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Effect of oleic acid plasticizer on chitosan–lithium acetate solid polymer electrolytes

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Abstract

Plasticized polymer electrolytes composed of chitosan as the host polymer, oleic acid (OA) as the plasticizer and lithium acetate (LiOAc) as the doping salt were prepared by the solution cast technique. These complexes with different amounts of salts and plasticizers were investigated as possible ionic conducting polymers. The highest ionic conductivity of the plasticized chitosan–LiOAc was $\sim 10^{-5}$ S cm^{-1} for the film containing 40.0 wt.% LiOAc and 10.0 wt.% of OA. Conductivity for the plasticized LiOAc-doped chitosan polymer was also studied as a function of temperature between 300 and 363 K. The plot of $\ln(\sigma T)$ versus $10^3/T$ for each sample obeys Arrhenius rule indicating the conductivity to be thermally assisted. XRD and FTIR spectroscopy techniques have been used for the structural studies.

Keywords: Chitosan; Lithium acetate; Oleic acid; Polymer electrolytes

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1. Introduction

Polymer electrolytes are receiving considerable attention as solid polymer materials in advanced applications such as rechargeable lithium ion batteries because their use allows the fabrication of safe batteries and permits the development of thin batteries and electrochemical devices with design flexibility [1,2].

Chitin is a natural polysaccharide (N-deacetylated-2-acetamido-2-deoxy-β-D-glucan) that exists in considerable amounts as the exoskeleton of arthropods and fungi [3]. The deacytelated chitin can dissolve in dilute acetic acid is called chitosan (see Fig. 1). Chitosan is a virtually non-toxic polymer with a wide safety margin [4]. Moreover, chitosan is a biodegradable, biocompatible, positively charged polymer, which shows many interesting properties, such as a biodegradable edible coating or film in food packaging [5], a dietary fibre [6], a biomaterial in medicine either on its own or as a blend component [7], a medicine against hypertension because of its scavenging action for chloride ions [8] and a membrane filter for water treatment [9]. In this study chitosan is used as a polymer electrolyte. Previous studies have proven that chitosan can be used as a polymer matrix for ionic conduction [10–16]. Each of the nitrogen and oxygen atoms in chitosan has a lone pair electron where complexation can occur [17,18]. Thus chitosan satisfies one of the criteria as pointed out by Armand [17] and Gray [18] for the chitosan to act as a polymer host for the solvation of salts.

The biocompability of the plasticizer is an important consideration for safe use of polymer electrolytes. The purpose of plasticizing the polymer electrolyte matrix is to reduce local viscosity, thereby facilitating the mobility of ions such as Li^+ within the medium, which in turn enhances the electrical conductivity. In this work, oleic acid (OA) is used as the plasticizer. OA (cis-9-octadecenoic acid) is a type of unsaturated fatty acids in palm oil. It has been shown that oleic acid could homogeneously distribute in poly(vinyl chloride) (PVC) at low

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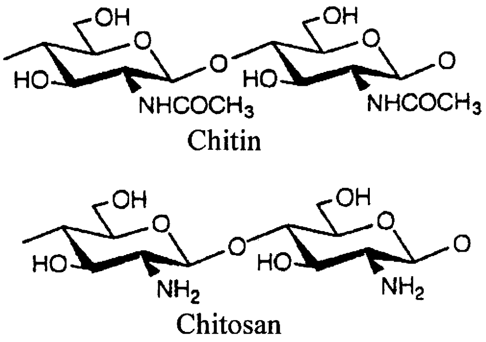

Fig. 1. Structure of chitin and chitosan.

concentrations [19]. Chitosan itself is a hydrophilic polymer, which absorbs water at ambient temperature. It is claimed that the cationic nature of chitosan makes it particularly suitable for sequestering fatty acids. On the other hand, the formation of hydrophobic aggregates has been indicated as a cause of lipid sequestering by chitosan or by chitosan–oleic acid associations [20]. This phenomenon may be an advantage in reducing the water present in chitosan-based polymer electrolyte, which will in turn help to reduce the back emf formed due to the polarization of water in the polymer [21]. Therefore the addition of OA in the chitosan-electrolyte may be useful for the good performance of such chitosan-based lithium ion polymer cells. Moreover, OA is non-toxic compared to commercially available plasticizers such as dioctyl phthalate (DOP) and trioctyl phthalate (TOP) [22]. The oleic-related plasticizer is also approved for use in dietary and medical applications [23]. Generally, it is known that oleic acid acts also as an efficient penetration enhancer for percutaneous drug delivery [24].

Infrared (IR) and X-ray diffraction (XRD) analysis were carried out to determine the occurrence of complexation and whether a material is amorphous or crystalline [25,26]. Solid-state chemistry has shown that polymers may form almost perfect crystals due to the spatial possibilities offered by chain folding. This disruption of the crystalline peaks by certain types of modification, such as the addition of an inorganic salt and plasticizer, renders the final material more amorphous. Although amorphous materials often have better ionic conductivity than their crystalline counterparts [17], Andreev and Bruce [1] are of the view that highly structured polymer electrolyte can lead to enhanced room temperature ionic conductivity and a better understanding of the conductivity or transport mechanism.

In this paper we present studies on biopolymeric electrolytes plasticized with fatty acid that can also be obtained from natural sources such as palm oil and many vegetable and animal fats.

2. Experimental

2.1. Sample preparation

1.0 g of chitosan powder was dissolved in several beakers containing 100 ml of 1.0% acetic acid solution. To these solutions, LiOAc was added in different quantities (9.1–50.0 wt.%) 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 from 2.7 to 21.7 wt.%. Two samples containing chitosan acetate and CA + OA, both without the inorganic salt were also prepared to act as controls.

2.2. X-ray diffraction

In this work, XRD were carried out using a Shimadzu XD-5 Diffractometer which employs Cu-Kα X-radiation of wavelength $\lambda = 1.5418$ Å between a 2θ angle of 10–70°. XRD was carried out to determine the nature of the materials whether a material is amorphous or crystalline.

2.3. Fourier transform infrared spectroscopy (FTIR)

FTIR spectroscopy was carried out to verify the occurrence of complexation using MAGNA-IR Spectrometer series II in the wave region between 4000 to 400 cm^{-1}. Some workers [27,28] have been successful in proving the occurrence of complexation between the salt and the polymer host. Complexation is known to occur between chitosan and an inorganic salt if there is a shift in O=C–NHR band at 1650 cm^{-1}, a shift in –NH$_2$ band at 1590 cm^{-1} and a shift in –NH$_3^+$ at 1560 cm^{-1} to lower wave numbers. However since the bands that require detailed investigation have wave numbers in the region between 1800 to 1200 cm^{-1}, this section will be enlarged in order to study the shift of the bands concerned.

2.4. Impedance spectroscopy

The ionic conductivity of the samples was measured with a HIOKI 3531-01 LCR Hi-Tester between the frequency ranges of 100 Hz to 1 MHz. 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 conductivity–temperature study was carried out in the temperature range of 300–363 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:

$$\sigma = \frac{t}{R_b A} \tag{1}$$

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

3. Results and discussion

Fig. 2 shows the XRD patterns of some of the samples prepared. The data show that LiOAc is obviously a crystalline phase with peaks at 2θ angles of 15.5°, 26° and 31°. The CA sample is partly crystalline with peaks at 2θ angles of 13.5° between of 16° to 18° and partly amorphous typical of polymers. The diffractogram of a sample containing LiOAc salt shows small peaks at 2θ angles of 15.5°, 20.5°, 25°, and 30°. Upon addition of plasticizer, the highest conducting CA-salt sample becomes amorphous. The absence of peaks in the XRD with addition of plasticizer indicates some evidence that complexation has occurred between the salt and the plasticized chitosan polymer.

Fig. 3 shows the FTIR spectrum of pure chitosan is quite similar to that given by Muzzarelli [29]. The acetate component was removed by soaking the material in sodium hydroxide solution. The spectrum for chitosan acetate (CA), Fig. 3(b), is almost similar to that of the plasticized CA, Fig. 3(c), because the plasticizer was homogeneously distributed within the film membrane. This implies that OA acts as a lubricant in the same manner as EC in chitosan acetate [30] and to PVC as described by Kusy et al. [31]. The position of the amine bands at 1590 cm^{-1} is very little affected by the introduction of the plasticizer. From Fig. 3(b)–(e), it can be observed that the amine band at 1590 cm^{-1} has shifted to lower wave numbers. This indicates that some complexation has occurred either between the salt and the nitrogen atom of the amine group or between the acetic acid and the nitrogen atom. As the salt is added, Fig. 3(d)–(e), the shift increases further towards lower wave numbers and overlaps with the $-NH_3^+$ band at 1560 cm^{-1}. Thus it can be concluded that complexation occurs when lithium from the salt interacts with the lone pair electrons of the nitrogen atom from the amine group of chitosan.

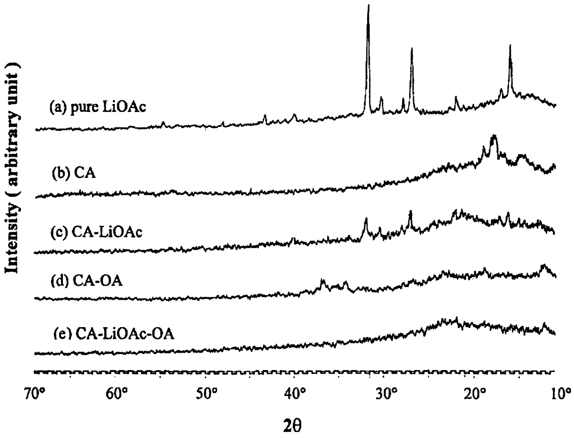

Fig. 2. X-ray diffraction patterns of (a) pure LiOAc, (b) CA, (c) CA(55.6)–LiOAc(44.4), (d) CA(83.3)–OA(16.7) and (e) CA(50)–LiOAc(40)–OA(10).

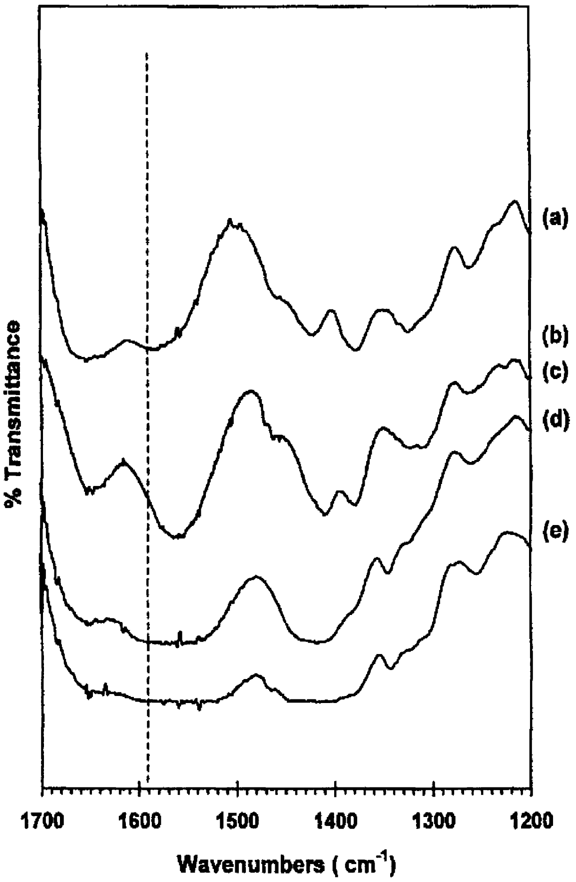

Fig. 3. FTIR spectra of (a) pure chitosan, (b) CA, (c) CA(83.3)–OA(16.7), (d) CA(55.6)–LiOAc(44.4) and (e) CA(50)–LiOAc(40)–OA(10).

The highest electrical conductivity obtained upon addition of 44.4 wt.% lithium acetate to chitosan indicating a conductivity of the order 10^{-7} S cm^{-1}. Upon addition of 10.0 wt.% oleic acid as a plasticizer, the conductivity at room temperature increases to a maximum of the order 10^{-5} S cm^{-1} as shown in Fig. 4. According to Muzzarelli [8], chitosan can bind anions such

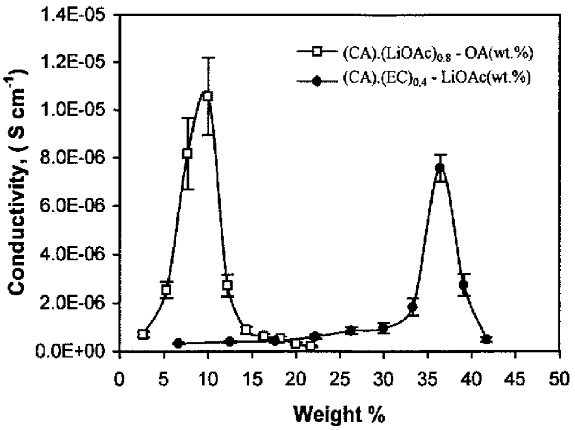

Fig. 4. Variation of conductivity with amount of CA–EC–LiOAc and CA–LiOAc–OA.

as free fatty acid (oleic acid) at low pH by ionic bonds. Oleic acid molecules (being relatively small in size compared with polymer molecules) penetrate into the chitosan matrix and establish attractive forces between plasticizer molecules and chain segments. These attractive forces reduce the cohesive forces between the polymer chains and increase the segmental mobility, thus enhancing electrical conductivity. It can be also seen that the conductivity increases with the amount of the oleic acid added up to 10.0 wt.% after which the conductivity decreases. This decrease in conductivity could be ascribed to ion aggregation [32]. This is because ion aggregation decreases the available number of charge carriers. It can be concluded that OA increases the dissociation of the LiOAc salt into lithium and acetate ions up to a certain concentration after which ion aggregation occurs at a faster rate than ion dissociation by OA and reduces the number of mobile ions in the sample. For comparison, it can be observed that a higher amount of ethylene carbonate (EC) is required to enhance the room temperature electrical conductivity to only 7.6×10^{-6} S cm^{-1}, as shown in Fig. 4.

In order to examine the temperature dependence of conductivity of the samples, the temperature dependent ionic conductivity measurements have also been carried out. Fig. 5 represents the Arrhenius plot that conductivity increases with temperature. The relationship between $\ln(\sigma T)$ and $10^3/T$ is almost linear. The regression value, r^2 lies in the range 0.989–0.997 and therefore the conductivity and temperature relationship obey Arrhenius rule, indicating that the conductivity mechanism is thermally assisted.

The effect of adding OA can be observed in Fig. 6. Upon addition of salt, 44.4 wt.% LiOAc the dielectric constant, $\varepsilon'(\omega)$ increases slightly. $\varepsilon(\omega)$ was calculated according to the equation:

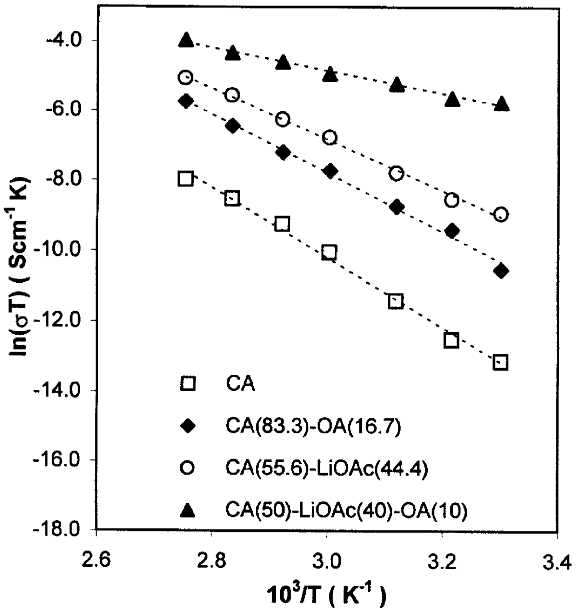

Fig. 5. Arrhenius plots of different polymer electrolyte composition based on CA, CA–LiOAc and CA–LiOAc–OA systems.

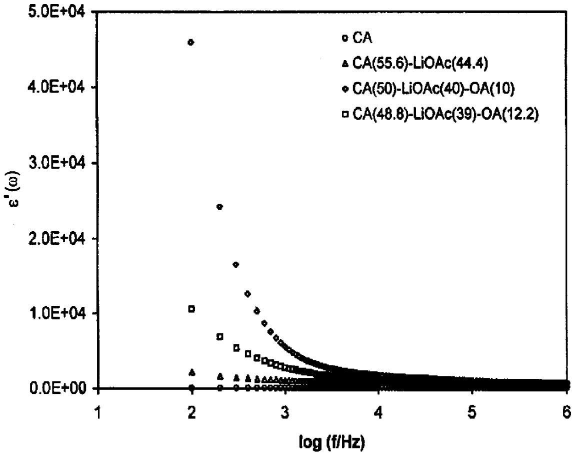

Fig. 6. Dielectric constant versus frequency with dopant contents for CA, CA–LiOAc and CA–LiOAc–OA systems.

$$\varepsilon'(\omega) = \frac{-\omega C_c Z''}{(\omega C_c)^2[(Z')^2 + (Z'')^2]} \tag{2}$$

Here $\mu = j\omega C_c$ where $C_c = \varepsilon_o A/t$, ε_o is the permittivity of free space, A is the sample-electrode contact area and t is the thickness of the sample. The imaginary part of the complex permittivity was calculated according to the equation:

$$\varepsilon''(\omega) = \frac{\mathrm{j}\omega C_c Z'}{(\omega C_c)^2[(Z')^2 + (Z'')^2]} \tag{3}$$

On addition of OA, $\varepsilon'(\omega)$ increases by one order of magnitude. The increase in $\varepsilon'(\omega)$ can be readily observed at low frequencies where the effects of blocking electrodes are observed. It is well known that the dielectric constant also plays a fundamental role in the ability of a polymer to dissolve salts. If the value of ε' increases with increasing plasticizer content and for a fixed frequency, the plasticizer has increased the ability of the biopolymer to dissolve the salt. The effect of the plasticizer in increasing the ability of a polymer to dissociate the salt has also been observed by the other workers [33,34]. Alternatively, plasticizers can also increase ionic mobility by reducing the potential barrier to ionic motion as a result of the decreasing cation–anion coordination of the salt [35].

Fig. 7 illustrates the dielectric loss, $\varepsilon''(\omega)$ values for the chitosan acetate film, film containing salt and plasticized films containing salt. For the plasticized film containing salt, $\varepsilon''(\omega)$ has high values at low frequencies. This implies that the mobile ions tend to accumulate at low frequency. It can also be observed that the dielectric loss value increases as the frequency decreases due to the free charge motion within the material [36]. This may be due to free charge build up at the interface between the material and the electrode. For very low frequencies there is practically time for charges to build up at this interface before the electric field changes direction giving a very large effective value of dielectric loss.

Figs. 8 and 9 depict the real part, $M'(\omega)$ and the imaginary part, $M''(\omega)$ of the modulus formalism, M with respect to frequency. Both parameters can be calculated as follows:

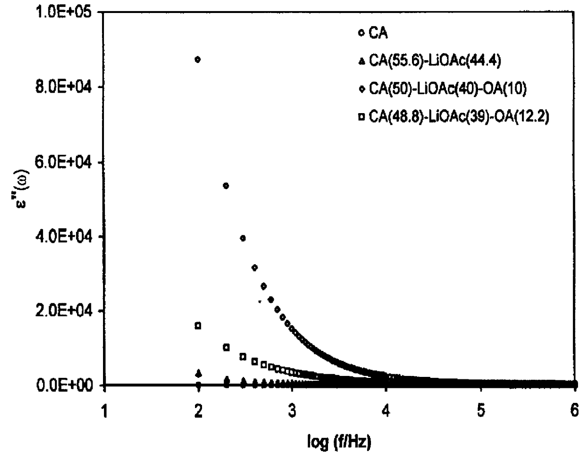

Fig. 7. Dielectric modulus versus frequency with dopant contents for CA, CA–LiOAc and CA–LiOAc–OA systems.

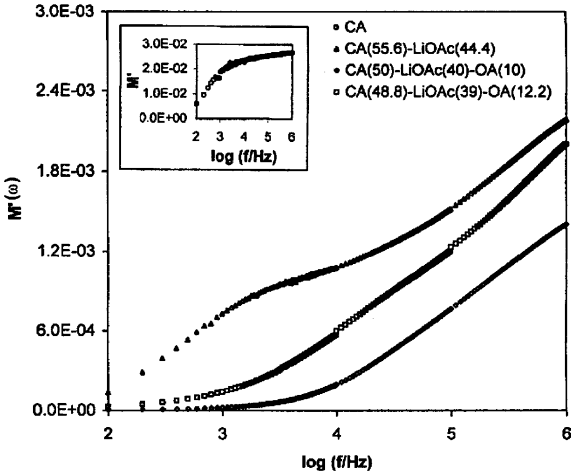

Fig. 8. Real modulus formalism versus frequency with dopant contents for CA, CA–LiOAc and CA–LiOAc–OA systems.

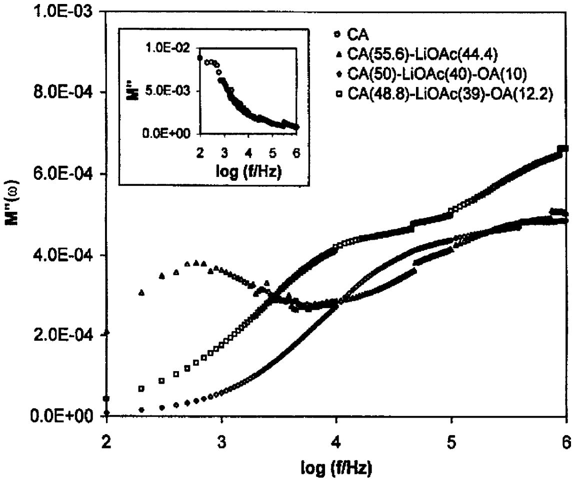

Fig. 9. Imaginary modulus formalism versus frequency with dopant contents for CA, CA–LiOAc and CA–LiOAc–OA systems.

$$M'(\omega) = -\omega C_c Z'' \tag{4}$$

$$M''(\omega) = \mathrm{j}\omega C_c Z' \tag{5}$$

It can be clearly observed from the imaginary part of the modulus formalism versus frequency plot there is a shoulder in the plot for the plasticized film containing salt. The shoulder reflects the expected conductivity relaxation peak for the distribution of relaxation times of the free charge [37]. The peak shifts to higher frequency as the conductivity increases indicating that the relaxation time decreases as conductivity increases. The existences of such peaks indicate that the samples are ionic conductors [38]. The tail in the $M'(\omega)$ versus $\log(f/\mathrm{Hz})$ plot indicates that the samples are capacitive in nature and the peaks observed in the $M''(\omega)$ versus $\log(f/\mathrm{Hz})$ implies the distribution of relaxation times of the ionic conductors.

4. Conclusion

These results show that OA can be used as a biodegradable plasticizer to increase the ionic conductivity of the electrolyte. The addition of OA has increased the dielectric constant, which implies that the plasticizer has helped to increase the dissociation of the salt thereby producing more free ions for conducting, and hence increases the ionic conductivity. OA is able to increase the electrical conductivity by a factor of 1.4. By virtue of the peaks present in the imaginary modulus formalism the OA plasticized chitosan–lithium acetate complex is an ionic conductor. The conductivity that has been obtained by adding LiOAc and OA to chitosan makes this material a potential candidate as an electrolyte in some electrochemical devices.

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