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Chemical and Electrochemical Grafting of Polyaniline onto Chitosan

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ABSTRACT

Conductive polymers are good candidates for preparation of conducting graft copolymers. Therefore, polyaniline was chemically grafted onto chitosan by using ammonium peroxydisulphate initiator, in the presence of 1 M HCl to obtain a product known as Chitaline (chit-*g*-PANi). Electrochemical polymerization was carried out by coating chitosan on the surface of Pt disk working electrode. Then, PANi grew onto chitosan in acidic solution and a graft copolymer was produced. The grafted copolymer was identified by FTIR, UV-visible, and ^{1}H and ^{13}C NMR spectroscopy techniques. Spectroscopic studies show the grafting and demonstrate that the electronic states are similar to those of the emeraldine and protonically doped emeraldine forms of polyaniline. The thermal properties of chit-*g*-PANi were studied by thermogravimetric (TGA) and differential scanning calorimetry (DSC). Morphology properties of chit-*g*-PANi have been studied by SEM images which confirm grafting polymerization. The effects of concentration of APS, ANi, reaction time and temperature on graft copolymerization were studied by determining the grafting percentage, grafting efficiency and percentage add-on. Electrical conductivity of copolymer has been studied by four-point probe method of having produced 4.6×10^{-2} S/cm conductivity.

Key Words:

conducting polymers;
graft copolymer;
polyaniline;
chitosan.

INTRODUCTION

Chitosan is a naturally occurring, biodegradable, non-toxic, non-allergenic biopolysaccharide derived from chitin, found in abundance in nature [1-3]. Chitosan has also been found to be a good candidate as a support material for gene delivery, cell culture and tissue engineering. However, practical use of chitosan has been mainly confined to the unmodified forms. Chitosan bears two types of reactive groups that can be grafted. First, the free amino groups on deacetylated units and secondly, the hydroxyl groups on the C3 and C6 carbons of acetylated or deacetylated units.

Grafting of chitosan allows the formation of functional derivatives by covalent binding of a molecule, the graft, onto the chitosan

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backbone. Recently researchers have also shown that after primary derivation followed by graft modification; chitosan would obtain much improved water solubility and bioactivities such as antibacterial and antioxidant properties [4].

Grafting of chitosan is a common way to improve its properties such as increasing chelation [5] or complexation properties [6], antibacterial effect [7] or enhancing adsorption properties [8]. Although the grafting of chitosan modifies its properties, it is possible to maintain some interesting characteristics [9] such as biocompatibility [10], biosynthesis [11] and fibre formation [12].

Many investigations have been carried out on the graft copolymerization of chitosan in view of preparing polysaccharide-based advanced materials with unique bioactivities and thus widening their applications in biomedicine and environmental fields. A few review articles on the potential applications of chitosan for pharmaceutical, veterinary medicine, biomedical and environmental field have already been reported [8,10].

Chitosan and several of its derivatives show good to excellent antimicrobial (antibacterial and antifungal) properties [8]. Chitosan blended with polyester and cellulose fibres renders antibacterial property to such fibres. The resulting fibres show excellent laundering durability and retention of antibacterial activity following several laundering cycles [13].

Chitosan and several of its water insoluble derivatives have shown excellent binding capacities against toxic, fatty acids and hazardous heavy metal ions such as Sn^{2+} and Sn^{4+} (including organic tins), Hg^{2+}, Pb^{2+}, U^{6+}; and transition metal ions e.g. Cd^{2+}, Cu^{2+}, Cr^{3+}, Zn^{2+}, Ni^{2+} and V^{4+} [14]. Low-molecular-weight carboxymethyl chitosan has been applied for flow injection chemiluminescence technologies.

Low-molecular weight carboxymethyl chitosan (CMCTSs) has been prepared by oxidative degradation method involving hydrogen peroxide (H_2O_2) without or with microwave radiation [15].

A number of initiator systems such as, ammonium persulphate (APS), potassium persulphate (PPS), ceric ammonium nitrate (CAN), thiocarbonation-potassium bromate (TCPB), potassium diperiodatocuprate (III) (PDC), 2,2'-azobisisobutyronitrile (AIBN) and ferrous ammonium sulphate (FAS) have been developed to initiate grafting copolymerization [16,17]. Therefore, conducting polymers and its derivatives can be used to other specific applications [18,19].

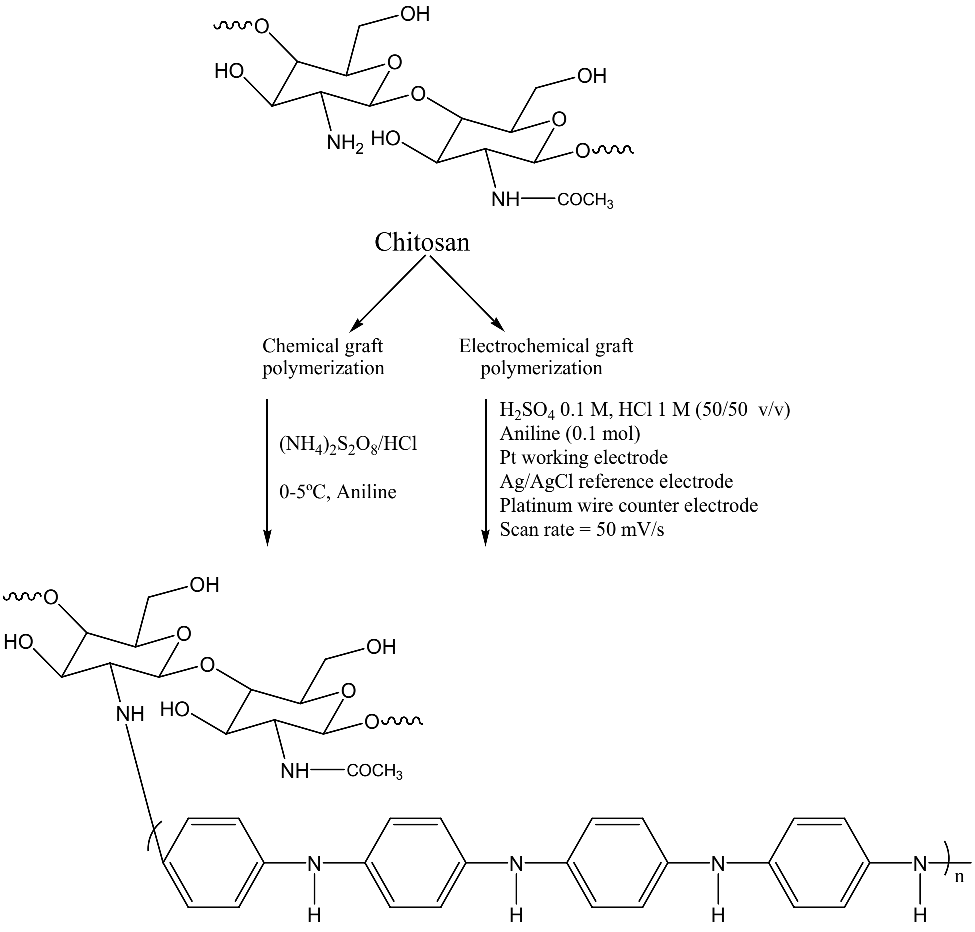
In the preceding works, we reported the chemical and electrochemical synthesis of conducting graft copolymer of vinyl acetate with pyrrole and studied its gas and vapour sensing [20] property. In continuation of our work we have synthesized PANi grafting onto polyvinyl-propionate [21]. The sensing effects of polyaniline grafted on polystyrene for cyanide compounds [22] and graft copolymer of polypyrrole grafted on polystyrene for some toxic gases [23] have been reported as well.

In this work conducting polymer was employed to initiate the graft copolymerization of aniline onto chitosan. So, the grafting of PANi onto chitosan (Chitaline) was carried out by chemical and electrochemical polymerizations. Therefore, the effects of concentration of APS, ANi, reaction time and temperature on graft copolymerization were studied by determining the grafting percentage, grafting efficiency and percentage add-on. On the other hand, chitosan or PANi's properties improved. Chit-*g*-PANi shows modification of PANi such as solubility, flexibility, film formation and sensor ability. In continue we measured the efficiency and grafting percentages and electrical conductivities of graft copolymer. Figure 1 shows all steps of Chitaline formation.

EXPERIMENTAL

Materials

Chemicals used in this study were American Chemical Society (ACS) grade. The sample of pure chitosan was obtained as a gift from Fluka Chemical Co. Its degree of deacetylation >85% and the molecular weight was 600,000. According to the publications chitosan flakes are being grinded to powders and dried under vacuum at room temperature. Aniline (Merck) was dried with NaOH, fractionally distilled under reduced pressure from sodium or CaH_2. Other chemicals and solvents were purified as per standard procedure before use.



Chitaline

Figure 1. Schematic illustration of chemical and electrochemical formation of Chitaline (chit-*g*-PANi).

Instruments

Conductivity changes were measured with a four-probe device (home-made, ASTM Standards, F 43-93). A Fourier transform infrared spectrometer, (Bruker) was used in spectral measurements of the polymer and graft copolymer and reported (as sharp, weak, medium, and broad peaks). Electrochemical polymerization was carried out using digital potentiostat (Metrohm 746 VA) by cyclic voltammetry. Proton and carbon nuclear magnetic resonance (FT-^{1}H and ^{13}C NMR) spectra were recorded at 250 MHz on a Bruker WP 200 SY spectrometer. NMR data are reported in the following order: chemical shift (ppm), spin multiplicity (as singlet, doublet, triplet, quartet, multiplet, and broad peaks), and integration. UV-visible spectra were obtained by Perkin Elmer Lambda 15 Spectrophotometer. Molecular weight was measured at 30ºC with a gel permeation chromatography (GPC), (Waters Associates, model 150-C). Three styragel packed columns with different pore sizes (104-106 Å) were used. The mobile phase was cresol with flow rate of 1.5 mL/min. The thermal properties (thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC)) of polymer were performed by STA 625-PL Thermal Science. Scanning electron microscopy (SEM) was employed to study the type of surface morphology of polymer. A Cambridge S-360 SEM was used for this purpose.

Chemical Synthesis of Chitosan/Polyaniline Graft Copolymer (Chit-*g*-PANi)

Chemical graft copolymerization was carried out in a 100-mL four-necked flask equipped with thermometer, condenser, stirrer and gas inlet. In a typical reaction, 0.4 g chitosan in 30 mL acetic acid 2% was added with constant stirring under nitrogen and degassed for 1 h. The solution from 1.23 g (0.0054 mol) APS in 20 mL distilled water was added to flask in 0-5ºC. The mixture was kept under N_2 atmosphere, then 0.5 g (0.0054 mol) aniline suspended in 10 mL distilled water and was added dropwise via a syringe through a rubber septum. The solution was reacted at room temperature with magnetic stirring in nitrogen atmosphere. After a further 12 h continuous stirring, the mixture became a black solution. The precipitate obtained was collected by filtration and thoroughly washed with distilled water. Dried at 40ºC for 24 h under vacuum, a green black powder was obtained.

Electrochemical Synthesis of Chitosan/Polyaniline Graft Copolymer (Chit-*g*-PANi)

Electrochemical polymerization was carried out by coating chitosan on surface Pt disk working electrode, and then PANi grew onto chitosan in acidic solution. Chit-*g*-PANi was perpared by applying intended potential to the electrode using potentiostat. In this electrolysis, a standard three-electrode cell without any cell partition, using a Pt working electrode, a Pt counter electrode, and Ag/AgCl electrode as a reference electrode were employed. The electrolyte solution consisted of 0.1 M aniline in 20 mL of 50:50 (v/v) mixtures of 0.1 M sulphuric acid and 1 M hydrochloric acid in water. The potential range for electrochemical polymerization and the scan rates were -0.5 to 2 V (versus Ag/AgCl) and 50 $mV.s^{-1}$, respectively.

RESULTS AND DISCUSSION

Chemical modifications open ways to various utilizations of polysaccharides. Of possible modifications, graft copolymerization is anticipated to be quite promising for developing sophisticated functions; it would enable a wide variety of molecular designs to afford novel types of tailored hybrid materials composed of natural polysaccharides and synthetic polymers. Graft copolymerization of synthetic polymers onto chitosan can introduce desired properties and enlarge the field of their potential applications by choosing various types of side chains.

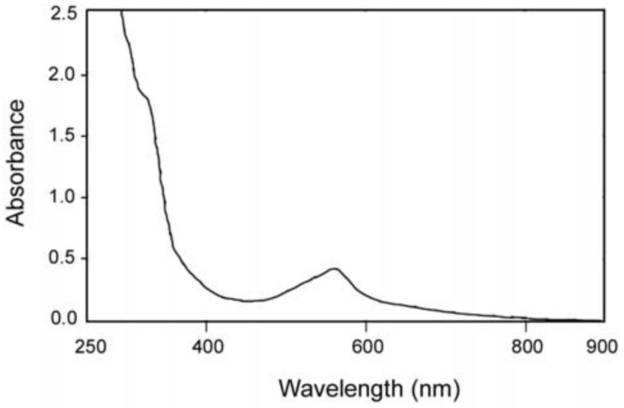


Figure 2. UV-visible of chit-*g*-PANi in *m*-cresol solvent.

Study of UV-visible Spectroscopy

Conductive polymers have a conjugate system of double bonds on their backbone. The conductive polymers have some of the conventional transfers in the UV region, such as *n*-π^*, π-π^*, etc. The π-π^* transfers of conjugated double bonds are related to near visible regions, associated to polaron and bipolaron status as well as solution of conductive polymers. Figure 2 shows UV-visible spectrum data for chit-*g*-PANi in *m*-cresol solvent. The above mentioned polymer (with aniline pattern) is expected to have two peaks in 260 nm and 320 nm with intensities of 3.5 and 1.8, respectively. The first transfer may be due to the *n*-π^* transfer and the second one due to the π-π^* of benzoic system. As we know, an increase in the chain length and subsequently, an increase in conjugated double bonds, a decrease in energy difference π-π^* occurs that causes an increase in the wavelength. UV-visible spectra data show that spectrum of 320 nm region is for the second peak of aniline groups and the π-π^* is a conjugate couple system for the benzenoid diamine and quinoid diimine units (for the polaron and bipolaron transfers) in 500-600 nm regions.

Infrared Spectroscopy

Structural changes of chit-*g*-PANi were confirmed by FTIR spectroscopy (Figure 3). The IR spectrum of the chitosan has strong peak around 3490 cm^{-1} due to the stretching vibration of O–H, the extension vibration of N–H, and inter hydrogen bonds of the polysaccharide. In graft copolymer the peak at 3200-3500 cm^{-1} is of quite reduced intensity and broad,

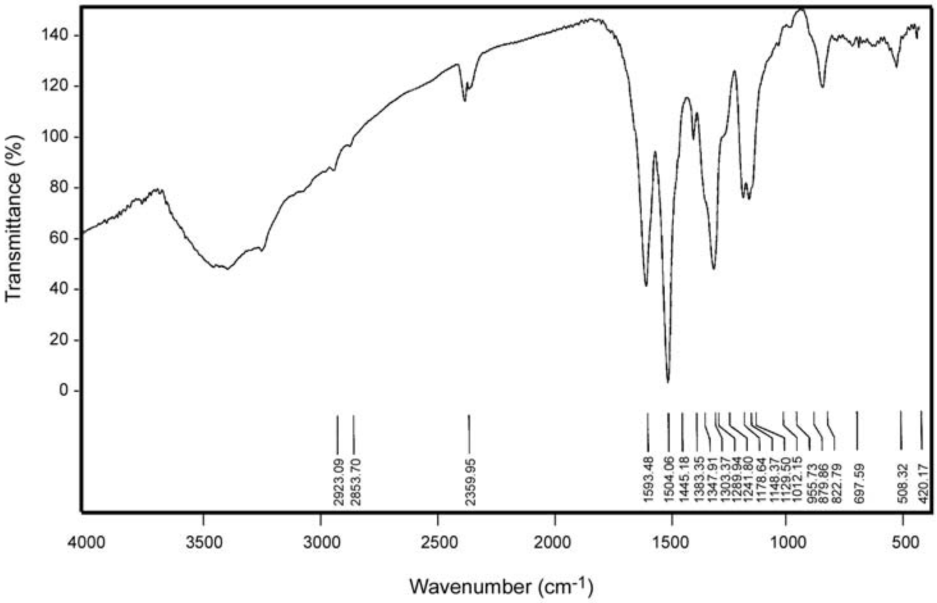


Figure 3. FTIR spectrum of chit-*g*-PANi.

(due to overlapping of O–H stretching of chitosan and N–H stretching of aniline groups at PANi grafts). Reduced intensity of this peak with respect to chitosan shows that appreciable amounts of O–H and N–H at chitosan have been grafted with PANi chain. The peak of 3100 cm^{-1} Ar-H stretching of PANi overlapped the O-H stretching of chitosan. The IR spectrum of chitosan shows other peaks assigned to the chitosan structure at 1148, 1012, and 879 cm^{-1} and a strong PANi characteristic peak at around 1593, 1504 and 1303 cm^{-1}. From the IR data it is clear that the grafted copolymer chit-*g*-PANi had characteristic peaks of PANi and of chitosan, which could be a strong evidence of grafting.

NMR Spectroscopy

Figure 4 shows FT-^{1}H NMR of chit-*g*-PANi. The FT-^{1}H NMR of chit-*g*-PANi shows the spectra in 1.71

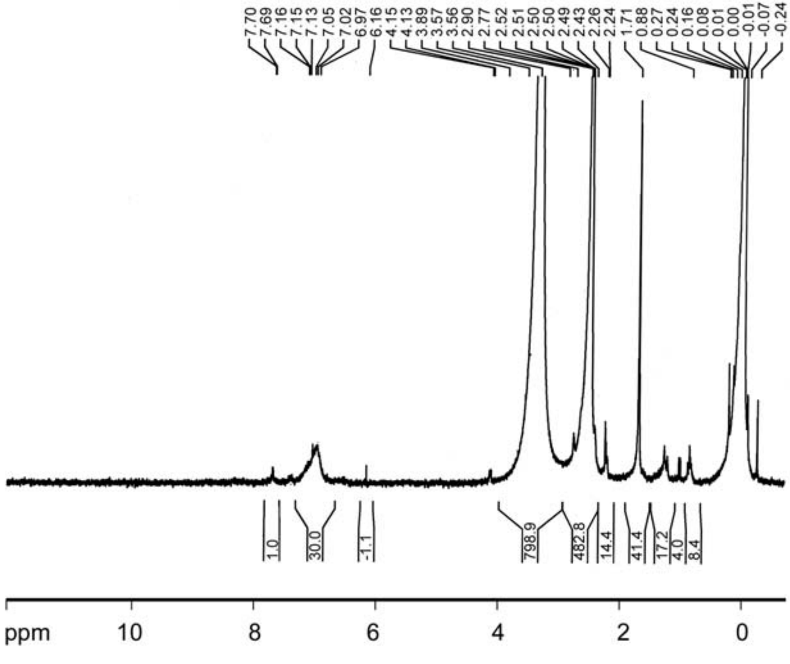


Figure 4. FT-^{1}H NMR spectrum of chit-*g*-PANi.

ppm region for different protons of CH_2 in the chain length as well as the lateral chains. The wide spectrum at 2.5 ppm seems to be related to the C-H protons on chitosan which are overlapped by the peak of DMSO protons. The wide spectrum observed in 3.7 ppm is also the specific peak of hydroxyl group along the chain that overlapped H_2O protons. Therefore, existing wide peak in 6.97-7.69 ppm region is for the aromatic and benzoic region of PANi protons.

Study of Differential Scanning Calorimetry and Thermal Gravimetry Analysis

Figures 5 and 6 show STA (DSC and TGA) thermograms of chitosan and chit-*g*-PANi, respectively. The STA curves show that chit-*g*-PANi has slightly higher thermal resistance than chitosan and still lower than PANi. The TGA curve for chitosan has a softening temperature at 200ºC and degradation initiation under 210ºC and for chit-*g*-PANi degradation initiation

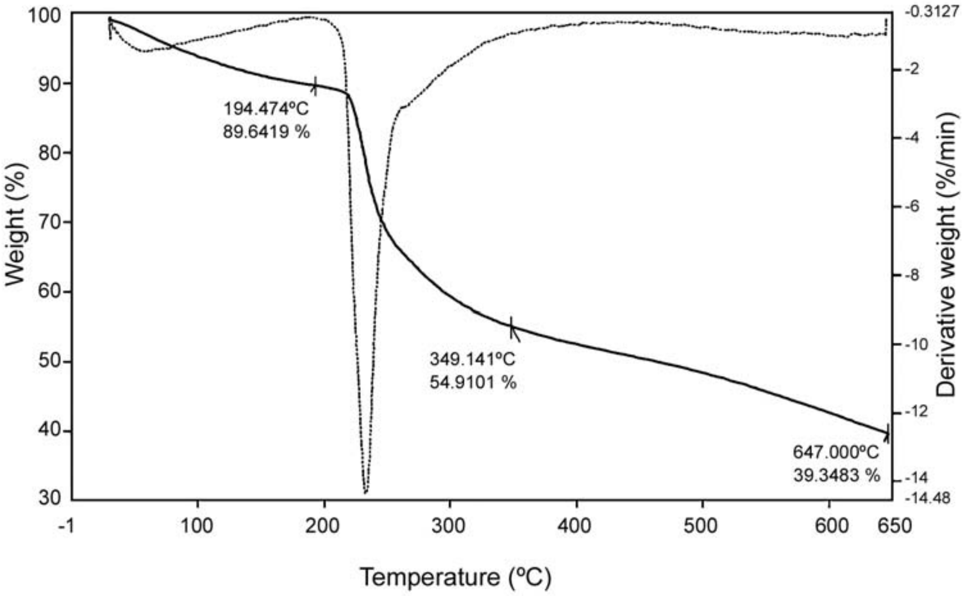


Figure 5. STA (TGA and DSC) thermograms of chitosan.

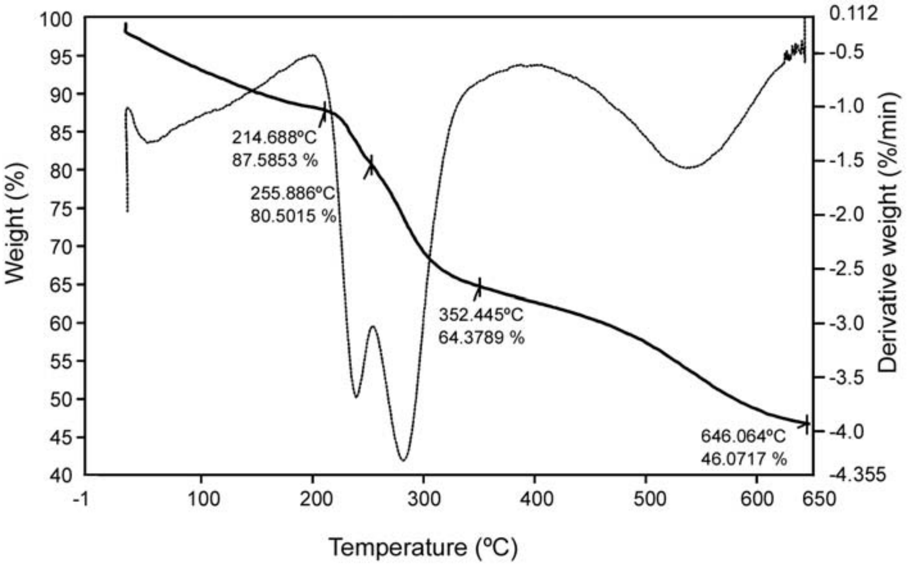


Figure 6. STA (TGA and DSC) thermograms of chit-*g*-PANi.

higher than 220ºC. In DSC curve for chitosan, one endothermic peak appeared in 230ºC region. As it is shown in TGA thermogram of chit-*g*-PANi, this polymer started to soften at 30ºC and up to 194ºC it lost approximately 10.4% of its weight which is due to the humidity and existing solvent in polymer chains, and above 210ºC it more or less degraded. Chit-*g*-PANi has a good stability below 200ºC. At above 220ºC polymer starts to degrade completely and it continues up to 400ºC. The TGA of chit-*g*-PANi for about 20% grafted PANi has illustrated that initial decomposition temperature (IDT), polymer decomposition temperature (PDT) and the maximum polymer decomposition temperature (PDT_{max}) are 214ºC, 255ºC and 352ºC, respectively. The residual weight (γ_c) of the polymer was reported at 646.64ºC to be 45.07%. A comparison between changes in thermal resistance of chit-*g*-PANi and its blends shows that chitosan and its blends have more thermal resistant as a copolymer.

Scanning Electronic Microscopy

Figures 7a and 7b show SEM of chit-*g*-PANi. As it is shown in pictures, PANi is in the form of needle and homogeneous particles. Homogeneity and single phase films are the implications of successful graft copolymer. Figure 7b is the cross cut of the same film which shows well the homogeneity and preparation of graft copolymer as well. The development of PANi chain length is sufficient on the base polymer.

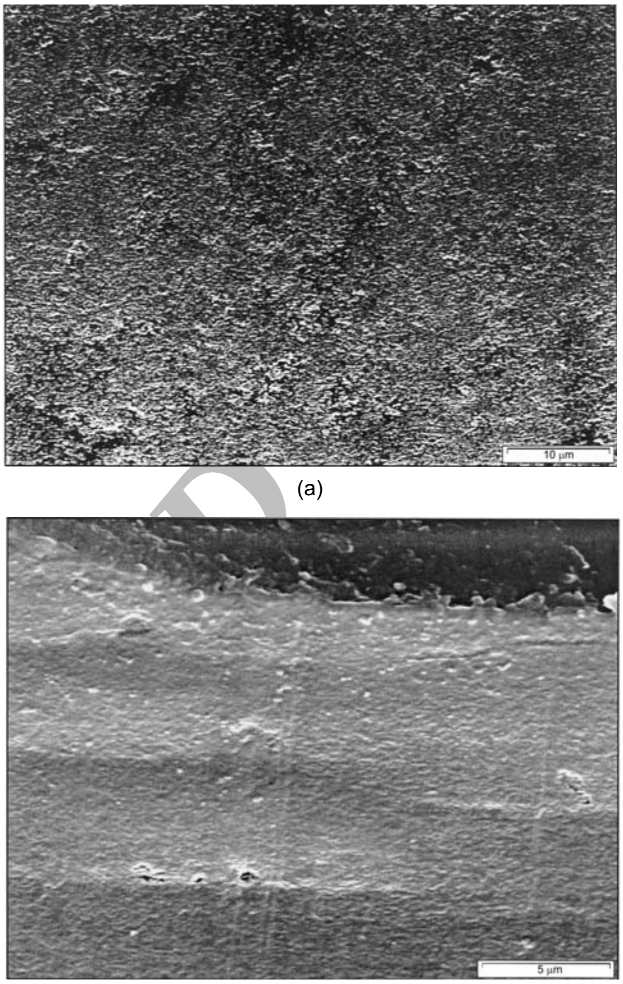
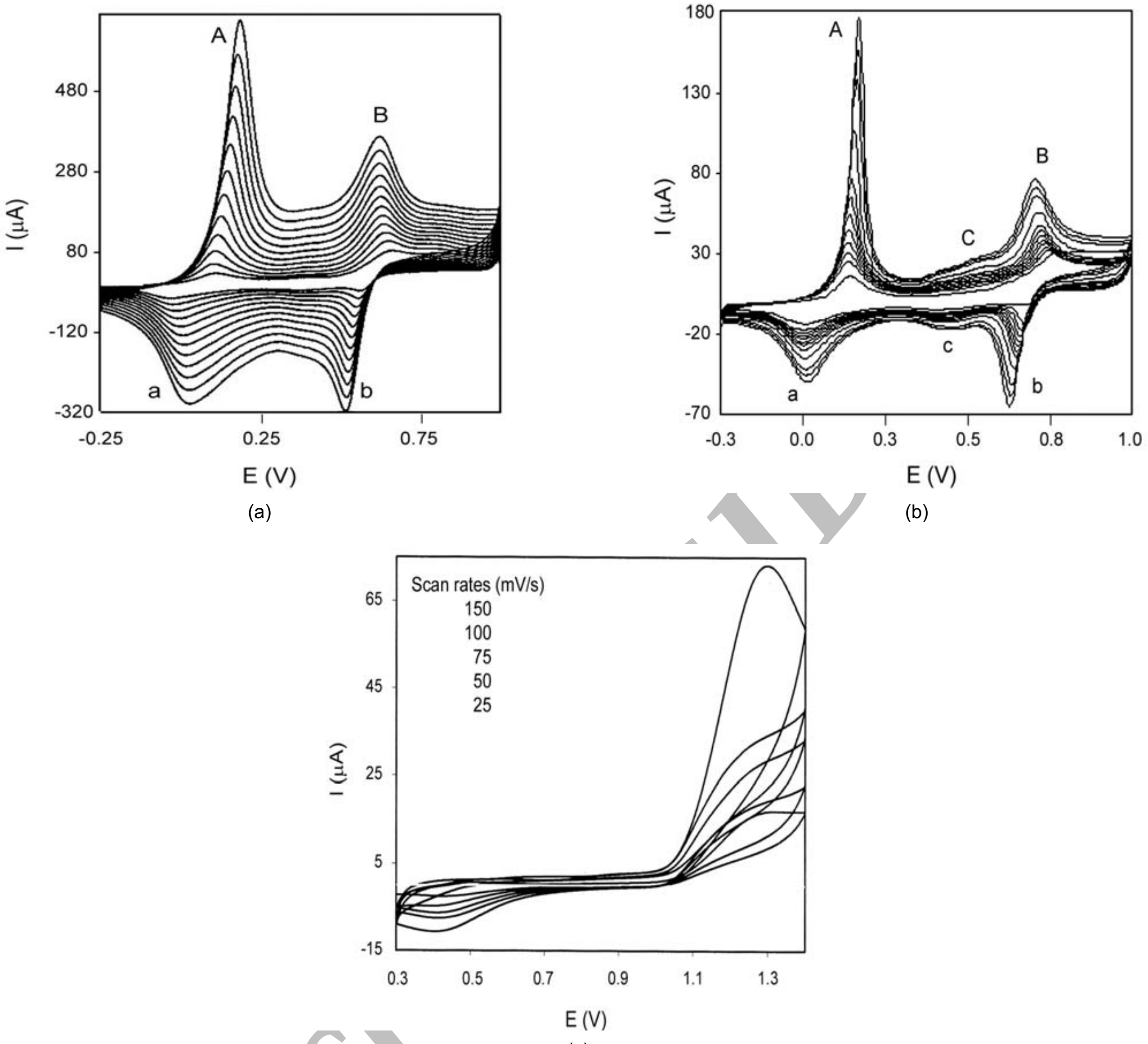


Figure 7. SEM micrographs of PVPr-*g*-PANi: (a) surface image, and (b) cross-section image of chit-*g*-PANi.

Cyclic Voltammetry

The cyclic voltammograms for aniline, grown chit-*g*-PANi films and blank at different scan rates in acidic solution, Pt disk as working electrode and Ag/AgCl reference electrode, with a reduced anodic potential limit are presented in Figures 8a to 8c. Two pairs of well resolved redox peaks A/a and B/b which progressively developed at 0.18 V and 0.68 V can be seen in Figure 8a. First curve shows the oxidation of chitosan moieties in the precursor starts to be oxidized for polymerization and for redox behaviour and it is completely electroactive. After several cycles, these peaks appeared and the newly formed redox anodic and cathodic peaks increase in intensity in each next cycles. The higher increase of maximum current and shifting of its peaks to higher potential imply that the PANi formation has started at the chitosan moieties in the precursor film and the ohmic conduction occurs between the electrode and the copolymers so that polymerization rate continuously increases for the subsequent potential cycles. The electrode is covered with a thick deposit and extensive dissolution occurs. The solution near the electrode surface has become an intensive green colour. Three redox peaks are detectable and the voltammograms show similar shapes as in the case for PANi [24,25]. It can be said that the identical redox process occurs during cycling of these two polymers.

Two pairs of well resolved redox peaks A/a and B/b which progressively develop at 0.2 V and 0.75 V can be seen in Figure 8b. This strongly resembles the behaviour of PANi. Only a third pair of redox peaks, the so called “middle peaks” C/c, which belongs to



(a) (b)

(c)

Figure 8. Cyclic voltammograms of: (a) polymerization of 0.1 M aniline (v = 50 mV/s), (b) graft copolymer formation of chit-*g*-PANi (v = 50 mV/s), and (c) blank of chit-*g*-PANi in different scan rates, in aqueous 0.1 M H_2SO_4, 1 M HCl solution, Pt disk electrode and Ag/AgCl reference electrode.

the degradation products [26] is poorly recognized. The potentials of the first peaks A/a in chit-*g*-PANi are slightly less positive than the corresponding values in PANi. With the same electrochemical conditions, the curve shapes of chit-*g*-PANi almost replicate the electrochemical behaviour of PANi, confirming once more that the mechanism of the redox processes in chit-*g*-PANi is the same as in the case of PANi. Figure 8c shows blank cyclic voltammograms of chit-*g*-PANi in different scan rates. Leucoemeraldine is converted into emeraldine by oxidation doping. Emeraldine is oxidized to pernigraniline and then the emeraldine is reduced to leucoemeraldine [27]. In both reduction systems, during electron transfer from polymer chain, to neutralize the load, the anions of the electrolyte transfer into the polymer structure.

Gel Permeation Chromatography

The GPC of chit-*g*-PANi has been analyzed using polystyrene standard and GPC curves obtained showing a unimodal distribution. The average molecular

Table 1. The molecular weight distribution averages for the PAN-*g*-PANi from GPC.

Molecular weight data	PAN-*g*-PANi
Number average	21982
Weight average	85730
Z average	190919
M_w/M_n	3.9

weight distribution for the polymer is presented in Table 1. As shown in Table 1, high molecular weight of the polymer shows the PANi growth on chit-*g*-PANi.

Efficiency and Grafting Percentage Determinations

The grafting parameters such as grafting percentage and grafting efficiency are greatly influenced by type and concentration of initiator, monomer concentration, reaction temperature and time. The properties of the resulting graft copolymers are widely controlled by the characteristics of the side chains, including molecular structure, length, and number. Till today, a number of research works have been done to study the effects of these variables on the grafting parameters and the properties of grafted chitosan polymers.

Percentage of grafting in copolymer was calculated by three methods: (i) the integration of the area under the peak [28,16]; (ii) by gravimetry [29]; and (iii) by measurement of %N in copolymer [12]. We have assumed that the weight of chitosan is W_1 (g) and the weight of grafted polymer along with the homopolymer is W_2 (g). The extraction was repeated until separation of the homopolymer from the grafted sample was completed. This was ascertained by drying the polymer in vacuum until constant weight, W3 (g). The difference in (W_3-W_1) gives the weight of the grafted polymer. The difference in (W_2-W_3) gives the weight of the homopolymer PANi.

$$W_1 = 1.51,\ W_3 = 2.27,\ W_4 = 2.51$$

$$Grafting\ (\%) = \frac{weight\ of\ chit-g-PANi}{weight\ of\ chitosan} \times 100$$

$$Grafting\ (\%) = \frac{W_3 - W_1}{W_1} \times 100$$

$$Grafting\ (\%) = \frac{2.27 - 1.51}{1.51} \times 100 = 50.33$$

$$Efficiency\ (\%) = \frac{weight\ of\ chit-g-PANi}{\begin{array}{c}weight\ of\ polymer\ grafted\\ and\ homopolymer\end{array}} \times 100$$

$$Efficiency\ (\%) = \frac{W_3 - W_1}{W4} \times 100$$

$$Efficiency\ (\%) = \frac{2.27 - 1.51}{2.51} \times 100 = 30.27$$

Conductivity

The results suggest that the chit-*g*-PANi films prepared in HCl solutions have high conductivity, and lower than PANi [28] under the same experimental conditions. Table 2 shows the effect of the molar ratio of chitosan/aniline on the conductivity (S/cm) and physical properties of the films. The conductivities of PANi and chit-*g*-PANi were found to be 0.01-5 $S.cm^{-1}$ and 0.01-0.07 $S.cm^{-1}$, respectively. It is not quite clear how the grafted polymer modifies the conductivity of the polymer. However, besides the chem-

Table 2. Effect of the molar ratio of chitosan/aniline on the conductivity (S/cm) and physical properties of the films.

Sample	Chitosan/Aniline ratio	Physical properties	Conductivity (S/cm)
1	0.5/1	Powder	0.015
2	1/1	Film, smoothless, brittle, strong	0.019
3	1/2	Film, smooth, flexible, strong	0.057
4	1/3	Film, smooth, flexible, strong	0.072

ical structure and chain conformation, there are many factors that may influence the conductivity, such as chain packing and morphology of the polymer. The backbone polymer, chitosan, can be expected to increase the torsional angle between adjacent rings to relieve the steric strain. This may contribute to the lower conductivities of chit-*g*-PANi as compared to the unsubstituted PANi.

CONCLUSION

Chitosan is a natural polymer and soluble, flexible, easily film forming with free NH_2. Application of chitosan grafted materials in biomedical gloves, cosmetic, artificial skin and dressings are very attractive. On the other hand, PANi is acted as a conducting polymer for fibre and film forming compound. Therefore, combination of these polymers produces a new compound with new properties. Chitosan was graft copolymerized with aniline in the presence of ammonium peroxydisulphate as a free radical initiator. Grafting percentage and efficiency have been calculated by gravimetry. Thermal and physical properties of chit-*g*-PANi increased with increase in grafting percentage. No residual monomer was found in the graft copolymer, even after storage for long periods. The graft copolymerization was carried out in a homogeneous system. Chit-*g*-PANi is a soluble and a flexible polymer with a good film and fibre formability, disperse, sensor and conductivity potentials as a backbone polymer. Chit-*g*-PANi synthesized by electrochemical method has higher conductivity and physical properties than chemically synthesized copolymer. Spectroscopy data confirm the formation of electro- and chemical graft copolymerization. TGA and SEM of chit-*g*-PANi show increase in thermal stability related to chitosan and copolymerization, respectively, and also confirm a successful copolymer grafting.

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