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Synthesis and characterization of biodegradable ultrasonicated films made from chitosan/al₂O₃ polymer nanocomposites

B.Prakash*, M.A.Jothirajanb, S.Umapathyc, Viji Amalaa

*Department of Physics, St. Joseph’s College, Trichy- 620 002, Tamil Nadu, India
bDepartment of Physics, Arul Anandar College, Karumathur – 625 514, Tamil Nadu, India
School of Physics, Madurai Kamaraj University, Madurai – 625 021, Tamil Nadu, India

Abstract

Chitosan is a biopolymer which is biodegradable, biocompatible, non toxic and cationic in nature. Due to these interesting properties, it finds advanced applications in sensors, drug delivery vehicle and gene therapy etc., In this present work, the biocompatible Al₂O₃ Nano particles were embedded into Chitosan Polymer matrix by ultrasonication route. XRD and FTIR studies confirm the presence of Al₂O₃ nanoparticle in the Chitosan polymer matrix. The morphological, optical, electrical properties of the polymer nano composite films are carried out by employing scanning electron microscopy (SEM), UV-Vis, LCR and Impedance studies.

Keywords: Nanocomposites; polymer; electrical properties

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1. Introduction

In recent decades, ionic conductors like solid polymer electrolytes (SPE) have been received more attention due to its wide applications in batteries, fuel cells, super capacitors, sensors etc [1-3]. The processability light weight and transparency are the main characteristics of SPE [4]. Non-toxicity, biodegradable, biocompatible and ability to cast bio films make Chitosan to be used in industrial devices than other SPE’s. Chitosan a natural polymer, β1-4 linked 2-amino 2-D glucopyronose, derivative of chitin, which is present in the shells of crustaceans, the cuticles of insects and cell walls of fungi[5,6]. The high glass transition temperature and high electrical conductivity at room temperature motivated many scientists to investigate on Chitosan as a polymer electrolyte [7].

* Corresponding author E-mail: prakashphys@gmail.com
Recently, chitosan has been widely studied for use in clinics, drug delivery systems, solid poly electrolytes, sensors, surfactants, and membranes on ultrafiltration, reverse osmosis, and evaporation. Considerable efforts are especially directed at modifying chitosan to improve its solubility in water [6] and other physicochemical properties [3]. At low pH, the positive charge on the NH$_3$ groups influences the Chitosan to be cationic polymer electrolyte [6]. Ding et.al reported that gold nano particles doped Chitosan films exhibits excellent biocompatible spatial structure and finds applications in cell based sensors and also studied the electrochemical behaviour of cells on surface of the films [8]. Winnie et.al observed that the conductivity of Chitosan increasing with addition of plasticizer [10]. Cathell et.al reported that the Chitosan and thiol Chitosan conjucate thin films can be used as a potential sensor for metals in aqueous solutions [9].

2. Experimental
2.1. Materials

All the chemicals used are of analytical reagent grade. The medium molecular weight Chitosan was obtained from central institute of fisheries technology, (ICAR), Kochi, Kerala state, India with degree of deactylation of (85%). The Al$_2$O$_3$ nanoparticle and glacial acetic acid were purchased from sigma Aldrich Pvt. Ltd. NaOH were purchased from Merck were used as such without further purification. Double distilled water was used for the preparation of aqueous solutions.

2.2. Methods

2 % (w/v) Chitosan solution were prepared by using 0.1M acetic acid solution and dissolved well to obtain a homogenous solution. The solution then filtered with whatmann no:1 filter paper.10 wt% of Al$_2$O$_3$ nano particles slowly added to the Chitosan solution by ultrasonication method with varying sonication period of 15, 30, 45 and 60 minutes. Transparent thin ultrafine polymer nanocomposites membranes are obtained by solution casting technique. The obtained membranes were immersed in 0.1M NaOH solution to remove the acidic components of the solvent. Further the membranes were soaked in distilled water to remove the residues present in the membranes. In this present work, the effect of sonication on the above mentioned polymer nanocomposites samples were studied.

2.3. Characterization:

XRD studies on thin films were carried out using Bruker D8 advanced X-ray diffractometer with Cu K$_\alpha$ source of 1.54 Å wavelength. UV Visible spectra of the sonicated films were taken using Lambda 35 model UV-Vis spectrometer in the range 300nm-1100nm. FTIR of each Chitosan/Al$_2$O$_3$ bio polymer nanocomposites films were subjected by a Perklin Elmer make spectrum RX1 model FTIR spectrometer in the range of 400-4000 cm$^{-1}$. The dielectric measurements of the samples were carried out with temperature range from 50°C to 200°C and the readings are measured using Novocontrol Impedance analyser. The thermal properties are studied using MDSC by TA instruments from 0°C to 200°C.
3. Results and Discussion
3.1 XRD Analysis

According to Owaga et. al. [10] there are three crystal polymorphs of semi crystalline Chitosan. First, the hydrated crystal structure gives a strong peak at \( \theta = 10^\circ \) (or peaks at 8\(^\circ\) or 12\(^\circ\)). Second, the anhydrous crystal structure of Chitosan gives a strong peak at \( \theta = 15^\circ \). Third, the amorphous nature gives a broad peak at \( \theta = 20^\circ \) [11]. It is generally known that, the structure of Chitosan is strongly dependent on its processing treatment, such as dissolving, precipitation and drying as well as its origin and characteristics such as degree of deactylation and molecular weight [12].

XRD patterns of the sonicated Chitosan- Al\(_2\)O\(_3\) polymer nanocomposites are shown in figure 1. The XRD pattern, shows an increase in intensity of a sharp peak at \( \theta = 15^\circ \) with respect to the increase in sonication time. It is evident that there is an increase in the anhydrous crystal structure of the Chitosan than the other structures due to the ultrasound irradiation. A broad hump from \( \theta = 20^\circ \) to \( \theta = 40^\circ \) shows the existence of amorphous nature of the Chitosan. This makes one to conclude that Chitosan-Al\(_2\)O\(_3\) nanocomposite is semi crystalline in nature [13]. On the other hand, the characteristic peaks of Al\(_2\)O\(_3\) nano particles are present at \( \theta = 34^\circ, 45.9^\circ \) and \( 67^\circ \) agree well with the literature [14] and the standard JCPDS 10-0173 data. It also confirms the presence of Al\(_2\)O\(_3\) nano particles in the Chitosan polymer matrix.

3.2 FTIR Analysis

FTIR spectra of the chitosan/Al\(_2\)O\(_3\) polymer nano composite films are shown in figure 2. From the spectra a broad hump from 3000 to 3600 cm\(^{-1}\) shows the presence of OH stretching of chitosan. Two absorption peaks corresponds to stretching of amide – I (CH-NH-) and amine (NH\(_2\)) deformation vibration of chitosan centered at 1656 cm\(^{-1}\) and cm\(^{-1}\) respectively, are found in the samples. The major absorption peaks of Al\(_2\)O\(_3\) are located at 1627 and 1398 cm\(^{-1}\) in the above spectra [7][x.liu]. An infrared
band appears in the region of 850 to 1050 cm\(^{-1}\) assigned to the surface vibrational mode of alumina nano particles, which arises due to the losing of free alumina hydroxyl groups. This confirmed the presence of Al\(_2\)O\(_3\) nanoparticles in the polymer nano composite membranes.

**Fig. 2.** FTIR spectra of sonicated Chitosan/Al\(_2\)O\(_3\) polymer nano composite sonicated films at (a) 15 min (b) 30 min (c) 45 min and (d) 60 min

**3.3 UV-Vis Analysis**

**Fig. 3.** UV-Vis- transmission spectra of Chitosan/Al\(_2\)O\(_3\) polymer nano composite films sonicated for (a) 15 min (b) 30 min (c) 45 min and (d) 60 min
Fig. 4. UV-Vis absorption spectra of Chitosan/Al₂O₃ polymer nano composite films
(a) 15 min (b) 30 min (c) 45 min and (d) 60 min

Fig. 5. Optical band gap determination curve of chitosan Al₂O₃ polymer nanocomposites

The UV-Vis transmission and absorption spectra of the chitosan Al₂O₃ polymer nano composite membranes were shown in Fig 3 and Fig 4 respectively. The optical bandgap of the membranes were determined using Scherrer’s formula. The optical band gap of the chitosan Al₂O₃ polymer nano composite is found to be 2.2 eV and it was observed that an increase in optical band gap with respect to increase in sonication period. From the transmission spectra, there is an increase in percentage of transmission with an increase in sonication period.
3.4 Dielectric studies

Fig. 6. Dielectric permittivity versus temperature of chitosan Al₂O₃ polymer nano composite films at (a) 8 kHz (b) 90 kHz (c) 500 kHz and (d) 3 MHz.

Fig. 7. Dielectric permittivity versus frequency of chitosan Al₂O₃ polymer nano composite films for various temperatures.
The conductivity behaviour of the chitosan Al₂O₃ polymer nano composites can be understood from the dielectric studies. Fig. 6 shows the dielectric constant as a function of temperature for various frequencies. There is a relaxation process observable at 160 °C correlated with DC conductivity which is found in dried chitosan polymer systems [19]. The relaxation process so called σ process. Fig. 7 shows the variation of dielectric constant as a function of frequency for various temperatures. The dielectric constant increased sharply at low frequencies indicating that electrode polarization and space charge effects have occurred confirming Non-Debye dependence [19]. On the other hand, at high frequencies periodic reversal of the electric field occurs so fast that there is no excess ion diffusion in the direction of field polarization due to charge accumulation decreases leading to the observed decreases in dielectric permittivity and dielectric loss.

The enhancement of dielectric permittivity may be due to the following reasons: the large scale heterogeneity in polymer nano composite is suppressed and the nano composite is replaced by small scale heterogeneity. The small scale heterogeneity is connected to the presence of Al₂O₃ nano particles which increases free volume due to looser segmental packing in chains confined to nano volume [20].

3.5 DSC studies:

![DSC curve](image)

Fig 8. DSC curve of sonicated Chitosan/Al₂O₃ polymer nano composite sonicated films
(a) 15 min (b) 30 min and (c) 45 min films

The DSC curve of the chitosan Al₂O₃ polymer nano composite membranes are shown in figure 8. From the graph, a sharp endothermic peak is observed at 150 °C which is known as dehydration temperature (T_d). It is due to the evaporation of water associated with the hydrophilic groups of the polymers and responsible for the strength of water-polymer interaction [21]. The T_d value obtained for chitosan is slightly increases with the increase in sonication time period

4. Conclusion

The biocompatible Al₂O₃ nanoparticles are embedded in to Chitosan Biopolymer matrix by ultrasonication route. From the XRD, the presence of Al₂O₃ nanoparticles are confirmed. The particle
size of the nano particles are found to be 24 nm from the Scherrer formula. The particle size of the nano particles are increases with increase in sonication time. The chemical finger prints of the Chitosan Al₂O₃ polymer nano composites were studies by FTIR and it confirmed the nano particle in the polymer system. The absorbance and transmittance of the above samples were studied and it is found that the optical transmittance of the samples increases with increase in sonication period. The optical band gap of the above samples are measured and found that the optical band gap is increasing with respect to the sonication time period. The glass transition temperature of the Chitosan were measured by DSC and the value of Tg is increasing with increasing sonication time. The electrical conductivity of the samples were studied by the Impedence analysis method. There is a relaxation process occurred at 160°C and it increases with increase in sonication.

References

[1]. Yahaya, M.Z.A., Harun, M.K., M.M.A, A., Mohammt, J. of App. Sci., 2006, 6(15), 3150-3154.
[2]. Park,C.H., Park, M., Im Yoo, S., Ki Joo, S., J.Power Sour., 2006, 158, 1442-1446.
[3]. Stephen,A.M., Nahm, K.S., Polymer 2006, 47,5952-5964.
[4]. Idris, N.K, Ni Aziz,, N.A., Zambri, Zakaria, N.A., Ionics, 2009, 15, 643-646.
[5]. Bhatt, A.S., Krishna Bhat, D., Santosh, M.S., Physica B, 2010, 405, 2078.
[6]. Yahaya, M.Z.A., Harun, Ali,M.M.A., Mohammt, J. of App. Sci., 2006, 6(6), 1287-1291.
[7]. Yahaya, Putesh, R., Arof, A.K., Mat. Sci. Forum Vols. 480-481, 2005, 95-100.
[8]. Ding, L., Hao, C., XueX, J., Ju, H.X., Biomacromolecules 2007, 8, 1341-1346.
[9]. Cathell, M.D., Szewcyk, Bui, F.A., Weber, C.A., Schauer, C.L., Biomacromolecules, 2008, 9, 289-295.
[10]. Ogawa, K., Hirano, S., Miyashita, T., Yui, T., Watanabe, T., Macromolecules 1984, 17, 973.
[11]. Wang, X., Bai, H., Yao, Z., Liu, A., and Shi, G., J. Mater. Chem., 2010, 20, 9032–9036.
[12]. Ling Liu, Y., Yuan Huu, C., Huei Su, Y., and Yih Lai, J., Biomacromolecules 2005, 6, 368-373
[13]. Whan rhim, J., In hong, S., Man park, H., Perry, K.W., J. Agric. Food Chem. 2006, 54, 5814– 5822.
[14]. Ricardo, M., Caridade, G., Roma’n, J., Mano, J., Reis, R.L., Biomacromolecules 2008, 9, 2132–2138.
[15]. Long, H.k., Guo, Y.J., Qin, L.S., Jian, L.C., Trans. Nonferrous. Met. Soc. China, 2007, 17, 633-637.
[16]. Feng, D., Wang, F., Chen, Z., Sensors and Actuators B, 2009, 138 539.
[17]. Kaushik, A., Solanki, P.R., Ansari, A.A., Sensor, Actuat. B-Chem, 2009,138 572.
[18]. Paulusse, Jos M.J. , sijbesma, R. P., Journal of Polym. Sci. Part A: Polym. Chem., 44 (2006) 5445.
[19]. Vicioso, M.T., Dionisio, M., Silva, R., J.F. Mano, Biomacromolecules, 2004,5,2073-2078.
[20]. Pradhann, D.K., Choudhary, R.N.P., Samantaray, B.K., Express Polymer Letters, 2008, vol:12, No:9, 630.
[21]. El-Hefian, E.A., Nasef, M.M., Yahaya, A.H., E-Journal of Chem, 8(1), 2011, 91.