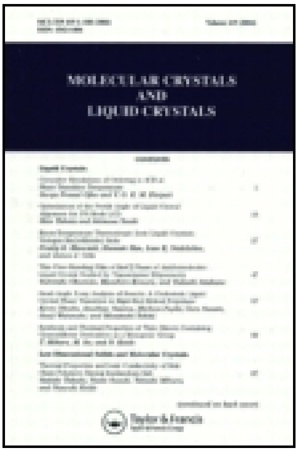

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Enhancement of Electrical Conductivity in Plasticized Chitosan Based Membranes

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Enhancement of Electrical Conductivity in Plasticized Chitosan Based Membranes

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Plasticized natural macromolecules-based polymer electrolyte samples were prepared and characterized. The plasticization of chitosonium acetate with glycerol increased the ionic conductivity value from 3.0 × 10^{-7} S/cm to 1.1 × 10^{-5} S/cm. The conductivity temperature relationship of the samples exhibits either VTF or Arrhenius type depending on the glycerol concentration in the sample. The dielectric studies evidencing the relaxation process in the plasticized sample at low frequency region are due to the electric polarization effect. Moreover, the samples were transparent in the Vis region, showed thermal stability up to 160°C and good surface uniformity.

Keywords Chitosan; gel polymer electrolytes; ionic conductivity; protonic conductor

Introduction

Natural polymers have received growing interest in the materials science due to their richness in nature, environmentally-friendly properties and their obtention from renewable sources such as fast growing plants or small crustaceans. Among the different polysaccharides investigated as ionic conducting membranes [1–3], chitosan based membrane have been prepared and characterized in different laboratories [4–6]. Chitosans' biocompatibility and bioactivity makes this polymer a promising macromolecule in biomedical, pharmaceutical and industrial applications [7]. The main reason is the characteristic to form transparent film and the possibility to introduce either acids or alkali salts, hence resulting in polymer electrolytes with high ionic conductivity and good electrochemical stability [5,8,9].

Recently, there have been reports on the electrical properties of chitosan-based polymer electrolytes (PEs) viz. chitosan complexed with lithium and ammonium salts [10,11]. The room temperature conductivities for chitosan/poly(ethylene oxide) (PEO) blends with LiTFSI salt [11] and for chitosan/poly(aminopropyl siloxane) (pAPS) with $LiClO_4$ [12] is in the order of 10^{-6} S/cm. Conductivity values between 10^{-5}–10^{-4} S/cm were reported for chitosan containing ammonium salts (NH_4NO_3 and $NH_4CF_3SO_3$) in which the hydrogen from the salt promotes the protonation of chitosan amino groups, consequently resulting in protonic conductivity [13,14].

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Plasticized polymer-based systems have also attracted the attention of various research groups. An increase in ionic conductivity of 1 to 2 orders of magnitude and decrease of Tg values by 40°C of the plasticized polymeric samples were reported by MacFarlane et al. [15] and Forsyth et al. [16]. The authors investigated the PEO samples plasticized with three different plasticizers molecules i.e. propylene carbonate, tetraglyme and dimethyl formamide. Other research groups have also studied the plasticized chitosan-based polymer electrolytes with ethylene carbonate and oleic acid, the ionic conductivities obtained were of around 10^{-5} S/cm [17–19]. We studied polymer electrolytes based on starch [20] and hydroxylethyl cellulose [21,22] plasticized with 30–48 wt.% of glycerol and ethylene glycol, respectively. The best samples showed very good ambient temperature ionic conductivity of 10^{-3} S/cm. To make progress in the research on natural macromolecules-based electrolytes, this paper reports on the conductivity enhancement of chitosan plasticized with glycerol and containing acetic acid.

Experimental

The electrolytes were prepared according to the following formula: 0.55 g of chitosan (Aldrich, No. 448877; average molecular mass of $3 \times 10^4 - 6 \times 10^4$; viscosity of 200–800 cps with 1% CH_3COOH and measured deacetylation degree of 70%) was dispersed in 55 mL of acetic acid solution (excess of 10.8, 21.7 and 40.4 times to amine groups, respectively) previously prepared with concentrations of 2.5, 5 and 10 wt.% (0.44, 0.87 and 1.75 mol/L) using Millipore Milli-Q water with resistivity of 18 $m\Omega^{-1}$ cm^{-1} at 25°C. This solution was then left under magnetic stirring for 24 hours for homogeneous gel formation. Next the solution was vacuum filtered and poured onto Petri plates to evaporate, dried at 50°C for 48 h and stored in a desiccator as chitosonium acetate membranes. The plasticized chitosan-acetic acid membranes were obtained by adding 0.4, 0.8 or 1.2 g of glycerol into the chitosan—5% acetic acid solution and continuously stirred until a viscous solution was formed and poured onto Petri plates before drying at 50°C to form transparent membranes. The prepared samples were designated as ChM (chitosonium acetate membrane) and ChGM chitosonium acetate (glycerol).

The ionic conductivity measurements were performed by placing 1.54 cm^2 round membranes between two mirror polished stainless steel electrodes fixed to a Teflon electrochemical cell. The conductivity values were obtained in vacuum by electrochemical impedance spectroscopy using a SOLARTRON SI 1260 Impedance/Gain Phase Analyzer coupled to a computer in the 10^6 to 10 Hz frequency range with amplitude of 5 mV. All measurements were taken in triplicate.

The UV-Vis measurements were taken with a Agilent spectrophotometer between 190 and 800 nm.

The thermal stability was studied by thermogravimetric analysis (TGA) in the temperature range of 25 to 700°C using a SHIMADZU TGA-50 with the N_2 flow of 50 mL/min and heat rate of 20°C/min. The DSC measurements were performed under the flowing argon atmosphere between -110 and 130°C and at the heating rate of 5°C/min using a SHIMADZU DSC-50 apparatus.

Results and Discussion

The thermal history of the polymer-based materials is an important feature in order to get more details on its possible practical application. Transitions such as melting, crystallization

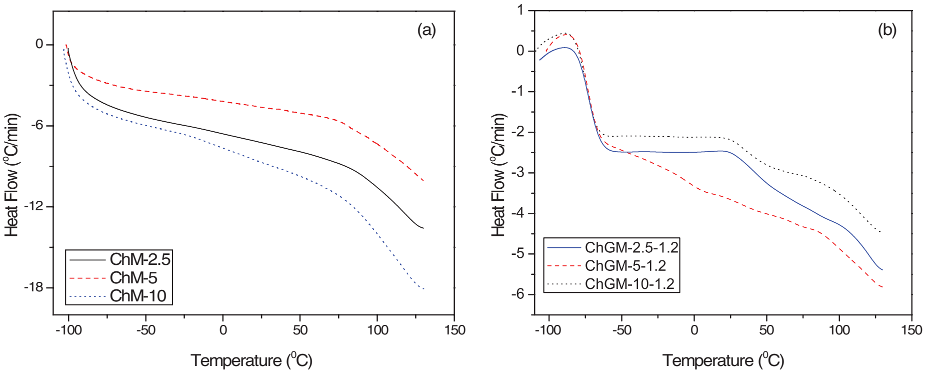

Figure 1. DSC measurements of chitosan based electrolytes with different acetic acid quantities 2.5% (—), 5% (- - -) and 10% (···) (a) and containing 1.2 g of glycerol (b).

and glass transition temperature (T_g) of the material can be observed by this analysis. In the case of polymer electrolytes the T_g represents an important property, as it can influence the ionic conduction mechanism and value and its conductivity-temperature behaviour [23]. The DSC analysis for the sample of chitosonium acetate membranes was obtained by dissolution of chitosan in 2.5, 5 and 10% of acetic acid in the temperature ranges from −110 to 130°C revealed no glass transition temperature was detected within this range (Fig. 1a). However at 70°C chitosonium acetate-based samples with different amounts of acetic acid showed an endothermic feature which can be attributed to acetylation reaction of chitosonium acetate to chitin [24]. The DSC curves of the glycerol plasticized samples (Fig. 1b) exhibit a very different behaviour, a noticeable change is observed for the baseline in the range of −80 to −70°C. According to Angles and Dufresne [26], the glass transition temperature of glycerol or glycerol-water association was reported at −120°C to −83°C. Hence this transition temperature can be assigned to the glass transition temperature of chitosan-glycerol sample with the fact that polysaccharide is linked by hydrogen bonding with the plasticizer. In analogous to starch based PEs water can also act as plasticizer for polysaccharide chains by hydrogen interaction with hydroxyl groups [28]. The same new glass transition temperature value has been observed in chitosan based ionic conducting membranes containing HCl [29].

Figure 2 shows the thermogravimetric analysis (TGA) of the studied samples. Similarly to the observation made by Toffey et al. [24], when the chitosonium acetate membranes are subjected to the thermogravimetric analysis (TGA) measurements, almost 15% of weight loss is recorded up to 250°C (Fig. 2a). In the temperature range of 250 to 350°C the degradation process of both chitin and chitosan was observed, followed by the next 25% of weight loss. This slow weight loss process continues up to 800°C with 30% of residues remaining. The addition of glycerol promotes a decrease in the degradation temperature of all investigated samples (Fig. 2b). This degradation process starts from 190°C until 350°C with 10% weight residues. The occurrence of the degradation depends on the quantity of glycerol, where two steps of degradation can be seen for samples with small quantities of glycerol and only one step of degradation process for the samples with high quantity of glycerol. The remaining residues are also lower when compared with chitosonium acetate membranes, where approximately 10 to 20% of weight is observed at 800°C. Moreover chitosan based electrolyte samples show lower weight loss up to 100°C and also a decrease of degradation temperature after glycerol addition when compared with pure chitosan

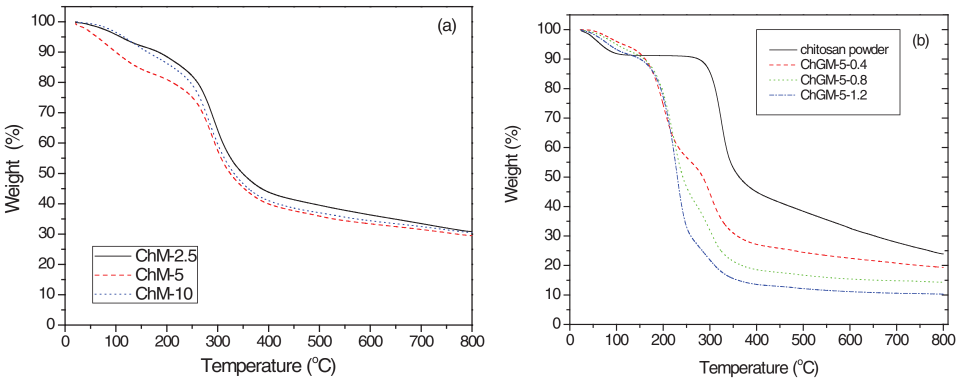

Figure 2. TGA results of chitosonium acetate membranes (a) and chitosonium acetate-glycerol membranes containing 5% of acetic acid and different glycerol quantities (b).

powder (Fig. 2b). At this point it should be noted that although glycerol is a hydrophilic substance, it does not promote the water absorption capacity of the film which is similar to chitosan-HCl [29] and agar based ionic conducting membranes [2].

Figure 3 shows that optical transmittance in the 200–1100 nm range of chitosonium acetate membranes with glycerol increases as a function of the wavelength from zero in the UV region at 280 nm to 88% in the Vis region, at 600 nm. It other studies on natural polymers based on ionic conducting membranes, the sample's transparency depends on the ionic conducting species, i.e., salt/acid and the plasticizer quantity [29]. In this work, the samples' transparency is independent with respect to the glycerol quantity, suggesting that the glycerol has better compatibility with chitosan when compared with

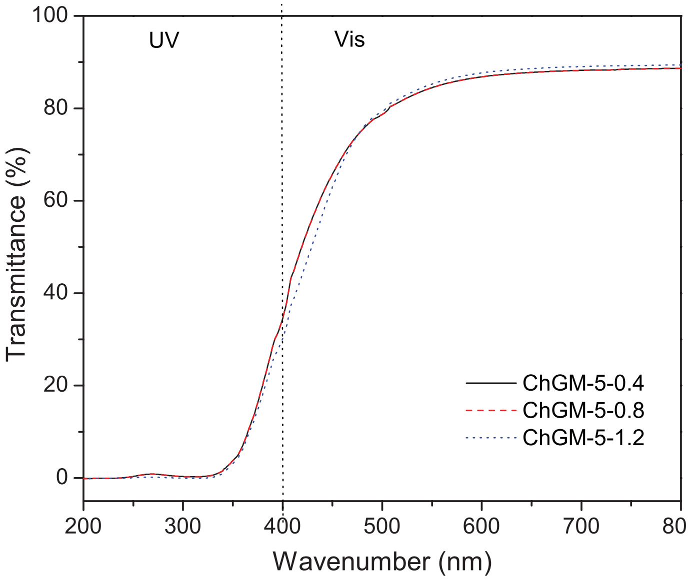

Figure 3. UV-vis spectra of the chitosan-based samples containing 5% of acetic acid and different glycerol concentrations.

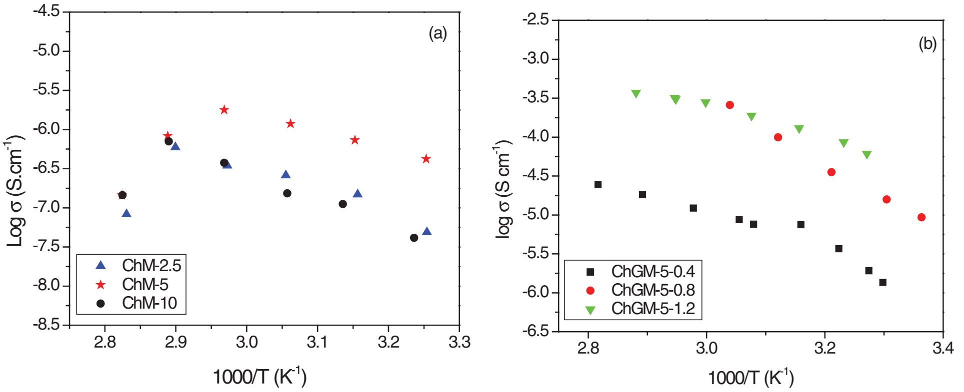

Figure 4. Ionic conductivity as a function of temperature of chitosan-based electrolytes with different acetic acid quantities (a) and with 5% of acetic acid and different glycerol quantities (b). (▲ – 2.5%; ★ – 5% and ♦ – 10%).

other polysaccharides [3]. These good transparency results up to 800 nm are similar to the gelatin-based electrolyte sample containing acetic acid [30], $LiClO_4$ [31].

To investigate the influence of glycerol on ionic conductivity of chitosonium acetate, Fig. 4(a & b) was plotted. The figure shows the conductivity values of the samples containing different amount of acetic acid increases as a function of temperature up to 70°C and then the decrease which may be due to the acetylation reaction at about 70°C as evidenced by DSC measurements shown in Fig. 2 [25]. The best value of 2×10^{-7} S/cm was obtained for the sample with 5% of acetic acid at 26°C which increase to 1.7×10^{-6} S/cm at 64°C.

The addition of glycerol to the chitosan-5% acetic acid sample caused an increase in the ionic conductivity and the thermal stability of the samples, which is evidenced in Fig. 4b. The ionic conductivity values of 1.4×10^{-6} S/cm, 1.6×10^{-5} S/cm and 6.1×10^{-5} S/cm at 30°C were obtained for the samples with 0.4, 0.8 and 1.2 g of glycerol, respectively. From these measurements, a change of linear to non-linear behaviour of the ionic conductivity is observed as a function of temperature after glycerol addition. These good ionic conductivity values are probably due to the chain movement, as already observed in other studies [31,32]. It means that glycerol promotes better separation of the macromolecular chains by hydrogen bond formation between chitosan side chains [25] and also increases the free volume, which is important to foment a vehicular mechanism of charge movement. A similar behaviour was already observed in the plasticized pectin-based system [3].

As shown in several studies the addition of acetic acid promotes the protonation of amine groups (NH_2) of chitosan, which leads to the formation of polycation chitosan-NH_3^+ [24]. As this molecule is a polyelectrolyte the ionic diffusion can occur in the whole system. Moreover, protonation of the remaining water molecules and formation of H_3O^+ and $H_5O_2^+$ is possible, which can participate in the ionic conduction.

Figure 5 shows real part of permittivity (ε_R) for chitosan-acetic acid and chitosan-acetic-glycerol samples at 303 K in the whole frequency range investigated.

In the case of chitosan-acetic acid, the highest dielectric constant at low frequencies is obtained for the sample containing 5 wt% of acetic acid either with 0.8 or 1.2 wt% of glycerol. Since the charge is produced by the protonation of the chitosan molecule, the increases in the dielectric constant indicate that the degree of protonation for the amine group in chitosan is increased. When there are more mobile ions, the conductivity is also

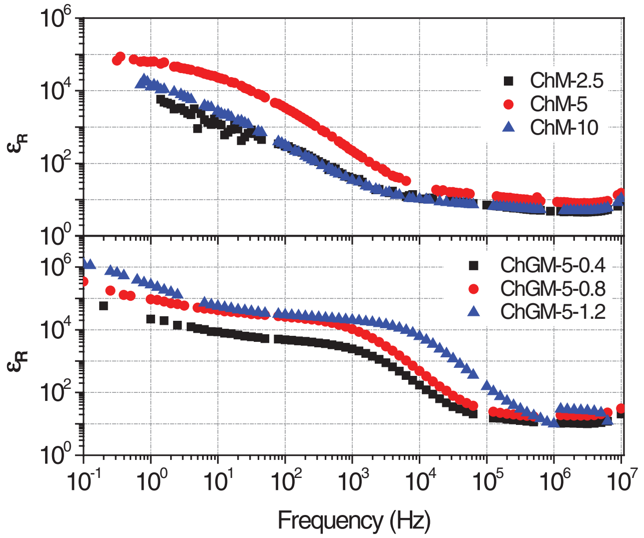

Figure 5. Real part of permittivity of chitosan films without (upper graph) and with glycerol (lower graph) at 303 K.

increased and optimized at 5 wt% acetic acid concentration. As the acetic acid concentration is further increased up to 10 wt% the acetate groups will have the tendency to hinder the mobile ions to conduct and therefore decrease the conductivity. However, the dielectric constant of this sample was further increased up to maximum, approximately $\varepsilon_R = 1 \times 10^6$ by incorporating glycerol into the chitosan-acetic acid sample. In this sample, the dielectric constant of glycerol is a result of the hydrogen bond network among the glycerol molecules [33], hence it is expected to play a role to dissociate acetic acid-like water to produce more free ions. Moreover, specific sites of chitosan macromolecule viz. $–NH_2$, $–CH_2OH$, $–NH_3{}^{+}\,{}^{-}OOCCH_3$, and $–NHOCCH_3$ can form hydrogen bonds with the alcoholic groups ($–CH_2OH$) from glycerol [34], leading to a regular structure and reducing the potential barrier for reorientational motions. Thus the mobility of free ions is expected to increase. The frequency dependence dielectric loss of chitosan-based electrolyte films, presented in Fig. 6, indicates the relaxation behaviour change by adding glycerol into the chitosan-acetic acid films.

By adding 0.4 wt% glycerol, a step frequency can be observed at about 1.6 kHz and shifts to higher frequencies with increasing glycerol content. The higher glycerol content and the higher intensity of dielectric loss are observed, suggesting an increased concentration and stronger dipole relaxation oscillation in the sample [35]. In addition, the occurrence of relaxation due to the motion of the polymer chains can be manifested from the dissipation loss peak ($\tan \delta$) at high frequency, as shown in Fig. 7.

A peak is observed in tangent loss versus frequency plot in the acetic acid sample. The magnitude of $(\tan \delta)_{\max}$ increases with the increase of acetic content, suggesting the enhancement in number of the charge carrier. The same behaviour is also observed after the glycerol has been added to the chitosan-acetic acid samples with an additional peak at the higher frequency region. To get further information on the relaxation behaviour in the investigated samples, real and imaginary parts of conductivity as a function of frequency were plotted and shown in Fig. 8.

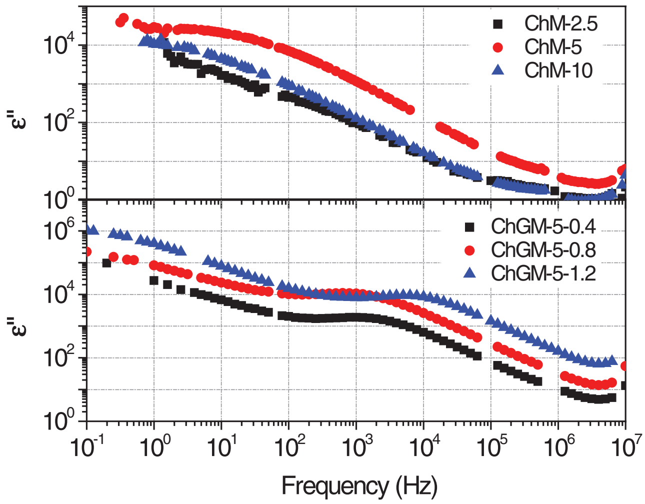

Figure 6. Frequency dependence of imaginary part of permittivity for chitosan membranes without (upper graph) and with glycerol (lower graph) at 303 K.

The conductivity behavior of chitosan-acetic acid is remarkably affected by glycerol. A rapid decrease of σ' can be seen in the low frequency region in all plots which can be attributed to space charge polarization for the electrode used [36–38]. The enhancement in the number density of charge carriers accumulated at the interface between the electrode and the sample will significantly cause the drop in the conductivity at the lower frequency region. This phenomenon is stronger in the higher glycerol content sample due to the enhancement of charge carrier mobility provided by the glycerol. After this region, a plateau which

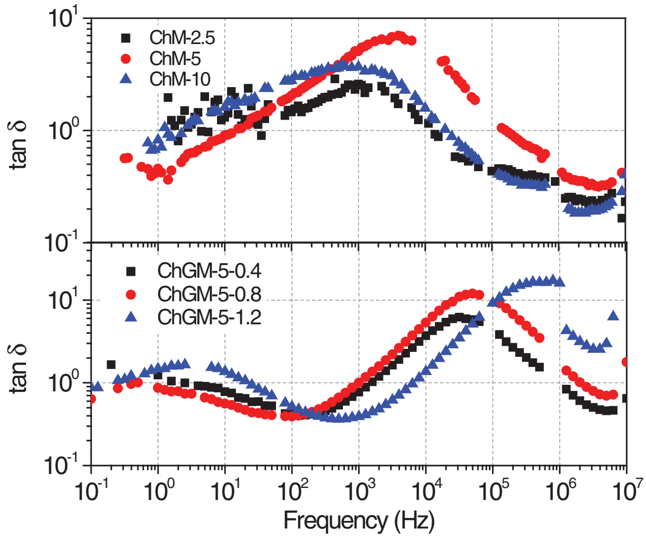

Figure 7. Frequency dependence of tangent loss for the chitosan-based membranes without (upper graph) and with glycerol (lower graph) at 303 K.

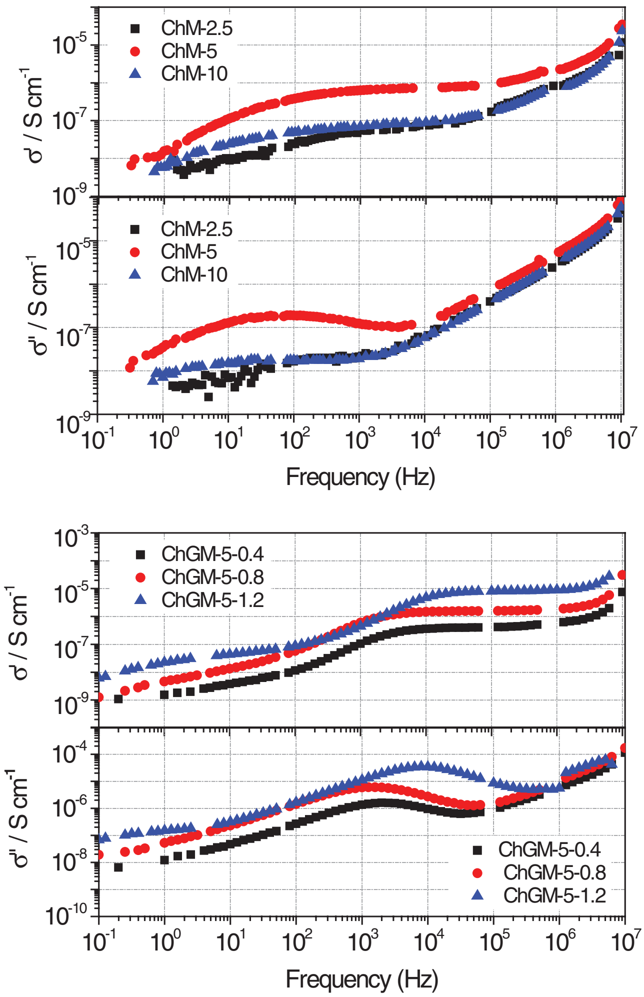

Figure 8. Frequency dependence of real and imaginary parts of conductivity for the chitosan-based membranes without (upper graph) and with glycerol (lower graph) at 303 K.

corresponds to DC conductivity is observed in all samples. In the case of chitosan with 5 wt% of acetic acid sample, DC conductivity plateaus are more distinguishable when the glycerol content is increased, (in the region f = 4.5 to 7). For better understanding Fig. 7 was compared with Fig. 8. Upon the plasticization of chitosan-acetic acid by glycerol, the electrode polarization effect was obviously found to begin at around 4 kHz towards the low frequency region and therefore the first peaking in dissipation loss peaks can be assigned as the relaxation due to electrode polarization. The second appreciable peak in the tangent loss plot is observed to associate with the DC conductivity plateau and this relaxation peak arises from the motion of the polymer chain. The shortest relaxation time is found for the sample 5HAC>0.4 glycerol>0.8 glycerol>1.2 glycerol and exhibits the conductivity trend as follows: 5HAC<0.4 glycerol<0.8 glycerol<1.2 glycerol.

Conclusions

Flexible and freestanding chitosan-based ionic conducting membranes were prepared and the conductivity enhancements were successfully achieved when glycerol was added as plasticizer. The increase in conductivity is attributed to the increase of charge carriers shown by dielectric constant. The frequency dependence imaginary part of the conductivity plots showed the electrode polarization effects at the lower frequency region. The value of the transparency for the best sample is 0% at 330 nm and 88% at 580 nm. Thermal analysis of electrolytes showed good thermal stability up to 180°C.

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