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## Synthesis and Characterization of a Novel Conducting Biopolymer Chitosan Grafted Polyaniline-Polypyrrole Flexible Copolymer



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### ABSTRACT

Conducting polymers like Polyaniline and Polypyrrole have been of interest as they combine the benefits of lightweight and low cost along with good electrical conductivity. However, the need for a more flexible and compatible matrix has led to the popularity of a bio-polysaccharide, Chitosan. In the present work, the copolymerization of conducting polymers; polyaniline and polypyrrole have been done along with subsequent grafting onto chitosan biopolymer to study the effect of alterations in molecular structures of polymer chains. The synthesis of the copolymer was carried out by chemical oxidative copolymerization. A 1:1 mixture of Aniline and Pyrrole monomers were used to prepare a polyaniline-polypyrrole copolymer (PAni-co-PPy). This was followed by its grafting onto chitosan to obtain a black powder of polyaniline-polypyrrole copolymer grafted with chitosan [Chit-g-(PAni-co-PPy)]. The Fourier Transform Infrared Spectroscopy (FTIR) spectroscopy and X-ray Diffraction (XRD) analysis confirmed the formation of a novel polymer with an altered structure. This fact was supported by the thermal studies, which also supports the formation of a compound with improved thermal stability. The addition of chitosan to PAni-co-PPy has been observed to retain the conductivity of these polymers which was found to be approximately  $0.4 \text{ S cm}^{-1}$  at 330K.



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## 1. INTRODUCTION

Conducting polymers have attracted numerous investigations due to the wide range of applications in the fields of sensors, batteries, electrochemical supercapacitors, microelectronics [1]. Among these conducting polymers, Polyaniline and Polypyrrole have proved to be the two most promising materials for potential applications. This is due to the high electrical conductivity, environmental stability and ease of preparation [2]. These properties are useful for the applications such as supercapacitors, sensors, solar cells and batteries. However, their properties like low solubility, flexibility and poor mechanical properties have paved the way for the need of incorporation of a more flexible and compatible matrix [3].

A bio polysaccharide, chitosan, has gained popularity in this context due to its excellent film-forming ability, flexibility, high mechanical strength and good adhesion property. Studies have suggested that the molecular structure of polymer chains is one of the significant factors that affect its properties, including electrical conductivity [1]. Chitosan has very interesting characteristics in such regards and is as chemically inert and has low cost as well.

In this work, PANi-pyrrole copolymer was grafted on the chitosan biopolymer by chemical polymerization. Due to grafting, many of the properties of the parent copolymer has been observed to be improved mainly the electrical conductivity. A black powder of polyaniline-polypyrrole copolymer grafted with chitosan (Chit-g-(PANi-co-PPy)) was synthesised. This polymer was then characterised by using FTIR, Differential Scanning Calorimetry (DSC), XRD and Four Point Probe method.

## 2. EXPERIMENTAL PROCEDURE

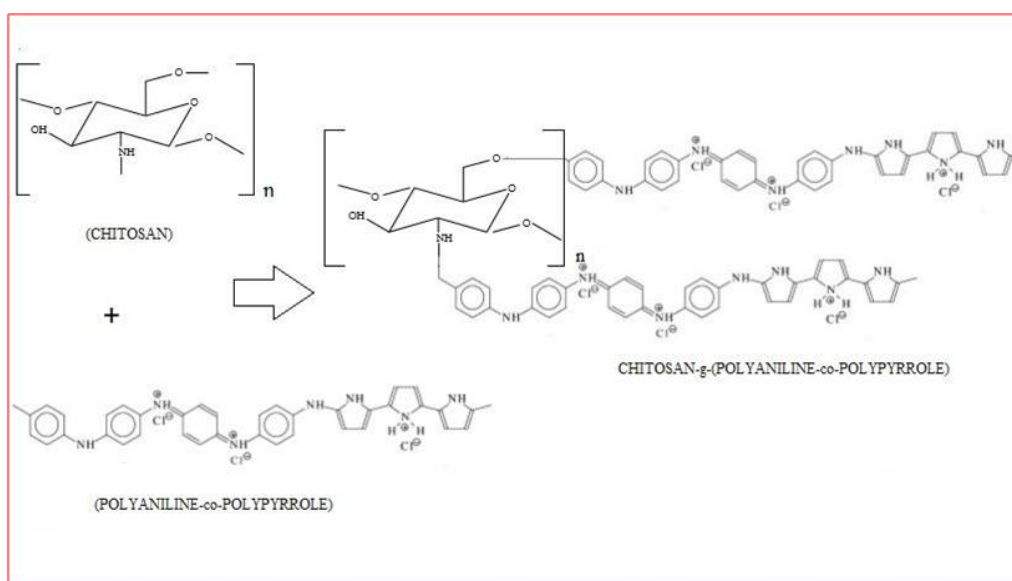
### 2.1 Preparation of Copolymer

For the preparation of the copolymer; 110 grams of HCl was added to 6 litres of distilled water to make a solution of 0.5M HCl. Then, 80.8 grams of distilled pyrrole (0.2M) was added to the solution and stirred well till the solution becomes clear. Again 112 grams of distilled aniline solution (0.2M) was added to the original solution and stirring was continued till the solution becomes clear. Thereafter, 60 grams of Ammonium Persulfate (APS) was added drop by drop to the final solution and the stirring was continued for 1 hr. The solution was kept undisturbed for polymerisation for 24h. After this, the solution was filtered, rinsed

with distilled water and acetone and then dried in oven at 60° for 12 h. The dark brownish black powder is the expected copolymer.

## 2.2 Preparation of grafted copolymer

For the preparation of grafted copolymer; 1.406 grams of chitosan was added to 105ml of acetic acid solution (2%) and stirred for 1h. Then, 4.3 grams of APS in 210ml of distilled water was added to the above solution. Another solution of 1.8 g (0.0054mole) of aniline in 35ml distilled water and 1.3g (0.0054mole) of pyrrole in 35ml distilled water was prepared and mixed together to form an aniline-pyrrole copolymerization solution. This solution was then added dropwise *via* a syringe to the original solution, along with continued stirring. This solution was kept for continuous magnetic stirring for 12 h. The mixture becomes black. Then, the precipitate is collected by filtration and washed with distilled water. Drying was carried out at 40° for 24 h, under vacuum to obtain a black powder of grafted copolymer. **Figure 1** shows the reaction during the formation of chitosan grafted polyaniline-polypyrrole copolymer.



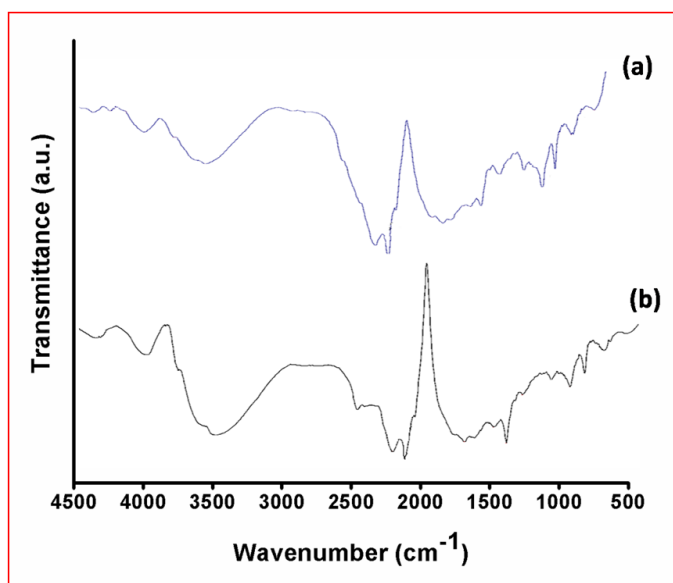
**Figure 1** Schematic Representation of formation of chitosan grafted polyaniline-polypyrrole

## 3. RESULTS AND DISCUSSION

### 3.1 FTIR Spectroscopy

The chemical structure of the synthesized polyaniline-polypyrrole copolymer as well as the chitosan grafted copolymer was studied using FTIR spectroscopy. **Figure 2 (a)** and **(b)** shows

the FTIR spectra of PANi-PPy copolymer and chitosan grafted polyaniline-polypyrrole copolymer respectively. The spectrum of PANi-PPy copolymer has a strong peak at  $3318\text{ cm}^{-1}$  due to the stretching vibrations of N-H bonds present in the corresponding homopolymer. The peaks present in between  $1045\text{ cm}^{-1}$  to  $1228\text{ cm}^{-1}$  represent the vibrations occurring due to the stretching of C-N bonds present in the aniline as well as pyrrole ring structure. The aromatic rings of pyrrole and aniline can be confirmed by the bending vibration frequencies in the range  $692\text{ cm}^{-1}$  and  $838\text{ cm}^{-1}$  [4-6].

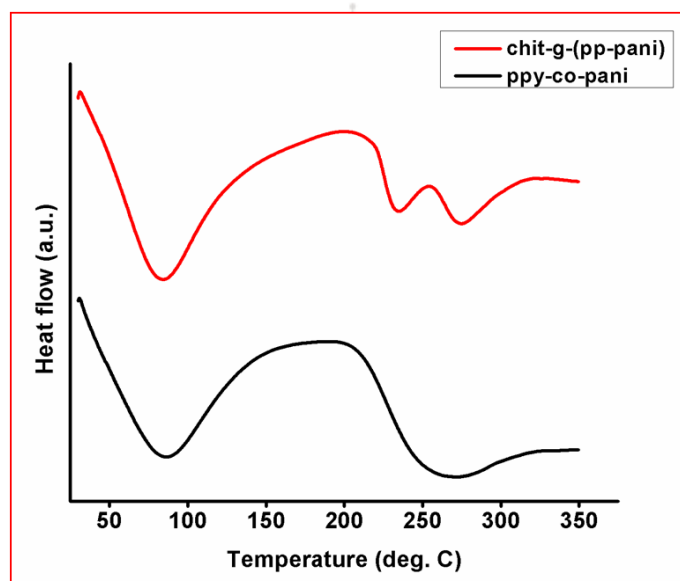


**Figure 2 FTIR Spectrum of (a) polyaniline-polypyrrole copolymer (b) chitosan grafted polyaniline-polypyrrole copolymer**

All the peaks in the copolymer have shifted from as compared to the spectra of individual polymers of polyaniline and polypyrrole; the reason for this change is attributed to the copolymerization which depicts the copolymerization has occurred completely [7-9]. The chitosan grafted polyaniline-polypyrrole copolymer shows an absence of peak corresponds to O-H vibration. Thus, it can be confirmed that grafting occurs via this active site of the chitosan structure [10, 11]. This can also be confirmed by the presence of peaks at  $1100\text{ cm}^{-1}$  and  $1231\text{ cm}^{-1}$  which represent phenylic C-O stretching. Also, the frequencies produced due to C-O stretching ( $1043\text{ cm}^{-1}$ ,  $1100\text{ cm}^{-1}$ ,  $1231\text{ cm}^{-1}$ ) are of much higher intensity in the grafted copolymer than that in pure chitosan denoting the presence of increased alkoxy bonding in the grafted copolymer. These observations indicate that chitosan has been successfully grafted onto the polyaniline-polypyrrole copolymer.

### 3.2 Differential Scanning Calorimetry

The thermal properties of the polymers were studied using differential scanning calorimetry. **Figure 3** shows the DSC thermograms for both the samples. Pure polyaniline is found to have an exothermic peak at around 195.74°C and pure polypyrrole shows an exothermic peak at 195.64°C. After copolymerization, the resulting copolymer shows a broadened exothermic peak at 196.45°C. This indicates an increase in the crystallization temperature of the copolymer due to the synergistic effect of its constituent homopolymers. The endothermic, melting peak for PAni-co-PPy is observed at 262.31°C. Chitosan experiences an exothermic peak at 306°C, indicating a higher degree of crystallinity. The DSC curve of chitosan grafted polyaniline-polypyrrole copolymer shows an exothermic peak with one at 199.12°C, followed by two endothermic peaks at 232.38°C and 274.35°C. This increase in the crystallization temperature of the copolymer can be attributed to the grafting of chitosan onto the copolymer leading to the formation of a compound with a melting point considerably higher than the ungrafted copolymer [6, 10]. Thus, we might conclude that grafting of chitosan onto polyaniline-polypyrrole copolymer causes an improvement in its thermal stability.



**Figure 3** DSC curve for (a) polyaniline-polypyrrole copolymer (b) chitosan grafted polyaniline-polypyrrole copolymer

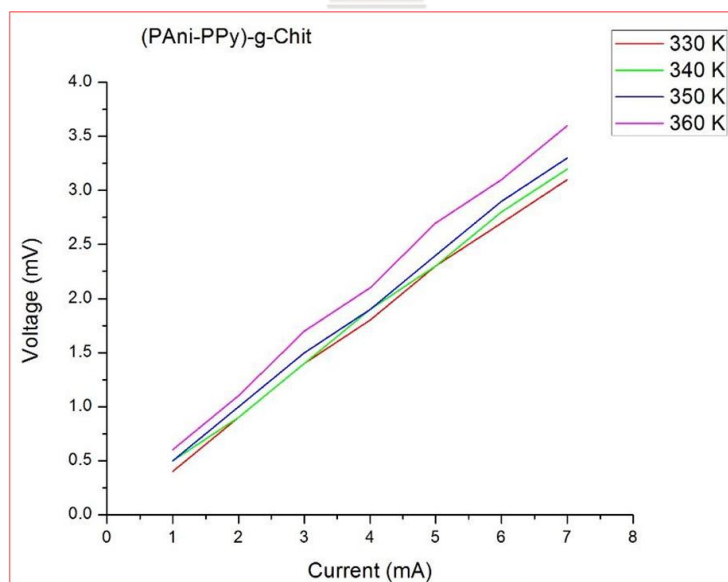
### 3.3 Electrical Conductivity Measurements

The fact that chitosan has successfully been grafted on the polyaniline-polypyrrole copolymer has been established by conductivity measurements. According to Mavundla *et. al.* [4] the electrical conductivity of polyaniline-co-polypyrrole is of the order  $10^{-5}$ , which is a

significant reduction from the values of the conductivities of the individual homopolymers. An even lower value has been obtained by Wasnik *et. al.* [12] who states the reason for this decrease as the formation of complex between the polyaniline and polypyrrole chains. On addition of chitosan to this copolymer, the conductivity values have been found to change significantly. The electrical conductivity values of the prepared chitosan grafted polyaniline-polypyrrole copolymer at four different temperatures are given in the **Table 1**. **Figure 4** shows the graph of current versus voltage for Chit-g-(PAni-co PPy) at different temperatures. The V/I plot of chit-g-(PAni-co-PPy) shows an approximately linear nature. This nature might be attributed to the formation of a conductive path [12-14]. These results lead us to the conclusion that the successful grafting along with the formation of a conductive polymer has taken place.

**Table 1. Value of electrical conductivity at different temperatures for Chit-g-(PAni-co PPy)**

Sr. No.	Temperature (K)	Electrical Conductivity (S cm <sup>-1</sup> )
1	330	0.43937
2	340	0.42492
3	350	0.40841
4	360	0.36524

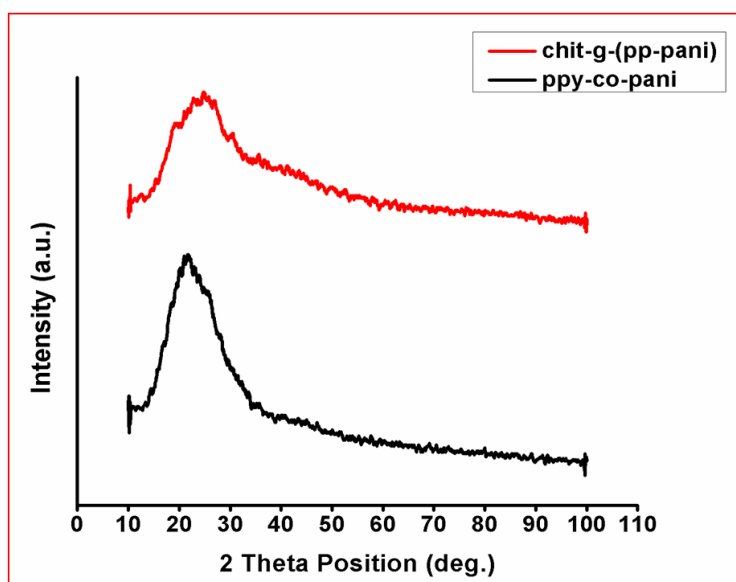


**Figure 4 Graph of V-I for Chit-g-PAni-co PPy graft polymer.**

### 3.4 X-Ray Diffraction Studies

**Figure 5** shows the diffraction pattern of PAni-co PPy and Chit-g-(PAni-co PPy) in a comparative manner. The X-Ray diffraction pattern for chit-g-(PAni-co-PPy) further

confirmed the grafting of chitosan onto the polyaniline-polypyrrole copolymer. The prepared copolymer shows a broad curve-like spectrum with peak at  $21.6^\circ$  which confirms the successful copolymerization of the polyaniline-polypyrrole copolymer [6]. Additionally, the chitosan grafted copolymer shows a broad hump containing several peaks at  $2\theta$  position. The presence of these peaks indicates that successful grafting has taken place leading to the formation of new phases with different properties [11]. Also, the XRD pattern is formed at a lower intensity when compared to PANi-PPy copolymer suggesting that the grafting of chitosan onto this copolymer chain leads to a decrease in the crystallinity of the chain. Also, the peak present in the initial copolymer chain is also seen in the XRD pattern of chit-g-(PAni-co-PPy). However, a shift in the maximum intensity peak value is observed, clearly highlighting that the grafted polymer exhibits different physical and chemical properties from its parent copolymer.



**Figure 5 XRD pattern for PANi-co-PPy and Chit-g-(PANi-co PPy) in a comparative manner**

## CONCLUSION

The results indicate that a novel graft copolymer was successfully synthesized. The parent chain of the polymer comprises a copolymer of polyaniline and polypyrrole. The grafted chain of the copolymer comprises of biodegradable polymer chitosan. The FTIR analysis and XRD studies confirm the same. The grafting of chitosan onto the parent chain leads to an enhanced thermal stability of the copolymer formed. Electrical conductivity measurements show that the formed polymer is conducting in nature with a conductivity value of  $0.43937 \text{ S cm}^{-1}$  at room temperature. The results in the study indicate that the synthesized polymer can

be used in a variety of applications requiring conductivity along with the inherent properties of chitosan like environmental stability, biocompatibility, etc.

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