

# Study of electrical percolation phenomenon from the dielectric and electric modulus analysis

SHUJAHADEEN B AZIZ

Advanced Polymeric Materials Research Laboratory, Department of Physics, Faculty of Science and Science Education, School of Science, University of Sulaimani, Sulaimani 46001, Kurdistan Regional Government, Iraq

MS received 24 March 2015; accepted 25 June 2015

**Abstract.** Chitosan : AgI solid polymer composite films have been prepared by the well-known solution cast technique. Electrical impedance spectroscopy was used to investigate the electrical percolation threshold phenomenon in this work. A wide dispersion can be seen in dielectric constant spectra at low frequencies. The dielectric constant at selected frequencies as a function of AgI concentration indicates the occurrence of electrical percolation threshold via the appearance of two distinguishable regions. The behaviour of dielectric constant and DC conductivity vs. AgI concentration are almost the same at low and high filler concentrations. The steep increase of dielectric constant and DC conductivity from 5 to 10 wt% of AgI was observed and a plateau was achieved from 10 to 20 wt% of AgI. The pattern of real part of electric modulus ( $M'$ ) at selected frequencies is similar to dielectric constant. The existence of distinct peaks in  $M''$  spectra with no corresponding peaks in  $\epsilon''$  spectra indicated that ionic and polymer segmental motions are strongly coupled. Argand plots of  $M''$  vs.  $M'$  was used to detect the relaxation type process. The Argand plots at different temperatures exhibit incomplete semicircular arc with a diameter below the real axis.

**Keywords.** Solid polymer composite; chitosan; AgI; dielectric constant; dielectric loss; electric modulus.

## 1. Introduction

The science of polymer electrolytes is a highly specialized interdisciplinary field which encompasses the disciplines of electrochemistry, polymer science, organic chemistry and inorganic chemistry.<sup>1</sup> Rapid growth in technologies requires the development of a new generation of high-performance energy sources. Polymer-based ion conducting materials have generated remarkable interest in the field of lithium batteries owing to their application as electrolyte. Since the work of Weston and Steele, the incorporation of solid nanometric fillers seems to be an alternative allowing increase of the ionic conductivity. The mechanisms responsible for the conduction improvement in these nano-composite polymer electrolytes have not yet been understood completely.<sup>2</sup> The dispersion of an electrically conductive phase within insulating host polymer, affects the overall performance of the heterogeneous system. Furthermore, if the dispersed filler is in sufficient quantity, a conductive or semi-conductive composite can be formed.<sup>3</sup> The term interface-mediated refers to an accumulation of local, uncompensated charges in bulk solids. Composite membranes are heterogeneous solid ionic conductors. The ionic conductivity of the composite membranes is of great interest to chemists and

engineers because of its wide application in commercial electrochemical devices. The higher conductivity in a wider temperature range and stability of electrochemical devices are the subject of research by a lot of researchers.<sup>4</sup> The use of solid polymer–ceramic composite materials as ionic conductors has in recent times attracted significant interest. The motivation for the interest is a commercial application as high conductivity and thermally stable membrane material for polymer electrolyte fuel cells.<sup>5</sup> From the fundamental point of view, dielectric relaxation spectroscopy has been widely used to investigate the relaxation process in complicated systems. The studies of dielectric properties of ion conducting polymers are useful to obtain information about the ionic and molecular interactions. The dielectric properties of ion conducting polymers are strongly influenced by the nature of additives and temperature.<sup>6</sup> Electrical conduction in polymers has been studied aiming to understand the nature of the charge transport prevalent in these materials.<sup>7</sup> According to the recent review of Bauhofer and Kovacs,<sup>8</sup> about the electrical percolation in polymer composites there is no work on chitosan-based polymer composites. The intensive and extensive survey of literature reveals that there is a very little work reported about the investigation of electrical percolation threshold from the behaviour of dielectric properties. Thus the main objective of this work is to use the dielectric constant and electric modulus formalisms to study the phenomenon of electrical percolation threshold in ion conducting chitosan-based polymer composites.

shujahadeenaziz@gmail.com, shujaadeen78@yahoo.com

## 2. Experimental

### 2.1 Materials and sample preparation

Chitosan (CS) and silver iodide (AgI) powders (with sizes of microns) obtained from Sigma Aldich have been used as raw materials to prepare the solid polymer composites (SPCs) using the solution cast technique. For this purpose 1 g of chitosan (CS) was dissolved in 60 ml of acetic acid (1 wt%) solution. The mixture was stirred continuously with a magnetic stirrer for several hours at room temperature until the chitosan has completely dissolved and a viscous liquid was obtained. Various amounts of AgI powder were added for the viscous liquid to produce the solid polymer composite samples. In viscous liquid it is possible to disperse and suspend the AgI powder finely, however in diluted solution it is impossible to disperse and suspend the filler powder. The AgI powder content in the prepared samples was varied from 5 to 20 wt% in steps of 5 wt% in volume fraction and the mixtures were stirred continuously until homogeneous solutions were obtained. The samples were coded as PC<sub>1</sub>, PC<sub>2</sub>, PC<sub>3</sub> and PC<sub>4</sub> for CS with 5 wt%, CS with 10 wt%, CS with 15 wt%, and CS with 20 wt% of AgI, respectively. The solutions were then cast into different clean and dry glass Petri dishes and allowed to evaporate at room temperature until solvent-free films were obtained. The films were kept in desiccators with blue silica gel desiccant for further drying.

### 2.2 Electrical impedance spectroscopy (EIS)

Complex impedance spectroscopy gives information on electrical properties of materials and their interface with electronically conducting electrodes. The solid polymer electrolyte (SPE) films were cut into small discs (2 cm diameter) and sandwiched between two stainless-steel electrodes under spring pressure. The impedance of the films was measured in the frequency range from 50 Hz to 1000 kHz using the HIOKI 3531 Z Hi-tester, which was interfaced to a computer. Measurements were also made at temperatures ranging between 303 and 363 K. The software controls the measurements and calculates the real ( $Z_r$ ) and imaginary ( $Z_i$ ) parts of impedance.  $Z_r$  and  $Z_i$  data were presented as a Nyquist plot and the bulk resistance ( $R_b$ ) was obtained from the intercept of the plot with the real impedance axis. The conductivity can be calculated from the following equation:<sup>9</sup>

$$\sigma_{dc} = \left( \frac{1}{R_b} \right) \times \left( \frac{t}{A} \right). \quad (1)$$

where  $t$  is film's thickness,  $R_b$  the bulk resistance of the sample, and  $A$  the active area.

The real ( $Z_r$ ) and imaginary ( $Z_i$ ) part of complex impedance ( $Z^*$ ) was also used for the evaluation of real and imaginary parts of dielectric and electric modulus using the following equations:<sup>10</sup>

$$\varepsilon' = \frac{Z_i}{\omega C_o (Z_r^2 + Z_i^2)}, \quad (2)$$

$$\varepsilon'' = \frac{Z_r}{\omega C_o (Z_r^2 + Z_i^2)}, \quad (3)$$

$$M' = \omega C_o Z_i, \quad (4)$$

$$M'' = \omega C_o Z_r. \quad (5)$$

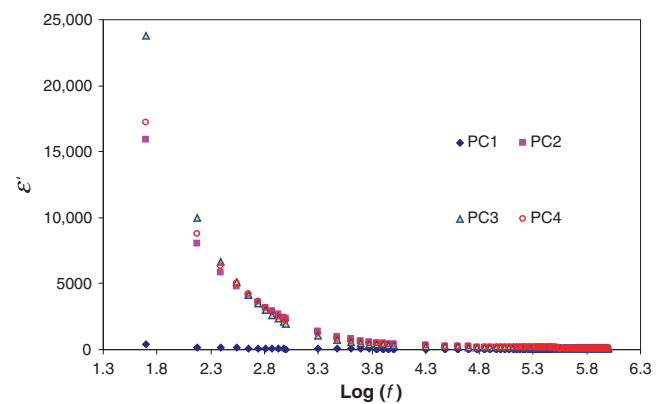
Here  $C_o$  is the vacuum capacitance and given by  $\varepsilon_o A/t$ , where  $\varepsilon_o$  is a permittivity of free space and is equal to  $8.85 \times 10^{-12}$  F m<sup>-1</sup>. The angular frequency is given as  $\omega = 2\pi f$ , where  $f$  is the frequency of applied field.

## 3. Results and discussion

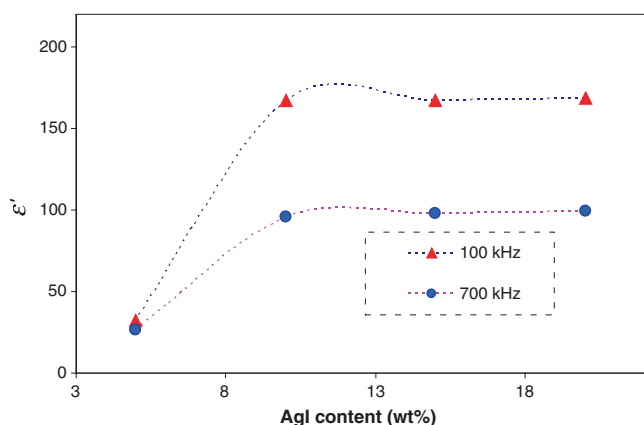
### 3.1 Dielectric constant and DC conductivity studies

Figure 1 shows the frequency dependence of dielectric constant for different silver iodide concentrations. It can be seen that dielectric constant increases with the decrease in frequency. This is because at low frequency the dipoles and charge carriers have sufficient time to orient in the direction of the applied electric field. Consequently a large amounts of charge carriers build up at the electrode/electrolyte interface and produces electrode polarization, which suppresses the high-frequency dielectric properties (bulk property).<sup>11</sup> It can be seen that above 5 wt% of AgI concentration the dielectric constant spectra of other concentrations (10–20 wt%) are very close to each other. This phenomenon may be related to the occurrence of percolation threshold especially above 5 wt%. To observe such a phenomenon the dielectric constant as a function of AgI concentration at some fixed frequency must be plotted.

Figure 2 shows the dielectric constant of chitosan as a function of AgI concentration at fixed frequencies. The steep increase of dielectric constant can be seen from 5 to 10 wt% of AgI and then a constant behaviour can be observed from 10 to 20 wt%. The nonsignificant change of dielectric constant above 10 wt% can be explained on the basis of percolation threshold theory. Plotting the dielectric constant and DC conductivity together in one figure is helpful to explain



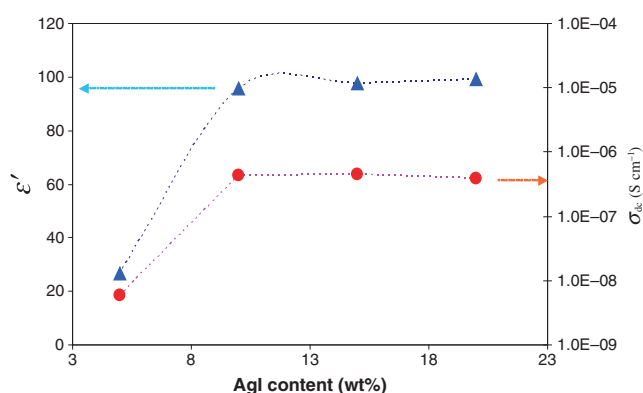
**Figure 1.** Frequency dependence of dielectric constant of chitosan at different AgI concentrations.



**Figure 2.** Dielectric constant of chitosan as a function of AgI concentration at fixed frequencies.

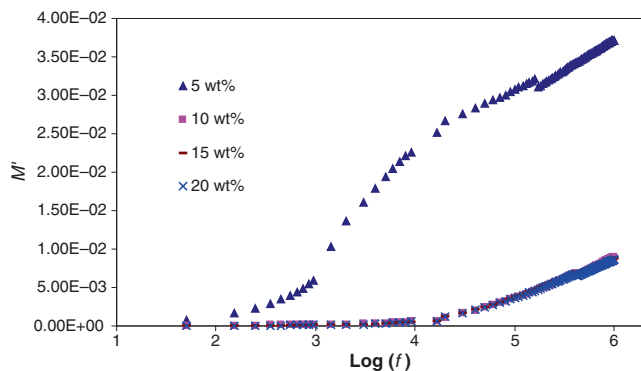
the fact that dielectric analysis can be used to detect the percolation threshold.

Figure 3 shows the DC conductivity and dielectric constant vs. AgI concentration. It is clear that the ionic conductivity and dielectric constant of the composite samples are progressively increases from 5 to 10 wt% of AgI content and then they reaches a plateau from 10 to 20 wt% of the doping phase. It was reported that further increases of the dopant beyond 20 wt% may decrease the conductivity, as it impedes the transport of charged species. A steady-state percolation occurs around 10 wt% of the dopant phase. The percolation threshold may vary depending upon the polymer matrix, particle size and the chemistry of the doping material.<sup>12</sup> The diverse range of electrochemical data on polymer–ceramic composite electrolytes reveals that the incorporation of a ceramic component such as  $\text{Al}_2\text{O}_3$  or  $\text{BaTiO}_3$  in a polymer matrix leads to enhanced conductivity (specifically at low temperatures), increased ion transport number and improved electrode/electrolyte interfacial stability. The results of this work demonstrate that the AgI superionic conductor can work as filler and as an ionic conductor that contributes the raise of DC ionic conductivity and dielectric constant. The behaviour of DC ionic conductivity and dielectric constant vs. AgI concentration as obtained in this work is similar to the pattern of DC conductivity, which is reported for other polymer composites in literature.<sup>13</sup> Percolation theory describes the transition from the state of limited and spatially restricted connections of conductive elements to the state of an infinite network of connections. The percolation threshold (PT) represents the critical concentration or volume fraction of the conductive inclusions, which is necessary for the beginning of conductive behaviour.<sup>14</sup> In literature a lot of work can be seen in which they explained the percolation threshold from the behaviour of the DC conductivity against filler concentration, however little attention has been given to interpret such a phenomena via the dielectric constant study.<sup>15</sup> The frequency dependence of relative permittivity and conductivity

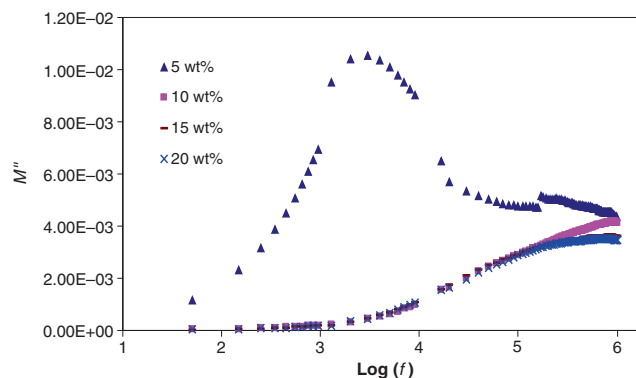


**Figure 3.** Bulk dielectric constant ( $\epsilon'$  at 1 MHz) and DC conductivity of chitosan (CS) as a function of AgI concentration.

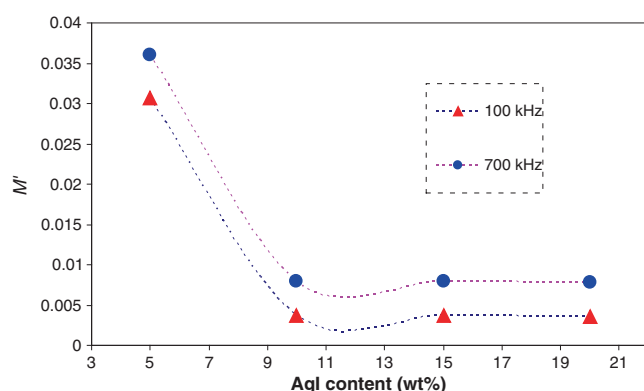
of disordered solids generally results from the polarization between the clusters and anomalous diffusion within each cluster. The capacitive effect between clusters on the conductivity and relative permittivity becomes significant at high frequency. As a result, the conductivity increases and relative permittivity decreases with frequency.<sup>16</sup> In all the cases, the effective dielectric constants obtained for all the composite samples are higher than that of pure chitosan ( $\epsilon' = 3.01$  at 1 kHz) as we reported previously.<sup>17</sup> The effective dielectric constant (high frequency region) of polymer composite material is influenced by many factors such as dielectric constants of the polymer, size and shape of filler, the volume fraction of the filler, the dielectric constant of the inter-phase region and volume of the inter-phase region.<sup>18</sup> The largest dielectric constant is 2422 (at 1 kHz) for chitosan : AgI composite with 10 wt% of AgI filler. Li *et al*<sup>15</sup> obtained the largest dielectric constant of about 3600 at 1 kHz for MWCNT/poly(vinylidene fluoride) (PVDF) composite with 8 vol% MWCNT. Thus the results of this work reveal that superionic conductors which are not dissolved in water-like solvent materials are good candidates to prepare high permittivity composites with polar polymers. The obtained DC conductivity ( $\sigma_{dc} = 6 \times 10^{-6} \text{ S cm}^{-1}$ ) in this work is higher than that reported by Zhao *et al* for PE/MWCNT composites ( $\sigma_{dc} = 10^{-12} \text{ S cm}^{-1}$ ), but very close to Zhang *et al* work for PE/single-walled carbon nanotube (SWCNT) composites ( $\sigma_{dc} = 10^{-6} \text{ S cm}^{-1}$ ).<sup>19</sup> Furthermore, the DC conductivity in the present work is too close to PVP :  $\text{KClO}_4$  (90 : 10) polymer electrolyte ( $\sigma_{dc} = 3.6 \times 10^{-6} \text{ S cm}^{-1}$ ) reported by Ravi *et al*.<sup>20</sup> It is important to mention that the DC conductivity in this work is two order higher than the DC conductivity of chitosan : AgTf system and four order higher than the DC conductivity of pure chitosan.<sup>21</sup> It is well known that AgTf is a dissolvable inorganic salt in polar polymers and thus some of  $\text{Ag}^+$  ions can be reduced to  $\text{Ag}^0$  nanoparticles.<sup>17,22</sup> This may reduce the number of ions that participate in DC ionic conductivity.<sup>21</sup> Thus, the use of AgI as filler which is insoluble in water-soluble polar polymers can solve the problems of silver ion reduction.



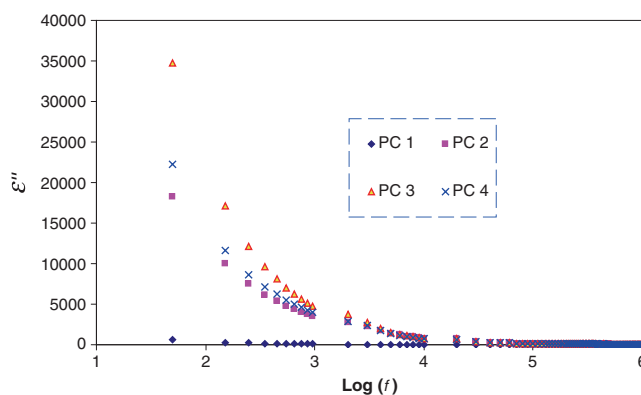
**Figure 4.** Frequency dependence of  $M'$  for different concentrations of AgI.



**Figure 6.** Frequency dependence of  $M''$  for different concentrations of AgI.



**Figure 5.** AgI concentration dependence of  $M'$  at fixed frequencies.



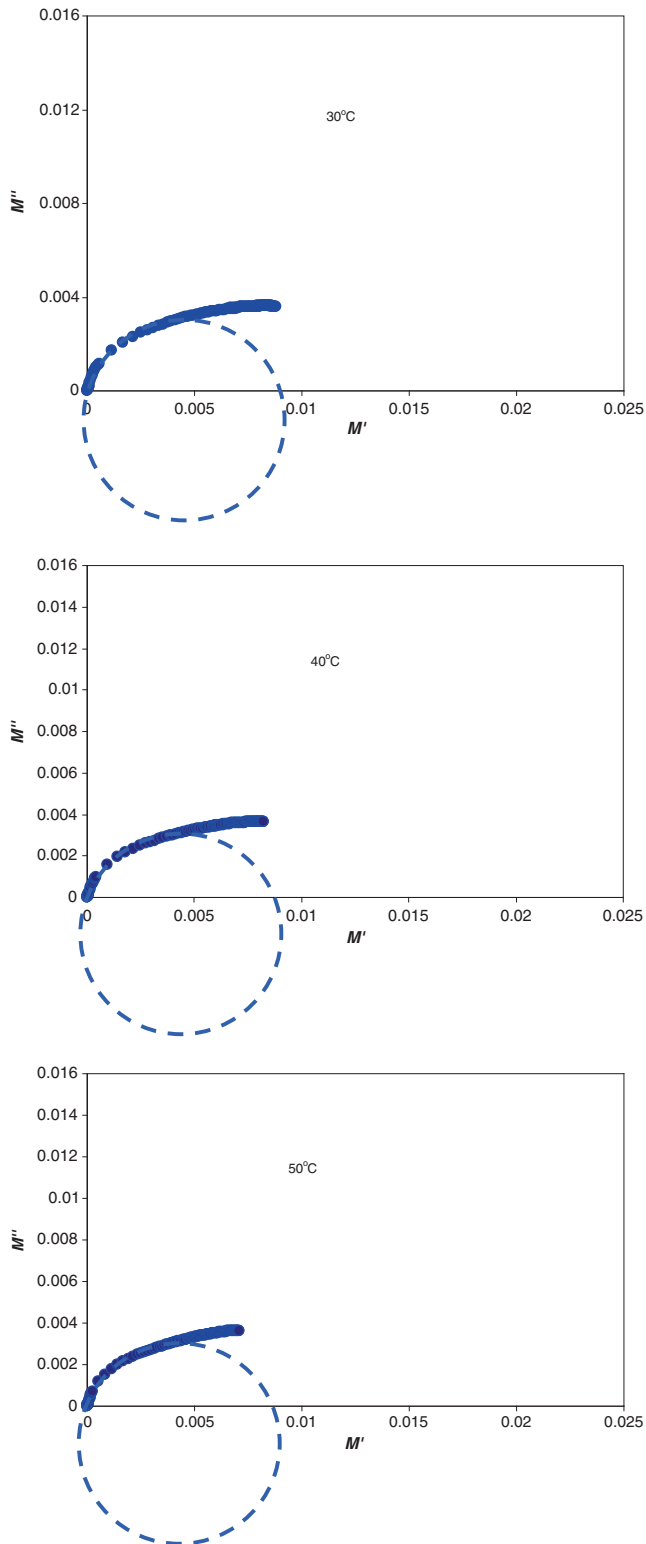
**Figure 7.** Frequency dependence of dielectric loss ( $\epsilon''$ ) at different AgI concentrations.

### 3.2 Electric modulus study

Broadband dielectric spectroscopy has proven to be a very useful tool to study the relaxation processes of polymeric systems. The complex dielectric function,  $\epsilon^*$ , which consists of dielectric constant and loss in materials property depending on frequency, temperature and structure. At low frequency both of them ( $\epsilon'$  and  $\epsilon''$ ) are very high due to electrode polarization (EP) effect.<sup>23</sup> To reduce the effect of electrode polarization, Macedo *et al* have established the electric modulus formalism.<sup>24</sup> In solid polymer electrolytes the movement of ions from one site to another will perturb the electric potential of the surroundings. Motion of the other ions in this region will be affected by perturb potential. Such a cooperative motion of ions will lead to non-exponential decay, or a conduction processes with distribution of relaxation time.<sup>25</sup> The frequency dependence of  $M'$  for different concentration of AgI is shown in figure 4. It is obvious that  $M'$  reaches a maximum saturation at high frequency. This is ascribed to the fact that at high frequency the dielectric constant decreases to a minimum value as can be seen in figure 1, and thus  $M'$  becomes maximum ( $M_\infty = 1/\epsilon_\infty$ ).<sup>26</sup> It is interesting to notice that the  $M'$  spectra for 10, 15 and 20 wt% of

AgI are coinciding to each other. The high value of  $M'$  at 5 wt% of AgI can be ascribed to its low dielectric constant compare to other sample. Thus plotting the  $M'$  as a function of AgI concentration at selected frequencies can be used to study the percolation threshold as depicted in figure 5. The observed plateau from 10 to 20 wt% of AgI can be ascribed to the occurrence of percolation threshold. The behaviour of  $M'$  vs. AgI concentration (figure 5) is similar to the pattern of  $\epsilon'$  vs. AgI content (figure 2) but in reverse manner. These noticeable results reveal that dielectric constant and electric modulus analysis are important to study the electrical percolation threshold in ion conducting polymer composites.

Figure 6 shows the frequency dependence of  $M''$  for different concentrations of AgI filler. It can be seen that in the imaginary part of modulus ( $M''$ ) spectra, a distinct relaxation peak is observed which is related to the conductivity processes, whereas no peak can be seen in the dielectric loss spectra as depicted in figure 7. This suggests that ionic and polymer segmental motions are strongly coupled manifesting as a single peak in the  $M''$  spectra with no corresponding feature in dielectric loss spectra.<sup>27</sup> Hence the conduction in polymer electrolytes takes place through charge migration of ions between coordinated sites of the polymer along with the



**Figure 8.** Argand plots for PC<sub>3</sub> sample at different temperatures.

segmental relaxation of polymer. It is clear that the position of the frequency corresponding to the maximum peak is the same for the AgI concentrations range from 10 to 20 wt%, while for 5 wt% of AgI filler the peak position occurred at

low frequency. This reveals the fact that the electric modulus studies can be used to detect the percolation threshold phenomena.

There are two relaxation processes in polymeric materials. The first one is called viscoelastic relaxation which is due to the dipolar relaxation. This relaxation occurred because of the existence of permanent dipoles on the side chains of the polymer backbone. The second one is called conductivity relaxation; this process due to the translational diffusion of ions which is responsible for ion conduction.<sup>27</sup> Argand plots of  $M''$  vs.  $M'$  can be used to detect the relaxation type process. Figure 8 shows the Argand plots for PC<sub>3</sub> composite sample at different temperatures. It is obvious that the Argand plots exhibit incomplete semicircular arc with a diameter below the real axis. This satisfies that the relaxation processes are a mixture of both relaxation processes mentioned above. This suggests that ionic motion and polymer segmental motion are strongly coupled and thus manifesting an incomplete semicircular arc with a diameter below the real axis. These reveal the fact that in polar polymers the dipolar relaxations have a strong effect on ion transport mechanism and cannot be ignored. It is clear that all the points cannot concur on the semicircular arc and thus a tail can be observed. This indicates the distribution of relaxation time and agrees well with our previous works,<sup>10,11</sup> while it completely disagrees with Ayesha<sup>27</sup> work in which he obtained a complete semicircular arc between  $M''$  vs.  $M'$  for PC : MnCl<sub>2</sub> polymer composites. It can be observed that with increasing temperature the Argand curves shift towards the origin. This is again ascribed to the increase of conductivity resulting in increase of ionic mobility with temperature and thus the decrease of both  $Z_r$  and  $Z_i$ .

#### 4. Conclusion

The fascinating results of the present work show that the percolation threshold can be studied from the behaviour of dielectric constant and electric modulus. A wide dispersion of dielectric constant spectra at low frequencies can be ascribed to electrode polarization. The steep increase of dielectric constant from 5 to 10 wt% of AgI content is attributable to the occurrence of percolation threshold because above 10 wt% of AgI a plateau was achieved. The behaviour of dielectric constant and DC conductivity vs. AgI concentration are almost the same, which are linear at low and nearly plateau at high filler concentrations and this reveals that dielectric constant study can be used to detect the percolation threshold. The pattern of real part of electric modulus ( $M'$ ) at selected frequencies is similar to dielectric constant. The existence of distinct peaks in  $M''$  spectra with no corresponding peaks in  $\epsilon''$  spectra indicates that ionic and polymer segmental motions are strongly coupled. Argand plots of  $M''$  vs.  $M'$  were used to detect the relaxation type process. The Argand plots at different temperatures exhibit incomplete semicircular arc with a diameter below the real axis, which indicates the distribution of relaxation times.

### Acknowledgement

I gratefully acknowledge the financial support from the University of Sulaimani, Faculty of Science and Science Education, School of Science-Department of Physics, for this research.

### References

1. Wang Y, Gao X-H, Li H-K, Li H-J, Liu H-G and Guo H-X 2009 *J. Macromol. Sci. Part A: Pure Appl. Chem.* **46** 461
2. Samir M A S, Alloin F and Dufresne A 2006 *Compos. Interfaces* **13** 545
3. Psarras G C, Manolakaki E and Tsangaris G M 2003 *Composites: Part A* **34** 1187
4. Kumar J, Rodrigues S J and Kumar B 2010 *J. Power Sources* **195** 327
5. Kumar B and Fellner J P 2003 *J. Power Sources* **123** 132
6. Bhargav P B, Sarada B A, Sharma A K and Rao V V R N 2010 *J. Macromol. Sci. Part A: Pure Appl. Chem.* **47** 131
7. Mohan V M, Bhargav P B, Raja V, Sharma A K and Rao V V R N 2007 *Soft Mater.* **5** 33
8. Bauhofer W and Kovacs J Z 2009 *Compos. Sci. Technol.* **69** 1486
9. Aziz S B and Abidin Z H Z 2013 *J. Soft Matter* Article ID 323868, p 8
10. Aziz S B, Abidin Z H Z and Arof A K 2010 *Express Polym. Lett.* **4** 300
11. Aziz S B and Abidin Z H Z 2015 *J. Appl. Polym. Sci.* **132** 41774
12. Kumar B and Rodrigues S J 2004 *Solid State Ion* **167** 91
13. Tchmutin I A, Ponomarenko A T, Krinichnaya E P, Kozub G I and Efimov O N 2003 *Carbon* **41** 1391
14. Psarras G C 2006 *Composites: Part A* **37** 1545
15. Li Q, Xue Q, Hao L, Gao X and Zheng Q 2008 *Compos. Sci. Technol.* **68** 2290
16. George S and Sebastian M T 2009 *Compos. Sci. Technol.* **69** 1298
17. Aziz S B and Abidin Z H Z 2014 *Mater. Chem. Phys.* **144** 280
18. Thomas P, Varughese K T, Dwarakanath K and Varma K B R 2010 *Compos. Sci. Technol.* **70** 539
19. Han M S, Lee Y K, Lee H S, Yun Ch H and Kim W N 2009 *Chem. Eng. Sci.* **64** 4649
20. Ravi M, Pavani Y, Bhavani S, Sharma A K and Rao V V R N 2012 *Int. J. Polym. Mater.* **61** 309
21. Aziz S B, Abidin Z H Z and Arof A K 2010 *Physica B: Condens. Matter* **405** 4429
22. Aziz S B, Abidin Z H Z and Kadir M F Z 2015 *Phys. Scr.* **90** 035808
23. Okutan M and Şentürk E 2008 *J. Non-Cryst. Solids* **354** 1526
24. Agrawal S L, Singh M, Asthana N, Dwivedi M M and Pandey K 2011 *Int. J. Polym. Mater.* **60** 276
25. Pradhan D K, Choudhary R N P and Samantaray B K 2008 *Int. J. Electrochem. Sci.* **3** 597
26. Kanchan D K, Padmasree K P, Panchal H R and Kulkarni A R 2004 *Ceram. Int.* **30** 1655
27. Ayesh A S 2008 *J. Thermoplast. Compos. Mater.* **21** 309