

Effect of Montmorillonite on Chitosan-Lithium Acetate Solid Polymer Electrolytes

Y. JAYA VINSE RUBAN*

Department of Chemistry, Annai Vellankanni College, Tholayavattam-629 157, India

E-mail: jayavinse201a@yahoo.com

Chitosan was prepared by deacetylation of chitin available from the crab shells. The degree of deacetylation of chitosan was calculated by pH-metric titration while its molecular weight by viscometric method. The structure of chitosan contains the amine group that can act as electron donor and in addition with that lithium acetate was doped to find out the conductance. The change in conductance upon the addition of montmorillonite was also studied on the chitosan-lithium acetate combined sample, which gave maximum conductance. The dielectric constant measurements were done by LCR meter with a fixed frequency of 1 KHz at room temperature.

Key Words: Chitosan, Lithium acetate, Montmorillonite, Conductance.

INTRODUCTION

Chitosan is a derivative of chitin consists of β -1,4-N-acetylglucosamine. Chitin is widely distributed in nature as a component of the skeleton structure of crustaceans, insects, mushrooms and the cell wall of fungi and it is the second most widespread natural polysaccharide. It may also be viewed as a positively charged polyelectrolyte and the versatile functions of chitosan have been ascribed to this cationic nature¹. Chitosan is a virtually non-toxic polymer with a wide safety margin. Moreover chitosan is a biodegradable, biocompatible, positively charged polymer which shows many interesting properties such as a biodegradable edible coating or film in food packing, a dietary fibre, a biomaterial in medicine either on its own or as a blend component, a medicine against hypertension because of its scavenging action for chloride ions and a membrane filter for water treatment². 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 proposed³.

An important criterion for the choice of a successful polymer host is the presence of hetero atoms such as O and N that possess lone pair electrons. These atoms are present in the polar groups of chitosan. Chitosan dissolves in dilute acetic acid and specially modified chitosan can dissolve in pure water. Hence when the film had formed such cation-hetero atom complexation had to be proven. If complexation did occur, then it is necessary to show that the complex is an ionic conductor. When a chitosan membrane is swollen in water the amino groups may be protonated, leaving the hydroxide ions free in water, which may contribute to the ionic conduction in the membrane. However, since there is not only electrolyte being added to the membrane before it was made the ionic conduction that membrane may show will be an intrinsic ionic conduction⁴. Intrinsically conducting polymers such as polypyrrole, polyaniline, polythiophene, *etc.* belong to the category of electroactive polymers, which reversibly change their chemical, physical and mechanical properties in response to a given stimulation. As in all polymer-salt complexes, conductivity can be attributed to both anions and cations. The mobility of each of these ions is known to be quite comparable.

Developing chitosan-layered silicate composite by inserting chitosan chains into interlayers of silicates can improve its mechanical properties. In recent years, polymer nanocomposites have received considerable interest because of their superior thermal and mechanical properties as compared with the polymer itself⁴. Polymer-clay composites are a class of hybrid materials composed of organic polymer matrices and nanoscale organophilic clay fillers. Of the nanoscale clays, montmorillonite is of particular interest and has been studied widely. Montmorillonite is a hydrated alumina-silicate layered clay made up of two silica tetrahedral sheets fused to an edge shared octahedral sheet of aluminium-hydroxide. Its advantage of high, large aspect ratio (50-1000) and platelet thickness of 10 Å make it purpose for reinforcement purposes⁵. The inorganic surface of montmorillonite has also been modified by organic replacement of the interlayer sodium ions by various organic cations to make the platelets more compatible with polymers.

The present study described the preparation of chitosan from crab shells and the degree of deacetylation and molecular weight of chitosan were studied by pH-metric and viscometric methods, respectively. Further, the montmorillonite doped chitosan-lithium acetate complexes were prepared and studied in terms of its ability as an ionic conductor.

EXPERIMENTAL

Preparation of chitosan: The samples of chitin and chitosan in pure form were prepared in the laboratory. The shells of crab were collected and brought to the laboratory for processing into chitosan. Dried shell waste, after washing with tap water was heated to boiling with 4 % NaOH at the

ratio of 2:3 (solid:liquid) in a glass container for 10 min. The alkali was then dried off and the shell was washed well and demineralized by treatment with 1 N HCl. The acid was drained off and the chitin was obtained when bleached with 10 % commercial hypochlorite for 10 min. The chitin prepared as above was deacetylated by treatment with 50 % NaOH for 2 h at 90-95 °C for the conversion of chitin into chitosan.

Determination of molecular weight: For the determination of average molecular weight (MW) of chitosan, five different concentrations of chitosan solution in CH₃COOH-CH₃COONa buffer were prepared. Then the relative viscosity was found out by a capillary viscometer at room temperature. Then the intrinsic viscosity was determined and the molecular weight of chitosan was calculated based on the Mark Hauwink equation⁵.

$$[\eta] = kMW^a, \text{ where } k = 0.076 \text{ and } a = 0.76.$$

Determination of degree of deacetylation (DDA): The pH-metric titration method was followed to determine the degree of deacetylation. According to this modified acid-base titration method 0.05 g of chitosan was dissolved in 20 mL of 0.1 N HCl and titrated pH-metrically with a standardized solution of 0.1 N NaOH. Then a plot of volume of NaOH against pH was drawn. The diagram has two equivalent points related to the excess of HCl and the protonated amino groups. The degree of deacetylation was calculated by the following equation⁵.

$$DDA = 16.1 (Y-X) f/w,$$

where Y and X are the consumed NaOH volumes of the equivalent points, f is the normality of the NaOH solution and w is the initial weight of chitosan⁶.

Preparation of films: 1 g of above prepared chitosan powder was dissolved in several beakers containing 100 mL of 1 % acetic acid solution. To these solutions lithium acetate was added from 0.1 to 0.4 g 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. Two samples containing chitosan and acetic acid and chitosan, both without the inorganic salt were also prepared to act as controls. 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-salt sample, this solution composition was used to prepare a montmorillonite-chitosan-salt film by adding different amounts of montmorillonite from 0 to 25 wt % of chitosan.

A.C. Impedance study: The ionic conductivity of the samples were measured in a LCR tester in a fixed frequency of 1 MHz. The samples were kept in a dessicator 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 the 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.

RESULTS AND DISCUSSION

Preparation of chitosan: The synthesis of chitosan from chitin was carried out by deacetylation with 50 % NaOH. Earlier the chitin was prepared from the crab shells by deprotonation with 4 % NaOH followed by demineralization by heating with 1 N HCl.

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. The 0.3 M $\text{CH}_3\text{COOH}/0.2$ M CH_3COONa 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 45,255 g/mol.

Degree of deacetylation: The pH-metric titration was performed with NaOH on chitosan to determine the DDA. And it was found that the percentage deacetylation of the chitosan prepared from crab shell was 86.94. The deacetelation was further confirmed by dissolving the chitosan in dilute aqueous acids.

A.C. Impedance study: Fig. 1 shows the conductivity plot of chitosan-lithium acetate polymer films with different weight percentage of lithium acetate. It was found that the conductance increased with the addition of lithium acetate with chitosan.

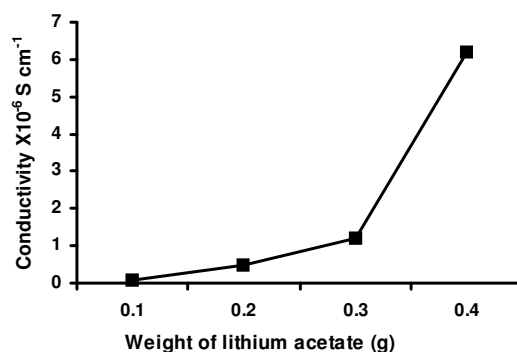


Fig. 1. Graph of conductivity against the weight of lithium acetate

The conductivity over the effect of montmorillonite on the chitosan-lithium acetate (40 wt %) was given in Fig. 2 which indicates there is a decrease in conductance with increase in weight % of montmorillonite.

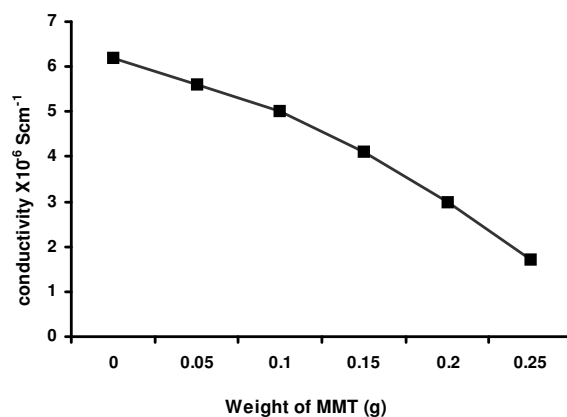


Fig. 2. Graph of conductivity against weight of montmorillonite

Conclusion

In this paper, the preparation of chitosan carried out from crab shells was described. The molecular weight of the bio polymer thus formed was found out by viscometric methods using Mark-Hauwink equation and it was found as 45,255 gm/mol. The degree of deacetylation was determined by the pH-metric acid base titrations and the value is 86.94. Then the polymer chitosan was converted into the polymer electrolyte by doping with lithium acetate and it was found that a maximum conductance was observed at the addition of 40 wt % lithium acetate, which is due to the increase in number of easy movement of ions. But films with clay as the fillers the movement of the ions were got restricted with the interlocking of these ions in excess of the clay particles. The decrease in conductance is also due to the decrease in flexibility of the polymer system due to the addition of the clay so that the ions are not easily moved. 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 clay.

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