Phosphoric Acid Doped N-phthaloylchitosan As Polymer Electrolyte Membrane

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Abstract

To diversify the applications of chitosan, structural modifications are required. In this wo the modified chitosan were synthesized using phthalic anhydride. N-phthaloylation is said be one of the potential methods to improve the solubility of chitosan in organic solvents. T precipitate obtained after drying in vacuum is yellowish in color and powdery in nature. FT proved the occurrence of phthaloylation. ^{1}H NMR spectrum exhibits two sets of broad pea The FTIR and ^{1}H NMR spectra verified the occurrence of phthaloylation at the amino gro of the chitosan. Phthaloyl chitosan shows excellent solubility in organic solvents such DMF, DMSO, DMAc, and pyridine. The chemically modified chitosan was able to fo transparent films by the solvent casting method. Phosphoric acid was introduced as the dop acid at various concentrations from 5 to 25 wt. %. The doped films are also evaluated for electrical properties using impedance spectroscopy. The maximum conductivity of PhCh fi was found to be 2.03 x 10^{-5} S cm^{-1} exhibited by the film containing 25 wt. % phosphoric aci

Keywords: polymer membrane, phthaloylation, chitosan

1. INTRODUCTION

Chitosan, containing the repeating structure of β-(1-4) linked 2-amino-2-deoxy-D-glucopyranose, is one of the promising membrane materials that have been studied widely as it contains amino group at C-2 and hydroxyl groups at C-3 and C-6 that are useful for chemical modification [1-5].

However, the rigid crystalline structure of chitosan shows poor solubility in organic solvents. Having great potential for application [6], chitosan has been efficiently modified to fully explore its ability and development by many possible ways, namely nitration, phosphorylation, sulphation, xanthation, acylation, hydroxylalkylation, graft copolymerization and alkylation [7]. N-phthaloylation is one the methods that have been shown to m chitosan soluble in organic solvents. T inability of chitosan to dissolve in orga solvents has limited its application. This due to its rigid crystalline structure that caused by the formation of intra/in hydrogen bonding between the NH_2 a OH^- groups [1-2,8]. Phosphoric a sulphuric acids are doping acid that c produce high conductivity polym electrolytes [9-12]. Proton conduction m occur according to the Grott mechanism [10]. In this work, we h used N-phthaloylchitosan to prod polymer electrolyte membranes by dop the modified chitosan with different wei percentages of phosphoric acid.

2. EXPERIMENTAL

2.1 Chemicals

Chitosan was purchased from Fluka. Phthalic anhydride was purchased from Aldrich, N,N-dimethylformamide (DMF) and phosphoric acid were supplied by R & M Chemicals. Ethanol was obtained from J. T. Baker and was distilled before used.

2.2 Instruments And Equipments

Fourier transform infrared (FTIR) spectra were recorded on Spotlight 400 Perkin-Elmer Spectrometer at a resolution of 4 cm^{-1} with 15 scanning number. Nuclear magnetic resonance (NMR) was taken at 270 MHz with JNM–GSX270 Fourier Transform Spectrometer using DMSO-d_6 as the solvent. HIOKI 3531 Z HiTester was used to measure the impedance of the films in the frequency range of 50 Hz to 1 MHz.

2.3 Procedures

2.3.1 Phthaloylation Of Chitosan

1 g of chitosan and 4.39 g phthalic anhydride dissolved in DMF were made to react at temperatures between 100 °C to 120 °C under nitrogen atmosphere for 6 h. The temperature was then reduced to 60 °C and the mixture was left overnight [1]. The clear yellowish solution was put into iced water to precipitate out the product. The precipitate was collected and washed with ethanol in a soxhlet extractor for 8 h. The product was dried in vacuum.

N-phthaloylchitosan (PhCh) was produced according to the equation shown in Scheme 1.

The synthesized PhCh was analysed for its solubility in various organic solvents such as dimethylformamide (DMF), pyridine, hexane, dimethylacetate (DMAc), chloroform, *p*-xylene, dimethylsulfoxide (DMSO), ethyl acetate, methanol and cyclohexanone at room temperature.

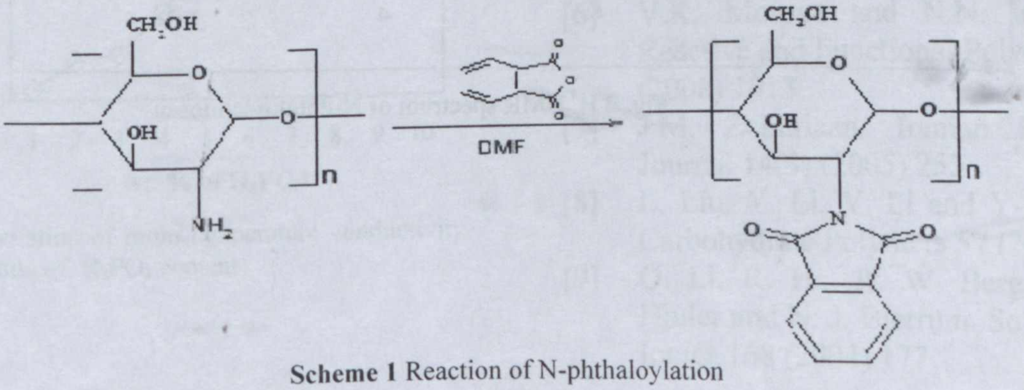
2.3.2 Film Forming of N-Phthaloylchitosan

PhCh film was prepared by solvent casting technique using DMF as the solvent. 0.5 g of synthesized PhCh was observed to dissolve completely in 10 mL DMF. Phosphoric acid, H_3PO_4 was introduced at various weight percentages from 5 to 25. The mixture was further stirred for 1 h before casting onto petri dishes. Then the solution was put into the oven with slow heating at 60 °C. The films were then stored in a vacuum desiccator before analysis.

2.3.3 Electrical Conductivity Measurements

The films were sandwiched between two stainless steel disc electrodes. The impedance data are presented in a complex impedance plot where the imaginary part, Z_i of impedance was plotted against its real part Z_r. The ionic conductivity of the samples can be calculated by using the R_B values in the equation (1).

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



Scheme 1 Reaction of N-phthaloylation

where t is the thickness of the film, R_B is bulk impedance and A is the film-electrode contact area.

3. RESULTS AND DISCUSSION

3.1 FTIR Analysis

FTIR spectrum of pure chitosan and N-phthaloylchitosan are shown in Fig.1.

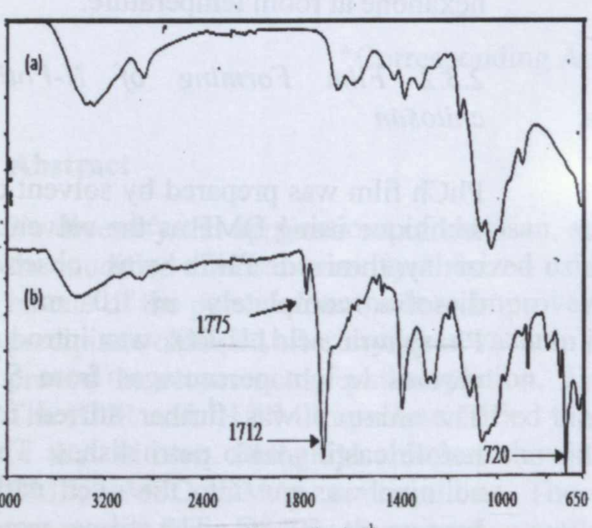


Fig. 1 FTIR spectra of (a) pure chitosan and (b) synthesized N-phthaloylchitosan

There are additional three main peaks in phthaloylchitosan compared to p chitosan. The spectrum of phthaloylchitosan exhibits two peaks 1775 and 1713 cm^{-1} corresponding to carbonyl anhydride on phthalimido gr similar to absorption bands that have b reported earlier [1-2,8,13]. There is a sh and intense absorption peak at 720 c indicating the presence of aromatic ring.

3.2 ^1H NMR analysis

^1H NMR spectrum is depicted in Fig. 2. NMR spectrum exhibits two sets of br peaks. One set consists of four pe centering at 7.5, 7.6, 8.0 and 8.2 p dedicated to the phthaloyl group. Pe that exist between 1.1 to 5.0 ppm assig to the chitosan backbone hydrogen 2,8,13]. Thus, the FTIR and ^1H N spectra verified that phthaloylation h occurred at the amino group of chitosan.

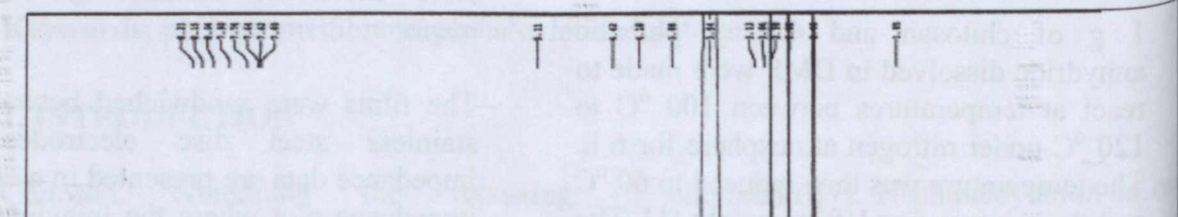


Fig. 2 H^1 NMR spectrum of N-Phtaloylchitosan

3.3 Solubility

Table 1 shows the solubility of PhCh in various solvents. PhCh dissolved completely in DMF, DMSO, DMAc, and pyridine giving clear solutions. Following the results from solubility, DMF was chosen to form the PhCh films. The films obtained were homogeneous, transparent and thin (in the range of 0.10 to 0.15 mm).

Table 1 Solubility of PhCh

Solvents	Solubility
DMF	√
THF	-
DMAc	√
DMSO	√
Chloroform	-
Pyridine	√
Hexane	-
p-xylene	#
Toluene	-
Methanol	-
Ethyl Acetate	-
Cyclohexanone	-

√: soluble -: insoluble #: swelled

3.4 Impedance Spectroscopy

The conductivity dependence on the acid doping level has been a subject of interest for various acid doped polymer electrolytes [14]. The acid doping level as a function of the weight percentage of the phosphoric acid in the film is shown in Fig. 3.

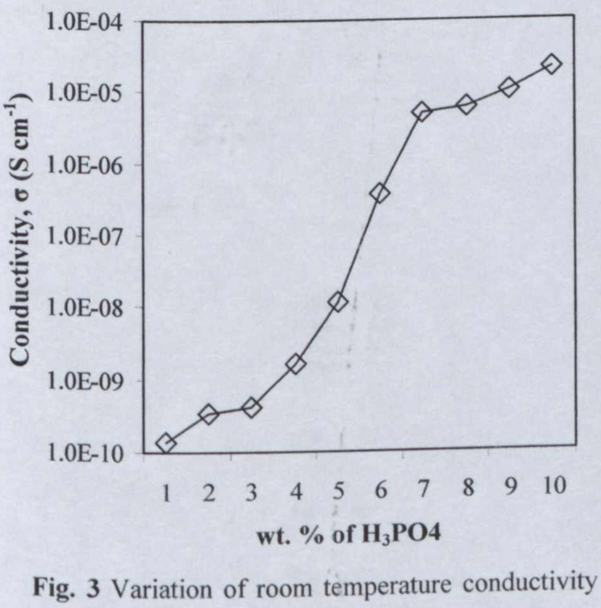


Fig. 3 Variation of room temperature conductivity as a function of H_3PO_4 content

The conductivity of the PhCh-H_3PO_4 films is observed to increase with respect to weight percentage of H_3PO_4. Pure PhCh film showed low conductivity compared to acid-doped PhCh films with 1.42×10^{-10} S cm^{-1}. The conductivity increased up to 25 wt. % of acid-doping in PhCh with a room temperature value of 2.03×10^{-5} S cm^{-1}. The increment in conductivity is due to the increase in the number of protons due to dissociation of the acid

4. CONCLUSIONS

In this study, N-phthaloylchitosan was synthesized using phthalic anhydride to improve hydrophobicity of chitosan, allowing excellent solubility in organic solvents and good film formation. The maximum conductivity of PhCh film was found to be 2.03×10^{-5} S cm^{-1} exhibited by 75 wt. % PhCh-25 wt. % H_3PO_4 film.

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