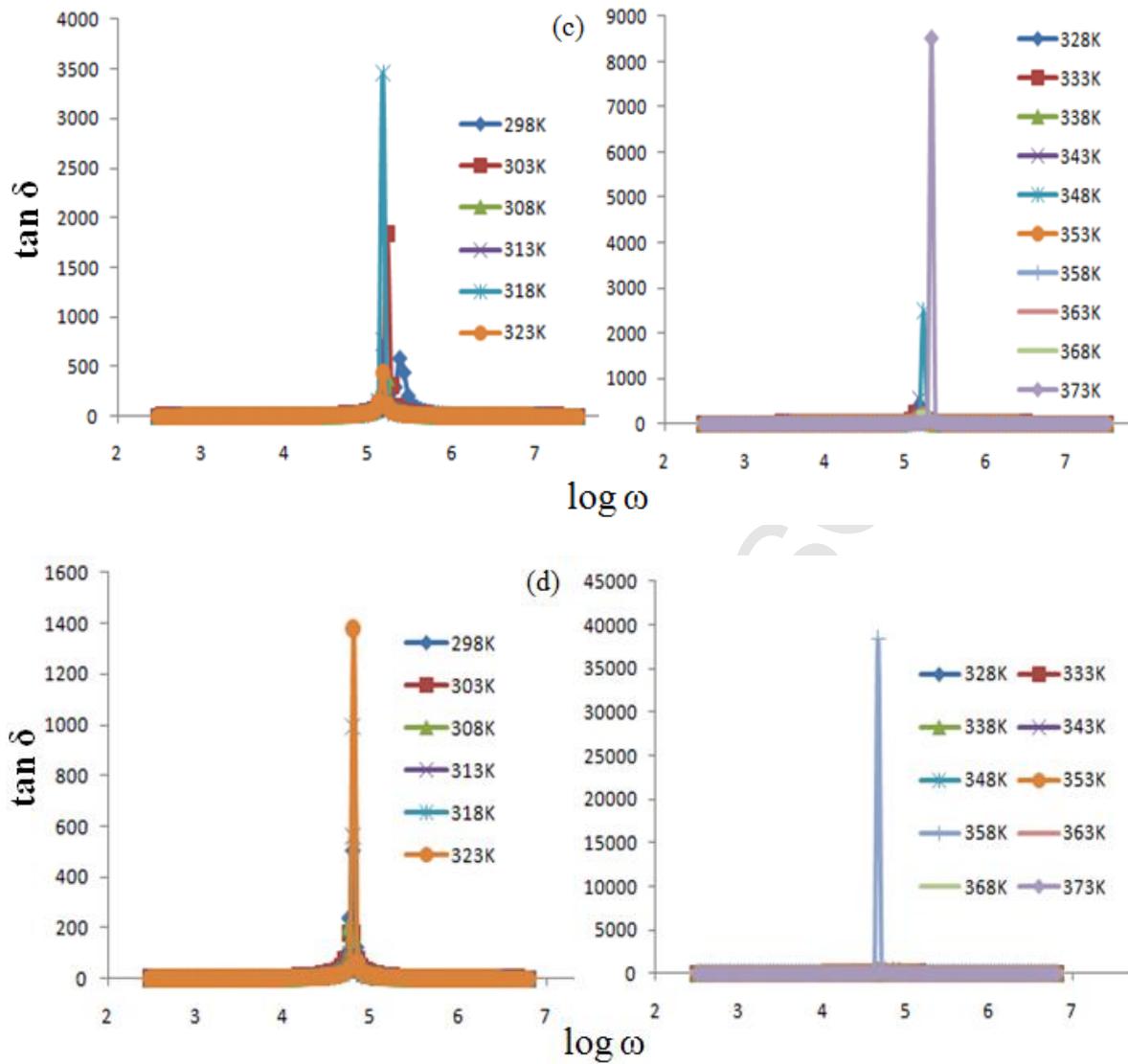


Fig. 7 Variations of loss tangent ($\tan \delta$) with frequency for (c) PEO+20wt%. LiPF₆+ 15 wt%. EC (d) PEO+20wt%. LiPF₆+15wt%. EC+5wt%. α -CNTs

Research Highlights.

- > The “dielectric” is typically used to describe materials with a high polarizability
- > The latter is expressed by a number called the dielectric constant
- > analyzed using the dielectric permittivity, loss tangent and electric modulus
- > dielectric permittivity rises towards low frequencies due to electrode polarization effects
- > maxima of loss tangent shifted and the height of the peak increases with increasing temperature.