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Ionic Conduction Model in Salted Chitosan Membranes Plasticized with Fatty Acid

M.Z.A. Yahya, A.M.M. Ali, M.F. Mohammat, M.A.K.M. Hanafiah,
M. Mustaffa, S.C. Ibrahim, Z.M. Darus and M.K. Harun
Faculty of Applied Sciences, Universiti Teknologi MARA, 40450 Shah Alam, Malaysia

Abstract: In this study, chitosan was used as the host with lithium acetate (LiOAc) as the doping salt and Palmitic Acid (PA) and Oleic Acid (OA) as plasticizers. The highest conducting film containing salt has composition 55 wt. % CA and 45 wt. % LiOAc. Complexation between chitosan and the salt can be proven by Fourier Transform Infrared (FTIR) method. The NH_2 and $\text{O} = \text{C-NHR}$ vibrations which can be observed at 1580 and 1655 cm^{-1} shift to lower wavenumbers when the complexes are formed. In this study, other than the salt, plasticizers are also added to the polymer with the aim of enhancing the electrical conductivity of the polymer, the mixing of these three components could lead to some interactions for the formation of the polymer electrolyte with its own unique properties. Hence, apart from justifying the occurrence of complexation, it is also essential to know the possible interactions between the salt and plasticizer, the plasticizer and the polymer and within the polymer-salt-plasticizer system. With such knowledge, a model of the polymer-salt and plasticizer system could be devised which might be able to explain the electrolytic property of the sample, in particular, the ion conducting mechanism.

Key words: Chitosan, polymer electrolytes, ionic conductivity, lithium acetate, fatty acid

INTRODUCTION

In the effort to find alternative polymers with a wide safety margin and good mechanical and electrical properties to act as an electrolyte in polymer batteries, chitosan was studied (Yahya and Arof, 2004; Yahya and Arof, 2002). Chitosan is a polysaccharide β -1, 4-linked 2-amino-2-D-glucopyranose which is a natural polymer obtained by extensive deacetylation of chitin isolated from the structural components of the shells of crustaceans, such as shrimps, lobsters and crabs (Okuyama *et al.*, 2000). Chitosan is obtained when deacetylated chitin is able to dissolve in dilute acetic acid. Usually 1% acetic acid is used to dissolve chitosan although other dilute acids such as formic acid and dilute hydrochloric acid can also be used. It is non-toxic, odorless and biocompatible in animal tissues and enzymatically biodegradable (Zhong *et al.*, 2000). Due to its special biological, chemical and physical properties, chitosan has been extensively used over a wide range of applications, such as a biomedical applications, e.g., a bacteriostatic agent, a flocculating agent, a drug delivery vehicle, an immobilization and encapsulation agent of toxic heavy metals, a biomaterial in medicine either on its own or as a blend component (Hasegawa *et al.*, 1994), a medicine against hypertension because of its scavenging

action for chloride ions (Muzzarelli, 1996), also as a biodegradable coating or film in food packaging (Butler *et al.*, 1996), a dietary fibre (Arvanitoyannis *et al.*, 1998), a cosmetics and a membrane filter for water treatment (Kawamura, 1995). Figure 1 shows the structure of chitosan. It can be observed that chitosan has a reactive amine site at the second carbon atom.

The biocompatibility of the plasticizer is an important consideration for safe use of polymer electrolytes. The purpose of plasticizing the polymer electrolyte matrix is to enhance the electrical conductivity (Yahya and Arof, 2004). In this study, Oleic Acid (OA) and Palmitic Acid (PA) were used as the plasticizer. Moreover, OA and PA are non-toxic compared to commercially available plasticizers such as Dioctyl Phthalate (DOP) and Trioctyl Phthalate (TOP) (Gibbon and Kussy, 1998). The oleic-related plasticizer is also approved for use in dietary and medical applications. Generally, it is known that oleic acid acts also as an efficient penetration enhancer for percutaneous drug delivery.

MATERIALS AND METHODS

Sample preparation: 1.0 g of chitosan powder (Aldrich) was dissolved in several beakers containing 100 mL of 1.0% acetic acid (Aldrich) solution. To these solutions

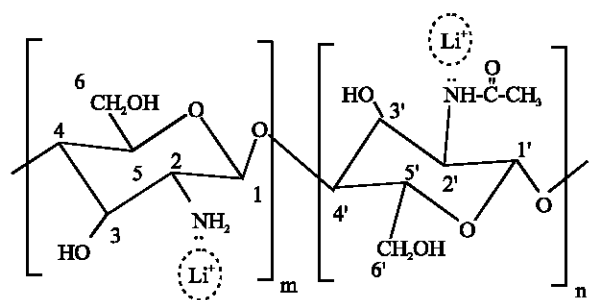


Fig. 1: Structure of chitosan

LiOAc (Aldrich) was added in different quantities (0.10 to 1.0 g) and stirred until complete dissolution was obtained. The solutions were then poured into different plastic petri dishes and left to dry at room temperature (27°C) for the films to form. To the highest chitosan-salt conducting sample, this solution composition was used to prepare a plasticized chitosan-salt film by adding different amounts of OA and PA from 2.7 to 21.7 wt.%, respectively. The preparation of these samples were carried out at Solid State Ionics and Devices (SSID) Research Lab, Universiti Teknologi MARA (UiTM).

Impedance spectroscopy: The ionic conductivity of the samples was measured with a HIOKI 3531-01 LCR Hi-Tester in the frequency range between 100 Hz and 1 MHz at SSID Research Lab UiTM. The samples were kept in a desiccator for several weeks to ensure that the films were fully dry so that water will not contribute to the ionic conductivity of the films before impedance measurements were carried out. Six different portions of the same film were used to obtain the average conductivity value and its standard deviation. The standard deviation of the conductivity value is graphed together with conductivity versus weight of dopant complexes. The conductivity-temperature study was also carried out in the temperature range between 300 and 363 K. A graph of negative imaginary impedance versus real impedance was plotted from which the bulk impedance, R_b of the sample could be determined and the electrical conductivity, σ calculated using the equation:

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

Here t is the thickness of the film and A is the film electrode contact area.

Fourier Transform Infrared (FTIR): FTIR spectroscopy was carried out to verify the occurrence of complexation using the MAGNA-IR spectrometer series II at the

Physics Department, University of Malaya. According to Osman and Arof (2003) complexation is known to occur between chitosan and an inorganic salt if there is a shift in $O=C-NHR$, $-NH_2$ and $-NH_3^+$ bands at 1650, 1590 and at 1560 cm^{-1} , respectively, to lower wavenumbers.

RESULTS AND DISCUSSION

The highest electrical conductivity achieved upon addition of 44.4 wt. % lithium acetate (LiOAc) to chitosan is $2.2 \times 10^{-7}\text{ S cm}^{-1}$. Upon addition 10.0 wt. % of OA and 7.7 wt. % of PA as a plasticizer, the conductivity increases to a maximum of $1.1 \times 10^{-5}\text{ S cm}^{-1}$ and $5.5 \times 10^{-6}\text{ S cm}^{-1}$ at room temperature, respectively as shown in Fig. 2. It can be seen that the conductivity increases with the amount of the OA added up to 10.0 wt. % and the PA added up to 7.7 wt. %. However, conductivity declines against increasing OA and PA content. According to Cowie (1987) ion aggregation limits conductivity. It can therefore be said that OA and PA increase the dissociation of the lithium acetate salt into Li^+ and CH_3COO^- ions up to a certain concentration after which ion aggregation occurs at a faster rate than ion dissociation and reduces the number of mobile ions in the samples.

In order to examine the temperature dependence of conductivity of the samples, the temperature dependent ionic conductivity measurement have also been carried out, Fig. 3. The relationship between $\ln\sigma T$ and $10^3/T$ is almost linear. The regression value, r^2 for the samples of pure CA, CA-LiOAc, CA-LiOAc-OA, CA-LiOAc-PA lie in the range 0.98 to 0.99 and the plotted points can be said to lie in a straight line. Hence, the conductivity mechanism is thermally assisted. The conductivity plot does not

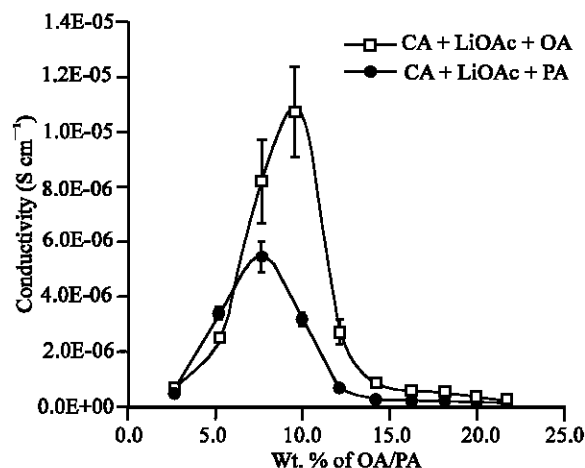


Fig. 2: Conductivity versus amount of PA and OA for CA +LiOAc+plasticizer films

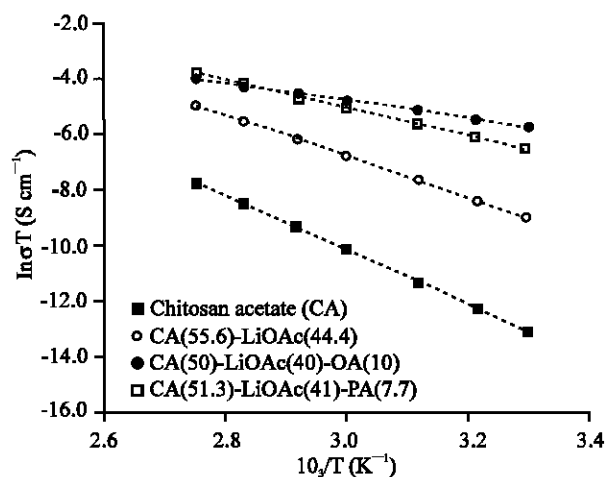


Fig. 3: Arrhenius plots of different polymer electrolyte composition based on CA, CA-LiOAc, CA-LiOAc-PA and CA-LiOAc-OA systems

show any abrupt jump indicating the fact that the chitosan-based polymer electrolyte exhibits a completely amorphous structure with no phase transition in this temperature range. It has been reported by Sakurai *et al.*, (2000) that the glass transition value, T_g for chitosan was 203°C. Thus it is possible that the T_g value for the samples studied is still above the temperature range investigated that the graphs do not show any deviation from linearity. The activation energies calculated from the Arrhenius plots are shown in Table 1. The activation energy (E_a) for the highest conducting plasticized film containing salt with PA is significantly lower compared to the highest conducting plasticized-salted sample with OA. This is due to the fact that the completely amorphous nature of the polymer electrolytes facilitates the fast Li-ion motion in the polymer network and it further provides a higher free volume in the polymer electrolyte system upon increasing the temperature (Micheal *et al.*, 1997).

Table 1: Activation energy variation with PA and OA plasticizer content in salted CA-LiOAc films

| CA+LiOAc+ wt. % plasticizer | Activation energy, E_a (eV) | |
|--------------------------------|-------------------------------|------|
| | PA | OA |
| 2.7 | 0.68 | 0.56 |
| 5.3 | 0.48 | 0.45 |
| 7.7 | 0.45 | 0.33 |
| 10.0 | 0.49 | 0.29 |
| 12.2 | 0.64 | 0.44 |
| 14.3 | 0.69 | 0.53 |
| 16.3 | 0.71 | 0.57 |
| 18.2 | 0.71 | 0.59 |
| 20.0 | 0.72 | 0.59 |
| 21.7 | 0.73 | 0.60 |

When chitosan is dissolved in 1% acid acetic solution, there is a possibility that a chitosan-acetic acid salt is formed at the nitrogen attached to the second carbon in the chitosan ring. This salt is chitosan acetate (CA) (Ritthidej *et al.*, 2002). Complexation between CA and lithium salt such as lithium acetate, LiOAc can be proven from FTIR studies (Fig. 4). The carbonyl and amine bands for CA peak at 1653 and 1571 cm^{-1} respectively. On addition of lithium acetate, the carbonyl band is shifted to 1646 cm^{-1} and the amine band shifts to 1564 cm^{-1} , respectively. On addition of plasticizer, oleic acid (OA) to CA, there seems to be no significant shift in the bands. The shift is even greater when salt and plasticizer are added to CA implying complexation between the salts and CA and also the possibility of salt-plasticizer interaction. Salt-plasticizer interactions have been shown by Osman and Arof (2003). For the sample with CA(50) + OA(10) + LiOAc(40), the amine band shifts to 1550 cm^{-1} . There is little shifting in the carbonyl band probably because its interaction with the salt has become saturated due to its smaller content in chitosan as a result of deacylation. Thus through FTIR studies, we have shown complexation between salt and chitosan.

The α -helix structure of chitosan is modeled in Fig. 5. For simplicity only the nitrogen atom of the amine groups attached to the second carbon of the chitosan monomer are shown. It is well known that the first carbon atom in a chitosan monomer is connected to the fourth carbon atom of the adjacent monomer through the interconnecting oxygen atom (Hasegawa *et al.*, 1994; Bodek and Bak, 1999). The monomers can rotate via the oxygen atom. The

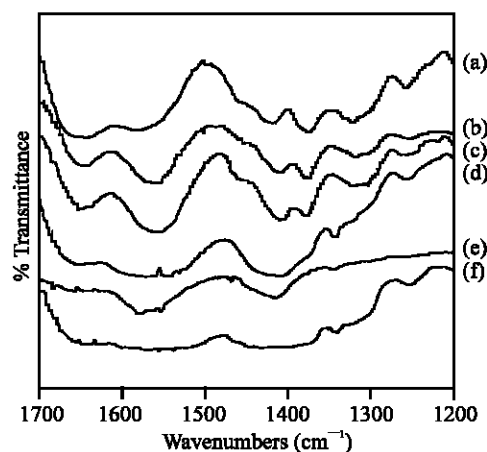


Fig. 4: The FTIR spectra of (a) chitosan acetate (CA) (b) CA(87) + PA(13) (c) CA(83.3) + OA(16.7) (d) CA(55.6) + LiOAc(44.4) (e) CA(51.3) + LiOAc(41) + PA(7.7) and (f) CA(50) + LiOAc(40) + OA(10)

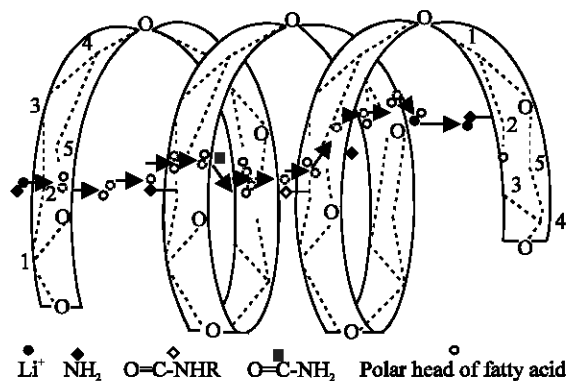


Fig. 5: Model of ionic conduction in chitosan acetate

length of two adjacent monomers in the linear configuration is 10.40 Å (Okuyama *et al.*, 2000). This implies that the distance N₂ – N₂' is less than 10.40 Å. Upon folding, as a result of hydrogen bonding between N₂ and O₆ the helical arrangement is formed. The N₂ – N₂' distance will be even shorter. Here N₂ – O₆' refers to nitrogen atom bonded to second carbon bonding monomer and O₆ refers to the oxygen in the six-membered ring in the chitosan “chair-structure”. In this arrangement the nitrogen atoms uniformly point towards the same direction.

In the model of Fig. 5, the salt is shown attached to the nitrogen atom in an amine group through its cation to illustrate complexation. These ions and all the atoms in the polymer have thermal energy at room temperature. Thus they vibrate about a certain equilibrium position. In the presence of an applied ac field, the ions are forced to move in the direction of the field and in doing so can collide with another lithium ion attached to another amine group. This can lead to energy transfer among the ions, resulting in some ions acquiring energy and some to lose energy. As the frequency of the ac source increases, the number of such motion and collisions will increase. Some ions will have enough energy such that when they collide with the lithium ion that is attached to the nitrogen atom in some of the amine groups, energy is transferred from the highly energetic lithium ion to the attached lithium ion. The energy transferred may be large enough to enable the attached ion to jump to the nearest amine group. If the nearest amine group is still vacant (no lithium ion attached to it yet), the lithium ion will reside there until it gets “knocked off” to the next amine site. If the nearest amine group is already occupied, the lithium ion may reside in an “interstitial” site within the polymer that is in between two adjacent amine sites. It can be felt that conductivity will not be high. In the present situation, conductivity should increase with an increase in the number of lithium ions.

This can be achieved by increasing the LiOAc content as long as the material does not become more crystalline. The presence of more lithium ions will increase the number of collisions, the rate of energy transfer, the number of energetic ions and the frequency of jumps from one amine group to another leading to an increase in conductivity. When the temperature increases, the lithium ions will acquire more energy and will be able to hop from one amine site to another with greater ease.

The introduction of plasticizers into the helix structure is like introducing stepping stones along the width of a river. In the context of the present material, the lithium ions can hop from one amine site to the next via the plasticizers. The plasticizers thus shorten the jumping distance from one amine group to another and the lithium ion will be able to jump from one amine group to the next via the plasticizers in between. The lithium ions can therefore hop through the material without having to acquire much energy. Hence, the activation energy needed is smaller, the lithium ion becomes more mobile and conductivity increases. As more plasticizers are added, the number of transit sites for the lithium ions to hop increases. The plasticizer thus provides a pathway for the lithium ions to reach another amine site with ease. As the amount of plasticizer increases, the lithium ions become more mobile and may be able to jump a larger distance if it has sufficient energy. If the energy it contains is insufficient to hop to another amine site, then it could transit at the oxygen atom of the polar group in the fatty acid plasticizers or at the oxygen atoms in EC, just like the interstitial mechanism in ionic crystals. It then requires lesser energy to hop from the oxygen atom to the next amine site, which may be just nearby. If the nearby amine site is occupied with a lithium ion, then this attached lithium ion may be knocked out from the amine site and its place taken over by the immigrant lithium ion. The exiled lithium ion will find itself on a transit plasticizer site and will continue to hop to another site when it acquires enough energy to do so. Thus a form of interstitially mechanism has taken place. A lithium ion that is attached to an amine site may also release itself by having sufficient energy and leaves a vacancy for the next mobile ion to reside, hence imitating the Schottky defect vacancy mechanism.

CONCLUSIONS

It has been shown that Li⁺ ion conduction do occur in chitosan polymer electrolytes. The transport of lithium ions can be visualized from the model of the material proposed. The model can help to explain the increase in conductivity with salt concentration and the enhancement

in conductivity upon plasticization in the permitted range of salt and plasticizer concentrations. The model can also explain how temperature assists ionic conduction

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