

Synthesis of Chitosan-graft-Polyaniline-Based Composites

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Abstract Chitosan was grafted with polyaniline through oxidative-radical copolymerization using ammonium persulfate in acidic medium. The grafting conditions were extensively studied by varying grafting parameters. All the findings have been discussed and proposed a plausible mechanism for the graft copolymerization. The representative chitosan-graft-polyaniline (Ch-g-PANI) was characterized using UV-VIS, FTIR, DSC, XRD and Scanning electron microscopy taking chitosan as reference. Ch-g-PANI exhibited electrical conductivity, which increases with the extent of grafting onto chitosan backbone. The application of conducting biomaterial such as Ch-g-PANI in the electronic devices especially for the fabrication of sensor devices would be attractive not only in terms of product cost and environmental safety but also from a materials science point of view.

Keywords: Biopolymers, Biocomposites, material testing, thermal properties, industrial applications

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1. Introduction

Chitosan is a N-deacetylated derivative of chitin, which is one of the most abundant organic materials found in crustacean, mollusks, and insects where it is an important constituent of the exoskeleton. Chitosan (Chi) is biodegradable, biocompatible nonirritant and exhibits good film-forming properties, high mechanical strength, and adhesion.[1] All these characteristics make it suitable for a wide range of applications such as controlled delivery systems, wastewater treatments, packaging separation membranes, and biosensors.[2] Chitosan gel may be easily obtained by a cross-linking reaction with glutaraldehyde.[3] These gels exhibit good swelling properties and efficient responses to external stimuli such as pH and temperature, which makes these materials eligible as artificial muscles.[4] However, in this domain of applications their developments are limited by the poor electrical conductivity resulting in a poor response time.

On the other hand, polyaniline (PANI) being the most promising organic conducting polymer finds wide applications, such as in rechargeable batteries, corrosion protection of metals, gas separation membranes, or molecular sensors.[5] It is easy to synthesize and it exhibits a wide range of conductivity, low operational voltage, and a good environmental, thermal, and chemical stability. PANI exhibits important advantages thanks to its unique and easy doping process. It is a pH-responsive material exhibiting different chemical forms, depending on acid/ base treatment. However, PANI has limitations due to its poor solubility in common organic solvents, its infusibility, and its poor mechanical properties. [6] To

overcome these drawbacks, many studies have been done either by using additives, specific doping chemicals, or through the formation of polymer matrix/PANI composites. In the latter, the polymer matrix brings specific properties as better solvent solubility or mechanical properties, while PANI provides conducting properties to the final composite. The obtained material will be stimulus-responsive and they may respond to various stimuli such as pH or electric stimuli. Moreover, they may be used in controlled delivery systems if the polymer matrix has hydrogel properties. Its swelling allows inclusion of active chemicals (among them drugs) and their release leading to being candidates for biomedical applications, as recently studied [7].

In the present study, composites have been made by mixing chitosan and PANI to combine good processability of the matrix and electrical conductivity. Recent works were reported on the synthesis of composites of chitosan with PANI or derivatives, and chitosan may also be used as a steric stabilizer for pH-responsive PANI colloids.[8] Another strategy was followed within the present work: chitosan PANI composite was obtained by a grafting reaction. The synthesis was based on a previous article, [9] and tridimensional hydrogels with a controlled architecture were obtained. In these composite polyaniline is statistically spread out within the chitosan network. In this work, chitosan was chosen for its film-forming properties and its chemical structure. Polyaniline is grafted onto the chitosan backbone before composite elaboration, thus, avoiding the migration of the polyaniline outside of the gel when swollen, and chitosan enables the enhancement of the conducting properties thanks to hydrogen bond occurring between chitosan hydrogel network and polyaniline.

2. Materials

Chitosan (from Sigma Aldrich degree of deacetylation was 0.76 and viscosity- average molecular weight was $M_n \cdot 5 \times 10^5$) Ammonium persulfate (APS; Aldrich; 248614, 98%), aniline (ANI; Acros Organics; 3,293-4, 99.8%), hydrochloric acid (Aldrich, 37%), ethyl alcohol (Atlantic labo, 96%), N-methylpyrrolidone (NMP, Sigma Aldrich), and acetic acid (Prolabo, 90%) were used as received. Glutaraldehyde was used as a 25 wt % solution in water.

2.1. Synthesis of Polyaniline

A total of 244.6 mg ammonium persulfate (10^{-3} mol) was added to a solution of 100 mg aniline (10^{-3} mol) in 200 mL of 0.1 M HCl. The reaction mixture was left under magnetic stirring for 4 h at room temperature. PANI particles were filtered and dried.

2.2. Synthesis of Chitosan-graft-Polyaniline-

220 mg chitosan (1.3×10^{-3} mono mol) and 100 mg aniline (1×10^{-3} mol) were introduced in 200 mL of 0.1 M HCl in a round-bottom flask. After solubilization, 244.6 mg of ammonium persulfate (1×10^{-3} mol) were added to

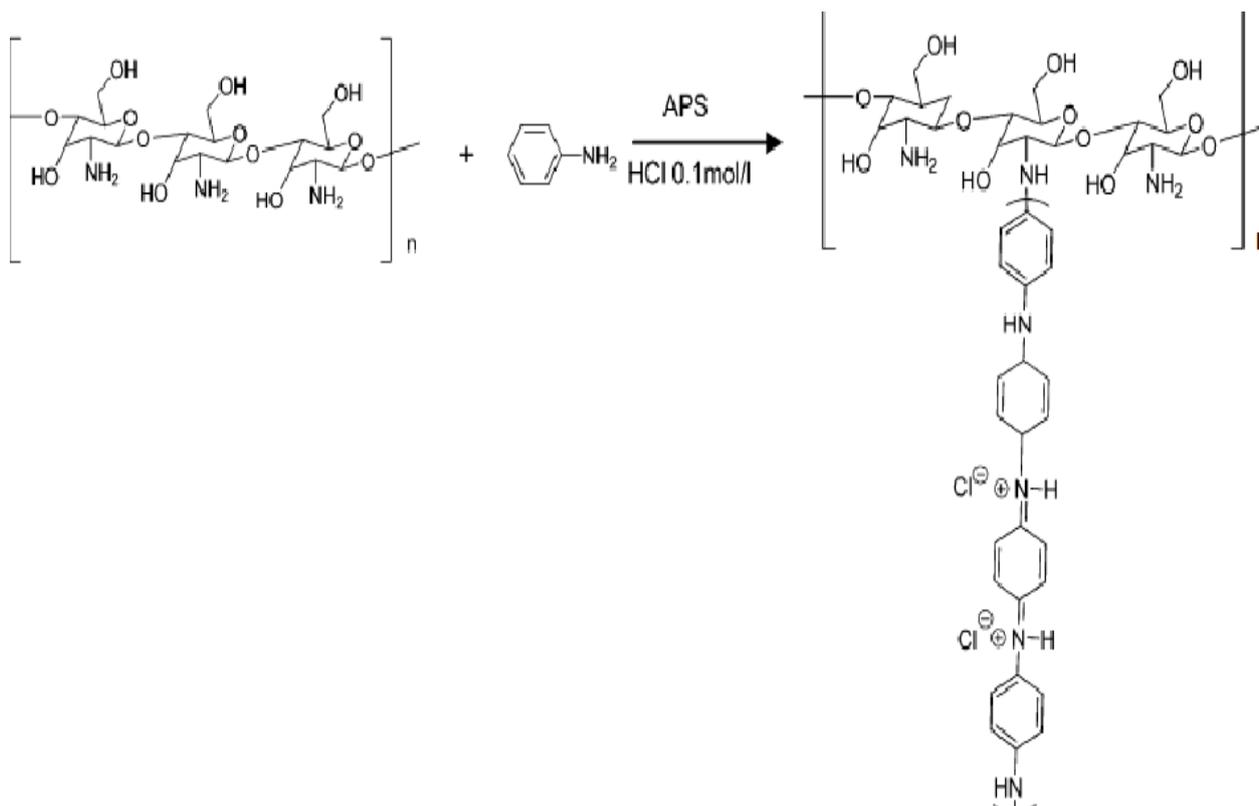
the reactive medium and left under stirring at room temperature for 4 h. The grafted copolymer was then neutralized by NaOH and precipitated with an excess of ethanol. The resulting precipitate was washed with NMP to remove free PANI. The latter was quantified by UV-vis spectroscopy (molar adsorption coefficient of $1600 \text{ L} \cdot \text{cm}^{-1} \cdot \text{monomol}^{-1}$ at 328 nm). Finally, the copolymer was rinsed with HCl 0.1 M and dried under soft conditions (room temperature and atmospheric pressure) to obtain doped copolymer [10].

The ANI grafting reaction being quantitative in our reaction conditions, total PANI weight is considered to be equal to initial ANI amount. As a consequence the grafting ratio of PANI on chitosan was calculated from the relation:

$$\% G = \frac{W1 - W2}{W0} \times 100$$

$$\% E = \frac{W1 - W2}{W0} \times 100$$

Where % G is Grafting Percentage and % E is Grafting Percentage $W1$, $W0$ and $W2$ denote, respectively, the weights of Ch-g-PANI, chitosan and aniline monomer.



Synthesis and Characterization of Chitosan-graft-Polyaniline Copolymers

In our study, aniline is polymerized in the presence of chitosan, we can assume that the reaction mechanism is of a chain nature due to the formation of the sulfate ion, radicals that are well known ion chain carriers for graft copolymerization. At the same time, per sulfate stimulates the oxidative polymerization of aniline via a medium of cationic radicals and forms ANI and PANI radicals. Finally, chitosan macro radicals and PANI cation radicals are combined to form Chi-graft-PANI graft copolymer. [11] On the other hand, the reaction of aniline on chitosan

amino groups is favored compared to its homopolymerization.

This phenomenon has already been described when grafting ANI onto poly(aminostyrene). On the contrary, a mixture of chitosan and PANI would be observed.

3. Characterization of Grafted Composite

The grafted composite obtained is characterized by IR, DSC, XRD, SEM analysis. The conductivity of chitosan

and Chitosan grafted composite is measured by four method.

3.1. UV-vis Spectroscopic Study

The UV-vis spectra of Ch-g-PANI at pH 1 (Figure 1) showed a broad absorption band at 300–350 nm due to overlapping of glucopyranose components of chitosan and π - π^* transition of benzenoid rings of grafted PANI with bands at 430 nm (due to polaronic peak of grafted PANI) and at 800 nm (assigned bipolaronic transitions of grafted PANI), while Ch-g-PANI at pH 10 (Figure 1b) clearly showed peak suppressed at 430 nm but appeared a new

peak at 620 nm (due to the transition of quinoid rings on the grafted PANI). These curves (Figure 1a and Figure 1b) indicating that the grafted PANI showed protonation-deprotonation.

Chitosan showed (Figure 1) a broad absorption band at 300 nm (due to glucopyranose components). Furthermore, the characteristic peaks of glucopyranose and PANI was significantly observed and it supports the grafting of PANI on to chitosan. Therefore, UV-vis spectra confirmed the chemical structure, conjugation, electronic transition and doping-dedoping behavior of Ch-g-PANI.

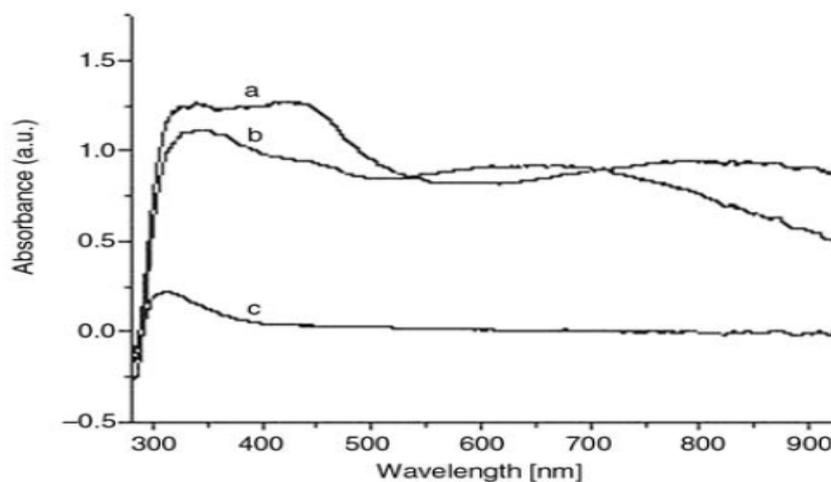


Figure 1. UV-vis spectra of (a) Ch-g-PANI at pH 1 (b) Ch-g-PANI at pH 10, (c) chitosan at pH 3

3.2. FTIR Spectra-

FTIR spectra of Ch-g-PANI (Figure 2) showed characteristic peaks of PANI as well as chitosan. The infrared band at 3040–3266 cm^{-1} corresponds to N–H stretching with hydrogen bonded 20 amino groups and free O–H stretching vibration, 3024 cm^{-1} corresponds to aromatic C–H stretching, 2930 and 2864 cm^{-1} (due to aliphatic C–H stretching), 1632 cm^{-1} (due to C=O stretching of carbonyl group, typical saccharide absorption), 1526 cm^{-1} (due to C=C stretching of quinoid rings), 1462 cm^{-1} (due to C=C stretching vibration of benzenoid rings), at 1284 cm^{-1} (due to C–N stretching).

The absorption band at 1110 cm^{-1} was assigned to N=C=N bending vibration shift towards the lower wave number correspond to the PANI. The shift of 1130 cm^{-1} band to lower wave number could be attributed to the hydrogen bonding between chitosan and imine group of the grafted chain of PANI. The absorption band at 1030 cm^{-1} (due to O–H bending), at 1076 cm^{-1} (characteristic peaks of a saccharine structure; C–O stretching) and at 830 cm^{-1} was assigned to aromatic C–H bending vibration band due to the 1, 4- disubstituted benzene ring, chitosan showed characteristic peaks of mucopolysaccharide [13,14].

Hence, FTIR studies clearly suggested the graft copolymerization of polyaniline on to chitosan.

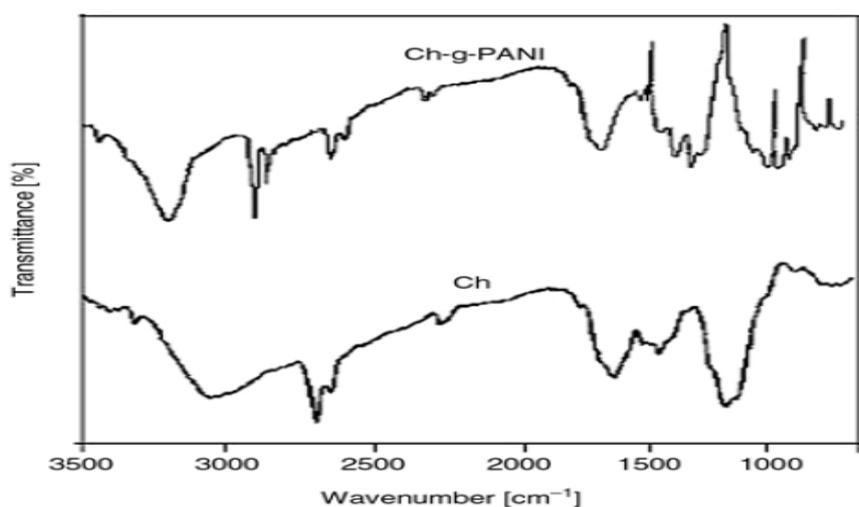


Figure 2. Figure 3 FTIR Chitosan and Chitosan graft polyaniline composite

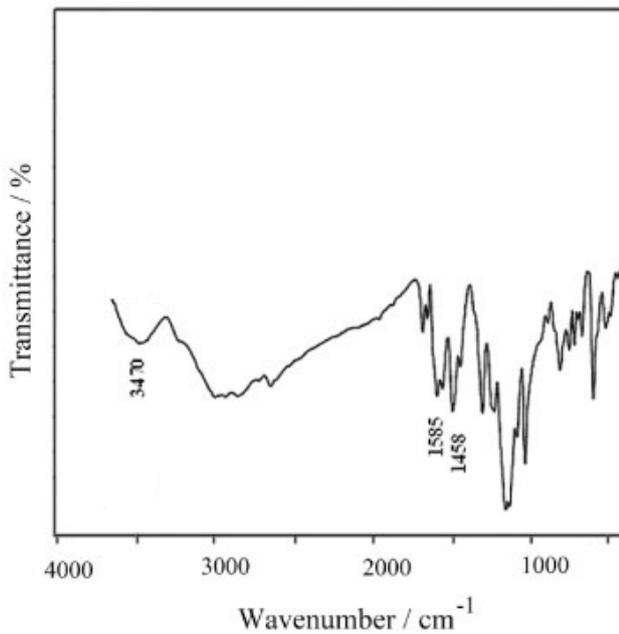


Figure 3. FTIR of Polyaniiline

The FTIR spectrum of PANI shows C=N in the polyaniline units appearing at 1585 cm^{-1} , the benzenoid stretches at 1485 cm^{-1} and N-H stretches at 3470 cm^{-1} .

3.3. Thermal Study of Composite

Differential scanning calorimetry (DSC) is the best analytical technique to find the polymer crystallinity, which measures the physical nature of the sample, i.e. to check it is heated, cooled or under isothermal conditions. In this technique a sample would heat or cool at linear intervals of temperature and measure the particular temperature and energy accompanied with any one of the range of thermal events. It is observed from DSC plot that chitosan undergoes dehydration at lower temperature as compare to Chito-Pani composite. However loss of water from composite is steady and periodically which shows that dehydration pattern is regular. (15)DSC of chitosan showed a weight loss in two distinct stages. The first stage ranges between 240°C and 300°C and showed about 42% loss in weight. This may correspond to the loss of adsorbed and bound water. The following figures 4b shows the DSC curves of chito-pani composite peak 360°C which shows dehydration of composite and thermally more stable. DSC suggests the high thermal stability of composites and uniform grafting is evidence.

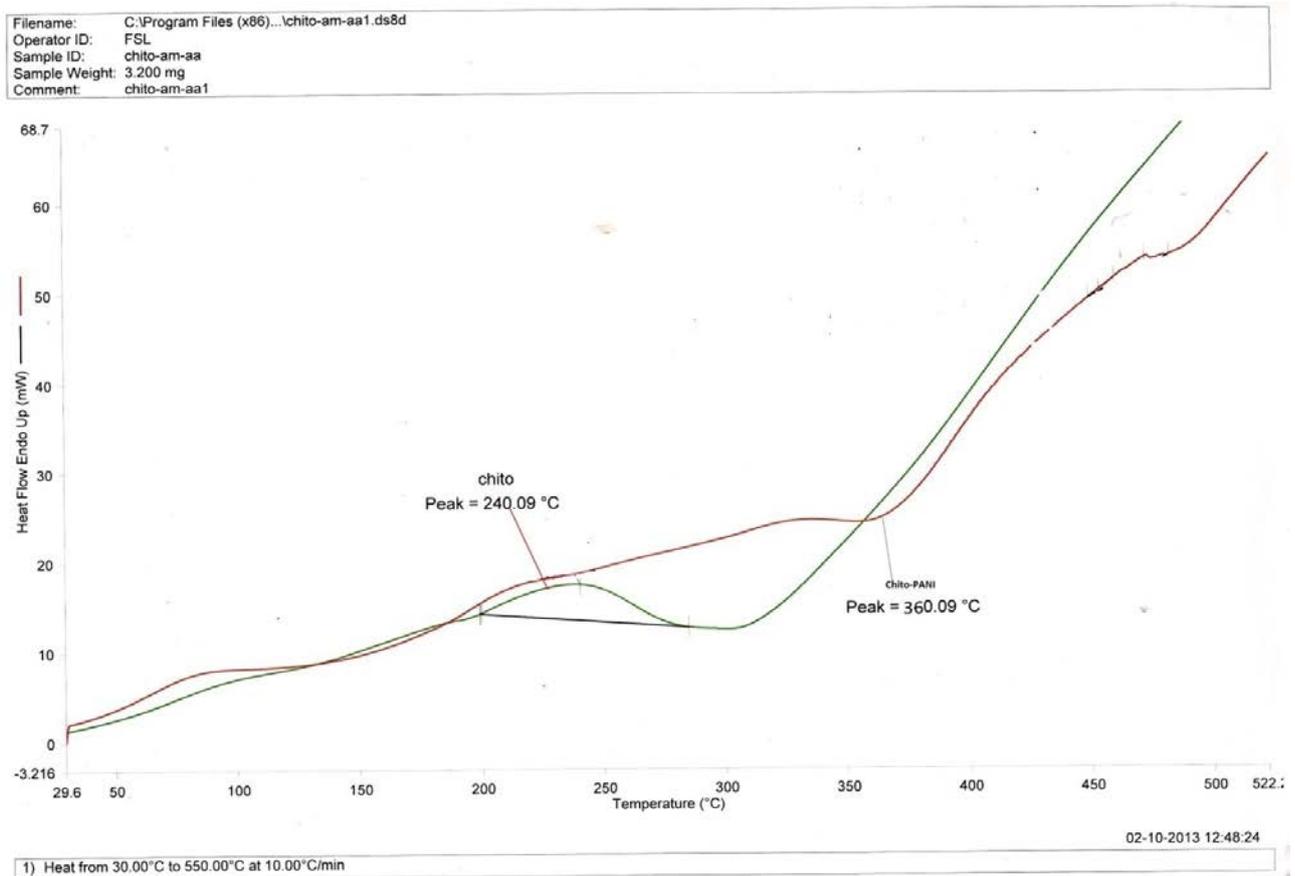


Figure 4. Study of Differential Scanning Calorimetry chitosan and chit-g-PANI

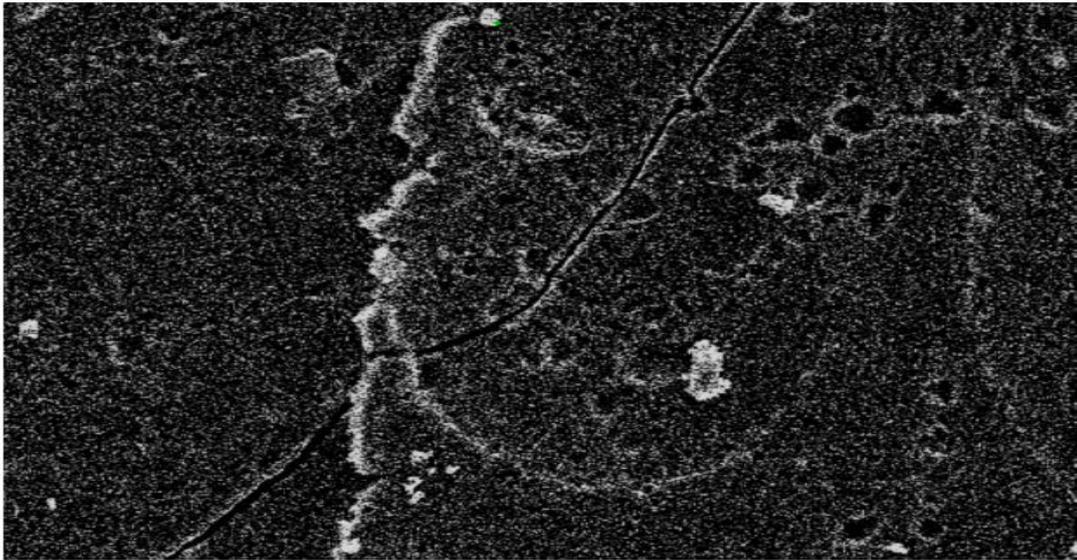
3.4. Scanning Electron Microscopy-

The surface topography of the Ch-g-PANI was studied by scanning electron microscopy (SEM) taking chitosan as reference. The exterior surface of the Ch-g-PANI seems like globules that were accumulated in contrast to the

interior structures and showed a porous surface. This fact can be attributed to the porosity of the globular surface in the grafted chitosan, while chitosan showed cotton like accumulation and bears an irregular shape with porous surface. Hence, the surface evidence supports the homogeneity of the uniform grafting of PANI on to the chitosan.

SEM Micrograph of Polymeric composite obtained in fig.6 from the composite shows that it is compact structure as compare to pure chitosan in Figure 5, pure chitosan sample have uniform but fracture surface whereas composite has porous structure which may be due to

presences of water molecule in this r beneath region. Porous structure support permeation and interfere site of external stimuli which hydrophilic group of grafted composite. (16)



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Figure 5. SEM surface images of chito-g- pani composite

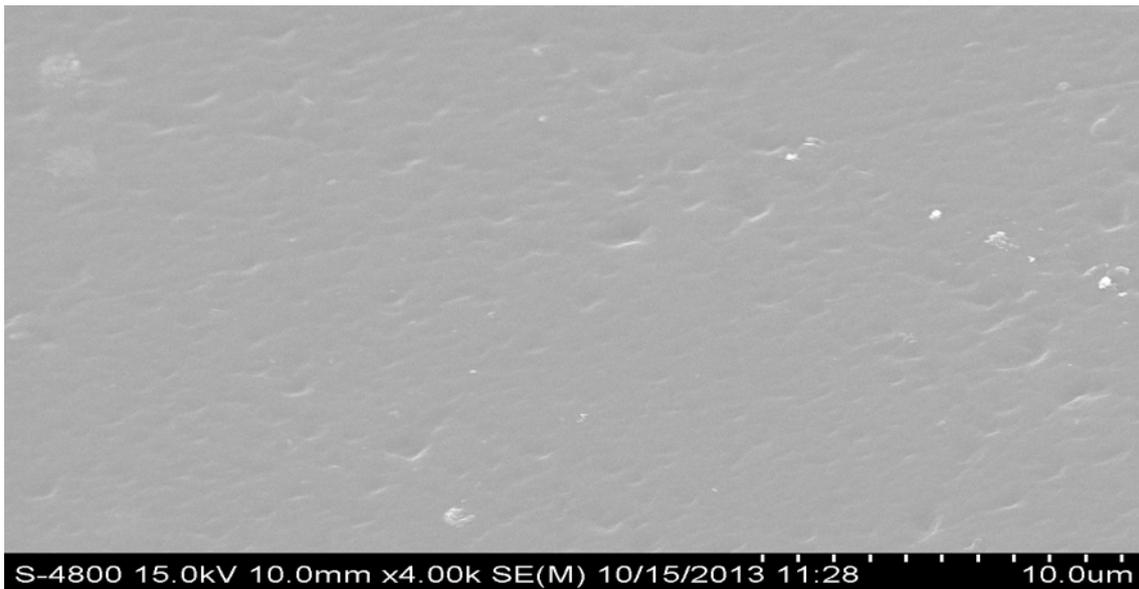


Figure 6. SEM cross-section images of chito-g- pani

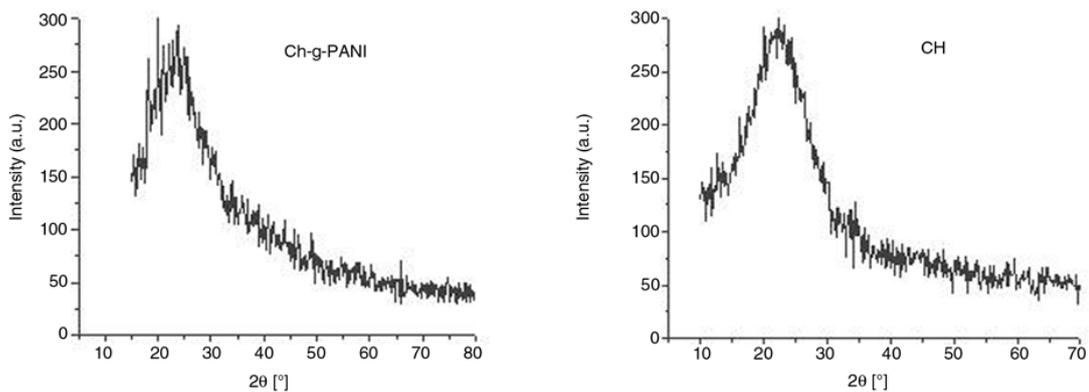


Figure 7. XRD spectra of Ch-g-PANI and Ch

3.5. XRD Spectra-

XRD of the Ch-g-PANI further supported the grafting (Figure 8). XRD spectra of the grafted chitosan showed a crystallinity area in the region of 2θ 18–24° due to the grafting of PANI onto the chitosan backbone, while XRD of the chitosan showed amorphous patterns.

3.6. Electrical Conductivity Measurement-

The surface DC electrical conductivity of the Ch-g-PANI rectangular pressed pallets (pressure 4 tons/cm²) was measured by the four-probe method [12]. The resistivity can be calculated by Equation (1):

$$\rho = 2\pi S \left(\frac{V}{I}\right) \quad (1)$$

where, S is the probe spacing [mm], which was kept constant, I is the supplied current in [mA], and V corresponding voltage was measured in [mV]. Conductivity can be computed using the Equation

$$\sigma = \left(\frac{1}{\rho}\right) \quad (2)$$

The DC electrical conductivity of grafted (120 %G) was measured at laboratory condition with reference to PANI and chitosan. The results are summarized in the Table 1.

Table 1. Conductivity measurement of polyaniline, chitosan and chitosan-graft-polyaniline

Sr.No.	Polymer	%G	pH	Conductivity
1	PANI	120	1	0.684
2	Chitosan	120	7	8.99×10^{-6}
3	Chito-PANI	120	1	3.99×10^{-2}

Table 2. Effect of % Grafting on electrical conductivity of chitosan-graft-polyaniline

Sr.No.	Polymer	%G	pH	Conductivity
1	Chito-PANI	50	1	5.49×10^{-4}
2	Chito-PANI	90	1	5.20×10^{-3}
3	Chito-PANI	120	1	1.2×10^{-2}
4	Chito-PANI	150	1	8.99×10^{-2}

4. Discussion

UV, IR studies suggest the graft polymerization of polyaniline on chitosan which is indicated by new peak in UV approximate at 620 nm further shifting of absorption band to lower wave number suggest the hydrogen bonding aniline supports the grafting chitosan backbone. Thermal studies of composite of DSC suggest the high thermal stability of composites and uniform grafting is invidances from SEM study. No residual monomer was found in graft polymer aft long storage time this suggest stability of flaxibility of polymer for further potential application in various field of chitosan.

The value of DC electrical conductivity was found almost 4500 times higher than that of the chitosan and is attributed to grafting of PANI on to chitosan backbone

[17]. The electrical conductivity was influenced with extent of grafting. The results are summarized in the Table 2. It has been clearly observed that increasing % grafting, electrical conductivity simultaneously increased. The finding was attributed to the electrical conduction in Ch-g-PANI material, which is purely electronic and occurred due to the grafting of PANI onto chitosan.

5. Conclusion

Chitosan was graft copolymerized with aniline in the presence of ammonium persulphate 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. Chit-g-PANi synthesized by electrochemical method has higher conductivity and physical properties than chemically synthesized copolymer. These grafted material may be considered as excellent advanced material for sustainable development in field of analytical chemistry. Spectroscopy data confirm the formation of electro- and chemical graft copolymerization. DSC and SEM of chit-g-PANi show increase in thermal stability related to chitosan and copolymerization, respectively, and also confirms a successful copolymer grafting.

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