



Polyaniline composite by *in situ* polymerization on a swollen PVA gel

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ABSTRACT

Interpenetrating polyaniline (PANI) formation in a 3D network of poly(vinyl alcohol) (PVA) hydrogel was developed. Polymerization was effected by immersing swollen PVA hydrogel previously soaked with ammonium persulfate (APS) in 1 M HCl solution of aniline hydrochloride (AnHCl). Gradual transformation of the swollen gel from colorless transparent gel to an opaque green color indicated the formation of PANI emeraldine salt (ES) on the surface and bulk of the PVA gel matrix. Characterization by UV–vis spectra, ATR–FTIR spectra and X-ray diffraction analyses supported the formation of PANI–PVA composite film. The surface morphology of the film was studied by FESEM. Electrical conductivity of the film was measured by four-probe method.

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1. Introduction

Polyaniline has attracted a lot of attention in the last decade because of its ease of synthesis, good environmental stability [1,2] high conductivity [3,4] and reversible doping/dedoping process compared to other conductive polymers [5,6]. Synthesis of nano-materials with well controlled morphology and size is a key issue in current nanoscience research because they are the key parameters to determine the optical, electronic, magnetic, and chemical properties [7–13]. PANI nanostructures have recently received much attention because the high surface area of these materials is of interest for the development of actuators, drug delivery systems, field emission displays, gas sensors, and biosensors [14–16]. PANI nanostructures, such as nanofibers/tubes, can be made by introducing 'structural directors' into the chemical polymerization bath. These structural directors include 'soft templates' such as surfactants [17], organic dopants [18] or polyelectrolytes [19] that assist in the self-assembly of the PANI nanostructures and 'hard templates' such as porous membranes [20] or zeolites [21]. Films containing PANI nanofibers can also be made by using the electrospinning [22] or electrochemical method to control the polymerization rate [23]. In spite of its excellent thermal and environmental stability, poor processability due to insolubility and brittleness limit its commercial applications. PANI can be made more processable in the composite form with another water soluble polymer such as PVA, poly(vinyl pyrrolidone), poly(acrylic acid) and poly(styrene sulfonic acid) (PSSA) which are used as stabilizers [24]. A function-

alized protonic acid can be added into the composites to chemically polymerize PANI. The PANI dispersion can then be cast to form composite film containing PANI nanoparticles [24]. Trivedi et al. [25], and recently Gangopadhyay et al. [26] have reported the preparation of a homogeneously dispersed PANI in an aqueous solution of PVA having stability for almost 6 months at room temperature. PANI–PVA composite exhibits microwave shielding property over the X-band [26] and is used in electrical connectors for display devices [27] and as a sensor for humidity [28]. Ali et al. [29] have synthesized PANI nanoparticles dispersed in PVA films using radiation technique. Dupare et al. [30] have synthesized PANI–PVA blend films by oxidative polymerization using chemical synthesis route and they have used the blend films for ammonia gas sensing. PANI and its blends with PVA and PVA–Cu (II) complex were synthesized by Murugesan and Subramanian [31] by *in situ* chemical oxidative polymerization technique with potassium persulfate (PDS) oxidant in aqueous sulfuric acid medium. Bhadra and Sarkar [32] have prepared ordered PANI nanorod arrays by dispersion polymerization of aniline in PVA. Amarnath et al. [33] have reported preparation of PANI dispersion in water using acacia gum (ACACIA). They observed that a blend of PVA with the composite PANI–(60 wt.%) ACACIA was highly conducting even for very low PANI with conductivity in the range 10^{-4} S cm $^{-1}$ to 10^{-5} S cm $^{-1}$.

In this study we report the synthesis of nanostructured PANI on maleic acid (MA) cross-linked PVA (MA–PVA) by oxidative polymerization of AnHCl using APS as oxidant. The novelty of this investigation lies in the *in situ* deposition of nanostructured PANI emeraldine salt on APS soaked and swollen cross-linked PVA substrate by the polymerization of AnHCl both on the surface and bulk of PVA hydrogel thus avoiding the problem of PANI insolubility. The obtained nanostructured materials were characterized by FESEM, FTIR and UV–vis spectroscopy, X-ray diffraction and elec-

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trical measurements. The effect of the APS/AnHCl molar ratio on the conductivity of the composite film was also studied.

2. Experimental

2.1. Materials

Poly(vinyl alcohol) (PVA) of molecular weight 57,000–66,000 was purchased from Alfa Aesar, USA. Aniline hydrochloride (AnHCl) and maleic anhydride were purchased from LOBA Chemie, India. Ammonium persulfate (APS), hydrochloric acid and sulfuric acid were purchased from E. Merck, India. All the aqueous solutions were prepared in deionized water (18.2 M Ω).

2.2. Synthesis of cross-linked PVA–PANI composite films

2.2.1. Preparation of cross-linked PVA film

An aqueous solution of PVA was prepared by dissolving 5 g of PVA in 50 ml of water. 2.25 g of maleic anhydride dissolved in 5 ml of water was added to it followed by addition of two drops of concentrated sulfuric acid. The resultant solution was stirred for 1 h followed by film casting on a flat Petridish. The film was formed through slow evaporation of water by keeping the Petridish with PVA solution containing MA in a covered glass chamber at ambient temperature. The evaporated water was expelled from the chamber by maintaining a flow of dust free air for 3 days. Then the air dried film was cured in a vacuum oven (500 mm of Hg) at 60 °C for 2 h to obtain a MA cross-linked PVA (MA-PVA) film through the formation of inter molecular ester bond.

2.2.2. Synthesis of PANI–MA-PVA composite

PANI–MA-PVA composite film was prepared by soaking of APS in a swollen gel of cross-linked PVA, i.e., MA-PVA followed by immersion of the APS soaked MA-PVA in the solution of AnHCl of a specific concentration. In actual preparation, the MA-PVA film was first kept immersed in water for 24 h to remove uncross-linked PVA and MA. The film was then dried by keeping in a covered glass chamber at ambient temperature for 24 h. A saturated solution of APS was separately prepared by dissolving 8 g APS in 10 ml water. Next the dry MA-PVA film was immersed in APS solution for a maximum time of 6 h during which the films swelled. The swollen gel was then immersed in a solution of 8 g AnHCl monomer in 10 ml of 1 M HCl. The swollen film started darkening immediately after immersion due to formation of PANI. The film was kept in the monomer solution for overnight to ensure complete polymerization in the MA-PVA matrix. Thus the PANI–MA-PVA composite films were prepared by using various initiator/monomer mole ratios and time of swelling in APS solution. Physical parameters and conditions of MA-PVA and PANI–MA-PVA film preparation are shown in Table 1. It may be pointed out here that the amount of APS trapped in the swollen MA-PVA gel after soaking was varied by varying the soaking time. The trapped amount of APS in the MA-PVA gel was calculated by iodometric estimation of the residual APS in the solution after soaking. The mole ratio (shown in Table 1) of APS/AnHCl was cal-

culated from the mole of trapped APS in the gel and mole of AnHCl in the solution in which APS soaked MA-PVA was immersed. The green colored composite film, thus obtained, was washed with distilled water, 1 M HCl to remove the soluble impurities, followed by washing with deionized water and acetone. The film was dried by keeping in a covered glass chamber at ambient temperature for 24 h and then heated in a vacuum oven at 60 °C for 2 h.

2.3. Characterization

2.3.1. Elemental analysis

Carbon, hydrogen, and nitrogen present in the PANI–MA-PVA composite films were analyzed by EURO EA Elemental Analyzer and chlorine was analyzed by Schöniger Combustion technique [34] using vacuum dried specimens.

2.3.2. FTIR spectroscopy

The ATR-FTIR spectra of the MA-PVA and PANI–MA-PVA composite films were recorded in NEXUS 870 FT-IR spectrophotometer. For this spectral analysis the purified film samples were dried in a vacuum oven at 60 °C for 6 h and stored in a vacuum desiccator.

2.3.3. UV–vis–NIR spectroscopy

UV–vis spectra of the MA-PVA and PANI–MA-PVA composite films were recorded in Perkin Elmer Lambda 750 spectrophotometer.

2.3.4. Mechanical properties

Tensile properties of the MA-PVA and PANI–MA-PVA composite films were measured following the standard procedure as laid down in ASTM D 882 by using Hounsfield H 10 K S Universal Tensile Testing machine.

2.3.5. Bulk and surface morphology

Both bulk and surface morphologies of the composite films were analyzed by field emission scanning electron microscopy (FESEM). The FESEM measurements were performed in Carl Zeiss Supra 40 scanning electron microscope. X-ray diffraction (XRD) patterns were obtained with Ultima III diffractometer using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$).

2.3.6. Electrical conductivity

Conductivity of the MA-PVA and PANI–MA-PVA composite film samples was measured by four-probe technique using Keithley 2400 Source Meter and Keithley 2000 Digital Multimeter. Four electrical contacts on the film were made using silver paste.

3. Results and discussion

3.1. Elemental analysis

The results of elemental analyses of all the PANI–MA-PVA composite films prepared at different conditions are shown in Table 2. It is observed from Table 2 that the conductivity of the composites

Table 1
Physical parameters and conditions of MA-PVA and PANI–MA-PVA film preparation.

Sample	MA-PVA film			APS/AnHCl mole ratio	PANI–MA-PVA		PANI in composite (%)
	Weight (mg)	Thickness (mm)	Swelling time in APS solution (h)		Weight (mg)	Thickness (mm)	
S ₁	19.49	0.10	1	0.014	19.93	0.11	2.26
S ₂	19.24	0.10	1	0.030	20.52	0.12	6.65
S ₃	24.31	0.11	2	0.090	25.90	0.12	6.54
S ₄	19.80	0.10	2	0.193	22.73	0.11	14.80
S ₅	24.22	0.11	6	0.115	28.15	0.18	16.23
S ₆	16.79	0.10	6	0.233	20.38	0.18	21.38

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