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CHEMICAL MODIFICATION AND CONTROL OF POLYANILINE NANOCOMPOSITES CONDUCTIVITY BY RADIATION TECHNIQUE IN PVA MATRIX

M.A. ALI[1,3*], E. SAION[1],Y. Noorhana[1], A. KASSIM[1],K.M. DAHLAN[2], K. A. Rabaeh[1], I. SHAHRIM[1], S. HASHIM[2]

[1]Department of Physics, Department of Chemistry, Faculty of Science, University Putra Malaysia, 43400 UPM Serdang, Selangor, MALASIA.
[2]Malaysian Institute for Nuclear Technology Research (MINT), 43000, Bangi, Selangor, MALAYSIA.
[3]Sudan University of Science & Technology, Medical Radiologic Science, Khartoum, SUDAN.
*Corresponding Author: alkajam@gmail.com

Abstract

A variables range of conducting polyaniline (PANI) nanocomposites hosted by polyvinyl alcohol (PVA) in a form of film has been prepared by using γ-irradiation technique to Aniline hydrochloride (AniHCl)/PVA composites. The conductivity of the film showed consequence increase following the radiation dose from 10 to 50 kGy for each different concentration of the monomer blend AniHCl in PVA matrix which have exponential relation. The maximum achieved dc conductivity $\sigma(0)$ was 10^{-1} (S/m) at high concentration of AniHCl and 50 kGy radiation dose, as being studied by LCR-meter. The composite films structure has also been studied by Raman spectroscope, which reveals that there is a new chemical bond structure as imines group of the form C=N (polarons) species has been formed by radiation and giving rise to Raman shift at 1637 cm^{-1}. The intensity of Polarons was also being increased exponentially following the radiation dose leading to increase of polyaniline conductivity. Moreover the morphological structure of the films were scanned by Scanning Electron Microscopy SEM, which intern reveals that the composite film is composed of polyaniline nanoparticles in the range size of 100 nm.

Keywords: Polyaniline, Nanocomposites, Radiation Processing.

Nomenclatures

D	Amount of applied radiation dose
D_0	Dose sensitivity of material
ml	Milliliters (volume unit)
nm	Nanometer (unit of size measurement)
S/m	Siemens per meter (conductivity unit)
wt %	Weight percentage
Y	Raman intensity at certain dose
Y_0	Raman intensity at zero dose

Greek Symbols

σ_{dc}	Direct current conductivity
γ	Gamma radiation

1. Introduction

Recently there is great interest in nano sized materials to be involved in many areas of applications such as electromagnetic shielding [1], anti corrosion [2],electronics, biosensors [3, 4] and biochemical/biomedical engineering [5]. The new materials with size ranging 1 – 100 nm are classified as nanomaterials because of their size, however they exhibit magnificent physical and chemical properties differ from those displayed by their molecular or bulky composites [6]. One of the most promising nanocomposites materials is the conducting nanocomposites polymers, which in general are so tunable in view of processing and control of properties either following chemical or electrochemical preparation [7] beside the other impracticable physical techniques such as ultra sound [8, 9] and ultra violet radiation [10]. Among the conducting polymers PANI showed high tunable conductivity, good environmental stability, processability and potential application in various fields' case it is hosted in water soluble polymer binder. The advantages of using gamma irradiation over the other techniques to prepare conducting PANI nanocomposites are no oxidizing agent required, no catalyst, the oxidation process occur at dry state, inexpensive, easy acquisitions and high production which encourage the commercial issues. The effects of γ-irradiation to AniHCl/PVA blend resulted in the formation of dissociation of hydrochloride HCl and free radical which are responsible for doping of amine group (N^-) and the polymerization of aniline respectively, then the potential chemical species as polarons will be formed within the polymer backbone which in turns responsible for high electrical conductivity in chemical doping of polyaniline [11]. The polaron species have also been traced by using Raman spectroscopy in a chemically prepared conducting polyaniline, and their Raman intensity directly influenced and increased the conductivity of the polymer composites [12, 13]. In this topic we would like to highlight the chemical modification by γ-irradiation which

intern govern the conductivity in addition to conductivity control based on the amount of radiation dose and the monomer concentration.

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 de-ionised distill water.

3. Experimental Procedure

The composites films of PVA/AniHCl were being prepared by dissolving 5 wt % of powder PVA in distilled de-ionized water (100 ml) under controlled temperature of 90^{o}C and continuous stirring for 3 h. then different concentration of AniHCl powder form (9.0, 16.7, 23.0, and 28.6 wt % were added into the PVA solution at room temperature and continuously stirring for 10 hours. The blend solution was divided in Petri-dishes as 50 ml/dish and left to dry under ambient temperature for 5 days. The free standing casting film was formed and the white film was cut into several pieces to facilitate for 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 Characterisation of PVA/PANI nanocomposites

The electrical properties of the films were determined from the conductivity measurement using an impedance analyzer (HP4248 LCR meter) versus different radiation doses (10 – 50 kGy) at room temperature. And the induced chemical functional group as C=N was traced by using Raman spectroscopy (RSI 2001, INC 25mW), while the morphological view was revealed by SEM model (Quanta 400, 132-2.5, serial No.9949-60810 ME)

4. Results and Discussion

The chemical bonds of all organic compounds have binding energy in the range of 10 – 15 eV, therefore are easily modified by γ-radiation which has ionizing potential of 12.4 eV or more [14]. Based on the radiochemical interaction formula at [15], the conductive polarons species in PANI ($C_6H_5N.HCl$) can be formed in addition to other detached charge carriers such as chlorine ion Cl^- and hydrogen ion H^+ to enhance the electrical conductivity.

4.1 Conductivity of Pure PVA upon Irradiation

Figure 1 shows the effect of radiation on the conductivity of pure PVA with 5 wt % concentration. In which the conductivity of insulator PVA is increased from 6.61×10^{-8} up to 1.9×10^{-6} S/m, this increment due to free electrons and charges carriers formed by irradiation. The increment of dc conductivity (σ_{dc}) of PVA upon irradiation is obeying the following relation $\sigma_{dc} = 2.0 \times 10^{-7} \exp(0.05D)$, where D is refer to the amount of applied radiation dose. Although there is increasing of conductivity with radiation dose but is still within the value of insulator [16]. PVA conductivity has been studied to see how far it participates in the general conductivity of PANI which almost seeks for binder.

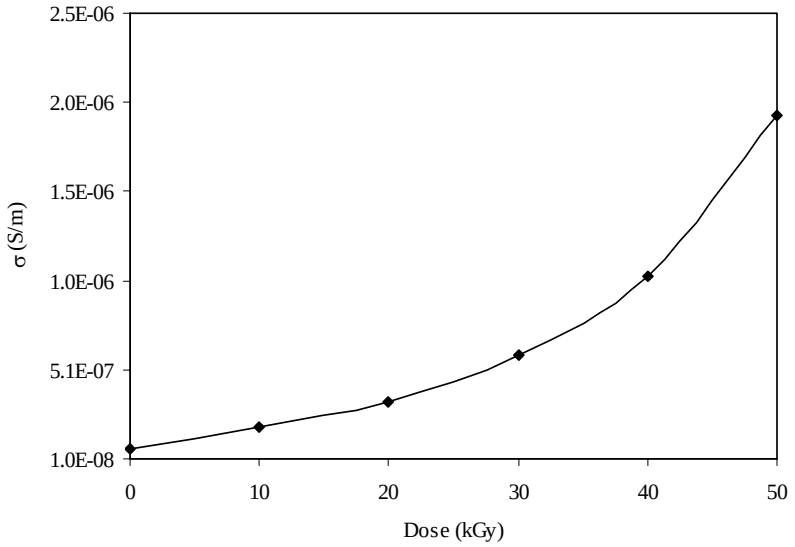

Fig. 1. Effect of Radiation on the Conductivity of Pure PVA with 5 wt % Concentration.

Figure 2 represents the effects of different concentrations of AniHCl blend on PVA dc conductivity. It shows that the conductivity of PVA has been increased by increasing the concentration of AniHCl from 6.61×10^{-8} S/m at 0.0 wt % AniHCl up to 1.0×10^{-4} S/m at 28.6 wt % AniHCl and there is subsequently dropped in conductivity at 33.0 and 38.0 wt % AniHCl. The increase of dc conductivity is attributed to more increase of charge carrier (Cl^-) in the blend compound, while the dropped in conductivity at high concentration of AniHCl (33.0, 38.0 wt% AniHCl) is due to high viscosity which causes high resistance opposing ions mobility [17, 18], as

has been shown that the ionic mobility has inversely proportion to viscosity as well as to formation of ion pairs [19].

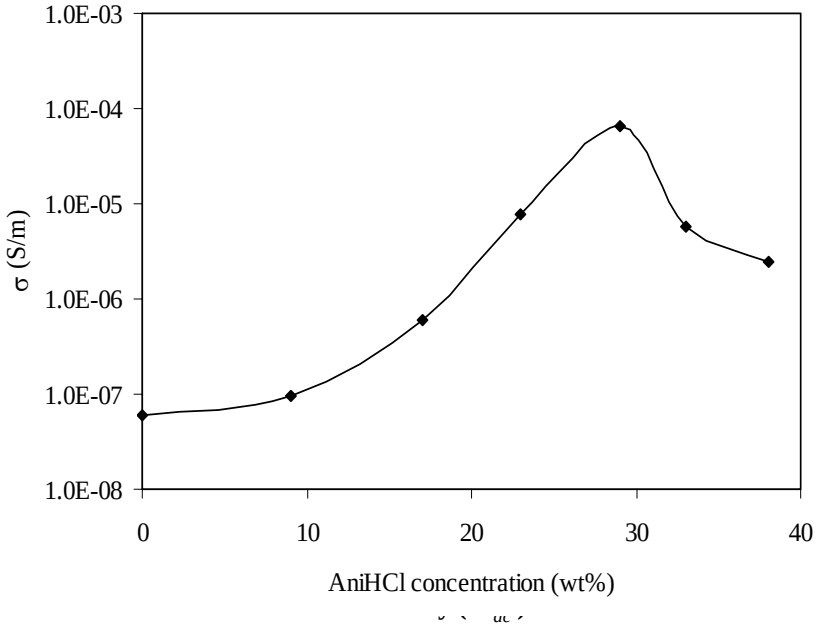

Figure 3 shows the dependant of dc conductivity of AniHCl/PVA film blend on the amount of radiation dose and AniHCl concentration. The study revealed that, the dc conductivity for all various concentrations were increased following the radiation dose in exponential relation of the form $\sigma_{dc} = \sigma_0 \exp(D / D_0)$, where D is the applied radiation dose, D_0 is the dose sensitivity of the material and σ_0 is the conductivity at zero dose.

We found that the dc component for 9.0 wt % AniHCl concentration increases from 5.75×10^{-7} S/m at 0 kGy to 1.32×10^{-3} S/m at 50 kGy, while for 16.7 wt % AniHCl concentration, the dc conductivity increases from 1.0×10^{-5} S/m at 0 kGy up to 2.9×10^{-3} S/m at 50 kGy. As for 23.0 wt % AniHCl concentration the conductivity increases from 2.4×10^{-5} S/m at 0 kGy to 1.3×10^{-2} S/m at 50 kGy. The highest conductivity measured was for 28.6 wt % AniHCl at which the dc conductivity increases from 7.8×10^{-5} S/m at 0 kGy up to 1.17×10^{-1} S/m at 50 kGy. The increment of dc conductivity is due to charge carriers (Cl^-) which detached by radiation from the composites and formation of polaron species which would be traced by Raman spectroscopy in Fig. 4, also the dc conductivity has been increased by increasing the

concentration of AniHCl in the composite, which is due to more charge carriers and high intense formation of polarons by increasing the target volume for irradiation.

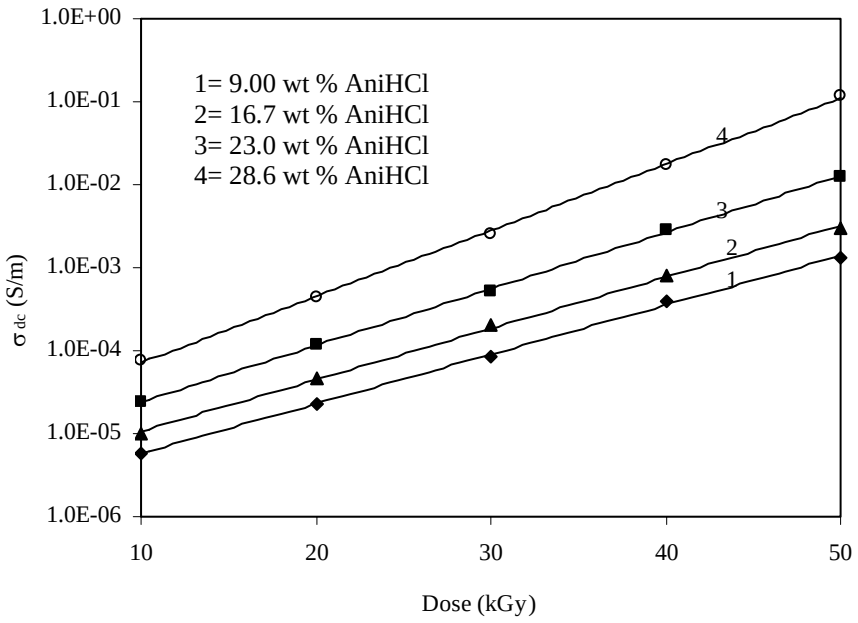

Fig. 3. Dependant of dc Conductivity of AniHCl/PVA Film Blend on the Amount of Radiation Dose and AniHCl concentration.

4.2 Radio-Chemical Modification

Figure 4 shows the intensity of the new chemical bond C=N as polaron species versus radiation doses for different AniHCl concentration traced by Raman spectroscopy at 1637 cm^{-1}. The intensity of polarons is being increased exponentially following the radiation dose and best fitted to the following relation $y = y_0 \exp(D/D_0)$, where y, y_0 are representing Raman intensity at radiation dose D and zero dose and D, D_0 are the applied radiation dose and dose sensitivity of the compound respectively.

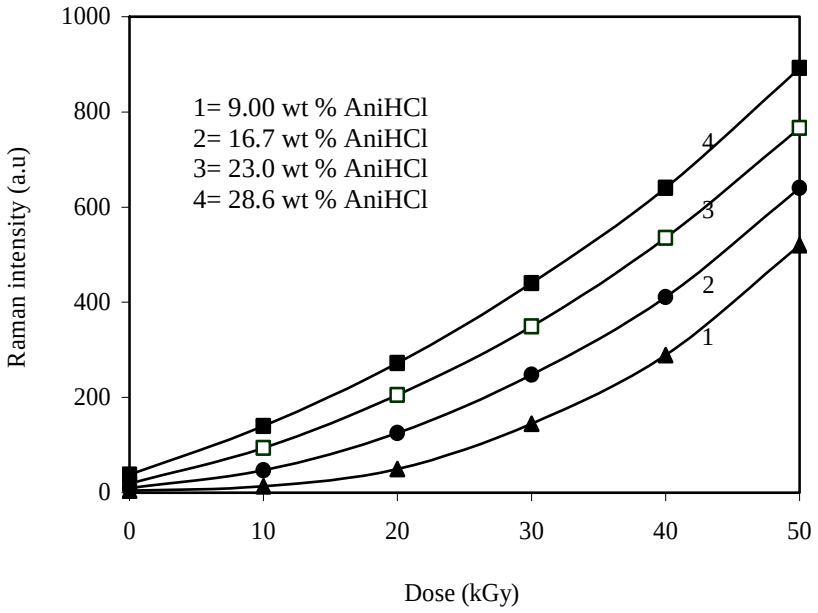

Fig. 4. Intensity of the New Chemical Bond C=N as Polaron Species versus Radiation Doses for Different AniHCl Concentration Traced by Raman Spectroscopy at 1637 cm^{-1}.

4.3 Morphology of PVA/PANI Nanocomposites

Figure 5-a shows micrograph of AniHCl/PVA at 50 kGy g-radiation dose by Scanning Electron Microscopy SEM. It exhibits even more evident of fully formed PANI nanoparticles aggregated in clusters having globular particle shape with an average diameter of about 100 nm, this in contrast with the same patch film Figure 5-b which shows only physical homogeneous blend paste of AniHCl with PVA in micro-size particles with no further details.

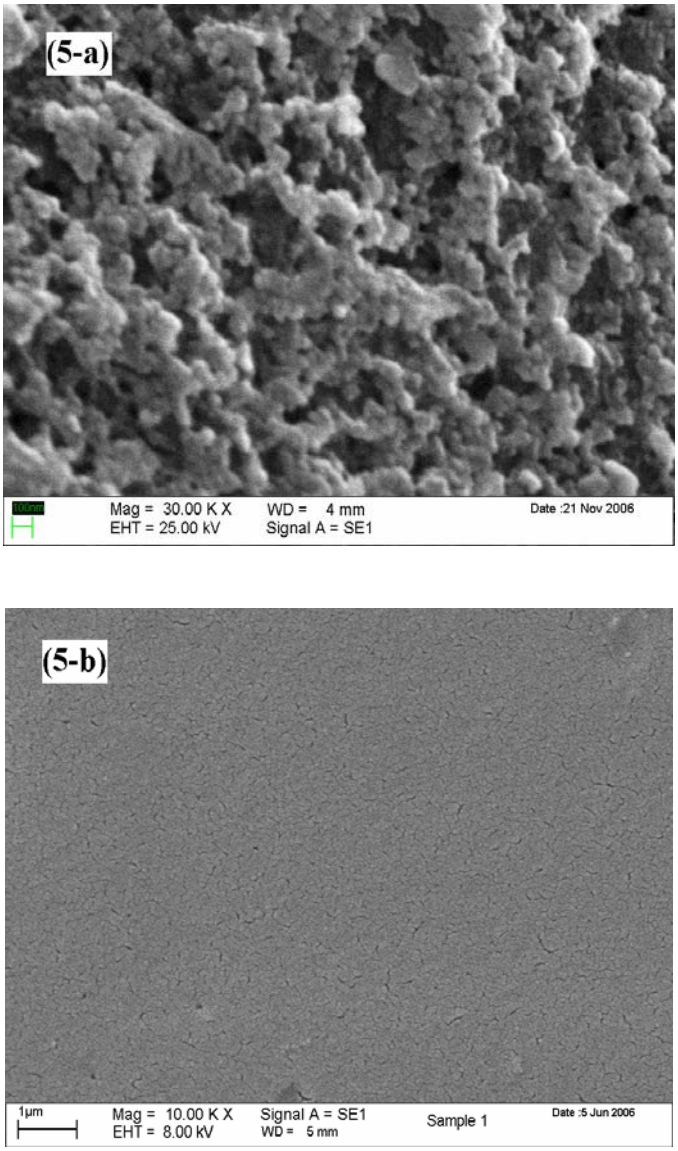

Fig. 5. Scanning Electron Microscopy SEM Micrograph of AniHCl/PVA (a) at 50 kGy γ-radiation Dose and (b) Before Irradiation.

5. Conclusion

For the importance of conducting nanocomposites polyaniline, many works have been done using either chemical or electrochemical technique; however the role of physics especially ionizing radiation as g-radiation is merely used in the current topic to prepare the conducting polyaniline nanocomposites.

The formation of conducting nanocomposites polyaniline with particles size of 100 nm has been well done by using γ-irradiation which has significant advantages in contrast with other used techniques. And such induced conductivity has great dependant up on the chemical modification (C=N) that took place due to irradiation. Also the conductivity range dependant on radiation dose has been confirmed, which has exponential relation as common radiation effect properties.

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