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### Gum Arabic-Graft-Polyaniline: An Electrically Active Redox Biomaterial for Sensor Applications

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# Gum Arabic-Graft-Polyaniline: An Electrically Active Redox Biomaterial for Sensor Applications

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The radical copolymerization of gum Arabic and polyaniline was done using peroxydisulfate as oxidant and initiator. The produced copolymer was electrically active, water-soluble and has redox property. The redox behavior of the copolymer was studied using cyclic voltammetry and compared with the pure polyaniline. The UV-vis, FTIR, <sup>1</sup>H-NMR, XRD, TGA and SEM techniques have been used for the characterization of grafted biomaterial. The copolymerization was systematically optimized and it was observed that solubility of the copolymers in water decreased with an increase in % G. The intrinsic viscosity of the copolymer has been estimated to be 10.8 dL/g, which indicates an appreciably high molecular weight for the copolymer. The shelf life and electrical conductivity of the copolymer were monitored to evaluate their potential application in the fabrication of semiconductor sensor devices. Results are discussed and proposed a plausible mechanism for the copolymerization.

**Keywords:** gum arabic; polyaniline; graft copolymer; conducting biomaterial; redox behavior; sensor

## 1 Introduction

The intrinsically conducting polymers (ICPs) have found wide applications (1–6) such as solar materials, sensors, artificial muscles, actuators, corrosion protection, electronic shielding, environmental sensitive membranes, visual displays and as components in high-energy batteries. The commercial CPs like polyaniline (PANI) has limitations (7) in synthesis, solubility and mechanical properties. The chemically synthesized PANI has low molecular weight, which results in low mechanical strength. The low mechanical strength of PANI is responsible for the poor adhesion on solid substrates (8) that has limited its utility in applications such as fabrication of sensor devices. The shortcoming of solubility of PANI has been effectively overcome by its copolymerization with water-soluble synthetic polymers (9–11). Recently, few works have been reported on the copolymerization of biopolymers and polyaniline (12–15), but having poor electrical conductivity. In the present work, considerable effort has been devoted to synthesize a novel biomaterial, gum Arabic-graft-polyaniline (GA-g-PANI) having better mechanical properties due to its high molecular weight, while maintaining redox behavior and electrical conductivity.

As water soluble, low cost, degradable, biocompatible, high molecular weight, branched, electrical conducting biopolymer (16) gum Arabic (GA) was used for the synthesis of GA-g-PANI. GA has unique physiochemical properties (17) (having –OH and –COOH groups offers self doping) that after copolymerization with PANI may act as excellent environmentally friendly and biocompatible redox electroactive material. However, no attention has been paid to the chemical copolymerization of electrically active biopolymer and polyaniline for the attractive fictionalizations of polyaniline for its broader *in vivo* and *in vitro* applications. GA exudated from *Acacia senegal* has a wide range of industrial applications (17) It is a ramified, hetero-polysaccharide and made up of D-galactose, L-arabinose, L-rhamnose, D-glucuronic acid and 4-O-methyl-D-glucuronic acid in 40:24:13:21:2 molar ratio (18). GA possesses a linear backbone of  $\beta(1 \rightarrow 3)$  linked D-galactopyranosyl units to which D-galactopyranosyl, L-arabinofuranose and L-rhamnopyranose are attached as the side chains through  $\alpha(1 \rightarrow 6)$ ,  $\alpha(1 \rightarrow 3)$  and  $\alpha(1 \rightarrow 4)$  linkages, respectively. The  $\beta$ -D-glucopyranose and 4-O-methyl- $\beta$ -D-glucuronopyranose units are found as terminating groups. These uronic acid components are responsible for the polyanionic character of the biopolymer (19).

In the present study, PANI was grafted on to GA in order to synthesize highly fictionalized, water soluble, biodegradable, high molecular weight, electrically conducting and redox biomaterial. In the serial of studies, the reaction mechanism,

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crystallization, morphology, electrical, thermal and redox properties were extensively investigated. It was expected that results would be helpful in leading to new promising conducting polymers useful in the fabrication of sensor devices. The major advantage of this work is for use as natural resources and to increase their utility in a broader perspective by chemical modification.

## 2 Experimental

### 2.1 Materials

Gum Arabic (E. Merck;  $M_w$   $1.64 \times 10^5$ ) and aniline (E. Merck) was used after purification. Ammonium peroxydisulfate (Aldrich) was used without further purification.

### 2.2 Preparation of Gum Acacia Dispersion

GA dispersion was prepared (19) by weight (wt%), known amounts of biopolymer powder were dispersed in deionized water under gentle stirring at  $40 \pm 2^\circ\text{C}$  for the period of 4–6 h. The initial pH of 1% GA dispersion was found to be 4.6.

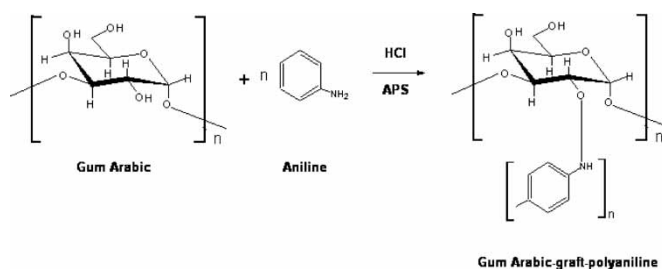
### 2.3 Synthesis of Polyaniline (PANI)

PANI was synthesized by oxidative polymerization (20) of doubly distilled aniline, dissolved in aqueous HCl (1 M), using ammonium peroxydisulfate (APS) in aqueous HCl (1 M) as an oxidant at  $4^\circ\text{C}$ . Aniline (0.5 M) dissolved in 200 ml of an aqueous solution of HCl (1 M) and APS (0.54 M) was dissolved in 200 ml HCl (1 M). The oxidant solution was then added slowly to the aniline solution with continuous stirring for 2 h and then kept in a refrigerator overnight. The reaction mixture was filtered and washed with HCl (1 M) till the filtrate became colorless and then with doubly distilled water until the filtrate became acid free. The polymer was ground to a fine powder, and low molecular weight oligomers were removed from polyaniline by soxhlation with acetone. The resulting PANI was dried at  $60^\circ\text{C}$  in an air oven for 48 h and stored in a desiccator.

### 2.4 Synthesis of GA-g-PANI

Gum Arabic-graft-polyaniline (GA-g-PANI) was synthesized by a calculated amount of the GA dissolved in a minimum required amount of distilled water in a 150 ml flask. To this solution, a calculated amount of the aniline and hydrochloric acid (HCl) were added and the total volume was made up to 25 ml. The flask was thermostated at  $40 \pm 0.2^\circ\text{C}$  with continuous stirring (Scheme 1).

After 30 min, a definite amount of peroxydisulfate was added and this was taken as zero time. Grafting was allowed for 2 h. The reaction mixture was neutralized by 5% aqueous NaOH and copolymer was precipitated with



**Sch. 1.** Gum Arabic-graft-polyaniline formed from the chemical oxidative-free radical copolymerization.

absolute ethanol. The resulting precipitate was washed with NMP in order to separate PANI (homopolymer) from the copolymer. The copolymer was ground to a fine powder and low molecular weight PANI oligomers were removed from GA-g-PANI by soxhlation with acetone. Finally, the products were dried for several days in a vacuum oven at  $50^\circ\text{C}$ .

The percentage and efficiency of grafting were calculated by the following equations (21):

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

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

Where  $W_1$ ,  $W_0$  and  $W_2$  denote the weight of the GA-g-PANI, respectively, the weight of GA and weight of the aniline monomer were used.

### 2.5 Cyclic Voltammetry Measurement

Cyclic voltammetry (CV) for GA-g-PANI and PANI solutions was carried out on a Potentiostat-Galvanostat, using a three-electrode cell configuration platinum wire as working electrode, platinum foil as counter and Ag/AgCl as a reference electrode, respectively. The CV (1% GA-g-PANI and 1% PANI dissolved in 1 M HCl) was run between  $-400$  mV to  $1600$  mV.

### 2.6 Intrinsic Viscosity Determination

The intrinsic viscosity of the copolymer (sample obtained at optimum condition; 149% G) was measured using dilute solution viscosimetry with an Ubbelohde viscometer at  $30^\circ\text{C}$ . In each case, flow time for the aqueous solutions of the copolymer samples was measured at five different concentrations.

### 2.7 Biodegradability Measurement

Biodegradability of the copolymer was measured by preparing a copolymer solution, a weighed quantity of the copolymer was dissolved in a minimum quantity of water by soaking overnight, followed by stirring, and then it was made up to a desired concentration and agitated vigorously for about 15 min till the solution became viscous and

homogeneous. The measurements were made using UV-Vis at 30°C. UV-Vis spectra of GA-g-PANI (samples with 149%G) solution were taken after different time intervals.

### 2.8 Electrical Conductivity Measurement

The surface DC electrical conductivity of the GA-g-PANI rectangular pressed pallets (pressure 6 tons/cm<sup>2</sup>) was measured (8) by a Kithley four-probe system using a 224 programmable current source, 181 nano voltmeter and 195A digital multimeter. The electrical conductivity ( $\sigma$ ) was calculated using the following equations:

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

$$\sigma = 1/\rho \quad (4)$$

Where  $\rho$ ,  $R$ ,  $A$ ,  $l$  and  $\sigma$  are resistivity ( $\Omega$  cm), resistance ( $\Omega$ ), area of the pallet (cm<sup>2</sup>), length of the pallet (cm) and conductivity (Scm<sup>-1</sup>), respectively. The electrical conductivity measurements were carried out at intervals of 20 min. The effect of pH on electrical conductivity of GA-g-PANI was studied. All the measurements were repeated three times at intervals of 20 min.

### 2.9 Characterization of GA-g-PANI

An Ocean Optics HR 4000 High Resolution Spectrophotometer using an aqueous solution of samples recorded the UV-vis spectra. FTIR spectra were recorded on a PK-1310, Perkin-Elmer instrument by making a pellet with dehydrated KBr in reflectance mode.

<sup>1</sup>H-NMR was done on a Bruker DRX-300 NMR spectrometer with (CD<sub>3</sub>)<sub>2</sub>SO as a solvent and SiMe<sub>4</sub> as an internal standard. X-ray diffractogram was taken by a Rigaku Rotaflex, RAD/Max-B, Rigaku Corporation, Japan instrument with a scanning speed of 1° per minute. TG was recorded on a Rigaku Thermoflex, PTC-10A, Rigaku Corporation, Japan with 10°C per min heating rate and Alumina as reference material. A scanning electron microscope (SEM) was done on a JEOL-840, JEOL Corporation, Japan by making a film of desirable size and coated with gold. The DC electrical conductivity of the samples was measured by making rectangular pressed pallets (pressure 10 tons/cm<sup>2</sup>) and using a Kithley four-probe system using a 224 programmable current source, 181 nano voltmeter and 195A digital multimeter. Cyclic voltammetric measurements were carried out on a Potentiostat/Galvanostat (Princeton Applied Research, Model No. 273A) hooked to a computer.

## 3 Results and Discussions

### 3.1 Determination of Optimal Grafting Conditions

To optimize the condition for grafting of PANI on to the GA, a concentrations of ammonium peroxydisulfate, hydrochloric

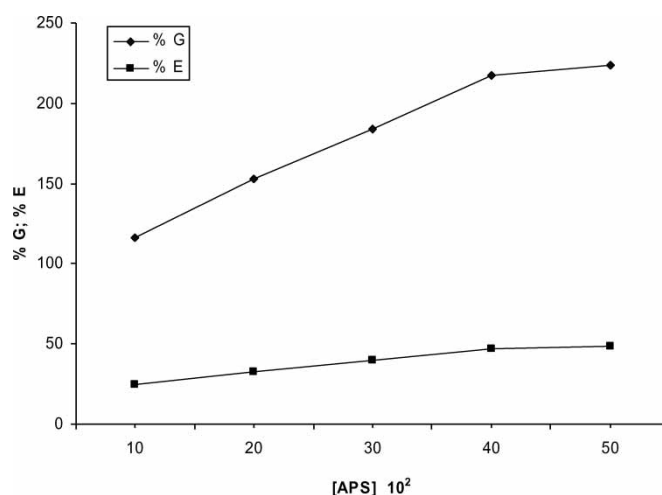
acid, aniline monomer, weight of the GA, reaction temperature and time for the copolymerization were varied keeping the total volume of the reaction mixture fixed at 25 ml, respectively. It was observed that the (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>/hydrochloric acid system can be efficiently used to graft copolymerization of polyaniline on to GA, where maximum 64.09% E could be achieved.

### 3.2 Effect of Ammonium Peroxydisulfate Concentration

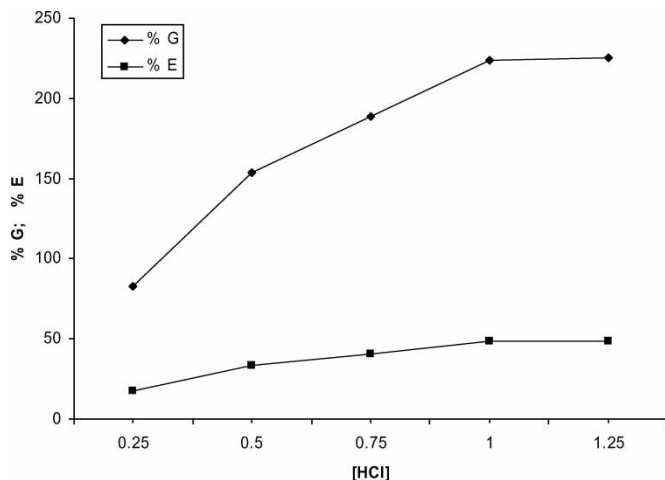
%G increased with an increase in initiator/oxidant concentration and reached a maximum value at 0.5 M of peroxydisulfate at a fixed concentration of 0.2 M aniline, 1 M hydrochloric acid and 4 g/L GA at 40 ± 0.2°C for 2 h (Figure 1). It was observed that %G increases within the peroxydisulfate concentration range from 0.1–0.5 M. It may be due to the fact that at this concentration range, the produced sulphate ions radical activate the backbone of GA and simultaneously produced PANI ion radical takes place immediately followed by the graft copolymerization of the monomer onto the backbone. Therefore, %E was increased with the increase in the concentration of peroxydisulfate.

### 3.3 Effect of HCl Concentration

The effect of acid was studied in the range 0.25–1.25 M at a fixed concentration of 0.5 M peroxydisulfate, 0.2 M aniline and 4 g/L GA at 40 ± 0.2°C for 2 h (Figure 2). It was observed that both %G and %E increases with the increase in concentration of acid, which may be due to the additional protonation of aniline monomer and accelerates the propagation of aniline, which can generate more PANI ion radicals.



**Fig. 1.** Effect of ammonium peroxydisulfate concentration at fixed concentration of 0.2 M aniline, 1 M hydrochloric acid and 4 g/L GA at 40 ± 0.2°C for 2 h.



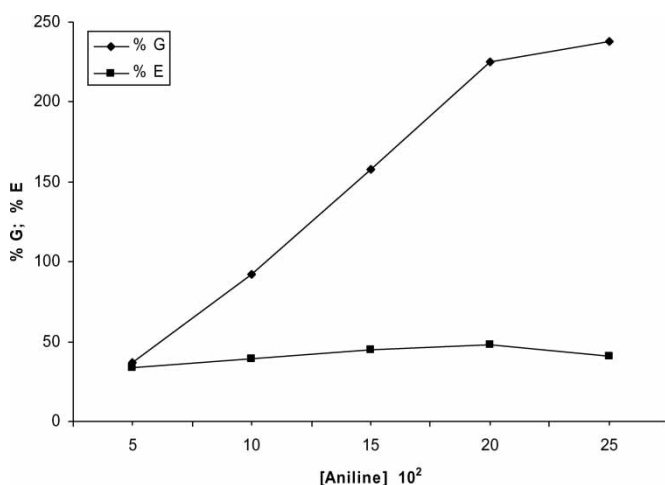
**Fig. 2.** Effect of HCl concentration at a fixed concentration of 0.5 M peroxydisulfate, 0.2 M aniline and 4 g/L GA at  $40 \pm 0.2^\circ\text{C}$  for 2 h.

### 3.4 Effect of Monomer Concentration

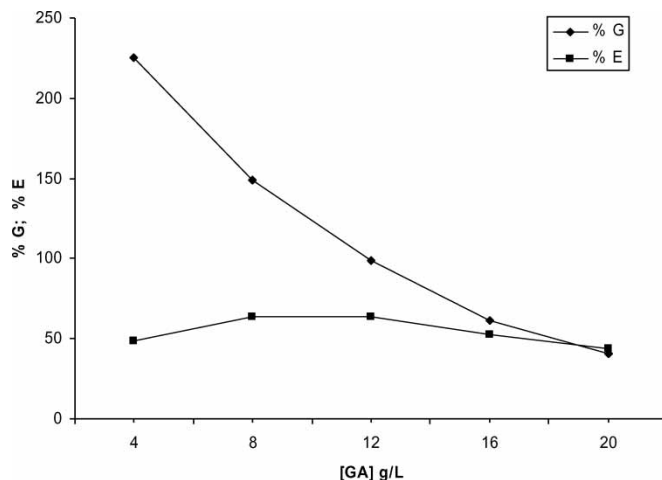
The increase in the concentration of monomer from 0.05–0.25 M, results in the increase of %G and %E (up to 0.2 M) under the fixed concentration of 0.5 M peroxydisulfate, 1.25 M HCl and 4 g/L GA at  $40 \pm 0.2^\circ\text{C}$  for 2 h (Figure 3). The increase in %G and %E may be due to the formation of more PANI radical ions, while generating more grafting sites and availability of extra aniline monomer for grafting. When increasing concentration beyond 0.2 M, the %E decreases slightly, and this may probably be due to the formation of PANI homopolymer.

### 3.5 Effect of Gum Arabic Concentration

The effect of GA concentration was studied in the range of 4–20 g/L with the constant concentration of [peroxydisulfate]



**Fig. 3.** Effect of aniline monomer concentration under the fixed concentration of 0.5 M peroxydisulfate, 1.25 M HCl and 4 g/L GA at  $40 \pm 0.2^\circ\text{C}$  for 2 h.

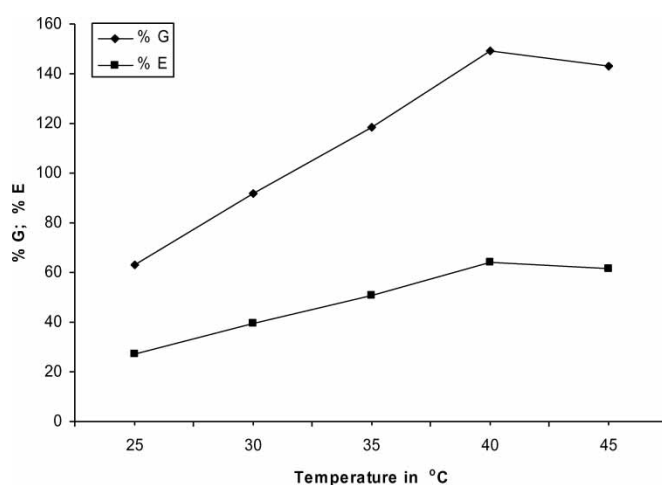


**Fig. 4.** Effect of gum Arabic concentration with the constant concentration of [peroxydisulfate] 0.5 M, [acid] 1.25 M, [aniline] 0.2 M at  $40 \pm 0.2^\circ\text{C}$  for 2 h.

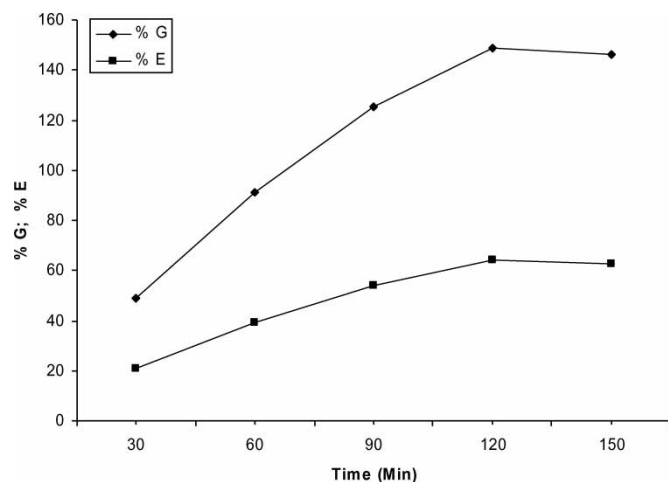
0.5 M, [acid] 1.25 M, [aniline] 0.2 M at  $40 \pm 0.2^\circ\text{C}$  for 2 h (Figure 4). It was found that %E increased up to 8 g/L GA concentration, (which may be due to the additional availability of the macro radicals), thereafter the %G and %E decreases, which may be due to the increase in viscosity of the reaction medium causing an obstacle in the normal reaction.

### 3.5 Effect of Temperature

The grafting reaction was carried out at different temperature ( $25\text{--}45^\circ\text{C}$ ) keeping other variables constant; [peroxydisulfate] 0.5 M; [acid] 1.25 M; [aniline] 0.2 M and [GA] 8.0 g/L for 2 h (Figure 5). Maximum %G was obtained at  $40^\circ\text{C}$ . The observed increase in %G may be attributed to the increase in the number of collisions between the monomer and the gum Arabic molecules that results in a decrease in the viscosity of the medium at higher temperature. However, beyond  $40^\circ\text{C}$ , the



**Fig. 5.** Effect of temperature keeping other variables constant; [peroxydisulfate] 0.5 M; [acid] 1.25 M; [aniline] 0.2 M and [GA] 8.0 g/L for 2 h.



**Fig. 6.** Effect of grafting time keeping other variables constant; [peroxydisulfate] 0.5 M; [acid] 1.25 M; [aniline] 0.2 M and [GA] 8 g/L at  $40 \pm 0.2^\circ\text{C}$ .

%G was slightly decreased which may be due to an increase in the ionic mobility of PANI ion radical and forms additional homopolymer.

### 3.6 Effect of Grafting Time

The grafting reaction was carried out at different times (30–150 min) keeping other variables constant; [peroxydisulfate]

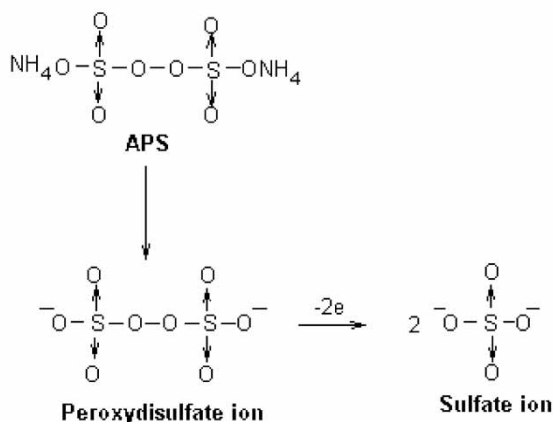
0.5 M; [acid] 1.25 M; [aniline] 0.2 M and [GA] 8.0 g/L at  $40 \pm 0.2^\circ\text{C}$  (Figure 6). Maximum % G was obtained at 120 min. The %G increased rapidly with an increase in time up to 120 min. after which it levels off. It could be attributed to a decrease in concentration for both initiator and monomer, thereby a reduction in the number of sites on the backbone accessible for grafting as the reaction procedure.

### 3.7 Mechanism for Graf Copolymerization

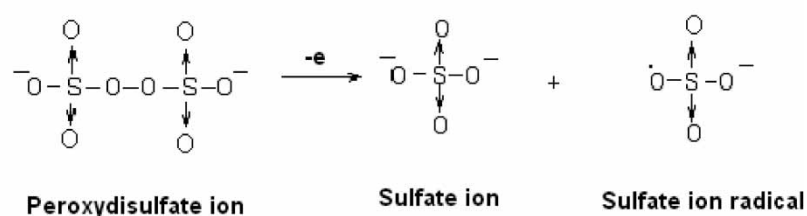
Many workers (21, 22) have explored free radical copolymerization of vinyl monomers on to biopolymers using peroxydisulfate. A chain mechanism (21) is involved due to formation of sulphate ion radicals ( $\text{SO}_4^{\cdot-}$ ), which are well-known ion chain carriers for the graft copolymerization (Scheme 2). At the same time, APS stimulates the oxidative polymerization reaction of aniline (23) via a medium of cationic radicals and form PANI and PANI radicals (Scheme 3). Finally, GA macro radicals and PANI cation radicals are combined to form a GA-g-PANI copolymer. The mechanism may be written as below:

$\text{SO}_4^{\cdot-}$  is the primary radical, generated from the ammonium peroxydisulfate (APS) by the reduction of one electron and are expressed as R $\cdot$  in Scheme 4. Simultaneously, APS generate  $\text{SO}_4^{2-}$  ions by the reduction of two electrons and act as oxidant. They initiate the oxidative polymerization of aniline, as the polymerization of the monomer is reported to be faster than the H abstraction from the biopolymer

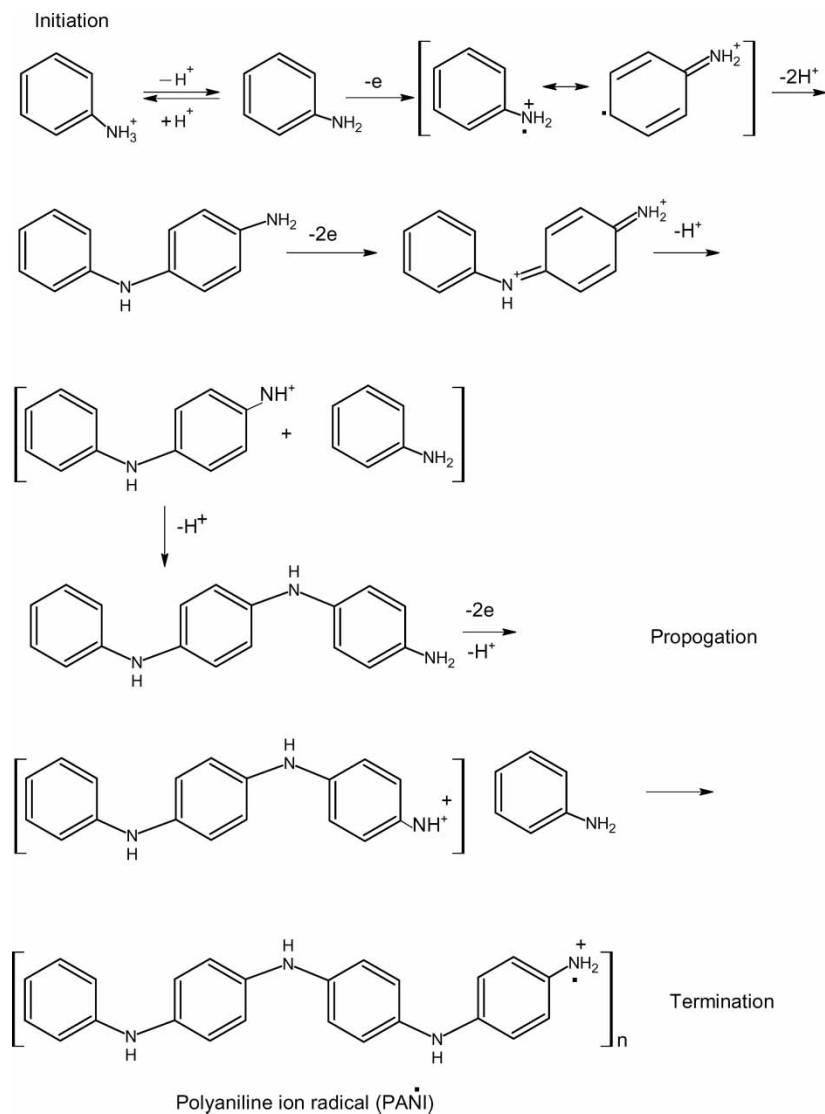
(1) Act as oxidizing agent, get reduced accepting  $2e^-$



(2) Formation of ion radical by one electron reduction

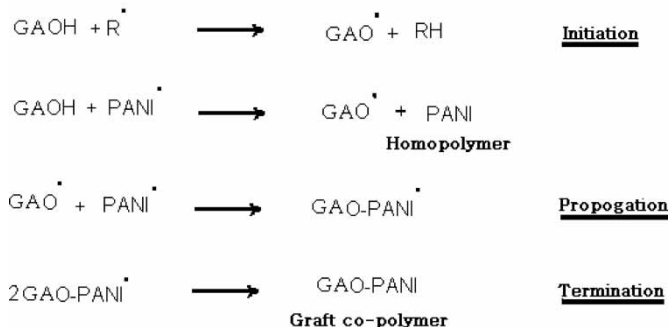


**Sch. 2.** Generation of primary radicals.



### Sch. 3. Formation of secondary radicals.

Where  $R^{\cdot}$  is  $1^{\circ}$  anion radicals i.e.  $SO_4^{\cdot-2}$  generated from Scheme-1  
 $Pani^{\cdot}$   $2^{\circ}$  cation radicals generated from Scheme-2  
 GAOH represents gum Arabic



### Sch. 4. Copolymerization of gum Arabic and polyaniline.

backbone (22). The macro radicals GAO may be generated by the abstraction of H by the growing polyaniline ion radical (PANI $^{\cdot}$ ) in the medium of acid, which may add onto the GAO $^{\cdot}$  macro radical generating new radical GAO-PANI $^{\cdot}$ . This chain will grow till it combines with other such chains to give a graft copolymer (Scheme 4).

### 3.8 Characterization of the Grafted Gum

A representative GA-g-PANI sample (sample with maximum %E) was characterized by UV-Vis, FTIR,  $^1H$ -NMR, XRD, TGA and SEM.

### 3.9 UV-Vis Spectra

The UV-Vis spectrum of the aqueous GA solution (0.1 wt%) showed a broad absorption peak at 298 nm due to the

presence of arabinogalactan components of the gum Arabic (19), while the solution of PANI in NMP had an absorption peak at 325 nm corresponding to the  $\pi$ - $\pi^*$  transition of benzenoid rings. 420 nm indicates the inter band charge transfer associated with the excitation of benzenoid to quinoid moieties resulting in protonation and doping (Figure 7B). The aqueous solution of GA-g-PANI (0.1 wt%) showed an absorption peak in the UV range at 299–325 nm, 430 nm, 520 nm and 600 nm. These are characteristic peaks of GA and PANI, respectively, but the peaks are shifted a little due to the effect of the solvent (Figure 7).

### 3.10 FTIR Spectra

FTIR spectra of the GA biopolymer (Figure 8C), show a broad strong band at  $3418\text{ cm}^{-1}$  due to stretching of the -OH group, band at  $2932\text{ cm}^{-1}$  indicating C-H linkages, at  $1720\text{ cm}^{-1}$  due to the -COOH group, at  $1634\text{ cm}^{-1}$  due to C=O stretching of the carbonyl group, at  $1423\text{ cm}^{-1}$ , the -OH bending of the acid group and another characteristic peak of the carboxylic group found at  $1254\text{ cm}^{-1}$  due to C=O stretching. Figure 8B showed the characteristic peaks of the emeraldine salt form of PANI (24), while GA-g-PANI showed the additional peaks to GA at  $2970\text{ cm}^{-1}$  due to aromatic C-H stretching,  $3361\text{ cm}^{-1}$  and  $3129\text{ cm}^{-1}$  N-H stretching and N-H stretch with hydrogen bonded  $2^0$  amino groups. Peaks at  $2864\text{ cm}^{-1}$  and  $2503\text{ cm}^{-1}$  due to C-H stretching of the -COOH group and at  $1527\text{ cm}^{-1}$  due to -CO-NH- stretching of the grafted chain and  $1460\text{ cm}^{-1}$  of N-H stretching with conjugation, these peaks confirm

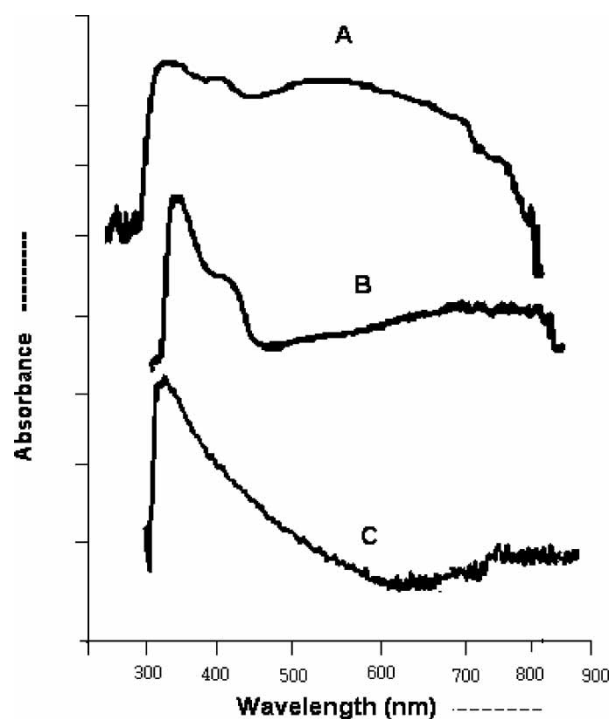


Fig. 7. UV-vis spectra of (A) aqueous solution of GA-g-PANI, (B) PANI in NMP, (C) aqueous solution of GA.

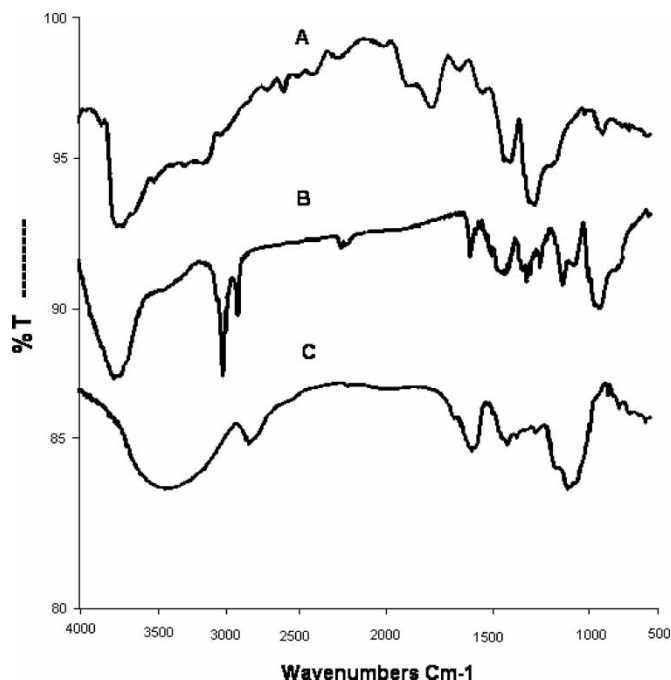


Fig. 8. FTIR spectra of (A) GA-g-PANI, (B) PANI, (C) GA.

grafting of PANI on to GA at the -OH sides of the biopolymer (Figure 8).

### 3.11 $^1\text{H-NMR}$ Spectra

$^1\text{H-NMR}$  of GA showed a peak at  $\delta$  2.51 ppm due to acid protons present in the sugar moiety and at  $\delta$  3.48 ppm due

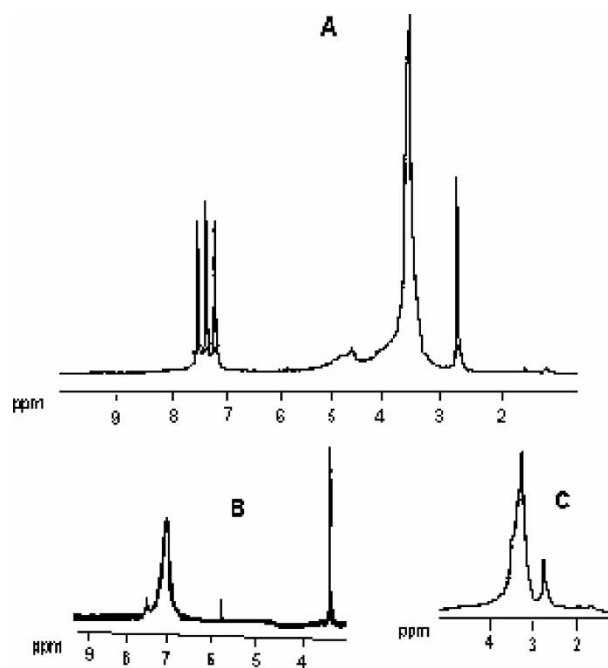
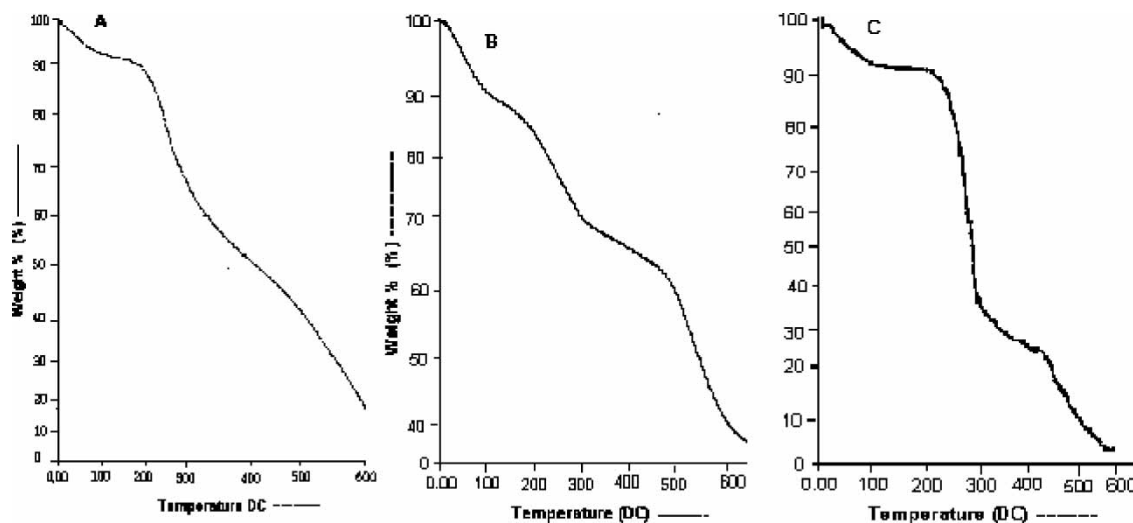


Fig. 9.  $^1\text{H-NMR}$  spectra of (A) GA-g-PANI; (B) PANI; (C) GA.





**Fig. 10.** TGA spectra of (A) GA-g-PANI; (B) PANI; (C) GA.

to sugar protons, while PANI-HCl showed a sharp peak at  $\delta$  3.35 ppm which corresponds to -NH- and -NH<sub>2</sub>-protons and the peak around 7 ppm assigned to protons on the benzene ring. The peak at 5.75 ppm assigned to a trace amount of water. The spectra of grafted GA showed peaks at  $\delta$  2.50 ppm,  $\delta$  3.50 ppm,  $\delta$  4.55 ppm, 7.17 ppm, 7.34 ppm and 7.51 ppm corresponded acid protons, sugar protons, -NH- and protons of benzene ring, respectively. The peak for -NH- of the grafted GA shifted; this may be due to intramolecular hydrogen bonding with the grafted PANI chain (Figure 9).

### 3.12 TGA

TGA of GA and PANI showed that decomposition onsets at 120 °C and 215 °C respectively, while in GA-g-PANI it starts at 249 °C indicating the grafted gum is more thermally stable than the pure GA and PANI, but once decomposition starts, the rapid weight loss was observed (Figure 10).

### 3.13 XRD Spectra

XRD of the GA, PANI and GA-g-PANI further supports grafting. (Figure 11). XRD spectra of the grafted GA showed a crystallinity area due to grafted PANI on GA backbone in the region of  $2\theta$  20–30°, while XRD of the GA and PANI showed that it was amorphous in nature.

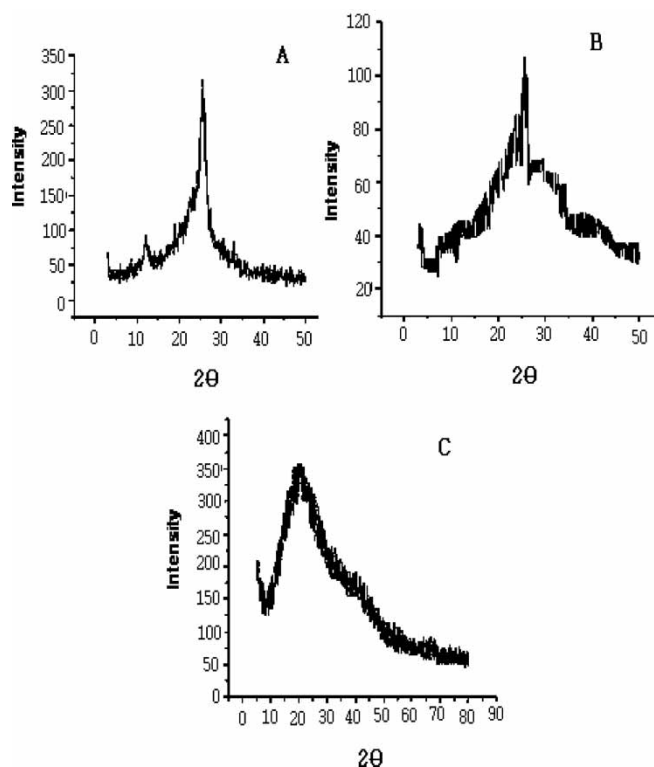
### 3.14 SEM

The scanning electron microscopy (SEM) was used to characterize the surface morphologies of the resulting GA-g-PANI. The SEM photographs of the grafted PANI (Figure 12A) were different than PANI (Figure 12B) and GA (Figure 12C). The surface evidence supports the

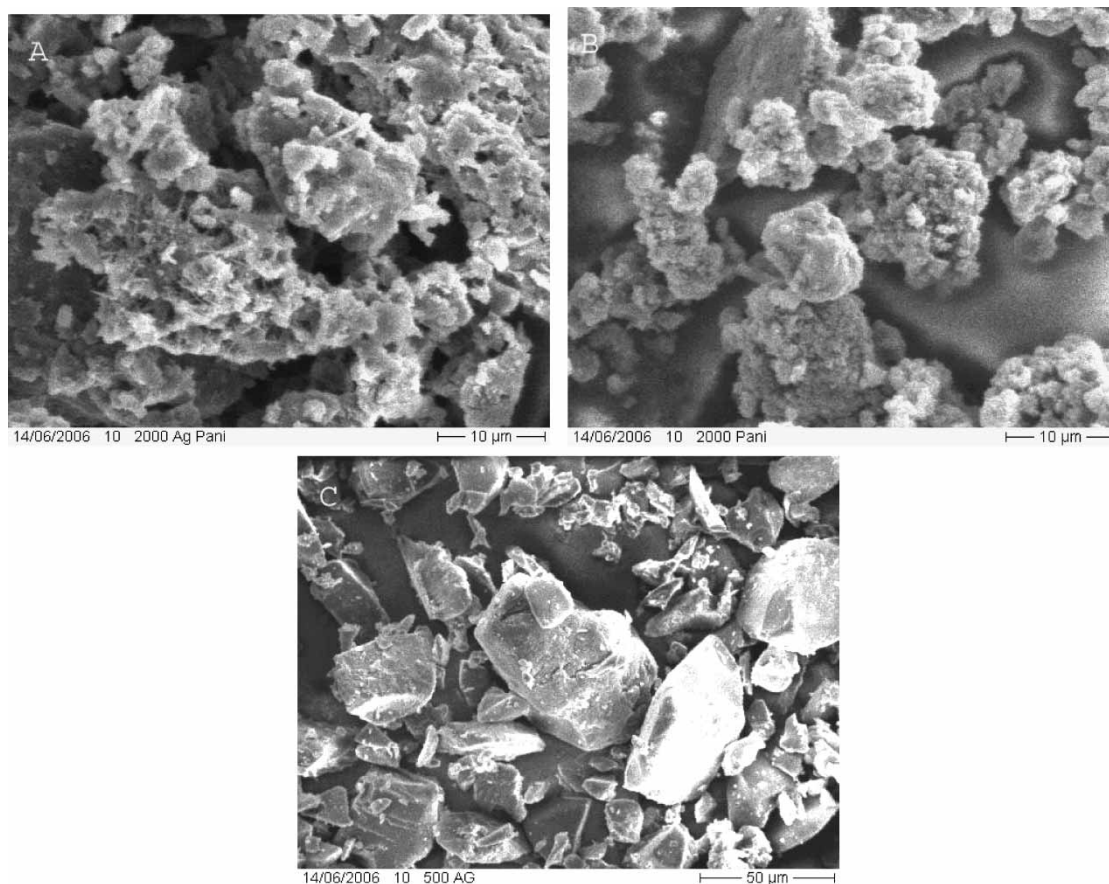
homogeneity of the uniform grafting of PANI on to the GA backbone.

### 3.15 Cyclic Voltammetry Measurements

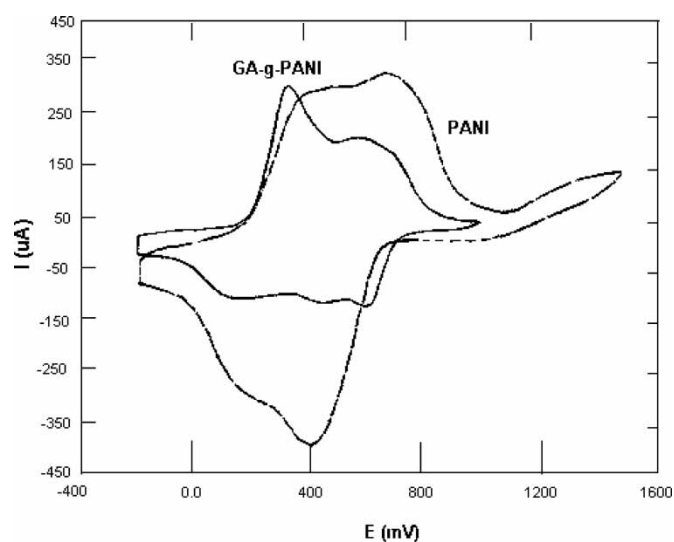
The redox property of the graft copolymer was investigated with cyclic voltammetry. Figure 13 shows a typical cyclic voltammogram of 1% PANI and 1% GA-g-PANI in 1M HCl at 50 mV/s scan rate, indicating that the grafted



**Fig. 11.** XRD spectra of (A) GA-g-PANI, (B) PANI, (C) GA.



**Fig. 12.** SEM pictures of (A) GA-g-PANI, (B) PANI, (C) GA.



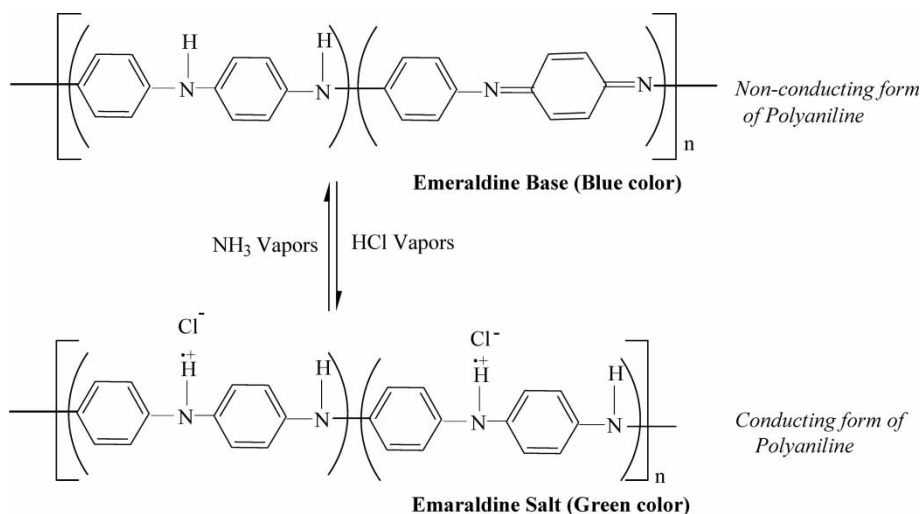
**Fig. 13.** Cyclic voltammograms of GA-g-PANI solution and pure PANI in 1M HCl, scan rate 50 mV/s.

**Table 1.** Conductivity measurement of polyaniline, gum arabic and grafted gum arabic

| Polymer   | %G   | pH | Conductivity                           |
|-----------|------|----|--|
| PANI      | —    | 1  | $0.742 \text{ Scm}^{-1}$               |
| GA        | —    | 1  | $4.73 \times 10^{-6} \text{ Scm}^{-1}$ |
| GA-g-PANI | 40.6 | 1  | $3.59 \times 10^{-4} \text{ Scm}^{-1}$ |
| GA-g-PANI | 92   | 1  | $6.83 \times 10^{-3} \text{ Scm}^{-1}$ |
| GA-g-PANI | 116  | 1  | $1.96 \times 10^{-2} \text{ Scm}^{-1}$ |
| GA-g-PANI | 149  | 1  | $5.18 \times 10^{-2} \text{ Scm}^{-1}$ |

**Table 2.** Effect of pH on conductivity of GA-g-PANI

| Polymer   | %G  | pH | Conductivity                           |
|-----------|-----|----|--|
| GA-g-PANI | 149 | 1  | $5.18 \times 10^{-2} \text{ Scm}^{-1}$ |
| GA-g-PANI | 149 | 3  | $9.06 \times 10^{-2} \text{ Scm}^{-1}$ |
| GA-g-PANI | 149 | 7  | $3.92 \times 10^{-3} \text{ Scm}^{-1}$ |
| GA-g-PANI | 149 | 10 | $7.31 \times 10^{-4} \text{ Scm}^{-1}$ |
| GA-g-PANI | 149 | 12 | $2.46 \times 10^{-6} \text{ Scm}^{-1}$ |



**Sch. 5.** Conversion of grafted PANI Emeraldine base form into PANI Emeraldine salt.

biomaterial has almost similar anodic peak potentials and peaks separation similar to that of PANI. These results indicate that the PANI grafted gum Arabic has almost similar redox behavior similar to pure PANI (24).

### 3.16 Intrinsic Viscosity Determination

The intrinsic viscosity  $[\eta]$  of the GA-g-PANI (149% G) was calculated by plotting  $\eta_{sp}$  vs.  $C$  and  $\eta_{inh}$  vs.  $C$  and then taking the common intercept at  $C=0$  of the best fitting straight line through the two sets of points. Here,  $C$  represents copolymer concentrations in g/dL. The  $\eta_{sp}$  and  $\eta_{inh}$  are specific and inherent viscosities and were calculated from the relation  $\eta_{sp} = \eta_{rel} - 1$  and  $\eta_{inh} = \ln \eta_{rel}/C$ . The  $[\eta]$  of the GA-g-PANI (149%G) was found to be 10.8 dL/g.

### 3.17 Biodegradation Study

The aqueous (sample of optimum conditions; 149% G) remains stable up to 3000 h at laboratory conditions, but beyond 3000 h, the copolymer solution biologically degraded. The degradation of GA-g-PANI solution was tested by taking UV-Vis spectra and observed no peaks.

The shelf life of the powder sample of GA-g-PANI was observed at laboratory conditions and has more than one year.

### 3.18 Electrical Conductivity Measurements

The DC electrical conductivity of grafted (sample of optimum condition; 149%G) and native biopolymer GA was measured under laboratory conditions. The results are summarized in Table 1. The value of DC electrical conductivity was found to be almost 10,000 times higher than that of the parental GA biopolymer. It is due to grafting of PANI on to the GA backbone. Doping with HCl gas and dedoping with  $\text{NH}_3$  vapors tremendously affected the electrical

conductivity of grafted GA. The surface conductivity of the rectangular pallet of the grafted GA was increased with the increasing exposure time of HCl gas and decreased with the increasing exposure time of  $\text{NH}_3$  vapors. The color of grafted GA was immediately changed from green to blue. It is due to formation of emeraldine salt to emeraldine base of the grafted PANI chain (23). The electrical conductivity of GA-g-PANI was found to be higher at pH 1 and very low at pH 12 (Table 2). It is also explained on the basis of conversion emeraldine salt to emeraldine base of the grafted PANI (Scheme 5). Therefore, GA-g-PANI could hold promise for sensor applications due to a redox surface like PANI.

## 4 Conclusions

A water-soluble, biodegradable, polyfunctional, high molecular weight, conducting and redox copolymer of gum Arabic and polyaniline was synthesized in aqueous acidic media using peroxydisulfate as initiator and oxidant. The optimum grafting condition was found to be at:  $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$  0.5 M; [aniline] 0.2 M; [hydrochloric acid] 1.25 M; GA 8.0 g/L, temperature,  $40 \pm 0.2^\circ\text{C}$ ; time, 2 h and it was found to have 64.09% efficiency. The solubility of copolymer in water was not obtained up to 149% G. The redox behavior of grafted biomaterial was almost similar to that of pure polyaniline. The intrinsic viscosity of the copolymer was calculated to be 10.8 dL/g. The aqueous solution of GA-g-PANI was biodegradable after 3000 h and the maximum electrical conductivity of the copolymer was  $5.18 \times 10^{-2} \text{ Scm}^{-1}$  at pH 1. The grafted materials have hybrid properties of both GA biopolymer and polyaniline. In conclusion, grafted biopolymers from renewable plant sources, like *Acacia senegal*, can be usefully explored for making environmentally friendly semiconductor devices by grafting with polyaniline,

and would be novel biomaterial for the fabrication of various sensors.

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