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Synthesis and Evaluation of Chitosan -Polyaniline Copolymer in Presence of Ammonium Persulfate as Initiator

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Abstract

Chemical grafting of Polyaniline (PAni) and chitosan (CS) as has been carried out with formaldehyde as grafting agent and ammonium persulfate as an initiator. For this reason aniline monomers were copolymerized with chitosan and were chemically polymerized. The synthesized copolymer was Characterized using Fourier transform infrared spectroscopy (FT-IR), UV-Visible, scanning electron microscopy (SEM) and differential scanning calorimetery (DSC) techniques.

Keywords: *Polyaniline, Copolymers, Chitosan, Biocompatible, Spectroscopic techniques, UV-Visible.*

Introduction

PAni as a conductive polymer has attracted the most of the attentions, due to simple preparation and doping procedure, good environmental stability, relatively high conductivity and low cost and also due to its wide spectrum of applications. PAni, like many other conductive polymers, is insoluble in common solvents and infusible because it decomposes before melting [1-4]. Because of these problems many methods are reported. Grafting with other polymers having good mechanical and physical properties is one of them. Many potential applications of PAni are demonstrated recently [5-8]. The polymers should be insoluble in whole range of pH to gain some of the applications. One way to overcome these problems is chemical grafting of PAni onto the radiation cross linked CS. CS is a polysaccharide derived from the chitin of crustaceans. The properties of cationic polysaccharides are the low toxicity and good

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biocompatibility that make them interesting for study as a drug excipient [9]. The nitrogen electrons in the amino and N-acetyl amino groups can establish dative bonds with transition metal ions and some hydroxyl groups in CS may function as donors [10]. CS can chelate metal ions by itself, especially those listed transition metals. It can apply as a matrix for immobilization of enzymes too [11].

Due to its physical and chemical properties, CS is used in different products such as pharmaceutical and cosmetic products to water treatment and plant protection. In different applications, different properties of CS are required [12, 13]. Recently, much attention has been paid to utilize CS in biomedical applications, for example, as a wound dressing, skin grafting template, hemostatic agent, hemodialysis membrane and drug delivery vehicle, etc. [14, 15]. Despite these high potential of CS, its insolubility in common organic solvents and non-thermal plasticity have delayed its utilization and basic research. Of the possible chemical modifications of this rigid amino polysaccharide, grafting with synthetic polymers has been explored as an interesting alternative method to develop novel hybrid materials, such as CS-graft-polystyrene, CS-graft-poly- (methyl methacrylate), CS-graft-poly(ethylene glycol) and so on [16].

Experimental

Materials and methods

Acetic acid, hydrochloric acid, N-methyl pyrrolidine (NMP) and ammonium persulfate (APS) with 98% purification prepared from Merck Company and used without further purification. All infrared spectra were obtained from samples in KBr pellets using a Bruker Tensor27 Ger FT-IR spectrophotometer. 1H NMR spectum was taken by a Bruker WP 200 SY spectrometer operating at 250 MHz in DMSO. To review the samples UV-Vis has been used (model Perkin Elmer Lamer Lambda25) too. Scanning electron microscopy (SEM) instrument models was XL30, Philips, Holland. Also the thermal behavior of the polymers obtained from the STA STA S-1500 Scinco model that is made in Korea. Finally the samples mixed together with Alfa magnetite stirrer (model: Hs- 860).

Preparation of polyaniline

First, 2 ml freshly distilled aniline was dissolved in 60 ml of hydrochloric acid (1M) and was brought to temperature 4-0 °C by ice bath. Then a certain amount of APS was added to 40 ml of hydrochloric acid (1M) and stirred. The prepared solution was added to the first solution drop by drop. A few minutes after injection of the oxidant, the solution turned bluish-green color. The color intensity of the reaction was greater by the time. After 5 hours of stirring, the solution was filtered through filter paper. Greenish black deposits remaining on the filter paper was washed by water and was dried in an electric oven at 60 °C for 12 hours finally. Quantitative details of this process are given in Table 1.

Table1. Quantitative details of PAni synthesis in presence of APS.

Electrical conductivity (S/cm)	Equivalent weight (mol) (i): initiator (ii): aniline	Compounds HCl(mL) :(i) (gr) initiator :(ii) aniline (mLit)(iii)	Precipitate (gr)	Sample
$9/3\times10^{-2}$	(i):1×10^{-2} (ii):1×10^{-2}	(i):50 (ii):2/45 (iii):1	0/424	I_{APS}
$8/5\times10^{-2}$	(i):1×10^{-2} (ii):1×10^{-2}	(i):50 (ii):2/70 (iii):1	0/405	II_{KPS}
$7/2\times10^{-2}$	(i):1×10^{-2} (ii):1×10^{-2}	(i):50 (ii):5/48 (iii):1	0/326	III_{CAN}

i) : Acetic acid, ii: APS, iii: Ani

Synthesis of chitaline

Chitasan was solved in 30 ml acetic acid solution and stirred for 1hr. Then 20 ml of APS solution was added to the first solution drop by drop at 5 °C. A solution of certain amount of freshly distilled aniline in 20 ml of distilled water was prepared and was added to the final solution drop by drop over 20 minutes. Stirring continued for 12 h. Then the solution was filtered and dried. Dark green to black powder is the expected copolymer (Figure 1). This experiment was carried for different ratios of PAni and CS as it is shown in Table 2.

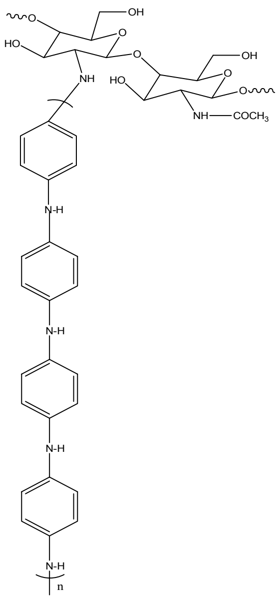

Figure 1. Partial structure of synthesized PAni-CS copolymer.

Table 2. Different amount of ingredients for preparing PAni-CS copolymer in presence of APS.

Electrical conductivity (S/cm)	Solubility in	Equivalent weight (mol)	Compounds	Sediment (gr)	Sample
6.8×10^{-4}	a: weak b: medium	i: 5.36×10^{-3} ii: 5.36×10^{-3}	i: 1.23 gr ii: 0.5 ml iii: 0.40 gr	0.622	A
4.1×10^{-4}	a: medium b: good	i: 5.36×10^{-3} ii: 2.68×10^{-3}	i: 1.23 gr ii: 0.25 ml iii: 0.40 gr	0.541	B
7.8×10^{-4}	a: weak b: medium	i: 5.36×10^{-3} ii: 1.07×10^{-2}	i: 1.23 gr ii: 1 ml iii: 0.40 gr	0.793	C
5.6×10^{-4}	a: weak b: good	i: 5.36×10^{-3} ii: 5.36×10^{-3}	i: 1.23 gr ii: 0.5ml iii: 0.2 gr	0.661	D

i): APS, ii: Ani, iii: CS, a: Acetic acid, b: NMP)

Synthesis of graft copolymer

Chitaline was dissolved in 30 ml of 2M ammonia and stirred at room temperature for 1hr. Then was filtered and the precipitate was dried in an oven at 60 °C for 3 hr.The obtained solid was stirred with 2 ml of 1M acetic acid until fully dissolved. So by adding excess amounts of acetic acid the pH raised to 4. Meanwhile by adding drop by drop a certain amount of formaldehyde the grafting process is started. Stirring was continued for 12 hr at room temperature. The solid was filtered, washed with distilled water and dried at 60 °C for 12 hr. A dark green powder was obtained including the chitosan grafted polyaniline (chit-g-c-PAni). Different ratios of aniline and formaldehyde were examined. In Figure 2, the structure of cross linked copolymer is shown.

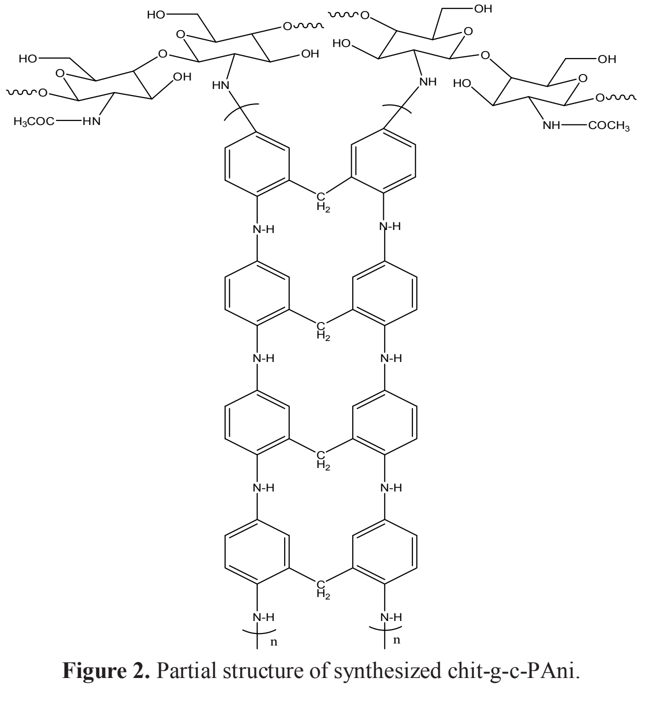

Figure 2. Partial structure of synthesized chit-g-c-PAni.

Result and discussion

Fourier transforms infrared analysis

Various vibrations of final grafted product (Figure 3) is analyzed. The wide peak is observed in the area of 3200-3500 cm^{-1} is due the overlapping between O-H stretching vibrations in CS and NH stretching vibrations in PAni. Also there are peaks at the areas of 2858 and 2925 cm^{-1} which are owned to CH stretching vibrations and the peak at 1636 cm-1 is due to C = O stretching vibrations of CS. The area at 11459 cm^{-1} is belonging to the C=C and C=N stretching vibrations in benzoid rings of PAni. Stretching vibrations of the aromatics is approximately at 1301 cm^{-1}.

As can be seen stretching vibrations of N = Q = N, after linking CS with PAni, has shift from 1132 cm^{-1} to 1040 cm^{-1}. NH vibration of CS has seen in the region around the peak at 1655 cm^{-1} too.

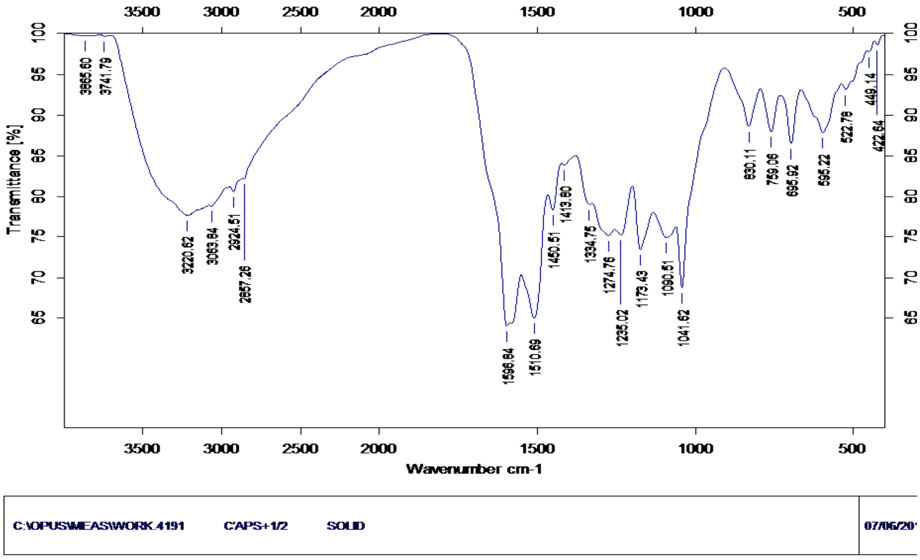

Figure 3. FT–IR spectrum of PAni- CS copolymer in presence of APS.

UV-vis characterization of CS-graft-PAni copolymer

Conductive polymers are containing a conjugated system of double bonds. That's why some of their electron transfers occur in the UV-Visible region. UV-Vis spectrum of PAni has two absorption bands at 630 and 330 nm wavelengths. The presence of these two peaks can be attributed to existence of two unequal rings (benzoid and quinoid) in polymer chains. According to the aniline pattern, expected peak of the benzoid ring is observed at 330 nm. But double bonds increasing in a conjugated system can cause a red shift (shift to lower frequency or higher wavelengths). So the absorption area of π-π* transition has been transferred from 330 nm to 350 nm that is due to double bond increasing in the chain as it shown in Figure 4.

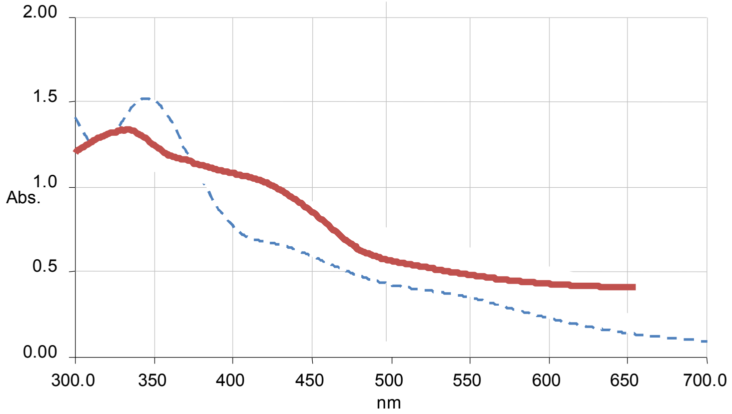

Figure 4. UV-Vis spectrum of PAni- CS copolymer in presence of APS blue and Chit-g-c-PAni red line.

TGA-DSC and SEM characterization of CS-graft-PAni copolymer

In Figure 5 the STA spectrum of graft copolymer is shown. As can be seen the polymer begins to soften from the temperature about 50 °C, and it continues until the temperature of 210 °C. This issue is caused by the loosening of connections between PAni and CS. At this point, the player loses almost 10% of its weight. This mass loss can be due to loss of moisture and solvent of polymer. Degradation begins at 210 °C and continues to 500 °C. The reason is PAni and CS chain degradation that caused to 50% mass reduction. Complete degradation occurs above 500 °C temperatures that continue to 600 °C. Instead of burning the polymer remains less than 10% ash.

There are almost three endothermic areas and one exothermic region in STA curve. Three endothermic regions are at 110, 240 and 290 °C temperatures which region of 110 °C is related to the first fracture and two subsequent regions are depended to second fracture. This shows that the second fracture involves both of the PAni chains and CS side groups connections that it was unclear in the TG curve. Exothermic area is due to degraded groups reconnection and gas formation that is along with heat production. Heating process was started from 25 °C and continued to 700 °C temperature. Complete degradation of 56% of the polymer mass was occurred and the remaining ash is close to 4% of the mass of the polymer.

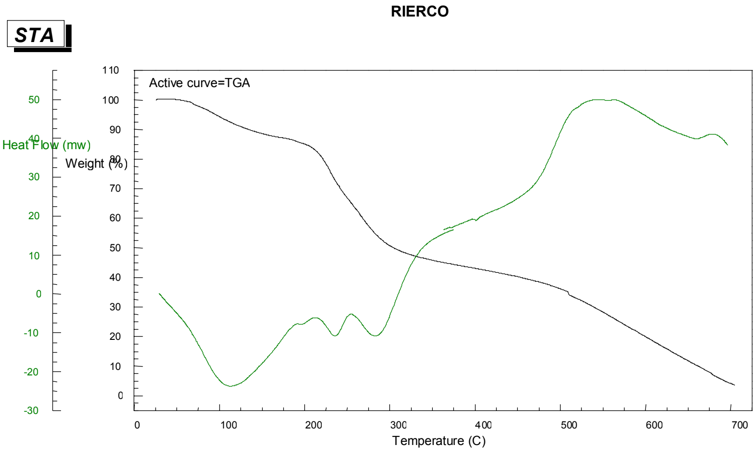

Figure 5. STA spectrum of Chit-g-c-PAni in presence of APS.

SEM images of PAni- CS copolymer in presence of APS

SEM images are shown in Figure 6 that indicates that the polymer surface is relatively smooth and slick.

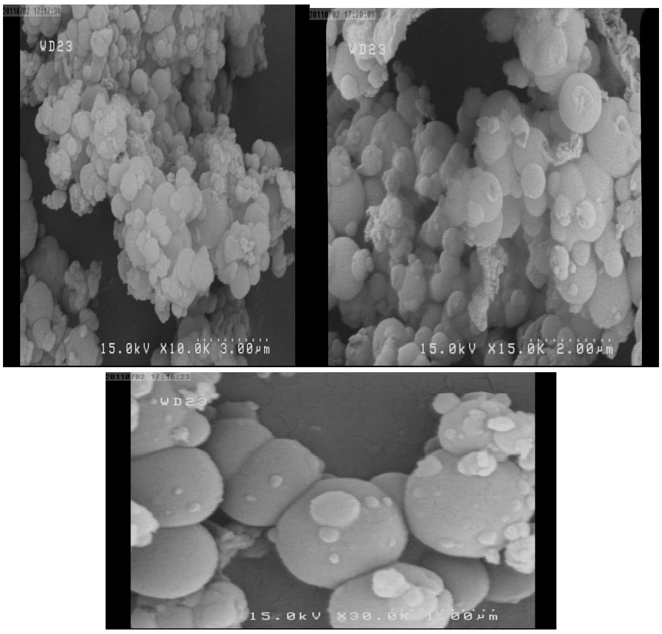

Figure 6. SEM images of PAni- CS copolymer in presence of APS with different magnifications.

Conclusion

In this work radical-cation of CS was formed under the influence of initiator and then exposed to Ani, graft copolymer was gained. The information of 1HNMR, FT-IR, UV-visble, STA and SEM spectra were produced the structure of synthesized copolymer. Solubility test results showed that the synthesized copolymer link is sparingly soluble in solvents tested also electrical conductivity of grafted copolymer is less than Ani with unclear reason. Besides the chemical structure, many factors including the morphology and shape of the polymer chain may effect on the electrical conductivity also molar ratio of Ani and APS are effective on the electrical conductivity of the synthesized copolymer as it shown in Table 2. The electrical conductivity increases when the initiator amount is greater than the Ani. In general, high value of initiator or high temperature has a positive effect on the polymerization rate, but it reduces the degree of polymerization. Also half of CS amount led to a slight increasing in electrical conductivity but the quality of the synthesized copolymer would not be good. It is known that the electrical properties of the conducting polymer are depended on the size and shape of the particles. SEM images indicate that the polymer surface is relatively smooth and slick. Usage of this copolymer with these properties is recommended for various applications, including preparation of polymer-resistant coatings, chemical sensors and storage containers.

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