

## Short Communication

## Conductivity enhancement due to ion dissociation in plasticized chitosan based polymer electrolytes

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**Abstract**

Cast films of chitosan acetate, plasticized chitosan acetate, chitosan acetate containing salt and plasticized chitosan acetate–salt complexes were used to obtain some insight on the mechanism of ionic conductivity in chitosan-based polymer electrolytes. The films are largely amorphous. The conductivity is due to the mobile ions from the salt. The role of the plasticizer is to dissociate the salt thereby increasing the number of mobile ions, which lead to conductivity enhancement. The conductivity was calculated using the bulk impedance obtained through impedance spectroscopy. The Cole–Cole plots illustrating the variation of the negative imaginary impedance with the real impedance do not always show the double layer reactance but the plot of dielectric constant  $\epsilon_r$  versus frequency tends to a maximum at low frequencies. The real and imaginary parts of the electrical modulus of samples containing salt show a “long tail” feature, which is not found in the electrical modulus spectra of the unsalted samples. This long tail feature can be attributed to high capacitance, which further supports the plasticizer’s role as an agent to dissociate the salt into ions. © 2001 Elsevier Science Ltd. All rights reserved.

**Keywords:** Chitosan; Plasticizer; Polymer electrolytes

**1. Introduction**

In the effort to find alternative polymers with good mechanical and electrical properties to act as an electrolyte in polymer batteries, chitosan was studied (Mohamed, Subban & Arof, 1995; Subban & Arof, 1996; Subban, Arof & Radhakrishnan, 1996). This biopolymer has a variety of uses (Muzzarelli, 1977). It has several polar groups (OH and  $\text{NH}_2$ ) in its structure. These can act as electron donors and interact with inorganic salts. Interaction between a lithium-cation and a nitrogen donor has been proven by X-ray photoelectron spectroscopy (Arof, Morni & Yarmo, 1998). X-ray diffraction has shown that a chitosan film is amorphous and its glass transition temperature,  $T_g$  is also quite high ( $\sim 200^\circ\text{C}$ ) (Sakurai, Maegawa & Takahashi, 1996). In polymers, the addition of salt at levels higher than required for optimum conductivity is known to increase  $T_g$  (Mellander & Albinson, 1996). The addition of plasticizers such as propylene carbonate (PC) and ethylene carbonate (EC) on the other hand can help to reduce  $T_g$ , thus increasing segmental motion of the polymer resulting in conductivity enhancement. The addition of 50% (w/w) tetraglyme and 50% (w/w) PC to a polymer decreases  $T_g$

by  $30\text{--}40^\circ\text{C}$  and increases the conductivity by 1 to 2 orders of magnitude (MacFarlane, Sun, Maekin, Fasouloupoulos, Hey & Forsyth, 1995). In another paper (Forsyth, Maekin & MacFarlane, 1995a), it has been shown that the addition of 50% (w/w) dimethyl formamide (DMF) decreases  $T_g$  by more than  $40^\circ\text{C}$ . The increase in the glass transition temperature, on the other hand, will make the polymer backbone more rigid and disallows conductivity enhancement through segmental motion. In the temperature range from ambient to about  $50^\circ\text{C}$  (Morni, Mohamed & Arof, 1997) and to as high as  $90^\circ\text{C}$  (Morni, 1998; Yahya, 1999), the temperature dependence of conductivity of the plasticized chitosan complex obeys an Arrhenius relationship rather than the Vogel–Tamman–Fulcher (VTF) law. Perhaps this is because  $T_g$  of the chitosan complex has not been sufficiently reduced for segmental motion to occur. It is therefore important to develop an understanding of the conductivity mechanism in chitosan based films in the temperature range below  $T_g$ . It is the aim of this paper to try and do so. For this, plasticized chitosan acetate films without salt and plasticized films containing salt will be prepared. The room temperature electrical conductivity, the dielectric constant and the dielectric loss as well as the real and imaginary parts of the electrical modulus will be analyzed. An unplasticized chitosan acetate film and a chitosan acetate film containing salt but unplasticized were also analyzed as controls.

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Table 1  
Film content

| Base material | Salt content (g) | Plasticizer (EC) content (g) | Sample number |
|---------------|------------------|------------------------------|---------------|
| A             | 0                | 0                            | S1            |
| A             | 0                | 0.1                          | S2            |
| A             | 0                | 0.2                          | S3            |
| A             | 0                | 0.3                          | S4            |
| A             | 0                | 0.4                          | S5            |
| A             | 0                | 0.5                          | S6            |
| A             | 0                | 0.6                          | S7            |
| A             | 0                | 0.7                          | S8            |
| A             | 0.3              | 0                            | S9            |
| A             | 0.3              | 0.1                          | S10           |
| A             | 0.3              | 0.2                          | S11           |
| A             | 0.3              | 0.3                          | S12           |
| A             | 0.3              | 0.6                          | S13           |
| A             | 0.3              | 0.9                          | S14           |
| A             | 0.3              | 1.3                          | S15           |

## 2. Experimental techniques

### 2.1. Sample preparation

Contents of the various films prepared are listed in Table 1. Here 'A' denotes the base material, i.e., 1g chitosan dissolved in 100 ml 1% acetic acid solution. 1 g of chitosan (Fluka) was dissolved in 100 ml 1% acetic acid solution.  $\text{LiCF}_3\text{SO}_3$  (Aldrich) and EC (Fluka) were added accordingly. After complete dissolution of the chitosan, salt and plasticizer, the solutions were cast in petri dishes and left to dry at room temperature to form films of (a) chitosan acetate (CA)—without salt and plasticizer, (b) CA–EC, (c) CA– $\text{LiCF}_3\text{SO}_3$  and (d) CA–EC– $\text{LiCF}_3\text{SO}_3$ . The films were then placed in a desiccator. Silica gel was continually renewed allowing the samples to dry for one week before they were used for conductivity measurement.

### 2.2. X-ray diffraction

To study the extent of crystallinity X-ray diffraction was carried out with a Shimadzu XD-5 diffractometer which employs a  $\text{CuK}\alpha$  X-radiation.

### 2.3. Impedance spectroscopy

The impedance,  $Z(\omega)$  and phase angle,  $\theta(\omega)$  were measured from 42 Hz to 5 MHz with a computer-interfaced HIOKI 3531-01 LCR bridge. The software controlling the measurement also calculates the real and imaginary impedance. From the plot of negative imaginary impedance versus real impedance with the horizontal and vertical axes having the same scale, the bulk resistance,  $R_b$  can be obtained, Fig. 1. The room temperature electrical conductivity of the sample ( $\sigma$ ) can then be calculated using the

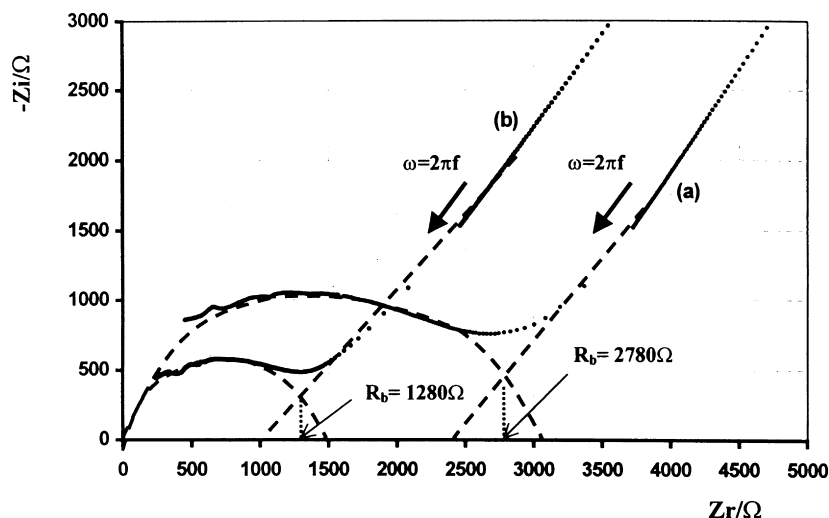


Fig. 1. Cole–Cole plot for chitosan acetate–salt complexes containing (a) 0.1 g EC (b) 0.3 g EC.  $R_b$  is taken at the intersection of the depressed semicircle and the tilted spike.

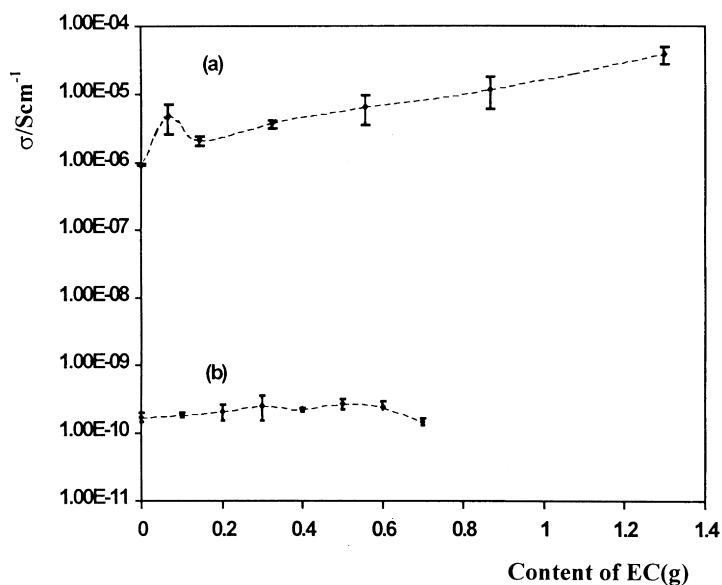


Fig. 2. Variation of electrical conductivity versus EC content in (a) chitosan acetate-EC-LiCF<sub>3</sub>SO<sub>3</sub> and (b) chitosan acetate-EC systems.

equation

$$\sigma = \frac{t}{R_b A} \quad (1)$$

where  $t$  is thickness of the film and  $A$  the cross-sectional area. A micrometer screw gauge was used to measure the thickness of the polymer films. In order to verify the presence of residual water, the impedance data was transposed into real and imaginary permittivity data. According to Wintersgill and Fontanella (1987), the dielectric loss,  $\epsilon_i$  probes a wide variety of phenomena along with any relaxation which may be present in the material. It is therefore

expected that if water is present a relaxation peak can be observed in the dielectric loss ( $\epsilon_i$ )-frequency spectrum.

The relationships between complex impedance, admittance, permittivity and electrical modulus can be obtained from MacDonald (1987). From these relationships and writing  $Z = Z_r + jZ_i$  where  $Z_r$  and  $Z_i$  are the magnitudes of the real and imaginary impedance, the equations for the dielectric constant,  $\epsilon_r$ , the dielectric loss,  $\epsilon_i$  the real electrical modulus  $M_r$  and the imaginary electrical modulus  $M_i$  can be shown to be:

$$\epsilon_r = \frac{Z_i}{\omega C_e (Z_r^2 + Z_i^2)} \quad (2)$$

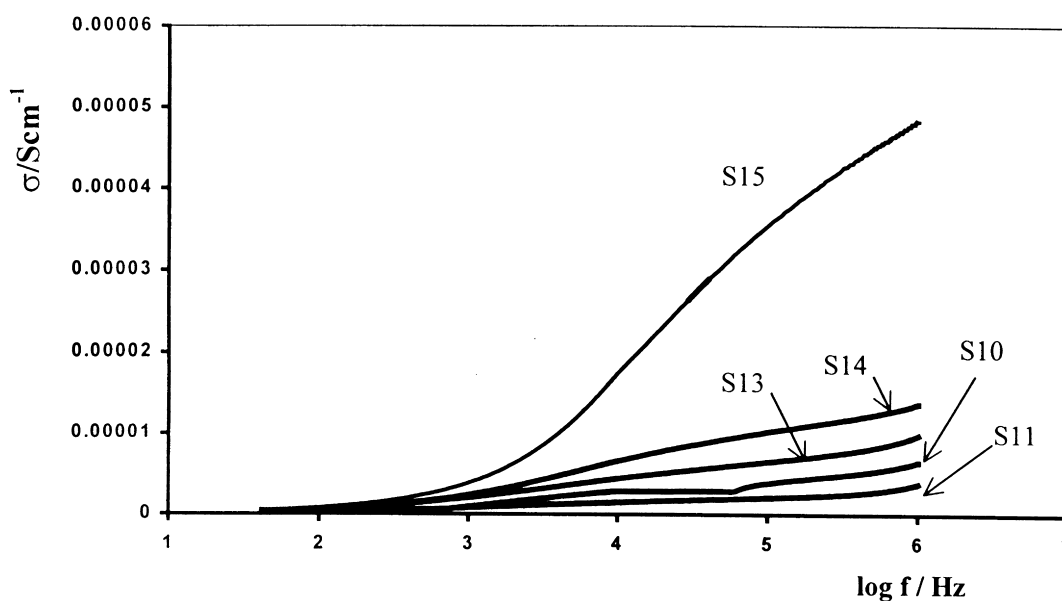


Fig. 3. Conductivity-frequency dependence for plasticized films containing salt.

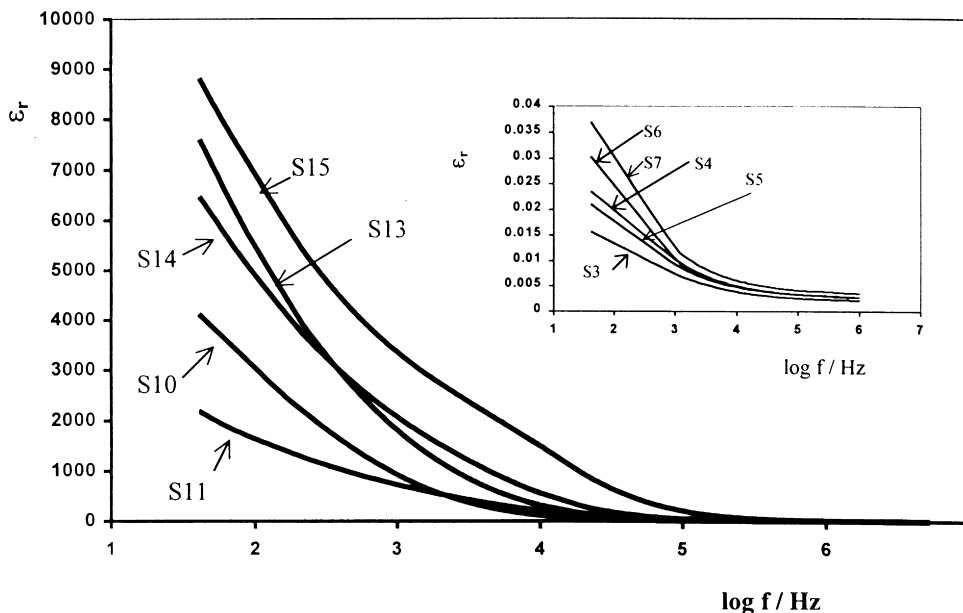


Fig. 4. Dielectric constant versus frequency for plasticized films with salt and without salt (inset).

$$\epsilon_i = \frac{Z_r}{\omega C_c(Z_r^2 + Z_i^2)} \quad (3)$$

$$M_r = \frac{\epsilon_r}{(\epsilon_r^2 + \epsilon_i^2)} \quad (4)$$

$$M_i = \frac{\epsilon_i}{(\epsilon_r^2 + \epsilon_i^2)} \quad (5)$$

$Z_r$  and  $Z_i$  are related to the magnitude of the complex impedance via the equation,  $Z_r(\omega) = Z(\omega) \cos \theta(\omega)$ ,  $Z_i(\omega) = Z(\omega) \sin \theta(\omega)$  and  $C_c = \epsilon_0 A/t$ .  $\epsilon_0$  is permittivity of free space.  $\omega = 2\pi f$ , where  $f$  is frequency. In all graphs, the values are averages of three sets of data obtained from three sets of impedance measurements.

### 3. Results and discussion

X-ray diffractograms showed that the films were largely amorphous. Fig. 1 shows typical impedance plots for the samples prepared.  $R_b$ , was determined and used to calculate  $\sigma$  from Eq. (1). Whenever  $R_b$  was difficult to obtain from the complex impedance data, the impedance data was converted into admittance data and plotted according to the admittance formalism from which  $1/R_b$  may be easier to obtain (Ali, Mohamed & Arof, 1998). Fig. 2 shows the plots of conductivity versus EC content for the plasticized and unplasticized films with and without salt. The salt containing film with 1.3 g EC has the highest conductivity i.e.  $4.0 \times 10^{-5} \text{ S cm}^{-1}$ . For the plasticized films without salt, the value of conductivity is approximately the same, irrespective of the EC content. On addition of salt, the conductivity value increases to  $\sim 10^{-6} \text{ S cm}^{-1}$  and continues to increase with increasing plasticizer content. It can be inferred that the

salt is responsible for the conductance of the chitosan-based films. On addition of 0.3 g salt, the increase in conductivity of the sample containing about 0.15 g EC is almost four orders of magnitude and with increasing in plasticizer content, the conductivity value rises to  $10^{-5} \text{ S cm}^{-1}$ .

Fig. 3 shows the variation in conductivity with frequency for the salt containing plasticized films. The bulk conductivity is very low at low frequencies ( $<1 \text{ kHz}$ ). This can be attributed to the accumulation of charged species at the electrode–electrolyte interface at low frequencies. Hence there are less mobile ions in the bulk material to contribute towards conductivity. The dielectric constant,  $\epsilon_r$  versus frequency plots for the plasticized films containing salt are shown in Fig. 4. The inset shows  $\epsilon_r$  values for the plasticized films that do not contain salt.  $\epsilon_r$  has high values at low frequencies. This implies that the mobile ions tend to accumulate at low frequencies. This is supported by the  $\sigma$ – $\log f$  graph, which shows  $\sigma$  with very low values at low frequencies. The value of  $\epsilon_r$  for the salt containing films is much (up to 200,000 times) higher than that of the films that do not contain salt. The dielectric constant plays a fundamental role in the ability of a polymer to dissolve salts (Wintersgill & Fontanella, 1987). With increasing plasticizer content and for a fixed frequency, the value of  $\epsilon_r$  for the films increases. This shows that the plasticizer has increased the dielectric constant of the biopolymer and increased its ability to dissolve the salt. Therefore the number of mobile ions in the samples increases and since conductivity is proportional to the number of mobile ions the conductivity is therefore increased. The effect of the plasticizer in increasing the ability of a polymer to dissociate the salt has also been observed by other workers (Forsyth et al., 1995a; MacFarlane et al., 1995). Alternatively, plasticization can also increase ionic mobility by reducing the potential barrier to

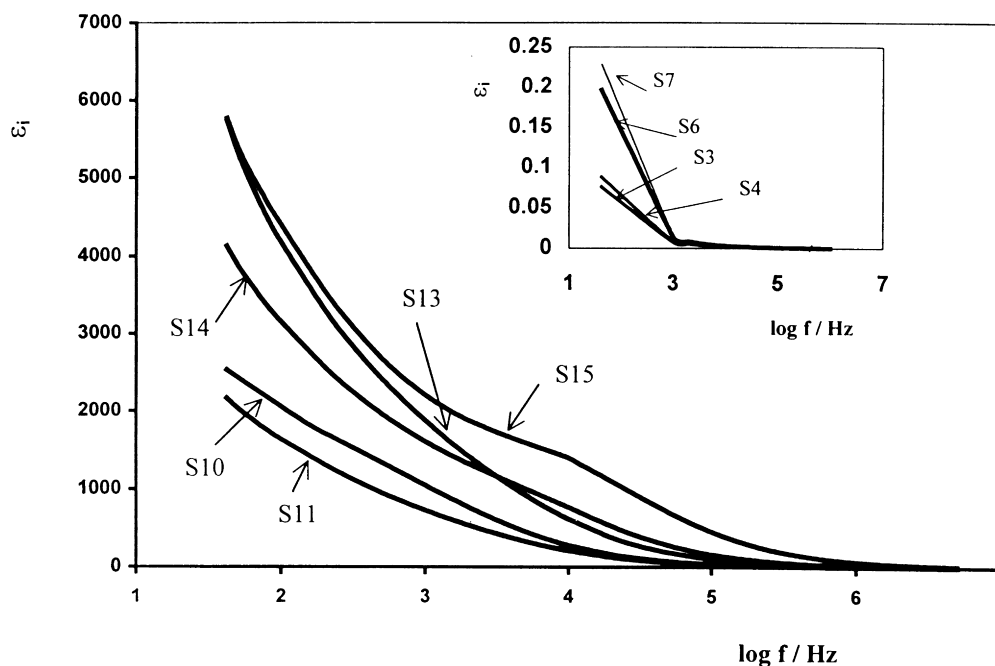


Fig. 5. Dielectric loss versus frequency for plasticized films with salt and without salt (inset).

ionic motion as a result of the decreasing cation–anion coordination of the salt (Forsyth, MacFarlane, Maekin, Smith & Bastow, 1995b).

Since no significant relaxation peaks are observed in the dielectric loss–frequency spectrum of Fig. 5 it is therefore inferred that residual water does not contribute towards conductivity enhancement. Fig. 6 depicts the modulus formalism,  $M$  with respect to frequency for the plasticized films

containing salt and Fig. 7 for the plasticized films that do not contain salt. For the films containing salt, a long tail is observed in the frequency range between 42 Hz and up to  $\sim 100$  kHz. This indicates that the material is very capacitive which again implies that the plasticizer has helped to dissociate the salt into ions that accumulate at the electrode–electrolyte interface at low frequencies. For the plasticized films that do not contain salt, there is no long tail

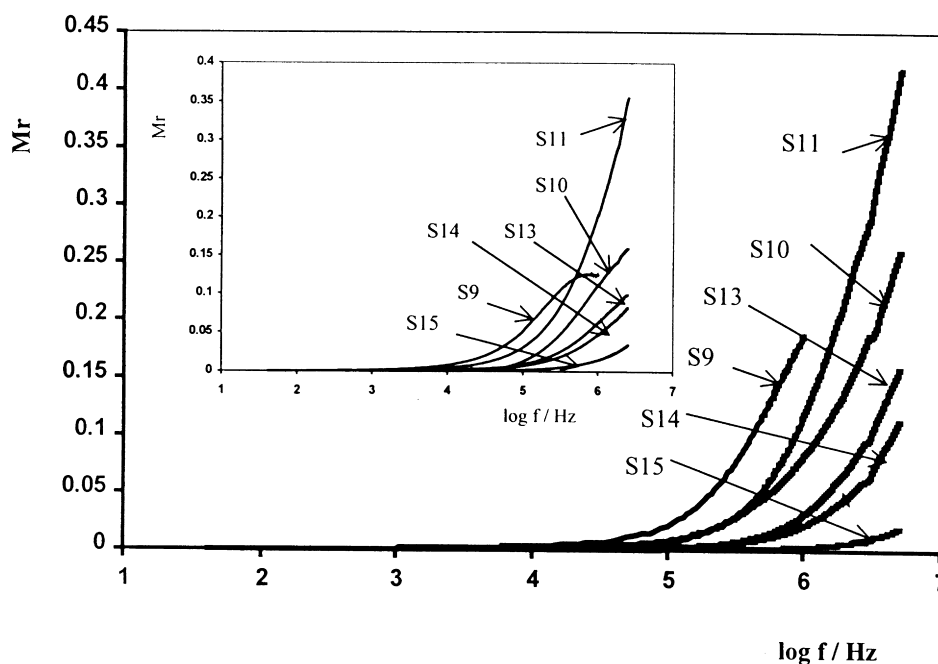


Fig. 6. Electrical modulus versus frequency for plasticized films containing salt.

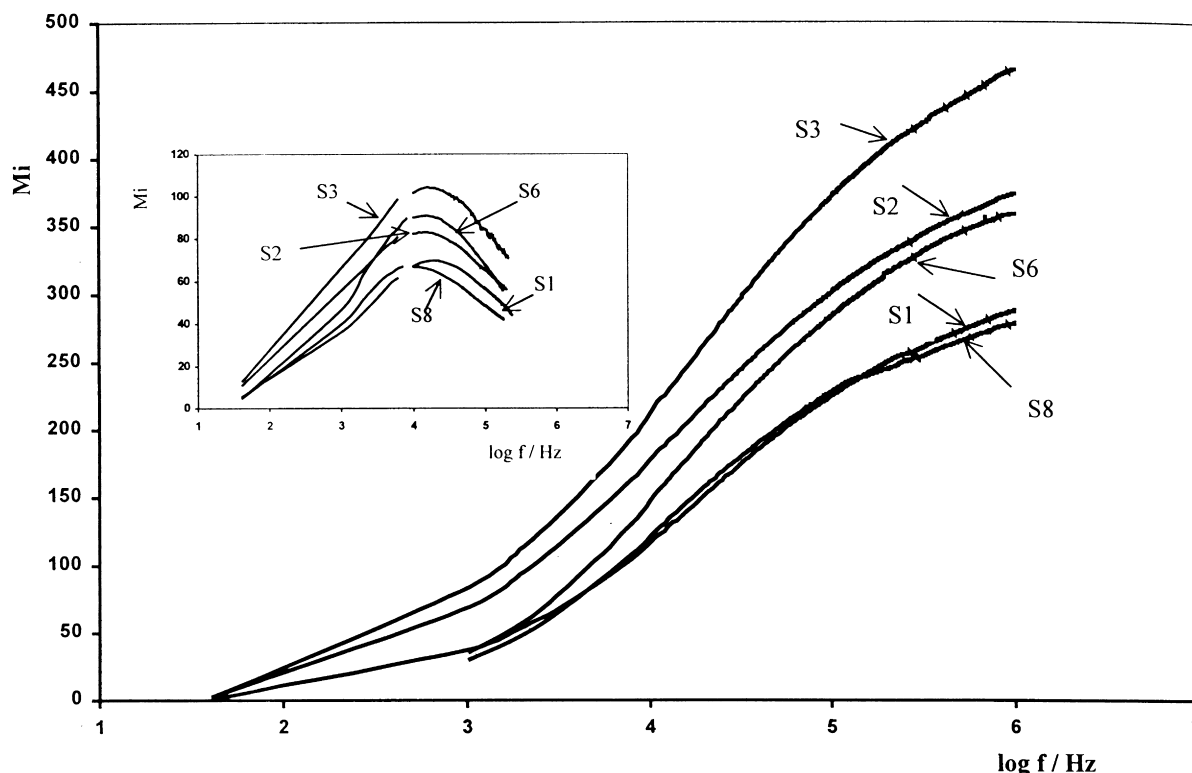


Fig. 7. Electrical modulus versus frequency for plasticized films without salt.

feature as observed for the plasticized films containing salt. This again shows that salt is the agent responsible for conductivity and the plasticizer seems to help the salt dissociate into mobile ions or increases the mobility of the ions so that the conductivity of the films can be enhanced.

#### 4. Conclusions

The conductivity of the plasticized chitosan acetate–salt complexes is due to the salt and can be enhanced by plasticization. From the present investigation, the value of conductivity in the plasticized films containing salt increases with EC and with frequency. Highest conductivity in plasticized film containing salt is  $4.0 \times 10^{-5} \text{ S cm}^{-1}$  and for the plasticized films not containing salt is  $3.0 \times 10^{-10} \text{ S cm}^{-1}$ .

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