Synthetic Metals 222 (2016) 162–169

Contents lists available at ScienceDirect

Synthetic Metals

journal homepage: www.elsevier.com/locate/synmet

Synthesis and characterization of polyaniline doped with polyvinyl alcohol by inverse emulsion polymerization

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ARTICLE INFO

Article history:
Received 19 June 2016
Received in revised form 14 October 2016
Accepted 18 October 2016
Available online 24 October 2016

Keywords:
Polyaniline
PVA
Composites
Cyclic voltammetry

ABSTRACT

The properties of conducting polymers (CPs) such as polyaniline (PANI) and its derivatives can be modified, improved and even enhanced by making composites with materials which can change the extent and level of doping in the CPs. This paper reports on the synthesis of PANI in the presence of various concentration of polyvinyl alcohol by inverse emulsion polymerization. The as synthesized PANI and PANI/PVA were characterized with UV/VIS, FTIR, XRD, TGA, SEM, conductivity and electrochemical measurements. The results demonstrated the formation of polyaniline doped with polyvinyl alcohol showing high thermal stability and improved room temperature conductivity. The synthesized composites were found to be soluble in common organic solvents such as N-methylpyrolidinone (NMP), Chloroform, 2:1 mixture of toluene and 2-proanol, 1:1 mixture of chloroform and toluene and 2:1 mixture of toluene and methanol. Cyclic voltammetric studies showed good redox properties of synthesized PANI and PANI/PVA.

1. Introduction

Polyaniline (PANI) is the most amazing and extensively studied polymeramong the conducting polymers and is gaining additional interest due to its potential applications in the field of anticorrosion coatings, electrochromic devices, light emittingdiodes, chemical and biosensor, chromatography, as an electro rheological fluid [1,2] and electrode material in batteries. In order to synthesize the different dimensional PANI structures such as nanorods [3], nanoparticles [4,5], nanotubes [6], nanofibers [7], microspheres [8] and microboxes [9] several methods have been investigated. There are two main methods for the synthesis of micro/nanostructures of PANI i.e. the hard template and soft template. The hard template method includes porous alumina [10], tracked etched polycarbonates [11], nanochanne ls of zeolite [12], manganese oxide [13], sodium dodecylsulfate [14], self-degradable MnO_2 [15] while the soft template method includes micelles [16], swollen liquid crystals [17], surfactants [18] and emulsions [19]. Other synthetic approaches for the synthesis of PANI micro/nano structures includes template free method [20], seeding polymerization [21], interfacial polymerization [22], and electrochemical synthesis [23].

Polyvinyl alcohol (PVA) being water soluble with a hydroxyl group attached with long and soft polyvinyl chain has remarkable adhesive, emulsifying and film foaming properties. The PVA is employed as a stabilizer to synthesize PANI colloids [24]. The synthesis of flower like micro/nanostructures of PANI/PVA in the dilute aqueous PVA solution was investigated in the chemical oxidative polymerization of aniline by using strong oxidizing agent like ammoniumperoxydisulfate (APS) [25]. Adhikari and Benerji-have used swollen PVA gels, soaked in acidic solution of APS, for *insitu* synthesis of PANI-PVA composites with low conductivity [26]. They reported the role of PVA gel in the morphology of composites. Similarly Misra et al. [27] reported the effect of potassium dichromate loading on the conductivity of PANI-PVA interpenetrating network synthesizedvia *in situ* polymerization. Honmute et al. [28] have used ammonium persulfate as an oxidizing agent for the synthesis ofinterpenetrating polymer network thin film of polyaniline-polyvinyl alcohol (PANI-PVA). They carried out oxidative polymerization of different concentration of aniline to form the composites. The PANI particles were dispersed in PVA matrix and composites have good storage capacity and film forming ability on glass plate, however, the

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http://dx.doi.org/10.1016/j.synthmet.2016.10.017
0379-6779/

Table 1
% Yield in terms of aniline and conductivity of PANI and its composites with PVA.

Sample	Concentration of PVA Solution added	% yield	Conductivity (S/cm)
PANI	–	94.36	0.019
PANI/PVA 1%	1% PVA	61.65	0.022
PANI/PVA 2%	2% PVA	80.30	0.049
PANI/PVA 3%	3% PVA	67.23	0.066
PANI/PVA 4%	4% PVA	66.99	0.053
PANI/PVA 5%	5% PVA	49.46	0.052
PANI/PVA 6%	6% PVA	55.33	0.052

composite were found to be less conductive and stable up to only 200 °C. The literature shows that the conductivity of PANI decreases by composite formation with PVA. Similarly there is no report on the formation of process able composites of PANI and PVA.

In the present paper we are reporting on the synthesis and characterization of soluble PANI/PVA composites by using inverse emulsion polymerization, because, normally insoluble and poor quality of PANI is obtained by the direct oxidative polymerization method. The inverse emulsion polymerization method have the advantage of synthesizing better quality of PANI with improved solubility in common organic solvents [29], and thus the processability and chances of industrial application are also maximized. The composites were prepared by the introduction of PVA during inverse emulsion polymerization of aniline. The composites were characterized with UV/VIS, FTIR, XRD, TGA, SEM and electrochemical measurements. The composites exhibited high thermal stability, improved conductivity and good redox properties.

2. Experimental

2.1. Procedure

Aniline reagent grade was purchased from Acros organics and distilled twice before use. DBSA (Acros),2-propanol (Merck), benzoyl peroxide (Merck) and Toluene (BDH) were used as received. Polyvinyl alcohol (PVA) was purchased from BDH having molecular weight of 22000 a.m.u and 98% minimum degree of hydrolysis. The samples were synthesized according to the procedure mentioned in literature [30]. In a typical experiment 50 mL of toluene was taken in a 100 mL round bottom flask. 0.40 g of benzoyl peroxide was added to it under mechanical stirring. To the above solution 10 mL of 2-propanol was added. 1.5 mL DBSA, 0.2 mL aniline and 10 mL deionized water was added to the above mixture respectively to form a white milky emulsion. The oxidant monomer ratio was 1.96. The reaction mixture turned greenish brown after 7 h and was allowed to proceed for 24 h. The aqueous layer was separated from the organic layer in a separating funnel. The organic layer obtained was suspended in 50 mL acetone. The relatively denser PANI phase was separated from the acetone layer. This process of separation was repeated 4 times for each sample. The product obtained was transferred in to a petri dish and dried in oven for 24 h at 40 °C. The polymer was broken in to flakes by the addition of small amount of acetone. The polymer was separated from the petri dish and was labeled as PANI. PANI/PVA samples were prepared by following the same procedure with different concentration (1%, 2%, 3%, 4%, 5% and 6%) of PVA 10 mL solution instead of deionized water.

2.2. Characterization

The conductivity measurements of the PANI/PVA composites were carried out by using four point probe Jandel Model RM2. Four electrical contacts were made with the solid pellet compressed under high pressure of 800 bar.

To record the UV/Vis spectra a Shimadzu UV/Vis 1700 spectrophotometer was used. The spectral region from 900 to 200 nm was selected and the spectra were recorded with a sampling interval of 0.5 nm. The spectra were recorded using chloroform solution of the samples.

FTIR spectra of solid samples were recorded by using IR prestige-21 FTIR spectrophotometer Shimadzu Japan in a region ranging from 400 to 4000 cm^{-1}. The spectra were collected with 10 numbers of scans for each sample.

The TGA was performed on solid samples at temperature ranging from 30 to 600 °C by using Diamond TG/DTA Perkin Elmer USA in the Centralized Resource Laboratories University of Peshawar Pakistan. The samples were heated from 30 °Cto 600 °C at a rate of 10 °C/min after holding them for one minute at 30 °C.

The XRD of solid samples was carried out by using Siemens diffractometer D 5000 at the Polymer Electronic Research Centre, University of Auckland New Zealand. The SEM was carried out in Centralized Resource Laboratories University of Peshawar Pakistan by using scanning electron microscope Model JSM-5910 JEOL Japan.

Electrochemical measurements were carried out by using ALS/DY 2323 Biopotentiostate. Goldsheet and wire were used as working and counter electrodes. Saturated calomel electrode was used as reference. A thin film of the polymer was deposited on the gold substrate and CVs were recorded in 0.5 M H_2SO_4 solution as supporting electrolyte at scan rate of 50 mV s^{-1}.

3. Results and discussion

The% yield in terms of aniline are calculated for various PANI/PVA products and their conductivities determined by four probe

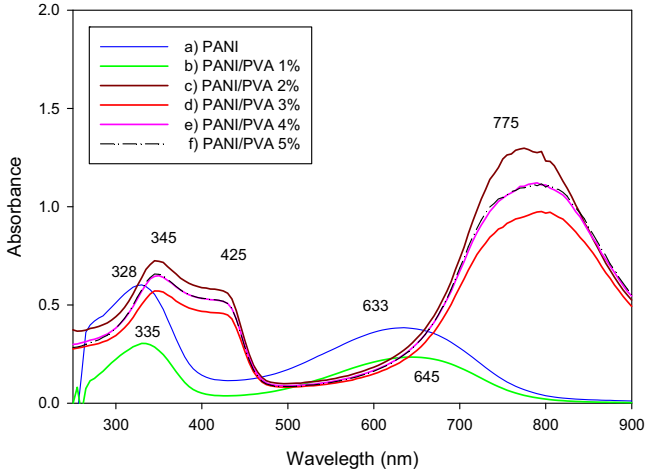

Fig. 1. UV/Vis spectra of a)PANI b) PANI/PVA1% c) PANI/PVA 2% d)PANI/PVA 3% e) PANI/PVA 4% and f) PANI/PVA 5%using chloroform as solvent.