

SYNTHESIS OF CONDUCTING POLYANILINE NANOCOMPOSITES BY RADIATION DOPING

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Abstract

Electrically conducting polymers have been most widely accomplished using chemical and electrochemical processing techniques. The present article aims at reporting the synthesis of polyaniline (PANI) nanoparticles dispersed in polyvinyl alcohol (PVA) films using radiation technique. The PANI nanoparticles were obtained by irradiating solvent casting PVA/aniline hydrochloride (AniHCl) blend films with gamma rays under ambient conditions. The formation of PANI nanoparticles has been seen by the color change from white to dark green following radiation doping. The SEM images exhibit spherical aggregates of PANI nanoparticles about 50-100 nm in diameter randomly distributed in the films. The UV-Visible spectrophotometer measurement revealed that the absorption band at 790 nm increases with dose owing to the formation of PANI with green color that increases with increasing dose. The conductivity measurement shows that the initially electrically insulating PVA/AniHCl blend has been remarkably transformed into the electrically conducting PVA/PANI nanocomposites where the conductivity increases by 5 orders of magnitude after exposure to 50 kGy.

Keywords: Polyaniline, PANI Nanoparticles, Radiation Scission, Radiation Doping

1. Introduction

Since the discovery of electrically conducting polymer by Alan MacDiarmid, Alan J. Heeger, and Hideki Shirakawa in 1976, intensive investigations have been carried out on the new generation of "synthetic metals" due to their unique combination of electronic and optical properties and processing advantages [1-2]. The electrical

Nomenclatures

σ_{dc}	Frequency-independent DC Conductivity
σ_{ac}	Frequency-dependent AC Conductivity
λ	Wave Length

conductivity is achieved in the conjugated polymers by means of delocalised of the π -electrons that allow charge mobility along the backbone of the polymer chain. The synthesis of conducting polymers has been accomplished by oxidising or reducing process either through chemical doping [3] or electrochemical doping [4].

Various applications of conducting polymers have been proposed as transducers of biosensor [5], electrodes of rechargeable batteries [6], artificial nerves and muscles [7], gas sensors [8], solid electrolytic capacitor, diodes and transistors [9], anti-static electromagnetic shielding [10], and biomedical applications [11].

Polyaniline (PANI) continues to attract considerable attention because its electrical and optical properties can be changed by oxidation and protonation of the amine nitrogen atoms. PANI is known for its excellent thermal and environmental stability but poor processibility due to insolubility and brittleness that limits its commercial applications. PANI could be more processible in the composites form with another water soluble polymers such as PVA, poly (vinyl pyrrolidone), poly (acrylic acid) and poly (styrene sulfonic acid) (PSSA) which are used as stabilisers. A functionalised protonic acid can be added into the composites to chemically polymerise PANI. The PANI dispersion can then be casted to form composite film containing PANI nanoparticles [12]. To improve the conductivity further, conducting polymers have been irradiated with x-rays [13, 14], gamma radiation [15], and gamma and electron beams [16]. When ionising radiation interacts with polymer materials active species such as free radicals are produced, thereby initiating chemical reactions including crosslinking, chain scission, and grafting. The ionic carriers induced by radiation scission can improve the conductivity of PANI.

In this paper, we wish to report the synthesis of PANI nanoparticles dispersed in PVA films directly using radiation doping with gamma rays. The influence of absorbed dose on the optical and electrical properties is presented. The advantages of the radiation method for polymerization of PANI nanoparticles are that it is simple and fast method. This might be an important step for processing advantages in industrial-scale production and applications in microelectronics and lithography.

2. Chemicals

The chemicals used in this study are: polyvinyl alcohol PVA (Mw = 72,000 g/mol) (Fluka), aniline hydrochloride (AniHCl, Mw = 129.59g/mol) (Merck-Schuchardt) and distilled water.

3. Experimental Procedure

The PVA bulk solution was first prepared by dissolving PVA powder (5 g) in distilled water (100 ml) under controlled water bath temperature at 90°C and continuous stirring for 3 hours. AniHCl powder (1.5 g) was added into the PVA solution at room temperature and continuously stirred for 10 hours. The blend solution was allowed to dry from casting glass under ambient temperature. Free standing casting film was formed and the white film was cut into several pieces to facilitate different radiation exposures. The average thickness of the blend films was 1.98 ± 0.02 mm.

The PVA/AniHCl blend films were exposed to gamma rays using ^{60}Co radiation facility (J.L. Sherperd model) at a constant dose rate at room temperature. The doses were delivered up to 50 kGy in a step of 10 kGy. The samples were placed inside a polystyrene block as a build up material for the secondary charge particle equilibrium. The dose rate was measured with a Fricke dosimeter.

3.1 Characterization of PVA/PANI composites

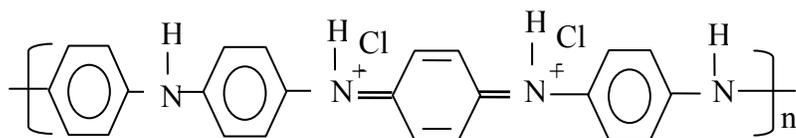
The structural morphology of the PANI nanoparticles was studied by a scanning electron microscope (SEM). The electrical and optical properties of PVA/PANI film composites were investigated at different doses to establish the amount of conducting PANI formed in the films. The optical characteristics were studied by a naked eye observation and a UV-VIS spectrophotometer (Camspec, M350) in the wavelength range from 200 to 800 nm. The electrical characteristics were determined from the conductivity measurement using an impedance analyser (HP4248 LCR meter) in the frequency range from 20 Hz to 1 MHz. All measurements were performed at room temperature.

4. Results and Discussion

Gamma rays (γ -radiation) imparted its energy in the medium through various processes such as ionisation and excitation of atoms, chemical bond scission, grafting, cross-linking, and disintegration of molecules. In our case after irradiation, AniHCl ($\text{C}_6\text{H}_5\text{N.HCl}$) undergoes dehydrochlorination (bond scission) and induced hydrochloric acid. The chlorine Cl^- from HCl agent in turns doped aniline molecules for the formation of conducting polymer of PANI Salt. The possible reaction in the formation of PANI from AniHCl by radiation doping may be written as follow:



The conducting PANI might take in the form of polyemeraldine structure as shown below, where the chlorine ion Cl^- doped the nitrogen ion N^+ of the imines group. This conducting polyemeraldine structure implies the conducting species polarons where each chlorine ion is being associated with one proton model (1).



Model 1. PANI Takes in the Form of Polyemeraldine Salt Structure.

4.1 Morphology of PVA/PANI nanocomposites

Figure 1 shows the SEM surface structure micrograph of PANI nanoparticles synthesised by radiation doping at 50 kGy. At high magnification of 10,000 times, it shows both the spherical PANI nanoparticles and some fibrous clusters of PANI nanostructures. The average size of the nanoparticles is about 50 - 100 nm in diameter and for the fibrous clusters is about 100 – 200 nm in diameter and 300 – 400 nm in length.

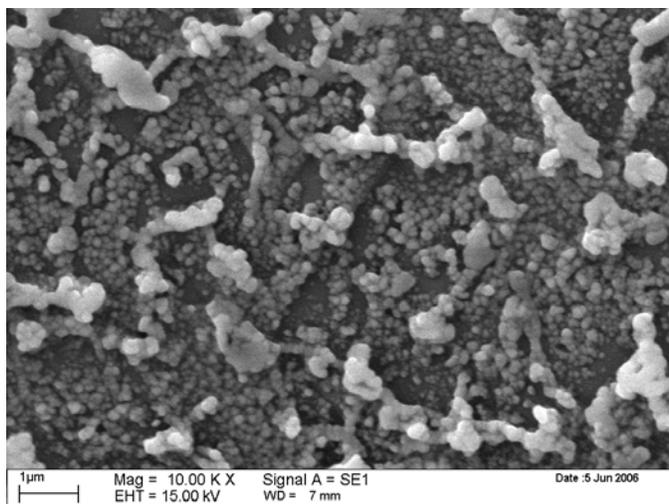


Fig. 1. SEM Micrographs 10,000 Times of Magnification Showing the Distribution of Fibrous Clusters and Spherical Aggregates of PANI Nanoparticles Synthesised by Radiation Doping at 50 kGy.

4.2 The Optical characteristics

The UV-Vis absorption spectra of the films were measured at different doses as shown in Fig. 2. For the film untreated with radiation there is no absorption peak in the UV region and no peak in the visible region. For the films irradiated with gamma rays, two absorption bands peaking at 315 and 790 nm are present. These optical absorptions are associated with the electronic transitions from highly occupied molecular orbital (HOMO) π -band to lowly unoccupied molecular orbital (LUMO) π^* -band of electronic states. The absorbance of both peaks increases with increasing dose as shown in Fig. 3. The absorbance at 315 nm band is due to HCl which is formed by radiation scission from AniHCl and seemed to be increases with radiation dose as shown in Fig. 3. The absorbance at $\lambda = 790$ nm band increases with the increase of dose, suggesting the formation of PANI is being formed. Thus, more polymerisation is takes place at higher doses Fig. 3. The result is in agreement with the recent study on PANI nanoparticles synthesised by HCl doping dispersed in PVA, where the characteristic absorption bands were at 740 – 800 nm wavelengths [13].

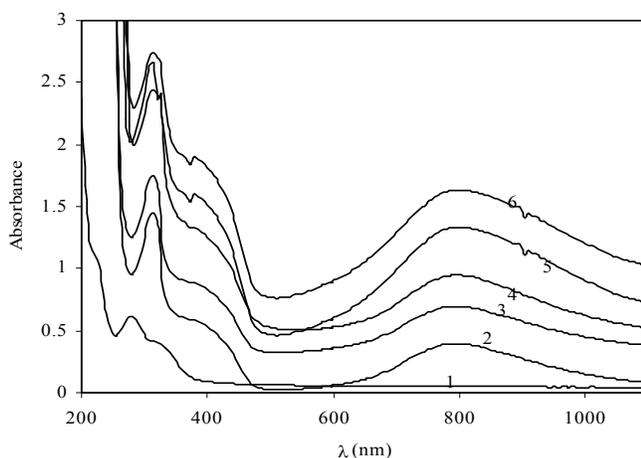


Fig. 2. UV-Visible Absorption Spectra of PANI Nanoparticles of Blend Film Irradiated at Different Doses up to 50 kGy and 23 wt% AniHCl.

4.3 Electrical conductivity

Figure 4 shows the variation of the total conductivity as a function of frequency for PVA/PANI composite films at various doses. The total conductivity can be expressed as in equation (1)

$$\sigma_T(\omega) = \sigma_{dc} + \sigma_{ac}(\omega) \quad (1)$$

At frequency independent, the conductivity is served by weakly disassociated ions by irradiation such as Cl^- , H^+ and OH^- while at frequency dependant the conductivity is served by relaxed ions and phonon assisted process [14].

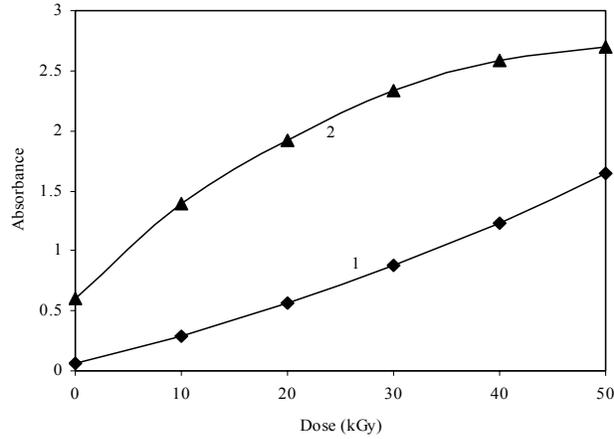


Fig.3. The Absorbance of 315 and 790 nm Absorption Bands as a Function of Dose Corresponds to the Formations of HCl and PANI Nanoparticles Respectively.

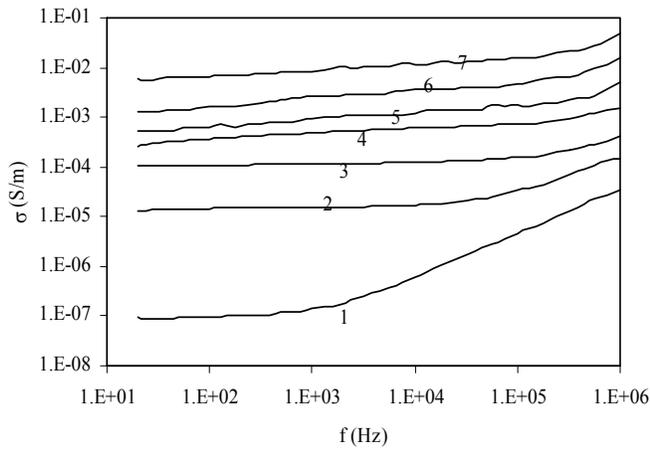


Fig. 4. The General Conductivity of PVA/PANI Nanocomposite (1 = pure PVA, 2 = PVA+1.5g AniHCl and 2-7 are Doses from 0 up to 50 kGy).

Figure 5 shows the dc conductivity derived by direct extrapolating of the general conductivity from Fig. 4. It shows that the dc conductivity of the blend is increased by

increasing the radiation dose and at 0 kGy the conductivity is 9.13×10^{-6} S/m and at 50 kGy is 2.4×10^{-2} S/m. The dc conductivity component comes from free charge carriers including Cl^- and H^+ ions originated from radiation scission of AnilHCl. The ac conductivity component is the result of the charge carriers that trapped in PVA and hopping between the sites over a potential barrier separating them. At doses of 20 kGy and higher, the electrical conduction is dominated by the formation of polarons from PANI of the polyemeraldine structure. The remarkable increase in conductivity indicates that there is a transition from PVA/AnilHCl dielectric polymer blend to PVA/PANI conducting nanocomposites following radiation doping.

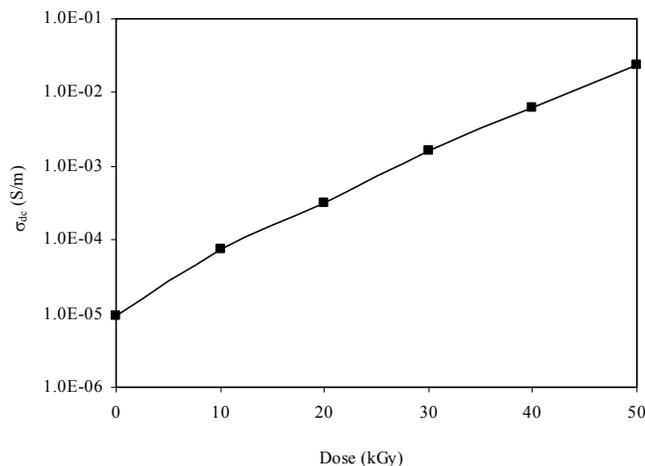


Fig. 5. The DC Conductivity of the PVA/PANI Nanocomposite Film with 23 wt% AnilHCl at Different Doses.

5. Conclusion

Polymerisation of aniline monomer and the synthesis of conductive polyaniline nanoparticles were synthesised by gamma irradiation having the conductivity up to 2.4×10^{-2} S/m for 30.1 wt. % of aniline hydrochloride i.e. 1.5 g AnilHCl at 50 kGy of radiation dose, such conductivity has proportional relation with the applied radiation dose. The conductive polyaniline salt i.e. PANI-HCl form showed an absorption band of ultraviolet visible spectrum at $\lambda = 790$ nm (range of green colour) and the intensity of such absorption was increased following the radiation dose. The usage of radiation technology in this field compared to chemical one has the advantages of pureness, no chemical catalysts, wider applications, easy process and commercial production.

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