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Electrical characteristics of PVA-PANI-ZnS nanocomposite film synthesized by gamma irradiation method

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This work presents the synthesis of PANI-PVA-ZnS nanocomposite films by gamma irradiation approach. The samples were irradiated with different doses ranging from 10 kGy to 40 kGy. Subsequently, structural, morphological, optical and electrical characteristics of the samples were investigated. Fourier transform infrared (FT-IR) spectroscopy was employed to study the chemical structure of the samples. Field emission scanning electron microscopy (FE-SEM) was used to investigate the morphology of nanocomposites. The electronic absorption characteristics of the samples were measured by means of UV-Vis spectroscopy. The AC and DC electrical behaviors of the samples were characterized using LCR meter in the frequency range of 20 Hz to 1 MHz. The impedance values of the samples were extracted from Cole-Cole plots and consequently DC conductivity was calculated.

Keywords: *nanocomposite; polyaniline; FT-IR; LCR meter; impedance analysis*

1. Introduction

Discovery of conductive polymers has made it possible to employ these substances as a low cost substitute, modifier or reinforcement for metallic and semiconductor materials [1, 2]. Among conducting polymers, polyaniline (PANI) has attracted much interest of many researchers due to its tunable properties and high conductivity, good environmental and thermal stability, ease of synthesis and many potential applications [3–5]. PANI has been found in different forms raging from insulating to conducting.

The combination of zinc sulphide (ZnS) nanoparticles and PANI is an interesting composite for optical, electrical and medical applications because of variable properties of PANI at different oxidation states as well as functional properties of the ZnS nanoparticles with the wide range of band gap. Incorporation of these two materials combines and enhances the properties of both phases.

PANI-ZnS nanocomposite is a new subject with a tremendous potential into the various applications, which makes it interesting to investigate. To the best of our knowledge, this compound has been scientifically studied in six different studies [6–11]. At present, two methods are used for the preparation of ZnS/conducting polymer composites: the dispersion of ZnS nanocrystals in polymer solution and the chemical polymerization of the monomer in the presence of ZnS nanoparticles [10]. The method of synthesis has a direct impact on chemical and physical properties of the final product. Therefore, finding a cheap, easy and processable method would be crucial for the large area application.

PANI shows better processability upon addition of another water-soluble polymers such as polyvinyl alcohol (PVA). Besides, PVA with the molecular formula of $(C_2H_4O)_n$ is a viscous medium or capping agent which provides flexibility, processability and control of the growth of nanoparticles [12].

In this study, we synthesized PVA-PANI-ZnS nanocomposite films by a single step in situ

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polymerization of PANI and simultaneous reduction of ZnS nanoparticles with the help of ionizing radiation. Gamma radiation has been considered as an interesting route since no oxidizing agent, reducing agent and metallic catalyst is required. It provides a pure product at a low cost. In addition, this process can be done in a solid state condition with a possibility of size control.

2. Materials and methods

Polyvinyl alcohol (PVA, Mw 30,000 g/mol, 98 % hydrolyzed) was purchased from Merck Company and used as a binder. Aniline hydrochloride (AniHCl, Mw 129.59 g/mol) and thioacetamide (CH_3CSNH_2) were supplied by Sigma-Aldrich and used as precursors. Zinc acetate ($Zn(CH_3COO)_2 \cdot 2H_2O$), purchased from R&M Chemicals was used as a source of zinc. All materials were used without any further purification.

In a typical procedure, the PVA solution was prepared by dissolving 30 g PVA powder in 600 mL deionized water at room temperature in a water bath at fixed temperature of 80 °C for 2 hours. The solution was then left to cool at room temperature.

After temperature equilibration, 12 g of aniline hydrochloride was added into 600 mL PVA solution. The same molar ratio ($1:1 \times 10^{-3}$ mol/L) of zinc and sulphur source was also added to the PVA solution. The mixture was continuously stirred for 10 hours in nitrogen atmosphere. The blend solution was divided into 50 mL portions and poured into a specially made glass caster. The casted solutions were left to dry at ambient temperature in a dark room for at least 6 days. The films were removed and cut into several pieces with the dimension of 2.5 cm × 2.5 cm. The thickness of the samples was determined by a digital micrometer model Mitutoyo No. 293-521-30-Japan. The average thickness of the films was 0.12 mm. The casted films were packed in six sealed plastic bags and sent for gamma irradiation from 0 kGy to 40 kGy. The samples were exposed to gamma irradiation at the room temperature using ^{60}Co producing gamma rays with the average energy of 1.25 MeV.

3. Results and discussion

The FT-IR spectrum of PVA-PANI-ZnS film is shown in Fig. 1. The PVA film is used for setting the background. The IR signatures indicate presence of both emeraldine base (EB) and emeraldine salt (ES) forms of PANI [13]. EB-polyaniline is the neutral and the most stable form of PANI at room temperature. It can form ES-polyaniline followed by protonation and exhibit electrical conductivity.
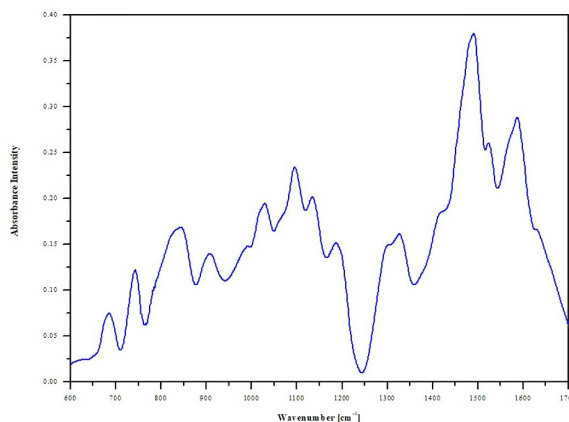

Fig. 1. FT-IR spectrum of PVA-PANI-ZnS nanocomposite film.

The FT-IR result indicates that HCl of Ani-HCl precursor is dissociated and forms free radicals of H^+ and Cl^- as the consequence of gamma irradiation. Subsequently, Cl^- radicals are doped on amine group and form the protonated state of PANI. The doping process creates a local distortion, resulting in a local polarization, centred on the charge carriers, that is known as polaron. Therefore, the protonation process produces the polarons and consequently results in high electrical conductivity.

The bands at 1592 cm^{-1} and 1495 cm^{-1} are assigned to the quinoid and benzoid ring stretching vibrations. Higher absorbance intensity of benzoid ring vibration confirms that the formed PANI is mainly at ES state. The peaks centred at 1335 cm^{-1} and 1305 cm^{-1} correspond to C–N stretching vibration. The peaks in the region of 1000 cm^{-1} to 1200 cm^{-1} are attributed to the in plane bending vibration of aromatic C–H.

The peak at 850 cm^{-1} is characteristic of C–H out of plane bending vibration. The bands at 747 cm^{-1} and 693 cm^{-1} are due to the mono-substitution on the benzene ring [13–17].

The morphology images of PVA-PANI-ZnS nanocomposite films subjected to 10 kGy and 40 kGy irradiation are shown in Fig. 2a and Fig. 2b, respectively. It can be seen in Fig. 2a that ZnS nanoparticles (bright spherical objects) and PANI nanoparticles are spherical and agglomerated. At higher dose of radiation more PANI nanoparticles are formed and agglomerated while ZnS nanoparticles are dispersed within the PANI structure. Therefore, at higher dose, a tight uniform structure of the nanocomposite is formed.
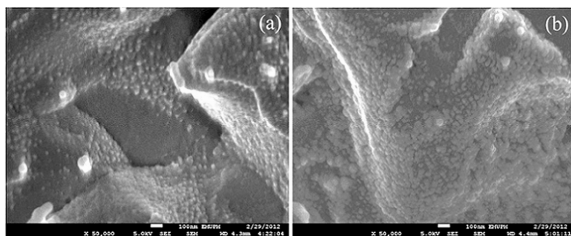

Fig. 2. FE-SEM images of PVA-PANI-ZnS nanocomposite films synthesized at (a) 10 kGy and (b) 40 kGy gamma irradiation.

Electronic absorption spectra of PVA-PANI-ZnS nanocomposite films are depicted in Fig. 3. The PVA film is set as the background. Both spectra reveal 5 main absorption peaks centred at 252 nm, 309 nm, 405 nm, 580 nm and 805 nm. The first peak at 252 nm is due to the polyanilinum cations and becomes smaller at 40 kGy irradiation indicating higher polymerization of PANI at higher doses. The peak observed at 309 nm confirms the formation of ZnS nanoparticles [18]. The peak centred at 580 nm is associated with the exciton transition of quinoid in the undoped state of PANI (EB) and the other two bands at 405 nm and 805 nm are due to polaron band transitions, indicating formation of conducting form of PANI (ES) [19]. Therefore, similar to FT-IR result, it is confirmed that PANI is present in both EB and ES forms. As the dose of radiation increases, the intensities of the peaks at 405 nm and 805 nm is increasing, indicating

the formation of more doped state of PANI. Consequently, the formation of more doped state would increase the conductivity of the sample irradiated at higher dose.
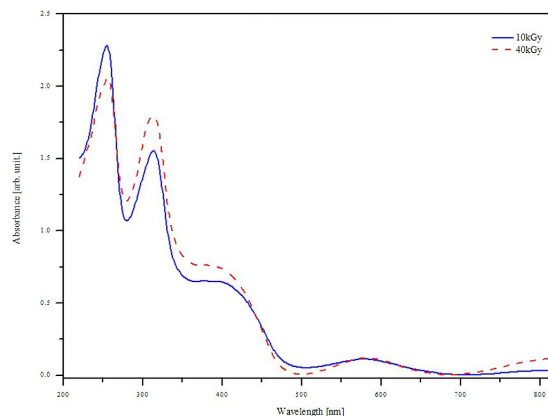

Fig. 3. UV-Vis spectra of PVA-PANI-ZnS nanocomposite films synthesized at 10 kGy and 40 kGy gamma irradiation.

Fig. 4 shows the general conductivity of PVA and PVA-PANI-ZnS as a function of frequency for gamma irradiated samples from 10 kGy to 40 kGy. The general conductivity plot is a combination of both real and imaginary part of conductivity. The general conductivity of the samples has increased compared to PVA.

According to Jonscher et al. [20], the conductivity is the summation of direct current (DC) conductivity and alternating conductivity (AC), which can be expressed as:

$$\sigma(\omega) = \sigma_{DC}(0) + \sigma_{AC}(\omega) \qquad (1)$$

The DC conductivity is a consequence of free charge carriers. The movement of these carriers in the applied electrical field is independent of frequency. In contrast, the AC conductivity arises form trapped charge carries or ions. Therefore, according to the known mechanism of ionic hopping, an alternating filed with a certain frequency causes the movement of ions from one centre to another.

At lower frequency, conductivity behaves independently of frequency representing DC conductivity. At higher frequency, conductivity shows
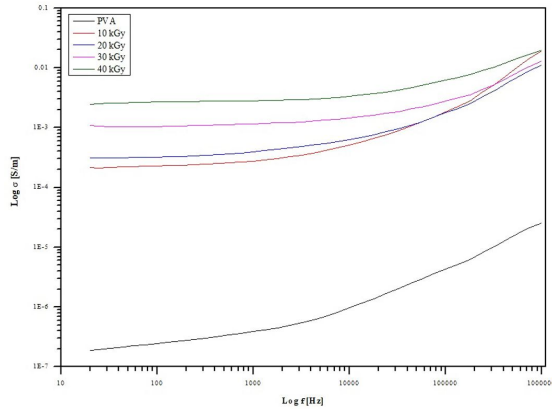
Fig. 4. General conductivity of PVA-PANI-ZnS samples irradiated from 10 kGy to 40 kGy.

Fig. 5. Cole-Cole plots of PVA-PANI-ZnS nanocomposite films irradiated from 10 kGy to 40 kGy.

frequency dependency and the AC conductivity becomes more dominant. The AC conductivity behavior at higher frequency is due to the trapped ions within the nanocomposite matrix. As the gamma irradiation is increasing, the frequency dependent conductivity shifts toward higher frequency. The shift of dispersion and increment of conductivity as a function of gamma irradiation indicates the less concentration of trapped ions and increased formation of free charge carriers within the film matrix.

Fig. 5 shows the Cole-Cole plots of PVA-PANI-ZnS samples from 10 kGy to 40 kGy gamma irradiation. The plot of complex impedance Z'' vs. Z' results in a semicircle graph in which the equivalent circuit is in a form of a capacitance in parallel with a resistance. This indicates that the grains are the main participants in conductivity and charge transfer while the grain boundaries have no effect on conductivity. This result is in agreement with the FE-SEM image, which shows a uniform polymerization within the film matrix.

Impedance Z_0 is obtained by extrapolating the semicircle curves to the real impedance axis Z' at zero frequency. The DC conductivity is then calculated by:

$$\sigma_{DC} = \frac{d}{A \times Z_0} \qquad (2)$$

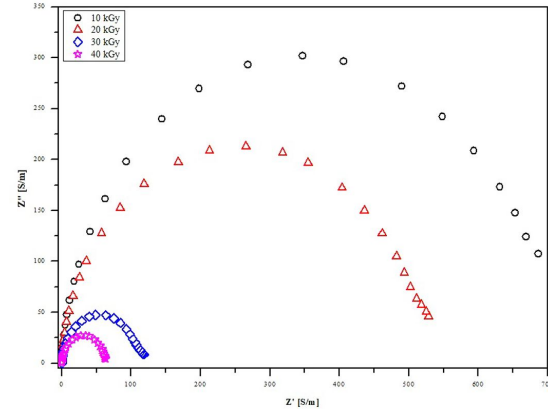where d is the thickness and A is the surface area of film.

The measured values of DC conductivity are 2.47×10^{-7} S/m, 2.1×10^{-4} S/m, 2.98×10^{-4} S/m, 1×10^{-3} S/m and 2.6×10^{-3} S/m for PVA, samples irradiated at 10 kGy, 20 kGy, 30 kGy and 40 kGy, respectively. The DC conductivity has increased by increasing the gamma irradiation dose from 10 kGy to 40 kGy. The increase in DC conductivity is due to the formation of higher amount of ES state of PANI, as a result of higher concentration of free charges present in the sample. It is worth to mention that the conductivity of PVA has increased by a factor of almost 10000 after polymerization of PANI at 40 kGy.

4. Conclusions

The PVA-PANI-ZnS nanocomposite was successfully synthesized by gamma irradiation method at 10 kGy to 40 kGy radiation doses. The FT-IR spectroscopy indicated the presence of EB and ES forms of PANI wherein the ES form was responsible for electrical conductivity of the samples. The FE-SEM images showed the formation of spherical ZnS and PANI nanoparticles where the PANI particles were agglomerated along the matrix. The PANI nanoparticles formed a uniform structure at higher dose. The UV-Vis spectroscopy also confirmed the formation of ZnS nanoparticles and both EB and ES forms of PANI. The result indicated that large quantity of ES was formed at higher dose. The electrical properties of the samples were enhanced

by increasing the gamma irradiation doses because of formation of higher amount of ES form of PANI. The measurements of impedance and DC conductivity revealed a significant increment in conductivity of the samples by a factor of 10^4.

Acknowledgements

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