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Optical Properties of Radiopolymerized Polyaniline Hydrochloride Hosted in Polyvinyl-Alcohol Matrix

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ABSTRACT: Aniline hydrochloride monomer was polymerized to polyaniline salt (emeraldine salt) and rendered as electro-chromatic material i.e. colored conducting material by direct γ-radiation exposure to high dose up to 50 kGy. The optical color of the material was shown as light green color to dark green color following the radiation doses rather than colourless indicating the polymerization of aniline salt. The optical color and the polymerization was confirmed by using UV-visible spectroscopy, which gave rise to an absorbance band at 790 nm, the absorbance band in turn increased following the dose exponentially. The band gap energy of PANI was obtained and shown to decrease with radiation dose down to 1 eV at 50 kGy indicating the electrical conductivity of PANI. Raman spectroscopy showed a new bond C=N as a part of polaron conducting species created by irradiation, which has a Raman shift of 1637 cm^{-1}. The double bond of C=N, responsible for the appearance of the green color, increased was increase exponentially with radiation dose.

KEYWORDS: *Optical properties, Radiopolymerized polyaniline.*

INTRODUCTION

Electromagnetic materials are characterized materials are characterized by redox state with distinct UV-visible absorption spectra or generation of new absorption band due to switching between redox states [(1,2)]. However the recent interest in electro-chromic devices (ECDs) for multi-spectral energy modulation by reflectance and absorbance has extended the definition to include the general response of the materials to the electromagnetic region regardless of human eye detection[(3)]. The color changes in an object give visual signals that can be used to convey useful information to an observer [(1)].

Many chemical species can be switched between redox states that have distinct electronic absorption spectra either due to moderate energy internal electronic excitation or to an inter-valence optical change transfer where the chemical species has two different valence or oxidation states. [(4-6).] The electro-chromic materials can be classified into three basic types: i) soluble in (redox) state such as: (i) Prototype viologen,1’1’-dimethyl-4,4-bipyridium (methyl viologen), ii) soluble in one redox state but form a solid film on the surface of electrode following electron transfer such as 1,1’ di-heptyl-4-4’bipyridium (heptyl viologen),and iii) materials of solid state in both cases of redox such as conductive polymers.

However two types of electromagnetic materials (ii and iii) are considered having an optical memory that is because once their redox state is switched, no further change injection needed to retain the new electro-chromic state [7]. The electro-chromic materials still have shortcoming in term of switching speed, stability, contrast and ease of synthesis and processing. However the conducting conjugated polymers are the most promising as electro-chromic materials because of their better stability, faster switching speeds and ease of processing compared to inorganic electro-chromic materials.

The importance of the electro-chromic materials is based on the applications in field of display devices and bio-analysis; hence the aim of this study is to reveal the effects of radiation as a polymerization tool for analine hydrochloride monomer.

MATERIALS and METHODS

Aniline hydrochloride (AniHCl) monomer with molecular weight (Mw) 129.59 g/mol from Merck-Schuchardt Company was used with different concentrations (9.0, 16.7. 23.0 and 28.6% wt. Polyvinyl alcohol PVA (Mw = 72,000 g/mol) (Fluka), has been chosen as a binder to form the composites in a film form.

Experimental Procedure: The PVA bulk solution was first prepared by dissolving PVA powder (5 wt %) in distilled water under controlled water bath temperature at 90 ^{o}C and continuous stirring for 3 h. AniHCl powder (1.0 g) was added into the PVA solution at room temperature, nitrogen atmosphere and continuously stirred overnight for 10 h. The blend solution was poured in Petri-dishes (20×20 cm) as 40 ml/dish and allowed to dry to form films by casting under ambient temperature for 5 days. A 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.

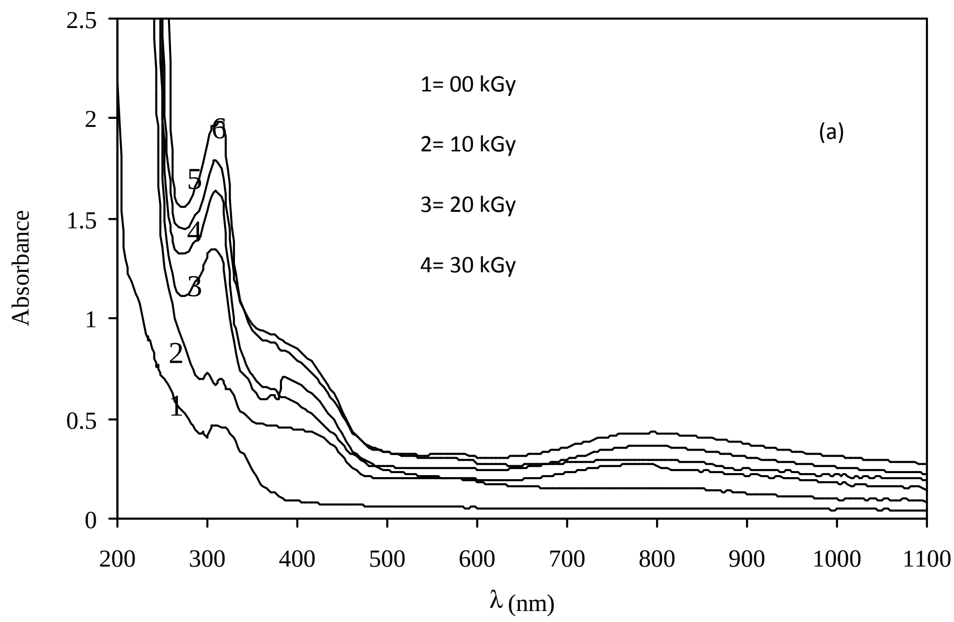
The PVA/AniHCl blend films were exposed to gamma rays using ^{60}Co radiation facility (J.L. Sherperd model) at a constant dose rate at room temperature. The doses were delivered up to 50 kGy in a step of 10 kGy. The samples were placed inside a polystyrene block as a build up material for the secondary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

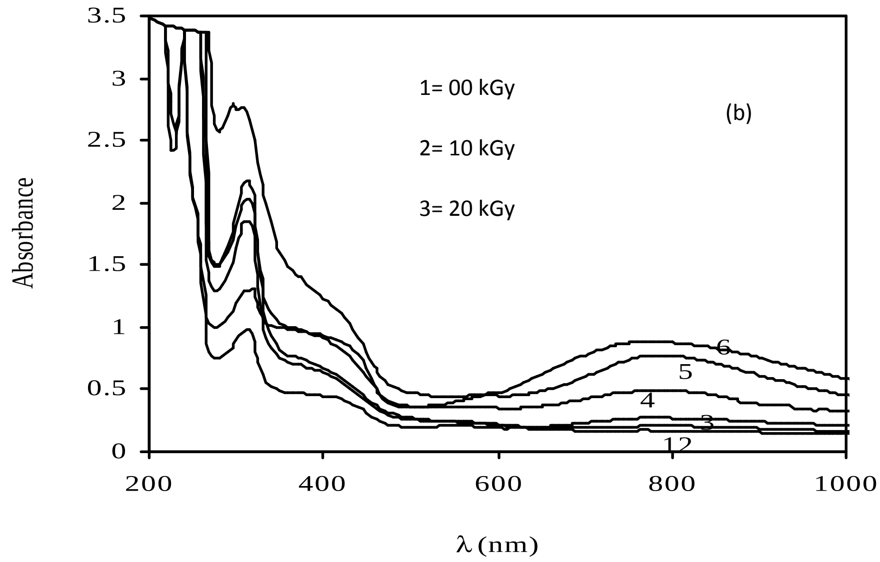
RESULTS and DISCUSSION

Figure 1 shows the response of electro-chromic (PVA/AniHCl) composites to gamma radiation (γ-radiation) with appearance of light green colour to dark green colour following the radiation dose. Such coloration indicates that PVA/PANI is electro-chromic material as well as the polymerization of aniline monomer to polyaniline. This result agrees with Jiaxing *et al*,[8].

Fig. 1: the response of PVA/AniHCl composite to γ-irradiation, indicating the electro-chromic and polymerization of aniline monomer.

Figure 2 illustrates the UV-visible spectra of PVA/AniHCl at 9.0, 16.7, 23.0 and 28.6% w/v of AniHCl concentrations. The composites UV-spectra revealed that there are prominent peaks at 315 and 790 nm. The absorbance band at 315 nm assigned for the electronic transition of Cl- while the absorbance at 790 nm is due to the creation of C=N imines group, the double bond of imines group representing the polarons species in conducting PANI that gives the green colour. This result is in agreement with previous study carried out by Rao, *et al.*[9]. The absorbance increased with the increase in dose and AniHCl concentration. Both peaks become sharper with dose increase, indicating the amount of Cl- and polarons formed (represented by C=N) have increased with dose increment.

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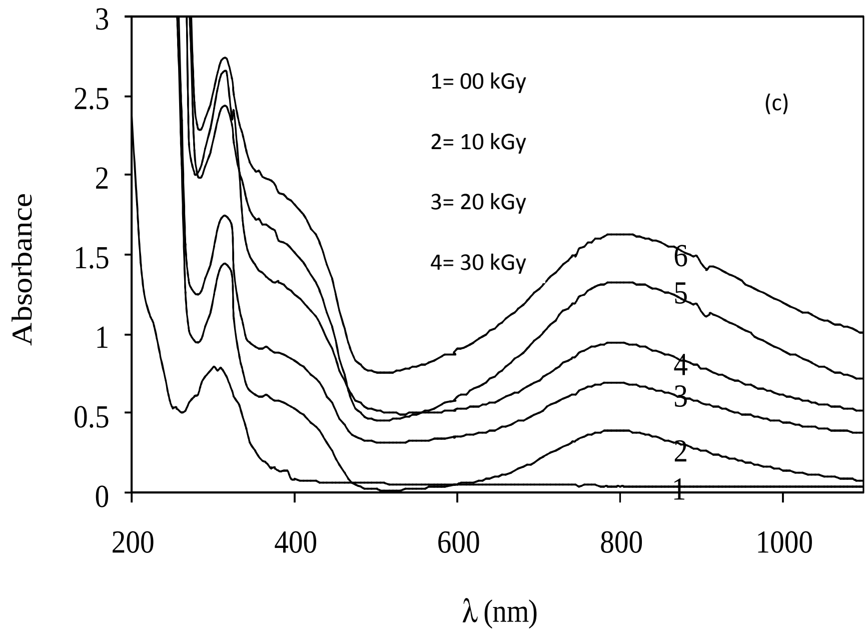
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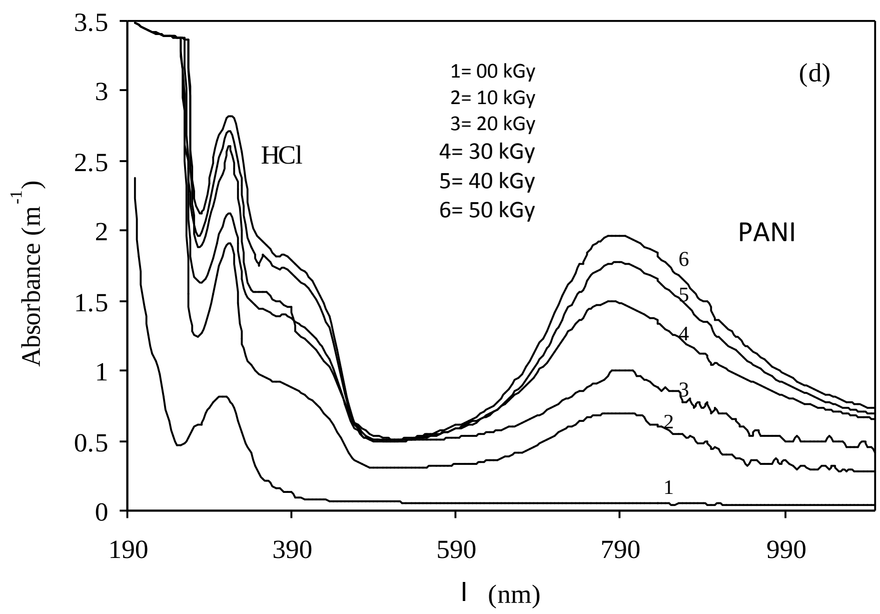

Fig 2: UV-visible spectra of PVA/AniHCl at different concentrations of AniHCl (a) 9.0, (b) 16.7, (c) 23.0 and (d) 28.6 % w/$_v$ and radiation dose up to 50 kGy.

Figure 3 shows the dependence of the absorbance band at 790 nm on radiation dose and the monomer concentration, this result indicated that the formation of polyaniline is exponentially dependant up on the radiation and fitted to the empirical relation of the form $y = y_0 \exp(D / D_0)$,

Where y is the absorbance at dose D, y_0 is the absorbance at zero doses and D_0 is the dose sensitivity parameter, as well as the increasing of imines group C= N, which response for the green color (electro-chromic response).

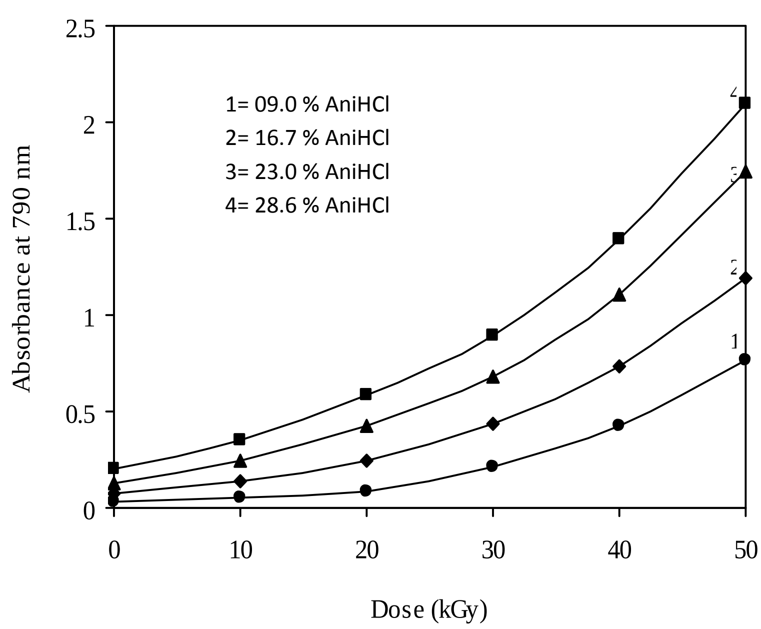

Fig. 3: Variations of absorbance band at 790 nm with radiation dose and the monomer concentration.

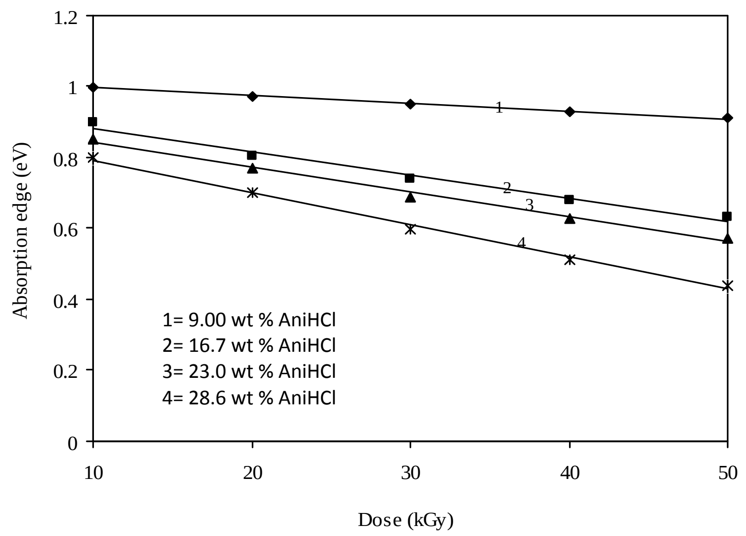

Fig. 4:Influence of AniHCl concentrations on absorption edge

Figure 4 shows the absorption edge vs. dose for different AniHCl concentrations. The absorption edge denotes to the minimum energy of light absorbed by the material leading to electronic transitions which can be deduced from the theory described by Uma *et al*. [(10)], The absorption edge decreased with increasing monomer concentration and also decreased with increasing dose as more C=N polaron species were formed by γ - irradiation.

Figure 5 shows the Raman intensity versus Raman shift spectrogram of the irradiated PVA/AniHCl up to 50 kGy. The spectrum revealed that the formed new bond C=N at 1637 cm^{-1} together with other bonds due to PVA radiolysis. While Figure 6 shows the increasing formation of imines group C=N following the radiation dose and AniHCl concentration with the following relation $y = y_0 \exp(D / D_0)$. The intense formation of C=N led to increase intensity of green color as dark green color.

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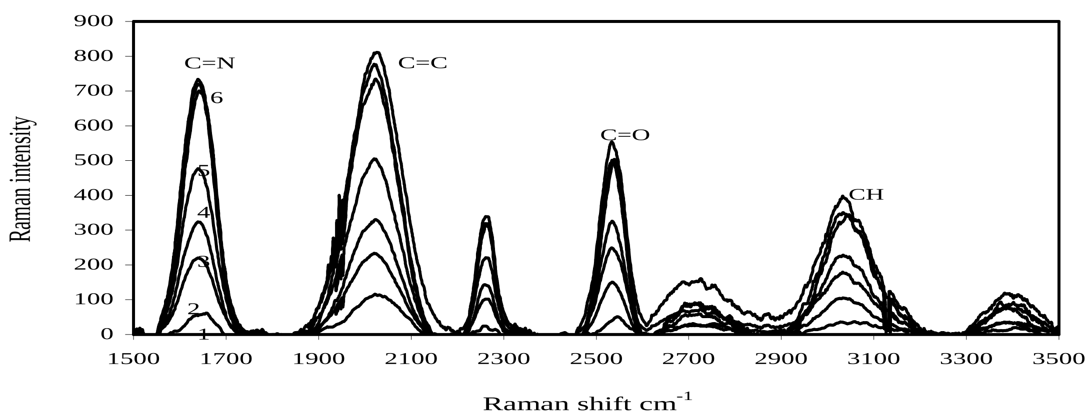

Fig 5: Raman intensity versus Raman shift spectrogram of the irradiated PVA/AniHCl up to 50 kGy.

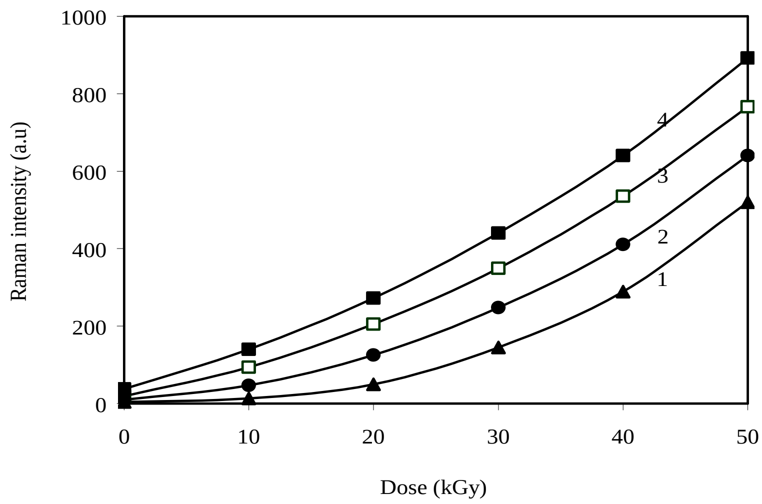

Fig 6:Influence of radiation dose and AniHCl concentration On formation of imines group C=N following the

CONCLUSIONS

Polyaniline is a typical Radioochromic material that has been prepared by γ-irradiation in a dose range of 10 – 50 kGy, the obvious response as Radioochromic material has been shown by naked eye as stepwise green color and confirmed by UV-visible spectroscopy. The cause of chromatic appearance was the formation of double bond between the carbon atom and the nitrogen (C=N) which represents the conducting polaron species that were detected by Raman spectroscopy.

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