Synthesis and thermal analysis of polyaniline (PANI)

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Abstract

An attempt was taken to prepare polyaniline (PANI) using chemical oxidative polymerization method with surfactant i.e sodium dodecyl sulfate (SDS) followed by treating with HCl and NH₄OH dopants. Raman spectroscopy, differential scanning calorimetry (DSC) and thermogravimetry analysis (TGA) techniques were used for the characterization studies. The electrical conductivity of polyaniline was measured using two probe method. Raman spectroscopy results confirm the formation of an emeraldine oxidation state of PANI. Thermal analysis of polyaniline up to 700°C was investigated using thermo gravimetric analysis technique.

Keyword: Polyaniline, Sodium dodecyl sulfate, Thermal degradation.

1.0 Introduction

Conducting polymers are exceptional organic polymers that can conduct electricity because of alternative single-double bond conjugated system [1]. Among various conducting polymers Polyaniline (PANI) is a promising candidate for technological applications in various areas like sensors [2], light-weight batteries [3-4], Supercapacitors [4], Corrosion inhibitors [5-7] and EMI shielding [8]. Polyaniline (PANI) has unique electrical conductivity along with other properties such as low cost, redox behaviour excellent environmental stability [9]. The scientific community has carried out good research work on the thermal reactions and thermal stability of polyaniline [10]. The degradation mechanism and various conditions are very important to know the stability of the polyaniline. Some recent studies done on the basis of the subject of thermal properties of polyaniline. The evolution of water, loss of dopants and eventually breakdown of polymer backbone are the steps in the degradation of polyaniline shown by thermogravimetric results [11].

In the present study chemical oxidative polymerization method has been followed for the preparation of polyaniline using ammonium persulphate (NH₄)₂S₂O₈, aniline hydrochloride,
hydrochloric Acid (HCl), sodium dodecyl sulphate (SDS), hydrochloric acid (HCl) and ammonium hydroxide (NH\textsubscript{4}OH) as a surfactants and dopants. The thermal behaviour of PANI has been studied in detail.

2.0 Experimental work

Materials Used

Aniline hydrochloride (Loba Chemie, purity 99.60%), ammonium peroxydisulfate (Qualigeng Fine Chemicals, purity ≥98%), NH\textsubscript{4}OH, HCl, SDS (LOBA Chemie, purity ≥80%)

2.1 Synthesis of polyaniline using dopant

Aniline hydrochloride (2.59g) and ammonium peroxydisulfate (5.71g) was added in 50ml of water separately and stirred for one hour. After that both the solutions were mixed together with dropwise addition and kept for 24 hours at room temperature for complete polymerization. The above solution was filtered using Wattman paper followed by 0.5M NH\textsubscript{4}OH. The same reaction has been repeated in the second time and solution was treated with 0.3M HCl in place of 0.5M NH\textsubscript{4}OH. Both products were dried in an oven at 60 degree celsius under the vacuum for 12 hours are represented as PANI-HCl and PANI-NH\textsubscript{4}OH.

2.2 Synthesis of polyaniline using surfactant

Polyaniline (PANI) powder was synthesized using 2.59g of aniline hydrochloride added with the solution of SDS (2.0g) surfactant in 50 ml of deionised water. Both solutions were mixed ultrasonically. The mixed solution was added with solution of 5.71g ammonium peroxydisulphate (in 50ml of ionised water) and was stirred for next 1 hour. After that the solution was kept at room temperature for 24 hours for polymerization. It was found that precipitation was occurred. The precipitates were filtered and washed with 0.3M HCl as a dopant followed by acetone which than dried in vacuum oven for 12 hours are represented as PANI-SDS.

Instrumentation

Raman Spectroscopy was carried out by STR 300 micro Raman spectrometer (Seki Technotron Corp., Japan) using 532 nm laser using 1200g/mm grating for 15 sec to determine the chemical structure of PANI. Thermo gravimetric analysis (TGA, TA instruments Q-500)
determine the thermal degradation property of the polyaniline (Pani) were heated from 30 to 700°C with gas flow rate of 60 mL/min and a heating rate of 10°C/min. Conductivity is measured by two probe technique.

3.0 Results and Discussion

3.1 Raman Spectroscopy:

To investigate the compositional changes inside polyaniline (PANI-HCl, PANI-NH$_3$OH and PANI-SDS) due to synthesis process Raman scattering was done. The STR micro Raman spectrometer was first calibrated using a single crystalline Si wafer and then the spectra were taken using two set-ups; 1) using 1200 g/mm grating and 2) using 600 g/mm grating, for 15 sec in each case with 532nm laser source. Figure 1, shows the Raman spectra of PANI doped HCl, NH$_3$OH and PANI-SDS. The Raman spectra of polyaniline obtained in this work were splited in different regions of wave numbers [12]. The region corresponding to C – C ring stretching vibrations, between 1650 and 1520 cm$^{-1}$ and C – N stretch modes may prevail, between 1400 and 1310 cm$^{-1}$ [13].
Figure 1: Raman spectroscopy of samples: PANI doped with (A) 0.3M HCl, (C) 0.5M NH₄OH and (D) with surfactant SDS.

3.2 Differential Scanning Calorimetry (DSC) and Thermogravimetric analyses (TGA)

The DSC of PANI-HCl and PANI-NH₄OH in air atmosphere have been shown in figure 2 (a and b) respectively. In figure 2a, a very intense endothermic peak is observed at 123°C for PANI-HCl. This peak can be associated to the evolution of water in the form of moisture absorbed by the polymer, one less intense endothermic peak appear at 281°C, in the DSC thermogram of PANI-HCl [14-15]. For PANI-NH₄OH the intense endothermic peak is at 101.94°C and less endothermic peak appears at 255.44°C.

Figure 2: DSC curve of polyaniline doped with (a) 0.3M HCl and (b) 0.5M NH₄OH

The TGA and differential thermogravimetry (DTG) curves of PANI-SDS are depicted in Figure 3. A three-step weight loss was observed in the TGA curve of the PANI-SDS. In DTG curve, two major minima were observed which revealed the majority weight loss of the particular steps. The first weight loss at 100 degree Celsius was ascribed due to the loss of absorbed water. The second weight loss between 100 and 300 degree Celsius might be because of the decomposition of dopant. It has been found that the third weight loss started close to 300 degree Celsius was attributed to the degradation and decomposition of the backbone units of PANI. The degradation of polymeric backbone units leads to the generation of substituted aromatic fragments.
Figure 3: TGA degradation curve of Polyaniline with surfactant SDS.

4.0 Conclusion:

Chemical oxidative polymerization method was used for the synthesis of Polyaniline (PANI) with aniline as monomers in an aqueous medium with SDS as surfactants, 0.3M HCl and 0.5M NH₄OH used as dopant in polyaniline. Its chemical structure is confirmed by Raman measurements. In thermal analysis it was found that the endothermic peaks observed at different temperature conformed by DSC. The TGA of PANI-SDS shows the evolution of water in the form moisture absorbed by polyaniline.

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