

Ion Conducting Mechanism of Carboxy Methylcellulose Doped With Ionic Dopant Salicylic Acid Based Solid Polymer Electrolytes

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Abstract

A conducting polymer electrolyte based on carboxy methylcellulose (CMC) complexed with different concentrations of salicylic acid (SA) has been investigated. The ionic conductivity of the solid polymer electrolyte (SPE) of pure CMC obtained at room temperature is $8.49 \times 10^{-10} \text{ S cm}^{-1}$. The maximum ionic conductivity achieved in the solution-cast films at room temperature is $9.50 \times 10^{-8} \text{ S cm}^{-1}$ for CMC incorporated with 7 wt. % SA. In addition, the temperature dependence of the SPE system exhibits Arrhenius behavior. Dielectric data were analyzed using complex permittivity ϵ^* and complex electrical modulus M^* for the sample with the highest ionic conductivity at various temperatures and found is non Debye behavior.

Keywords: polymer electrolyte; ionic conductivity; transport properties.

1. Introduction

In the world of a new era, there are so many product of battery with high cost fabrication and not environmentally friendly. The widespread use of batteries has created many environmental concerns, such as toxic metal pollution. Battery manufacture consumes resources and often involves hazardous chemicals. Used batteries also contribute to electronic waste (Stephan and Nahm, 2006). Electrolytes used in the commercial batteries and electronic devices today are high in conductivity, but it is hazardous and non-biodegradable, thus, it is danger to the environment and also human. One of the main issues of concern in studies of polymer electrolytes is the question of what types of polymers might be useful. A distinctive structural feature of cellulose materials is heterogeneity owing to its fiber structure (Nigmatullin et al, 2004). Several researches done on this very famous cellulose were largely investigated by various scientists around the world due to its mysterious and unexplored properties. The solubility behavior of cellulose was the main concern of the previous researches. Nevertheless, this behavior was extensively studied and several solutions were proposed to increase the solubility. Work done by (Miller and Krotcha, 1997) and some other researches concentrate on the application of cellulose as coatings of food product. Therefore, it is a very urging to come up with a very abundant known polymer as the main composition for an ionic conductor.

The potential of CMC as SPE will be studied extensively by means of conductivity. Studies on SPEs have been improving actively due to their potential application in solid state electrochemical cells, high energy density batteries, fuel cells and electro chromic devices (Aziz et al, 2010; Michael et al, 1997). The cellulose was found to act as sacrificing agents retarding moisture loss from food products. Carboxyl methylcellulose (CMC) is a naturally occurring polysaccharide and the most abundant organic substance on the earth. Due to the abundance, low cost and easier process ability, cellulose based electrolytes is expected to bring better future of green nations than non biodegradable, toxic and harmful materials used in the commercial batteries today (Siddhanta et al., 2009).

In this study, solid polymer electrolyte or SPE is presented to overcome this problem. Thus, development of cellulose or cellulose derivative based electrolyte is an evolutionary research where the well-known insulator material (cellulose is the wall cell of plant – wood) is manipulated to be an ionic conducting materials. The CMC would be explored in term of its electrical conductivity as well as to improve previous researches in understanding the potential of this material as an ionic conductive polymer. The introduction of ionic dopant into the CMC would expect to increase the cellulose film electrical properties for further usage of the SPE in today's electrochemical application.

2. Methodology

2.1 Sample Preparation

1 g of CMC from Acros Organics Co. was dissolved in distilled water. Then, varied amount of salicylic acid (SA) in weight percent (1-9 wt. %) was added in CMC solution. The mixtures were stirred continuously with magnetic stirrer and bar until complete dissolution became homogenous. The mixtures were then poured into several Petri dishes and allowed to evaporate slowly at ambient temperature for films to form. To ensure there is no water content in biopolymer films, films were kept in desiccators. The composition of the samples and their designation are tabulated in Table 1.

2.2 Electrical Impedance Spectroscopy

The polymer electrolyte samples were cut into small discs of 2 cm diameter and sandwiched between two stainless steel electrodes under spring pressure. The samples were characterized via Electrical Impedance Spectroscopy (EIS) using HIOKI 3532-50 LCR Hi-Tester interfaced to a computer in a frequency range between 50 Hz and 1 MHz. The measurements were carried out at room temperature of 303K until 393K. The conductivity of electrolyte can be calculated from the equation (Samsudin and Isa, 2012)

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

Here A (cm^2) is the electrode-electrolyte contact area of the film and t its thickness. R_b is bulk resistance obtained from the complex impedance plot (Cole-Cole plot) at the intersection of the plot and the real impedance axis.

3. Result and Discussion

3.2 Ionic conductivity study

Figure 1 depicts the semicircle and spike for the sample (E) at room temperature. Two well defined regions can be observed, a high frequency incomplete semicircle followed by a spur (an inclined spike) at the low frequency region. The semicircle obtained is related to the conduction process of the polymer electrolyte, indicating that the ions have plural relaxation time (Armstrong, 1974). Since the blocking electrodes have been used in the impedance analysis, the electrolyte or electrode interface could be regarded as a capacitance (Samsudin et al., 2012). When the capacitance was ideal, it should show a vertical spike in the impedance plot. However, the spike inclined at an angle (θ) less than 90° has been found instead of the vertical spike which may be attributed to the non-homogeneity or roughness of the electrolyte or electrode interface. The bulk resistance, R_b can be retrieved from the intercept of high frequency semicircle and low frequency spike on the Z_r axis and equation (1) was used to calculate the conductivity, σ and bulk resistance, R_b of the sample at room temperature. The conductivity, σ of the sample at room temperature is illustrated in Figure 2.

There are several factors that influence the ionic conductivity, such as ionics conducting species concentration, cationic or anionic types charge carriers, the charge carrier's mobility and the temperature (Samsudin et al., 2012; Ellen et al., 2010). From Figure 2, it can be observed that the ionic, conductivity increases with addition of SA; this can be attributed to the increase in the number of mobile charge carriers. The highest conductivity at the room temperature is $9.5 \times 10^{-8} \text{ Scm}^{-1}$ for sample (D) containing 7 wt. % of SA. With the addition of the more 7 wt. %, the conductivity starts to decrease. In the case of non-aqueous polymer electrolytes, the dissociation of salt shall depend upon the dissociation constant of the salt, dielectric constant of the solvent and nature of the dopant. According to (Yahya and Arof, 2003), the dependence of ionic conductivity on the salt concentration provides information on the specific interaction among the salt and the polymer matrix.

The initial increase of ionic conductivity can be explained by association of ions at higher salt concentration, which leads to the formation of ion clusters and the number of charge carriers and their mobility. The decrement of conductivity is due to the increase amount of SA contribute to the over crowded of the ionic dopants thus reduces the number of charge carriers further gives limitation of the mobility of ions (Idris et al., 2009).

The temperature-dependent ionic conductivity measurement was used to analyze the mechanism of ionic conduction of polymer electrolytes. Figure 3 shows the plot of log conductivity, σ versus $1000/T$ for the CMC-SA based on SPE system in temperature range 303 K to 393K. The increases in conductivity with temperature in CMC-SA SPE system can be due to the increases in the free volume of the system. Thus, the segmental motion either permits the ions to hop from site to another or provides a pathway for ions to move (Vieira et al., 2007). The log conductivity, σ versus $1000/T$ was found to be a straight line with regression value and this linearity are observed in all of the polymer electrolytes. For other results was shown indicates that is no phase transition occurs in the polymer matrix or domains were formed by addition of salts. From Figure 3, the linear relationship where the values of R^2 found to be close to unity confirms that the variation in ionic conductivity with temperature obey the Arrhenius-type (Hema et al., 2008; Samsudin et al., 2011). It can be observed that the conductivity of the electrolyte increases with increasing to all composition given by the relation:

$$\sigma = \sigma_0 \exp(-E_a/kT) \quad (6)$$

where σ_0 is the pre-exponential factor, E_a the activation energy and k is the Boltzmann constant.

The activation energy, E_a which is combination of the energy of defect formation and the energy for migration of ion was calculated from the slope of the log conductivity, σ versus $1000/T$ plot for all the samples. E_a is the energy required for an ion to begin movement. In the context of polymer electrolytes, the ion is usually "loosely bound" to site with donor electrons (Buraidah et al., 2009). The movement from one site to another result in the conduction of charge and the energy for this conduction is the E_a . When the ion has acquired sufficient energy, it is able to break away from the donor site and move to another donor site (Samsudin and Isa, 2012). The E_a value for all samples is listed in Table 2. It was noticed from Table 2 that E_a for the conduction decreased gradually with increment an ionic conductivity of CMC-SA SPE system. Decreasing the value of E_a implies that the ions highly conducting samples require lower energy for migration. Since the ion transfer is greatly affected by the polymer segmental motion: an electrolyte with lower value of E_a implies rapid ionic conduction and then increase conductivity to the higher value. This is in agreement with the fact that the amount of ions in the biopolymer electrolyte increases with increasing in salt content, the energy barrier for the proton transport decreases and leading to a decrease in the activation energy. The low activation energy for CMC-SPE system is also due to the completely amorphous nature of polymer electrolyte that facilitates the fast H^+ ion motions in the polymer network.

Ionic conductivity of an electrolyte depends on the number of mobile and mobility of ions as expressed by the equation

$$\sigma = \eta q \mu \quad (4)$$

where σ is ionic conductivity, η is number, μ is mobility of mobile ions and q is electron charge. It is a very important parameter in understanding the transport properties of PEs (Shuhaimi et al., 2010). The number of mobile ions was estimated from the Rice and Roth, 1972 equation shown below

$$\sigma = \left(\frac{2(Ze)^2}{3kTm} \right) \eta E_a \tau \exp(-E_a/kT) \quad (5)$$

Here Z , E_a and m is the valency, activation energy and mass of the conducting ion respectively. ℓ is the mean free path or distance between coordinating sites (electron donating atoms) and $v = \sqrt{2E_a m}$ is velocity of the free ions. In using the Rice and Roth equation, ℓ for CMC must be known. Yokota et al., 2007 [20], had found that the length of 40 rigid chain segments of bendable molecular cellulose is (60 ± 15) nm. From this result, the length of one chain segment is 1.5 nm is used in the Rice and Roth equation for of ℓ .

Table 2 depict the ionic mobility, μ and diffusion coefficient, D and found to be related with the ionic conductivity of MC-GA PCBES system.

According to Majid and Arof, 2004 and Samsudin et al., 2012, the ionic conductivity in a polymer is generally linked to the number of ions and the mobility of conducting species in the polymer complexes. However, in this study, the number density of mobile ions does not give significant contribution to the conductivity compared to diffusion coefficient and mobility. These results clearly reveal that the conductivities of the CMC–GA SPE are strongly influenced by the diffusion coefficient and its mobility (Ellen et al., 2010; Selvasekarapandian et al., 2005). Instability the value of η in CMC-SA SPE system with the conductivity can be attributed to the increment of SA composition made; it does not favor the association of ions count, but it shows the increment of mobility and diffusion parallel with the conductivity (Samsudin et al., 2011). When conductivity increased, irregular value of η increasingly hard to move and this reflected in the E_a values become smaller that required the ions to move with higher in μ . The decrease in conductivity value at higher salt content can be explained by aggregation of the ions, leading to the formation of ion cluster where the dipole interaction between the protons in the medium increases, which reduces the ion mobility and thus the conductivity (Selvasekarapandian et al., 2005).

3.3 Dielectric study

The study of dielectric behavior in polymer electrolytes helps to understand the conductivity behavior. The variation of dielectric constant, ϵ_r and loss, ϵ_i are shown in Figure 4 (a) and (b). From Figure 4, it can be observed that there were no appreciable relaxation peaks observed in the frequency range employed in this study. Both ϵ_r and ϵ_i rise sharply at low frequencies indicating that electrode polarization and space charge effects have occurred confirming non-Debye dependence (Khiar et al., 2006) implying that the conductivity exhibits relaxation that is non-exponential in time. On the other hand, as frequency increased, the rate of reversal of the electric field increased, and so there was no time for charge to build up at the interface. Therefore, the polarization due to charge accumulation decreased that lead to the decreasing in the value of dielectric loss (Khiar and Arof, 2010).

Further analysis of the dielectric behavior would be more successfully achieved using the formulation of electrical modulus, which suppresses the effect of electrode polarization (Ramly et al., 2011). The variations of real, M_r and imaginary, M_i parts of electrical modulus are depicted in Figure 5 respectively. Both plots show an increase at the higher frequency end, with well defined dispersion peaks observed in the imaginary plots. The presence of such relaxation peaks in the imaginary plots indicates that the sample is ionic conductor (Ramesh and Arof, 2001). From the Figure 5, both M_r and M_i approached to zero at low frequency and showed an increase at the higher frequency. The plot exhibited low value at lower frequencies which might be due to the large value of capacitance associated with the electrodes. This further confirmed the non-Debye behavior in the samples. The frequency range on the lower side of the peak frequency determined the range in which charge carriers were mobile over long distances (Khiar et al., 2006).

4. Conclusion

Carboxy methylcellulose (CMC) based solid polymer electrolyte (SPE) was prepared by solution casting technique, with doping of different composition of salicylic acid (SA). XRD measurements confirmed that the SPE system predominantly amorphous in nature. The amount of SA has been found to influence the proton conduction and the high ambient temperature ionic conduction value of $9.50 \times 10^{-8} \text{ S cm}^{-1}$ has been obtained for CMC with 7 wt. % SA composition. The temperature dependence of ionic conductivity of these electrolytes exhibited Arrhenius behavior. Conductivity enhancement in the CMC–SA solid polymer electrolyte is caused not only by the increase in the concentration of free ions but also by the increase in mobility and diffusion coefficient of ions. The dielectric behaviors of the prepared samples show strong dependence on frequency and temperature. The frequency dependence of ϵ^* and M^* is non-Debye type.

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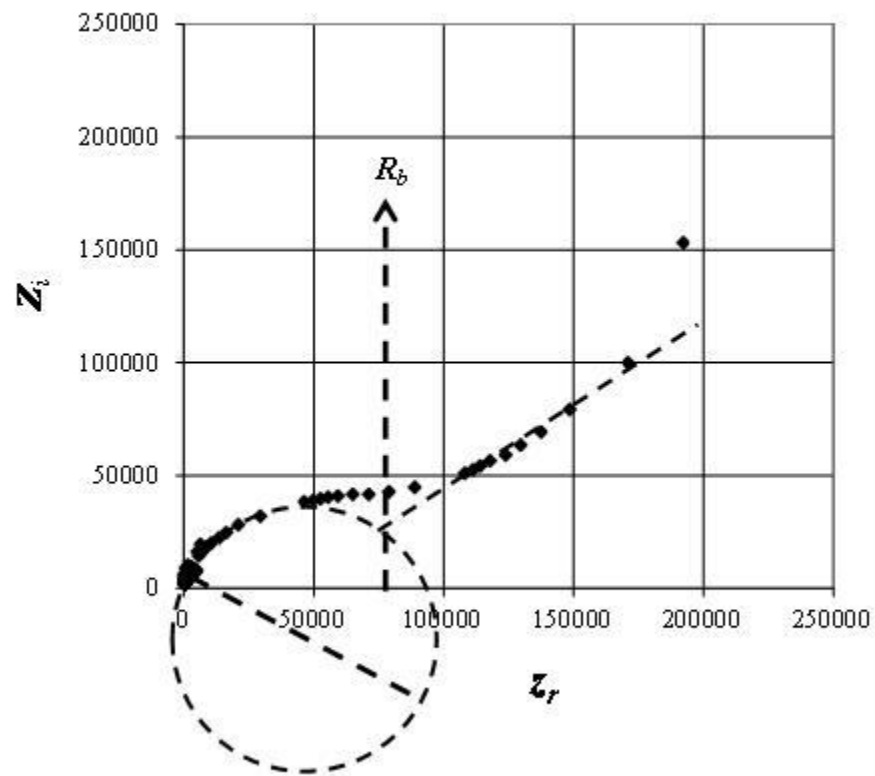


Figure 1: Cole-Cole plot for sample containing 7 wt. % of SA at ambient temperature

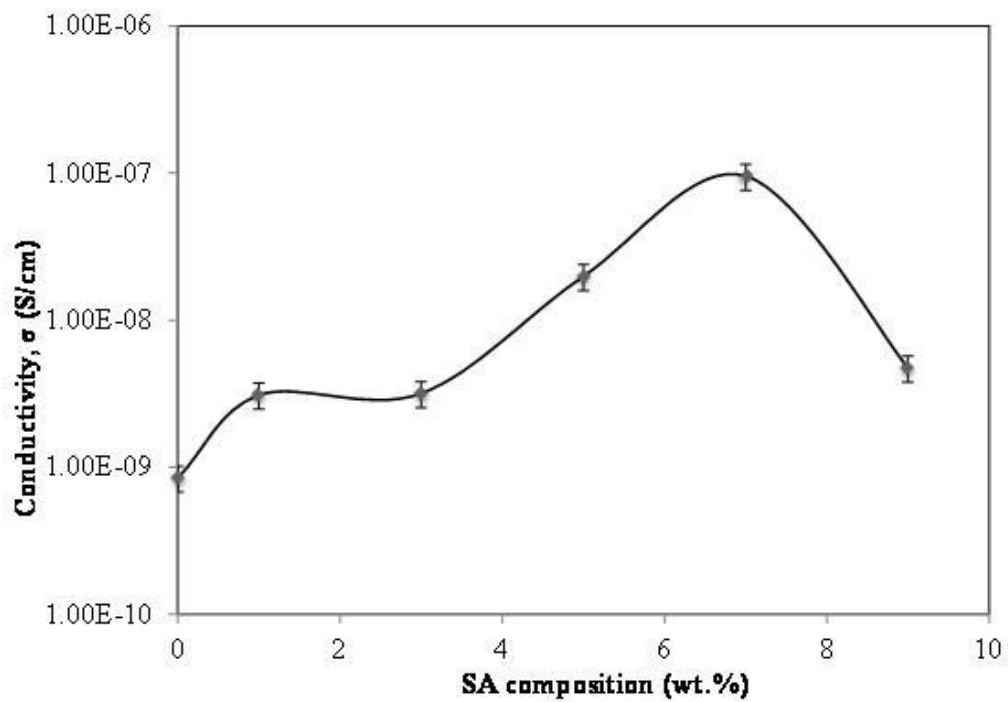


Figure 2: Conductivity versus SA composition at ambient temperature

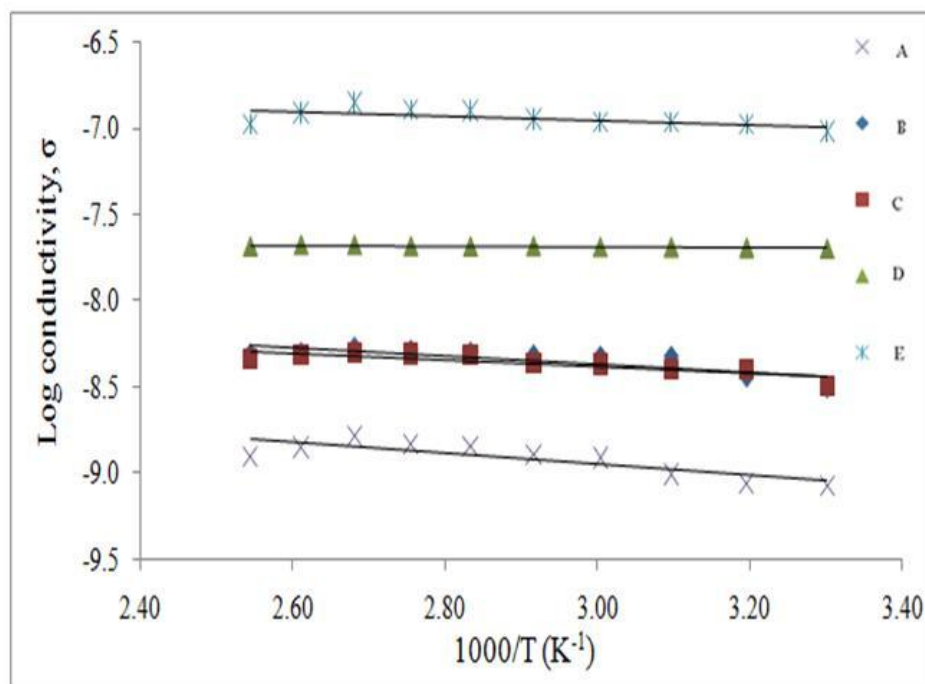
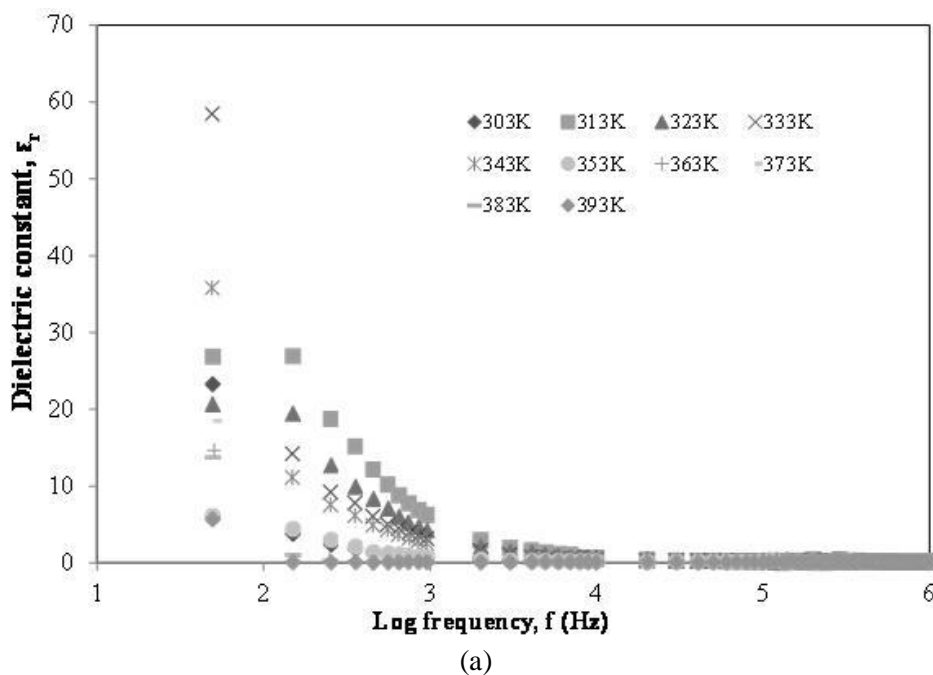
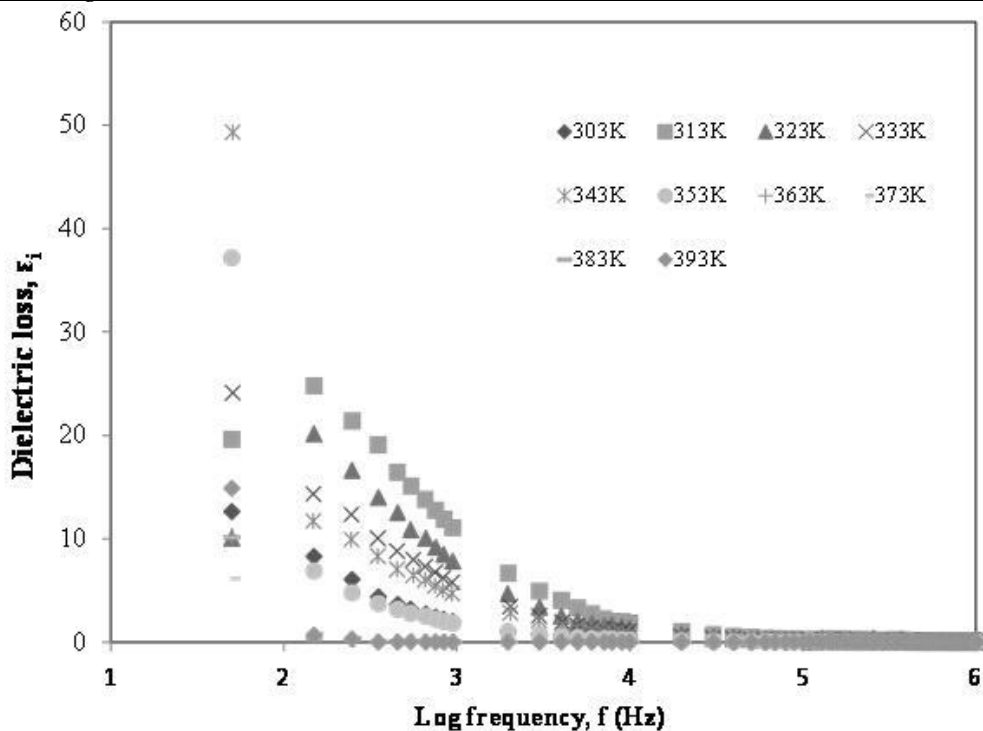


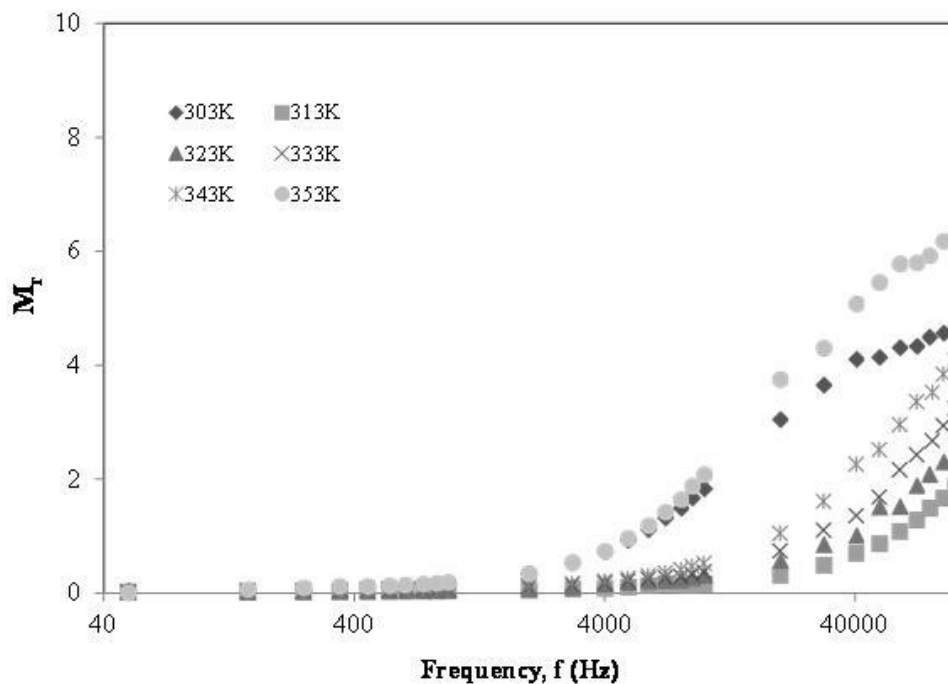
Figure 3: Plot of $\log \sigma$ vs. $1000/T$ for the CMC-SA system





(b)

Figure 4: Frequency dependence of (a) dielectric constant, ϵ_r and (b) dielectric loss, ϵ_i at various temperatures for sample SA 7 wt. %.



(a)

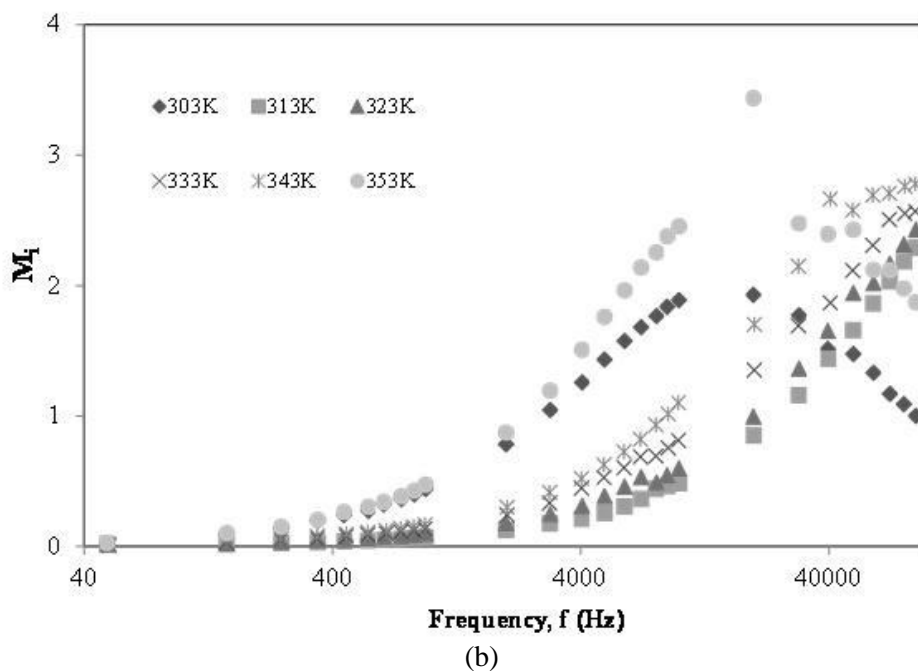


Figure 5: Frequency dependence of (a) real part, M_r and (b) imaginary part, M_i of modulus study at various temperatures for sample SA 7wt. %.

Table 1: Composition of CMC and SA

Designation	SA (wt. %)	CMC (g)
(A)	0	
(B)	1	
(C)	3	1
(D)	5	
(E)	7	
(F)	9	

Table 2: Transport properties of CMC-SA based SPE at ambient temperature

Sample	E_a (eV)	t ($\times 10^{-13}$) (s)	η ($\times 10^{-23}$) (cm^3)	μ ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	D (cm^2s^{-1})
(A)	0.58	1.42	1.36	3.90×10^{-14}	1.02×10^{-15}
(B)	0.54	1.48	79.80	2.44×10^{-13}	6.36×10^{-15}
(C)	0.53	1.49	61.50	3.24×10^{-13}	8.46×10^{-15}
(D)	0.47	1.59	39.10	3.18×10^{-12}	8.31×10^{-14}
(E)	0.40	1.71	17.60	3.39×10^{-11}	8.86×10^{-13}
(F)	0.50	1.54	31.00	9.57×10^{-13}	2.50×10^{-14}