

Effect of ammonium persulfate (aps) concentration on chitosan grafted polyaniline

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Chitosan was grafted with polyaniline (PANI) through oxidative radical copolymerization using ammonium persulfate (APS) initiator to obtain a product called Chitosan-graft-polyaniline (Chit-g-PANI). Chit-g-PANI samples were synthesized by varying the APS concentration. The grafted polymer was characterized by using Fourier Transformation Infrared Spectroscopy (FTIR), X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Dielectric Studies and AC Conductivity taking Chitosan as a reference material. The application of conducting biomaterial such as Chit-g-PANI in the electronic devices is especially for the fabrication of sensor devices. FTIR spectra of the Chit-g-PANI revealed that there is a strong interaction between PANI and Chitosan. Morphological studies were carried out to confirm the grafting polymerization and it was further confirmed by XRD pattern. Chit-g-PANI exhibited electrical conductivity, which increase with increase in the APS concentration.

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1. Introduction

Chitosan is one of the promising natural polymers with characteristics such as biodegradability, chemical inertness, biocompatibility, high mechanical strength, good film-forming properties, and low cost [1]. Chitosan is a linear polysaccharide obtained from the N-deacetylation of chitin with a strong alkali [2]. Its structure is basically constituted of D-glucosamine units, with contents of N-acetyl-D-glucosamine in the range of 0-50% [3]. This polymer possesses hydrogel-like properties through a reaction with glutaraldehyde as a crosslinking agent. In the form of a hydrogel, chitosan is used in for wide range of applications such as waste water treatment, separation membranes, food packing, drug delivery systems, and biosensors [4]. However, in sensor applications, the poor electrical conductivity of hydrogels results in a poor response time and a high operational voltage limits its applicability in devices. Hence, composites have been attempted by incorporating a rigid conducting polymer (such as PANI) into a flexible matrix (such as chitosan) to combine the good processability of the matrix and the electrical conductivity of the conductive polymer. Therefore, chitosan is a low cost, degradable, biocompatible, high molecular weight, branched biopolymer with unique physiochemical properties. It is a good candidate to introduce functional groups in PANI, and enhance its selectivity for sensors. In the present study, PANI was grafted onto chitosan in order to synthesize electrically conducting tailor made pH-switching

properties [5]. In the accomplished studies, the reaction mechanism, crystallite, morphology and electrical properties were extensively investigated. It was expected that the results would be promising for biomaterial based sensors fabrication. Fig.1 shows the general polymerization mechanism of Chitosan-g-Polyaniline.

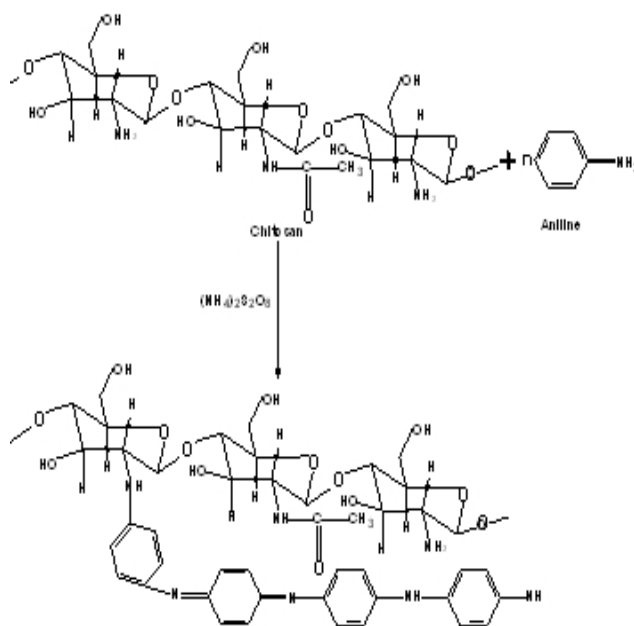


Fig.1, Scheme for the synthesis of Chitosan-g-polyaniline (Chit-g-PANI).

2. Experimental details

2.1. Materials

Chitosan middle-viscus was purchased from Fluka (Japan). Aniline monomer and APS were purchased from M/s Merck (India). The aniline monomer was distilled under reduced pressure prior to use. AR grade chemicals of N-methyl-2-pyrrolidone (NMP), acetic acid, and methanol were used as received.

2.2. Synthesis of chitosan-g-polyaniline (Chit-g-PANI)

Chit-g-PANI was synthesized by dissolving 1g of chitosan in 75 ml of acetic acid in 150 ml flask. The solution was stirred for an hour. To this solution, different mole ratio of APS dissolved in 20ml of distilled water was added slowly to prevent the warming of the solution (addition time almost 30 minutes). Stirring was continued for half an hour. Then 1 g (0.0108 mol) of aniline was dissolved in 200 ml of aqueous solution added drop wise to this solution. After 12 hours of continuous stirring, the mixture turned to a black solution. The precipitate obtained was collected by filtration and thoroughly washed with distilled water, NMP and acetone. The precipitate was dried under vacuum at 50°C for 48 hours and a deep green powder of Chit-g-PANI was obtained.

2.3. Characterization

The FTIR spectrum of chitosan and Chit-g-PANI samples were recorded using a Perkin Elmer spectrophotometer using KBr Pellet with spectrum of frequency range from 4000 to 400 cm^{-1} with an accuracy of 2 cm^{-1} . The XRD pattern of chitosan and Chit-g-PANI samples were characterized with the help of Rigaku X-ray diffractometer. The scan range 2θ was 10°-75°. The surface morphology of the Chitosan and Chit-g-PANI were investigated using Scanning Electron Microscopy (SEM) JSM 6390 JEOL. The dielectric studies were carried out by HIOKI 3532-50 HITESTER LCR meter.

3. Results and discussion

3.1. FTIR spectra

FTIR spectra of chitosan and Chit-g-PANI are shown in Figure 2. For pure chitosan in figure 2(a), the broad band at 3416.69 cm^{-1} is due to overlapping of -O-H and -NH₂ stretching [6]. The band around 1596.76 cm^{-1} is ascribed to -NH₂ bending. The bands around 2807.77 cm^{-1} and 2720.98 cm^{-1} are assigned to the C-H stretching mode in chitosan [7]. The band occurs around 1351.38 cm^{-1} is described to the C-OH vibration of the alcohol groups in the chitosan [8]. The spectrum also shows band at 1225.06 cm^{-1} that could be attributed to the saccharide structure [9]. For the FTIR spectrum of pure PANI in the emeraldine base form, absorption peaks can be observed at

1567, 1493, 1305, and 828 cm^{-1} corresponding to the C=N stretching of the quinoid structure, C-N stretching of the aromatic conjugation, and the vibration of symmetrically substituted benzene, respectively [4].

The FTIR spectrum of Chit-g-PANI in Figures 2(b)-(d) show all significant peaks correspond to chitosan and polyaniline. The following key characteristic bands are observed.

1) 3406.27 cm^{-1} (overlapping of O-H stretching and N-H stretching). 2) 2888.77 cm^{-1} (aliphatic C-H stretching). 3) 1637 cm^{-1} (C=O stretching of carbonyl group of typical saccharide absorption. 4) 1521.35 cm^{-1} (C=C stretching vibration of benzenoid ring) and 1307.68 cm^{-1} (C-H stretching). The absorption band of the N=Q=N bending vibration of pure PANI is observed at 1226.75 cm^{-1} but shifted to 1111.86 cm^{-1} in the Chit-g-PANI due to the steric effect of chitosan [10]. These data confirm the formation of Chit-g-PANI effectively.

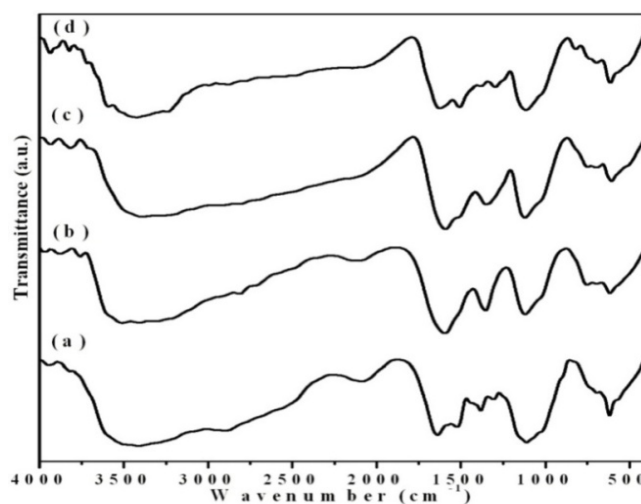


Fig.2. FTIR spectrum of Chitosan (a), Chit-g-PANI (APS 0.616g) (b), Chit-g-PANI (APS 1.23g) (c), Chit-g-PANI (APS 2.469g) (d).

3.2. X-ray diffraction (XRD)

The XRD pattern of pure chitosan and Chit-g-PANI samples are shown in figures 3(a-d) and chitosan samples shows distinct crystalline peaks at around 10° and 25° compared to Chit-g-PANI. This is because plenty of hydroxyl and amino groups exist in the chitosan structure, which form stronger inter molecular and intra molecular hydrogen bonds and the structure of chitosan molecules has certain regularity which results in easy crystalline formation of Chitosan molecules [11].

In case of Chit-g-PANI the peak at 10° and 25° are weakened obviously, due to the destruction of the intermolecular hydrogen bonds and the crystalline region of chitosan, which indicates that the PANI side chains are introduced onto chitosan main chains [12]. Moreover, the intensity of the peak appeared around 25° is increased gradually with the increasing APS concentration, which indicates that the crystalline structure of the Chit-g-PANI increases with increasing the APS concentration.

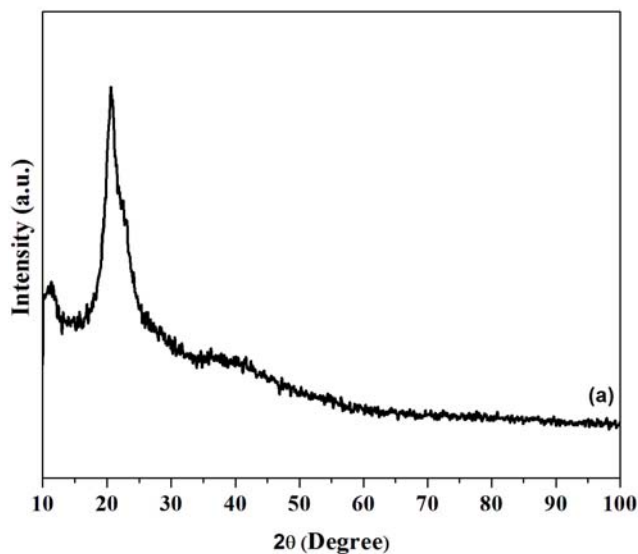


Fig.3 (a) XRD spectrum of Chitosan

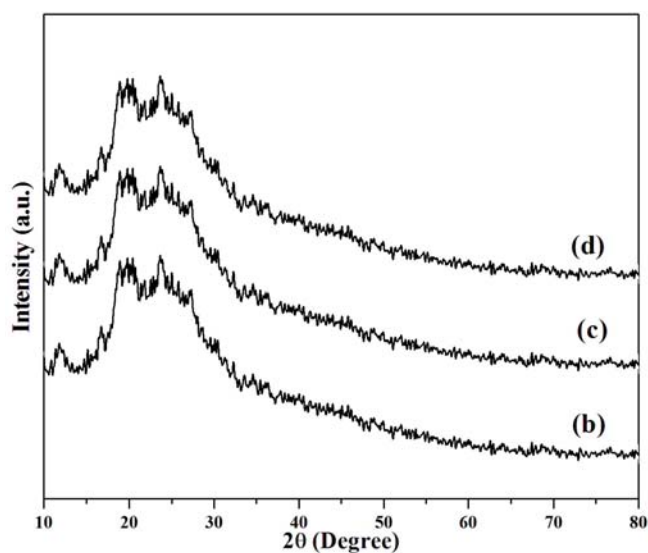


Fig.3 (b-d) XRD spectrum of Chit-g-PANI (APS 0.616g) (b), Chit-g-PANI (APS 1.23g) (c), Chit-g-PANI (APS 2.469g) (d).

3.3. Scanning electron microscope (SEM)

SEM image of pure chitosan in figure 4(a) shows larger cluster structure due to the stronger interactions between chitosan molecules. Fig. 4(b)-(d) represent the SEM images of the Chit-g-PANI. The image 4(b) shows Chit-g-PANI as needle like structure which arises due to the presence of PANI in separate phase on the surface. As the APS concentration increases the needle lines separate phase of PANI grafted with chitosan changes into plate like structure as seen in the figures 4(c) and 4(d). This fact can be attributed to the polar difference between chitosan and PANI and the destruction of the inter molecular hydrogen bonds and the crystalline regions of chitosan [11].

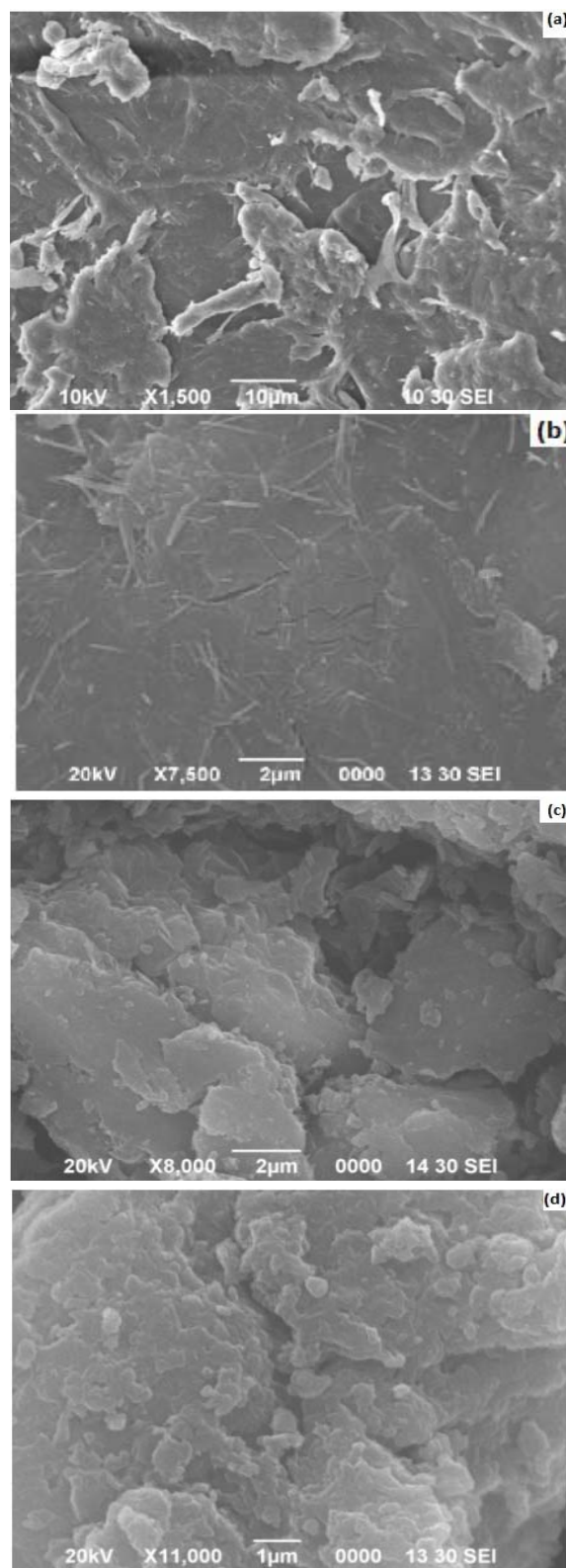


Fig.4 SEM Studies of Chitosan (a), Chit-g-PANI (APS 0.616g) (b), Chit-g-PANI (APS 1.23g) (c), Chit-g-PANI (APS 2.469g) (d).

3.4. AC Conductivity

Fig. 5 shows the AC conductivity of Chitosan and Chitosan-g-PANI with different concentrations of APS. It shows that ac conductivity increases with increase in the frequency range. On increasing the APS concentration the conductivity also increases and reaches a maximum value at 2.46g of APS.

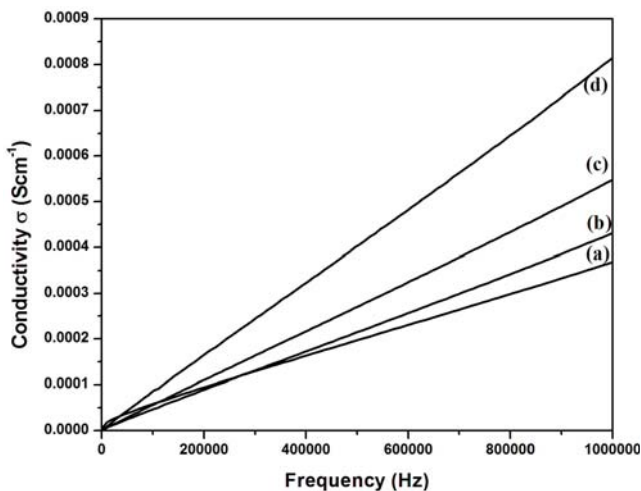


Fig. 5. AC Conductivity of Chitosan (a), Chit-g-PANI (APS 0.616g) (b), Chit-g-PANI (APS 1.23g) (c), Chit-g-PANI (APS 2.46g) (d).

3.5. Dielectric Studies

Fig. 6.1 and 6.2 show the dielectric loss (ϵ'') and dielectric constant (ϵ') of Chitosan and Chit-g-PANI with different concentrations of APS. These figures show that the dielectric loss (ϵ'') and dielectric constant (ϵ') decrease with increasing frequency. At low frequencies, there is sufficient time for the charge carriers to move over macroscopic distance and build up at the interfaces between the sample and the electrodes within half cycle of the applied ac field, resulting in very high values of the dielectric constant (ϵ') and loss (ϵ'') [13], whereas, at higher frequencies there is practically no time for building up of charges at the sample electrode interfaces, however, the transport of charges take place over microscopic dimensions and charges build up at the boundaries of conducting species in the materials. In the high frequency range, the charges cannot follow the changes in the electric field and only bulk polarization mechanisms of the molecular structure contribute to the electric polarization [14]. It shows very high dielectric constant (ϵ') value that could be attributed to the presence of semi conducting grains dispersed in insulating grain boundaries.

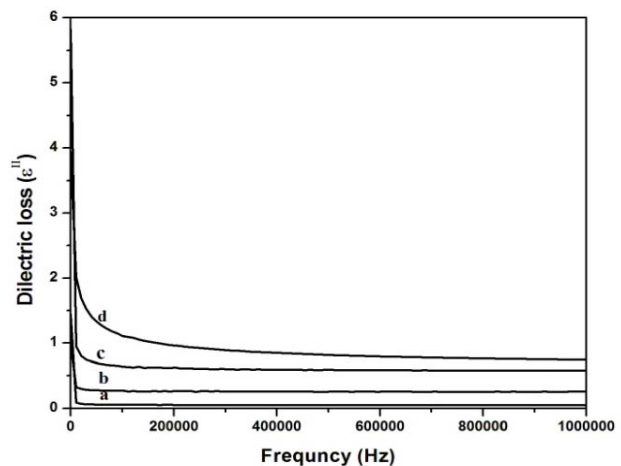


Fig.6a. Dielectric Loss of Chitosan (a), Chit-g-PANI (APS 0.616g) (b), Chit-g-PANI (APS 1.23g) (c), Chit-g-PANI (APS 2.46g) (d).

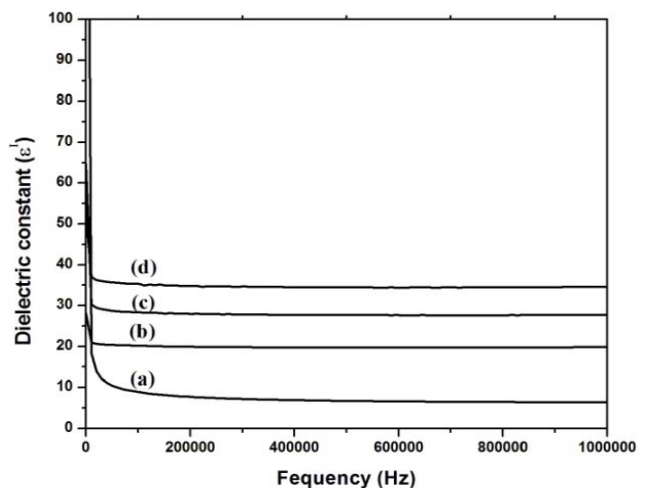


Fig.6b. Dielectric Constant of Chitosan (a), Chit-g-PANI (APS 0.616g) (b), Chit-g-PANI (APS 1.23g) (c), Chit-g-PANI (APS 2.46g) (d).

4. Conclusion

The Chit-g-PANI was synthesized by grafting of polyaniline onto Chitosan using Ammonium persulfate as initiator in acetic medium. FTIR spectra confirmed the grafting of PANI onto chitosan. The unique and homogeneous structure of Chit-g-PANI was confirmed from SEM studies. This smooth morphology can be reason for its higher conductivity. In XRD studies of Chit-g-PANI the semi crystalline nature is due to the grafting of PANI onto the Chitosan backbone. Dielectric studies showed that, the dielectric loss and dielectric constant decreased with the frequency. The results suggest that the grafted polymer can be used in sensor applications.

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