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Conductivity and Dielectric behavior of PVdF-HFP/PEMA – Magnesium perchlorate solid polymer electrolyte Films for Mg-ion batteries

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Abstract - *A new series of gel polymer electrolytes (GPEs) composed of Poly (vinylidene fluoride – co - hexa fluoro propylene)(PVdF-HFP) and Poly (ethyl methacrylate) (PEMA) as a host polymer and $Mg(ClO_4)_2$ as a salt are prepared by solution casting technique. The XRD reveals that the crystalline phase of the polymer host and it has completely changed into other side with the addition of the dopant. The formation of the polymer and salt complex has been confirmed by FT-IR spectral studies. The conductivity vs temperature plots are obey the Arrhenius relation. Arrhenius plot shows the decrease in activation energy. The dielectric behavior of the sample is analysed using dielectric permittivity (ε'), dielectric loss (ε'') and electric modulus (M'') of the samples. The high frequency semi-circle in the impedance plot is due to the bulk effect of the material and the depression in the semicircle shows the non-Debye nature of the materials. The ionic conductivity is found to be 2.8×10^{-5} Scm^{-1} at room temperature.*

Keywords - *Solid polymer electrolytes, PVdF-HFP, Magnesium perchlorate, dielectric, FTIR*

I. INTRODUCTION

Presently a great deal of scientific interest is emergent a new energy storage system [1, 2]. Because the globe moves towards the electricity and transportation based on renewable sources of energy and also the world require lower cost, high energy density electrical storage is attractive further apparent and eco friendly. Many types of energy storage systems are available, since the battery has much more attention and also preferable one. The Magnesium battery has numerous promising properties [3]. Compared to Li ions, the Mg has two electrons per atom, so they are potentially more efficient energy-storage systems. Then the Mg is relatively earth abundant material, cheap, lightweight, environmentally friendly and also safer [4, 5].

In batteries, the electrolytes play an important role and also it act as a medium for the transfer of charges a pair of electrodes i.e., anode and cathode. To improve the mechanical strength, increasing the conductivity and also retain the crystallization of polymer chains in the following way, i.e., blending of two polymers, Co-polymerization, comb formation and polymer alloying, nano fillers [6]. To design the polymer electrolytes with a wide variety of polymer blends. The polymer blending is an effective technique. The polymer electrolytes have many advantages compared with liquid, it has a longer shelf life, leak proof and easy fabrication into a variety of dimension and shapes.

The manifestation of improving the properties depends upon the miscibility of the blend, moreover, the changing of the blend composition that give rise to a range of properties in the final product [7]. The suitable selection of the polymer, which may have the advantage of lowering the degree of crystallinity. The Poly (vinylidene fluoride-co-hexa fluoro propylene) (PVdF - HFP) has fascinated a lot of researchers because of it has low crystallinity, high free volume due to the incorporation of an amorphous phase of HFP, good compatible nature, high mechanical stability, high dielectric value ($\varepsilon \sim 8.4$) helps to dissolve more ionic species in the polymer matrix, support to the ion transport and also good electrochemical stability [8, 9]. on the other hand the PEMA exhibit very good mechanical, excellent chemical resistance, high surface tension, high optical transparency, elasticity, good adhesion onto substrates and electrochemical. The PEMA reveal very good mechanical and electro-chemical properties compared with PMMA [10, 11].

II. MATERIALS AND EXPERIMENTAL TECHNIQUE

PVdF-HFP, PEMA and Magnesium perchlorate $Mg(ClO_4)_2$ were used as starting materials and were purchased from Sigma Aldrich and dried at 90°C for 5 hrs. The polymer electrolytes were prepared using a solution cast technique. The THF (Tetra hydrofuran) solvent was used in this work. The appropriate amount of polymers were dissolved separately in solvent and mixed well. Then the fixed amount of salt was added to the polymer mixture. The mixture was stirred up to 12 hrs to obtain a homogeneous solution. The solution was then poured into the glass petri dishes and evaporated slowly under 50°C for 5 hrs under vacuum. The polymer electrolyte samples were then transferred into desiccators. The compositions of the polymers are shown in the table 1.

In order to calculate the ionic conductivity, this was carried out with the help of stainless steel blocking electrodes using a computer controlled autolab type III. Potentiostat in the frequency range of [10Hz – 100Hz] over the temperature range of 303 – 363K. The amorphous nature of the blend polymer electrolytes has been investigated by XRD analysis with the help of X'pert PROPAN analytical X-ray diffractometer. The complex formation between the polymer and salt has been confirmed by FTIR spectra using SPECTRA RXI, Perkin Elmer spectrophotometer in the range of 400-4000 cm^{-1}.

Table 1. The composition of the Polymers

Sample code	PVdF-HFP (wt%)	PEMA (wt%)	$Mg(ClO_4)_2$ (wt%)
S_1	100	0	8
S_2	75	25	8
S_3	50	50	8
S_4	25	75	8
S_5	0	100	8

III. RESULT AND DISCUSSION

A. XRD Analysis

The X-ray diffraction patterns of the Pure PVdF-HFP, PEMA, $Mg(ClO_4)_2$ and their complexes are shown in figure 1. The peaks at 20.2˚and 39˚correspond to (110) and (021) corresponds to semi-crystalline nature of PVdF-HFP shown in figure 1. The pure PEMA represents the amorphous nature. Pure $Mg(ClO_4)_2$ shows high intense peaks at angles 2θ = 10.7˚, 21.55˚, 22.94˚, 31.63˚, 34.18˚, 39.40˚, 49.86˚, 51.99˚, 55.41˚, which reveal the crystalline nature of the ionic salt. The different blend ratio of the polymers, that induces a significant disorder in the polymer structure; hence the crystallinity of polymer decreases as evident from fig 4.1 (S_1 – S_5). Invariably in all complexes a less intense and broad peak has been observed at 2θ = 20.9◦corresponding to (101) in all complexes. The broad XRD peak revealed that the polymer blend PVdF-HFP (69)/ PEMA (23)/ $Mg(ClO_4)_2$ (8) (S2) is more amorphous. The amorphous nature results in greater ionic diffusivity with high ionic conductivity, as amorphous polymers have flexible backbone. The peaks corresponds to salt have completely disappeared in the polymer complexes, this reveals the interaction between the polymer and the salt. When $Mg(ClO_4)_2$ dissolves in the polymer host, the interaction between PVdF-HFP/PEMA host matrix and $Mg(ClO_4)_2$, leads to a decrease of the intermolecular interaction among the polymer chains which reduces the crystalline phase and hence increases the amorphous region [12].

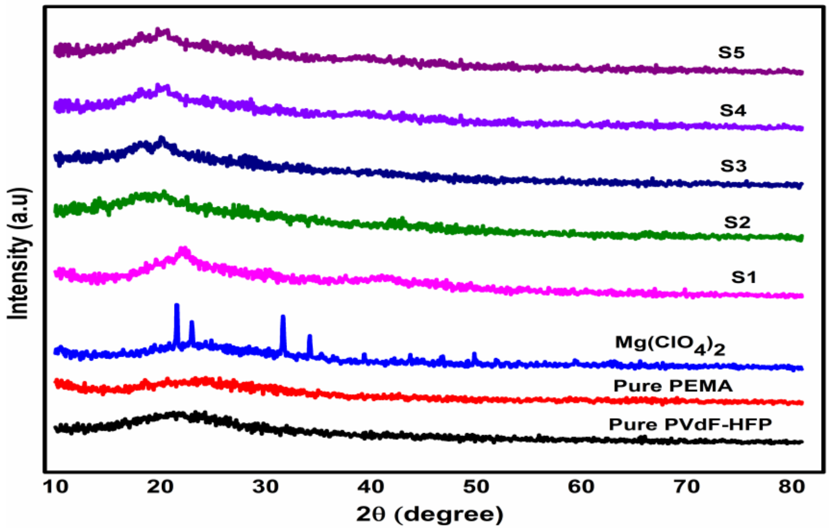

Figure 1. XRD pattern of pure PVdF-HFP, PEMA, $Mg(ClO_4)_2$ and PVdF-HFP/PEMA with different concentration of $Mg(ClO_4)_2$

B. Fourier Transform Infrared Spectroscopy

The FTIR transmittance spectra for pure PVdF-HFP, PVAc, $Mg(ClO_4)_2$ and their complexes of EMITF are shown in Figure 2(a-h) respectively. The crystalline phase of the pure PVdF-HFP polymer is identified by the vibrational bands at 1402, 877, 517 cm^{-1} respectively. Symmetrical stretching of –CF, $-CF_2$ groups, vinylidene group, bending vibrations of $-CF_2$ groups. The crystalline phase of VdF unit is identified by the vibration bands of 981, 759 and 618 cm^{-1} are due to the non-polar trans-gauche conformation of the semi-crystalline PVdF-HFP.

The vibration bands of 1732, 1487, 942 and 762 cm^{-1} are attributed to the C=O carbonyl group, $-CH_2$ scissoring, $-CH_2$ wagging and $–CH_2$ rocking modes of pure PEMA [13]. In the polymer complexes some of the bands are shifted slightly, some bands disappear in the complexes. This observation indicates the substantial conformational changes in the crystalline texture of the PVdF-HFP. Due to the interaction with the PEMA and salt electrolytes. The stretching vibration mode of ClO_4^- anion observed in the range of 650-600 cm^{-1} has been probed to get the information associated with the degree of salt dissociation in the polymer electrolyte. The above observed peaks are shifted in S_1, S_2, S_3, S_4 and S_5. The changes in the frequently characteristics of the electrolyte and it confirm the complexation in the measured polymer electrolytes .

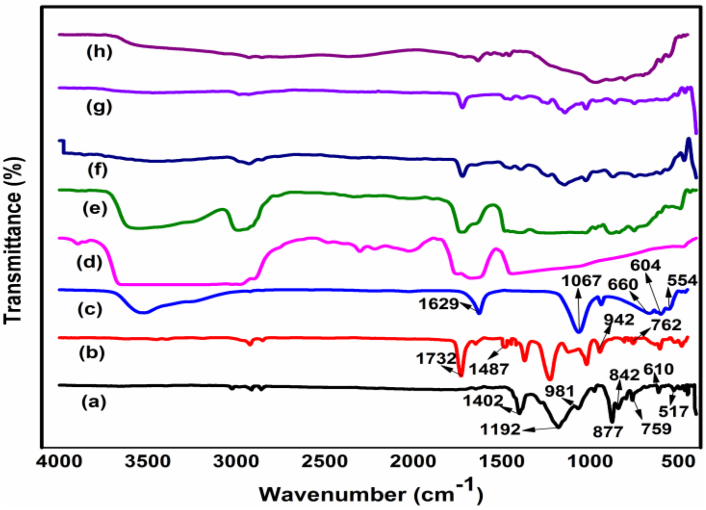

Figure 2. FTIR spectra of pure PVdF-HFP, pure PEMA, pure $Mg(ClO_4)_2$ and PVdF-HFP/PEMA with various concentration of $Mg(ClO_4)_2$

C. Conductivity studies

Figure.3 shows the room temperature complex impedance plots of the prepared samples. The frequency response analyses carried out over a wide frequency range from 100 Hz to 300 KHz. In this figure, the semicircular portions corresponding to the high frequency region are absent, which indicates that the majority of the current carriers in the electrolyte medium are ions and that the total conductivity is mainly due to ion conduction. The obtained spike corresponding to the lower frequency region is ascribed to double layer capacitance in a cell with an ion-blocking electrode configuration. The ions present in the polymer segments in amorphous region of the complex are responsible for the increase in conductivity. For that blend polymer electrolyte (S_2) the relative number of effective charge carriers diminishes at equivalent levels of segmental mobility. For the other blend polymer electrolyte, the decrease in conductivity is observed due to the increase in the fraction of ion pairs as neutral species do not contribute to ionic transport. The remaining free ions and ion pairs are dominant species present in the electrolyte. This is due to the increase in the electrolyte viscosity resulting from the formation of transient cross links preferably by linking one or more polymeric chains via positively charged triplets. The decrease in ionic conductivity could be due to an increase in ion-ion interaction that blocked the motion of ions and reduced the conductivity pathway [14]. The activation energy for all the prepared polymer electrolytes is calculated by linear fit of VTF plot (figure 5). The activation energy decreases. This is due to the increase in amorphous nature of the polymer electrolyte. The activation energy is found to be low of the order of 1.69 eV for the highest conducting sample. The conductivity and the activation energy values are tabulated in table 2 and the plot is shown in figure 4. The room temperature conductivity is found in the range of 10^{-6} Scm^{-1}

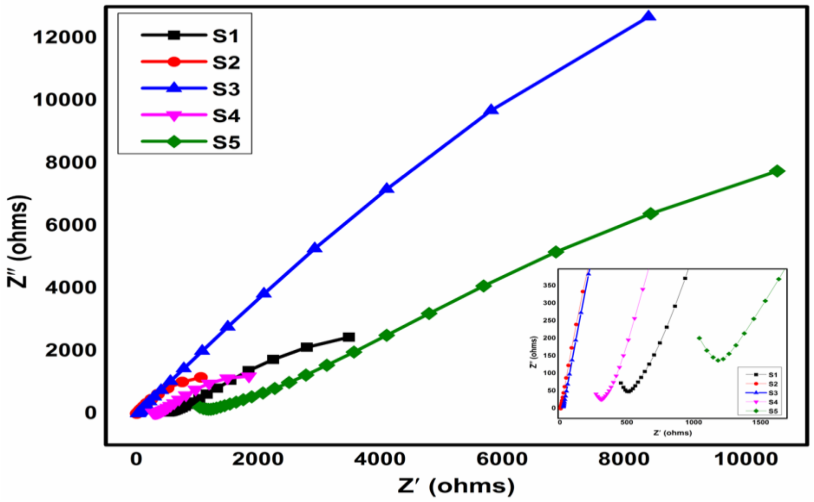

Figure 3. Room temperature of the complex impedance plot of the prepared samples.

Table 2. Conductivity and Activation energy values of solid polymer electrolyte films

Polymer composite electrolytes	**Ionic conductivity (S/cm)**							**Activation energy(Ea) (eV)**
	303K	**313K**	**323K**	**333K**	**343K**	**353K**	**363K**	
S_1	**0.223×10^{-7}**	**0.256×10^{-7}**	**0.578×10^{-7}**	**0.751×10^{-7}**	**1.502×10^{-7}**	**3.432×10^{-7}**	**1.201×10^{-6}**	**3.342**
S_2	**0.845×10^{-6}**	**1.024×10^{-6}**	**1.672×10^{-6}**	**2.454×10^{-6}**	**3.867×10^{-6}**	**1.768×10^{-5}**	**2.612×10^{-5}**	**1.694**
S_3	**1.192×10^{-7}**	**2.095×10^{-7}**	**4.190×10^{-7}**	**1.892×10^{-6}**	**2.129×10^{-6}**	**3.247×10^{-6}**	**4.042×10^{-6}**	**3.059**
S_4	**2.037×10^{-7}**	**2.901×10^{-7}**	**3.091×10^{-7}**	**3.448×10^{-7}**	**1.048×10^{-6}**	**2.588×10^{-6}**	**2.902×10^{-6}**	**5.076**
S_5	**2.017×10^{-7}**	**3.493×10^{-7}**	**4.042×10^{-7}**	**5.802×10^{-7}**	**6.145×10^{-7}**	**1.712×10^{-6}**	**2.034×10^{-6}**	**7.177**

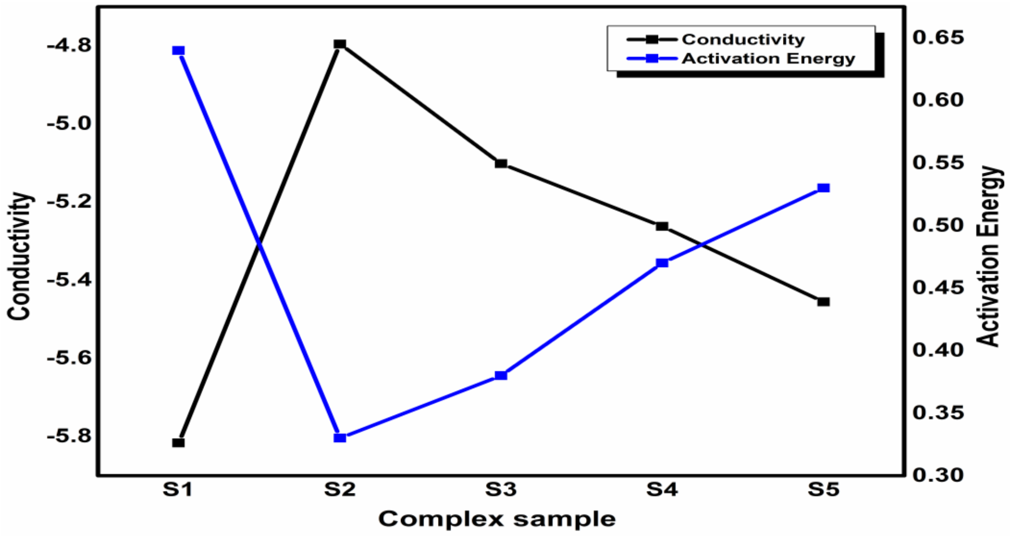

Figure 4. The variation of the conductivity and activation energyt for the prepared polymer electrolytes

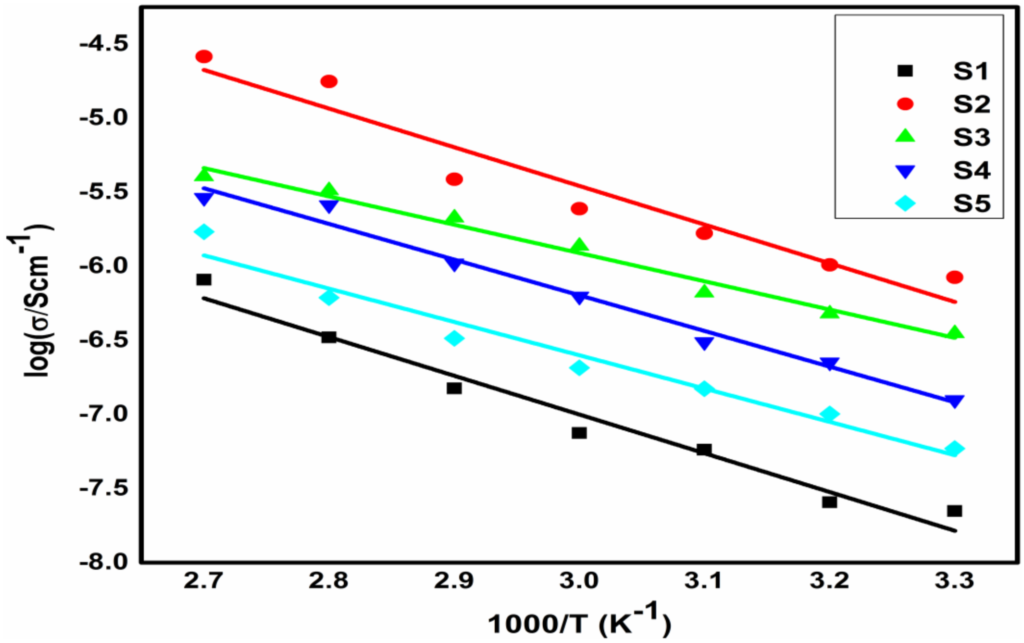

Figure 5. Temperature dependent ionic conductivity plot of the prepared samples.

D. Dielectric Spectra Analysis

The dielectric behavior of a material is broadly distinguished by complex permittivity as

$$\varepsilon^* = \varepsilon' - i\varepsilon''$$

Where, ε′ - dielectric constant, ε″ - dielectric loss

Dielectric relaxation and frequency dependent conductivity is sensitive to the apparent movement of charge species and dipoles present in the polymer dielectric relaxation is a consequence of the reorientation process of dipoles in the polymer chains, which shows maxima in ε″ spectra. Hence the analysis of the relative permittivity of polymer electrolyte helps to understand the correlation between ionic relaxation time with conductivity and the polarization effects at the electrode/electrolyte interface. Where ε′, ε″ at are real and imaginary components represent storage and loss of energy in each cycle of applied electric field. Figure 6 and 7. shows the variation of dielectric permittivity (ε′) and dielectric loss (ε″) with frequency (logω) for PVdF-HFP/PEMA complex with 8 wt% of $Mg(ClO_4)_2$ at room temperatures and the frequency dependence of imaginary part dielectric loss (ε″). The increased value of ε′ and ε″ at the low frequency part is due to dielectric polarization. The reduction of dielectric permittivity (ε′) with increasing frequency is due to the electrical relaxation process. Under the inference of an electric field, ions tend to defuse and migrate along the orbit. But the ions are unable to cut across the electrode-electrolyte interface due to the stainless steel electrode.

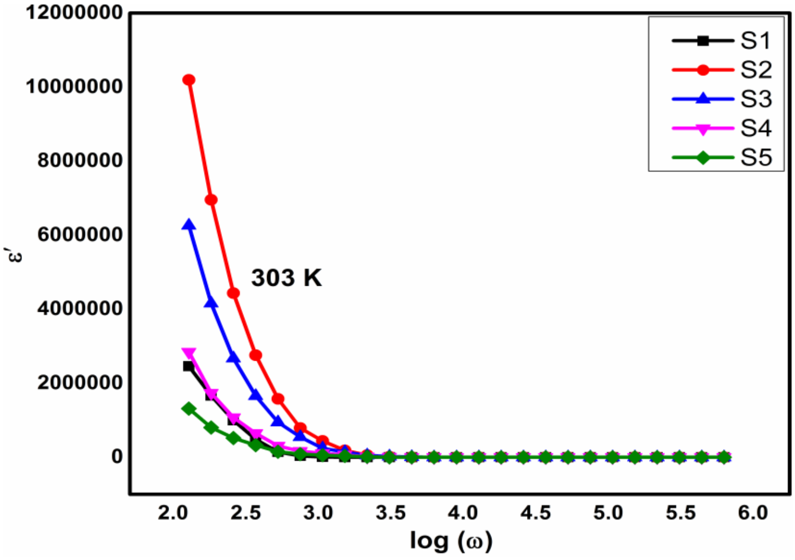

Figure 6. Variation of dielectric constant ε′ of PVdF-HFP and Mg(ClO$_4$)$_2$ as a function of frequencies at room temperature.

The charge density increases rapidly when the thickness of the electrolyte is greater than that of the hetero charge layer which results in electrode of the subject at the interface. The dielectric constant result is in agreement with increments of the conductivity of the electrolyte system. The observed decrease in the value of ε′ and ε″ at above 100 KHz can be ascribed by the decrease in the in the charge accumulation at high frequencies, which is already observed in the impedance plot [15].

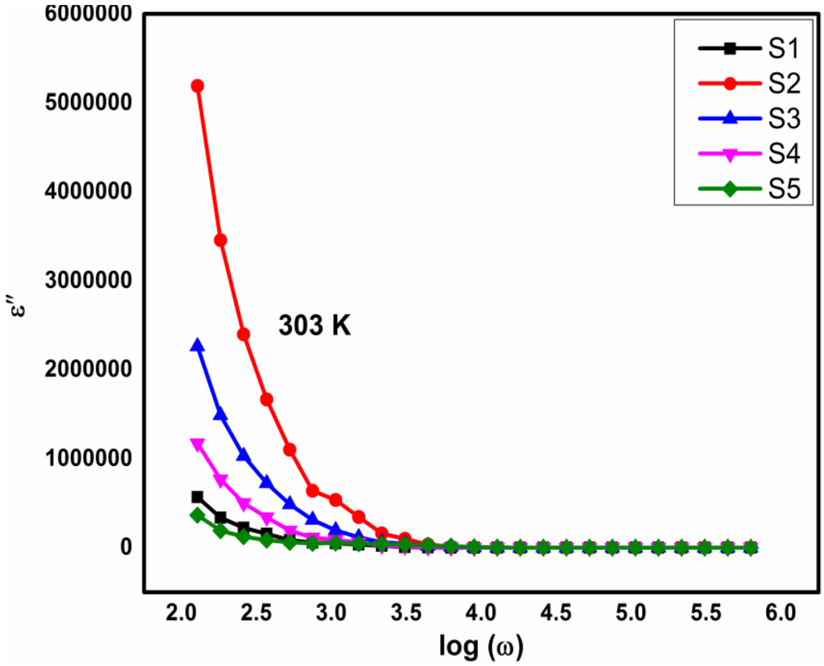

Figure 7. Variation of dielectric loss of ε″solid polymer system PVdF-HFP and Mg(ClO$_4$)$_2$ as a function of frequencies at room temperature.

E. Dielectric Modulus Analysis

A further analysis of electric behavior would be more successfully achieved by dielectric modulus (M′ and M″), which inhibited the effect of electrode polarization to give a clear indication of electrical property of the polymer electrolyte. The dielectric modulus spectrum was shown in figure 8 and 9.

The dielectric modulus was analyzed using the pattern

$$M' = \varepsilon'/ (\varepsilon'_2 + \varepsilon''_2)$$

$$M'' = \varepsilon''/ (\varepsilon'_2 + \varepsilon''_2)$$

Where calculated values of real part M′ and imaginary part M″ versus log(ω) for PVdF-HFP/PEMA complex with 8wt% of $Mg(ClO_4)_2$ at room temperatures. From the spectra, it is noted that both M′ and M″ increase at higher frequencies and decreases with increasing temperature. Increasing module (M′ and M″) values at higher frequencies might be assigned to the bulk effect with the wage increase of temperature, height decreases suggesting a multitude of relaxation mechanism, lower frequencies, it is observed that modules values are vicinity of zero indicating that the issue of polarization is small, which is the main advantage of M′ and M″ modules studies [16].

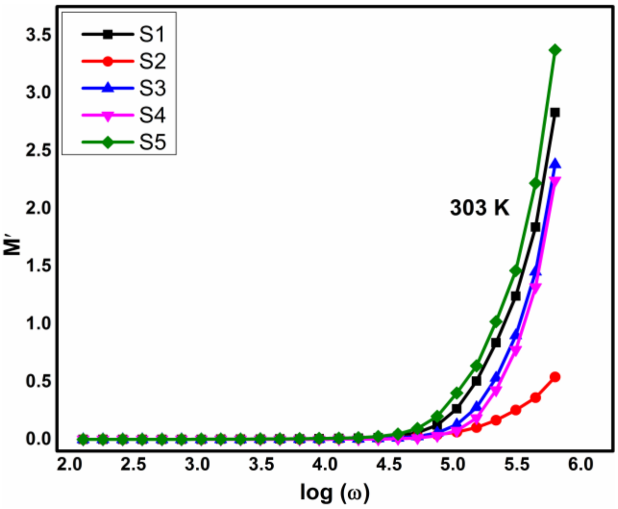

Figure 8. Variation of real part of electric modules M" for solid polymer system at room temperature.

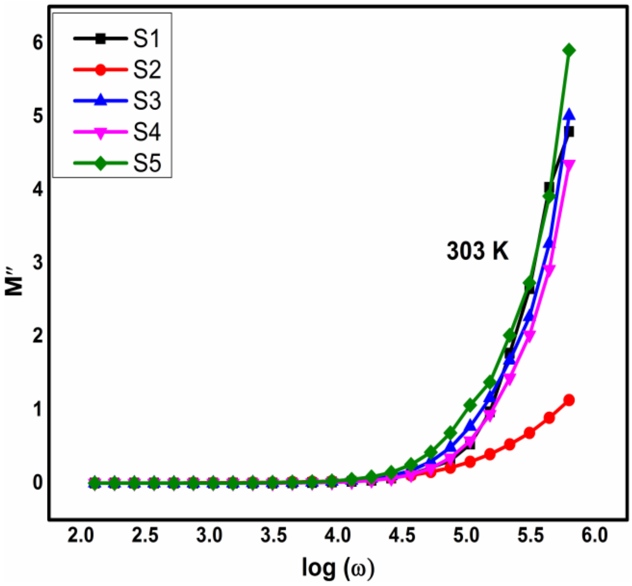

Figure 9. Variation of imaginary part of electric modules M" of solid polymer system at room temperature.

F. Loss tangent spectra

The dielectric relaxation parameter of the polymer electrolytes can be obtained from the following relation

$$\tan\delta = \varepsilon''/\varepsilon'$$

The variation of the tanδ with frequency for all the prepared electrolytes at room temperature is shown in figure 10. It has been observed that the tender increase with increasing frequency it reaches the maximum. Then further increase the frequency also decreases. For maximum dielectric loss at a particular temperature the loss tangent peak is described by the relaxation. This relaxation time (τ) can be calculated by using the following relations, $\tau=1/\omega$ is the relaxation time, ω is the angular frequency of the applied electric field. As the temperature increases the charge carrier has been thermally activated and the loss tangent peak shifts towards higher frequency. The peak is shifted to the high frequency range with temperature increases, which indicates the reducing of relaxation time and this shifting of peaks is attributed to the fast segmental motion coupled with the mobile ion.

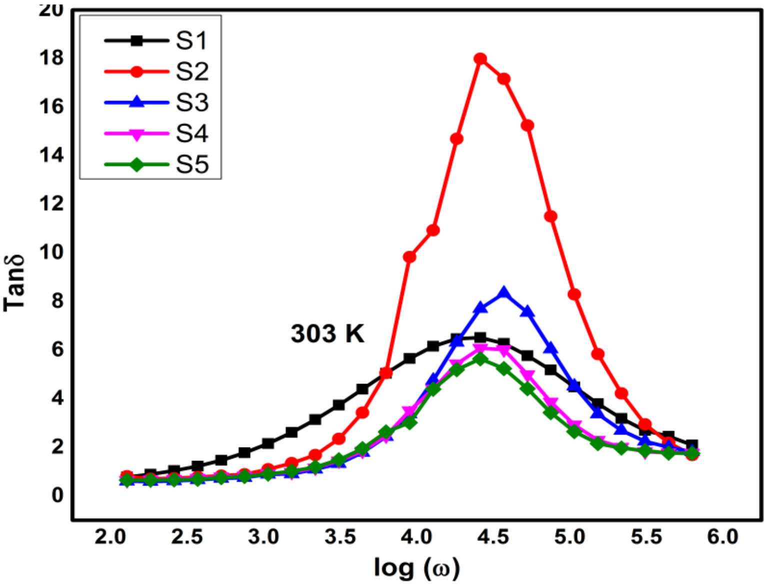

Figure 10. Frequency dependent loss tangent spectra of solid polymer electrolytes at room temperature.

IV. CONCLUSION

The novel blend polymer electrolytes based on Poly(vinylidene fluoride-co-hexafluoropropylene)/Poly(ethyl methacrylate) have been prepared by using the solvent casting technique for magnesium ion battery applications. The structural and complex formation of the polymer matrices has been confirmed by XRD and FTIR. The high ionic conductivity was observed for the PVdF-HFP (69)/PEMA (23)/$Mg(ClO_4)_2$ (8) – (S_2) blend polymer electrolyte. The temperature dependent ionic conductivity shows the VTF relation, which indicates that the ions transport together. With the kinetical movement of polymer chain. The dielectric studies show the conductivity relaxation. From the tangent spectra, it obeys the non-Debye relation.

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