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SYNTHESIS AND CHARACTERISATION OF POLYANILINE GRAFTED CHITOSAN FILMS

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ABSTRACT

Polymers were used as insulators of electricity & considered as non conducting material. Polyaniline (PANI) is one of the most commonly studied organic conducting polymer having wide applications. Chitosan is one of the most abundantly used biomaterial, which is similar to cellulose having easy biodegradability. Chitosan has various applications in industries such as medicine, food, textiles etc. It has potential to be used as sensing element in chemical and biosensor. The objective of the present work is to synthesize polyaniline grafted chitosan film followed by its characterization using FTIR, SEM & Electrochemical potential difference studies. Five film samples CP1- CP5 of varying proportions of these two materials are prepared. From the interpretation of IR data it is clear that the grafted copolymer PANi-*g*-chit has characteristic peaks of PANi and chitosan, which could be a strong evidence of grafting. SEM images of samples CP1 to CP5 have clearly indicated grafting of polyaniline on the surface of chitosan, however the distribution may not be uniform and as homogenous at places. The Electrochemical potential difference of electrode made of polyaniline grafted chitosan is more than graphite powder coated electrode by magnitudes of 10 to 20 %. Hence it can be concluded that the present work has demonstrated successfully the development of composite film of polyaniline grafted chitosan with enhanced electrochemical properties. The work is demonstrative and more experimental runs are required to validate the claim further.

KEYWORDS: Polyaniline grafted Chitosan, NMP, Composite film, electrochemical potential difference

INTRODUCTION

For a long time, polymers were used as insulators of electricity and considered as non conducting material. Polyaniline (PANI) is one of the most commonly studied organic conducting polymer having wide applications, mainly in rechargeable batteries, corrosion protection of metals, biosensors, gas-separation membranes, electronic devices like printing circuit board etc. PANi also called as aniline black, exists in different forms based on its oxidation level, pernigraniline base is the fully oxidized, half-oxidized emeraldine base and fully reduced leucoemeraldine base of PANi. Emeraldine base form of PANi, is the most stable and conductive. It bears thermal, chemical and good environmental, electrical and optical properties. Chitosan is one of the most abundantly used biomaterial, which is similar to cellulose having easy biodegradability. Chitosan has various applications in industries such as medicine, food, textiles etc. It has potential to be used in chemical and biosensor. The present work aims at synthesis of polyaniline grafted chitosan followed by its characterization.

LITERATURE SURVEY

Tiwari and V. Singh have investigated mucopolysaccharide chitosan that 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, TGA, X-ray diffraction and Scanning electron microscopy taking chitosan as reference. Ch-g-PANI exhibited electrical conductivity, which increases with the extent of grafting onto chitosan backbone. Its electrical conductivity is further influenced by pH and showed pH switching electrical conduction behavior when exposed to NN_3/HCl vapors. The application of conducting biomaterial such as PANI-g-Ch 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 material science point of view.

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Ayse Gul Yavuz et.al investigated that substituted polyaniline/chitosan (PANIs/Ch) composites that were chemically synthesized by using ammonium peroxydisulfate as oxidant and characterized by measurements of conductivity, FTIR, UV–vis, SEM and TGA techniques. FTIR spectra of the composites revealed that there is a strong interaction between substituted polyanilines & chitosan. Among the substituted polyaniline/chitosan composites synthesized, poly(N-ethylaniline)/chitosan PNEANI/Ch has the highest conductivity with a value of1.68 10^{-4}S/cm. The PANI/Ch composite exhibited higher thermal stability than the other composites. SEM images of the composites showed an agglomerated granular morphology of substituted polyaniline particles coated on the surface of chitosan.

Cheng-Ho Chen, Jian-Yuan Jian, and Si-Yuan Huang reported, the chitosan/polyaniline (CS/PANI) conductive blend films that were fabrication by solution blending method. The surface resistance and morphology of the CS/PANI blend films were examined and discussed. Results illustrated that the surface resistances of the CS/PANI blend films were decreased as the amount of PANI was increased.

E. Yu. Rosova, et.al investigated Electroconductive and mechanically strength of composite systems based on polyaniline and chitosan on the polyethylene porous substrate. A method to synthesize the conductive form of polyaniline in the solution of chitosan was developed. Molecular characteristics of chitosan in the solutions of acetic and hydrochloric acids and in their mixtures have been investigated. Optimal composition of solvent for the synthesis of polyaniline in a chitosan solution was determined. Electrical conductivity and mechanical characteristics of polyaniline/chitosan composite systems on porous polyethylene fi lm were measured.

S. Hossein Hosseini et.al reported that 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 1H and 13C 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.

MATERIALS AND METHODS

The objective of the present work is to synthesize polyaniline grafted chitosan film followed by its characterization using FTIR, SEM & Electrochemical potential difference studies.

Materials

Emeraldine base form of polyaniline, distilled water, N methyl 1-pyrroledone (NMP), chitosan, glutaraldehyde, glycerin, laboratory grade acetic acid, polyethelene (PE) sheet.

Method

The details of the steps followed in synthesis of composite films are as given below.

- Commercial grade Emeraldine base form of Polyaniline is crushed into fine particle for better dispersion in solvent
- Known quantity of Polyaniline is dissolved in solvent, N-methy1-2 pyrrolidone(NMP) for 6 hours .
- Commercial grade Chitosan is added with known a quantity of aqueous acetic acid. The mixture is stirred and heated till gel formation results.
- Polyaniline and NMP solution is mixed with chitosan gel and stirred so that uniform mixture is formed, 1 ml of glycerin is added as across linking agent
- The uniform mixture is cast on PE sheet and dried for 48 hours
- Dried film of chitosan grafted with polyaniline is obtained.
- The process is repeated with varied ratio of chitosan/polyaniline to synthesize five films.

The block diagram and actual photographic representation of the process steps are shown in figure numbers 1&2. The details of experimental observations are as shown in table 1.

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Table 1. Observation table.

Sr. No.	Sample Name	Polyaniline (gm)	NMP (ml)	Chitosan (gm)	Acetic Acid (ml)	Distilled Water (ml)
1	CP1	0.5	25	0.5	2	40
2	CP2	0.4	15	0.4	2	40
3	CP3	0.3	20	0.3	1	40
4	CP4	0.6	25	0.6	3	40
5	CP5	0.3	10	0.3	1	40

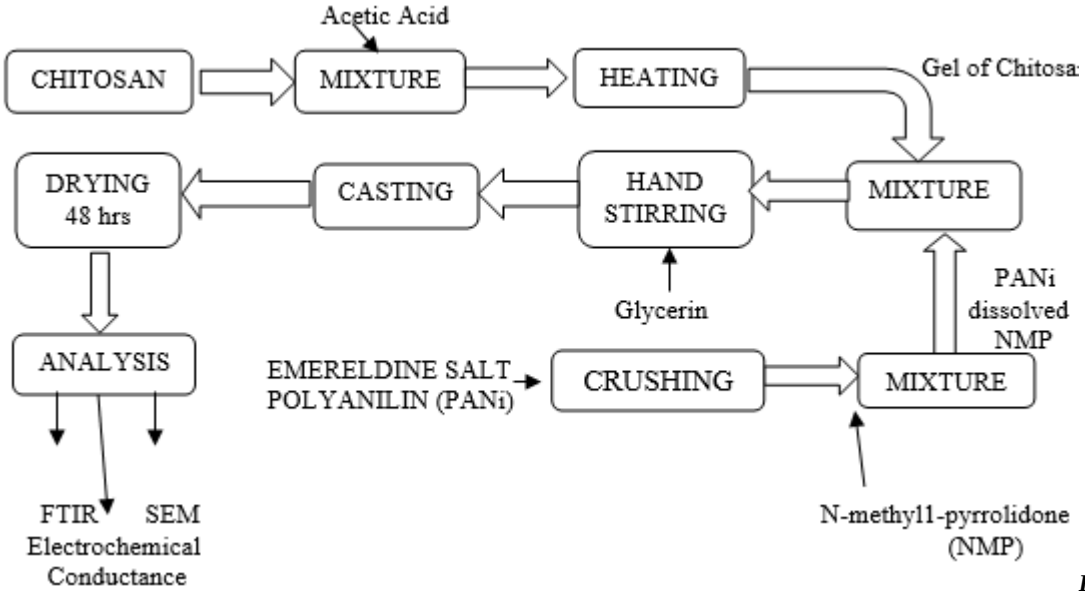


Fig.1: ***Block diagram of process steps.***

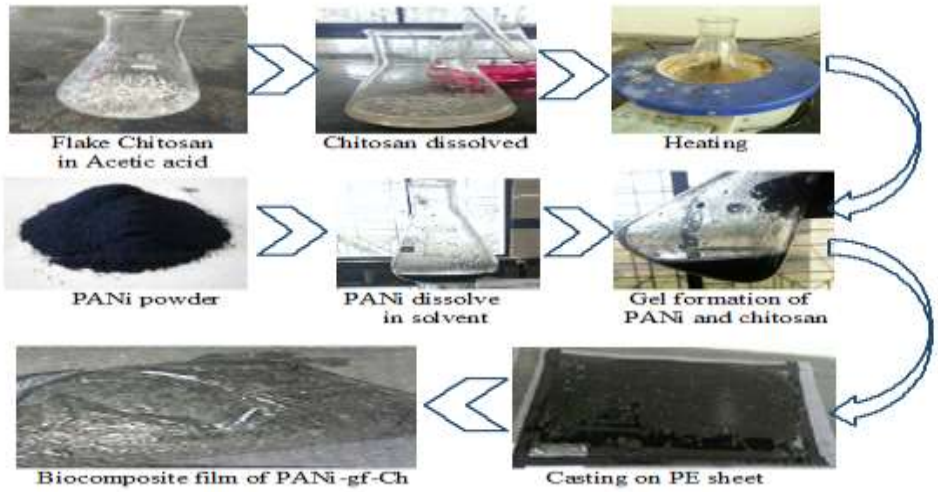


Fig 2: Photographic Representation of Process Steps.

RESULTS AND DISCUSSION

The polyaniline grafted chitosan films synthesized are analyzed using FTIR, SEM & electrochemical potential difference studies.

Interpretation of Infrared Spectroscopy

Structural changes of PANi-*g*-chit were confirmed by FTIR spectroscopy. FTIR analysis of samples CP1 & CP2 are shown in Figures 3 &4. The interpretation of the FTIR analysis is done by comparing wave numbers with

that reported in literature [5]. Almost similar wave numbers have been observed in both the samples except for additional wave number 2881.32 has been seen in sample CP2.

The detailed discussion is as follows:

The IR spectrum of the chitosan has strong peak around 3252 cm^{-1} due to the stretching vibration of O–H, the extension vibration of N–H, and inter hydrogen bonds of the polysaccharide. The band peak 2881.52 as seen in sample CP2 is due to chitosan. In graft copolymer the peak at 3200- 3500 cm-1 is of quite reduced intensity and broad 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 may have been grafted with PANi chain. 1532.10 peak shows strong characteristic feature of chitosan as seen in both the samples. Similarly 1376 peak indication of PANi characteristic From the IR data it is clear that the grafted copolymer PANi-*g*-chit has characteristic peaks of PANi and of chitosan, which could be a strong evidence of grafting.

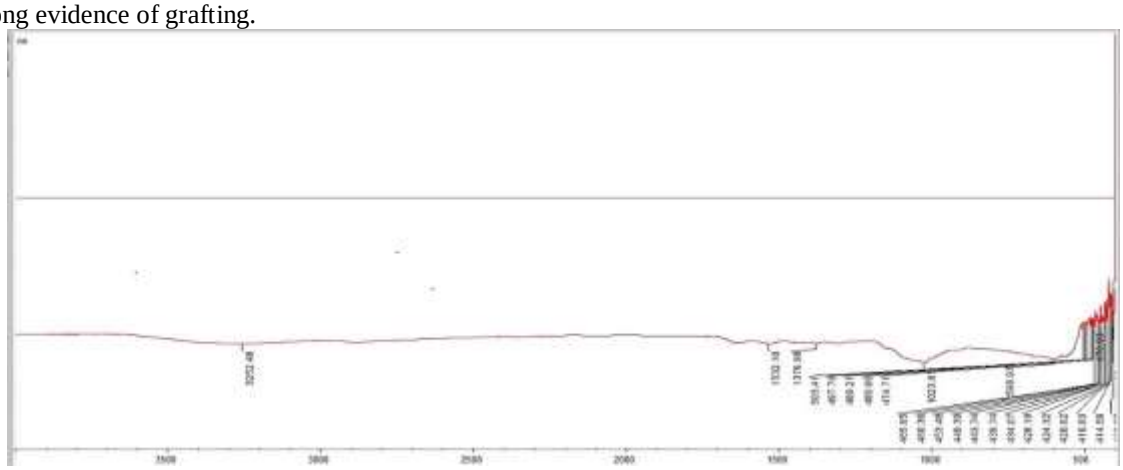


Fig 3: FTIR spectra of polyaniline-grafted-chitosan sample CP1

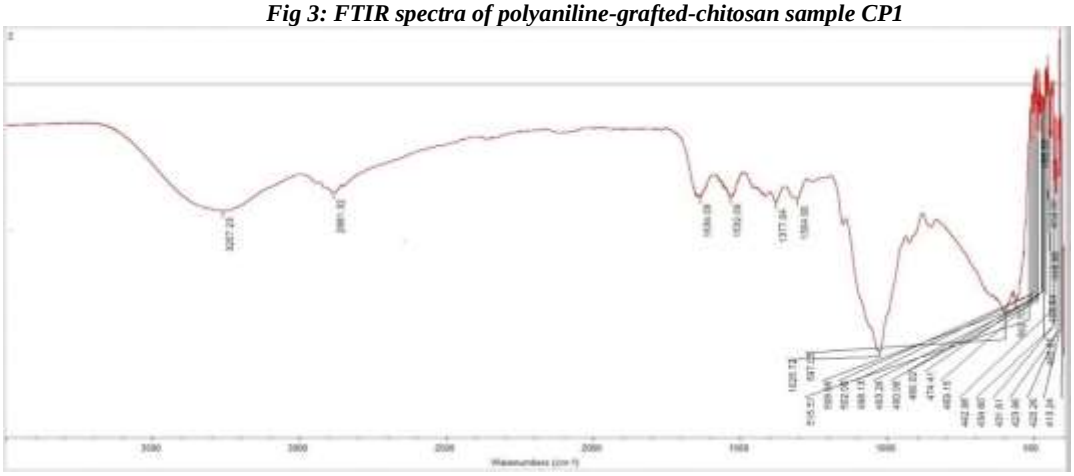
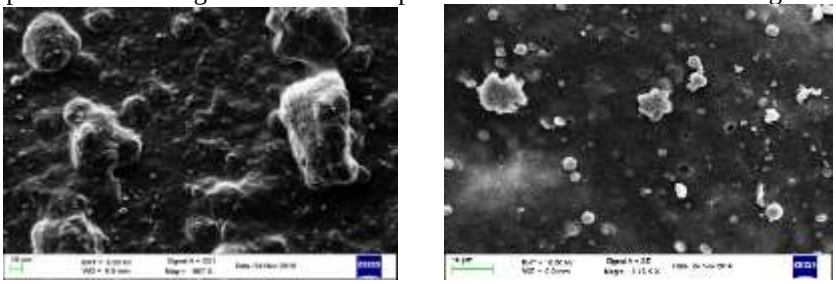


Fig 4: FTIR spectra of polyaniline-grafted-chitosan sample CP2

Morphology

The surface topography of the film made from composite of chitosan and polyaniline are studied by scanning electron microscope. The SEM images of the film samples CP1 to CP5 are as shown in figures 5 to 9.



(a) ***(b)***

Fig. 5: SEM images of sample CP1

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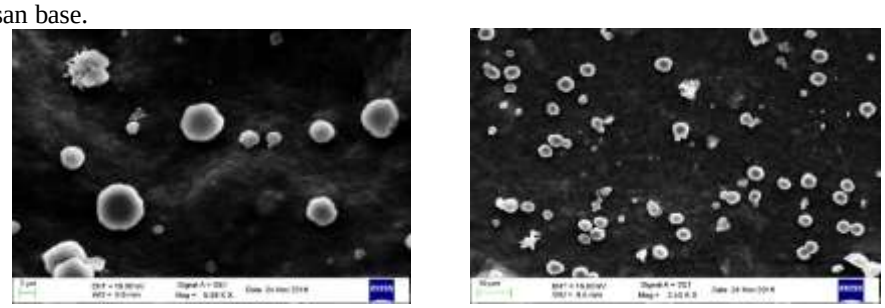
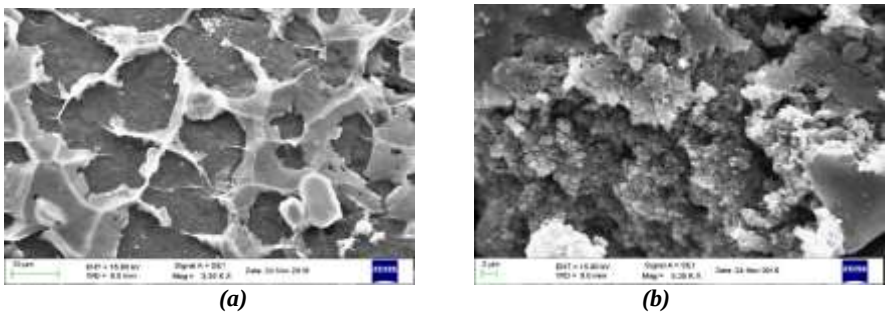
SEM images of sample CP 1 show the topmost exterior surface with granular material scattered across the possible chitosan base.



(a) *(b)*

Fig. 6: SEM images of sample CP2

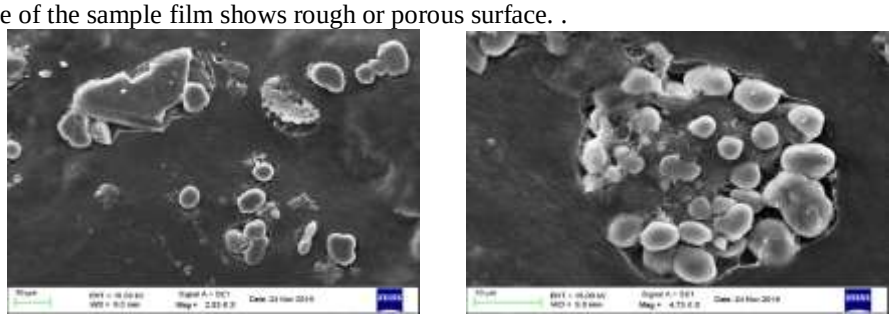
SEM images of Sample CP2 show the similar structure as sample 1, however with even distribution over the surface.



(a) *(b)*

Fig. 7: SEM images of sample CP3

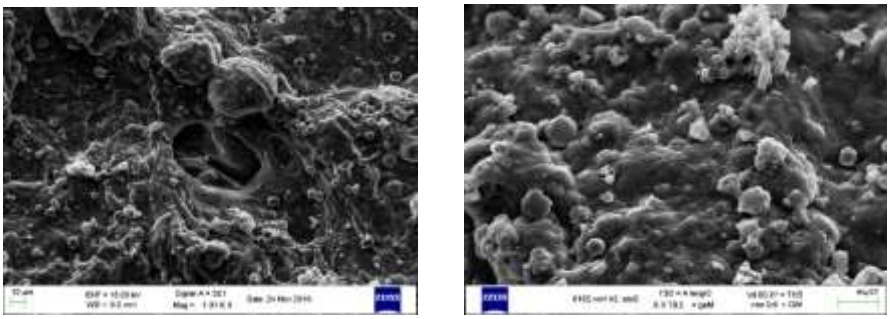
SEM image of sample CP3 shows exterior surface with inter connected chitosan and mixed polyaniline, whereas the other image of the sample film shows rough or porous surface. .



(a) *(b)*

Fig. 8: SEM images of sample CP4

SEM images of sample CP4 show surface with accumulated mass of granular material with non-uniform distribution.



(a) *(b)*

Fig. 9: SEM images of sample CP5

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SEM images of sample CP5 show the surface with uneven exterior, it may be said that material is distributed on the surface with varying degree of uniformity.

Electrochemical potential difference measurement

Electrochemical potential difference measurement is done by using lab made electrochemical cell. Known quantities of water are taken in separate beakers with dilute acetic acid & dilute hydrochloric acid as electrolytes. Two electrodes are used aluminum foil & another made by using polyaniline grafted chitosan film. Fig no 10 shows photograph of electrode cloth that include enamel coated cloth, enamel coated cloth with graphite powder & enamel coated cloth with polyaniline grafted chitosan film & fig 11 shows strips of electrode cloth. The potential difference generated because of the electrochemical conductance is recorded by using digital multimeter. The details of the observations are shown in table number 2 & photographic representation in figure no 12.As can be seen from the table, the highest magnitudes of potential difference of 503mV & 365 mV are obtained for enamel coated cloth with polyaniline grafted chitosan film. These values are 10 to 20 % more than other electrodes used in present work. This highlights the success of present work in development of polyaniline grafted chitosan film with enhanced electrochemical conductance.

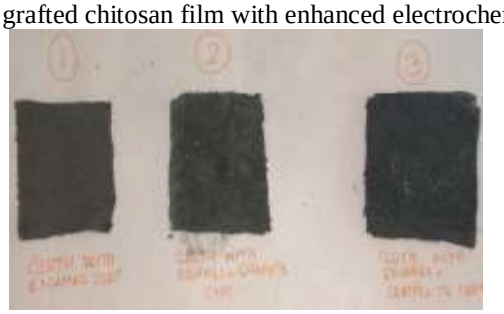

Fig 10 Electrode cloth

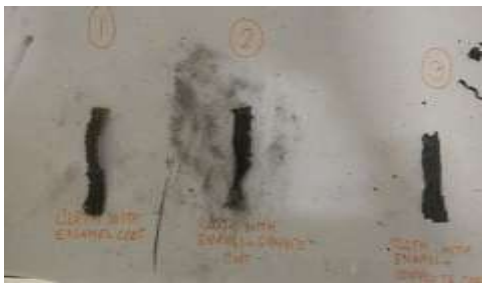

Fig 11 Cloth strip as electrode

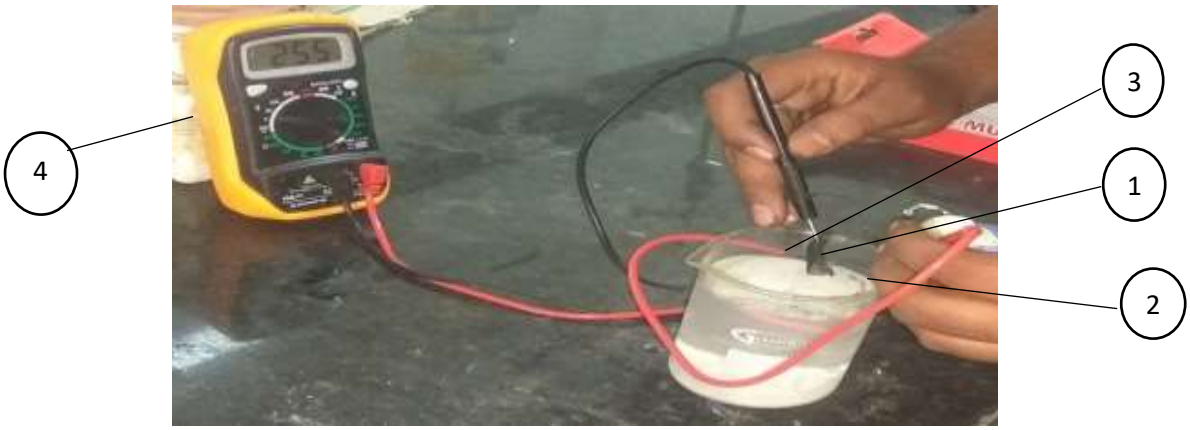

Fig. 12 Conductance measurement setup

Nomenclature

1 potential difference of PANI-gf-Chitosan film.
2. Aluminum foil as a reference electrode
3. Acetic acid in aqueous solution as an electrolyte solution
4. Digital Multimeter

Table 2. Electrochemical conductivity of cotton cloth and PANI-gf-Ch film

Sr. No.	Type Of Material	HCL 2% PD (mV)	Acetic Acid 1% PD (mV)
1	Cotton cloth coated with enamel base	407	230
2	Cotton cloth coated with enamel base paint and graphite powder	460	257
3	Cotton cloth coated with enamel base and PANI-gft-Ch film	503	365

CONCLUSION

The objective of the present work is to synthesize polyaniline grafted chitosan film followed by its characterization. Various proportions of chitosan and polyaniline have been used in synthesizing various sample films CP1 to CP5.

The characterization is done by FTIR, SEM & Electrochemical Conductance studies. Interpretation of FTIR analysis of samples CP1 &CP2 is done by comparing spectragram with that reported in the literature. Comparison validated the grafting of polyaniline on chitosan. SEM images of sample CP1 to CP5 have clearly indicated grafting of polyaniline on the surface of chitosan, however the distribution may not be uniform and as homogenous at places.

The Electrochemical potential difference of electrode made of polyaniline grafted chitosan is more than graphite powder coated electrode by magnitudes of 10 to 20 %. Hence it can be concluded that the present work has demonstrated successful development of composite film of polyaniline grafted chitosan with enhanced electrochemical potential difference. The work is demonstrative and many more experimental runs are required to validate the claim further.

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