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Morphological Behavior of Polyaniline Prepared By Oxidative Polymerization Method

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Abstract

Polyaniline (PANI) has been prepared with and without solvent followed which lead to develop the different morphologies. The chemical oxidative polymerization was used for the preparation of the polyaniline. The prepared PANI was characterized using Scanning electron microscopy (SEM). The PANI prepared with solvent develops the mixed morphology granular and fibrillar, however, PANI without solvent shows granular morphology

Keywords: Polyaniline, fibrillar, morphology, granular

Introduction

Conducting polymers are the kind of organic compounds that associate with the various characteristics of polymers like mechanics and chemicals[1].Among these polymers intrinsically conductive polymers (ICP) represent class of materials which are light weighted, versatile, low cost and have attractive electrical and optical properties[2]. The conductivities (σ) and dielectric constants (ε_r) of ICPs are high that are easy to designand handle through chemical processing.The redox properties of these conjugated organic polymers may be tuned according to multiple independent structural and processing characteristics. Recently,polyaniline (PANI) is the most popular polymer have attracted much attention during the last decade because of their chemical, environmental stability, presence of reactive NH- groups in polymer chain and anomalous behavior[3-4]. The general formula of polyaniline is [(-B-NH-B-NH-) n (-B-N=Q=N-) 1−n] m in which Q and Brepresent the rings in the quinonoid and benzenoidforms having3 idealized states (oxidation): the fully reduced (leucoemeraldine) and oxidized (pernigraniline)system. Moreover, the partially oxidized form of emerdine is attractive because ofits tunable states: EB (emeraldine base)and ES (emeraldine salt)out of which protonated

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emeraldine (ES) is most important form of polyaniline appear as green and electrically conducting[5-6]. Its conductivity approach to the value of common semiconductor which exceed the value of general polymer $<10^{-12}$ Scm^{-1}. However, its value is lower than the typical metals $>10^{4}$ Scm^{-1}. PANI has the potential applications in various areas such as electronic device sensors, respectively. Various methods have already been reported for the preparation of polyanilineincludingchemical polymerization, plasma polymerization and electrochemical polymerization etc.[1].

Experimental section

Chemicals

Aniline monomer ($C_6H_5NH_2$, M=93.13 g/ mol, 99%) was doubly distilled in laboratory,$(NH_4)_2S_2O_8$, M=228.20 g/mol, ≥98%), HCl (M=36.46 g/mol, 37%), were purchased from Merck. All reagents were used as received without further purification.

Synthesis of PANI

To a solution of HCl (2.5M) in DI water (1:4) was placed at stirring in ice bath below 5°C, APS(2.4g) was added slowly till 5-10 minutes. Double distilled aniline(1ml) was added drop wise into the above solution upto 15 minutes and again I ml aniline was added at once. The mixture was placed at vigorous stirring in air tight flask for 3hrs. For the complete polymerization of aniline solution was kept at room temperature for 10-15hrs. During the polymerization color of the dispersion appear as dark green followed by filtering and washing it 2-3 times by DI water and 2-3 times by acetone and dried at 80˚C in incubator. The obtained precipitate was softly grinded tofine powder and kept in vacuum desiccators designated as PANI S (Polyaniline prepared with solvent).

Solvent-Free (SF) Synthesis of PANI.

The double distilled aniline was added into the mortar (prepared with porcelain). Afterwards, hydrochloride (2.5M) was added drop wise into it and simultaneously grinding it for 10 minutes R.T (room temperature), the process leads to the appearance of white paste. Separately, grinded APS in small portion (0.5g) was added to the above reaction mixture for 1-2 minutes to ignore the overheating and simultaneously grinding till complete batch is uniformly grinded.This

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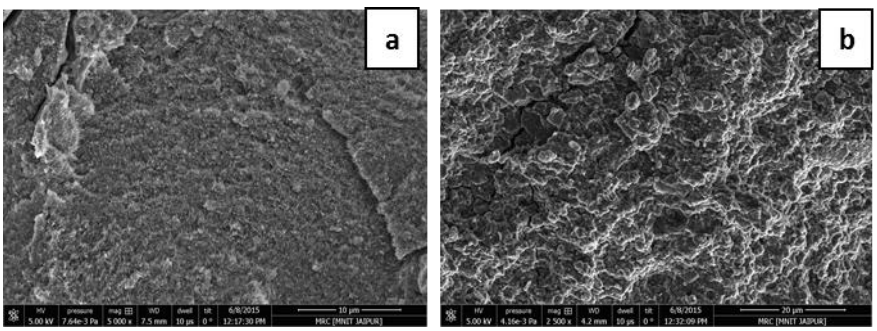
process of addition of APS leads to the appearance of green colour of mixture. This powder was transferred into the 2L beaker in which 100 milli litre of acetone, 800 milli litre DI water and100 milli litreof ethanol was taken and put it for 1hr for complete polymerization and to remove oligomer impurities. Then this was followed by washing with nearly 500 ml DI water, ethanol and acetone until the brown precipitate has no colour. Then it dried at 80℃ for 48 hrs. Then dark green powder PANI was obtained which is grinded gently into a fine powder and kept in desiccators designated as PANI SF (Polyaniline prepared without solvent).

Characterizations

The surface morphology of the prepared polyaniline were examined using FESEM (Nano 450, FEI)

Results & Discussion

Fig. 1shows the scanning electronic micrograph (SEM) image of PANI S (figure 1a) and PANI SF. The two types of morphology granular and fibrillar is shown by PANI S and only granular morphology is by PANI SF. The mixed morphology in PANI S is because of incorporation of aniline monomer in the prepared solution[7-8]. The drop-wise addition of the aniline monomer occupies more space for their growth inparticular direction. However, theagglomerated grains are well interconnected with each other represents enough binding energy to associated with closegrains is due to the quick incorporation of the monomer (aniline).On the other side, Fig 1b for PANI SF has only granular morphology. As the used synthetic method for PANI SF is solid state polymerization, so there is no more space for the growth of polymeric chains. The grains get bonded with the solid-solid interaction appeared as granular morphology[9-11].



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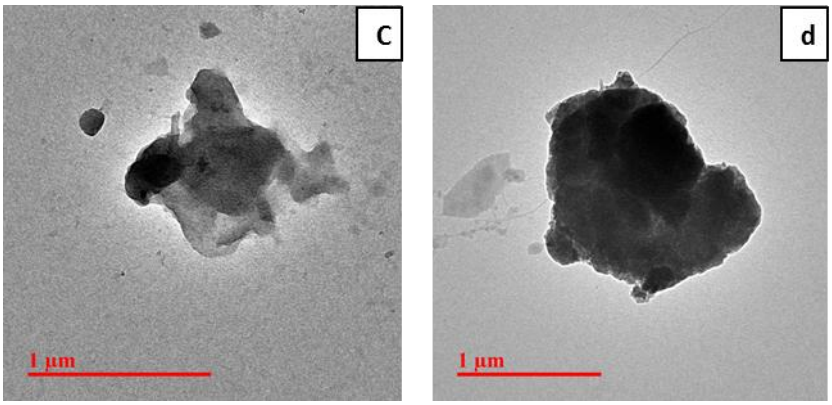

Fig.1:SEM image of PANI S prepared with solvent (a) and PANI SF prepared without solvent (b)TEM micrographof prepared PANI S with solvent (c) and PANI SF prepared without solvent (d)

The morphology of PANI S and PANI SF was alsoconfirmed by TEM (Transmission Electron Morphology)(**Fig.1c-d**). In **Fig. 1c**, it has been shown that there is growth of small fibers along with granular as conformed by SEM images. In **fig.** 1d, there is only granular morphology as not solvent is used there.

Conclusion

The main contribution in this work is to prepare the polyaniline with and without solvent. It has been found that the morphology of the prepared PANI with solvent was granular along with fibrillar. However, in case of PANI which was prepared without solvent had only granular. It was due to the rate of addition of the aniline monomer.

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