

Effect of aniline concentration on chitosan grafted polyaniline

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Graft copolymerization of polyaniline onto chitosan using ammonium persulphate (APS) as an initiator was carried out to obtain a product called chitosan grafted polyaniline (chit-g-PANI). Chit-g-PANI samples were synthesized by varying aniline concentration. The structural, thermal and electrical properties of the chit-g-PANI were characterized by measuring UV-Vis, FT-IR, XRD, TGA techniques and DC conductivity measurements, taking chitosan as reference. The chit-g-PANI products have a lower thermal stability than chitosan as revealed by TGA analysis. X-Ray diffraction curves show changes in crystallinity pattern. Spectroscopic analysis suggested a grafting mechanism that proceeds via oxidation and chain scission of chitosan. The DC conductivity is measured in the temperature range of 300-370K and is found to increase with temperature.

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1. Introduction

Chitosan obtained from chitin poly- β -(1 \rightarrow 4)-N-acetyl-D-glucosamine through deacetylation using strong aqueous alkali solution is a more versatile form of this polysaccharide, which is one of the most abundant natural polymers on earth. [1]. Its structure is basically constituted of D-glucosamine units, with contents of N-acetyl-D-glucosamine in the range of 0-50% [2]. It possesses the special properties such as biocompatibility, biodegradability, and biological activities; as a result it has been widely applied to biomedical applications. However, chitosan is only soluble in few dilute acid solutions which limit its wide applications. Recently, the increasing importance and interest in chemical modification of chitosan through graft copolymerization has been showed to be a promising method for the preparation of new materials, which enables to improve its solubility and widen its applications. Graft copolymerization of synthetic monomers such as PANI onto chitosan has attracted the interest of many scientists in the last three decades [3, 4, 5]. Therefore, chitosan is a good candidate to introduce functional groups in PANI, and enhance its selectivity for bio sensors [6]. This polymer possesses hydrogel-like properties through a reaction with glutaraldehyde as a crosslinking agent. In the form of a hydrogel, chitosan is used for wide range of applications such as food packing, drug delivery systems, and biosensors [7]. In the present work, the grafting of aniline onto chitosan in terms of

different monomer concentration has been studied. Some properties of the grafted chitosan are compared with that of the unmodified chitosan. It is expected that the results would be promising for fabrication of biosensors.

2. Experimental details

2.1 Materials

Chitosan middle-viscus was purchased from Fluka (Japan). Aniline monomer and ammonium persulphate (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

In a typical grafting reaction, an exact amount of chitosan was dissolved in 100 ml of 1% (wt) acetic acid solution with constant stirring for overnight. To this solution, different concentration of aniline 0.25M, 0.50M, and 0.75M was dissolved in 20 ml of distilled water at room temperature, was added dropwise for 20 minutes with constant stirring. The resulting solution was brought to below 5°C by immersing the reaction flask in freezing mixture. The polymerization was carried out by the addition of a known amount of ammonium persulphate

dissolved in 20 ml of distilled water was added dropwise to this solution. During the addition, the solution slowly turned to emerald green which confirmed the grafting. The stirring was continued for 5 hours by maintaining the same temperature to ascertain the completion of grafting. The solution obtained was collected by filtration and thoroughly washed with distilled water, methanol, N-methyl pyrrolidone and acetone to remove the unmodified soluble low molecular weight chitosan. The washing procedure was repeated until the polymerization solution became colourless. 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 UV-Visible spectra of chitosan and chit-g-PANI were performed between 200 nm and 1000 nm on Perkin Elmer lambda 35 UV-Visible spectrophotometer. The FTIR spectra of the samples were recorded using a Perkin Elmer spectrometer using KBr Pellet with spectrum of frequency from 4000 cm^{-1} to 400 cm^{-1} with an accuracy of 2 cm^{-1} . The XRD pattern of chitosan and chit-g-PANI were characterized with the help of Rigaku X-Ray Diffractometer. The TGA measurements were investigated using Perkin Elmer, Diamond TG/DTA under a Nitrogen atmosphere at a heating rate of 10°C between room temperature and 900°C. The DC conductivity measurements of chitosan and chit-g-PANI were performed by a Kiethly 6571B high resistance meter and electrometer using a four probe-setup (DFP.2 model).

3. Results and discussion

3.1 UV-Visible spectroscopy

Fig. 1 shows the UV-visible spectra of chitosan (a), and chit-g-PANI graft copolymer with different aniline concentrations (b-d). The absorption band that appears in (a) around 330 nm is due to the glucopyranose components of chitosan. The absorption bands in (b-d) around 300 and 305 nm are due to overlapping of glucopyranose components of chitosan and π - π^* transition of benzenoid rings of grafted PANI with band appeared around 404 nm is due to polaronic peak of grafted PANI which supports the grafting of PANI onto chitosan [8]. The increase of aniline concentration in the chit-g-PANI samples leads to increase of absorption intensity of all peaks as shown in figure 1(b-d). [9].

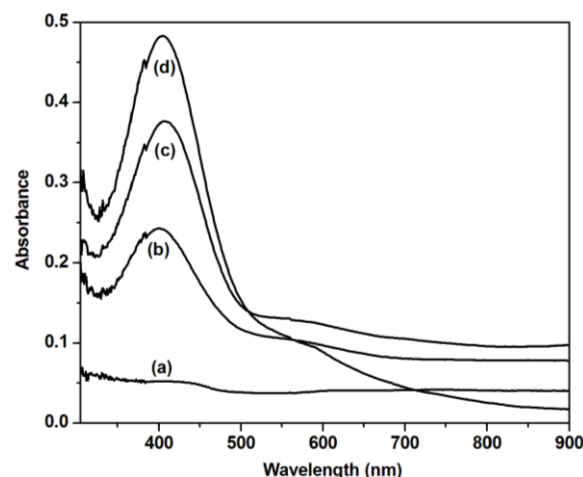


Fig. 1. UV spectra of chitosan and chit-g-PANI copolymer: (a) chitosan; (b) 0.25M aniline; (c) 0.50M aniline; and (d) 0.75M aniline.

3.2 FTIR spectroscopy

Fig. 2 illustrates the FTIR spectra of chitosan (a), and chit-g-PANI with various aniline concentration (b-d). For chitosan in figure (a), the broad band around 3420 cm^{-1} is due to the stretching of O-H, extension vibration of N-H, and inter hydrogen bonds of the polysaccharide. The bands around 2810 cm^{-1} and 2720 cm^{-1} are ascribed to the C-H stretching mode in chitosan. The band occurring at 1596 cm^{-1} is ascribed to $-\text{NH}_2$ bending. The peak appearing at 1351 cm^{-1} is due to the C-OH stretching mode in chitosan. The spectrum also shows band at 1225 cm^{-1} that could be attributed to the saccharide structure. In graft copolymer (b-d) the peaks at 3427 cm^{-1} are of quite reduced intensities and broad, (due to overlapping of O-H stretching of chitosan and N-H stretching of aniline groups at PANI grafts). Reduced intensities of these peaks with respect to chitosan show that appreciable amount of O-H at chitosan has been grafted with PANI chain [10]. The bands around 1121 cm^{-1} in the chit-g-PANI copolymer are due to the steric effect of chitosan [11]. The bands around 761 cm^{-1} correspond to the C-H out-of-plane bending mode in PANI. The bands around 617 cm^{-1} were attributed to the C-OH out-of-plane deformation. The comparatively weaker bands around 2809 cm^{-1} were ascribed to the C-H stretching mode of chitosan [12]. The bands around 1593 cm^{-1} belong to $-\text{NH}_2$ bending. The bands occurring around 1349 cm^{-1} are ascribed to the C-OH vibration of the alcohol groups in the chitosan [13]. Fig. 2 (b-d) show the characteristic absorption peaks of PANI which become more dominant with increasing monomer concentration [14]. Hence FTIR studies clearly suggest the graft copolymerization of polyaniline onto chitosan.

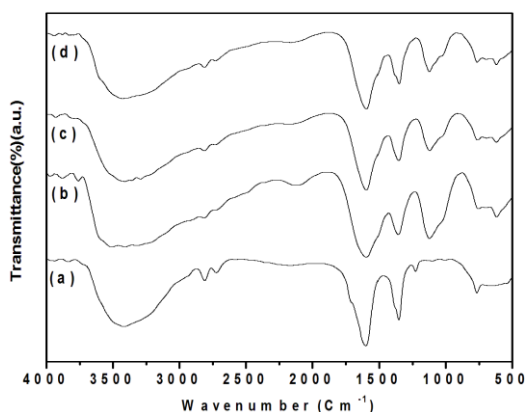


Fig. 2. FTIR spectra of chitosan and chit-g-PANI copolymer: (a) chitosan; (b) 0.25M aniline; (c) 0.50M aniline; and (d) 0.75M aniline.

3.3 X-Ray analysis

The XRD curves of chitosan (a) and chit-g-PANI graft copolymer with various aniline concentration (b-d) are shown in Fig. 3. Chitosan shows the two distinct major crystalline peaks at 11° and 20° due to existence of hydroxyl and amino groups in the chitosan structure [15]. In case of chit-g-PANI (b-d) the peak at 11° disappeared and the peak at 20° decreased sharply. A decrease in crystallinity may be due to the PANI side chains being introduced onto chitosan main chains [16]. Moreover, the intensity of the peak appearing at 20° is suppressed gradually, which indicates that crystalline structure of chit-g-PANI decreases with increasing aniline concentration.

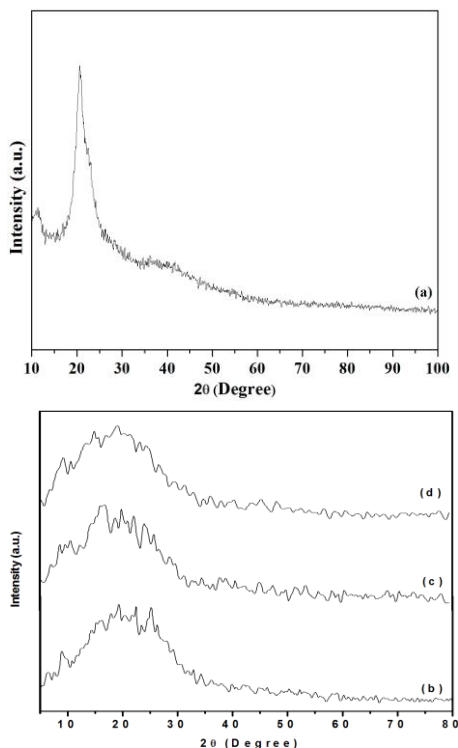


Fig. 3. XRD studies of chitosan and chit-g-PANI copolymer: (a) chitosan; (b) 0.25M aniline; (c) 0.50M aniline; and (d) 0.75M aniline.

3.4 TGA analysis

Fig. 4 shows the TGA traces of chitosan (a) and graft copolymer chit-g-PANI with various aniline concentration (b-d). The TGA of chitosan shows a weight loss in three stages. The first stage ranges between 50°C and 136°C and shows about 10% loss in weight. This may be attributed to the loss of absorbed and bound water indicating its hygroscopic nature [17]. The second weight loss occurs in the range 258 to 327°C , which is about 34% which corresponded to the scission of ether linkage of chitosan back bone [18]. The last stage shows a weight loss of 22% in the range of 327°C to 952°C , which is responsible for the thermal decomposition of glucosamine residue.

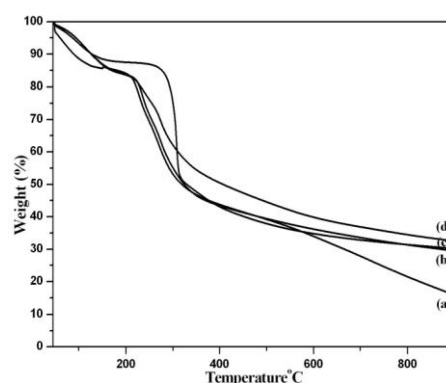


Fig. 4. TGA traces of Chitosan and chit-g-PANI copolymer: (a) chitosan; (b) 0.25M aniline; (c) 0.50M aniline; and (d) 0.75M aniline.

However, the chit-g-PANI copolymer in figure 4 (b-d) has different course of the thermal degradation compared to chitosan. The first stage shows that a loss of absorbed water started at about 40°C and continues up to 145°C , and weight loss was about 12%; the second stage between 210 - 320°C , shows a weight loss of about 31% which corresponds to the scission of the ether linkage in the chitosan back bone. The onset temperature of both the dehydration and the thermal degradation was lower than the chitosan, revealing slight decrease of the thermal stability of chitosan after graft copolymerization. This is because more hydroxyl and amino groups exist in the chitosan structure and crystalline regions form easily compared to chit-g-PANI copolymer [18]. The third stage from about 363°C - 890°C which attributes to the thermal decomposition of the PANI side chains.

3.5 DC conductivity

I-V characteristics of chitosan (a) and graft copolymer chit-g-PANI with different aniline concentration (b-d) are recorded at different temperatures and are found to be linear as shown in Fig. 5(i).

DC electrical conductivity was calculated from the relation,

$$\sigma_{dc} = 1 / \rho_{dc} = (1/R) \times (L/A)$$

where, R, the resistance, L, is the thickness, A, the cross sectional area, σ , the conductivity, and ρ , the resistivity of the sample.

Fig. 5 (ii) shows the variation of DC conductivity with temperature for chitosan (a) and graft copolymer chit-g-PANI with different aniline concentration (b-d). The electrical conductivity of all the samples has been determined in the temperature range from 303 K to 373 K. In all cases conductivity increases rise in temperature in the whole range, this is the characteristic of semiconducting behaviour [19, 20].

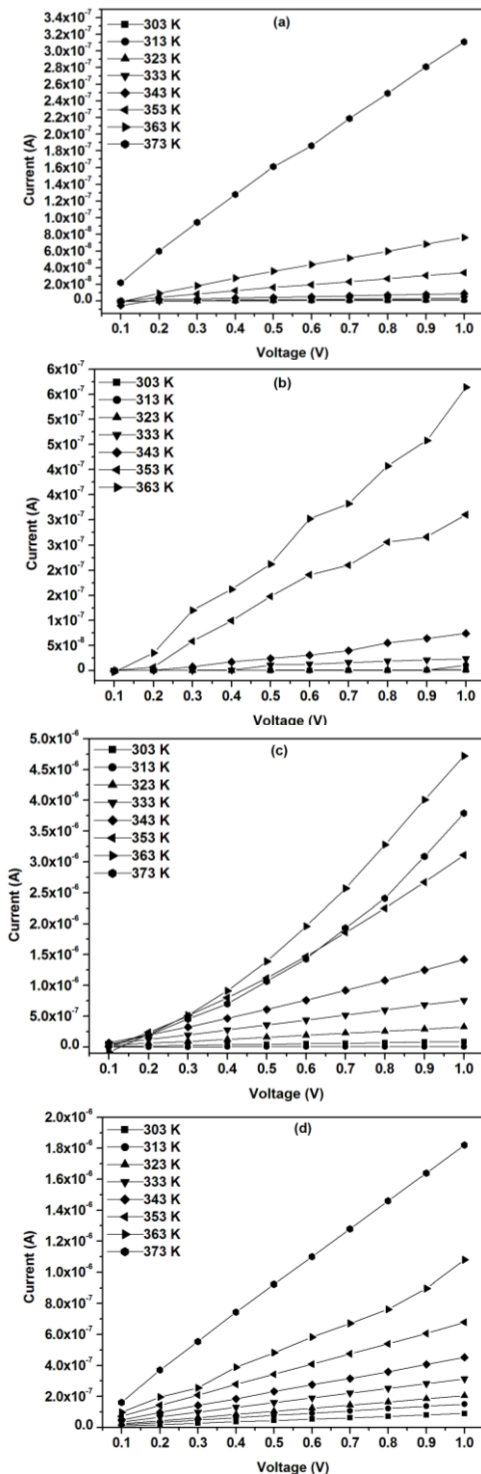


Fig. 5.(i), V-I characteristics of chitosan and chit-g-PANI copolymer: (a) chitosan; (b) 0.25M aniline; (c) 0.50M aniline; and (d) 0.75M aniline.

The DC conductivity of pure chitosan measured at room temperature is 4.96×10^{-11} S/cm. After copolymerization with different aniline concentrations the conductivity was found to be change from 10^{-8} to 10^{-10} S/cm.

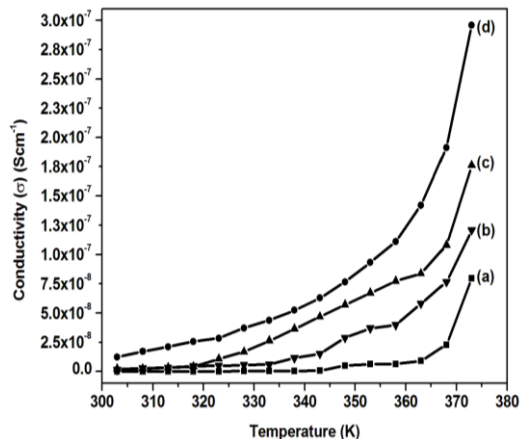


Fig. 5. (ii), Temperature vs. DC conductivity plots of chitosan and chit-g-PANI copolymer: (a) chitosan; (b) 0.25M aniline; (c) 0.50M aniline; and (d) 0.75M aniline.

4. Conclusion

The chit-g-PANI was prepared by a graft copolymerization of polyaniline onto chitosan by chemical oxidation using APS as an initiator. Chitosan and chit-g-PANI samples were characterized by means of UV-Visible, FTIR, XRD, TGA technique and DC conductivity measurement. Spectroscopic data confirm the formation of chemical copolymerization. XRD reveals change in crystallinity of grafted copolymers. The TGA results show that the thermal properties of chitosan are slightly changed by the grafting copolymerization and also confirm a successful copolymer grafting. The DC electrical conductivity results confirm the semiconducting behavior of the samples.

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