

## Preparation and Characterization of Amino Acids Doped PANI

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### ABSTRACT

The preparation of polymer-amino acid composites combining the synthesized polyaniline and two amino acids namely L-glutamine (Q) and L-arginine (R) has been demonstrated. The prepared samples were characterized by DSC and atomic force microscopy. DSC thermograms showed the structural changes occurred during composite formation. DC electrical conductivity of the samples were measured in the temperature range 80 K - 310 K and found to be supported by a three-dimensional variable range hopping charge transport mechanism. The sample R doped PANI show higher conductivity than the conductivity offered by Q doped PANI is the novel observation. The carboxyl group of the both amino acids played an important role in the electrical conductivity through hydrogen bonding.

**Keywords:** differential scanning calorimetry; DC conductivity; atomic force microscope.

### INTRODUCTION

Polyaniline (PANI) with the dopant acids is of fundamental importance in exploiting the electrical properties.<sup>1</sup> It has attracted much attention because of its low cost, easy synthesis, good processibility and excellent environmental stability.<sup>2-3</sup> PANI-amino acid composite has potential applications as biomimetic, biosensor,

biochip and in tissue engineering.<sup>4,5</sup> Amino acids L-glutamine (Q) and L-arginine (R) are having physiochemical properties of neutral polar and basic polar respectively. It has been believed that in amino acids the carboxylic group is called as proton donor.<sup>6-8</sup> Due to weak intermolecular interaction, charge carriers are localized and variable range hopping (VRH) charge transport mechanism in disordered organic solid

materials had been found. In the present study it was seen that the carboxyl group of the amino acids Q and R form a hydrogen bond with the nitrogen of PANI so that the resultant composites were found with an improved electrical conduction. There are few reports on the synthesis and optical studies of polymer/amino acid composites.<sup>6,9,10</sup> However to the best of our knowledge no studies have been reported on heat flow and temperature dependent dc conductivity of PANI/Q and PANI/R composites. Herein, we report the preparation of Q and R doped polyaniline composites which have improved electrical responses. The structure, morphology and dc electrical conductivity of Q and R doped PANI composites were also investigated.

## EXPERIMENTAL

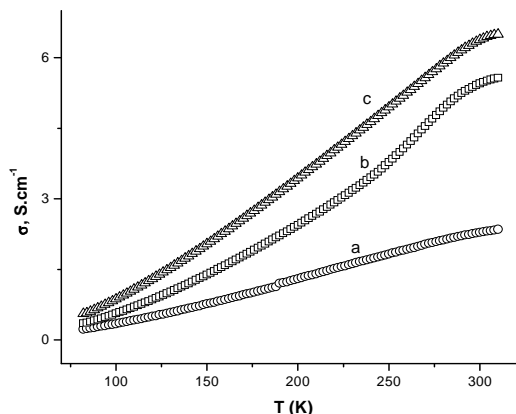
In this study aniline hydrochloride (0.20 M, 25.9 g; s.d.fine Chem. Ltd, India) and ammonium peroxydisulfate (APS) (0.25 M, 57.1 g; Merck, India) were dissolved in deionized water (500 mL in each case). The solutions were then mixed at room temperature, and aniline was left to polymerize. After 24 hours the precipitated PANI hydrochloride was collected on a filter and washed copiously with 1M ammonium hydroxide. The resulting PANI base was dried in vacuum at 60 °C for seven hours. The process protonation of PANI in the solid-state was used.<sup>1,6,11</sup> PANI base was mechanically blended for fifteen minutes with Q (C<sub>5</sub>H<sub>10</sub>N<sub>2</sub>O<sub>3</sub>) and R (C<sub>6</sub>H<sub>14</sub>N<sub>4</sub>O<sub>2</sub>) (99%, Central Drug House (P) Ltd, Bombay, India) in a mortar and two composite samples with the molar fraction of [Amino acid]/[PANI] with 0.05 (PANI-Q) and 0.01

(PANI-R) respectively were prepared. A differential scanning calorimeter (DSC; Model 2910 MDSC V4.4E) was used to examine the thermal properties of the Q and R doped PANI in the temperature range from 323 K to 473 K with a heating rate of 10 K/min. DC resistivity of the samples were measured from 80 K to 310 K by standard four-probe method on the sample pellets compressed at 250 KN/m<sup>2</sup>, 10mm in diameter and 2-5 mm thick.

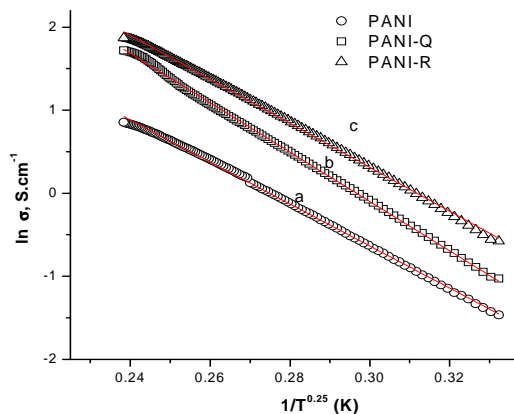
## RESULTS AND DISCUSSION

### D.C. Conductivity measurements

Fig.1 shows the temperature dependent dc conductivity of the samples were measured in the temperature range 80 K - 310 K and found to be supported by a three-dimensional variable-range hopping charge transport mechanism with Arrhenius fitting (Fig. 2).<sup>1,6</sup> The improved electrical responses were found from the dc conductivity measurement for both PANI-Q, PANI-R samples (curves b and c of Fig. 1). The sample R doped PANI show higher conductivity than the conductivity offered by Q doped PANI is an interesting observation though the molar fraction of the later is high. This can be attributed to the basic polar nature of the R. The carboxyl group of the both amino acids played an important role in the electrical conductivity through hydrogen bonding. The conductivity of the samples at room temperature was 5.5 and 6.5 Scm<sup>-1</sup> respectively.



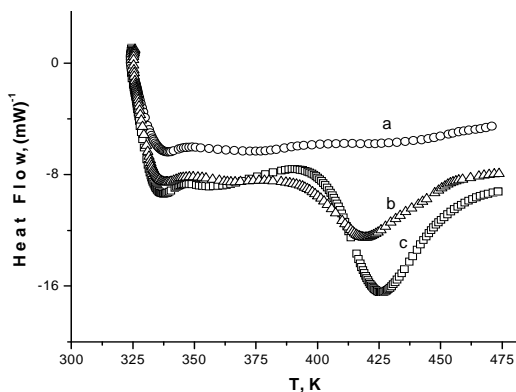
**Fig. 1** DC conductivity plot of (a) PANI, (b) PANI-Q and (c) PANI-R.



**Fig. 2** Arrhenius plots of  $\ln \sigma$  vs  $1/T^{0.25}$ .

**DSC thermal analysis**

PANI/LG composite samples were studied by DSC to examine its thermal stability (Fig. 3). From 323 K to 473 K, there were three different broad endothermic transitions for pure PANI (Fig. 3a), PANI-Q (Fig. 3b) and PANI-R (Fig. 3c) respectively.



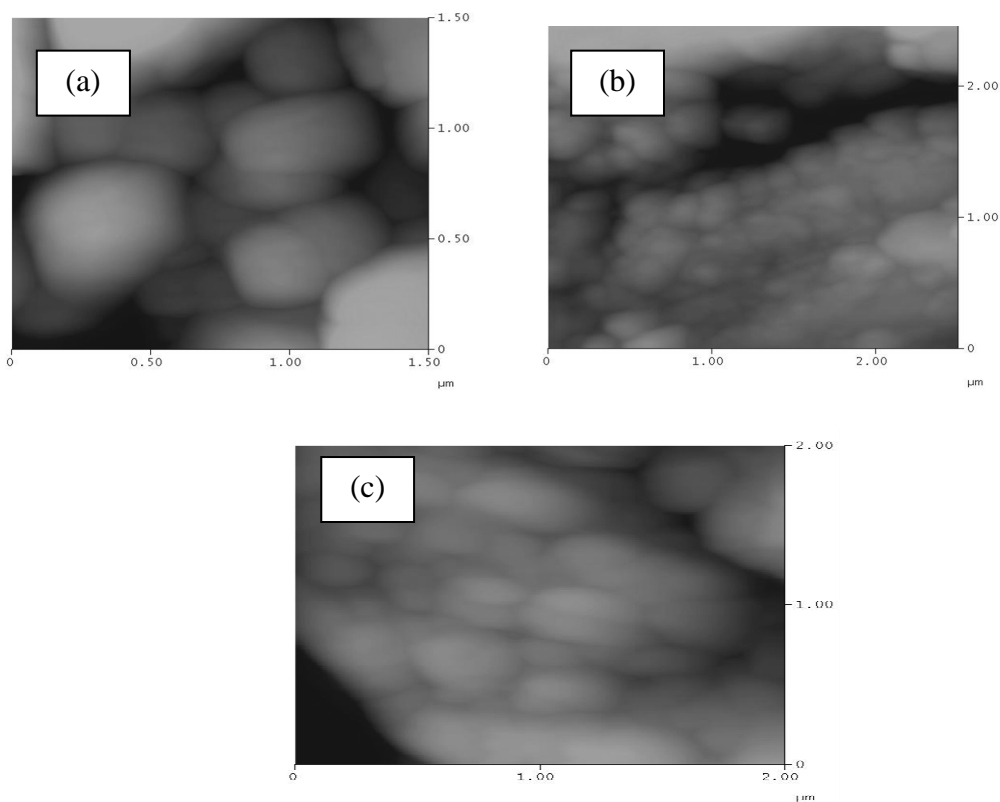
**Fig. 3.** DSC plot of (a) pure PANI, (b) PANI-Q and (c) PANI-R.

The maximum heat flow values observed for those samples were at 375, 395 and 378 K respectively. There was a small conversion seen before 353 K say about 338 K which can be attributed to evaporation of moisture. The endothermic peaks at 420 K

for PANI-Q and 425 K for PANI-R samples indicate the changes in structural transformation. Bond scissoring is normally an endothermic process while bond formation is an exothermic one, the overall reaction being an endothermic process.<sup>12</sup> The presence of the endotherms in the samples could be due to different chains length. It can be concluded, that Q and R doped polyaniline forms cross linked structures at higher temperatures than the PANI.

**AFM images**

The AFM images (a), (b) and (c) of Fig. 4 exhibits a disordered arrangement of grains in 1X1 and 2X2  $\mu\text{m}$  frames of 2D images. The AFM images (a), (b) and (c) of Fig. 4 revealed that the topological surface of sample pellets are covered by grain size varying approximately from 0.1 to 0.5  $\mu\text{m}$  in diameter. The volume of the PANI chains with Q and R show significantly varying compared to pure PANI. This is shown by AFM images (b) and (c) of Fig. 4 and this proves the incorporation of Q and R into PANI chain.<sup>6</sup>



**Fig. 4. AFM images of (a) pure PANI, (b) PANI-Q and (c) PANI-R.**

## CONCLUSION

In summary, we report the synthesized PANI doped with Q and R in solid-state which proves the possibility of partial solid-state protonation. A possible 3D-VRH mechanism for the charge transport in Q doped PANI and R doped PANI samples was found with Arrhenius fitting. DSC thermograms show the crosslink between the chains of Q doped PANI and R doped PANI. AFM images show the disordered grains with different size with volumes of the samples.

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