This chapter deals with the different formalism obtained from impedance spectroscopy data viz., impedance, bulk conductivity, AC conductivity, dielectric, relaxation and modulus of samples at different temperatures.
5.1 Introduction

The impedance spectroscopic technique is employed to understand ion conduction mechanism. When we apply a DC bias to a sample, polarization at the electrodes, due to the failure of the mobile ions to traverse the electrolyte/electrode interface, is observed because ionic current drops to zero. This problem can be solved by using AC techniques, alternately, called as Impedance spectroscopy [1-7]. In AC impedance measurements, a small sinusoidal potential perturbation is applied to the sample [1], the response to the applied perturbation is, generally, different in phase and amplitude from the applied signal. Measurement of the phase difference and the impedance allows analysis of the electrode process relating to contributions from diffusion, kinetics, double layer capacitance and coupled homogeneous reactions, etc. The plot between real and imaginary part of impedance is called the Nyquist plot or the complex impedance plot [5]. It should be noticed that in the Nyquist plot of impedance spectroscopy data, each point corresponds to the impedance at one specific frequency; low frequency data are on the right-hand side, while those of higher frequencies are on the left-hand side of the plot.

Frequency dependence conductivity and dielectric studies are useful techniques to obtain the detailed information of ionic conduction mechanism in solid electrolytes [6]. Using dielectric relaxation study, the dynamic and relaxation behavior of the electric dipoles in the polymer matrix can be understood by studying the electrode polarization effect in the polymer electrolytes [8-10]. Conductivity relaxation refers to the time that is required to build up the charge carriers at the electrode electrolyte interface before the electric field changes its direction [8]. The resulting in a net cumulative moment will give
rise to a relaxation. The buildup of the charge carriers are known as polarization [9-12]. The polarization disappears when the voltage is removed [12].

Dielectric and modulus formalisms have their own advantage at particular circumstances. Among these principal quantities \((Z^*(\omega) \& \varepsilon^*(\omega))\) have a long history while the modulus \(M^*(\omega)\), was introduced relatively recently [13] and it seems to be useful in analysis of the electric response of the materials where the parasite capacitance effects, such as the electrode polarization, double layer formation etc. are occurring [14]. Relaxation processes occurring inside the ionic materials can be visualized and distinguished by impedance, electric modulus and dielectric permittivity. Variation of AC conductivity with temperature as well as compositions is presented and discussed. Dielectric and modulus studies were carried out and discussed to understand the relaxation phenomenon. The modulus study is used to discuss the distribution of relaxation times. The real, \(Z'\) and imaginary, \(Z''\) parts of complex impedance \(Z^*\) are directly measured from the instrument. The increase in ionic conductivity with temperature is due to ions receiving more thermal energy and because the number of defects in solids increases with temperature.

Ionic conductivity measures the ability of a charged particle (an ion) to move through the crystalline / amorphous structure of a material. Compounds and elements able to accept the movement of an ion through their structure are called electrolytes.

In the present study, electrical properties of prepared samples were carried out at different temperatures using the impedance spectroscopy in the frequency range of 10Hz to 1MHz. Complex impedance data can be drawn directly from the instrument.
5.2 Complex impedance plot and conductivity

The following given systems of polymer electrolytes were prepared to study the conduction mechanism in these polymer blend films using the method described in Chapter III:

**Series I:** \((PEO)_x(PMMA)_{100-x} - 5\text{ wt}\% \text{AgNO}_3\) [PPS]

where \(x\) is varied from 10-70 wt\% in steps of 10.

**Series II:** \(PPS\text{ system }+ x\text{ wt}\% \text{PEG}\) [PPSP]

where \(x\) is varied from 5-15 wt\%.

**Series III:** \(PPS\text{ System }+ x\text{ wt}\% \text{EC}\) [PPSE]

where \(x = 5, 7, 10, 12, 15\).

**Series IV:** \(PPSP\text{ System }+ x\text{ wt}\% \text{nano-filler} \text{Al}_2\text{O}_3\) [PPSPA]

where \(x\) is varied from 1-5 wt\% in steps of 1.

**Series V:** \(PPSE\text{ System }+ x\text{ wt}\% \text{nano-filler} \text{Al}_2\text{O}_3\) [PPSEA]

where \(x\) is varied from 1-5 wt\% in steps of 1.

To understand the effect of blending of semi-crystalline polymer PEO with amorphous and rigid polymer PMMA, the complex impedance data at different frequencies and temperatures is recorded. The impedance plots for different concentrations of PEO in PPS electrolyte films are obtained at different temperatures. Figs. 5.1 to 5.5 show the complex impedance plots for PPS-10, PPS-20, PPS-30, PPS-40, and PPS-70 samples. The impedance plots which show the semicircles for the PPS system at all temperatures indicate that the sample is partially resistive and capacitive in nature. The obtained impedance plots were fitted using Zview2 program. The intercept of
Fig. 5.1 Plot of $Z'$ vs. $Z''$ for PPS-10 polymer film at different temperatures.

Fig. 5.2 Plot of $Z'$ vs. $Z''$ for PPS-20 sample at different temperatures.

Fig. 5.3 Plot of $Z'$ vs. $Z''$ for PPS-30 sample at different temperatures.
Fig. 5.4 Plot of $Z'$ vs. $Z''$ for PPS-40 sample at different temperatures.

Fig. 5.5 Plot of $Z'$ vs. $Z''$ for PPS-70 sample at different temperatures.

Fig. 5.6 Fitted impedance plot (equivalent circuit-inset) for PPS-10 sample at 313 and 343K.
the fitted semicircle on the real axis (Z’ axis) is used to obtain the bulk resistance ($R_b$) of the sample [15]. The intercept of real axis shifts towards origin i.e., the bulk resistance of the sample decreases with increase of temperature in all the samples. The fitted impedance plots represent a series combination of two parallel lumped RC circuits. Fig.5.6 shows the fitted curve for PPS-10 polymer film and its inset shows its equivalent fitted circuit. The first semicircle arises due to the bulk resistance of the sample while the other semicircle ($R_2C_2$ couple) arises due to polarization of mobile $\text{Ag}^+$ ions at the electrode–electrolyte interface [15, 16]. The temperature dependence of the obtained impedance plots can be divided in two regions: region - I; below melting temperature $T_m$ of PEO, and, region - II-above $T_m$. Below $T_m$ (region I), a gradual decrease in the $R_b$ values and a sudden/large decrease of $R_b$ near $T_m$ is observed. In region II (above $T_m$), the decrease in $R_b$ value is quite substantial compared to below $T_m$. Similar behavior with different quantitatively values in other samples is observed. The impedance plot for various concentrations of PEO in polymer blend system (PPS-system) in Fig. 5.7 shows that the polymer films with 30 wt% and 50wt% demonstrate the lowest bulk resistance.
values compared to other samples.

To understand the variation of conductivity due to blending of PEO with PMMA, the plot of logarithmic of ionic conductivity versus reciprocal of temperature for various concentrations of PEO are shown in Fig.5.9. Two distinct regions of conductivity, one below $T_m$ and other one above $T_m$ are clearly seen. A sudden increase of slope in the curve near melting temperature $T_m$ has been reported by many a workers [17-19]. Beyond $T_m$, the rise in the conductivity with temperature is larger than that below $T_m$.

According to Druger et. al. [20, 21], the increase in conductivity with temperature in solid polymer electrolyte is due to segmental (i.e. polymer chain) motion and free volume of the system. This, in turn, results in the hopping of ions from one site to another and provides a pathway for ions to move. The segmental movement of the polymer facilitates the translational ionic motion, thus, increasing the charge carrier mobility. The matrix amorphosity supports the faster internal polymer chain movement in which bond rotations produce segmental motion to favor inter and intra-chain ion hopping, and thus
the degree of conductivity becomes high [22].

Below the transition temperature $T_m$, the rise in conductivity with temperature which is interpreted to be due to the hopping processes between coordination sites, local structural relaxations and segmental motion of the polymer chains, is observed to be very nominal. While above $T_m$, due to dominating amorphous regions in the polymer blend system, the polymer chains acquire faster internal modes in which bond rotations produce faster segmental motion resulting in the temperature assisted rise in the conductivity.

The conductivity isotherm for the first (PPS) system is plotted and shown in Fig. 5.9. Two conductivity maxima at PPS-30 and PPS-50 in 30 wt% and 50wt% of PEO in polymer blend electrolytes are observed in the conductivity isotherms. Also an enhancement in conductivity with increment in PEO concentration is observed. The observed enhancement in ionic conductivity might be occurring due to increased segmental motion and ionic mobility due to melting of PEO in the blend matrix. According to Straka et. al. [23], PEO crystalline regions are separated by amorphous layers of PEO and PMMA in PEO-PMMA polymer blend. The highest conductivity for PPS-50 polymer sample is obtained with a value of 9.42x10^{-9} S/cm at 328K. Occurrence of two conductivity maxima in ionic conductivity isotherms have been reported by several workers [24-28]. Singh et. al. [24] observed two maxima in conductivity plot in PEO-NH$_4$I-ZnS polymer electrolyte system due to two different percolation threshold for two mobile species i.e., cations and anions. While Chandra et. al. [25] have reported two maxima in conductivity isotherms in PEO-AgNO$_3$ polymer electrolytes, where first maxima is attributed to the amorphous phase of polymer complex and second maxima is probably due to the redissociation of non-conducting pairs. Several workers [26-28]
assigned the reason of two maxima in conductivity plot to percolation process in polymer electrolytes. According to Bunde et. al. [29], in a percolation process, percolating paths give rise to conductivities characteristic of metal salts in the polymer electrolytes. In the present case, the values of conductivity lie between the conductivity values of pure PEO and PMMA which suggests the optimization of the PPS-system with PEO: PMMA as 50:50 ratio of further study.

After, optimization of blend ratio in polymer complexes, the effect of plasticization using PEG and EC plasticizers in PEO-PMMA polymer blends has been undertaken. It is well known that a plasticizer is a low molecular weight polymer with high salt–solvating power, sufficient mobility of ionic conduction and reduction in crystalline nature of the polymer matrix as main features [30, 31]. Plasticizers are additives that increase the fluidity of the host material in which these are added. It is to be noted here that the addition of plasticizer does not supply ions to the system; but instead it dissolves enough charge carriers and provides a more mobile medium for the ions. Thus, plasticizer contributes to conductivity enhancement by opening up narrow rivulets of plasticizer-rich phases for ionic transport. In general, the addition of plasticizer enhances the conductivity of polymer electrolytes (i) by increasing the amorphousity of polymer electrolytes; (ii) by dissociation of ion aggregates and (iii) lowers the glass transition temperature $T_g$ of the polymer electrolyte system [32]. Plasticization of polymer, on one hand, generally enhances the electrical properties however; on the other hand, it may lead to decrease in mechanical, thermal, electrical and electrochemical stabilities.

Small working voltage range, narrow electrochemical window, high vapor
Fig. 5.10 Impedance plot for PPSP-I0 polymer film.

Fig. 5.11 Impedance plot for PPSP-I2 polymer film.

Fig. 5.12 Impedance plot for PPSP-I5 polymer film.
pressure and poor interfacial stability with electrodes are the disadvantages of plasticized–gel polymer electrolytes [33, 34]. The impedance plots at various temperatures for PEO-PMMA-AgNO₃-PEG polymer electrolytes i.e.; PPSP system are obtained (Fig.5.10 to Fig. 5.12) and equivalent-circuit fitted (Fig. 5.13). The impedance plots in this PPSP-system are depressed semicircles which is a general feature occur in solid electrolytes. The obtained depressed semicircles indicate distribution of relaxation times [16]. With the rise of temperature, the radius of the semicircle reduces. This implies a reduction in bulk resistance values with increase in temperature. A sharp decrease in bulk resistance value near the 333K is observed which is attributed to the melting of crystalline PEO in polymer complex. Fig. 5.14 shows the impedance plot of PPSP-system for different PEG concentrations. The impedance plots do not show any systematic change with PEG concentration, though the bulk resistance value for the polymer film with PEG-5 wt% is found to be lowest.

\[ Z''(\Omega) \]
\[ Z'(\Omega) \]
\[ C_1 \]
\[ C_2 \]
\[ R_s \]
\[ R_1 \]
\[ R_2 \]

**Fig. 5.13** Equivalent-circuit fitting of impedance plot for PPSP-12 sample at 313 and 343 K.

The conductivity isotherms as a function of PEG concentration (PPSP system) are presented in Fig.5.15. In PEO-PMMA-AgNO₃-PEG polymer matrix (PPSP-system), polyethylene glycol (PEG) has been varied from 5 to 15wt%. PEG is supposed to be a
soft PEO polymer with similar structure as PEO and having low molecular weight with lower dielectric constant. In PEO-PMMA-PEG polymer blend system, due to similar structure of PEO and PEG which promoted the organization of segmental units [35]. The decrease in the conductivity due to the addition of PEG in the polymer blend

![Impedance plot of PPSP (second) system.](image)

**Fig.5.14** Impedance plot of PPSP (second) system.

![Variation of ionic conductivity with PEG concentration.](image)

**Fig.5.15** Variation of ionic conductivity with PEG concentration.

![Logarithmic of ionic conductivity vs. 1000/T plot.](image)

**Fig.5.16** Logarithmic of ionic conductivity vs. 1000/T plot.

...system could be ascribed to the dielectric constant of the plasticizer, which played an important role in the modification of the conductivity of the polymer electrolytes. The differences of dielectric constant can cause the possibility of chemical interaction; thus, the chemical bonds and linkages in the polymer complex were expected to be affected by the addition of the PEG plasticizer.

The dielectric constant of PEG is smaller than that of PEO. The low dielectric
constant of PEG arises from the high ratio of alkyl segments and a strong crystallization correlated with the high organization and rigidity of segmental units in PEO. After PEG-5wt% concentration in PEO-PMMA polymer blends, the crystalline phase of the polymer blend increases and is supported by IR studies (In Chapter 4). Kumar and Sekhon [36] have suggested that polymer-polymer and/or polymer-plasticizer interactions depend on the molecular weight of plasticizer and polymer. The higher value of the dielectric constant of plasticizer helps in the dissociation of salt and ion aggregates. The ionic conductivity behavior of PEO-AgCF$_3$SO$_3$-PEG-SiO$_2$ system (plasticized polymer system) is reported to depend on the structure, molecular weight, viscosity and dielectric constant of plasticizer, polymer–plasticizer interaction, and ion–plasticizer coordination [35]. In general, charge carriers (Ag$^+$-ions) migrate through less viscous system due to plasticization effect which enhances the mobility of ions. Also, plasticizer occupies inter chains and intra-chains free volume by disrupting polymer-polymer interactions. In the present case, the used polymers are of approximately same molecular weights and the plasticizer PEG possesses a low dielectric constant than as that of PEO or PMMA.

The increase in degree of crystallinity beyond 5 wt% of PEG electrolyte films are in agreement with the results obtained from the increased value of $T_m$ from DSC and higher intensive peaks observed in FTIR.

To investigate the temperature dependence of conduction mechanism in PPSP-system, the conductivity measured from impedance plot is shown in Fig.5.16. A sudden increase/transition in the conductivity near $T_m$ is the main feature of the conductivity plots in this system. The non-linear nature of temperature dependent conductivity is generally observed for PEO based systems [37-39]. The observed rise in conductivity with
temperature can be explained on the basis of free volume model [40, 41] which explains that the coordination sites come closer due to increase in temperature enabling the ions to hop from the occupied site to the unoccupied site requiring lesser energy. Amplitude of vibration of the polymer backbone and side chains also supports in increase of the fraction of free volume in the polymer electrolytes. This facilitates ionic translational motion and/or hopping by the dynamical segmental motion of the polymer. And liquid like phase of PEO in PEO-PMMA polymer matrix due to melting near \( T_m \) increases larger segmental motion of polymer chains.

Further, the plasticization using ethylene carbonate (EC) plasticizer has been done in PEO-PMMA-AgNO\(_3\) system. The impedance plots of polymer electrolyte films plasticized with various concentrations of EC are obtained. Figs.5.17- 5.19 show the impedance plots PPSE-5, PPSE-7 and PPSE-15 at different temperatures and Fig.5.20 depicts equivalent-circuit (inset of Fig) fitted impedance curve for PPSE-15 polymer film at 313 and 323K. These curves show depressed semicircular arcs followed by a spur at low frequencies. The spur indicates the presence of the interfacial polarization. It can be observed that the size of the arcs reduces with temperature which implies that the bulk resistance decreases with increase of temperature. Fig.5.21 depicts the impedance plot obtained for different EC concentrations at 323K which shows that the bulk resistance value increases with the increase in EC concentration up to 10wt\% and after that a decrease in bulk resistance is observed.

The ionic conductivity plot for the PPSE system i.e., PEO-PMMA-AgNO\(_3\) system with varying amount of EC is given in Fig.5.22. It is observed from figure that conductivity initially drops at 7wt\% and thereafter it increases non-linearly with addition
Fig. 5.17  $Z'$ vs. $Z''$ plot for PPSE-5 polymer film.

Fig. 5.18  $Z'$ vs. $Z''$ plot for PPSE-7 polymer film.

Fig. 5.19  $Z'$ vs. $Z''$ plot for PPSE-15 polymer film.
Fig. 5.20 Equivalent-circuit fitting for PPSE-15 sample at 313 and 343 K.

Fig. 5.21 $Z'$ vs. $Z''$ plot for all samples of PPSE series and 323K.

Fig. 5.22 Compositional variation of ionic conductivity PPSE system.

Fig. 5.23 Temperature dependence of ionic conductivity.
of EC. The lowest conductivity in EC-7wt% is due to the increased degree of crystallinity as supported by its XRD and DSC studies. Generally, the plasticizer concentration in polymer complexes reduces the inter-ion Coulomb interactions and dissociates more salt content to make more number of cations available for conduction [36]. The addition of plasticizer has been found to lower the melting temperature, $T_m$ as well as increases the amorphous level of polymer blend system.

H.J. Rhoo et. al.[42] argued the opening of the narrow rivulets of plasticizer-rich phase and large free volume for higher conductivity. The increase in conductivity after 7 wt% of EC for PPSE-system may be ascribed to the dissociation of more salt supporting the enhancement in conductivity. Huang et. al.[43] described the presence of plasticizer as a lubricant in a polymer which makes the ions more mobile within the polymer system. Fig.5.23 shows the temperature dependence of ionic conductivity for PPSE system. The ionic conductivity of plasticized polymer with EC in blend complex increases with the temperature. Figure shows a sudden and/or sharp rise in conductivity near $T_m$ which is ascribed due to the softening of PEO polymer near $T_m$ in the polymer complexes and has been reported by several workers [17-19, 37-39]. For comparison, the variation of conductivity for both the plasticizers PEG and EC is shown in Fig.5.24 at

![Variation of ionic conductivity for plasticizer concentration in PEO-PMMA polymer blends system.](image)
**Fig. 5.25** Impedance plot for PPSPA-1 polymer electrolyte film.

**Fig. 5.26** Impedance plot for PPSPA-2 polymer electrolyte film.

**Fig. 5.27** Impedance plot for PPSPA-3 polymer electrolyte film.
Fig. 5.28  Impedance plot for PPSPA-4 polymer electrolyte film.

Fig. 5.29  Equivalent-circuit fitting of impedance plot for PPSPA-4 sample at 313 (left) and 343 K (right).

Fig. 5.30  Impedance plot for all PPSPA samples at 323K.
323K. The conductivity is nearly same at 5 wt% of both plasticizers. The minimum conductivity is observed at 7 wt% in EC system whereas at 10wt% for PEG. An increase in conductivity beyond minima is observed only in EC based electrolyte system.

The variation of conductivity with nano-filler concentration is an important feature in polymer composites. The presence of nano-filler is expected to favor additional transient sites for ion migration and also to promote amorphous phase in polymer that allows polymer chains to be more dynamic, thus providing favorable conducting pathways for charge carriers [44]. The effect of dispersion of nano-filler in the highest conducting plasticized polymer films is undertaken. The amount of nano-filler from 1 to 5wt% is varied in PPSP and PPSE systems.

The impedance plots of the polymer nano-composites plasticized with PEG (i.e.; PPSPA- polymer electrolyte system) with the nano-filler (Al$_2$O$_3$) concentration are obtained and analyzed at different temperatures. Impedance plots of plasticized polymer electrolyte films with Al$_2$O$_3$-from 1wt% to 4wt% nano-filler concentration are shown in Figs.5.25-5.28 and fitted impedance plot is shown in Fig. 5.29. Impedance spectra in these polymer nano-composites show two semicircles namely; one at high frequency and other at low frequency region. As temperature approaches $T_m$, the impedance spectra shows only single semicircle and the intercept of real axis shifts towards origin, i.e.; bulk resistance value decreases in solid electrolytes. Impedance plot obtained for different amount of nano fillers at 323K is shown in Fig. 5.30. The bulk resistance decreases with the nano-filler concentration in the system as is evident from the shifting of the intercept towards origin. However, polymer electrolyte film with 5 wt% of Al$_2$O$_3$ shows a reverse effect.
Fig. 5.31 represents the variation of ionic conductivity with nano-filler concentration in this PPSPA system at 323K. The ionic conductivity increases with the addition of nano-filler Al₂O₃ up to 4 wt%. The addition of nano-filler in the polymer system increases the flexibility with an enhanced level of amorphousity (observed from XRD and DSC studies). Ekanayake et al. [45] and others [46-48] reported the increased ionic conductivity due to creation of more conducting pathways for the migration of ions with the addition of nano-fillers. Johan et al. [49] reasoned the enhancement in conductivity due to increase in the amorphous phase with CuO nano-filler. Wieczorek et al. [46] suggested that migrating ionic species interact with O-OH surface groups on alumina grains of nano filler which provide transient hopping sites and conducting pathways for migrating ions.

In the present system, however, the favorable high conducting pathways for silver ions, created by alumina nano-filler grains, may be responsible for rise in ionic conductivity. The retarding effect in conductivity after 4wt% of Al₂O₃ nano-filler is attributed to the conglomeration of excessive nano-filler reaching a threshold which makes the long polymer chains immobilized leading to a decrease in the conducting pathways. This maximum shows the balance between the opposing forces: increase in free volume as well as chain flexibility and decreasing polymer segmental mobility. The results from characterization are also in good agreement with the results which support the drop in conductivity at 5 wt%. Temperature dependence of ionic conductivity for PPSPA-system is shown in Fig. 5.32. Figure shows the variation of the logarithm of ionic conductivity with inverse absolute temperature for various concentrations of nano-fillers. Similar to earlier-systems, this system shows two regions in temperature dependent
conductivity. It is observed that within the investigated temperature range, ionic conductivity increases with increasing temperature as suggested by free volume theory [20]. With the increase in temperature, the polymer matrix can expand easily and produce free volume in which ions, solvated molecules or polymer segments can move. This enhances the motion of Ag⁺-ion as well as polymer segmental mobility resulting in increase in ionic conductivity. The sudden rise in conductivity is attributed to the melting of PEO in host PEO-PMMA polymer matrix.

![Graph](image)

**Fig.5.31** Variation of ionic conductivity with nano-filler (Al₂O₃) concentration in PPSPA system at 323K.

**Fig.5.32** Temperature dependent variation of ionic conductivity

To understand the effect of nano-filler concentration in polymer blend system plasticized with EC, the impedance plots of polymer electrolyte with different concentration of nano-filler Al₂O₃ in PPSE-system at different temperatures is studied. Impedance spectra of PPSEA-2, PPSEA-4 and PPSEA-5 polymer electrolyte films at different temperatures are shown in Figs. 5.33-5.35, respectively and Fig. 5.36 shows the equivalent-circuit fitted curves for PPSEA-2. Impedance plots show the presence of two semicircles and as temperature approaches $T_m$ of PEO, the second semicircle at lower frequencies gradually disappears and the bulk resistance decreases with increase of temperature with a transition near the melting temperature of PEO as observed in other
Fig. 5.33 Impedance plot for PPSEA-2 sample.

Fig. 5.34 Impedance plot for PPSEA-4 sample.

Fig. 5.35 Impedance plot for PPSEA-5 sample.
systems also. Fig.5.37 depicts the impedance plot for different nano filler amounts obtained at 323K. The bulk resistance value decreases up to 4wt% of nano-filler concentration. However, in the polymer film with 5 wt% Al₂O₃, the $R_b$ value increases.

![Equivalent-circuit fitting for PPSEA-2 polymer film at 313 and 343 K.](image1)

Fig. 5.36  Equivalent-circuit fitting for PPSEA-2 polymer film at 313 and 343 K.

![Compositional impedance plot for PPSEA series (fifth series).](image2)

Fig. 5.37  Compositional impedance plot for PPSEA series (fifth series).

In general, the ionic conductivity increases as the degree of crystallinity decreases. The increase in ionic conductivity with nano-filler concentration is an indication of enrichment of amorphous phase as discussed above. The ionic conductivity in this system is shown in Fig.5.38. This system shows an enhancement in ionic conductivity with nano-filler concentration up to 4wt% and further addition in nano-filler
concentration results a drop in conductivity as was seen in PEG based system. The observed fall in conductivity at 5wt% of Al$_2$O$_3$ concentration is attributed to the conglomeration of nano-filler which make the long polymer chains more immobilized obstructing the migration of ions and provide a threshold value for the present system. A recent work by M.R. Johan et. al. [52] has also reported the drop in conductivity due to the aggregation of nano-filler in the polymer. Within investigated temperature range, the enhancement in ionic conductivity with temperature shows two regions as observed in other studied systems. Polymer matrix can expand easily and produce free volume due to rise in temperature [53].

![Fig. 5.38 Compositional variation of ionic conductivity with nano-filler.](image1)

![Fig. 5.39 Temperature wise variation of ionic conductivity.](image2)

Fig.5.39 depicts the temperature dependent ionic conductivity for PPSEA-system. The conductivity of PEG and EC based nano-composites can be summarized in Fig.5.40. The conductivity of EC based plasticized polymer electrolyte system is higher (nearly more than one order of magnitude) than the conductivity of PEG based polymer nano-composite system below melting temperature $T_m$ and 2 to 3 order higher for EC based
system above $T_m$.

![Graph showing conductivity as a function of nano-filler concentration for PPSPA and PPSEA systems at 323K.](image)

**Fig. 5.40** Conductivity as a function of nano-filler concentration for PPSPA and PPSEA systems at 323K.

### 5.3 Frequency dependent conductivity

The blending effect of PEO concentration with respect to PMMA in PEO-PMMA polymer blends in terms of frequency dependence of conductivity (or AC conductivity) at different temperatures is studied. Frequency dependent conductivity in the investigated temperature range shows two different features region-I and II (i.e.; below and above $T_m$) in conductivity spectra in polymer blend electrolytes (Figs. 5.41 (a)-(d)). In region-I i.e., below $T_m$, the AC conductivity shows two dispersion frequencies: one at low frequencies and other at higher frequencies. In this region, with the rise in temperature, the observed low frequency dispersion gradually shifts towards high frequency side while the high frequency dispersion does not shift markedly with the increment in temperature. As temperature approaches near $T_m$, low frequency dispersion starts disappearing and a systematic shift of the dispersion frequency towards high frequency is observed in high frequency dispersion. The frequency dependence of conductivity is a sum of conductivity due to movement of free charges and polarization conductivity due to movement of bound charges ($\sigma^* = \sigma_{\text{polarisation}} + \sigma_{\text{ion}}$) [54]. The conductivity value at low frequencies is
related to the accumulation of ions due to the slow periodic reversal of the electric field. In high frequency region, the conductivity sharply increases with frequency. The variation of conductivity with frequency in high frequency region is expressed by the well known power law of ac behavior \([16, 54, -57]\) given by the following equation,

\[
\sigma(\omega) = \sigma_0 + A\omega^n \quad \text{...(5.1)}
\]

where \(\sigma(\omega)\) is the conductivity at a particular frequency, \(\sigma_0\) is the conductivity at low frequencies, \(A\) is a constant and \(n\) is the frequency exponent. The curves of best fits to Jonscher’s Power law are shown in Fig. 5.42. The above expression is known as the power law of ac behavior. Because the power law of ac behavior is observed in wide range of materials, Jonscher called it “Universal Behavior” \([9, 55, 56]\). The frequency exponent \(n\) was calculated from the slope of the plot \(\log(\sigma' - \sigma_0)\) versus \(\log \omega\) (straight
line curve) and is a measure of degree of interaction with the environment. The exponent \( n \) values, in the range \( n < 1 \), indicates a preference on the part of ions that have hopped away to the site from where they started. It is documented that \( n \) can also hold values larger than one. Papathanassiou et.al. [58] suggested that there is no physical argument to restrict the value of \( n \) below one. Many researchers [59-61] have reported that \( n \) can have values \( 0 < n < 2 \). The values of \( n \sim 0.5 - 1 \) cover either ion conduction by translation motion or by displacive movement of caged ions while \( n \geq 1 \) values may be attributed to other ion movements such as vibrational etc. The calculated values of \( n \) from eq. 5.1 for PPS-System at different temperatures are tabulated in Table.5.1. In the present case, the values of \( n \) are found to be greater than one.

![Graphs showing fitting of conductivity spectra at different temperatures](image)

**Fig. 5.42** Fitting of conductivity spectra at different temperatures (the continuous lines are best fits to Jonscher’s Power law.)
All the samples show only 1-2 orders of magnitude rise in conductivity from region I to region II except for the samples with PEO- 30 and 50wt% possessing the highest conductivity, which have demonstrated the rise in conductivity of 3 and 5 orders of magnitude respectively.

The observed frequency dependence of conductivity below $T_m$ is due to presence of semi-crystalline as well as due to the amorphous regions [62] present in PEO-PMMA host polymer matrix. As temperature approaches near $T_m$, the semi-crystalline region of PEO melts and the amorphous region preponderates in the PMMA matrix. Above $T_m$, i.e.; in region II, the melted PEO penetrates in the PMMA polymer matrix, making the overall polymer system, a gel-like system in which polymer chains acquire faster internal movement and segmental motion dominates, giving only a single dispersion in high frequency region.

![Conductivity spectra for all the samples of PPS system at 333K.](image)

**Fig. 5.43** Conductivity spectra for all the samples of PPS system at 333K.

Such frequency dependent conductivity features are observed in all the polymer blend samples. The observed rise in conductivity with temperature can be explained on the basis of free volume theory [20] in which the system acquires more free space.
allowing, in turn, easy ion transport. Low frequencies variation of conductivity is due to accumulation of charges at the electrode-electrolyte interfaces producing polarization effects [63]. The conductivity is almost independent of frequency in low frequency region. As frequency increases, the conductivity increases continuously because charge carriers get enough excitation energy from the electrical signal. At high frequencies, mobility of charge carriers, Ag⁺-ions is high, the relaxation times decreases and hence conductivity rises. Frequency dependent conductivity spectra for all blended polymer electrolyte films of PPS-system at a 323K are shown in Fig.5.43.

It is clear that the ac conductivity \( \sigma_{ac}(\omega) \) for all the samples exhibit the same characteristics of the curve with increasing conductivity values with different PEO: PMMA ratios. PPS-50 composition, the highest conducting sample, is selected to investigate the effect of plasticizers PEG and EC in the blend.

Frequency dependence of conductivity at different temperatures for PEG system is studied. AC conductivity spectra for PPSP-12 and PPSP-15 samples are shown in Figs.5.44 (a) & (b), respectively. Temperature dependence of AC conductivity of polymer blends plasticized with PEG shows a frequency independent region at low frequencies below \( T_m \). The transition from the slow change in conductivity to its abrupt increase in conductivity signifies the onset of conductivity relaxation due to dipolar motions caused by the segmental and normal-mode dynamics of the polymer host.

The conductivity value at low frequencies is related to the accumulation of ions due to the slow periodic reversal of the electric field and the ions travel much slower at lower frequency enabling ion to jump from one site to another vacant sites. With the rise in temperature, the dispersion region at low frequency below \( T_m \) gradually starts
Fig. 5.44  Conductivity spectra at different temperatures for (a) PPSP-12 and (b) PPSP-15 samples of second series.

Fig. 5.45 Fitting of conductivity spectra for PPSP-12 and PPSP-15 polymer films at different temperatures (the continuous lines are best fits to Jonscher’s Power law.

Fig. 5.46 Conductivity spectra all samples of PPSP system at 323 K.

Fig. 5.47 Conductivity spectra for all samples of PPSE-system at 323 K.
Conductivity spectra for (a) PPSE-5, (b) PPSE-10, (c) PPSE-12 and (d) PPSE-15 polymer electrolyte films at different temperatures.

disappearing and dispersion at high frequency region shifts to higher frequency side. The curves of fitting of conductivity to Jonscher’s Power law at high frequency for PPSP-12 and PPSP-15 samples are shown in Fig. 5.45. Here again, within the investigated temperature range, the ac conductivity is observed to increase more than two orders of magnitude in all samples while the highest conducting polymer sample (PEG 5wt %) shows rise of four orders of magnitude. AC conductivity spectra with PEG concentration at 323K is shown in Fig.5.46. The sample with 5 wt% PEG depicts the highest conductivity at all frequencies.

The variation of AC conductivity with different concentrations of EC plasticizer at 323K is depicted in Fig.5.47. AC conductivity values are higher in the polymer films
with EC-5wt% and 15 wt%. Figs. 5.48 (a)-(d) represents the temperature dependence of AC conductivity spectra of different EC polymer films and Figs. 5.49 (a)-(d) show the Jonscher’s Power law fitted curves. AC conductivity shows two dispersion regions; one in low frequency region and other in high frequency region. Dispersion in low frequency region starts disappearing near to melting temperature and only high frequency dispersion is seen in all samples. In the high frequency region, mobility of charge carriers is high near to relaxation times and hence, conductivity increases with frequency. The system with EC shows an enhancement in conductivity of nearly four orders of magnitude for highest conducting samples.

Fig. 5.49 JPL fitting of conductivity spectra for (a) PPSE-5, (b) PPSE-7, (c) PPSE-12 and (d) PPSE-15 polymer films at different temperatures.
AC conductivity spectra of polymer nano-composite films plasticized with PEG (PPSPA systems) at different temperatures is studied and for PPSPA-1 and PPSPA-2 polymer films are represented in Figs.5.50 (a) & (b). The AC conductivity spectra for polymer electrolyte films show two regions below and above $T_m$. In all spectra, a frequency independent region at low frequency followed by two distinguishable dispersion regions in high frequency is observed. The observed frequency independent conductivity in low frequency region is attributed to electrode polarization which masks the ionic conduction of the bulk material. At higher frequencies, the mobility of charge carrier is high. AC conductivity increases with temperature and the relaxation frequency also shifts towards high frequency side. The observed frequency dispersion spectra are
fitted using Jonscher’s Power Law and fitted curves are shown in Figs.5.51 (a) & (b). The calculated values of power exponent \( n \) are tabulated in Table 5.1.

Fig. 5.52 Conductivity spectra for all samples of PPSPA-system at 323K.

Fig. 5.53 Conductivity spectra for PPSEA-system (fifth series) at 323K.

In nano-composite polymers with plasticizer, the increase in conductivity with temperature is discussed (Section 5.2) on the basis of free volume theory which favors the volume expansion with the rise in temperature. Near \( T_m \), a sudden rise in ac conductivity is attributed to increase in mobility of Ag\(^+\) ions due to formation of additional amorphous regions. Conductivity enhancement in this system is of nearly three orders of magnitude within investigated temperature range. It is noticed that different concentration of nano-fillers in the present studies show similar trend with different values, however dominance of the double dispersion decreases with nano-filler concentration with a reverse effect at PPSPA-5 polymer film. Compositional variation of AC conductivity for the samples of PPSPA-system at 323K is given in Fig.5.52.

AC conductivity spectra for different compositions of Al\(_2\)O\(_3\) nano-filler in PEO-PMMA -AgNO\(_3\)-EC polymer electrolyte (PPSEA-system in fifth series) at 323K is represented in Fig 5.53. The values of conductivity increase with nano-filler
concentration as observed in ionic conductivity results. The lower frequency dispersion seems to disappear at a temperature which gradually decreases with the addition of Al₂O₃, indicating some structural change in the electrolyte samples. Figs. 5.54 (a) & (b) and Figs. 5.55 (a) & (b) show the frequency dependent (AC) conductivity behavior for PPSEA-1 and PPSEA-4 samples and their respective JPL fitted conductivity spectrum respectively. Double dispersions are observed in \( T<T_m \) temperature range in the ac conductivity spectra. With the increase in temperature, the dispersion frequency shifts towards high frequency side.
Table 5.1 Frequency exponent ‘n’ values for PPS, PPSP, PPSE, PPSPA and PPSEA systems at 323K.

<table>
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<tr>
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5.4 Dielectric studies

Dielectric materials are understood as the materials in which electrostatic fields can persist for a long time. These materials offer a very high resistance to the passage of electric current under the action of the applied direct-current voltage. Materials are characterized by their dielectric response of either the bound or free charge. Generally, dielectric means insulator which has no free charge but produce change in electric field. Dielectrics are a class of materials that are poor conductors of electricity, in contrast to materials such as metals that are generally good electrical conductors [65].

In a dielectric substance, an electric field gives rise to no net flow of electric
charge because electrons are tightly held by individual atoms. However, when electric field is applied, nuclei are attracted to one side and the electron cloud to the other side. This process of alignment of dipoles is known as polarization. In addition to these dipoles, there may also be permanent dipoles in the crystal. The alignment of these dipoles may not give a zero dipole moment or a net dipole moment. The net dipole moment leads to certain characteristic properties to solids.

The dielectric constant is a measure of the influence of electric field on the capacitance of a condenser due to a particular dielectric material. It measures how well a material separates the plates in a capacitor and is defined as the ratio of the capacitance of a set of electrodes with the dielectric material between them to the capacitance of the same electrodes with vacuum between them.

Complex dielectric function, \( \varepsilon^* \) of the materials dependent on frequency is given by \( \varepsilon^* = \varepsilon' - i\varepsilon'' \). \( \varepsilon^* \) reflects the molecular relaxation and transport processes of the material [8, 66, 67]. The real part of dielectric permittivity, \( \varepsilon' \) has same significance as that of ordinary dielectric constant i.e.; it measures the elastically stored energy in the material during each cycle of applied alternating field and the energy returned to the field at the end of each cycle. The higher the value of \( \varepsilon' \), the better is the electrical conductivity. When an electrical field is applied to a material, the dipoles in the material show the tendency to orient them in the direction of the applied field [67]. However, the mobilization of the dipole depends on the ductility of the materials. The imaginary part of dielectric permittivity, \( \varepsilon'' \) corresponds to the dielectric loss factor due to the conduction of ionic species in the material when an electrical field applied. At higher temperatures, dipoles can orient easily whereas a highly cross-linked material finds difficulty in
orientation. The delayed response to a stimulus in a system is the called relaxation. The orientation involves a characteristic time called relaxation time $\tau$ [68].

The dielectric loss of a system can be explained as the ratio of the energy dissipated per radian in the material to the energy stored at the peak of polarization. This parameter is usually described by the so called loss tangent, $\tan \delta$ and is defined as [69]

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'}.$$ 

Frequency dependent dielectric behavior of prepared polymer electrolytes systems is investigated. In an ion conducting system, the dielectric constant has contribution from dipoles as well as from mobile ions to the relative permittivity of the materials. To study the dielectric properties of prepared blended, plasticized and nano-filled polymer electrolyte films, frequency dependent real and imaginary parts of dielectric permittivity are calculated and analyzed at different temperatures using formulas given in Chapter 3. At first the polymer blended system with various ratios of PEO to PMMA at different temperatures are studied. For this, real ($\varepsilon'$) and imaginary ($\varepsilon''$) parts of permittivity as function of frequency at different temperatures are plotted. Figs 5.56 (a)-(c) and 5.56 (d)-(f) show the variation of $\varepsilon'$ and $\varepsilon''$ for PPS-10, PPS-50 and PPS-70 polymer electrolyte films, respectively. Observing the data of dielectric properties, it is clear that dielectric constant decreases with increase of frequency and saturates at higher frequencies [71]. Both dielectric constant and dielectric loss rise sharply at low frequencies and this behavior have been attributed to the occurrence of electrode polarization and space charge effects [70-72]. The presence of this polarization effect indicates the non-Debye type of behavior and the periodic reversal of the electric field at high frequencies does not allow any excess ion diffusion in the direction of the field leading to decrease in
polarization resulting in a drop in dielectric constant and dielectric loss. The degree of salt dissociation of ion aggregates increases with temperature resulting in the increase in number of free ions or charge carrier density. The frequency of dispersion in the dielectric permittivity shifts towards higher frequency side implying the faster relaxation of polymer chain segments. This introduces flexibility in the polymer chain segment and

![Diagram of dielectric constant and loss factor vs. frequency for different temperatures](image)

**Fig. 5.56** Frequency dependent $\varepsilon'$ plots for (a) PPS-10, (b) PPS-50 and (c) PPS-70 and $\varepsilon''$ plots for (d) PPS-10, (e) PPS-50 and (f) PPS-70 samples at different temperatures.
Fig. 5.57 Frequency dependent logarithmic $\varepsilon'$ plots for (a) PPS-10, (b) PPS-50 and (c) PPS-70 and $\varepsilon''$ plots for (d) PPS-10, (e) PPS-50 and (f) PPS-70 samples at different temperatures. thereby its mobility. In logarithmic scale, dielectric constant steadily decreases with increasing frequency and becomes almost constant at higher frequencies (Figs. 5.57 (a)-(c)). Imaginary part of dielectric permittivity show higher values at low frequencies which is due to the free charge motion in the electrolyte material [8] and is observed to
Temperature dependence of permittivity and imaginary part of dielectric permittivity are seen in Figs 5.58(a)-(c) and 5.58(d)-(f) for PPS-10, PPS-50 and PPS-70 polymer electrolyte films, respectively. However, real ($\varepsilon'$) and imaginary ($\varepsilon''$) part of
permittivity values show a sudden rise near the melting temperature of PEO as observed in conductivity spectra in section 5.2. Saroj et. al [73] suggested that with increase in temperature, the crystalline phase in semi-crystalline polymeric materials dissolves progressively into amorphous phase. This behavior influences the polymer dynamics and thus the dielectric properties increase.

The variation of loss tangent with frequency for PPS-10 polymer film, shown in Fig. 5.59(a), decreases with increasing frequency and becomes constant at higher frequencies because ion migration mitigates at high frequency and a decrease in dielectric loss is observed. The loss increases with increase in temperature [73]. This high value of dielectric loss is due to the contribution of ion jump and dc conduction loss of ions in addition to the polarization loss. Similar behavior is observed in other samples. Fig. 5.59(b) shows the tan δ plot for different amount of PEO concentration in PPS-system. The figure clearly depicts that losses increase with PEO concentration and maximum for highest conducting samples i.e.; PPS-30 and PPS-50.

Both the values of the permittivity show a strong dispersion in frequency at the temperature above melting point. This type of dispersion in $\varepsilon'$ may be regarded as
Fig. 5.60  (a) $\varepsilon'$ and (b) $\varepsilon''$ plots for PPS-System at 353K and insets show the complete spectra.

relaxation behavior concerned with the high mobility of Ag$^+$-ions under the force of an external electric field. This increase in dielectric permittivity with temperature is ascribed due to the formation of molecular dipoles. These dipoles remain frozen when the temperature is low. At the melting temperature of PEO, the dipoles having more rotational freedom become more thermally activated. Such temperature dependence of dielectric permittivity has been reported in other solid electrolytes [8, 39].

Fig. 5.61  Variation of real part of permittivity for PPS-System at different frequencies.

Figs. 5.60(a) & (b) show the compositional variation of $\varepsilon'$ and $\varepsilon''$ for PEO blended with PMMA polymer complexes as a function of frequency at 353K. The dielectric constant values are found to increase with PEO concentration (in both $\varepsilon'$ and
$\varepsilon''$ spectra) and found to be highest for PPS-50 polymer electrolyte sample. Compositional variation of dielectric constant at different frequencies, depicted in Fig.5.61, also indicates that dielectric permittivity increases with PEO concentration and shows two maxima at PPS-30 and PPS-50 similar to the conductivity isotherm of PPS-system.

![Frequency dependent $\varepsilon'$ plots for (a) PPSP-10 and (b) PPSP-12 and $\varepsilon''$ plots for (c) PPSP-10 and (d) PPSP-12 samples at different temperatures.](image)

When plasticization is carried out in PEO-PMMA-AgNO$_3$ polymer electrolyte with PEG and EC, the system shows similar frequency dependent behavior of real and imaginary permittivity as observed in pure blended samples at different temperatures. Both the real and imaginary part of dielectric permittivity rise sharply near low frequencies indicating that electrode polarization and space charge effects are still there and confirm its non-Debye dependence (Figs.5.62 & 5.63). Plasticizer PEG having
Fig. 5.63 Frequency dependent logarithmic $\varepsilon'$ and $\varepsilon''$ plots for PPSP-10 ((a) & (b)) respectively at different temperatures.

Fig. 5.64 Temperature dependent $\varepsilon'$ and $\varepsilon''$ plots for (a & b) PPSP-10 and (c & d) PPSP-15 at different frequencies.

similar structure as PEO and low dielectric constant, promotes the organization of segmental units and in turn, modifies the blend structure. Figs.5.64 (a) - (d) show the temperature dependence of real and imaginary parts of permittivity at different frequencies for PPSP-10 and PPSP-15 samples. The steep rise above melting temperature
Fig. 5.65 (a) $\varepsilon'$ and (b) $\varepsilon''$ plots for PPSP-System at 353K and insets show the complete spectra.

Fig. 5.66 Variation of tan$\delta$ for (a) PPSP-10 polymer film at different temperatures (b) PPSP-System at 323K.

is the main feature of all the samples. Compositional dependence of dielectric permittivity (Fig. 5.65) reveals the high values for the polymer films above melting temperature than at below melting with highest values for PPSP-5 sample. The loss tangent values are slightly increased and the frequency of dispersion decreases with the addition of PEG whereas with temperature the frequency of dispersion shifts towards high frequency side in the system (Fig.5.66). Never the less, EC based polymer blended electrolyte system also shows similar behavior as observed in PEG system. Variation of dielectric constant and dielectric loss for different EC concentrations in silver-ion
conducting PEO-PMMA polymer blend is shown in Figs 5.68 and 5.69. The observed decrease in $\varepsilon'$ and $\varepsilon''$ values is due the fact that as the frequency increases, the polarizability contribution from ionic and orientation sources decreases and finally disappears due to their inertia [8, 39]. With the rise in temperature (Fig. 5.70), the ionic and electronic polarizability start to increase which result in enhancement in dielectric constant values. Compositional variation of $\varepsilon'$ and $\varepsilon''$ values initially decrease as

Fig. 5.68 Frequency dependent (a)-(c) $\varepsilon'$ and (d)-(f) $\varepsilon''$ plots for PPSE-5, PPSE-7 and PPSE-12 at different temperatures.
ethylene carbonate concentration increases up to 7 wt% and further addition of EC concentration leads to rise of more than one order of magnitude in the values of permittivity.
Variation of loss tangent (tan δ) with temperature for PPSE-5 and PPSE-12 samples is represented in Figs. 5.72 (a) & (b) respectively. A peak maxima in tan δ start to appear as temperature approaches near $T_m$. This peak maximum in loss tangent slightly shifts towards higher frequency with rise in temperature. It is worth mentioning here that
Fig. 5.75  Frequency dependent (a)-(c) $\varepsilon'$ and (d)-(f) $\varepsilon''$ plots for PPSPA-1, PPSPA-2 and PPSPA-4 at different temperatures.

tan $\delta$ is situated at low frequency region, where dc conductivity dominates. In addition to this, dielectric losses at lower frequencies are significantly higher than those occurring at higher frequency. This kind of dependence of tan $\delta$ on frequency is associated with losses by conduction. Consequently, the dielectric loss for samples with high conductivity
(PPSE-5 & PPSE-15) is higher than the samples with lower conductivity. The main advantages of the composite electrolyte are the enhancement of room temperature ionic conductivity and an improved stability at the electrode-electrolyte interface. The inert fillers, due to its large surface area, prevent the local chain reorganization with the result of locking in a high degree of disorder characteristic of the amorphous phase, which favors the high ionic transport. Therefore, the effect of nano-filler Al$_2$O$_3$ concentration on dielectric properties of polymer electrolytes plasticized with PEG behavior is observed.

![Figure 5.76](image)

**Fig. 5.76** Frequency dependent logarithmic (a) $\varepsilon'$ and (b) $\varepsilon''$ plots for PPSPA-4 and at different temperatures.

Fig.5.75 shows the frequency dependence of real and imaginary parts of dielectric constant at different temperatures for 1, 2 and 4 wt% of Al$_2$O$_3$ in PPSP sample. It is clear from the figure that permittivity decreases monotonically with increasing frequency and after a cross-over frequency, shows a saturation plateau in the higher frequency region. The accumulation of charge at the interface of electrode-PPSPA nano-composites at low frequency ascribes the polarization and the fast periodic reversal of electric field at higher frequencies charge accumulation decreases which is responsible for a fall in dielectric constant. At $T < T_m$ temperatures, in Fig. 5.76, $\varepsilon'$ plot reveals a step-like behavior or two
plateaus of dielectric which shifts to higher frequency side with the increase in temperature, and above $T_m$, double plateau region gradually converts into a single dispersion with the increase in temperature. Similar behavior is observed in other samples. A sudden increase in dielectric constant also features beyond the melting temperature and this increase is more pronounced at lower frequencies as is evident from Fig.5.77. It can be clearly made out from the Fig.5.78 that the values of the dielectric constant, both above and below the melting temperature of PEO, increase with the addition of nano-filler in the blend electrolyte samples except at 5wt%.

Figs.5.79 (a) & (b) show the frequency dependent loss tangent of the investigated polymer nano-composite system at various temperatures for PPSPA-4 and PPSPA-5.
samples. Observed from figure, it is apparent that the losses increase with temperature. At $T<T_m$, loss peak in tan $\delta$ spectra is very feeble with no shifting with the rise in temperature. The peak values at lower frequencies are high and its values decrease with
frequency. Loss peak at \( T > T_m \) shifts towards high frequency side with rise in temperature. The loss peaks and their shifts with temperature indicate a dielectric relaxation process. The dielectric losses also increase with the filler concentration up to 4 \text{wt}\% and decreases at higher amount of Al\(_2\)O\(_3\) (Fig.5.80).

![Image of Fig. 5.81](image)

**Fig. 5.81** Frequency dependent \( \varepsilon' \) and \( \varepsilon'' \) plots for (a) PPSEA-2 and (b) PPSEA-4 at different temperatures.

Similar observations in EC based polymer nano-composites are observed. The variations of real and imaginary parts of dielectric constant, as a function of frequency, are shown in Fig.5.81 (for PPSEA-2 and PPSEA-4 samples) and Fig.5.82 (for PPSEA-4 polymer film). The dielectric permittivity rises sharply towards low frequency due to electrode polarization effects [74]. A sudden increase in \( \varepsilon' \) and \( \varepsilon'' \) values near \( T_m \) (Fig. 5.83) is one of the main features in this system too. The highest values of \( \varepsilon' \) and \( \varepsilon'' \)
for PPSEA-4 sample indicates the enhanced charge carrier density at the space charge accumulation region, resulting in an increase in the equivalent capacitance.
Loss tangent of polymer nano-composite system plasticized with EC for PPSEA-2 and PPSEA-4 samples, shown in Fig.5.84 at various temperatures increase with the rise in temperature. Losses rise with the filler concentration up to 4 wt% but decrease at higher amount of Al₂O₃ (Fig.5.85). Dielectric constant values as a function of nano-filler concentration is given in Fig.5.86. It can be concluded from figure that the values are quite higher (more than one order of magnitude) in EC based nano-composites. This is found in good agreement with conductivity results shown in Fig.5.39.
5.4 Modulus Analysis

The electrode-electrolyte interface polarization due to accumulation of charges at low frequency is so much prominent that it is difficult to separate other relaxation effects apart from polarization. Hence, further analysis of the dielectric behavior, using the formulation of electric modulus, pioneered by Macedo et. al. [13] is used to overcome this [75, 76]. Electric modulus is an electrical analog to the mechanical shear modulus.

Electrical modulus formalism is useful to study the relaxation process in a wide variety of materials [76-78]. The electrical relaxation process is due to distribution of relaxation times which may be due to inhomegenity, conducting domain and mixture of phases etc. The modulus formalism transforms a monotonically increasing function of frequency (the real part of ac conductivity $\sigma'(\omega)$) into one exhibiting a peak in $M''(\omega)$ representation. The electric modulus data can be obtained from the complex impedance data [77] according to the relation given in Chapter 3.

The variation of $M'$ and $M''$ at low and high frequencies can be predicted by the following model proposed by Macedo et. al. [13]
and $M''$ passes through a maximum. At first, the effect of blending of different ratios of PEO with PMMA concentration on modulus spectra at different temperatures is studied. The modulus spectra of various concentrations of PEO in PEO-PMMA blended system at different temperatures are studied. The frequency dependent real and imaginary parts of modulus, $M'(\omega)$ and $M''(\omega)$ spectra for polymer blend PPS-10, PPS-20, PPS-30, PPS-50, PPS-60 and PPS-70 polymer electrolytes at various temperatures are shown in Figs. 5.88(a)-(f) and Figs. 5.89(a)-(f). It shows an increase in $M'(\omega)$ values with frequency and attain a constant value at higher frequency. The observed small value of $M'(\omega)$ in low frequency region facilitates the migration of ion conduction [76].

However, the frequency dependent values of $M'(\omega)$ at high frequencies decreases with the increase in temperature and the relaxation frequency shifts towards the higher frequency side with temperature. The reduction in the value of $M'(\omega)$ with increase in temperature is due to the increase in the mobility of the polymer segment and charge carriers with the temperature. Below $T_m$, $M'$ plot shows two dispersion regions (similar to regions observed in PPS and PPSP-systems) which turn into single one as temperature approaches $T_m$. The frequency dependent $M'(\omega)$ and $M''(\omega)$ spectra (Fig. 5.88 and Fig. 5.89.) are divided in two regions; region I and region II which are in the temperature range $T<T_m$ and $T>T_m$ respectively. In region I, $M'(\omega)$and $M'(\omega)$ spectra show two dispersions and two relaxation peaks, respectively. Low frequency dispersion and/or first
relaxation peak gradually shift towards high frequency side with temperature and finally disappear as temperature approaches near $T_m$. The second dispersion frequency observed in higher frequency region, does not shift but a reduction in the value peak height of $M''$ is observed. The low frequency relaxation peak of $M''(\omega)$ is observed to be centered at the first dispersion region of $M'(\omega)$. This peak is assigned to the transition region from long
range ionic mobility to dipole mobility (rotation). The double relaxation peaks in $M''(\omega)$ spectra is expected one due to the presence of semi-crystalline regions and other due to amorphous regions in the present polymer blends. As the temperature approaches near $T_m$, semi-crystalline region of PEO melts and amorphous region preponderates in the PMMA matrix. In region II, the melted PEO penetrates in PMMA polymer making the
polymer system as gel like system in which polymer chains acquire faster internal movement and segmental motion dominates giving rise to only a single relaxation peak in high frequency region. In this region, the frequency of $M''_{max}$ is found to shift systematically towards higher frequency side with the increase in temperature. Similar behavior is observed in other samples too. The observed shift in $M''_{max}$ either in low frequency region or in high frequency region with increase in temperature suggests that the increased movement of the charge carriers leading to decrease the relaxation time in their respective regions. This behavior suggests that the relaxation is a thermally activated process and occurrence of hopping of charge carriers. Effect of blending of PEO with PMMA on imaginary modulus spectra can be seen from Figs.5.90 (a) & (b).

$M'(\omega)$ and $M''(\omega)$ spectra show a long tail at the low frequency region. This long tail provides evidence of the large capacitance associated with the electrodes. This is due to accumulation of a large amount of charge carriers at the electrode-solid polymer electrolyte interface. Frequency dependent $M''$ plot shows asymmetric relaxation peak in the dispersion region of $M'$ and the occurrence of relaxation peak indicate long range to the short range mobility with increase in frequency [77]. The charge carriers are mobile...
over long distances in the left side region of the peak and they are spatially confined to their potential wells region in the right side of peak [76].

In optimized polymer blending ratio as 50:50 of PEO and PMMA polymers, effect of increasing plasticizer (PEG and EC) concentrations is studied. Figs. 5.91(a)-(d) and Figs. 5.92(a)-(d) show the frequency dependent $M'$ & $M''$ spectra for PPSP-5, PPSP-10, PPSP-12 and PPSP-15 polymer electrolyte films respectively at different temperatures. The occurrence of long tail at lower frequencies in $M'$ and $M''$ plots indicate the negligible contribution of electrode polarization. $M'$ shows increasing trend with frequency and level off at higher frequencies. Similar to PPS-system, $M''(\omega)$ spectra is divided in two regions in $T<T_m$ and $T>T_m$ temperature regions and shows two peaks.

**Fig. 5.91** Frequency dependent real part of modulus plots for (a) PPSP-5 (b) PPSP-10 (c) PPSP-12 and (d) PPSP-15 polymer films at different temperatures.
Fig. 5.92 Frequency dependent real part of modulus plots for (a) PPSP-5 (b) PPSP-10 (c) PPSP-12 and (d) PPSP-15 polymer films at T>T_m and inset shows the T<T_m temperatures.

Fig. 5.93 Frequency dependent (a) real, $M'$ and (b) imaginary, $M''$ parts of modulus plots for PPSP-system at 323K and 353K respectively.

With the increase in temperature the peak in low frequency region becomes feeble and disappears near $T_m$. The shifting of $M''$ peak towards higher frequencies side, with the increase in temperature is due to faster movement of the charge carriers (Ag⁺-ion), leading to decreased relaxation time. The presence of asymmetric relaxation peak
Fig. 5.94 Frequency dependent real part of modulus plots for (a) PPSE-5 (b) PPSE-7, (c) PPSE-10, (d) PPSE-12 and (d) PPSP-15 polymer films at different temperatures.

indicates non-Debye nature i.e., distribution of relaxation times. Figs.5.93 (a) & (b) depict the \( M' \) and \( M'' \) plots for various compositions of PEG plasticizer in silver ion conducting PEO-PMMA polymer blend. Polymer film with highest conductivity shows dispersion at higher frequency and lowest maxima values in their respective plots as
Fig. 5.95 Frequency dependent imaginary part of modulus plots for (a) PPSE-5, (b) PPSE-7, (c) PPSE-10, (d) PPSE-12 and (d) PPSP-15 polymer films at T>T<sub>m</sub> and inset shows the T<T<sub>m</sub> temperatures.

Compared to other samples.

Frequency dependent M'<sup>′</sup>and M'<sup>″</sup>spectra of various concentrations of EC in PEO-PMMA-AgNO<sub>3</sub> polymer films are shown in Figs.5.94 and 5.95, respectively. M'<sup>′</sup> and M'<sup>″</sup>spectra show an increasing trend with frequency at a particular temperature indicating the
bulk effect. The significantly lower or negligible values of $M'$ and $M''$ at lower frequencies indicates that the electrode polarization phenomena makes small contribution to electrical modulus. Below $T_m$, $M'$ plot shows two dispersion regions (similar to regions observed in PPS and PPSP-systems) which turn into single one as temperature approaches $T_m$. Similarly below $T_m$, frequency dependent $M''$ spectra (Fig.5.95) show two peak maxima and as temperature approaches $T_m$, first peak in low frequency region disappears and single relaxation peak in mid frequency region remains.

These double relaxation features at temperatures $T<T_m$ are also in agreement with ac conductivity behavior. This behavior can be explained as at higher temperatures i.e., $T>T_m$, the semi-crystalline regions of PEO melts, in other words, the system becomes amorphous which results in single dispersion in conductivity or single relaxation in modulus plots. At $T>T_m$, the frequency corresponding to $M'_{max}$ is found to shift systematically towards higher frequency side with the increase in temperature. Similar features in modulus spectra at below and above melting temperature $T_m$ of PEO in mixed electrolytes of MEEP-PEO doped with NaSCN are reported by Subramony et. al.[79]. The results obtained in the present system are in good agreement with the Macedo’s model [13].

![Graph showing frequency dependent (a) $M'$ and (b) $M''$ parts of modulus plots for PPSE- system at 323K.](image_url)
Further in the present work, the effect of incorporation of nano-fillers on both plasticized (PEG and EC) polymer electrolytes in terms of electrical modulus spectra has been undertaken. Figs.5.96 and 5.97 show the $M'$ and $M''$ plots at various temperatures for different concentrations of nano-filler Al$_2$O$_3$ in PPSPA-system, respectively. Similar to blended and plasticized systems, $M'$ and $M''$ variation as a function of frequency at different temperatures show two dispersion or relaxation regions, namely one prior to melting and other above melting temperature. $M'$ and $M''$ have S-shaped dispersion and a peak respectively in high frequency region. The electrode polarization effects are seems to vanish in this (modulus) formalism in contrast to dielectric formulation (Fig. 5.76 and 5.76).
Fig. 5.97  Frequency dependent $M'$ plots for (a) PPSPA-1 (b) PPSPA-2 (c) PPSPA-3 and (d) PPSPA-4 polymer films at $T>T_m$ and inset shows the $T<T_m$ temperatures.

Fig. 5.98  Frequency dependent (a) $M'$ and (b) $M''$ parts of modulus plots for PPSPA-system at 323K.

The observed peaks in $M''$ spectra are assumed to be related to the translational ion dynamics and mirror the conductivity relaxation of mobile ions. The observed frequency dependent $M''$ spectra for different compositions indicate a shifting of peak towards high frequency side with the increase in nano-filler concentration. However, a
shift towards lower frequency side is observed for the polymer film with 5 wt% of Al₂O₃ (Fig.5.98). This result is found to be in consistent with the characterization as well as conductivity results.

Fig.5.99 Frequency dependent $M'$ plots for (a) PPSEA-1 (b) PPSEA-2 (c) PPSEA-3, (d) PPSEA-4 and (d) PPSEA-5 polymer films at different temperatures.
Fig. 5.100 Frequency dependent $M''$ plots for (a) PPSEA-1 (b) PPSEA-2 (c) PPSEA-3, (d) PPSEA-4 and (d) PPSEA-5 polymer films at different temperatures.

Figs. 5.99 and 5.100 show $M'$ and $M''$ spectra as a function of frequency in the investigated temperature range for different concentrations of nano-filler Al$_2$O$_3$ in polymer blended electrolyte plasticized with EC system (PPSEA-system). In the low frequency region, both $M'$ and $M''$ values tend to zero indicating the fact that the electrode polarization make a negligible contribution. The long tail at lower frequencies is due to
the large capacitance associated with the electrodes. $M'$ and $M''$ variation as a function of frequency show an increasing trend towards high frequencies. The observed peak in $M''$ spectra for all polymer films imply that the polymer electrolyte films are ionic conductors. As discussed in previous sections, $M'$ and $M''$ variation as a function of frequency at different temperatures of these polymer electrolyte films also show two dispersion or relaxation regions which turns into single one as temperature approaches melting of PEO. $M'$ and $M''$ spectra for PPSEA-system at 323K is shown in Fig.5.101. Similar to PPSPA-system, this system also depicts that with increasing the nano-filler concentration, dispersion in $M'$ spectra and peak maxima in $M''$ spectra shift towards high frequency side with a reverse behavior in PPSEA-5 sample. This result is in good agreement with the characterization and conductivity results.

The modulus plots are non-symmetric which is in agreement with the non-exponential behavior of the electrical function and it is well described by the Kohlrausch-William-Watts (KWW) exponential function [80-82] as given in eq.2.33 and is known to provide satisfactory fit for the asymmetrical $M''$ peaks. The stretched exponent $\beta$ values can be evaluated by knowing the full width at half maximum (FWHM) of the $M''_{\text{max}}$ plot, where

$$\beta = \frac{1.14}{\text{FWHH}}$$

$\beta$ is a measure of the degree of deviation from the Debye behavior of single relaxation. $\beta \sim 0$ indicates the maximum interaction between ions and other factors which give rise to effects for ion transportation. The exponent $\beta$ is widely used to describe different kinds of relaxation processes in amorphous materials. The calculated values of $\beta$ for PPS, PPSP, PPSE, PPSPA and PPSEA systems are tabulated in Table 5.2. The $\beta$ values are found to be greater than 1 for all except for PPSEA system.
Fig. 5.101 Frequency dependent (a) real, $M'$ and (b) imaginary, $M''$ parts of modulus plots for PPSEA system at 323K.

Table 5.2 KWW exponential function $\beta$ values for PPS, PPSP, PPSE, PPSPA and PPSEA systems at different temperatures.

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In solid electrolytes, conduction of ionic carriers and dipoles gives the relaxation phenomenon and $M''$ peak position is a measure for the conductivity relaxation time, $\tau$, which is assumed to represent a characteristic time scale of the ionic motion. The observed peak in $M''(\omega)$ spectrum indicates the conductivity relaxation time of Ag$^{+}$-ion,
by \(2\pi f_{\text{max}} \tau = 1\) [83] where \(f_{\text{max}}\) is the peak frequency and \(\tau\) is the relaxation time [84]. Values of the relaxation time are found to decrease with the increase of temperature. Above the melting temperature of PEO in polymer complexes, the variation of relaxation time follows a systematic Arrhenius type behavior (Fig. 5.102). The activation energy for PPS-50 is 0.77 eV which is a slightly lower when compared with the activation energy calculated from conductivity plot (0.80 eV). In the same manner, for other plasticized and nano-composites systems, the variation of relaxation time is found to be Arrhenius in region II (above \(T_m\)) and the activation energies are found to be in the range of 0.6-0.9 eV. The difference in the values of activation energy indicates that the ions have to overcome different potential barriers in conduction and relaxation processes.

In case of an ideal circuit, the impedance and modulus spectroscopic plots i.e., \(Z''\), \(M''\) versus log \(f\) plots are completely super imposable and is given below:

\[
Z'' = R \frac{\omega RC}{1+(\omega RC)^2} \quad \text{and} \quad M'' = \frac{C_0}{C} \frac{\omega RC}{1+(\omega RC)^2}
\]  \(\text{…} \ (5.2)\)

The Debye like peak shapes in the spectroscopic plots is given by the term, \(\frac{\omega RC}{1+(\omega RC)^2}\) in the imaginary parts of both \(Z''\) and \(M''\). It can be seen that the \(Z''\) peaks are scaled by \(R\) where as the \(M''\) peaks are scaled by \(C_0/C\). But in practice, for solid electrolytes, they need to be represented by a series array of \(RC\) elements in order to account for various layers within the material, as observed in Section 5.2 [85]. As a result, there occurs usually a distribution of relaxation times, in which case the maxima in the impedance and modulus spectra no longer coincide [85].

To understand the non-Debye behavior of the present system, impedance and modulus spectrum at 343K have been plotted and shown in Fig. 5.103 for PPS-10, PPS-
Fig. 5.103  Frequency dependent $Z''$ and $M''$ plots for PPS, PPSP, PPSE polymer electrolyte films at 343K.
30, PPSP-10, PPSE-5, PPSE-15, PPSPA-1, PPSPA-3 and PPSEA-4 polymer electrolyte samples. It can be seen from the figure that $Z_{\max}$ and $M_{\max}$ in all spectra do not coincide at the same frequency. $Z''$ spectrum broadened on the low frequency side while $M''$ spectrum broadened on the high frequency side indicating distribution of relaxation times, i.e., non-Debye nature of polymer films. Similar impedance and modulus with log frequency behavior are also observed for other samples.

5.5 Scaling

Scaling and universality are important concepts that arise in many situations in our physical world [86]. Often one encounters processes in the laboratory that at first appear to behave differently for differing materials, but which when appropriately scaled, display an underlying common behavior among all materials. In these instances, scaling and universality provide to reduce the procedure to simpler parts so that a clear understanding might be achieved. Universality of conductivity and dielectric relaxation processes in an ion conducting materials can be established using scaling of respective spectra to show whether the processes are independent of charge concentration and/or are thermally activated. Scaling is an important property for any dynamic process to possess as it implies that one may separate the thermodynamics, entering only through the scales themselves, from the inherent physics involved in the dynamical process which is completely described by a single scaling function [87]. The ability to scale different data sets so as to collapse all to one common curve indicates the process can be separated into a common physical mechanism modified only by thermodynamic scales [88]. The conductivity, dielectric and modulus spectra are scaled using the different scaling laws given by different workers.
In general, the master curve of AC conductivity spectra can be obtained using the relation [89]:
\[
\bar{\sigma} = F\left(\frac{C}{\sigma_{dc}} \omega\right)
\]
where F is the function describing the master scaling, C may depend on variables like charge carrier concentration \(n\) and temperature \(T\) etc.

Different scaling approaches to scale AC conductivity and modulus spectra by many workers have been reported in past to establish time-temperature superposition principle (TTSP) of conduction or relaxation processes. In these scaling approaches, dc conductivity (\(\sigma_{dc}\)) is used to scale AC conductivity i.e.; \(\frac{\sigma'}{\sigma_{dc}}\) and frequency axis is scaled by different factors as \(\frac{\omega}{\omega_p}\) [90], \(\frac{f}{\sigma_{dc} T}\) [91], \(\frac{f}{\sigma_{dc} T} \chi\) and \(\frac{f \varepsilon_0 \Delta \varepsilon}{\sigma_{dc}}\) [88] etc. where \(\omega_p, \chi, \varepsilon_0\) and \(\Delta \varepsilon\) are hopping frequency, number density of mobile ions, the permittivity of free space (constant) and permittivity change respectively. Usually, the frequency- and temperature-dependent conductivity spectra obey the time-temperature superposition principle. This means that, for a given material, the conductivity isotherms can be collapsed to a master curve upon appropriate scaling of the conductivity and frequency axes. The master curves of different solids may have very similar shapes.

In the present studies, Ghosh scaling’s approach [90] is used to scale conductivity and modulus spectra, since it takes into account the dependence of the conductivity spectra on structure and the possible changes of the hopping distance experienced by the mobile ions. Ghosh’s scaling approach is given by the relation:
\[
\frac{\sigma' (\omega)}{\sigma_{dc}} = F\left(\frac{\omega}{\omega_p}\right)
\]
Figs. 5.104 (a)-(e) show the scaled spectra of AC conductivity, using Ghosh’s scaling law, for PPS-30, PPSP-12, PPSE-5, PPSPA-4 and PPSEA-4 polymer electrolyte films, respectively at different temperatures ($T > T_m$ temperature range). It is observed from figures that all AC conductivity spectra merge near perfectly onto a single master...
curve giving a TTSP spectra. Compositional AC conductivity spectra for all PPS, PPSP, PPSE, PPSPA and PPSPE polymer system at a particular temperature are plotted individually and analyzed. Scaled conductivity spectra for all the samples for PPSEA-system gives a nearly same curve only at a particular temperature (Fig.5.104(f)) while other systems revealed merging at higher frequencies with deviation at lower frequencies, which might be occurring due to dominance of polarization at electrodes at these frequencies.

The scaling behavior of the imaginary part of modulus spectra provides an insight into temperature and composition dependence of the relaxation dynamics. Imaginary part of modulus spectra is generally scaled using Ghosh’s scaling law in which the modulus axis (y-axis) is scaled by peak maximum value of modulus ($M_{max}$) value) and frequency axis (x-axis) is scaled by frequency corresponding to maximum value of modulus. In other words, scaling function can be defined as:

$$\frac{M''}{M_{max}''} = F\left(\frac{f}{f_{max}}\right)$$

A remarkable characteristic of this type of data representation is that a direct comparative analysis can be performed for each branch of curves $M''/M_{max}''$ versus log $(ff_{max})$. In the same way, any type of dispersion phenomenon can be easily detected. The scaling of the frequency by $f_{max}$ parameter gives a distribution of $M''/M_{max}''$ values considering logarithmic representation at around $(ff_{max})=1$. At frequency above this value, some degree of dispersion can be observed depending on the composition formulation and temperature of measurement.

Figs.5.105 (a)-(b) show the normalized spectra of imaginary part of modulus, $M''$ at different temperatures for PPS-30, PPS-50 and PPS-70. Fig.5.105 (c) represents the
normalized modulus spectra at 353K for different concentration of PEO. The normalized plot of imaginary part of modulus shows a single normalized peak i.e., merging of $M''$ plot at different temperatures and as well as for different concentrations of PEO at a particular temperature confirming the temperature and as well as compositional independence of relaxation in PEO: PMMA polymer blend electrolyte system. Similar behavior is observed for other samples as well. This time-temperature superposition attributes a temperature independent relaxation behavior or the dynamical processes occurring at different temperatures are independent of temperature. The asymmetrical shape of the plots attributes the existence of distribution of relaxation times.

Scaling approach in $M''$ spectra for PEG and EC containing systems are also

![Scaled M'' spectra for (a) PPS-30 (b) PPS-50, (c) PPS-70 at $T>T_m$ temperatures (inset shows the complete temperature range) and (d) PPS-system at 353K.](image)

Fig. 5.105 Scaled $M''$ spectra for (a) PPS-30 (b) PPS-50, (c) PPS-70 at $T>T_m$ temperatures (inset shows the complete temperature range) and (d) PPS-system at 353K.
applied. The perfect merging of scaled $M''$ versus normalized frequency plot at $T > T_m$ temperatures is observed and shown in Fig. 5.106(a) for PPSP-10. Other concentrations of this series also showed the similar behavior. A master plot of the
modulus isotherms for the PPSP system at 358K is shown in Fig. 5.106(b). The near perfect overlap of the data at different temperatures on a single master curve indicates that all the dynamic processes occurring at different time scales exhibit the relaxation mechanism involved is temperature independent or merely thermally activated. Similarly the normalized imaginary part of the modulus versus normalized frequency log \((f/f_{\text{max}})\) plots for PPSE-10, PPSE-12 and PPSE-15 polymer electrolyte films are shown in Fig. 5.107(a)-(c), respectively. It can be seen from figures that the plots are clearly superimposable and the data points are found to collapse very well for all the temperatures \((T > T_{m}\) temperatures) studied. The super imposition of the plots indicates that the dynamical processes of ion transport are same throughout the investigated temperature and frequency window. The scaled spectra of \(M''\) for different compositions of PPSE-system at 358K is shown in Fig. 5.107(d). The curves present nearly superimposition leading to the same master curve behavior at different compositions. This development suggests a common relaxation mechanism in these polymer electrolytes for the studied composition range.

Fig. 5.108  Scaled \(M''\) spectra for (a) PPSPA and (b) PPSEA-systems at 363K.

Next to plasticized polymer electrolyte systems, scaling in nano-composites plasticized with PEG and EC is carried out. Fig. 5.108 (a) & (b) depict the scaling of
modulus of PPSPA and PPSEA-systems at 363K, respectively. Perfect overlapping of $M''$ spectra for all compositions in their respective systems is observed indicating that the relaxation processes of conducting Ag$^+$-ions in PEG and EC containing polymer nano-composites are independent of composition. The temperature wise scaled $M''$ plots for
PPSPA-1 and PPSPA-2 samples are depicted in Fig. 5.109(a) & (b). The same plots for PPSEA-1, PPSEA-2, PPSEA-3 and PPSEA-4 samples are shown in Fig.5.110 (a) - (d). Temperature wise as well compositional perfect merging of modulus spectra giving single master curve is the beauty of polymer nano-composite system plasticized with PEG and EC.