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Physical investigations on chitosan graft polyaniline

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ABSTRACT

Conductive polymers are good candidates for preparation of conducting graft copolymers. Therefore, polyaniline (PANI) was chemically grafted with chitosan by using ammonium peroxydisulfate (APS) initiator to obtain a product called as chitosan-graft-polyaniline (CHIT-g-PANI). Polyaniline, chitosan and CHIT-g-PANI were characterized by fourier transform infrared spectroscopy (FTIR), UV-vis spectroscopy, X-Ray diffraction (XRD) and scanning electron microscopy (SEM). UV –vis and FT-IR studies confirmed the chemical structure and conjugation of CHIT-g-PANI. FTIR studies suggested the graft copolymerization of polyaniline on to chitosan. XRD of the CHIT-g-PANI further evidenced the grafting. The surface structure of CHIT-g-PANI was also verified by SEM.

Introduction

Polyaniline (PANI) is one of the most extensively studied conductive polymers. Potential applications include uses in rechargeable batteries, sensors, switchable membranes, anticorrosive coatings, and electronic devices [1-4]. Polyaniline is commercially attractive owing to its easy synthesis, either through chemical or electrochemical methods, good environmental stability, ease ot control conductivity and inexpensive production in large quantities. An important characteristic of PANI is that it undergoes two distinct redox processes as well as p^H switching between unprotonated and protonated states [5]. PANI can be rapidly switched by the addition of bases and acids that unprotonate and protonate the base sides within the polymer. However, the major disadvantage of PANI is its insolubility in common solvents and its infusibility [6]. In an attempt to overcome these problems, we have chemically grafted polyaniline on to the chitosan. In general, incorporation of PANI into flexible matrix could result in good processability with the electrical conductivity having the requisite processes like chemical stability towards dopants, thermal stability and insolubility under readily accessible conditions [7,8].

Chitosan is very interesting due to its characteristics such as biodegradability, chemical inertness, biocompatibility, high mechanical strength, good film-forming properties and low cost [6]. Chitosan, a copolymer of β (1,4) - linked 2-acetamido-2-deoxy-D-glucopyranoseand 2-amino-2-deoxy-D-glucopyranose, is generally obtained by deacetylation of chitin, which is the main component of the exoskeleton of crustaceans shells, such as shrimps [9].

In this work, conducting polymer was employed to graft on to chitosan by chemical polymerization. CHIT-g-PANI shows modification properties of PANI such as solubility, flexibility and season ability. Figure 1 shows the general polymerization mechanism of chitosan-g-polyaniline.

Experimental Details

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-pyrolidine (NMP), hydrochloric acid, acetic acid, ammonia solution and methanol were used as received.

Synthesis of polyaniline in emeraldine base form

The polyaniline in emeraldine base form PANI (EB) was chemically synthesized by oxidation of aniline with APS in aqueous HCl solution at room temperature [10]. In a typical experiment, a solution of 9.3 ml of aniline (0.1 mol) in 200 ml of 1 M aqueous HCl was taken in a 500 ml three-necked round-bottomed flask. A solution of 11g of APS (0.05 mol) in 200ml of 1 M aqueous HCl was then added drop wise over a period of 1 h to the above solution under vigorous stirring. The reaction was stirred for 24 h to complete polymerization of aniline and the precipitated product was then collected by filtration. Then dark green powder obtained was repeatedly washed with 2-3 l of distilled water and methanol in order to remove excess dopant and APS. Final washing was done with acetone to remove water. The $(PANI)_{HCl}$ complex was dedoped with 1% NaOH solution for 24 h and dried in a vacuum oven at 50 °C for 24 h. The dedoped PANI obtained is referred as PANI emeraldine base (PANI-EB).

Synthesis of chitosan-g-polyaniline (CHIT-g-PANI)

A calculated amount of the chitosan was dissolved in a 75 ml of acetic acid in a 150 ml flask. The solution was stirred for an hour. To this solution, 1.23 g (0.0054 mol) 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 and HCl (1 mol) added drop wise to this solution. After 12 hours of continuous stirring, the mixture became black solution. The

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precipitate obtained was collected by filtration and thoroughly washed with distilled water, NMP and acetone. The precipitate was dried under vaccum at 50^0C for 48 hours, a deep green powder of CHIT-g-PANI was obtained.

Instrumentation

The FTIR spectrum of PANI(EB), chitosan and CHIT-g-PANI 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 UV-visible spectrum of PANI(EB) was performed between 200 to 800 nm on the Syntronics double beam UV-visible spectrophotometer 2202. The XRD pattern of PANI(EB), chitosan and CHIT-g-PANI were characterized with the help of Rigaku X-ray diffractometer. The scan range 2θ was 10^o-75^o. The surface morphology of the PANI (EB), chitosan and CHIT-g-PANI were investigated using a scanning electron microscope JSM 6390 JEOL.

Results and discussion

FTIR spectra

FTIR spectra of PANI(EB) , chitosan, and CHIT-g-PANI are shown in Figure 2. For PANI (EB) in Figure 2(a), the prominent absorption peaks at 1594.14 cm^{-1} and 1502.78cm^{-1} are due to quinoid and benzenoid unit stretching modes of EB respectively. The band at 1152.24 cm^{-1} is from the quinoid units stretching modes of EB and the vibrations at 1226.75 cm^{-1} and 1350.44 cm^{-1} are the C-N stretch from the benzenoid units stretching modes of EB [11]. For pure chitosan in Figure 2(b), the broad band at 3416.69cm^{-1} is due to overlapping of –O-H and $–NH_2$ stretching [9]. The band around 1596.76 cm^{-1} is ascribed to $–NH_2$ bending. The bands around 2807.77 cm^{-1} and 2720.98 cm^{-1} were described to the C-H stretching mode in chitosan [12]. The band occurs around 1351.38 cm^{-1} was described to the C-OH vibration of the alcohol groups in the chitosan [13]. The spectrum also shows band at 1225.06 cm^{-1} that could be attributed to the saccharide structure [14].

The FTIR spectrum of CHIT-g-PANI in Figure 2(c) shows all significant peaks correspond to chitosan and polyaniline. The following key characteristic bands were 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 was 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 [15].

The absorption peaks at 1594 cm^{-1} and 1596 cm^{-1} for EB and chitosan respectively has been shifted to 1637 cm^{-1} in the CHIT-g-PANI due to C=O stretching of carbonyl group, typical saccharide absorption [16]. The FTIR results suggested that there is an interaction between aniline with the active sites of chitosan, that is –OH and $–NH_2$.

UV-vis spectroscopy

The UV-vis spectrum of PANI(EB) in Figure 3(a) shows the absorption bandat the 308.8-360.8 nm which is due to the Π-Π* transition of the benzenoid ring. The band at the 600-620 nm shows the absorption of the quinoid ring due to the exciton transition (n-Π*) between the HOMO of the benzenoid ring (non-bonding nitrogen lone pair) and the LUMO (Π*) of the quinoid ring [17, 18]. The spectrum of chitosan in Figure 3(b) shows absorption band at 398.03 nm due to the glucopyranose components of chitosan. The characteristic peaks at 391.05 nm and 844.31nm are related to the Π-Π* transition and polaronic transition. The spectrum of CHIT-g-PANI in Figure 3(c) shows absorption bands at 302 and 310 nm due to overlapping of glucopyranose components and benzenoid rings of grafted PANI. A new peak was appeared at 409 nm due to the Π-Π* transition of the grafted PANI which supports the grafting of PANI onto chtosan[16].

X-ray diffraction (XRD)

The XRD pattern of PANI(EB) in Figure 4(a) shows a broad peak with a maximum around 19.1^o which is characteristic peak of amorphous emeraldine base form of PANI [19]. The XRD pattern of chitosan in Figure 4(b) shows distinct crystalline peaks at around 11^o and 20^o compared to PANI(EB) and CHIT-g-PANI. This is because plenty of hydroxyl and amino groups exist in the chitosan structure, which can form stronger intermolecular and intramolecular hydrogen bonds, and the structure of chitosan molecules has certain regularity, so that chitosan molecules form crystalline regions easily. However, as regards CHIT-g-PANI, the peaks at 11^o and 20^o are weakened obviously as in Figure 4(c). The reason may be attributed to the destruction of the intermolecular hydrogen bonds and the crystalline regions of chitosan, which indicate that the PANI side chains were introduced into chitosan main chains [20].

Scanning electron microscope (SEM)

Figure 5(a) shows SEM images of PANI with an agglomerated granular morphology. The SEM image of chitosan in Figure 5(b) shows larger clustered structure due to stronger interactions between chitosan molecules. After grafting copolymerization of PANI on chitosan, there is a remarkable change of the surface morphology of chitosan as seen in Figure 5(c). A fluffy morphology and globular shapes with some irregularities were clearly observed. This fact can be attributed to the polar difference between chitosan and PANI and the destruction of the intermolecular hydrogen bonds and the crystalline regions of chitosan. This indicates intuitively that the PANI side chains were introduced into chitosan main chains [20].

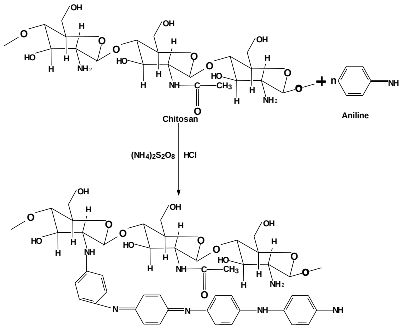

Fig. 1. Scheme for the synthesis of chitosan-g-polyaniline (CHIT-g-PANI)

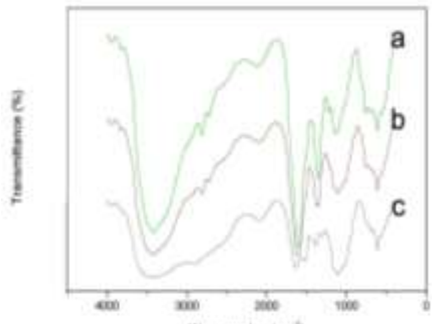

Fig 2. FTIR spectra of (a) PANI(EB) (b) chitosan and (c) CHIT-g-PA

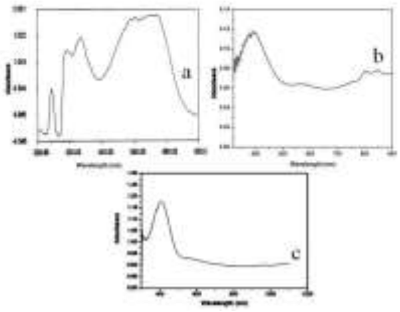

Fig 3. UV-vis spectra of (a) PANI(EB) (b) chitosan and (c) CHIT-g-PANI

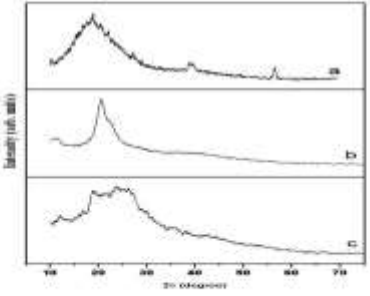

Fig 4. XRD spectra of (a) Polyaniline-EB (b) Chitosan and (c) CHIT-g-PANI

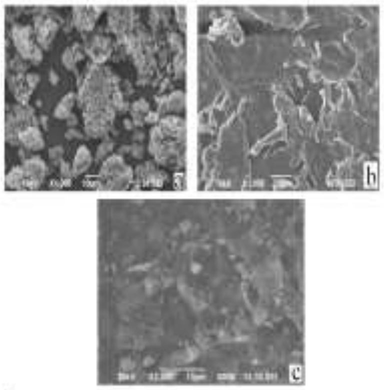

Fig 5. SEM images of (a) PANI(EB) (b) chitosan and (c) CHIT-g-PANI

Conclusion

CHIT-g-PANI was synthesized by chemical oxidation using ammonium persulfate as an oxidant in HCl acid medium. Polyaniline, chitosan and CHIT-g-PANI samples were characterized by means of FTIR, UV-vis, XRD and SEM. Spectroscopy data confirmed the formation of chemical graft copolymerization. The change of PANI and chitosan structure before and after graft copolymerization was investigated by means of XRD which was also confirmed by SEM. The prepared CHIT-g-PANIis expected to have good processability with improved solubility, mechanical strength and electrical properties and could be used for sensors applications.

References

1. Ayse Gul Yavuz, Aysegul Uygun, Venkat R. Bhethanabotla, Carbohydrate Polymers, 75, 448 (2009).
2. S. Roth, W. Graupner, Synth, Met., 55, 3623 (1993).
3. E.M. Genies, A. Boyle, M. Lapkowski, C. Tsintavis, Synth. Met., 36, 139 (1990).
4. A. Ohtani, M. Abe, M. Ezoe, T. Dol, T. Miyata, A. Miyake, Synth. Met., 55, 3696 (1993).
5. G.G. Wallace, G.M. Spinks, L.A.P. Kane-Magurie, P.R. Tesdale. Conductive Electroactive Polymers, 2nd ed., CRC Press, Boca Raton, FL, (2003) 121.
6. A.T. Ramaprasad, Vijayalakshmi Rao, Ganesh Sanjeev, S.P. Ramanani, S. Sabharwal, Synth. Met., 159, 1983 (2009).
7. X. Lu, C.Y. Tan, J. Xu, C. He, Synth. Met., 138, 429 (2003).
8. K. Takabashi, K. Nakamura, T. Yamaguchi, T. Komura, S. Ito, R. Aizawa, K. Murata, Synth. Met., 128, 27 (2002).
9. Tuspon Thanpitcha, Anuvat Sirivat, Alexander M. Jamieson, Ratana Rujiravanit, Carbohydrate Polymers, 64, 560 (2006).
10. A.G. Mac Diarmid, J.C. Chiang, A.F. Epstein, Synth. Met., 18, 285 (1987).
11. Su Ryon Shin, Sang Jun Park, Seoung Gill Yoon, M. Geoffrey Spinks, I. Sun Kim. Seon Jeong Kim, Synth. Met., 154, 213 (2005).
12. Ayse Gul Yavuz, Aysegul Uygun, Vekat R. Bhethanabotla, Carbohydrate Polymers 81, 712 (2010).
13. Yahya A. Ismail, Su Ryon Shim, Kwang Min Shin, Seong Gill Yoon, Kiwon Shon, I. Sun Kim, Seon Jeong Kim, Sensors and Actuators B, 129, 834 (2008).
14. Santos Adriana Martel-Estrada, Carlos Alberto Martinez-Perez, Jose Guadalupe Chacon-Nava, Perla Elva Garcia-Casillas, Imelda Olvas-Armendariz, Carbohydrate polymers, 81, 775 (2010).
15. A. Tiwari, S.K. Shukla.: Chitosan-g-polyaniline, eXPRESS Polymer Letters, Vol. 3, No. 9, 553 (2009).
16. A. Tiwari, V. Singh, eXPRESS Polymer Letters, Vol. 1, No. 5, 308 (2007).
17. Denice S.Vicentini, Guil herme M.O.Barra, Jose R.Bertolino, Alfredo T.N.Pires, European Polymer Journal, 43, 4565 (2007).
18. Palle Swapna Rao, S.Subrahmanya, D.N.Sathyanarayana, Synth. Met., 139, 397 (2003).
19. Dongxue Han, Ying Chu, Likun Yang, Yang Liu and Zhongxian Lv, Physicochem. Eng. Aspects 259, 179 (2005).
20. Wengui Duan, Chunhong Chen, Linbin Jiang, Guang Hua Li, Carbohydrate Polymers, 73, 582 (2008).