

PREPARATION AND CHARACTERIZATION OF CONDUCTING INK

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ABSTRACT

The inks for the specialized field of printable electronics have to be specially designed. Conductive inks are comprised of dispersed conductive particles commonly metal nano particles in a non conductive resin matrix. Conductivity can also be achieved by using polymers that exhibit electronic conductivity in a suitable solvent. Chitosan, an organic bio polymer bears good environmental, thermal and chemical stability, shows good electrical and optical properties. The presence of $-OH$ and $-NH_2$ groups in chitosan offers site for grafting. It is electrical conducting material having good pH switching properties. Poly aniline grafted chitosan (PGCS) was prepared and characterized using FTIR, SEM, XRD and DSC with reference to Chitosan (CS). PGCS/CS hydrogels were used to prepare conducting ink and resistance of lines drawn with these ink samples were measured. PGCS containing inks showed less resistance or greater conductivity as compare to inks constituting CS.

INTRODUCTION

The inks for the specialized field of printable electronics have to be specially designed. Both the intended application and the desired printing process will govern the composition of the ink. The term conductive polymer ink is used to generally characterize printing inks that are used for making conducting layers such as electrodes or wires (1, 2). Most commercially available conductive inks are comprised of dispersed conductive particles commonly metal nano particles in a non conductive resin matrix which bind the particles (3). Conducting polymers after a unique combination of properties make them attractive options in printed electronics. Polymeric materials are flexible, light weight and easily processed. The conductivity of these materials can be tuned by chemical composition, configuration, conformation of the polymer backbone, nature of dopant, degree of doping and by the volume fraction of the conducting polymer in the printing composition. Conductivity can be achieved by different mechanisms such as incorporating metallic or other conducting particles into a non conducting polymer vehicle or by using polymers that exhibit electronic conductivity in a suitable solvent (4). Furthermore, the presence of additives that are commonly included in regular printing ink formulations in order to meet process requirements such as viscosity, wettability and end use properties etc. may cause undesired change in electrical properties of materials and consequently performance of the final device (5).

Patterns of printing with inks having functional electrical conductivity provides the opportunity to print electrical circuiting or RFID antennas (6). Printing patterns with functionality like semi conductivity and electrical insulation opens routes to print polymer transistors and light emitting diodes (7). However, the potential of different printing technologies is not known yet. For the printing of electronic component, disrupted traces would be undesirable, e.g. in the manufacture of this film transistors continuous lines are essential.

Chitosan, an organic bio polymer finds wide applications in formulating drug delivery devices (8, 9). This material has also been used for several other biomedical purposes e.g. in gene therapy (10, 11), gene delivery (12), to suture and wound healing materials (13), skin culture (14, 15), vascular grafting (16), nerve cell generation (17), cartilage regeneration (18), vaccine delivery (19-21), and making contact lenses (22). Besides pharmaceutical applications it has been used in pollution control to remove toxic metal and dyes (23-25), in photography (26), to improve quality of film, in cosmetics due to its fungicidal and fungi static properties, as a food and nutrition supplement (27,28), paper finishing and sizing (29) and in dry batteries, sensor, gas and fan separation membranes etc. (30,31). It bears good environmental, thermal and chemical stability, shows good electrical and optical properties, also it has pH suitability behavior (32,33).

Chitosan, a high molecular weight polysaccharide composed of β (1 \rightarrow 4) 2-deoxy-2-amino-D-glucopyranose units and β (1 \rightarrow 4) linked 2-deoxy-2 acetamido-D-glucopyranose units, has found potential use in a wide range of chemical modifications like crosslinking, grafting etc. It is a brittle material, tends to absorb a quantity of moisture and to improve its toughness, solubility and rheological properties, grafting is commonly employed for several applications (34). It is a low cost, degradable bio compatible, branched biopolymer with unique physicochemical properties (35). The presence of $-OH$ and $-NH_2$ groups in chitosan offers self doping to enhance its selectivity for chemical sensors. It is electrical conducting material having good pH switching properties.

MATERIALS

Chitosan was purchased from India Sea Food Ltd., Kerala and was used as received. Its percentage of deacetylation after drying was 89%. Other chemicals used were of laboratory reagents. Parker blue quink ink manufactured by Luxor writing Instrument Pvt. Ltd., Noida was obtained from local market. Graphite was obtained from lead pencil and used in powdered form.

EXPERIMENTAL METHODS

Preparation of Polyaniline Grafted Chitosan

Chitosan graft polyaniline was synthesized as described by Tiwari and Singh (35). A 20 ml of HCl (0.5 M) was taken into 500 ml conical flask to dissolve 0.15 gm of Chitosan and continuous stirring was given for 1 hour. A mixture of 0.14 gm aniline in 20 ml of 0.5 M HCl was added to this solution and total volume was made up to 100 ml by adding HCl (0.5 M) and then kept it at 25°C in thermostat with continuously stirring

for 30 minutes. Now 2.85 gm of ammonium per sulfate was added and allowed to proceed the reaction for 1 hour.

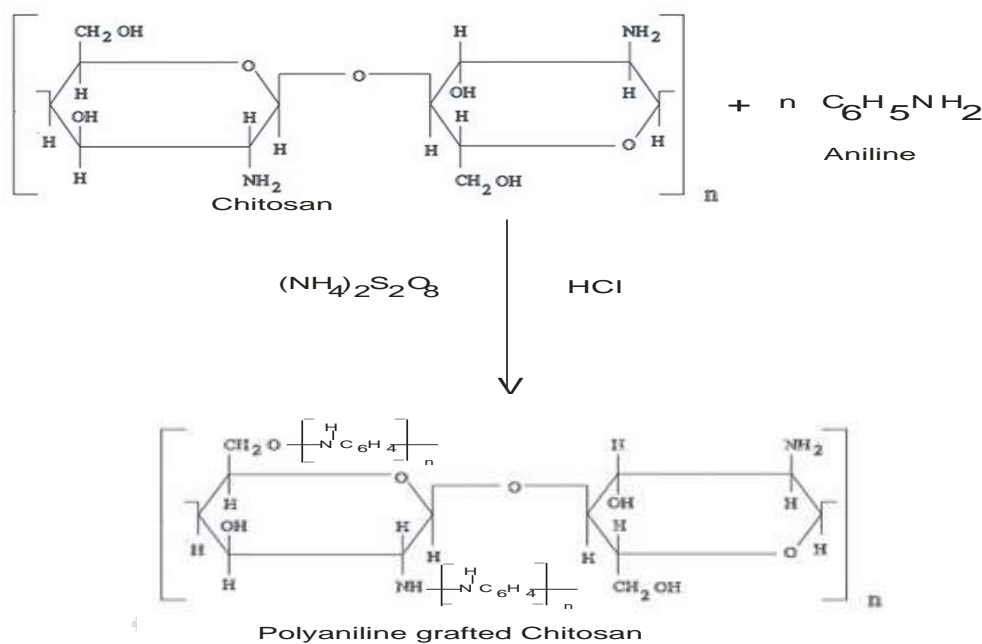


Figure 1- Polyaniline grafted chitosan (PGCS) preparation from chitosan (CS).

Chemical reaction is shown in figure 1. The reaction mixture was neutralized with 5% aqueous NaOH and graft polymer was precipitated with absolute ethanol. The material was finely powdered and washed with acetone and finally air dried.

Characterization of Polyaniline Grafted Chitosan

It is a scientific practice that the characterization of CS and PGCS prepared has been carried out using following techniques-

Fourier transform infra red (FTIR) spectroscopy

Dried samples were ground into powder and crushed with KBr for homogenization. A Nicolet economy sample press was used to obtain optically clear pellets. Pellets were analyzed using transmission FTIR using a Thermo Nicolet Avatar 370 FT-IR spectrometer system. The data was analyzed by Omnic software.

Scanning electron microscopy (SEM)

The FESEM QUANTA 200 FEG model “(FEI, The Netherlands make)” was used with operating voltage ranging from 200 V to 30 kV. FESEM micrographs were taken after coating with a thin layer of gold by using BAL-TEC-SCD-005 Sputter Coater (BAL-TEC AG, Balzers, Liechtenstein Company, Germany) under argon atmosphere to make the sample conducting.

Thermal analysis

Thermal gravimetric analysis (TGA), Differential thermal gravimetric (DTG) and Differential thermal analysis (DTA) were carried out simultaneously by using a (PYRIS Diamond). TG/DTA thermal analyzer model DSC-7, supplied by Perkin Elmer and the data was processed and analyzed by PYRIS muse measure and standard analysis software (V. 3.3U; #. 2002 Seiko instruments inc.). The sample was kept in Alumina pan with the reference material Alumina powder and heated at a rate 10°C/min under 200 ml/min flow rate of air or nitrogen atmosphere.

X-ray diffraction (XRD)

X-ray diffraction studies were performed by using Bruker AXS D8 Advance using CuK α Nickel filter and Copper as target at wavelength of 1.54 Å with goniometer and speed was kept at 2°/min wide angle X-Ray scattering patterns of the samples were obtained using DIFFRAC plus XRD commander software and analysis was done by DIFFRAC plus (version 8.0) software. The range of scanning angle for the sample was kept in the range 2 θ of 10 – 60°.

Preparation of conductive polymeric hydrogel

Polymeric hydrogel was obtained from Chitosan (CS) and Polyaniline grafted Chitosan (PGCS) separately. The definite quantity of conductive polymer CS or PGCS was dissolved in 80 ml of 2% acetic acid under stirring condition for 3 h at room temperature. A homogeneous mixture of different compositions as shown in Table-1 were obtained as conductive polymeric hydrogel.

Table – 1 : Composition of Conductive Polymeric Hydrogel

S. No.	% CS or PGCS	Sample code for CS hydrogel	Sample code for PGCS hydrogel
1	0.25	CS1	PG1
2	0.50	CS2	PG2
3	0.75	CS3	PG3
4	1.00	CS4	PG4
5	1.25	CS5	PG5
6	1.50	CS6	PG6

Electrical conductivity measurement

The measurement of electrical conductivity of conductive hydrogel and prepared conductive ink samples from suitable hydrogel of 1.25 % in the experiment were performed using a conductivity meter Elico CM 180.

Resistance measurement

The lines with prepared conductive inks have been drawn on paper with a sarkanda wood whose tip was carved in nip width of 2.5, 3.5 and 4.0 mm, and their resistance were measured with an Analog-Digital multimeter 30918 by Rishab Instruments Pvt. Ltd., Nasik, India.

RESULTS AND DISCUSSIONS

Characterization

FTIR

FTIR curve for CS and PGCS are presented in figure 2. Curve for CS exhibited a broad peak at 3450 cm^{-1} which was assigned to -NH- stretching vibration which might be due to deacetylation of chitosan. The peak at around 3500 cm^{-1} due to hydrogen bonded O-H vibrational frequencies and O-H bond stretch of gluco pyranose units. Peaks at 1639 cm^{-1} and 1319 cm^{-1} were observed due to C=O stretching of amide bond. The peak at 1613 cm^{-1} was assigned to strong N-H bending vibrations of secondary amide. Bands at 2919 and 2810 cm^{-1} represent the aliphatic C-H stretching vibrations. The observed sharp peak at 1384 cm^{-1} is due to CH_3 symmetrical deformation mode. Two peaks around 894 cm^{-1} and 1171 cm^{-1} appeared in spectra corresponding to saccharide structure. A broad band appearing near 1083 cm^{-1} indicated the >CO-CH_3 stretching vibration of chitosan. While, Spectra of PGCS showed additional peaks of poly aniline which may be assigned at 1526 cm^{-1} and 1462 cm^{-1} for C=C stretching of quinoid and benzenoid rings, at 1284 cm^{-1} for C-N stretching, at 1100 cm^{-1} characteristic of poly aniline and at 830 cm^{-1} for C-H bending vibrations due to 1,4 di substituted benzene ring. FTIR spectra clearly suggested the grafting of poly aniline on to chitosan.

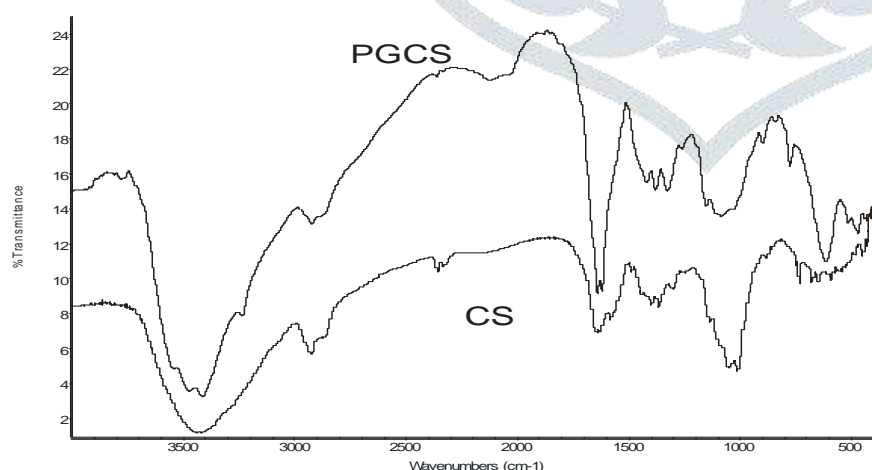


Figure 2- FTIR of CS and PGCS.

Thermal analysis

CS and PGCS were carried out to analyze for their thermal stability and results obtained were shown in figure 3 and 4 respectively. TGA curve for chitosan (figure 3) indicates that it decomposed in two steps

approximately 10% weight loss below 100°C, involves a smaller weight loss, may be due to initial loss of water molecules, and after 249°C and the total weight loss at 400°C was found to be about 60 %. In case of PGCS (figure 4) and the total weight loss at 400°C was of 44 % showing slow degradation.

DTG thermograms of chitosan in figure 3 indicated one peak at 290°C corresponding to higher rate of weight loss about 1.4 mg/ min in comparison to peaks at 229°, 268° and 420°C showing lower of rate of weight loss about 0.35, 0.45 and 0.22 mg/ min for PGCS in figure 4.

DTA thermograms for chitosan is presented in figure 3, showed endothermic peak at 65°C due to loss of free water and one exothermic peak at 296°C due to chemical transformation. While PGCS in figure 4 showed two exothermic peaks at 270° and 427°C due to chemical transformation.

Thermal analysis proved that the PGCS is more thermally stable as compare to CS.

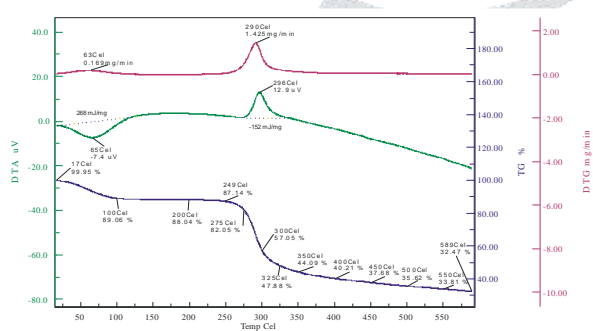


Figure 3- Thermal analysis of CS.

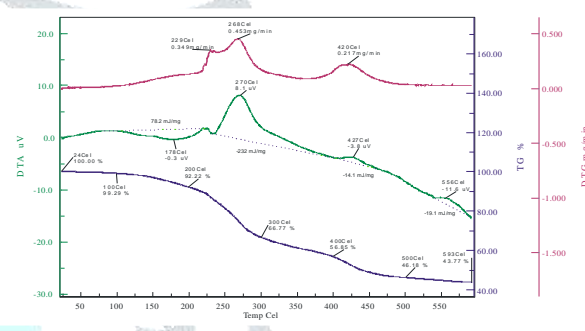


Figure 4- Thermal analysis of PGCS.

XRD

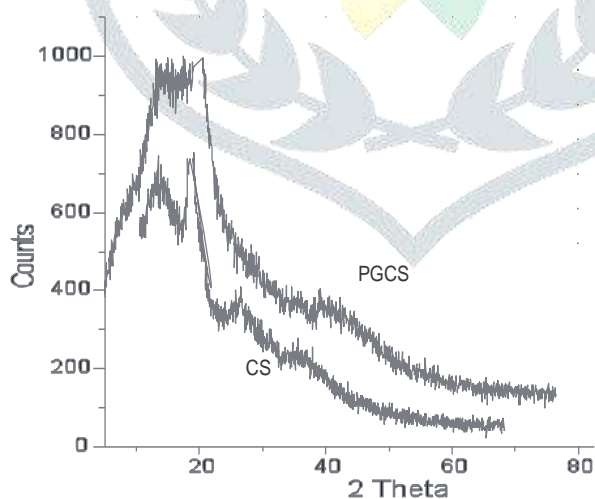


Figure 5- XRD of CS and PGCS.

The obtained XRD spectra for CS and PGCS are showed in figure 5. CS gave peaks at 2θ of 12° to 16°, 20° and 29° while PGCS produced peaks in region of 2θ of 16° to 24° clearly indicating that more crystalline nature of PGCS in comparison to CS.

SEM

The surface morphology of the PGCS with reference to CS was studied. The exterior of PGCS appears globular and porous surfaces bearing irregular shaped globules on to the interior (figure 6b) and chitosan seems like fiber having rough and porous surfaces with irregular wrinkles (figure 6a), hence the surface morphology also supports the grafting of poly aniline on chitosan backbone.

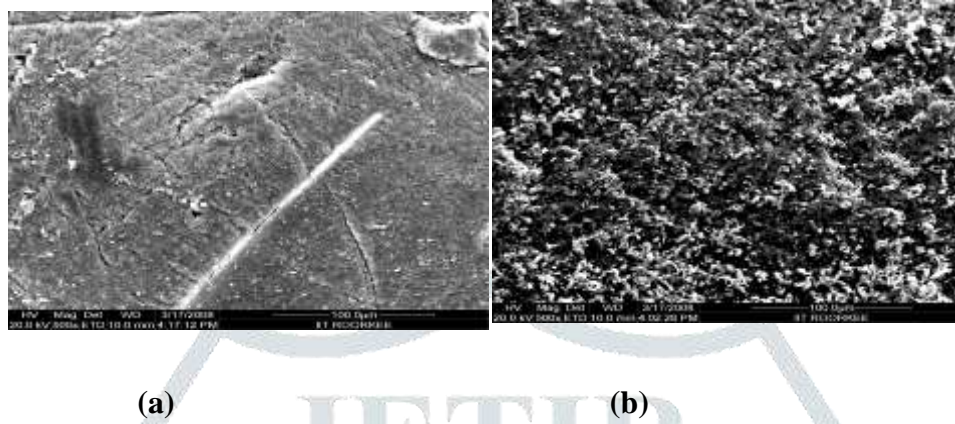


Figure 6- SEM micrographs of (a) CS and (b) PGCS.

Conductivity of hydrogels

Conductive polymer hydrogels from Chitosan (CS1-CS6) and from PGCS (PG1 – PG6) were prepared and electrical conductivities were determined which are shown in table 2.

Table – 2 : Conductivity of CS or PGCS Conductive Polymer Hydrogels

Chitosan (CS)		Polyaniiline Grafted Chitosan (PGCS)	
Sample Codes	Conductivity s/cm	Sample Code	Conductivity s/cm
CS1	0.8×10^{-3}	PG1	0.42
CS2	1.24×10^{-3}	PG2	0.62
CS3	1.75×10^{-3}	PG3	0.79
CS4	2.27×10^{-3}	PG4	1.13
CS5	2.56×10^{-3}	PG5	1.28
CS6	3.03×10^{-3}	PG6	1.48

As indicated from table-2 electrical conductivity of polymeric hydrogels obtained from PGCS (PG1-PG6) were quite high as compared to the hydrogel obtained from CS (CS1-CS6). Conductivities were found to be increased exponentially on increasing CS (figure 7) and PGCS (figure 8) polymer concentration.

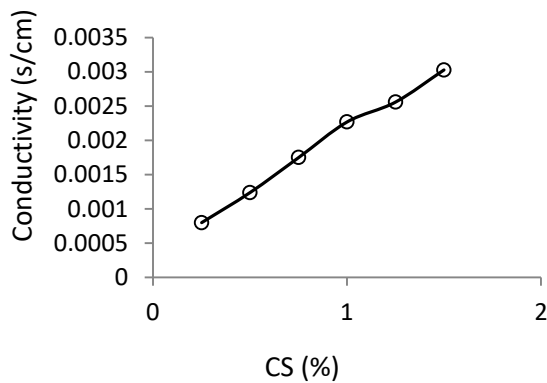


Figure 7–Plot showing variation of hydrogel conductivity with CS quantity.

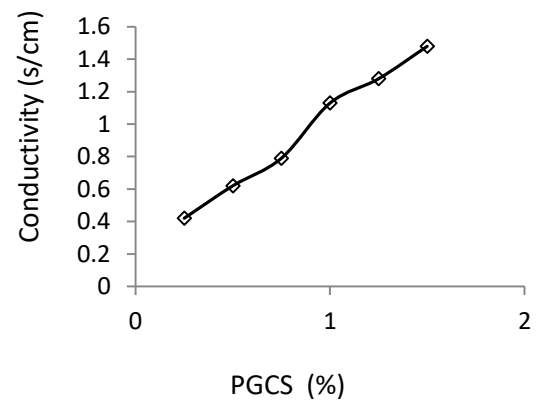


Figure 8–Plot showing variation of hydrogel conductivity with PGCS quantity.

Conducting ink samples

As hydrogel samples constituting 1.25 % of CS or PGCS was able to draw uniform and smooth lines without clogging was chitosan for preparing conducting ink. 1.25 % hydrogel, graphite and Quink ink were mixed in a definite proportion to obtain conducting ink samples A1 to C1 containing CS and A2 to C2 constituting PGCS which were formed as a homogeneous thick and dense liquid. The composition of conductive ink samples is shown in table-3. The pH of all conductive ink samples was kept almost neutral (pH 6 – 7).

Table – 3 : Composition of Conductive Inks showing Conductivity

CS/PGCS Hydrogel (ml)	Graphite (gm)	Quink ink (ml)	Conductivity s/cm			
			Sample Codes	CS	Sample Codes	PGCS
10	2.0	10	A1	2.05×10^{-3}	A2	0.92
10	3.0	10	B1	2.17×10^{-3}	B2	1.02
10	3.5	10	C1	2.33×10^{-3}	C2	1.18

The conductivity of ink samples were increased with the increasing concentration of graphite and conductivity of PGCS containing inks are quite high as compared to CS containing inks. Similar results were obtained from conductive hydrogels and it is to be noted that conductivity from PGCS was found greater about 500 times as that of conductivity of samples containing CS.

Resistance Measurement

Sarkanda Wood was shaped into a writing tool to mark lines on paper by carving it in a way so that it can draw lines of definite width of 2.5, 3.5 and 4.0 mm. The lines were marked on paper using each of the ink sample A to C by dipping wooden carved tool in ink and ten lines for each of the width (2.5, 3.5 and 4.0

mm) and same length of 1.0 cm were drawn on applying two coatings of ink as presented in figure . The ink showed good adhesion on paper surface and formed a uniform layer, but take time to be dried.

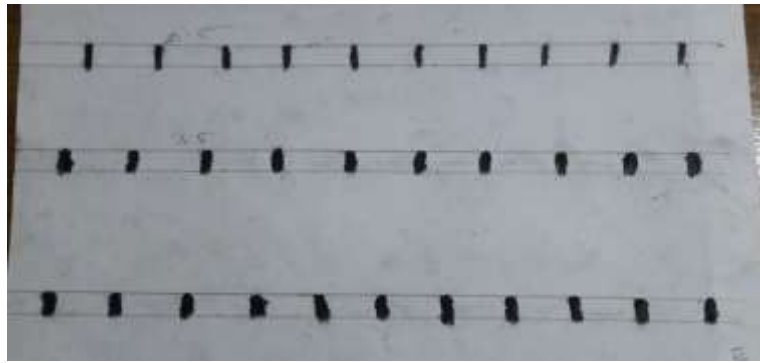


Figure 9 – Photograph of sample patterns drawn with conducting ink on paper.

Resistance was measured for each of ten lines and then average resistance is calculated which was reported in Table-4, for each and every conducting ink sample obtained from CS (A1-C1) and from PGCS (A2-C2).

Table – 4 : Average Resistance of lines drawn from conductive inks

Line Width (mm)	Average Resistance (Ω)					
	CS Ink (CS5)			PGCS Ink (PG5)		
	A1	B1	C1	A2	B2	C2
2.5	55.82×10^3	25.7×10^3	20.6×10^3	121.0	51.5	41.2
3.5	44.4×10^3	16.2×10^3	3.24×10^3	89.3	32.5	6.43
4.0	19.5×10^3	13.3×10^3	2.80×10^3	38.9	26.4	5.34

Resistance of marked lines obtained from ink containing PGCS is very low as compared to lines marked with ink constituted CS as conductive polymer, hence PGCS containing hydrogel and inks definitely have better electrical conductivity.

CONCLUSION

Polyaniline grafted Chitosan polymeric hydrogel and inks containing it, exhibited better electrical conductivity than CS-hydrogel and ink containing it. In future, it requires more investigations to decide its conductive performance and writing or printing properties.

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