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STRUCTURAL AND COMPLEX AC IMPEDANCE STUDIES ON PROTON CONDUCTING POLYMER ELECTROLYTES BASED ON CHITOSAN /H^+-MMT

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ABSTRACT- In this study the development and characterization of on modified montmorillonite incorporated on the chitosan based biopolymer matrix by the solvent casting technique in the form of dimensionally stable and free standing films.The surface modification of MMT has been confirmed by the FTIR analysis. Significantly the effects of modified MMT incorporated bio polymer were investigated by X-Ray diffraction method. From the AC impedance spectroscopic analysis , the proton conductivity has been found to be increases with increasing modified nano clay concentration up to 25% beyond which the conductivity decreases and the highest ambient temperature conductivity has been found to be $5.074X10^{-3}$ S/cm. Dielectric data's like using complex impedance Z^*, Dielectric constant and tangent loss were analyzed for prepared polymer electrolyte membrane for the highest conductivity sample at various temperature. Based on the study of relaxation spectra, it is found that the relaxation time decrease with increase in temperature and dopant concentration.

Keywords- [modified nano clay, Proton conductivity, Dielectric loss, Tangent loss].

1. INTRODUCTION

In recent years, polymer/clay nanocomposites have attracted considerable interest because they combine the structure and physical and chemical properties of inorganic and organic materials. Smectite group clay minerals have large adsorption capacities for polymer molecules due to their unique crystal structure [1]. Montmorillonite (MMT) is layered silicate clay which belongs to the smectite clay group with a wide range of applications in medicine, polymer industry, ceramic industry and nano materials. Raw formula of montmorillonite (MMT) is $(Na,Ca)_{0.3}(Al,Mg)_2Si_4O_{10}(OH)_2,nH_2O$. MMT has the wider acceptability for use in polymer nanocomposites because of its ease availability, well known intercalation / exfoliation chemistry, high surface area and high surface reactivity [2]. Polymer clay nano composites received intense attention because of their unique properties which can never be attained by micro size fillers or by other nano fillers. The enhancement of properties by the addition of Montmorillonite clay, without sacrificing the pure polymer process ability, mechanical properties and light weight, make this clay more and more important in modern polymer industry [3]. Comparatively little attention has been paid to natural polymer / clay nano composites. The polymers in the montmorillonite dispersions interact with the clay particles, according to their ionic or non-ionic character. The ionic polymers induce electrostatic interactions, but the non-ionic polymers are adsorbed on the surface of clay minerals by the steric interactions. Generally, oppositely charged polyions can interact electrostatically to form polyelectrolyte complexes (PECs) [4]. Polyelectrolyte complexes have recently attracted considerable attention due to their applications in different fields, such as separation membranes and medical applications. Chitosan/clay nanocomposites are economically interesting because they are easy to prepare and involve inexpensive chemical reagents. In the same way, clays are abundant and low-cost natural materials [1]. Due to the presence of polar functional groups in chitosan's chemical structure, this natural polymer can be a promising polycation to interact with polyanions and salts electrostatically and form a new kind of PECs [5]. Acetic acid can be used to dilute chitosan polymer to produce chitosan polymer membrane with high rigidity. The presence of hydroxyl groups in the acetic acid facilitates the dissolution of chitosan via hydrogen bonding with the carboxyl group and amine group from the chitosan. To obtain efficient nanocomposites, the MMT nanolayers must be uniformly dispersed in the polymer matrix, as opposed to being aggregated as tactoids or simply intercalated[6]. Organically modified MMT has an improved capability of dispersing, gelling, adsorption and nanocomposite formation in organic systems. The aim of this study is to develop a low cost and environmental friendly chitosan/H^+-MMT composite membranes for fuel cell application.

2. EXPERIMENTAL PROCEDURE

2.1 Preparation of Protonated MMT (H^+MMT)

The protonation of montmorillonite (MMT) was completed through the following procedure. First, raw MMT (Na^+-MMT; Cloisite Na^+, Sigma Aldrich,German) was converted into H^+-MMT via stirring with abundant 1 N H_2SO_4 solution at room temperature for 2 h. Figure.1 shows the fictionalization modification on the layered silicate MMT.

2.2 Electrolyte Preparation

The Chitosan- protonated MMT (H^+-MMT) nano clay based proton conducting polymer electrolytes were prepared by the solution casting method. In this preparation, biopolymer chitosan (Mw~6x10^5 gmol^{-1}, 85% degree of Deacetylation, source: SRL) was dissolved in 100 ml 1% acetic acid (NICE) and stirred for a few hours at room temperature. Different weight percentages (5,10,15,20,25 %) of H^+-MMT were added and further stirred for 24 h. The mixtures were then cast into petridish. The solvent acetic acid was allowed to evaporate to form a film slowly at room temperature over night and 40^0C for 6 h. Flexible thin films with thickness of about 0.59 mm were obtained and the films were kept in the desiccators to ensure that the films were dry.

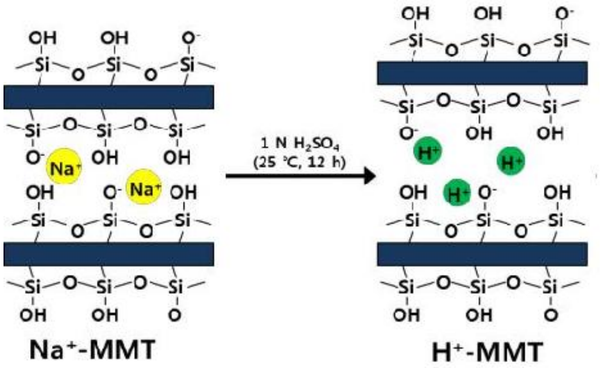

Figure 1- Schematic representation for the functionalization of layered silicates.

RESULTS AND DISCUSSION XRD-Analysis

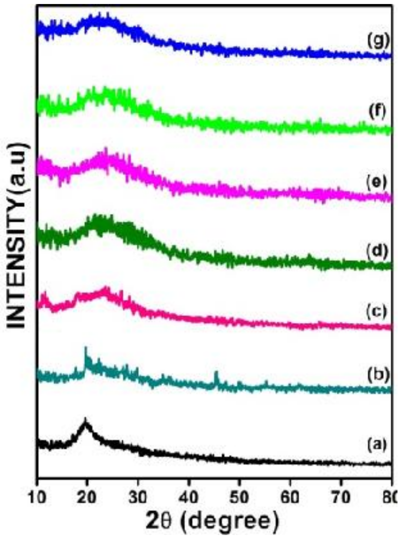

Figure 2- XRD spectra of all the prepared polymer electrolytes.(a) Pure Chitosan (b) H$^+$MMT(c)95:05 of CS/H$^+$MMT(d)90:10 of CS/H$^+$MMT(e)85:15 of CS/H$^+$MMT(f)70:30of CS/H$^+$MMT(g)75:25 of CS/H$^+$MMT

The persuasive evidence for the intercalation of a modifier into the interlayer of MMT can be obtained from XRD patterns of the nano composites. By monitoring the position, shape & intensity of diffraction peaks, the embedded or intercalated structure of the nanocomposites can be identified. Radical scan were recorded in the reflection scanning mode with 2Θ being changed from 10^0 -80^0. Figure.2 depicted the diffraction pattern of CS/H$^+$MMT composite polymer membrane that were prepared by adding with various amount of H$^+$MMT fillers. In general, a sharp peak with high intensity corresponds to semi crystalline materials and a broad peak corresponds to an amorphous material. A broad peak of chitosan at about 20^0 (2Θ) for the (100) plane (jcpds.no:361894). There are two peaks, one at 26^0 (2Θ) with the high intensity and another is appeared at about 19^0 (2Θ) with less intensity appears in the H^+MMT. The relative peaks value for all the prepared polymer electrolytes are shown in figure.3. Two peaks are present in the composite polymer matrix one at 11^0(2Θ). A broad peak between 15^o to 31^0 (2Θ) related to amorphicity of the polymer has been presented for every complex and pure chitosan. The relative intensity peak values of CS/MMT composite membrane are decreased with increase of additive H^+MMT concentration.Peak of protonated MMT are completely absent in the spectrum. Hence every grain of H^+MMT might have been well surrounded by the polymer matrix.

FTIR Spectra Analysis

The surface chemistry analysis of MMT before and after its surface modification was investigated by FTIR analysis. As shown in Figure.3, most important peaks needed for the identification of MMT, the peaks at 3437 and 1640 cm^{-1} corresponded to the –OH stretching and bending vibrations of H–O–H on the MMT surface, respectively [7]. The FTIR spectra corresponding to the characteristic peaks of MMT structure which was assigned to Si–O and Al–O stretched at $1031cm^{-1}$ and 1000–1300 cm^{-1} respectively, indicating that the main structure of MMT still exists afer the surface modification by ion exchange resin. The splitting of the first band indicates the presence of more than one type of hydroxyl bonds, due to their different absorption frequencies. The modification performed on MMT was able to reduce the intensity of –OH stretching bond vibration of pure MMT [8]. This phenomenon describes the consumption of the MMT hydroxyl groups by condensing with the silanol groups. The MMT surface modification also decreased the water adsorption on its surface due to the bonding formation between MMT and H_2SO_4.

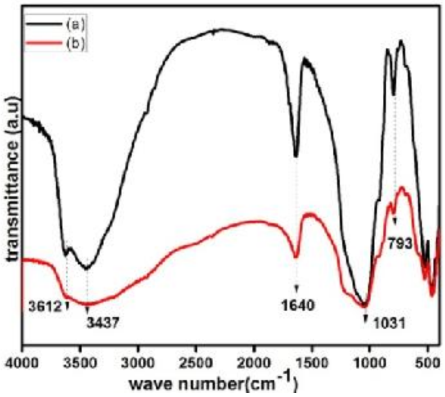

Figure 3- FT-IR spectra of (a) H^+-MMT (b) Pure MMT

Ac Impedance Spectra Analysis

Proton conductivity is the most important property for the polymer electrolyte membranes.The conductivity of all the prepared polymer electrolyte films has been characterized using ac impedance spectroscopic technique at different concentration of protonated MMT using a computer controlled µ-autolab type III potentiostat/Galvanostat in the frequency range of 10 Hz to 1MHz. Figure.4, shows the Nyquist plot for 75:25 wt% of CS/H^+-MMT polymer electrolyte at various temperature. The impedance can be calculated from the intercept of spike on the $Z^{'}$ axis. The ionic conductivity values are calculated by using the equation $\sigma = \frac{t}{R_b A}$ where t and A are the thickness and area of the prepared polymer electrolyte film respectively. R_b is the bulk resistance of the electrolyte film. All the prepared membranes were placed in 10 V% H_2SO_4 solution about 12 hrs at room temperature. After this treatment, the membranes were rinsed with DI water several times to remove the excess of acid content present in the membrane. The temperature is increases the bulk resistance is decreased, the mobility of polymer chain increases, which enhance the ionic conductivity. The membranes with modified MMT delivered higher proton conductivity because of their strong affinity to the water molecules. The hydrophilicity along with its high surface area provides the ionic clusters of side chains lead to more absorption of water content which is capable for easy of proton transfer [9]. The high proton conductivity value achieved for the 75:25 wt% CS/H^+MMT membrane is $5.074X10^{-3}$ S cm-1. The reason for this increase in proton conductivity could be the hydronium ions from CS polymer and protons from the H^+ MMT.

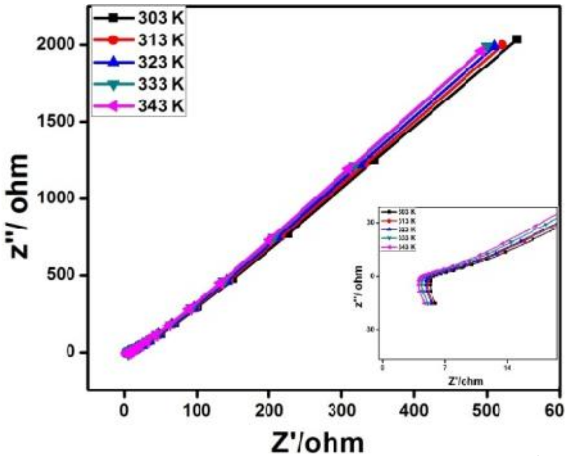

Figure 4- Protonic conductivity of the 75:25 wt% of CS/ H^+MMT with different temperatures

Dielectric Constant & Loss tangent Spectra Analysis

The dielectric relaxation behavior of the polymer electrolyte brings about important insights into ionic transport phenomenon. Figure 5a&b shows the dielectric constant and loss tangent spectra of 75:25 wt% CS/H^+MMT electrolyte at various ambient temperature. It has been observed from the figure at high frequency the dielectric constant has been found to be constant, this is because of the inability of the charge carriers to follow the periodic reversal of the electric field. The dielectric constant is high at the low frequency due to the presence of space charge effects, which are contributed by the accumulation of charge carriers near the electrodes. The dielectric relaxation of the polymer electrolyte can be obtained as a function of frequency it can be defined by the equation $\tan\delta = \frac{\varepsilon^{'}}{\varepsilon^{''}}$. The absorption peak is described by the relation ωτ=1 where τ is the relaxation time and ω is the angular frequency of the applied signal. As the temperature increases the relaxation peak shift to high frequency indicating that the charge carrier is thermally activated.

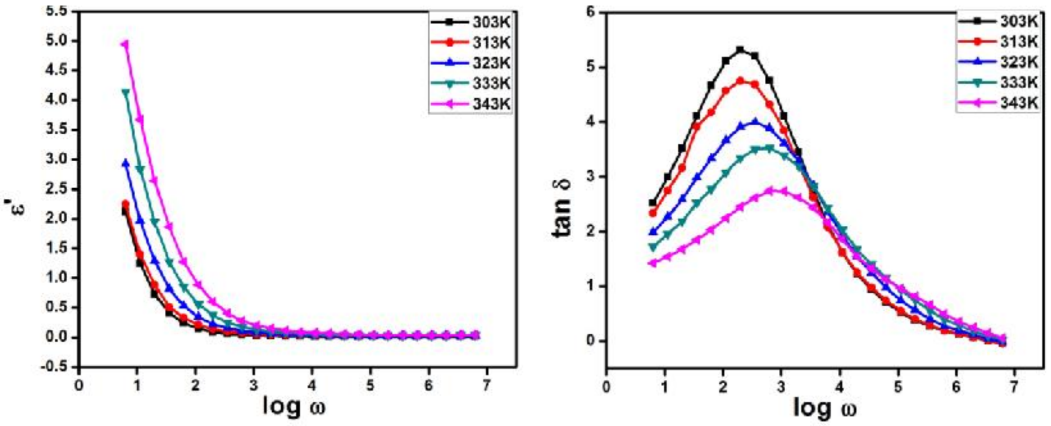

Figure 5-a&bDielectric Constant and loss tangent spectra of 25% of H^+MMT with different temperatures

Chitosan: H^+MMT(75:25 WT%)	Relaxation Frequency log ω_m (Hz)	ω_m (Hz)	Relaxation Time
303 K	2.291	$1.95X10^2$	$5.1X10^{-3}$
313 K	2.344	$2.20 X10^2$	$4.54 X10^{-3}$
323 K	2.480	$3.01 X10^2$	$3.33 X10^{-3}$
333 K	2.632	$4.28 X10^2$	$2.33 X10^{-3}$
343 K	2.856	$7.17 X10^2$	$1.39 X10^{-3}$

TABLE 1- Relaxation parameters of the 25wt% H^+ MMT polymer electrolytes at different temperature

CONCLUSION

Proton conducting polymer electrolyte based on chitosan & protonated MMT have been prepared. The presence of more hydroxyl group of H-MMT improved the phase interaction between chitosan and H^+-MMT due to the interaction between hydroxyl groups of H^+- MMT and hydroxyl groups or amide groups of the chitosan polymer chain.The XRD analysis reveals the increase in amorphous nature of the electrolytes. The dielectric behavior of the prepared samples shows strong dependence on frequency and concentration of H^+-MMT.From the relaxation spectra relaxation time decreases with increase of temperature which results in an increase in conductivity.

REFERENCES

[1]. S.Pandey, S. B. Mishra, Journal of Colloid and Interface Science, **361** (2011) 509–520.

[2]. F.Bergaya, B.K.G. Theng, and G.Lagaly, Handbook of Clay Science, 1st ed, Elsevier Publications, (2006)289-309.

[3]. Y.Han ,S.Lee,K.H. Choi, Journal of Physics and Chemistry of Solids, **71** (2010) 464-467.

[4]. E.Gunister et. al, Carbohydrate Polymers **67,** (2007) 358–365.

[5]. S. E. Shakeri et al, Journal of Macromolecular Science Part B: Physics, **52** (2013) 1226–1241.

[6]. P.Mochammad et .al, RSC Adv, **6** (2016) 2314-2322.

[7]. J.Madejova, and P.Komadel, Institute of Inorganic Chemistry, Clays and Clay Minerals, **49**, No. 5, pp. 410–432 (2001).

[8]. M.L.Suédina.et.al., Infrared Spectroscopy - Materials Science, Engineering and Technology book, online publication (2012).

[9]. K. Miyatake, K. Oyaizun, E. Tsuchida, A. S. Hay, Macromolecules, **34** (2001) 2065.