CHAPTER 6

MODULS AND DIELECTRIC ANALYSIS

Analysis of frequency dependent electric modulus & dielectric properties, including relaxation time and dielectric constant, as well as dielectric loss factors respectively of solid polymer electrolytes are discussed in this chapter.
6.1 Introduction

The term dielectric is broader than the term insulating material. Here the dielectric material term means the substance whose basic electrical property is the ability to be polarized and in which electrostatic field can exist. For most of the applications of dielectric materials, the vital properties are the dielectric constant \(\varepsilon'\) and the dielectric loss factor, (i.e., \(\tan\delta\)) [1].

Dielectric polarization results due to the existence of atomic and molecular forces. It appears whenever charges in a material are somewhat displaced with respect to one another under the influence of an electric field. In a capacitor, the negative charges (-ve) within the dielectric are displaced towards the positive electrode (+ve), while the positive charges shift in the opposite direction. As charges are confined in an insulator, restoring forces are activated which either do work, or cause work to be done on the system in short, energy is transferred. During charging a capacitor, the polarization effect opposing the applied field draws charges onto the electrodes, storing energy and on discharge, this energy is been released. A result of which the interaction in certain materials, which possess easily polarizable charges, will greatly influence the degree of charge which can be stored in a capacitor. The proportional increase in storage ability of a dielectric with respect to vacuum is defined as the dielectric constant of the material [1, 2].

6.2 Dielectric Analysis

In general, dielectric analysis of the material provides the measure of electrical characterization of polymer material where the real part of dielectric permittivity \(\varepsilon'\) is proportional to the capacitance and measures the alignment of dipoles and imaginary part of dielectric permittivity \(\varepsilon''\) is proportional to the conductance and represents the energy required to align dipoles and move ions.

Therefore, in order to understand the effect of variation of silver salt concentration on the dielectric properties in PEO-AgCF\(_3\)SO\(_3\) polymer electrolytes (PS-system), the frequency dependence real \((\varepsilon')\) and imaginary \((\varepsilon'')\) part of permittivity at different temperature are plotted and shown in Fig. 6.1 and 6.2 respectively. The plot of real part of
permittivity ($\varepsilon'$) shows dispersion at low frequency region with a gradually decrease in mid-frequency region and finally attain a constant value at high frequency. The increase in $\varepsilon'$ values at lower frequencies results mainly due to the contribution of the electrode.

![Graph (a)](image(a).png)

![Graph (b)](image(b).png)

![Graph (c)](image(c).png)

![Graph (d)](image(d).png)

![Graph (e)](image(e).png)

**Fig. 6.1** The real part of dielectric permittivity, $\varepsilon'$ plots for (a) PA-2, (b) PA-3.5, (c) PA-5, (d) PA-7 and (e) PA-11 of PA series at various temperatures.
polarization and Maxwell-Wagner interfacial polarization [3-5]. The electrode polarization phenomena occur due to formation of electric double layer capacitances by buildup of free charges at the interface between the electrolyte and the electrode [6]. This buildup of electrical polarization and drop of the electric field in the bulk are reflected by the increase in the complex dielectric function at low frequencies.

In the Maxwell-Wagner phenomena, the free charges build up during the electromigration at the interfacing boundaries of different dielectric constants in the dielectric
material, which results in the formation of nano-capacitors in the dielectric material [7].

![Graphs showing dielectric constant at 313K](image)

**Fig. 6.3** The plot of (a) real part $\varepsilon'$ and (b) imaginary part $\varepsilon''$ of dielectric permittivity with different amount of AgCF$_3$SO$_3$ for PA System at 313K.

At sufficiently high frequencies, the free charges do not follow the fast changes developed in the ac field and thus only molecular polarization occurs at these frequencies [8-13]. In other words, dielectric constant decreases sharply with increase in frequency and becomes constant at high frequencies [8]. Both $\varepsilon'$ and $\varepsilon''$ rise sharply at low frequencies with temperature and this rise shifts towards high frequency side and saturates [9] for all the samples of the PA-series. Figs. 6.3 (a) and (b) represent plots of real ($\varepsilon'$) and imaginary ($\varepsilon''$) part of dielectric constant as a function of log frequency for different amount of AgCF$_3$SO$_3$ containing PEO polymer electrolytes.

At higher frequencies i.e.; in the range of $10^4$ to $10^6$ Hz, the measured dielectric constant is almost independent of the composition. The dielectric constant of the polymer film with 7wt% of AgCF$_3$SO$_3$ is observed to be highest and this sample shows maximum dispersion frequency. It is observed from figure that at low frequencies, the real ($\varepsilon'$) and imaginary ($\varepsilon''$) parts of permittivity remain almost constant for PA-2wt% and PA-3.5wt%, whereas for PA-5wt% and PA-7wt% it increases and finally for PA-11wt% its value decreases. Figs. 6.7 (a) to (e) depict the frequency dependent dielectric constant plots for different concentrations of nano-filler SiO$_2$ in polymer salt system (PAS-system). According to Agrawal et.al., [14] the decrease of $\varepsilon'$ and $\varepsilon''$ with increasing frequency may be attributed to electrical relaxation or inability of dipoles to rotate rapidly leading to a lag between frequency of oscillating dipoles and that of applied field. They added that, as the frequency increases, the ionic and orientational source of polarizability decreases and finally disappear due to inertia of mobile ions to result in a nearly constant
value of dielectric permittivity. Figs. 6.6(a) and (b) shows the variation of dielectric permittivity i.e.; \( \varepsilon' \) and \( \varepsilon'' \) with frequency for different SiO\(_2\) concentration in PAS system at 313K. Non-uniform variation in the dielectric permittivity values with addition of SiO\(_2\) are the main feature of the present system. Both \( \varepsilon' \) and \( \varepsilon'' \) values remain nearly same for PAS-5, PAS-10 and PAS-15 % of SiO\(_2\) dispersed in PEO- AgCF\(_3\)SO\(_3\) composite electrolyte and an increase in the values is observed only at higher concentration of SiO\(_2\) i.e.; PAS-20wt%. This type of behavior indicates that the filler provides almost constant crys-
talline domain channels initially and then it starts segregating due to non complexation in polymer matrix. The alignment of these extra domains enhances the dielectric value of the materials. Agrawal et al. [14] discussed that dispersion at lower frequencies seems to be higher in case of composite electrolyte (PEO–SiO:NH4SCN) compared to SPEs.

**Fig. 6.5**  The plots of frequency dependent $\varepsilon''$ for (a) PAS-5, (b) PAS-10, (c) PAS-15, (d) PAS-20 and (e) PAS-25 of PAS series at various temperatures.

The effect of plasticizer PEG in polymer nano-composites PASP-system in terms of dielectric permittivity is studied. The frequency dependent $\varepsilon'$ and $\varepsilon''$ variation of all the samples of PASP-system at different temperatures are shown in Figs. 6.7 and 6.8, re-
Fig. 6.6  The plot of (a) real part $\varepsilon'$ and (b) imaginary part $\varepsilon''$ of dielectric of various amount of SiO$_2$ for PAS System at 313K.

Fig. 6.7(a)-(d)  The plots of real part of dielectric permittivity, $\varepsilon'$ for (a) PAS-5, (b) PASP-10, (c) PASP-15 and (d) PASP-20 of PASP series at various temperatures.

respectively. A strong frequency dispersion of permittivity is observed in the low frequency region followed by a nearly frequency independent behavior. In the dielectric plots of PASP system shown in Fig. 6.9, the frequency of dispersion are not wide and well separated as observed for PAS system and are very close to each other. In this system, the as
Fig. 6.7(e) The plot of $\varepsilon'$ for PASP-25 at various temperatures.

Fig. 6.8 (a)-(d) The plots of $\varepsilon''$ variation as a function of frequency for (a) PASP-5, (b) PASP-10, (c) PASP-15 and (d) PASP-20 of PASP series at various temperatures.

sociation of PEG with polyethylene oxide (PEO) results in the reduction in system flexibility. S.K. Tripathi and co-researchers [15] mentioned that on addition of nanofiller Al₂O₃ to plasticized polymer electrolyte the dielectric constant and dielectric loss showed dispersion mainly near lower frequency region. R.H.Y Subban et. al. [16] mentioned that the variation in $\varepsilon'$ and $\varepsilon''$ with angular frequency could be attributed to the formation of a
space charge region at the electrode and electrolyte interface, which is known as the non-Debye type behaviour. The compositional variations of real and imaginary parts of dielectric permittivity are shown in Figs. 6.9 (a) and (b), respectively. The highest conducting film depicts the highest dielectric constant value as well as highest losses too.

Fig. 6.9  The plots of (a) real part $\varepsilon'$ and (b) imaginary part $\varepsilon''$ of dielectric permittivity for for PASP System at 313K

In Li-ion conducting series (PLA system), the variation in $\varepsilon'$ and $\varepsilon''$ as a function of frequency for different polymer films at different temperatures are depicted in Figs. 6.10 (a) to (e) and Figs. 6.11 (a) to (e) respectively. According to Saroj et.al., [17], the rise in $\varepsilon'$ and $\varepsilon''$ values with the increase in temperature are due to progressively dissolution of crystalline phase into amorphous phase. Dielectric permittivity plots of various concentrations of Al$_2$O$_3$ in PLA-series are shown in Figs. 6.12 (a) and (b) at 313 K. A sharp rise is observed for 1wt% of Al$_2$O$_3$ but, beyond this concentration of Al$_2$O$_3$, it decreases and becomes constant. A gradually increase in Al$_2$O$_3$ content must have prompted the cluster formation which in fact hinders the conducting channels resulting in gradually
decreases in $\varepsilon'$ and $\varepsilon''$ values.

![Graphs](image)

Fig. 6.10(a)-(d)  Plot of $\varepsilon'$ for (a) PLA-1, (b) PLA-2, (c) PLA-3 and (d) PLA-4 of PLA series at various temperatures.

Fig. 6.10(e)  Frequency dependent $\varepsilon'$ variation for PLA-3 of PLA series at various temperatures.

With different PEG concentrations in lithium ion conducting nano-composite system i.e., PLP series, are shown in Figs. 6.13 and 6.14 at different temperatures. It is observed that on increasing the temperature, dielectric permittivity values increase which can also be attributed to the enhanced flexibility as well as segmental mobility of polymer chains resulting from rise in free volume due to addition of plasticizer. S. Ranjendran and coworkers [18] reported that in PMMA–LiClO$_4$–DMP polymer electrolytes, the rise of $\varepsilon'$
Fig. 6.81 Frequency dependent $\varepsilon''$ variation for (a) PLA-1 and (b) PLA-2 at various temperatures.

Fig. 6.11 Frequency dependent $\varepsilon''$ variation for (c) PLA-3, (d) PLA-4 and (e) PLA-5 of PLA series at various temperatures. and $\varepsilon''$ towards low frequency with increase in temperature are also due to electrode polarization effects. The decrease of $\varepsilon'$ and $\varepsilon''$ with frequency is attributed to the electrical relaxation process, but at the same time the material electrode polarization cannot be ignored as the samples are ionic conductors.

The material electrode interface polarization of the composites masks the other re-
laxation process at low frequencies. There is a significant effect of plasticizer on the value of $\varepsilon'$ and $\varepsilon''$ with strong low frequency dispersion. The plasticizer results in more localization of charge carriers along with mobile ions causing higher ionic conductivity. This may be the reason for higher $\varepsilon'$ and $\varepsilon''$ strong low frequency dispersion [17, 18].

Fig. 6.12 The plot of (a) real part $\varepsilon'$ and (b) imaginary part $\varepsilon''$ of dielectric permittivity for PLA System at 313K.

Fig. 6.13 Plot of $\varepsilon'$ for (a) PLP-5, (b) PLP-10, (c) PLP-15, and (d) PLP-20 of PLP series at various temperatures.

It is observed that on increasing the temperature, dispersion frequency shifts towards higher frequency side in all the samples indicating that (i.e. above $T_g$) the polymer
chain becomes more flexible and increases charge carrier density with the increase in temperature. At high frequency, the data at different temperatures merges, revealing that dielectric constant \(\varepsilon'\) and dielectric permittivity \(\varepsilon''\) are independent of temperature.

![Graphs showing \(\varepsilon'\) and \(\varepsilon''\) as a function of frequency for different temperatures.](image)

Fig. 6.14  \(\varepsilon''\) variation as a function of frequency for (a) PLP-5 and (b) PLP-10 of PLP series at various temperatures.

![Graphs showing \(\varepsilon'\) and \(\varepsilon''\) as a function of frequency for different temperatures.](image)

Fig. 6.14  \(\varepsilon''\) variation as a function of frequency for (c) PLP-15 and (d) PLP-20 of PLP series at various temperatures.

![Graphs showing \(\varepsilon'\) and \(\varepsilon''\) as a function of frequency for different temperatures.](image)

Fig 6.15  The plot of (a) real part \(\varepsilon'\) and (b) imaginary part \(\varepsilon''\) of dielectric permittivity for PLP System at 313K

Figs.6.15 (a) and (b) show variation of dielectric permittivity i.e.; \(\varepsilon'\) and \(\varepsilon''\) of PLP system at 303K. In this system, the dielectric constant increases with the increase in the PEG content up to 10wt% thereafter it reduces.
6.3 Modulus Analysis

Fig. 6.16 A plot of real part $M'$ of Modulus for PA series for different amount AgUF$_3$SO$_4$ at 513K.

Fig. 6.17 The real part $M'$ of Modulus plots for (a) PA-2, (b) PA-3, and (c) PA-3 of PA series at various temperatures.

The dispersion behaviour of the conductivity in the frequency domain is more conveniently interpreted in terms of conductivity relaxation time $\tau$, using the electrical modulus $M^* = 1/\varepsilon^*$ representation [19].

Complex electric modulus $M^*$ formalism is used frequently when the relaxation behaviour is supposed to be due to the motion of ions or electrons [19-21]. Although, initially modulus analysis employ to separate space-charge effects from the bulk conductivity, but
now the $M'$ representation is widely used to analyze ionic conductivities by associating a conductivity relaxation time ($\tau$) with the ionic process [22]. The use of modulus formalism is presenting frequency dependent dielectric or conductivity data has the advantage of eliminating any spurious effect due to contacts or interfaces (Maxwell-Wagner effects) [20]. The dielectric modulus parameter also represents the bulk dielectric behaviour of the polymer electrolytes because of the elimination of polarization effect [21].

**Fig.6.17 (d) & (e) $M'$ plot for (d) PA-7 and (e) PA-11 of PA series at various temperatures.**

**Fig.6.18 A plot of real part $M'$ of Modulus for PAS series for different amount SiO$_2$ at 313K.**

Figure 6.16 shows the real part of the modulus spectrum of PA system for various composition of salt AgCF$_3$SO$_3$ at 313K. The value of $M'$ at different concentration of AgCF$_3$SO$_3$ approaches to zero, at low frequencies, which indicates that the electrode polarization make negligible contribution to $M'$ and lack of restoring force flow of charges under the influence of steady electric field [20]. At higher frequencies, $M'$ attains a max
Fig. 6.19 $M'$ plots for (a) PAS-5, (b) PAS-10, (c) PAS-15, (d) PAS-20 and (e) PAS-25 of PAS series at various temperatures. The dispersion is observed in the range from $10^3$ to $10^4$ Hz.

While looking into the spectra (Figs. 6.17(a) to (e)) of all the samples of this series at various temperatures, it is observed that the dispersion spreads over wide range of frequencies. And the maximum value of $M'$ decreases with increase in temperature. This decrease in peak value indicates increase in the mobility of the polymer segment and ions with the temperature because the orientation of the charge carriers and molecular dipoles is easier at high temperature.
When, the nano-filler SiO₂, which generally increases the amorphous level in the electrolytes [23], is added in PA system, the real part of modulus (Fig. 6.18) shows the large change in dispersion frequency i.e., $10^3$ to $10^5$ Hz and a shifting of dispersion towards higher frequency side with nano-filler except for 25 wt% of SiO₂. The real part of modulus ($M'$) of all the samples at different temperatures (Fig. 6.19) shows the shift of dispersion towards high frequency side as in the case of PA system. The peak values of $M'$ are increased with the addition of nano-filler in PASP system which indicates the increase in conductivity of the samples.

![Fig. 6.20](image)

*Fig. 6.20* A plot of real part $M'$ of Modulus for PASP series for different amount PEG at 313K.

Generally, with the intention to increase the flexibility of polymer matrix low molecular weight plasticizer is added to nano-composite polymer electrolyte. As plasticizer can interrupt polymer-polymer interactions by occupying inter and intra-chain free volume [24]. This decrease in polymer-polymer interaction affects the flexibility of the polymer matrix. The plot of real part of modulus $M'$ for the next system, where the amount of plasticizer PEG is varied and the amount of salt (AgCT₃SO₃) and nano-filler (SiO₂) are kept constant is shown in Fig. 6.20 for various PEG contents at 313K. It is observed that on increasing the PEG amount, the dispersion is confined to particular frequency ($10^4$ Hz). PEG instead of increasing inter- and intra chain separation, it forms long chains due to the similar structural nature of PEO and PEG. This reduces the flexibility and level of amorphous nature of the system. In addition to this, Fig. 6.20 indicates the shifts of dispersion towards higher frequency side on increasing the plasticizer content except for 25wt%. Temperature dependence of $M'$ variation plots for different compositions of PASP-system are depicted in Fig. 6.21 (a) to (e). With the increase in temperature, the
dispersion frequency shifts towards high frequency side.

The real ($M'$) part of all samples of PLA series in which salt AgCF$_3$SO$_3$ is been replaced by LiCF$_3$SO$_3$ and nano-filler SiO$_2$ by Al$_2$O$_3$ are shown in Fig. 6.22. It is obvious that at lower frequencies, $M'$ values are very small and tend to zero, indicating the suppression of electrode polarization [25]. The nature of the graph does not alter for LiCF$_3$SO$_3$ salt and nano-filler Al$_2$O$_3$. The temperature dependence of real part of modulus (Fig. 6.23) at high frequency is observed, suggesting singularity of relaxation mechanism. The sample with 3wt% of Al$_2$O$_3$ shows dispersion along with shifting with increasing
temperature.

The real $M'$ part of modulus for different amount of plasticizer PEG as a function of frequency at 313K is shown in Fig. 6.23 for PLP series. A wide range of dispersion

![Fig. 6.22 $M'$ plot for PLA series at 313K.](image)

![Fig. 6.23 $M'$ plot for PLP series at 313K.](image)

![Fig. 6.24 $M'$ plots for (a) PLA-1, (b) PLA-2, (c) PLA-3, and (d) PLA-4 of PLA series at various temperatures.](image)

i.e., from $10^2$ to $10^5$ Hz along with the shifting towards higher frequency side is observed. The real part of modulus ($M'$) at different temperatures are shown in Figs. 6.24(a) to (e),
in which the spectrum shifts towards lower frequency side except for 10wt% PEG. All the plots are observed to show ‘S’ shaped characteristic feature which is an indication of ionic conductors [26].

Fig. 6.24 (c) \( M' \) plot for PLA-5 of PLA series at various temperatures.

Fig. 6.25 (a)-(c) The \( M' \) spectra for (a) PLP-5, (b) PLP-10 and (c) PLP-15 of PLP series at various temperatures.
Fig. 6.25 (d) & (e) The $M'$ spectra for (d) PLP -20 and (e) PLP -25 of PLP series at various temperatures.

![Graphs of $M'$ spectra for different temperatures](image)

Fig. 6.26 $M''$ spectra for (a) PA-2, (b) PA -3.5, (c) PA-5 and (d) PA -7 of PA series at various temperatures.

![Graphs of $M''$ spectra for different temperatures](image)

Now, the variation of the imaginary part of the modulus ($M''$) with frequency at different temperatures for all the samples for PA series is shown in Fig. 6.26 (a) to (e). Similar to $M'$ spectra, the $M''$ plots also show a long tail at low frequencies. It is also seen that $M''$ spectra have an asymmetry of the peak approximately centered in the dispersion region of $M'$. The observed long tail behavior at low frequencies is the result of the large capacitance associated with the electrodes [27, 28]. In the low frequency region which the ions can move over long distance i.e., ions can perform successful hopping from one site to
the neighboring site. On the other hand, the high frequency wing of the $M''$ peak suggests
that the ions are spatially confined to their potential wells and can make only localized
motion within the wells [29]. It is clear from above figure that the shape of the spectrum
remains constant but the frequency of the modulus maximum $M''_{max}$ shifts to higher fre-
quency side with increase in temperature. It may also be noted that the magnitude of $M''$
peak with temperature is found to be constant. The constancy of the height of the mod-
ulus plot suggests the invariance of the dielectric constant and distribution of relaxation
times with temperature [30, 31]. The imaginary part $M''$ of modulus spectra for various
amount of AgCF$_3$SO$_3$ at 313 K are shown in Fig. 6.27. It is observed that with increasing
the amount of AgCF$_3$SO$_3$, the $M''_{max}$ peak shifts towards higher frequency side i.e., relaxation
time decreases till 7wt%. It means, the increasing amount of salt content

![Fig. 6.26 (e) $M''$ spectra for PA-11 of PA series at various temperatures.](image)

![Fig. 6.27 $M''$ plot for PA series at 313K.](image)

supplies the larger number of charge carriers but after 7 wt%, the process of ion associ-
ation must have started and the system turning into less flexible resulting into the shifting of $M''_{max}$ peak towards the lower frequency side.

The variation of the imaginary part of modulus, $M''$ with frequency at different
temperatures for all sample of PAS system in which the amount of nanofiller SiO$_2$ is va-
ried is shown in Fig. 6.28. The shape of the spectrum remains same as that observed in
PA series but, in the present case not only the peak of $M''_{max}$ shifts towards the higher fre-
quency side, but an increment in the peak height is also observed along with rise in tem-
perature. The inconstancy of the height of modulus plot is an indication the variance of
dielectric constant.

The Fig. 6.29 shows the $M''_{max}$ Peak shift towards higher frequency side with in-
creasing the amount of SiO₂ till 20wt%. The presence of SiO₂ makes the system more amorphous and increases the intra chain distances. However, the flexibility reduces due to the cluster formation after optimum value, resulting into the shifting of $M''_{max}$ peak towards lower frequency side.

**Fig. 6.28** $M''$ spectra (a) PAS-5, (b) PAS-10, (c) PAS-15, (d) PAS-20 and (e) PAS-25 of PAS series at different temperatures.

In the polymer nano-composite composition with highest ionic conductivity (Chapter 5), the plasticizer PEG is added. Generally, plasticization of polymer nano composites improves the ionic conductivity and the amorphous content of polymer electro
Fig. 6.29 $M''$ spectra for PAS series at 313K. Figs. 6.30 (a) to (e) show the plot of imaginary part of the modulus ($M''$) with frequency for all samples of PASP series at different temperatures. Beside, the shifting of peak values towards higher frequency side, the magnitude of the peak levels off on addition of plasticizer PEG. However, no appreciable shifting is observed on increasing the amount of PEG in the values of imaginary part of modulus in Fig. 6.31. But, for sample with 20wt% PEG, the peak intensity has shifted slightly towards higher frequency side, which is in accordance with conductivity variation.

The frequency dependent $M''$ plots at different temperatures for all the samples of PLA series, wherein the silver salt is replaced by lithium salt and nano-filler SiO$_2$ is replaced by Al$_2$O$_3$, are shown in Figs.6.32 (a) to (e). Similar to silver and other solid electrolytes [25, 27, 28], the spectra of $M''$ shifts towards high frequency side with the rise in temperature. $M''$ spectra for various concentrations of Al$_2$O$_3$ in PLA systems at 313 K are shown in Fig. 6.33. With increasing the amount of Al$_2$O$_3$ the $M''_{max}$ peak shifts towards lower frequency side after 1wt%. This observation clearly indicates that larger amount of the nanofiller Al$_2$O$_3$ does not support conduction mechanism because the system becomes more crystalline confirmed from XRD results.

The frequency dependent plot of imaginary part of modulus, $M''$ for various amounts of PEG in PLP series (Fig. 6.34) indicates the shift of peak of $M''_{max}$ towards higher frequency side up to 10wt% PEG thereafter in opposite side. The temperature dependent $M''$ spectrum of different samples of PLP series are shown in Figs.6.35 (a) to (e).

The peaks of $M''$ are related with the translational ion dynamics and mirrors the
Fig. 6.31 $M''$ spectra for (a) PASP-5, (b) PASP-10, (c) PASP-15, (d) PASP-20 & (e) PASP-25 of PASP series at various temperatures. Conductivity relaxation of the mobile ions. It is worth noticing that the relaxation peak is owing to ‘fast segmental motion’ which is responsible for reducing the relaxation time consequently the transport properties. It is clear from all above figures that the frequency of the modulus maximum $M''_{max}$ shifts to higher frequency side with increase in tempera-
ture. The magnitude of $M'$ peak with temperature is found to be constant for samples with plasticizer.

![Graphs showing $M'$ spectra for different temperatures](image)

**Fig. 6.32** $M'$ spectra for (a) PLA-1, (b) PLA-2, (c) PLA-3, (d) PLA-4 and (e) PLA-5 of PLA series at different temperatures.

The peak frequency ($f_{max}$) of the modulus peak ($M''_{max}$) is assumed to represent a characteristic frequency of the conductivity relaxation [30]. Various parameters can be determined from its data. The obtained modulus plots are non-symmetric and are in agreement with the non-exponential behaviour of the electrical function [33] which is
well described by the Kohlrausch–William Watts (KWW) exponential function. This stretched exponential function was first introduced by R. Kohlrausch [34] in 1854 to describe the discharge of a capacitor. This exponent is often used as a phenomenological description of relaxation in disordered systems. But, in 1970, G. Williams and D.C. Watts used the Fourier transform of the stretched exponential to describe dielectric spectra of polymers; in this context, the stretched exponential or its Fourier transform are also called the Kohlrausch-Williams-Watts (KWW) function. [35]. Generally, the value of stretched exponent $\beta$ lies between 0 and 1 has great significance, but compressed exponential function of value greater than 1 i.e. $\beta>1$ has less practical importance, with the notable exception of $\beta=2$, which gives the normal distribution.

In present case, the value of stretched exponent $\beta$ can be evaluated by knowing the full width at half height (FWHH) of the $M''$ plot, where $\beta = (1.14/ \text{FWHH})$ value. The value of $\beta$, at ambient temperature for other samples are given in table 6.1, which gener-

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**Fig. 6.33** $M''$ plot for PLA series at 313K.

**Fig. 6.34** $M''$ spectra for PLP series at 313K.

**Fig. 6.35(a)&(b)** $M''$ spectra for (a) PLP-5, (b) PLP-10 of PLA series at different temperatures.
ally lies between 0 and 1. Considering $\beta$ parameter smaller than 1, some authors [39-41] have suggested that it can be correlated to a distribution of relaxation times in the materials. In the PA series, the width at half height of the modulus spectrum for the sample with 7 wt% of AgCF$_3$SO$_3$ at different temperature is close to 2.2 decades and the $\beta$ results in the value of 0.50.

![Graph](image)

**Fig. 6.35 (c)-(e) $M''$ spectra for (c) PLP-15, (d) PLP-20 and (e) PLP-25 of PL4 series at different temperatures.**

In the present investigated systems, the values of $\beta$ seems to level off in the range 0.56 - 0.67, which is found to be insensitive to the variation of temperature and composition. At low temperature, the relaxation occurs via isolated non interacting dipoles, becoming more and more Debye like and $\beta$ values tend towards unity [42] and also there is a general tendency of $\beta$ to decrease with temperature.

In the PAS series, the width at half height of the modulus spectrum at different temperatures is 2.05 decades and the $\beta$ results in the value of 0.67 for 20wt% of SiO$_2$ and the values of $\beta$ ranges from 0.47 to 0.67 for different amount of SiO$_2$. While the width
at half height of the imaginary part of modulus is close to 1.5 decades in the PASP series, where the amount of PEG has been varied, and the $\beta$ value of sample 5wt% of PEG is observed to be 0.76 and the value for different amount of PEG are confined between 0.6-0.7.

Table 6.1 KWW exponential function $\beta$ from modulus plot of all five series

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\beta$</th>
<th>Sample</th>
<th>$\beta$</th>
<th>Sample</th>
<th>$\beta$</th>
<th>Sample</th>
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<td>PAS-5</td>
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<td>PAS-10</td>
<td>0.54</td>
<td>PASP-10</td>
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<td>0.76</td>
<td>PLP-10</td>
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</tr>
<tr>
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<td>0.67</td>
<td>PAS-15</td>
<td>0.47</td>
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<td>PLA-3</td>
<td>0.63</td>
<td>PLP-15</td>
<td>0.87</td>
</tr>
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</tr>
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<td>PAS-25</td>
<td>0.47</td>
<td>PASP-25</td>
<td>0.76</td>
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<td>0.95</td>
<td>PLP-25</td>
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</tbody>
</table>

In a series with Lithium triflate i.e., PLA series, the modulus spectrum at different temperatures provides $\beta$ values in the range of 0.5 to 0.9. On the other hand, with the addition of plasticizer PEG in PLP series, such a large distribution is not observed and the width at half height is close to 1.5 decades and the $\beta$ value of the sample 25wt% of PEG is found to be 0.76.

The efforts carried out by ionic charge carriers within the polymer materials to follow the change in the direction of applied field results in the occurrence of relaxation time [30]. Relaxation time $\tau$ is obtained from the frequency corresponding to $M''_{max}$ value and from the condition $\tau = 1/2\pi f_{max}$, where $\tau$ is the estimated relaxation time for the ionic charge carrier [42]. The shift of $M''_{max}$ towards high frequency with increasing temperature indicates that relaxation time decreases with temperature. The variation of relaxation time with temperature for sample PA-5 is presented in Fig. 6.36 (a) and it reveals that the temperature dependence of relaxation time appears to obey Arrhenius law [43-44]. The activation energy calculated from the slope of the Arrhenius plot is 1.02 eV. The variation of relaxation time $\log \tau$ as a function of composition (AgCF$_3$SO$_3$) salt at 313 K for PA series given in Fig. 6.36(b), reveals that with the increase in conductivity, the relaxation time decreases and vice versa. The relaxation time for sample 10wt% nano-
Fig. 6.36  Variation of relaxation time, \( \tau \) (a) with temperature for PA-5 sample and (b) for different amount of \( \text{AgCF}_2\text{SO}_3 \) in PA-system at 313K.

Fig. 6.37  Variation of relaxation time, \( \tau \) (a) with temperature PAS-20 sample and (b) for different amount of \( \text{SiO}_2 \) PAS system at 313K.

Fig. 6.38  Variation of relaxation time, \( \tau \) (a) with temperature PASP-20 and (b) for different amount of PEG system at 313K.

filler \( \text{SiO}_2 \) in a PAS series shows [Fig. 6.37(a)] a thermally activated process and the activation energy obtained from the slope is observed to be 0.73 eV. It is clear that on addition of nano-filler, new conducting pathways are formed and the activation energy is decreased. The variation of relaxation time as a function of nano-filler \( \text{SiO}_2 \) at 313 K for PAS series in Fig. 6.37(b) shows the non-uniform behavior because of the generation of uneven conducting channels by nano-filler due to random dispersion.

On plasticization (PASP series), the relaxation time decreases with the tempera-
ture indicating again a thermally assisted process as shown in Fig. 6.38 (a). The activation energy obtained from the slope is 0.93 eV, which is higher than that of the sample in PAS series. With the addition of PEG, viscosity of polymer system changes and instead of decreasing, the overall effect is the increase in activation energy. The variation of relaxation time as a function of plasticizer is similar as observed for conductivity in Fig. 6.38 (b).

![Graph](image1)

**Fig. 6.39** Variation of relaxation time, $\tau$ (a) with temperature PLA-1 sample and (b) for different amount of Al$_2$O$_3$ PLA system at 313K.

![Graph](image2)

**Fig. 6.40** Variation of relaxation time, $\tau$ (a) with temperature PLP-15 sample and (b) for different amount of PEG for PLP systems at 313K.

In Lithium salt polymer electrolyte with 1wt% of Al$_2$O$_3$, relaxation time decreases with increase in temperature shown in Fig. 6.39(a). The activation energy in PAL system is found to be very low i.e., 0.12 eV whereas in silver based system (PAS), it is 0.73 eV ascribing that the conduction of lithium ions is faster than that of silver ion because of the smaller size of lithium ions. However, the variation of relaxation time with Al$_2$O$_3$ in PLA series [Fig. 6.39 (b)] is not similar to the variation of conductivity. The activation energy increases from 0.12 eV to 0.5 eV. In PAS and PLA series, the logarithm relaxation time and conductivity do not vary accordingly with composition. Due to the Lewis-acid base interaction between the filler surface and the CF$_3$SO$_3^-$ anion, the nano filler (Al$_2$O$_3$) acts
as anionic acceptors and the surface area of filler grows which is responsible for increase in free volume. The drift of the motion of cations may be random in nature resulting in different relaxation times at different concentration of nano-fillers. For PA, PASP and PLP systems, the variation in relaxation time is observed to be in accordance with the variation in conductivity with the composition.

### 6.4 Scaling of Modulus

Universality of conductivity and dielectric relaxation processes in an ion conducting material can be established using scaling of respective spectra to show whether the processes are independent of charge concentration and/or are thermally activated. According to Sidebottom [45], for any dynamic process, by scaling, one may separate the thermodynamics from the inherent physics involved in the dynamical process which is

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**Fig. 6.41** Plot of $M''/M'_{\infty}$ Vs. $\log(f/f_{\max})$ (a) with temperature PA-5 sample and (b) for different amount of AeCF$_2$SO$_4$ in PA system at 313K.

**Fig. 6.42** Plot of $M''/M'_{\infty}$ Vs. $\log(f/f_{\max})$ (a) with temperature PAS-15 sample and (b) for different amount of SiO$_2$ in PAS system at 313K.
completely described by a single scaling function. To collapse all different data sets to one common curve is an indication that the process can be separated into a common physical mechanism modified only by thermodynamic scales [46].

The scaling in ac conductivity was proposed by Isard [47] for ion conducting glasses. In 1996, Sidebottom et al. [46] observed the conductivity master curve for alkali oxide glasses, polymers and doped crystals and concluded that the ion dynamic processes are independent of temperature.

In 1997, Roling et al. [48, 49] analyzed the scaling properties of the conductivity spectra of sodium borate glasses containing different amounts of sodium oxide. Subsequently, Ghosh and his coworker [50] argued that the scaling formalism of Roling et. al. was unable to merge all of the conductivity isotherms into a single master curve for lithium tellurite glasses, even in the higher composition range. In present case Ghosh’s scaling law [50] is used to scale modulus spectra in which Y-axis (imaginary part of modulus) is scaled by the peak value of \( M' \) and X-axis (frequency axis) is scaled by the frequency corresponding to \( M''_{\text{max}} \).

To have further look into the relaxation mechanism of polymer electrolyte systems, the imaginary part of dielectric modulus (\( M''/M''_{\text{max}} \)) is plotted as a function of frequency \( \log(f/f'_{\text{max}}) \) for 5wt% AgCF₃SO₃ for PA series given in Fig. 6.41(a). The superimposability of all the data points at all temperatures has been observed except a small proportion at higher frequencies which results in a time-temperature superposition (TTSP) principle. The non-merging of compositional plot on a single master curve for different

![Fig. 6.43 Plot of M''/M''_{\text{max}} Vs. log(f/f'_{\text{max}}) (a) with temperature for PASP-15 sample and (b) for different amount of PEG in PASP system at 313K.](image)
compositions of PA series at 303K shown in Fig. 6.41 (b) indicates that the microscopic dynamic process occurring at different compositions do not follow the similar relaxation mechanism. Further modification of PA system by incorporating nano-filler SiO$_2$ to form PAS system, the data points in the modulus plots neither coalesce for different temperatures Fig. 6.42(a) nor for different compositions of SiO$_2$ [Fig. 6.42(a)].

![Graph](image1)

**Fig. 6.44**  Plot of $M'/M'_{\text{max}}$ Vs. log($t/t_{\text{max}}$) (a) with temperature for PLA-2 sample and (b) for different amount of Al$_2$O$_3$ PLA system at 313K.

![Graph](image2)

**Fig. 6.45**  Plot of $M''/M''_{\text{max}}$ Vs. log($t/t_{\text{max}}$) (a) with temperature for PLP-5 sample and (b) for different amount of PEG in PLP system at 313K.

However, the data points for the imaginary part of dielectric modulus ($M''/M''_{\text{max}}$) for 15 wt% PEG in PASP system coalesced at different temperatures [Fig. 6.43(a)] but the plots do not scale with composition (PEG) at all [Fig. 6.43(b)]. In the Lithium based polymer electrolyte (PLA) system, the modulus plots at different temperatures coalesce, while for different amounts of nano-filler (Al$_2$O$_3$) at 313 K do not coalesce as shown in Fig. 6.44 (a) & 6.44 (b). The addition of plasticizer (PEG) into the nano-composite systems i.e., PLP series shown in Fig. 6.45(a), the dielectric modulus ($M''/M''_{\text{max}}$) coalesce at
all temperatures but not for different PEG concentrations [Fig. 6.45(b)].

Fig. 6.46  Plot of $Z''$ and $M''$ vs log $f$ at 318K for (a) PA-7, (b) PAS-5, (c) PASP-10, (d) PLA-3 and PLP-10 samples.

The plotting of data in terms of impedance, electric modulus and dielectric permittivity simultaneously is extremely advantageous for distinguishing the different relaxation processes occurring inside the materials. For an ideal circuit, the impedance and modulus spectroscopic plots i.e., $Z^*$, $M^*$ vs log $f$ plots are completely super imposable and is given by eqn. (as below):
\[ Z'' = R \left( \omega RC \right) / \left( 1 + \omega RC \right)^2 \] and \[ M'' = \left( C_0 / C \right) \left( \omega RC \right) / \left( 1 + \omega RC \right)^2 \] Therefore, comparison of \( Z'' \) and \( M'' \) data is very useful and the Debye like peak shapes in the spectroscopic plots is thus given by the term, \[ \left( \omega RC \right) / \left( 1 + \omega RC \right)^2 \] in the imaginary parts of both \( Z'' \) and \( M'' \). It can be seen that the \( Z'' \) peak is scaled by \( R \) whereas the \( M'' \) peaks are scaled by \( \left( C_0 / C \right) \). But in the case of practical solid electrolytes, they need to be represented by a series array of RC elements in order to account for various layers within the materials [28]. As a result, there is usually a distribution of relaxation times, in which case the maxima in the impedance and modulus spectra no longer coincide. To understand the non-Debye behaviour of the prepared systems, impedance and modulus spectrum have been plotted. Figs. 6.46 (a) to (c) show plots of \( Z'' \) and \( M'' \) vs \( \log f \) for 7wt% of AgCF₃SO₃, 5 wt% of SiO₂ and 10 wt% of PEG for PA, PAS and PASP series respectively. It can be seen from these figures that \( Z''_{\text{max}} \) and \( M''_{\text{max}} \) do not coincide at the same frequency and a broadened modulus spectra is obtained which is an indication of the broad distribution of relaxation times. It also reveals that the \( Z'' \) spectra are broadened on the lower frequency side of the peak maximum and \( M'' \) spectra are broadened on the high frequency side. The large rise in \( Z'' \) occurring at low frequencies is caused mainly due to the electrode polarization [51]. Figs.6.46 (d) and 6.46(e) show plot of \( Z'' \) and \( M'' \) vs \( \log f \) at 313K of 2wt% of Al₂O₃ for PLA series and 25wt% of PEG in PLP series. Here also, the peaks of \( Z''_{\text{max}} \) and \( M''_{\text{max}} \) do not coincide at the same frequency and the broadening is not as large as for silver salt system indicating narrow distribution of relaxation time in lithium system.
References: