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Y Jaya Vinse Ruban
 Department of Chemistry, St.
 Xavier's College (Autonomous),
 Palayamkottai, Tamil Nadu,
 India

S Mary Jelastin Kala
 Department of Chemistry, St.
 Xavier's College (Autonomous),
 Palayamkottai, Tamil Nadu,
 India

S Ginil Mon
 Department of Chemistry,
 Nesamony Memorial Christian
 College, Marthandam,
 Tamil Nadu, India

T Leon Stephan Raj
 Department of Botany, St.
 Xavier's College (Autonomous),
 Palayamkottai, Tamil Nadu,
 India

Correspondence
Y Jaya Vinse Ruban
 Department of Chemistry, St.
 Xavier's College (Autonomous),
 Palayamkottai, Tamil Nadu,
 India

Effect of organoclay on chitosan-magnetite solid polymer electrolytes

Y Jaya Vinse Ruban, S Mary Jelastin Kala, S Ginil Mon and T Leon Stephan Raj

Abstract

Chitosan was prepared by deacetylation of chitin available from the crab shells. By the use of pH-metric titration the degree of deacetylation (DDA) of chitosan was studied and viscometric method allows to find out its molecular weight. The structure of chitosan contains the amine group that can act as electron donor, and in addition with that Fe_3O_4 (magnetite) was doped to find out the conductance. The change in conductance with addition of organoclay was also studied on the chitosan-magnetite combined sample which gave the maximum conductance. The polymer films were prepared by the solution casting technique. The dielectric constant measurements were done by LCR (Induction, Capacitance, Resistance) meter with a fixed frequency of 1 KHz at room temperature.

Keywords: Chitosan, Organoclay, Fe_3O_4 , conductance

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]. Chitin is the second, after cellulose, most abundant natural polymer. It is widespread in the animal world, in particular in crustacea, molluscs and insects where chitin is an important constituent of the exoskeleton and appears also in the cells of fungi and moulds. Chitosan is a polysaccharide, cationic in nature, composed mainly of (1, 4) linked 2-amino-2-deoxy- β -D-glucan and soluble in acidic solutions, but insoluble in alkaline solutions [2]. Because chitosan has ionized amino groups, both its reactivity and solubility are much higher than those of its precursor, chitin, and so it has become the most applied of the chitin derivatives. It also has some other specific favorable properties, such as non-toxicity, tastelessness, heat stability, resistance to alkalis, and resistance to corrosion, that have drawn people's attention [3]. Blending natural polymers with different additives is a very interesting methodology to modify the properties of natural polymers and to develop novel composite materials based on natural polymers. It is important to clarify whether the polymer blends are miscible or immiscible systems when composite materials are prepared [4]. An important criterion for the choice of a wonderful polymer host is the presence of heteroatom such as O and N that possess lone pair electrons. These atoms present in the polar groups of chitosan. Chitosan dissolves in dilute acetic acid and specially modified chitosan can also dissolve in pure water. When a chitosan membrane is swollen in water the amino groups may be protonated and leaving the hydroxide ions free in water, which may contribute to the ionic conduction in the membrane. Intrinsically conducting polymers such as polypyrrole, polyaniline, polythiophene etc. belong to the category of electro active polymers, which reversibly change their chemical, physical and mechanical properties in response to a given stimulation. Ever since the discovery by Wright, the polyethylene oxide (PEO)-salt complexes can support ionic conductivity and many other polymeric materials have been tested and found to support ionic conductivity. Examples of other polymeric materials include poly vinyl chloride (PVC), polyethylene glycol (PEG), polyvinylidene fluoride and several mechanisms of conductivity have been proposed [5].

This study began with the synthesis of a conducting polymer, consisting of magnetite particles and chitosan, then its ability to maintain its conductance with the addition of organoclay was tested under uniform condition.

2. Experimental

2.1 Materials

Iron-Oxide (Fe_3O_4) nanopowder with the nominal size < 40 nm, and density of 5.11 g/cm³ was purchased from sigma Aldrich Inc., USA and used as received. Montmorillonite clay was purchased from Sigma Aldrich Inc., USA. Tetradecyltrimethylammonium bromide was kindly supplied by Sisco Research Laboratories, Mumbai, sodium chloride was provided by Central Drug House, New Delhi and silver chloride, hydrochloric acid, sodium hydroxide, sodium acetate and acetic acid were purchased from Merck India Ltd., India.

2.2 Preparation and characterization of chitosan

Chitosan has been synthesized and characterized by following the procedure we reported earlier [6]. In brief, crab shells were collected, cleaned, powdered and then heated to boiling with sodium hydroxide at the ratio of 2:3 (solid: liquid) in a container for 10 minutes. The alkali was then dried off and the shell was washed well and demineralised by treatment with 1N HCl. The acid was drained off and the chitin was obtained when bleached with 10% commercial hypochlorite for 10 minutes. The chitin prepared as above was deacetylated by treatment with 50% aqueous sodium hydroxide for 2 hours at 90–95 °C for the conversion of chitin into chitosan. Then the molecular weight of chitosan was determined by measuring the intrinsic viscosity of the chitosan solution and calculated by the Mark Hauwink equation. The degree of deacetylation of the prepared chitosan was established by the pH-metric method.

2.3 Preparation of Organoclay

The purification of montmorillonite was achieved by sedimentation, centrifugation and drying. A portion of the montmorillonite was crushed in a mortar in order to obtain a fine powder. The clay was dispersed in deionised water using an ultrasonic bath during ten minutes. The obtained solution was stirred overnight. As stirring stopped, particles started to sediment. The solutions containing particles still in suspension (which are less than $\approx 2\mu\text{m}$) was siphoned off. This solution was subjected to 20000 rpm during 15 minutes so that particles sedimented rapidly in the centrifugal field. Particles were then redispersed in a small amount of purified water. The concentrated solution obtained was dried at 50 °C in a ventilated oven during 4 days.

In order to increase swelling properties of montmorillonite (MMT), sodium activation was performed to convert into Na-montmorillonite. Montmorillonite clay was first dispersed in 1N solution of sodium chloride and stirred. The stirring was continued for 24 hours at 70 °C. Upon centrifugation of the solution at high speed an opaque layer accumulates in the bottom of the centrifuge tubes beneath a translucent gel. The gel was isolated and washed several times with deionised water until no chloride was detected in the centrifugate by testing with one drop of 0.1 N silver nitrate solution. The purified clay was dried at 70 °C and stored in a desiccator.

Purified Na-montmorillonite clay of 15 g was dispersed into 1,200 ml of distilled water at 80 °C.

Cetyltrimethylammonium bromide, 5.7 g, in 300 ml distilled water was poured in the hot montmorillonite/water solution and stirred vigorously for 1 h at 80 °C. A white precipitate formed, was isolated by filtration and washed several times with hot water/ethanol (1:1) mixture until no chloride was detected in the filtrate by one drop of 0.1 N AgNO_3 solution. The cetyltrimethylammonium ion exchanged montmorillonite (organoclay) was then dried for several days at 75 °C, ground with a mortar and pestle, and then the <50 μm fraction was collected. The organophilic nanoclay was stored in a desiccator for further use [7].

2.4 Preparation of films

About one gram of the above prepared chitosan powder was dissolved in several beakers containing 100 ml of 1% acetic acid solution. To these solutions Fe_3O_4 was added from 0.1 to 0.5g and mixed. The mixtures were stirred with a magnetic stirrer for several hours at room temperature until chitosan and the salt were completely dissolved and become thick and gel like in the acetic acid solution. When complete dissolution has taken place, the solution was poured into different plastic petri dishes according to the amounts of dopants and left to dry in air at room temperature until the films have formed. The films were then transferred into a desiccator for continuous drying. Then the film which gives a maximum conductance was checked. From the maximum conducting chitosan- Fe_3O_4 sample, this solution composition was used to prepare a organoclay-chitosan- Fe_3O_4 film by adding different amounts of organoclay from 0 to 25 wt% of chitosan.

2.5 FT-IR spectroscopy

The IR spectra were recorded on a Perkin-Elmer (Model RX1) FT-IR spectrometer, with KBr pellets, for solid samples. For viscous liquid samples, the spectra were carried out by placing the sample between two KBr pellets.

2.6 AC Impedance Study

The ionic conductivity of the samples was measured in a LCR tester in a fixed frequency of 1MHZ. The samples were kept in a desiccator for several days 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. Four different portions of the same film were used to obtain the average conductivity value. The conductivity measurement was carried out at 300±1 K.

3. Results and discussion

3.1 Spectral analysis

The IR spectrum (Fig: 1b) of cetyl ammonium exchanged montmorillonite (C-MMT) contains several new signals corresponding to the cetyl ammonium group at 2927 cm⁻¹ (CH_2 asym. stretch), 2864 cm⁻¹ (CH_2 sym. stretch), 1479 cm⁻¹ (C-H def.), 3452 cm⁻¹ (N-H stretch) and 1045 cm⁻¹ (Si-O-Si asym. stretch of MMT). The strong and intense absorption frequency at 1045 cm⁻¹ characterizes the silicate layers which are found in both MMT and C-MMT (Fig: 1a and 1b).

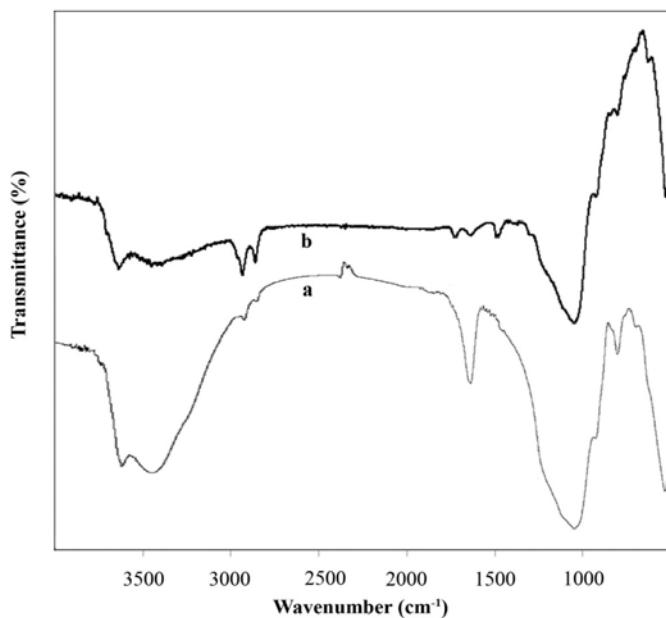


Fig 1: FT-IR spectra of (a) pristine MMT and (b) organo-MMT

The FTIR spectrum of chitosan (Fig. 2) shows peaks assigned to the saccharide structure at 891 and 1148 cm⁻¹ and a strong amino characteristic peak at around 1581 cm⁻¹. The

absorption bands at 1650 and 1321 cm⁻¹ are characteristic of N-acetylated chitin^[8].

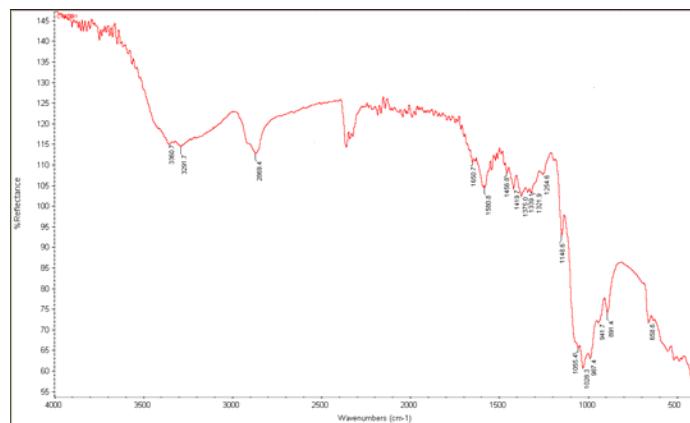


Fig 2: FTIR spectrum of Chitosan prepared from crab shells

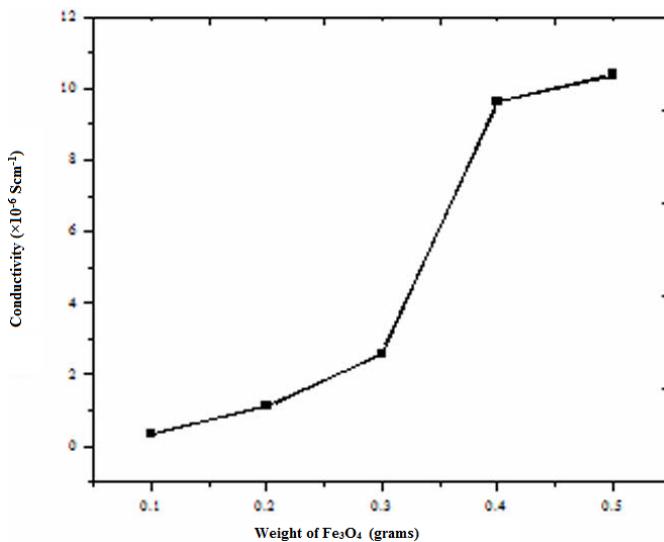
3.2 Degree of deacetylation and molecular weight

The pH-metric titration method was performed with NaOH on chitosan to determine the DDA as explained earlier^[8]. The percentage of deacetylation was calculated using the relation $16.1(y-x)/f/w$. And it was found that the percentage deacetylation of the chitosan prepared from crab shell was 79.41%. The deacetylation was further confirmed by dissolving the chitosan in dilute acids. Viscometry is the most common method for determining the molecular weight of polymers by using Mark-Hauwink equation. The use of viscometry in the case of chitosan, however is not always straight forward because of its complex hydrodynamic behaviour, which greatly depends upon its DDA and the solvent system used as well as temperature. Several authors have reported different coefficient and exponential values in Mark-Hauwink equation for chitosan in various solvent

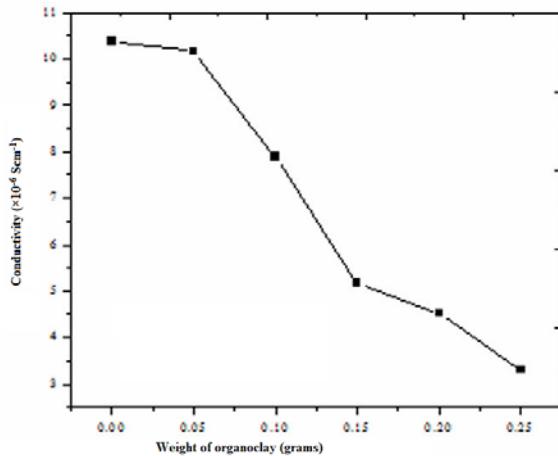
systems. The 0.3M CH₃COOH/0.2M CH₃COONa solvent system has been chosen here because the viscosity-average molecular weight of chitosan obtained using this solvent system is independent of its DDA in a range above 60%. And it was found that the molecular weight of chitosan from crab shell was 52,729 g/mol.

3.3 A.C. Impedance Study

The figure 3 shows the conductivity plot of chitosan-Fe₃O₄ polymer films with different weight percentage of Fe₃O₄. It was found that the conductance increases with the addition of Fe₃O₄ with chitosan and attained a maximum of 10.385×10^{-6} S cm⁻¹ for 0.5 g of Fe₃O₄. The increase in conductance of the films with increase in concentration of Fe₃O₄ is due to the presence of free Fe³⁺ ions in the sample which are the carriers of electric charge.

**Fig 3:** Graph of Conductivity against the Weight of Fe_3O_4

Then the conductivity over the effect of organoclay on the chitosan- Fe_3O_4 (50 wt%) is given in figure 4, which indicates there is a decrease in conductance with increase in wt% of organoclay. The movement of the ions restricted more with the interlocking of the ions in the layers of the organoclay. This decrease in conductance is also due to the wrapping mechanism of long cetyl groups linked into the galleries of montmorillonite.

**Fig 4:** Graph of Conductivity against the weight of Organoclay

4. Conclusion

In the present study, the preparation of chitosan carried out from crab shells is described. The molecular weight of the chitosan thus formed was found out by viscometric methods using Mark-Hauwink equation and it was found as 52,729 gm/mol. The degree of deacetylation was determined by the pH-metric acid base titrations and the value is 79.41%. Then the polymer chitosan was converted into the polymer electrolyte by doping with Fe_3O_4 and it was found that a maximum conductance was observed at the addition of 50 wt% Fe_3O_4 , which is due to the increase in number and easy movement of Fe^{3+} ions. But films with organoclay as the fillers the movement of the ions were get restricted with the interlocking of these ions in the gallery of the clay particles and due to the wrapping mechanism of long cetyl groups linked into the galleries of montmorillonite. The decrease in

conductance is also due to the decrease in flexibility of the polymer system due to the addition of the organoclay so that the ions are not easily move. So when the fillers are added more, the movement of the ions further restricted more with the interlocking of the ions in the layers of the organoclay.

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