Synthesis and Characterization of Biopolymer-Based Electrical Conducting Graft Copolymers

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ABSTRACT: The naturally occurring Guar gum (GG) was chemically modified with polyaniline (PANI) using ammonium persulfate (APS) as oxidant/initiator in acidic condition. The representative graft copolymer was characterized using UV–vis, FTIR, H^1 NMR, XRD, TGA, and SEM taking GG and PANI as reference. The affinity of the upper limit for the graft copolymerization has been extensively studied by varying different chemical and physical parameters. All the findings have been discussed, and proposed a plausible mechanism for the graft copolymerization. The grafted GG exhibited hybrid properties of biopolymer as well as PANI, and has electrical conductivity in the range of 1.6×10^{-2} S/cm at room temperature. The electrical conductivity of the grafted biomaterial was quite sensitive with pH, and it could be interesting to combine a biopolymer, isolated from the natural resources with synthetic polymer from petrochemical origin, and yielded an eco-friendly material of high performance. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 1169–1177, 2008

Key words: polyaniline-*graft*-guar gum; water soluble; electrical conductivity; sensor application

INTRODUCTION

Polyaniline (PANI) has emerged as one of the most promising conducting material[1,2] and has wide applications[3–5] viz. fabrication of sensors, artificial muscles, solar materials, actuators, electronic shielding, etc. It has some limitations in synthesis, solubility, and mechanical strength.[6,7] It has found that the chemically synthesized PANI has low molecular weight, which results in low mechanical strength.[8] The low mechanical strength of PANI is responsible for the poor adhesion on solid substrates[9] that has limited its utility in the fabrication of electronic devices. The copolymers of PANI are potentially synthesized for the technological applications[10] such as plastic transistors and logic gates, photovoltaic cells, antistatic coatings, field-effect transistors, etc. The considerable research has been done on biopolymers-based conducting materials[11–13] and owing new classes of advanced materials having unique physicochemical properties. Among these, many reports have focused on the combination of biopolymer with conducting PANI, and resulting materials would be versatile for making in eco-friendly highly efficient electronic devices. For making attractive PANI, considerable affords have been made through copolymerization of PANI with few other biopolymers.[14] However, not much attention has been paid on the chemical copolymerization of biopolymer with PANI. This work clearly indicates a unique compatibility between PANI and biopolymer through graft copolymerization of PANI onto Guar gum (GG). It would be expected that the produced conducting biomaterials might be potentially used in the eco-friendly electronic devices and probes for the sensors fabrication.

GG is an edible carbohydrate polymer[15] isolated from the seeds of *Cyanaposis tetragonolobus*. It is a nonionic, branched-chain polymer (Structure 1), consisting of a straight chain of mannose units joined by $\beta(1\rightarrow4)$ linkages having α-D-galactopyranose units attached to this linear chain by $\alpha(1\rightarrow6)$ linkages with molecular ratio of 1 : 2. GG is cold-water swelling biopolymer, and is reported to be one of the most highly efficient water thickeners and tablet binder.[16]

In this study, PANI was grafted onto GG to synthesize water-soluble electrical active biomaterial for the *in vivo* and *in vitro* sensor applications. In the series of studies, the reaction mechanism, crystalline and morphological features, electrical and thermal properties of the grafted product were extensively investigated. It has been expected that results would be leading to new promising conducting polymers especially for the sensor applications. The major advantage of this work is to use natural recourses and increase their utility in broader prospective by chemical modification.
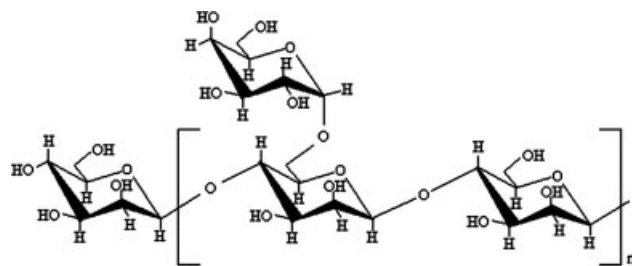
Structure 1   Chemical structure of Guar gum.

EXPERIMENTAL

Materials

GG (E. Merck, Germany; M_w 2.47 × 10⁶) and aniline (E. Merck) was used after purification, while ammonium persulfate (APS; Aldrich, USA) was used without further purification. Doubly distilled water was used in all the experiments.

Purification of GG

GG was purified[17] by barium complexing, preparing 2.5% (w/v) aqueous gum solution by continuous stirring for 12 h at 60°C and precipitating with saturated barium hydroxide solution. The produced complex was separated by centrifugation and dissolved in 1M acetic acid with stirring, centrifuged it, and precipitated with ethanol. The precipitate was further washed with 70, 80, 90, and 95% ethanol.

Synthesis of PANI

PANI was synthesized[18] by oxidative polymerization of aniline using peroxydisulfate as oxidant. The doubly distilled aniline (0.5M in 200 mL 1M HCl), APS (0.54M in 200 mL 1M HCl) was added dropwise with stirring at 4°C. The reaction mixture was kept under continuous stirring for 2 h, and then stored overnight in a refrigerator. The precipitated PANI was filtered and washed with 1M HCl until filtrate became colorless. It was finally washed with distilled water and made acid-free product. Finally, product was ground as fine powder and low-molecular weight PANI oligomers were removed by exhaustive extraction with acetone. The resulting PANI was dried at 50°C in air oven for 48 h.

Synthesis of GG-*graft*-PANI

A calculated amount of the GG was dissolved in minimum quantity of distilled water in a 500-mL flask. To this solution, calculated amount of aniline and hydrochloric acid were added and kept total volume of 200 mL. The flask was then thermostated at 25°C ± 0.2°C with continuous stirring. After

30 min, a definite amount of APS was added dropwise and this was taken as zero time. The reaction was further allowed for 45 min. After completion of reaction, reaction solution was neutralized with 5% aqueous NaOH and graft copolymer was precipitated with absolute ethanol (Scheme 1). The precipitate was then washed with N-methyl pyrrolidinone (NMP) to separate PANI (homopolymer) from the copolymer. Finally, resulting copolymer was dried for 72 h in a vacuum oven at 50°C.

The %grafting and %efficiency of the graft copolymers were calculated using the following equations[19]:

$$\%\text{Grafting } (\%G) = \frac{W_1 - W_2}{W_0} \times 100 \qquad (1)$$

$$\%\text{Efficiency } (\%E) = \frac{W_1 - W_2}{W_2} \times 100 \qquad (2)$$

where W_1, W_0, and W_2 denote, weight of GG-*graft*-PANI, weight of GG, and weight of aniline monomer used, respectively.

Characterization of GG-*graft*-PANI

Ocean optics HR 4000 high-resolution spectrophotometer was used to record the UV–vis spectra of the samples. FTIR spectra were recorded on PK-1310, Perkin-Elmer instrument by making a pellet with dehydrated KBr in reflectance mode. ¹H NMR was done on Bruker DRX-300 NMR spectrometer with $(CD_3)_2SO$ as solvent and $SiMe_4$ as internal standard. X-ray diffractogram was taken by Rigaku Rotaflex, RAD/Max-B with a scanning speed of 1°/min. TGA was taken from Rigaku Thermoflex, PTC-10A with 10°C/min heating rate and taking alumina as reference material. Scanning electron microscope (SEM) was done on JEOL-840, JEOL by making a film of desirable size and coated with gold. The DC electrical conductivity of the samples was measured by making rectangular pressed pellets (pressure 6 ton/cm²) and using Keithley four-probe system with 224 programmable current source, 181 nanovoltameter, and 195A digital multimeter.

Electrical conductivity measurement

The surface DC electrical conductivity of the GG, PANI, and GG-*graft*-PANI rectangular pressed pellets (pressure 6 tons/cm²) was measured by Keithley four-probe method.[20] The electrical conductivity (σ) was calculated using the following equations:

$$\rho = R(A/l) \qquad (3)$$

$$\sigma = 1/\rho \qquad (4)$$
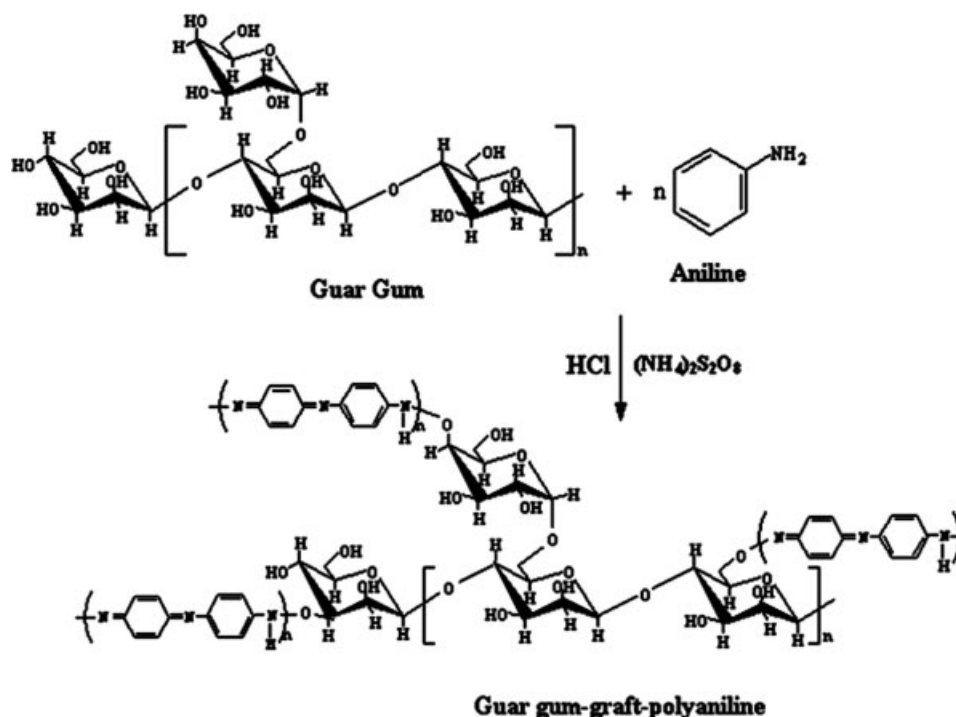
Scheme 1 Graft copolymerization of polyaniline onto Guar gum.

where ρ, R, A, l, and σ are resistivity (Ω cm), resistance (Ω), area of the pallet (cm^2), length of the pallet (cm), and conductivity (S/cm), respectively. The electrical conductivity measurements were carried out at intervals of 20 min, and measurements were repeated three times.

RESULTS AND DISCUSION

Determination of optimal grafting condition

The grafting conditions of GG-*graft*-PANI have been optimized with varying [APS], [HCl], [aniline], and [GG] chemical components. The temperature and time for the copolymerization were also tailored, where total volume of the reaction mixture was kept at 200 mL. The graft copolymerization of PANI onto GG using APS was find as a function of [oxidant], [HCl], [aniline], [GG], and influenced with temperature and reaction time. It was observed that $(NH_4)_2S_2O_8$/HCl system can be efficiently used for the graft copolymerization of PANI onto GG, where maximum 230 %G and 65.71 %E could be achieved.

Effect of APS concentration

%G increased with increase in initiator/oxidant concentration and reached a maximum value at 0.55M of peroxydisulfate at fixed concentration of 0.15M aniline, 0.5M HCl, and 4 g/L GG at 25°C ±

0.2°C for 45 min. It was observed that %G increase within the peroxydisulfate concentration range from 0.35 to 0.55M. It may be due to the fact that at this concentration range, produced sulfate ion radicals that activate the backbone of GG and form GG macroradicals; simultaneously, it oxidized the aniline monomer and produced PANI cation radicals[21] that immediately grafted onto the GG backbone by the graft copolymerization. Therefore, %G was increase with the increase in the concentration of APS.
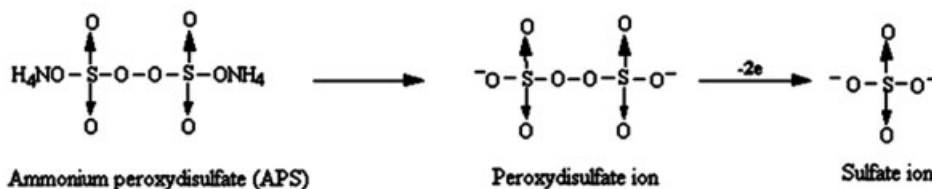
Effect of HCl concentration

The effect of acid was studied in the range of 0.1–0.5M at fixed concentration of 0.55M APS, 0.15M aniline, and 4 g/L GG at 25°C ± 0.2°C for 45 min. It was observed that both %G and %E increases with the increase in the concentration of acid, which may be due to the more protonation of aniline monomer; accelerate the propagation of aniline for the formation of PANI cation radicals.[22]
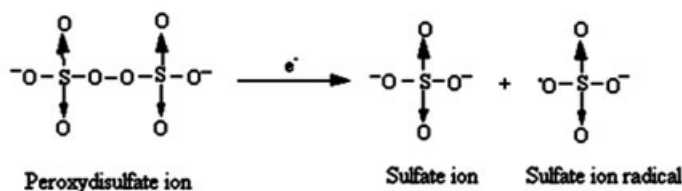
Effect of monomer concentration

The increase in the concentration of aniline from 0.15 to 0.35M resulted in the increase of %G under the fixed concentration of 0.55M APS, 0.5M HCl, and 4 g/L GG at 25°C ± 0.2°C for 45 min. The increase in %G may be due to the more formation of PANI

1) Oxidizing action of APS

Ammonium peroxydisulfate (APS)   Peroxydisulfate ion   Sulfate ion

2) APS act as initiator

Peroxydisulfate ion   Sulfate ion   Sulfate ion radical

Scheme 2   Generation of primary sulfate ion radicals.

cation radicals that generates more grafting sites onto the GG backbone. Increasing the concentration beyond 0.15M the %E decreases, this may be probably due to more formation of PANI homopolymer or PANI oligomer of lower molecular weight.

Effect of GG concentration

The effect of GG concentration was studied in the range of 2–6 g/L with the constant [APS] 0.55M; [HCl] 0.5M; [aniline] 0.15M at 25°C $\pm$ 0.2°C for 45 min. It was found that %E increased up to 4 g/L GG concentration, which may be due to the more availability of the macroradicals. Thereafter, %G and %E both decreased simultaneously, probably due to the increase in the viscosity of the reaction medium causing hindrance for the normal reaction. Therefore, copolymerization of GG-*graft*-PANI was a combined function of oxidant, HCl, monomer, and GG mole ratio.
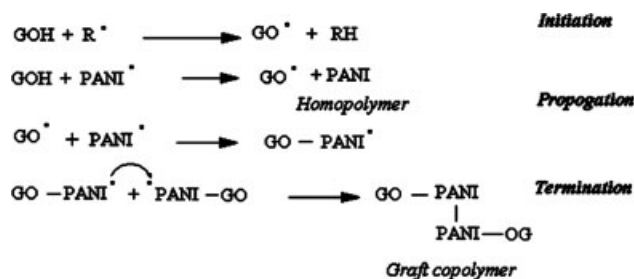
Effect of temperature

The grafting reaction was carried out at different temperature (15–35°C) keeping other variables constant; [APS] 0.55M; [HCl] 0.5M; [aniline] 0.15M, and [GG] 4.0 g/L for 45 min. It was observed that %G was increased up to 25°C. It is attributed that with increasing temperature range from 15 to 35°C, which may be probably due to the increase in the number of collisions between the monomer and the GG macromolecules, simultaneously decreased in the viscosity of the medium at higher temperature. But

beyond 25°C, %G was slightly decreased, which may be due to increase in ionic mobility of PANI cation radicals that resulted to form more homopolymers.
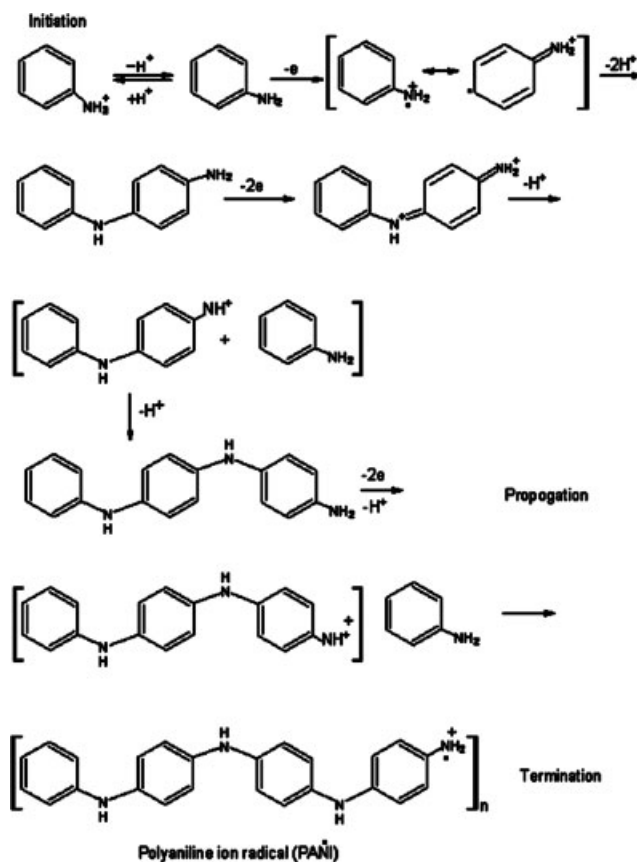
Scheme 3   Formation of secondary PANI radicals.

Scheme 4   Copolymerization of Guar gum and polyaniline.

Effect of grafting time

The grafting reaction was carried out at different time (15–75 min) keeping other variables constant; [APS] 0.55M; [HCl] 0.5M; [aniline] 0.15M, and [GG] 4.0 g/L at 25°C $\pm$ 0.2°C. Maximum %G was obtained at 75 min. The %G increased with increasing in time up to 75 min, after which it levels off. It could be attributed to decrease in concentration for both initiator and monomer, thereby a reduction in the number of sites on the backbone accessible for grafting as the reaction procedure.

Mechanism for Graft copolymerization

The peroxydisulfate initiated graft copolymerization of vinyl monomers onto biopolymers has explored free radical copolymerization mechanism.[23,24] A chain mechanism[25] is involved due to the formation of sulfate ion radicals (SO_4^-), which are well-known ion chain carriers for the graft copolymerization (Scheme 2). At the same time, APS stimulates the oxidative polymerization reaction of aniline[26] via a medium of cationic radicals and form PANI radicals (Scheme 3). Finally, GG macroradicals and PANI cation radicals are combined to form GG-*graft*-PANI copolymer. Mechanism may be written as follows.

SO_4^- is the primary radical, generated from the APS by the reduction of one electron and are
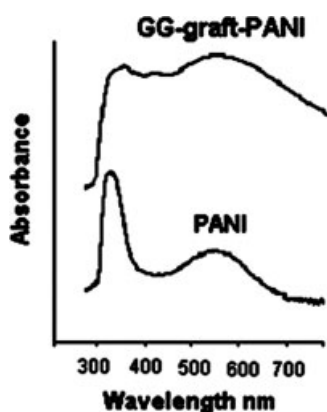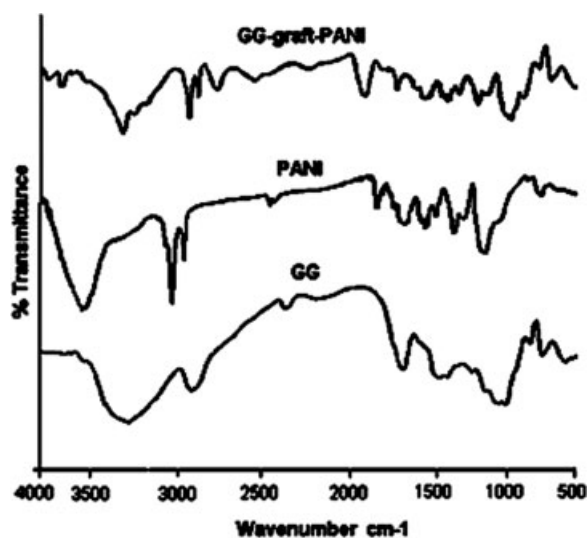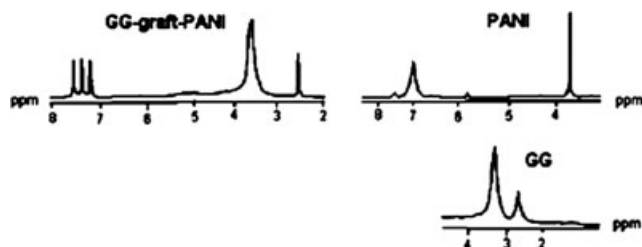

Figure 1   UV–vis spectra of GG-*graft*-PANI and PANI.

Figure 2   FTIR spectra of GG-*graft*-PANI, PANI, and GG.

expressed as R˙ in the Scheme 4. Where R˙ is 1° anion radicals, i.e., SO_4^-˙ generated from Scheme 1, PANI˙ is 2° cation radicals generated from Scheme 2, GO˙ macroradicals and GOH represents Guar gum. Simultaneously, APS generate SO_4^{-2} ions by the reduction of two electrons and act as oxidant. They initiate the oxidative polymerization of aniline, as the polymerization of monomer is reported to be faster than the H abstraction from the biopolymer backbone.[27] The macroradicals GO˙ may be generated by the abstraction of H by the growing PANI cation radical (PANI˙) in the medium of acid, which may be added onto the GO˙ macroradical that generates new radical GO-PANI˙, and this chain will grow till it combines with other such chains to produce a graft copolymer (Scheme 4).

Characterization of GG-*graft*-PANI

The UV–vis spectrum of the aqueous GG-*graft*-PANI solution (0.1 wt %) showed absorption peak in the UV range at 328 and 560 nm these are characteristic peaks of undoped PANI, whereas PANI solution in NMP had absorption peak at 325 and 558 nm that correspond to excitations of amine nitrogen of the

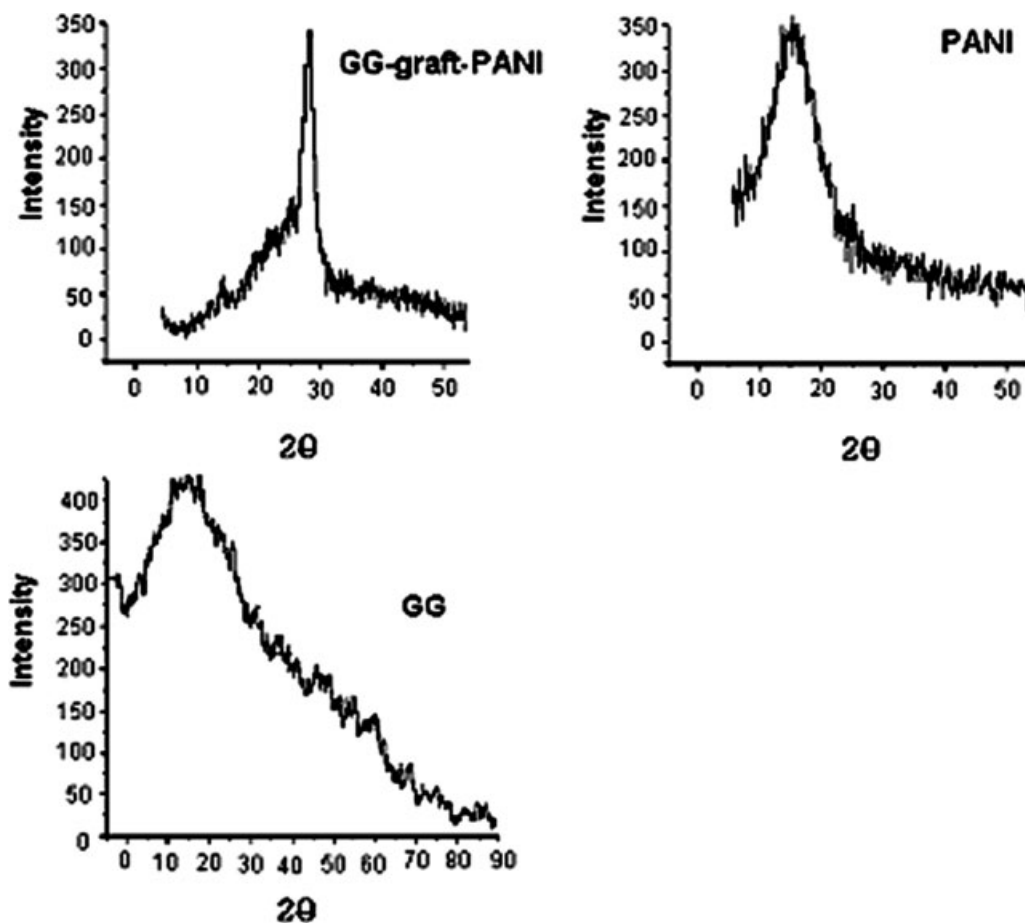Figure 3   H^1 NMR of GG-*graft*-PANI, PANI (low M_w), and GG.

Figure 4 XRD spectra of GG-*graft*-PANI, PANI, and GG.

benzenoid and imine nitrogen of the quinoid segments of PANI, respectively (Fig. 1). It was observed that UV absorbance for GG-*graft*-PANI is higher than PANI. It may probably be due to the effect of solvent (GG-*graft*-PANI dissolved in water whereas PANI dissolved in NMP) or occur due to interaction between PANI chains and water-soluble polymer, GG, or due to both. GG-*graft*-PANI showed a band at 410–470 nm that is attributed to the formation of delocalized polarons.[28] The smeared polaron peaks, which appear around that region indicate an enhanced polaron delocalization. This behavior indicates a more expanded coil conformation of the chains entailing a larger conjugation length that may happen only if the chains are less branched.

FTIR spectra of the GG showed typical polysaccharide absorption at v_{max} 3318 cm^{-1} (stretching of —OH group), v_{max} 2930 cm^{-1} (C—H stretching), v_{max} 1632 cm^{-1} (C=O stretching of carbonyl group, a typical saccharide absorption). FTIR of PANI showed the characteristic peaks of the emeraldine salt form of PANI,[29] while GG-*graft*-PANI showed some additional peak at v_{max} 2994 cm^{-1} due to aromatic C—H stretching, v_{max} 3421 cm^{-1}, and v_{max} 3149 cm^{-1} (bonded and free N—H stretching). Peaks

at v_{max} 2906 cm^{-1} due to C—H stretching of —CH$_2$ groups and at 1527 cm^{-1} due to —N—C— (Quinoid form of PANI) stretching of the grafted chain and v_{max} 1460 cm^{-1} of N—H stretching with conjugation, confirms formation of GG-*graft*-PANI (Fig. 2).

^{1}H NMR of the pure GG showed a peak at δ 3.4 ppm for anomeric hydrogens and at δ 2.6 ppm due
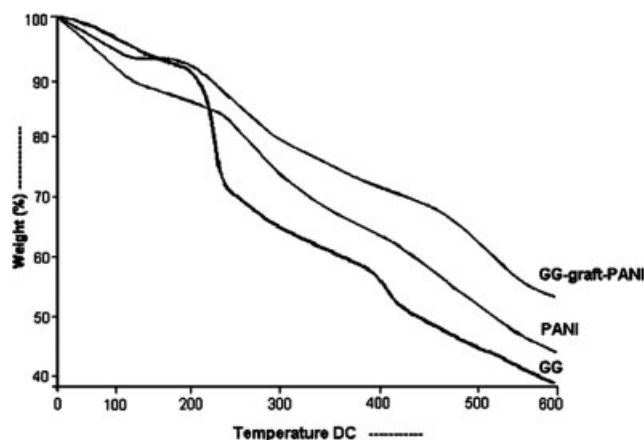

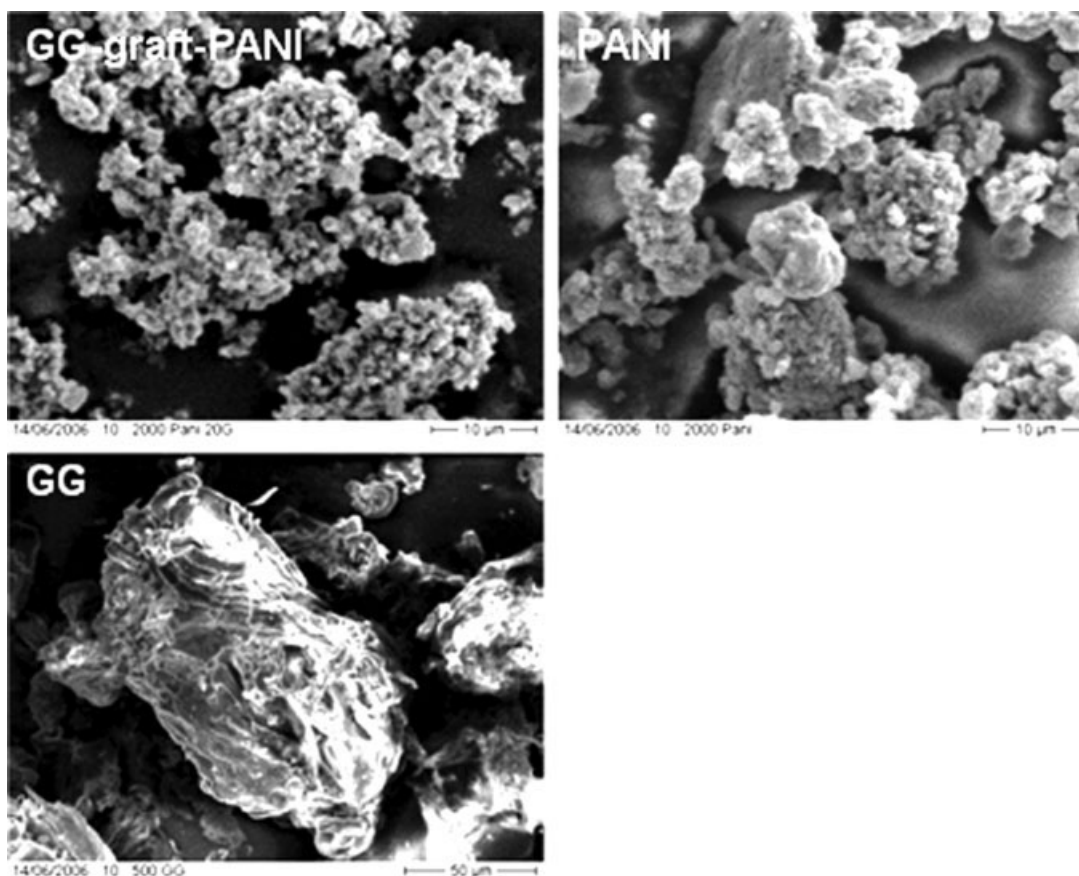**Figure 5** TGA spectra of GG-*graft*-PANI, PANI, and GG.

Figure 6 SEM pictures of GG-*graft*-PANI, PANI, and GG.

to sugar protons, while PANI (low M_w) showed a sharp peak at δ 3.28 ppm that corresponds to —NH and —NH$_2$ protons, and the peak around 7.1 ppm assigned to protons on the benzene ring. The peak at 5 ppm assigned to trace amount of water. The ^{1}H NMR of GG-*graft*-PANI showed peaks at δ 2.49, 3.60, 7.19, 7.36, and 7.58 ppm corresponded to anomeric hydrogens, sugar protons, —NH—, and protons of benzene ring, respectively. Peak for —NH— of the GG-*graft*-PANI has shifted; this may be due to intramolecular hydrogen bonding between —OH of GG with the incorporated PANI chains (Fig. 3).
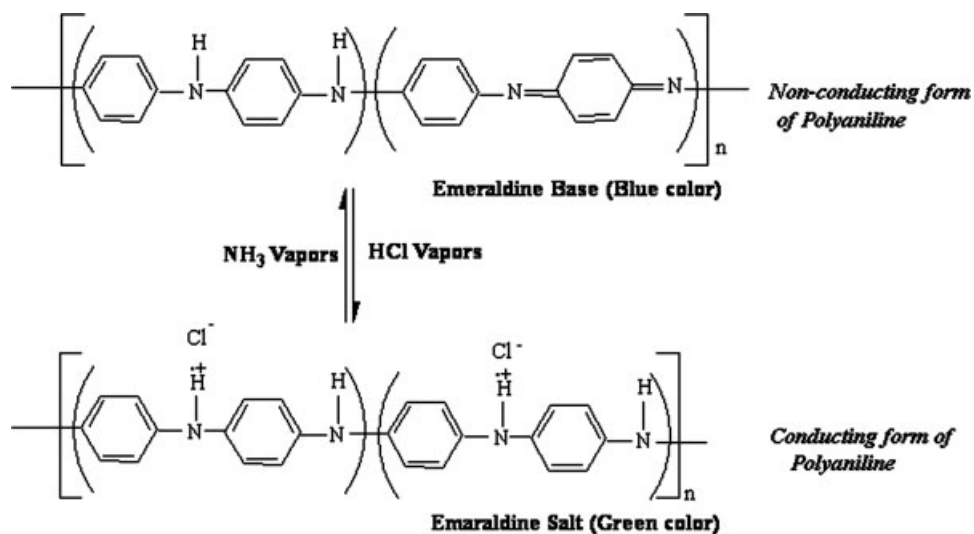
Scheme 5 Conversion of grafted PANI emeraldine base form into PANI emeraldine salt.

TABLE I
Electrical Conductivity of Parental Polymers and Graft Copolymers at pH Different Conditions

S. No.	Polymer bulk sample	%G	pH	Solubility in water	Electrical conductivity (S/cm)
1.	PANI-HCl	–	1	Insoluble	0.457
2.	PANI	–	12	Insoluble	3.1×10^{-5}
3.	GG	–	6.8	Soluble	11.95×10^{-6}
4.	GG-*graft*-PANI	230	1	Soluble	1.6×10^{-2}
5.	GG-*graft*-PANI	230	12	Soluble	6.8×10^{-5}
6.	GG-*graft*-PANI	220	1	Soluble	1.08×10^{-2}
7.	GG-*graft*-PANI	107	1	Soluble	4.7×10^{-3}
8.	GG-*graft*-PANI	58	1	Soluble	5.2×10^{-4}

XRD of the pure GG, PANI, and GG-*graft*-PANI further supported the copolymerization (Fig. 4). XRD spectra of the grafted GG showed increased crystallinity of 2θ 20–30°, due to grafting of PANI onto GG backbone, while XRD of the GG and PANI showed amorphous in nature.

Grafting is clear from the TGA that the GG-*graft*-PANI has more thermal stability than the GG and PANI both. In GG the first weight lost (∼ 8%) is due to loss of adhered water, thereafter the decomposition onsets at 200°C and up to 220°C, 32% weight loss was observed while up to 600°C, almost 63% weight is lost. In PANI, three stages of weight loss is observed, the first 10% weight loss was observed up to 120°C which may be due to loss of bound and adhered water, up to 300°C, a second weight loss of 28% was observed, and third weight loss triggers 300°C and about 56% weight is lost up to 600°C. Whereas in case of GG-*graft*-PANI, 6% weight loss is observed due to bound water up to 185°C, and first weight loss is triggered at and up to 400°C only 27% loss in weight is observed, after this it degrades slowly and a total loss of 42% is observed till 600°C (Fig. 5).

The surface morphology of GG has been modified with the incorporation of PANI that is clearly evidenced by the SEM pictures (Fig. 6). In the GG, aggregated molecules form porous clusters with rough surface topology, while PANI has clustered in to flower-like structure. The copolymer showed mixed pattern, where clusters are bigger, more symmetrical, and porous with flower-like appearances.

The GG-*graft*-PANI showed interconversion from emeraldine base to emeraldine salt, and color changed blue to green during the process of doping–dedoping with HCl. It is evidenced that grafted biomaterial has redox property of PANI.[30] Scheme 5 shows interconversion of grafted PANI emeraldine base form into PANI emeraldine salt like PANI along the GG backbone and created redox surface onto the GG-*graft*-PANI.

The DC electrical conductivity of GG-*graft*-PANI, PANI, and GG of bulk sample were measured under laboratory conditions. All the results are summarized in Table I. The value of DC electrical conductivity of GG-*graft*-PANI was found almost 10^4 times higher than that of pure GG. It is due to incorpora-

tion of PANI onto GG backbone. The bulk electrical conductivity of GG-*graft*-PANI was found to increase with increasing the %grafting. When pellet of the GG-*graft*-PANI was exposed with HCl vapors, the color of the pellet was immediately changed from blue to green, and again with NH_3 vapor the color of the pallet turns back to blue. It is due to interconversion of emeraldine salt to emeraldine base of the PANI chains grafted onto GG backbone, therefore electrical conductivity of GG-*graft*-PANI (bulk sample) was shifted at lower side.[31] Hence, GG-*graft*-PANI holds redox surface like PANI and may be promising alternative smart material for the sensor applications.

CONCLUSIONS

A water-soluble conducting copolymer of PANI onto GG was synthesized in aqueous acidic medium using peroxydisulfate as initiator/oxidant. The optimum grafting conditions were found to be at $[(NH_4)_2S_2O_8]$ 0.55M; [aniline] 0.15M; [hydrochloric acid] 0.5M; [GG] 4.0 g/L; temperature 25°C ± 0.2°C, and time 75 min, and found 65.71 %efficiency with 230 %G. The solubility of copolymer in water was not obtained up to 230 %G. The maximum bulk electrical conductivity of the copolymer was 1.6×10^{-2} S/cm at pH 1. The grafted materials have hybrid properties of GG biopolymer and PANI both. In conclusion, grafted biopolymers from renewable plant sources, like, *Cyanaposis tetragonolobus* could be usefully exploited for making environmental-friendly semiconductor devices by grafting with PANI, and would be novel materials for the fabrication of various electronic sensors.

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