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Electrochemical Polymerization of Aniline by Current Pulse Method in the Presence of *m*-Aminobenzoic Acid in Chlorhydric Acid Solution

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Summary: Electrical and structural properties of polyaniline powder doped by chloride and *m*-aminobenzoic acid on graphit electrode through current pulse method have been investigated by conductivity measurement, infrared spectroscopy, thermal analysis and scanning electron microscopy. The infrared spectra for the both products showed the clear presence of benzoid and quinoid ring vibrations at 1567 cm^{-1} and 1489 cm^{-1}, respectively. The microstructural observation by scanning electron microscopy showed a knitted morphology of polyaniline doped by *m*-aminobenzoic acid the conductivity of which was found 0.635 S/cm, higher than that of polyaniline synthesized in chlorhydric acid solution (0.368 S/cm). The conductive materials were decomposited at about 380 degree.The detail results will be discussed below.

Keywords: *m*-aminobenzoic acid; current pulse method; polyaniline

Introduction

The 'synthetic metal' such as polyacetylene, polypyrole, polythiophene and polyaniline were being investigated intensively in last years for many applications in high technology. Among them, polyaniline is one of the most studied material because of its high electrochemical reversibility, high conductivity, easy preparation by both chemical way[1] and electrochemical polymerization,[2] good stability in air and environment. Therefore, it is regarded as an excellent candidate material for batteries,[3,4] sensors,[5,6] corrosion protections,[7,8] ect.. Its properties depend much on experimental parameters such as monomer and anion concentration, temperature, synthese-method, ect.. The electrochemical method is the most useful as it provides grater control over the rate of polymerization and results in a more reproducible product. In comparision with chemical oxydation of aniline, electropolymerization has better advantage of getting product with similar electrochemical and electrical properties, especially, the galvanostatic pulse method was being applied to control the morphology of polyaniline film.[9] However, like it was reported in previous literature the height of current pulse plays an important role in synthesis process of polyaniline in powder form and the best suitable value of which could be found at 20 mA/cm^2.[10] This paper reports some results about polymerization and characterization of PANi powder synthesized by galvanostatic pulse current at 20 mA/cm^2 in the presence of *m*-aminobenzoic acid (*m*-ABA) at a concentration of 0.02M in chlorhydric acid solution of 1M.

Experimental Part

Chemical agents were provided by Merck Co. from Germany. Aniline (0.3M) was dissolved into HCl 1M containing and non-containing *m*-aminobenzoic acid (0.02M).

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PANi was prepared in two electrode cell at the room temperature under the condition of galvanostatic pulse current at 20 mA/cm^2 with the wide at 60s and the rest at 10s. PANi was deposited on the graphit electrode used as working electrode. A graphit or lead electrode was used as counter electrode. The obtained PANi was filtered and washed firstly by distilled water and then by acetone. After drying it in *vacuum* oven at 40 °C, the structure of which was carried out by infrared spectrum on IMPACT 410-Nicolet unit. The conductivity measured by cyclic voltammetry (CV) through two-point-electrode method on an electrochemical workstation IM6 (Zahner-Elektrik, Germany). The thermal stability was analyzed by a Thermal Detector

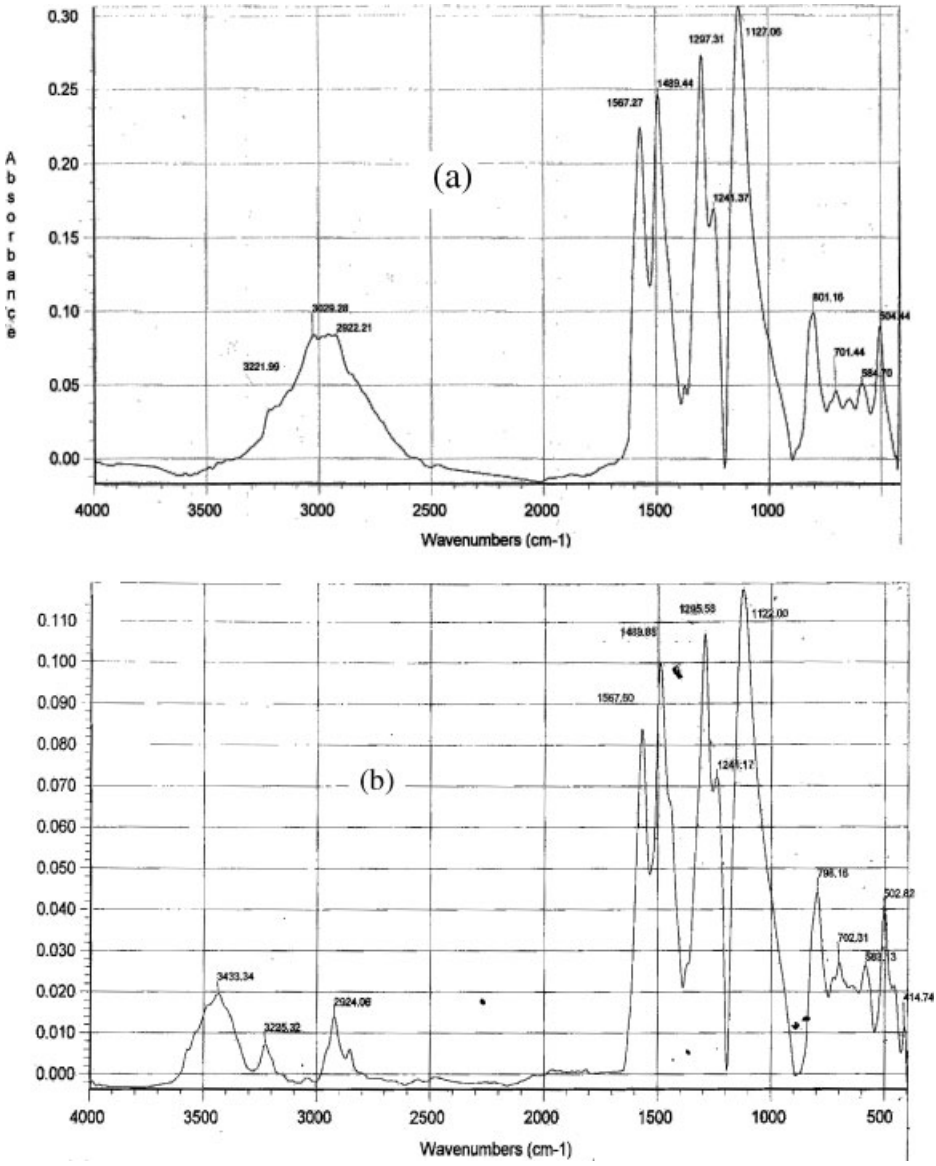

Figure 1.
IR- Spectra of doped PANi products. PANi doped by Cl^- ion and *m*-ABA (a); PANi doped by only Cl^- ion (b).

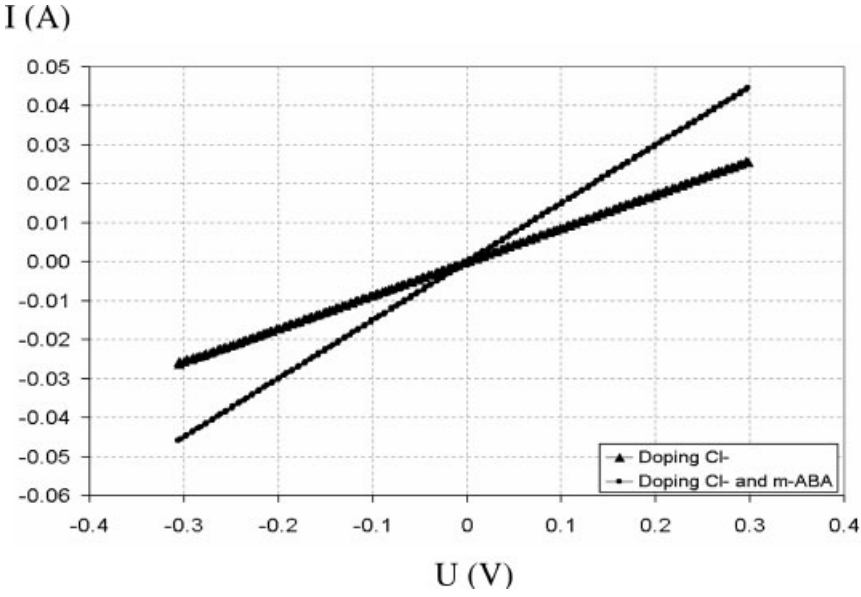

Figure 2.
CV-diagrams of polyaniline product doped by two different anions. Scan rate: 100 mV/s.

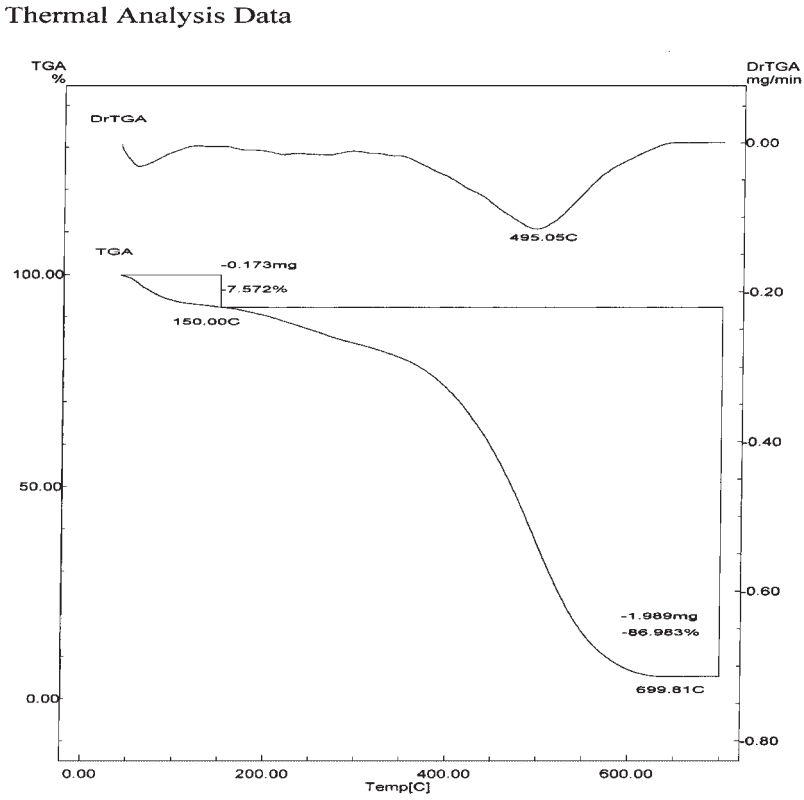

Figure 3.
TGA diagram of polyaniline powder synthesized by pulse galvanostatic method at 20 mA/cm^2 in HCl 1M.

(Shimadzu TGA 50Hz, Japan). The material morphology was carried out by electron scanning microscopy on an equipment FE-SEM Hitachi S-4800 (Japan).

Results and Discussion

Infrared Spectra

Figure 1 shows the spectra of the two kinds of doped PANi. Both spectra exhibit the clear presence of benzoid and quinoid ring vibrations at 1567 cm^{-1} and 1489 cm^{-1}, respectively. The band from 3433 cm^{-1} to 3221 cm^{-1} is assigned to the N–H stretching mode, from 3029 cm^{-1} to 2922 cm^{-1} (aromatic C–H), from 1297 cm^{-1} to 1122 cm^{-1} (–N = quinoid = N–), from 702 cm^{-1} to 583 cm^{-1} (Cl^- ion). The signal at 1241 cm^{-1} was determined due to the C–N^+ group. The peak near 800 cm^{-1} was confirmed due to the absorption of the N–H group.

However, there was no signal at 3433 cm^{-1}, but a new one was observed at 3029 cm^{-1} in the spectrum (a) in comparing with (b). That means *m*-ABA affected on forming the structure of polyaniline.

Conductivity

The conductivity of PANi was determinated through CV-diagrams from Figure 2 below. The higher slope has the CV-line, the lower electric resistance has the PANi. The conductivity was calculated by the following equation:

$$\sigma = (\Delta I \times d)/(\Delta U \times A)$$

where, σ is conductivity (S/cm), ΔU is potential difference (V), ΔI is responsive current difference (A), d is thickness of sample (cm) and A is area (cm^2). The main obtained result from this study is that, the

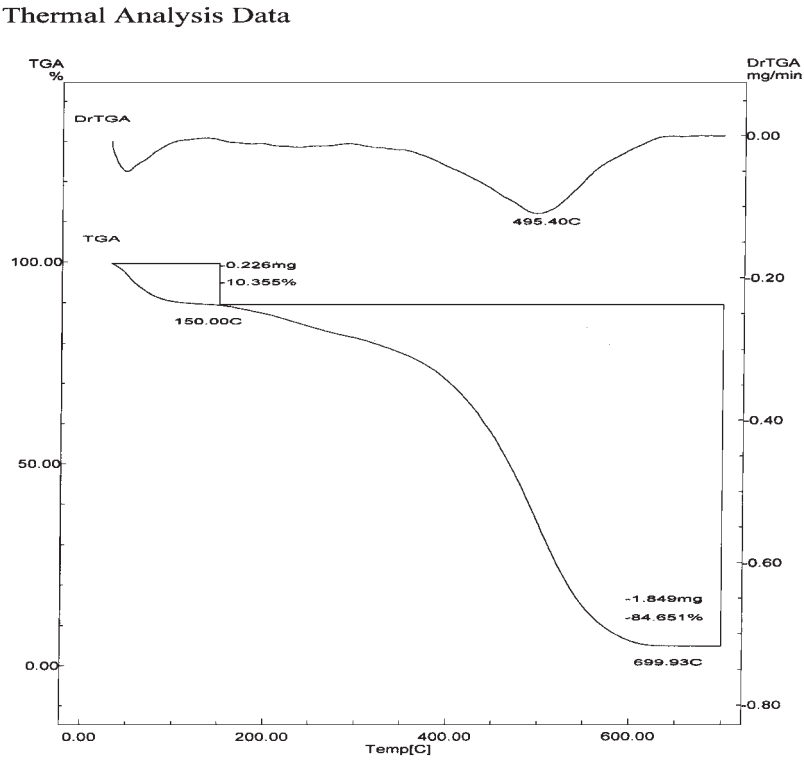

Figure 4.
TGA diagram of polyaniline powder synthesized by pulse galvanostatic method at 20 mA/cm^2 in mixed solution of HCl 1M and *m*-ABA 0.02M.

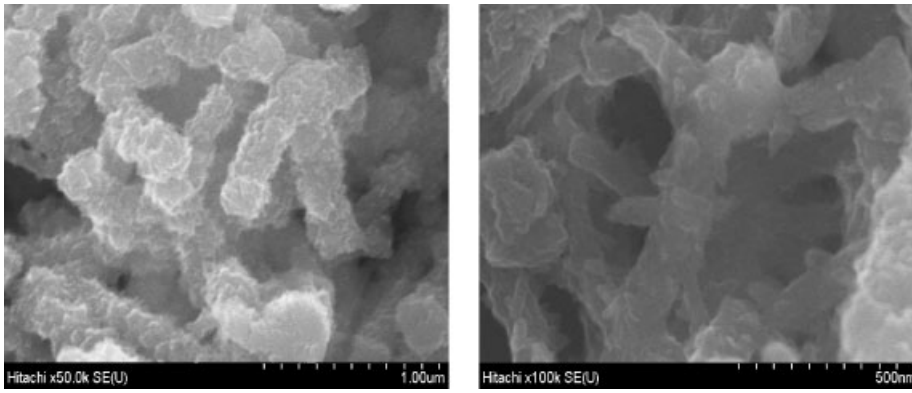

Figure 5.
Migrographs of the PANi prepared by current pulse method. Solution: HCl 1M containing aniline 0.3M and *m*-ABA 0.02M. Pulse characteristics: height: 20 mA/cm^2; wide: 60s ; rest: 10s.

conductivities of PANi got by current pulse method were 0.368S/cm and 0.635S/cm for the case of being doped by only Cl^- ions and being doped additionally by *m*-ABA, respectively. It might be said that the conductivity of PANi was improved through *m*-ABA.

Thermal Analysis

Firstly, we can see from thermal diagrams that the physical dehydration of material at the temperature of 150 °C was about 10% when doping *m*-ABM and only 7% if nondoping it. However, there was almost no difference in the thermal analysis data between two kinds of these PANi products. They both started being decomposited at about 380 degree and decomposited completely at over 699 degree.

Morphology

The SEM micrographs of obtained PANi showed that there is a distinct difference between doping and non-doping *m*-ABA. In the presence of *m*-ABA during polymerization, many small branches of fibre in the chain of PANi knitting together were found (Figure 5). The reason for that is, the

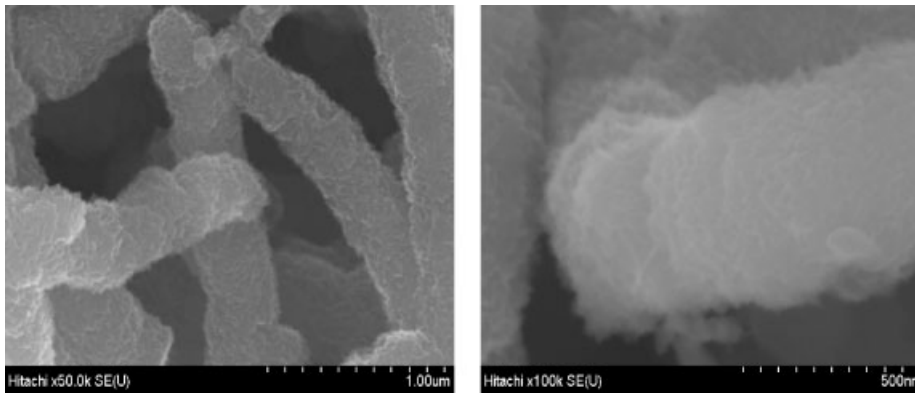

Figure 6.
Migrographs of the PANi prepared by current pulse method in HCl 1M containing aniline 0.3M. Pulse characteristics: height: 20 mA/cm^2 ; wide: 60s ; rest: 10s.

structure of this PANi product was varied by doping *m*-ABA. However, in the case of PANi doped by only Cl^- ion (Figure 6), the unconnected fibre structure with big diameter was observed. This results suggested that these fibres didn't knit together which results in the fact this PANi has a smaller conductivity than that in the case of PANi doped additionally by *m*-ABA.

Conclusion

The morphology of PANi doped extra by *m*-ABA was in the form of knitted fibre. Therefore, its conductivity might increase significantly, about double time higher than that doped only by chloride ion. The thermal stability of the both products were the same.

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