

Synthesis of Processible Doped Polyaniline-Polyacrylic Acid Composites

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ABSTRACT: Processible composites of emeraldine salt form of polyaniline (PANI) with polyacrylic acid (PAA) are synthesized and studied for their structural, electrical, mechanical, thermal, and electrochemical properties. The processible conducting composites of various weight percentage from 20 wt % to 90 wt % (of PANI) have been prepared by mixing the PANI and PAA under vigorous stirring and sonication conditions. Self-standing films of electroactive homogeneous composites are obtained by solution casting method. A significant improvement in processibility, crystallinity, and thermal stability is observed in the composites; however, the electrical conductivity decreased remarkably as the percentage of PANI is decreased in the composites. The 60 wt % PANI-PAA composite showed crystalline structural

property with orthorhombic crystal system and cell parameters as $a = 5.93\text{\AA}$, $b = 7.57\text{\AA}$, and $c = 10.11\text{\AA}$. The 60 wt % PANI-PAA composite also showed better thermal stability and highest capacitance amongst all the composites and used as an active material for development of electrochemical capacitors (parallel plate assembly). The processible composites based electrochemical capacitors using 0.5 M NaClO₄-Acetonitril electrolyte showed super capacitance with ease in fabrication and cost effectiveness in comparison to other similar materials based capacitors. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 874–882, 2009

Key words: conducting polymer; polyaniline; polyacrylic acid; polymer composite; electrochemical capacitor

INTRODUCTION

Polyaniline (PANI), one of the most studied conducting polymers, has attracted considerable attention over recent years due to environmental and thermal stability as well as its electrical properties for many technological applications,^{1–4} such as semiconducting devices,⁵ sensors,^{6–8} batteries and capacitors,^{9–16} electrochromic display devices,^{17,18} etc. PANI is composed of benzenoid and quinoid rings bound by nitrogen atoms, which form amine or imine groups. Amine groups exist in the fully reduced PANI structure (leucoemeraldine base), however, fully oxidized polymer chains (pernigraniline base) contain imine groups solely. Both of these states of the polymers or intermediate oxidized states are non-conducting. Emeraldine base (EB) form of PANI composed of equal numbers of amine and imine groups, which can be easily transformed to the conducting form (emeraldine salt, ES) by protonation (doping) with acid.¹⁹ In protonation or doping, acid molecules react with imine groups and introduce positive charges (polaron and bipolarons)

into the chain, which is responsible for conductivity.²⁰

Doped conducting polymers (including PANI) are hard to process due to their poor solubility in common solvents and exhibit poor physical and mechanical properties.^{21,22} To overcome this problem, one of the recent trends is the formation of PANI composites with conventional polymers. In this modification PANI is allowed to diffuse in an insulating polymer matrix such as polymethyl methacrylate,²⁰ polyvinyl carbazole,²³ poly(vinyl alcohol),^{24,25} nylon 6,²⁶ polycarbonate,²⁷ etc. The use of insulating polymer improves the mechanical, thermal, and chemical properties of the PANI. However, due to insulating polymer matrix electroactivity and conductivity of such composites decrease significantly. Another alternative method to improve the PANI is by doping with macromolecular/poly acids such as polyacrylic acid (PAA),^{11,28–32} polystyrenesulfonic acid,³³ etc. However, the electroactivity, processibility, and conductivity of the composites are still a challenge for the researchers. Moreover, formation of homogeneous composites is rather difficult. There is a need to get a real composite of conducting polymer of desired properties.

Two methods are common and used for the composite formation, one by mixing of pre prepared PANI with insulating polymers in various weight

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percentages (simple solution mixing) and second by polymerization of PANI in the presence of insulating polymer (in-situ technique).^{11,28,29,31} However, homogeneity and doping of conducting polymers in composites are major problems in both the methods due to insoluble nature of doped PANI and weak acidic nature of macromolecular acids. In addition, in in-situ technique it is also difficult to control the percentage of PANI in the composites. To achieve homogeneous composite with improved stability, mechanical property, crystallinity and electroactivity, we report a modified method for composite formation by slow addition of chloride doped PANI (emeraldine salt, ES) in dilute PAA aqueous solution under vigorous stirring and sonication condition at higher temperature. The synthesized processible doped PANI-PAA composites of various weight percentages are discussed and reported for the first time as an active material for the development of electrochemical capacitor using NaClO₄-Acetonitril electrolyte.

EXPERIMENTAL

Materials

Aniline, ammonium peroxodisulphate ((NH₄)₂S₂O₈) and acetonitrile (HPLC grade) were obtained from Merck, India. Polyacrylic acid (PAA, $M_w = 2100$) and sodium perchlorate were obtained from Aldrich (Milwaukee, WI) chemicals. Acetonitrile (AN) was obtained from Sisco Research Laboratory (SRL), India. Aniline was purified by vacuum distillation before use. ITO glass plates were purchased from Vision Tek System Ltd. United Kingdom of surface resistance 12 ohms per square cm and 90% transmittance at 550 nm. All other chemicals used were of analytical grade. Double distilled water was used in the experiment.

Instruments

Four probes assembly (Raman Scientifics, Roorkee, India) connected with Keithly, make digital multimeter and current source measurement instrument (model 2000) is used for conductivity measurements. Electrochemical workstation (mode I700C), CH-Instrument Inc., is used for the electrochemical characterization using three electrodes assembly. UV-visible study was done with Lamda 25 spectrophotometer of Perkin Elmer, Germany (Obtained under DAAD Instrument grant). XRD and FTIR characterizations were carried out using 18 kW rotating anode powder X-ray diffractometer, Rigku, Japan and Thermo model 5700 FTIR (Germany) respectively. TGA studies were carried out using Perkin Elmer, Germany (Pyris Diamond) and SEM studies were carried out using JEOL840A (Japan), respectively.

Chemical synthesis of PANI

PANI is synthesized using ammonium per oxodisulphate as an oxidizing agent. Ammonium per oxodisulphate solution of ~ 0.1 M (4.5 g in 200 mL of 2.5 N HCl) was made and pre-distilled aniline (2 mL) was drop wise added with vigorous stirring at bath temperature below 5°C. After complete addition of aniline (in 30 minutes), it was stirred for another 2 h at low temperature in stoppered conical flask. The solution was kept in air tight flask for 10–15 hrs at room temperature ($\sim 28^\circ\text{C}$) for complete precipitation of PANI. A dark bluish precipitate was obtained and it was filtered followed by 3–4 times washing with 0.1 M HCl. Finally precipitate was washed with 5–10 ml of methanol and dried at 80°C in vacuum oven. PANI in powdered form was obtained with 85% yield and stored in vacuum desiccator for further use.¹¹

Synthesis of PANI-PAA composites

A typical composition of PANI-PAA composite was prepared by dissolving 200 mg of doped (emeraldine salt) PANI and 800 mg of PAA in 2 mL of water to get a composite of 20 wt % PANI-PAA composition (i.e., PANI is 20 wt % and PAA is 80 wt %). PANI (emeraldine salt) was added slowly in aqueous solution of PAA with vigorous stirring and ultrasonication for 15–20 minutes followed by 6 hrs stirring in a closed flask at higher temperature. PANI was introduced in the PAA matrix through diffusion to get homogeneous composites. Other compositions viz. 40, 50, 60, 80, and 90 wt % were made under similar conditions as used for 20 wt %.

Development of electrochemical capacitor

An electrochemical capacitor was developed using doped PANI-PAA composites using parallel plate assembly. The processible conducting composite film was coated over ITO glass plates (one side conducting) by dip coating/solvent evaporation technique. Electrical connections from each ITO plates were taken by soldering a copper wire with silver paint. Composite coated ITO plates were assembled in a small glass cell using Teflon separator and filled with 0.5 M NaClO₄-AN electrolyte. The geometrical area of the capacitor was maintained as 1 cm².

RESULT AND DISCUSSION

Various compositions of PANI-PAA composites were prepared and studied for their structural, electrical, mechanical, thermal, and electrochemical properties. Composites were prepared by mixing the PANI and PAA in water by stirring followed by sonication at

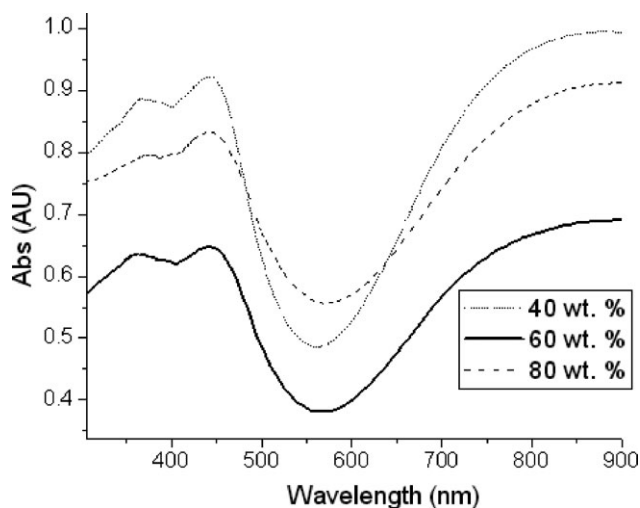


Figure 1 Absorbance spectra of PANI-PAA of (A) 40 wt %, (B) 60 wt %, and (C) 80 wt % of PANI taken in 0.1 M HCl.

room temperature as discussed under experimental. It was observed that initially doped PANI was insoluble in PAA aqueous solution, however, while stirring and sonication it started to disperse in the solution probably due to diffusion in the PAA matrix and interaction with the carboxylic functional group of PAA polymer. After 6 h of stirring followed by sonication a complete homogeneous aqueous solution was obtained, even when the PANI was present above 80 wt %. Blue coloured aqueous solutions of the PANI-PAA composites were obtained and the solution of all the percentage of doped PANI viz. 20 wt % to 80 wt % was stable. Self-standing polymer composite films were also formed by solution casting method and used for further characterizations.

Structural characterization

UV-visible absorption spectra of the composites of various weight percent was taken at low pH by dissolving in 0.1 M HCl. PANI-PAA composite at acidic pH showed two sharp peaks at 362 nm and 445 nm due to π - π^* and polaronic transition (emeraldine salt and base form of the PANI), respectively, and a broad absorbance starting from 650 nm to higher wavelength due to bipolaronic transition^{11,28} was observed as shown in Figure 1 for 40, 60, and 80 wt % of PANI in PANI-PAA composites. Using UV-vis data optical band gap was also calculated for all the compositions of composites as shown in Figure 2 (A-C). In the various composites band gap varies from 2.12 to 2.31 eV. The band gap decreases with the increase of PANI amount in the composite.

FTIR studies supported the assumption of the PAA incorporation in the PANI matrix and interac-

tions of the two polymers. When PANI added in the PAA solution, an acid-base reaction took place between the $-\text{N}-\text{H}$ (base) of PANI and $-\text{COOH}$ (acid) of PAA polymers. This acid-base reaction resulted remarkable changes in the characteristic PAA spectrum at 3312 cm^{-1} corresponding to $\text{O}-\text{H}$ stretching of carboxylic group and at 1728 cm^{-1} due to the stretching of $\text{C}=\text{O}$ group of PAA chain. The $-\text{OH}$ peak of PAA at 3312 cm^{-1} diminished due to the acid-base interaction of both the polymers during composite formation. In addition, peak at 1728 cm^{-1} due to $\text{C}=\text{O}$ group of PAA chain also shifted to 1709 cm^{-1} due to the interaction of the polymers³² as shown in Figure 3. No change was observed with the variation of the PANI percentage in the composite.

The interaction of the PAA and PANI chains result ordering of chains and well-aligned chains were evident by XRD studies. Two broad characteristic

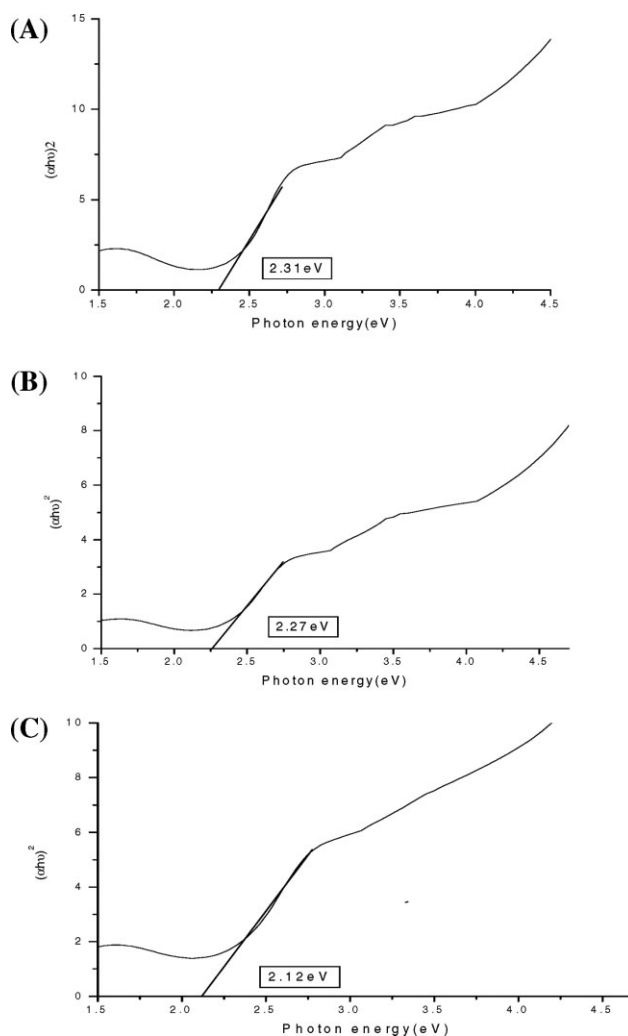


Figure 2 Optical and gap calculation for PANI-PAA composites for (A) 40 wt %, (B) 60 wt %, and (C) 80 wt % of PANI.

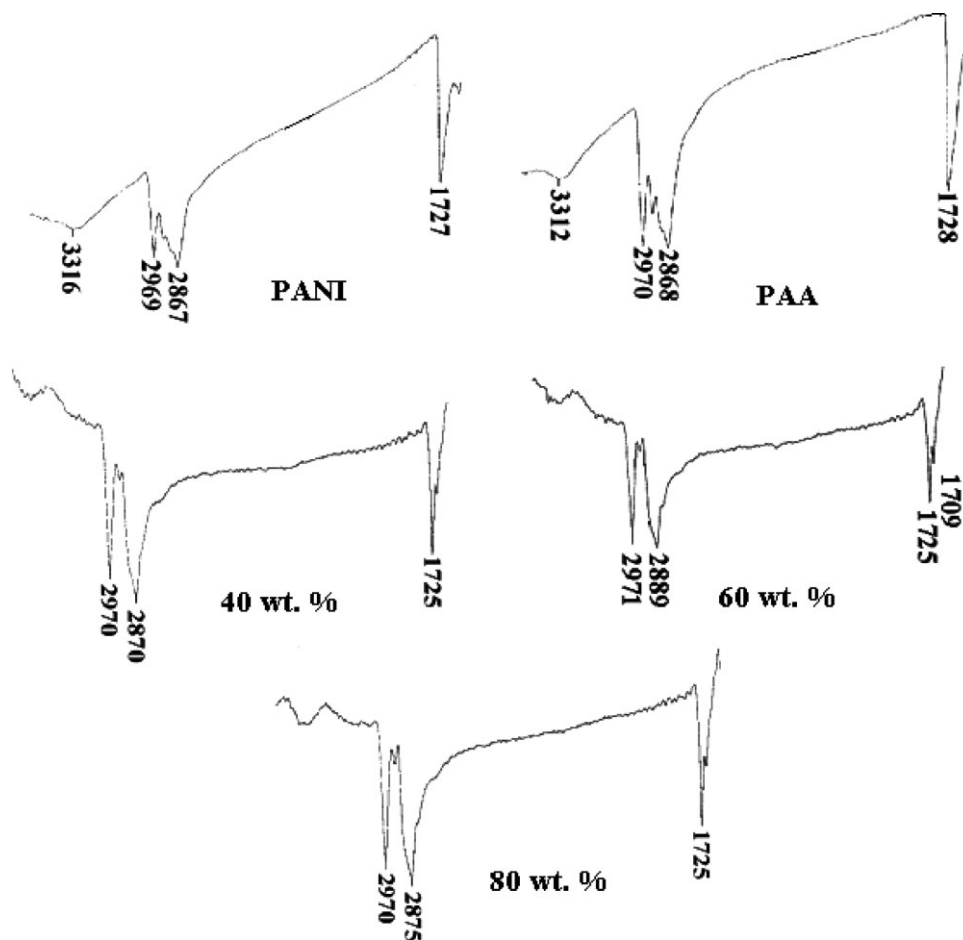


Figure 3 FTIR spectra of PAA, PANI, and PANI-PAA composites for 40 wt %, 60 wt %, and 80 wt % of PANI taken in KBr matrix.

amorphous peaks for doped PANI were appeared at $2\theta = 22.25^\circ$ and 25.12° and for PAA at $2\theta = 19^\circ$ and 33° . However, PANI-PAA composites showed crystalline nature as showed in Figure 4 along with PANI and PAA. The crystallinity and chain alignments are seems to be highest around 60 wt % composite probably due to having 1 : 1 ratio of PANI and PAA chains (as PANI may have lower molecular weight than PAA). PANI-PAA composite of 60 wt % showed many additional peaks at $2\theta = 18.88^\circ, 27.88^\circ, 28.84^\circ, 31.95^\circ, 33.69^\circ, 38.43^\circ, 48.63^\circ$ as shown in Figure 4. The crystalline nature probably appeared due to the interaction of the PANI and PAA chains through acid base reaction, i.e., doping of the PANI with carboxylic group of PAA. This interaction caused an alignment of the chains to form a regular geometry. The XRD pattern shows that PANI and PAA are amorphous whereas the PANI-PAA composites are crystalline and 60 wt % composite is highly crystalline in nature. The crystal structure of PANI-PAA composite was analyzed by considering the orthorhombic crystal system. The cell parameters obtained by using this data are $a = 5.93\text{\AA}$, $b = 7.57\text{\AA}$, and $c = 10.11\text{\AA}$ (these were deter-

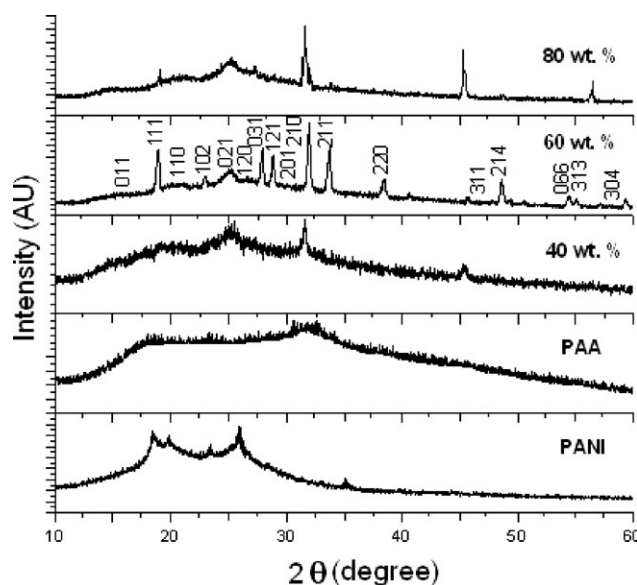


Figure 4 XRD of pure PANI, PAA, and PANI-PAA composites for 40 wt %, 60 wt %, and 80 wt % of PANI.

TABLE I
Conductivity of PANI-PAA Composites

Polyaniline, wt%	Conductivity in S/cm
Cl ⁻ doped PANI (pure pellet)	Order of 10 ¹
20 of PANI-PAA	$8.5 \pm 0.5 \times 10^{-6}$
40 of PANI-PAA	$2.2 \pm 0.5 \times 10^{-5}$
50 of PANI-PAA	$7.8 \pm 0.4 \times 10^{-4}$
60 of PANI-PAA	$4.7 \pm 0.4 \times 10^{-3}$
80 of PANI-PAA (pellet)	Order of 10 ⁻¹

mined by using Unit Cell program, Method of TJB Holland & SAT Redfern 1995) which is in good agreement with the previously reported value for PANI.^{11,34} The miller indices corresponding to reflections from different planes are shown in same Figure 4.

Electrical characterization

Electrical conductivity of the composite film coated over glass substrate or in pellet form was measured using mini four probes assembly connected with a 6-1/2 digit digital multimeter at room temperature.¹¹ An increase in conductivity was observed in the composites films with increasing percentage of PANI as shown in Table I. The conductivity above 80 wt % PANI-PAA composites or pure PANI could only be measured after pellet formation due to brittle nature of the films. The pellets were formed of 1 cm diameter and 0.1 cm thickness at 50 kN pressure using stain less steel die and hydraulic press. I-V study was carried out by current voltage plot for PANI-PAA composites, which showed an ohmic current with a symmetric current plot both side in positive and negative voltage range as shown in Figure 5 for 40, 60, and 80 wt % of composites. A similar plot was also observed for doped PANI.

Morphological characterization

The surface morphology of the various composites was studied by SEM. A single phase, homogeneous and uniform globular structure of PANI-PAA composites were obtained as shown in Figure 6. Most of the PANI composites with insulating polymers showed two distinguished phases,³⁵ however, the composite formed using our method showed single phase even using doped PANI. Single phase formation also evident the interactions between the two components and formation of homogeneous and uniform composites. In case of higher percentage of insulating polymer (PAA) as 40 wt % composite, more compact, however, with separated granules like structure of typical thermoplastic polymers was obtained due to dominating property of PAA.

Thermal characterization

The TGA results for the PANI-PAA composites showed three major stages of weight loss. The first weight loss was observed at 70–126°C, which could be attributed to the moisture evaporation. Second weight loss for the doped PANI-PAA started around 200°C due to carbon dioxide removal.³⁶ The third stage of weight loss took place at the 350°C, which finally (up to 650°C) lost up to the 45% of the 60 wt % composite, however, loss was more than 60% in the case of other two wt % composites as shown in Figure 7. It was observed that 60 wt % PANI-PAA composite is more stable than other composites, however, all the composites are more stable to that of pure doped PANI, which loses a total of 90% of its weight by the time it acquires a temperature of ~ 500°C. The better thermal stability is probably due to the interaction of PANI chains with PAA in the composites.

Electrochemical characterization

Composite was characterized using cyclic voltammetry by coating the film over platinum wire electrode or in solution state in three electrode system using Pt as counter and Ag/AgCl as reference electrodes. Three pairs of well-defined redox peaks were obtained in 1 M HCl due to oxidation of PANI at 0.26 V, 0.51 V, and 0.68 V vs. Ag/AgCl and reduction at 0.15 V, 0.413 V, 0.632 V vs. Ag/AgCl as shown in Figure 8. Similar results were observed with the other compositions, however, with decrease in peak current as the electroactive component (PANI) decrease in the composite. The study revealed that the electroactivity of the PANI retained

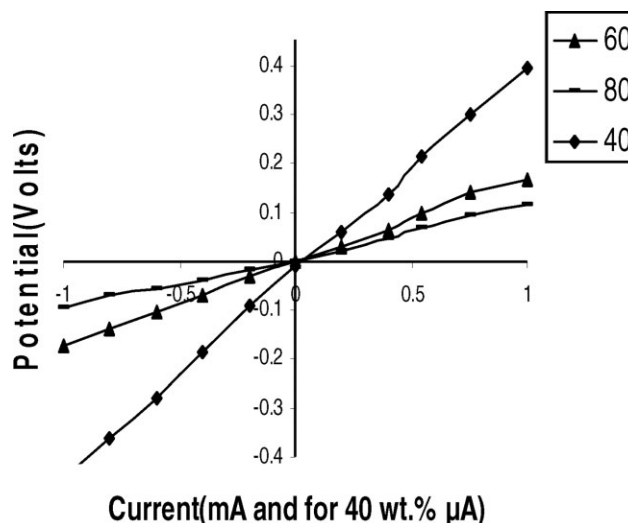
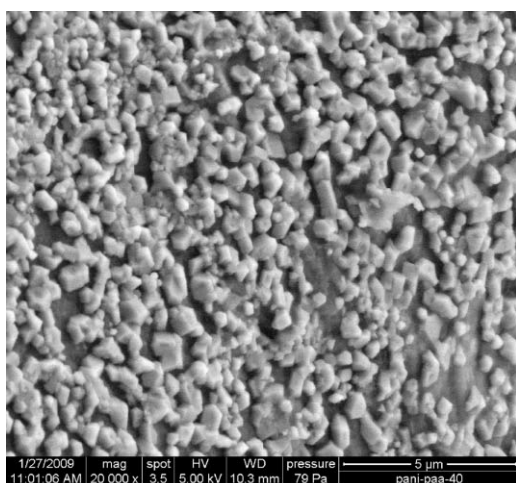
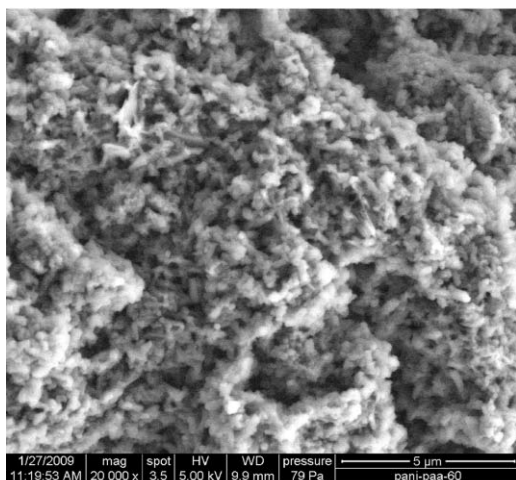


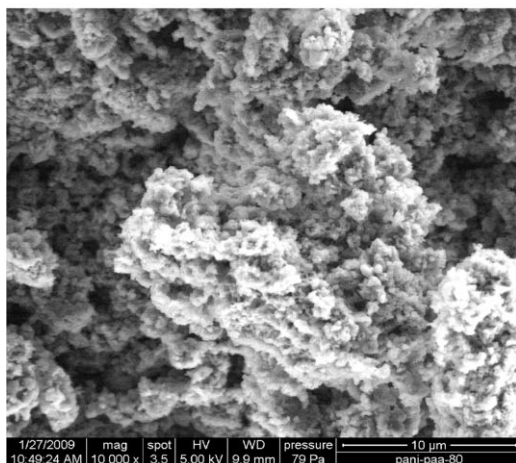
Figure 5 I-V plot of PANI-PAA composites for 40 wt %, 60 wt %, and 80 wt % of PANI.



a)



b)



c)

Figure 6 SEM of PANI-PAA composites for a) 40 wt %, b) 60 wt %, and c) 80 wt % of PANI.

even after formation of composite with insulating non-electroactive component. Electroactivity of the same composite was also studied in non-aqueous medium using acetonitrile and 0.1 M NaClO₄ electrolyte. Although the redox peaks were not well

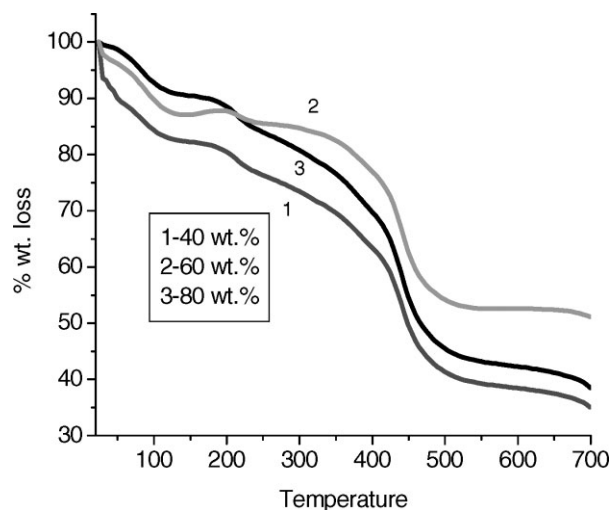


Figure 7 TGA of PANI-PAA composites for 40 wt %, 60 wt %, and 80 wt % of PANI.

resolved in the composites, however, it showed reproducible reduction and oxidation as shown in Figures 8 inset. The long-term stability of conducting polymers is an important consideration for their applications in charge storage devices and electrochemical capacitors. To test the cycle-life of PANI-PAA composites, consecutive scans were performed in acetonitrile using 0.5 M NaClO₄ electrolyte over 60 wt% PANI-PAA composite, where a cycle is defined as scanning from -0.2 to 1.0 V and then back to -0.2 V at a scan rate of 50 mV/s. The scan was given for more than 100 cycles and last 10 cycles are recoded as shown in Figure 9. The loss in the electroactivity or redox property of the polymer composite was negligible even more than 100 numbers of cycles.

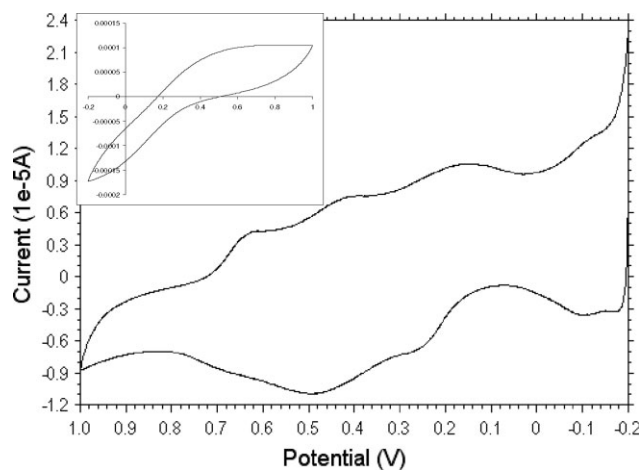


Figure 8 Cyclic voltammogram for 60 wt % of PANI-PAA composite dissolved in 0.1 M HCl (in solution state). In set: Cyclic voltammogram for 60 wt % of PANI-PAA composite (film form) in acetonitrile using 0.1 M NaClO₄.

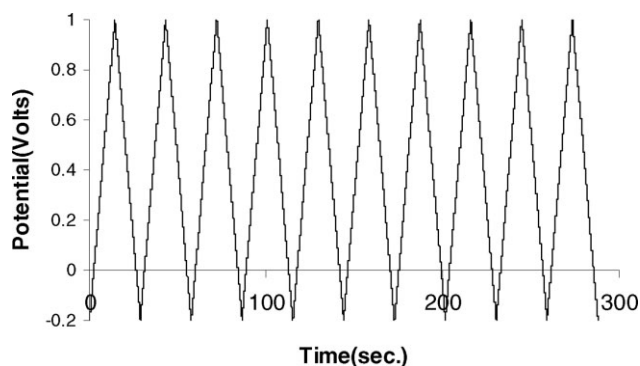


Figure 9 Galvanostatic charge-discharge cycles in acetonitrile- NaClO_4 (0.5 M) solution between -0.2 to 1.0 V for 60 wt % PANI-PAA.

Capacitance measurement

The specific capacitance for both electrodes was calculated from the cyclic voltammograms obtained as shown in Figure 10 for acetonitrile (0.5 M NaClO_4), using the following equation in the same three electrode cell used for impedance analysis:

$$C = \frac{q_a + q_c}{2m \Delta V}$$

where q_a , q_c , m , and ΔV are indicative of the sums of anodic and cathodic voltammetric charges on the anodic and cathodic scans, mass of the electro-deposited material and the potential window of the cyclic voltammogram, respectively.^{9,11}

The specific capacitance can be calculated using impedance data according to the following formula:

$$C_p = -1/(\omega Z'' m)$$

where ω is the angular frequency, which has the relationship with frequency as follows, $\omega = 2\pi f$, Z''

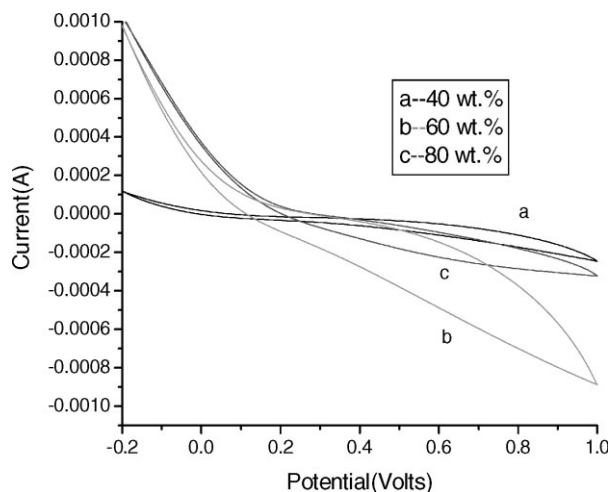


Figure 10 Cyclic Voltammograms of PANI-PAA composites in acetonitrile- NaClO_4 (0.5 M) solution.

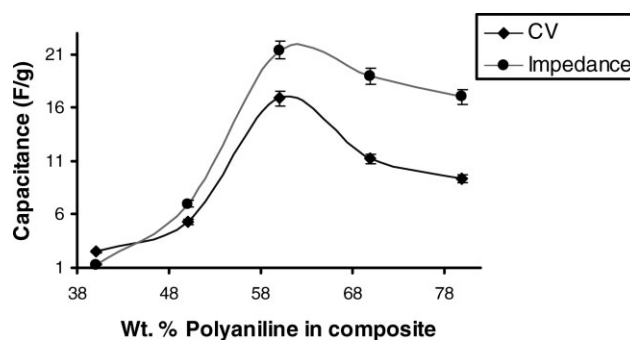


Figure 11 Variation in capacitance with weight percent of PANI in the composites taken in acetonitrile- NaClO_4 (0.5 M) solution.

is the imaginary impedance of impedance spectrum, m is the mass of the polymer.¹⁴ The impedance analysis of various composites were carried out in acetonitrile using 0.5 M sodium perchlorate in the frequency range 0.01 Hz to 1×10^4 Hz. Electrochemical capacitance was calculated for various compositions of the composites as shown in Figure 11 using CV and impedance data. The maximum capacitance was obtained for 60 wt % of PANI composite by both CV and impedance data probably because of the better alignment and interactions of the polymer chains in the composite and homogeneous distribution of the PAA in the PANI matrix. A typical example for 60 wt % PANI-PAA composite Nyquist plot is shown in the Figure 12 (curve with brick shape symbols). The equivalent-circuit model was obtained by using Z Simpwinn software as shown in the inset of Figure 12. The equivalent-circuit model from Z Simpwinn software was used for the calculation of various parameters viz. geometrical capacitor (C), solution resistance (R_s), impedance of the PANI electrolyte interface (Z_i), bulk faradaic impedance (Z_f), ionic charge-transfer resistance at the PANI-electrolyte interface, (R_{ct1}), electron-transfer resistance of the redox transitions (R_{ct2}), double-layer capacitance (C_{dl}), and bulk faradaic pseudo capacitance (C_F). The various elements shown in the circuit have its physical meaning and value of various electrochemical parameters based on the best fit for the Figure 12 (curve with square shape symbols) are summarized in the Table II. C_{dl} and C_F do not behave as an ideal capacitor at applied potential, and have to be replaced by T'_1 and T'_2 , respectively, due to the constant phase element, which is usually defined as $1/T(j\omega)^n$, where " n " is the correction factor, which has been associated with the roughness of the electrode surfaces, T is capacitance and $j\omega$ is angular frequency. The non-ideal responses of C_{dl} should be associated with the factor due to surface roughness.³⁵ The composite is porous and rough as also observed in SEM photograph (cf. Figure 6). The non-

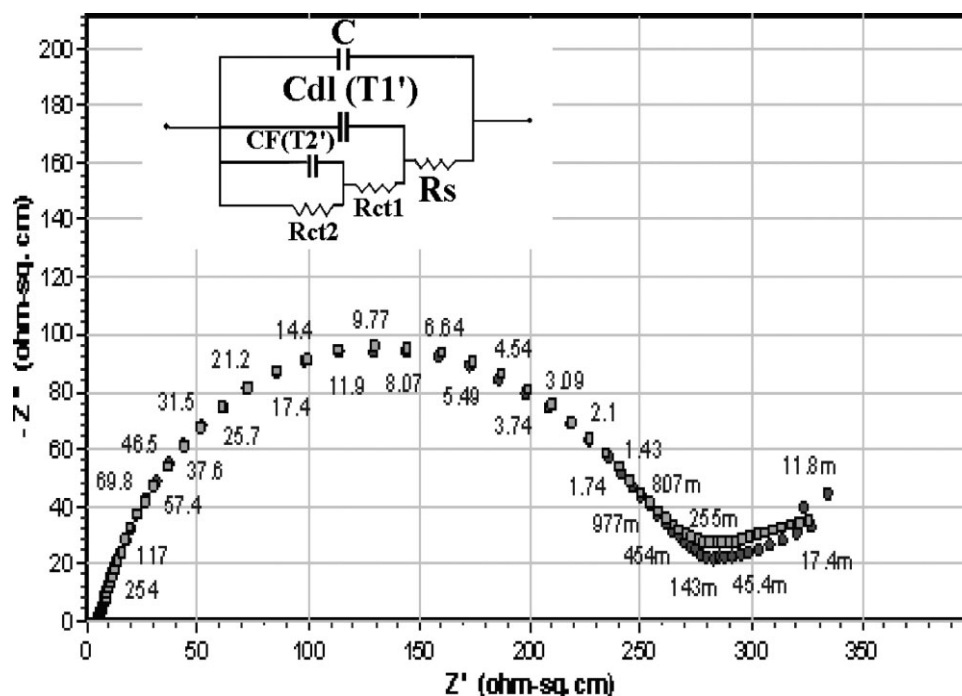


Figure 12 Equivalent-circuit model (inset) obtained by best fit model for Nyquist Plot of 60 wt % PANI-PAA composite at 0.2 V applied potential taken in acetonitrile- NaClO_4 (0.5 M) solution.

ideal behavior of C_F may reflect the kinetics of the electrochemical reactions on the electroactive sites of capacitors plate. The total capacitance of electrochemical parallel plate capacitor was observed as 14.02 F/g of 60 wt % PANI-PAA composite material in acetonitrile (0.5 M NaClO_4).

CONCLUSION

Processible, electroactive and homogeneous conducting PANI-PAA composites have been prepared by mixing the two polymers in various weight percentages under vigorous stirring and sonication condition. Homogeneous composite with continuous network structure and high crystallinity is obtained

with improved thermal and structural properties. Composites showed orthorhombic crystal system as evolved based on XRD studies. PANI-PAA chains interactions and formation of uniform composites showed the potential of the material towards the various technological applications. The composite is for the first time used as an active material for the development of an electrochemical capacitor based on parallel plate assembly in acetonitrile 0.5 M NaClO_4 electrolyte. The composite based electrochemical capacitors showed super capacitance of the order of 14 F/g and long cycle life.

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TABLE II
Various Electrochemical Parameters Based on the Best Fit for the Figure 12

Parameter	At applied potential 0.2 V vs. Ag/AgCl
R_s	5.3423
C	9.77 E-6
R_{ct1}	191.8
T_1'	0.000133
n_1	0.791
R_{ct2}	246.6
T_2'	0.0251
n_2	0.386

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