

OPTICAL RADIO-CHROMIC PROPERTIES OF POLYANILINE FILM IRRADIATED WITH GAMMA RADIATION

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Abstract

Aniline hydrochloride monomer has been polymerized to polyaniline salt (emeraldine salt) and the characterization reveal that it is an electro-chromic material after direct γ -radiation exposure to high dose up to 50 kGy. The electro-chromic material which deduced by direct step wise appearance of light green color to dark green color following the radiation doses rather than colorless. The Radio-chromic and polymerization confirmed by using UV-visible spectroscopy, which gave rise to absorbance band at 790 nm, the absorbance band in turn increased following the dose exponentially. The band gap energy of PANI was obtained and showed to be decreases by increase of radiation dose down to 1 eV at 50 kGy. Raman spectroscopy showed a new bond C=N as a part of polaron conducting species is created by irradiation, which has Raman shift of 1637 cm^{-1} . The double bond at C=N which is responsible for the appearance of the green color has been increases exponentially following the radiation dose.

Keywords: Polyaniline, Radio-chromic Film, Radiation Processing.

1. Introduction

The electro-chromic materials are referring to that exhibit redox state with distinct UV-visible absorption spectra or generate new absorption band due to switching

Nomenclatures

D	Amount of applied radiation dose, kGy
D_0	Dose sensitivity of material, kGy
y	Raman intensity at certain dose, kGy
y_0	Raman intensity at zero dose, kGy

Greek Symbols

γ	Gamma radiation
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Abbreviations

ECD	Electrochromic device
eV	Electron volt
kGy	Kilo gray (radiation unit)
Mw	Molecular weight, g/mol
ml	Millilitres (volume unit)
Redox	Reduction/oxygenation
UV	Ultraviolet

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 to 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].

There are 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 which are classified into three basic types:

- (i) Soluble in (redox) state such as Prototype viologen, 1,1'-dimethyl-4,4'-dipyridinium (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'-diheptyl-4,4'-bipyridinium (heptyl viologen) and,
- (iii) Materials of solid state in both case of redox such as conductive polymers).

However two types of them (ii and iii) are considered having an optical memory that is because once their redox state switched, no further change injection needed to retain the new electro-chromic state [7]. The electro-chromic materials still has 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 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.

2. Experiment

2.1. Materials

Aniline hydrochloride (AniHCl) monomer with molecular weight (Mw) 129.59 g/mol from Merck-Schuchardt Company has been chosen 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.

2.2. 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°C and continuous stirring for 3 hours. AniHCl powder (1.0 g) was added into the PVA solution at room temperature, nitrogen atmosphere and continuously stirred overnight for 10 hours. The blend solution was poured in Petri-dishes as (20×20 cm), 40 ml/dish and allowed to dry to form the films by casting under ambient temperature for 5 days. 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°C 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.

3. Results and Discussion

Figure 1 shows the response of electro-chromic (PVA/AniHCl) composites to gamma radiation (γ -radiation) with appearance of light green color to dark green color 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 is in agree with Jiaying et al. [8].

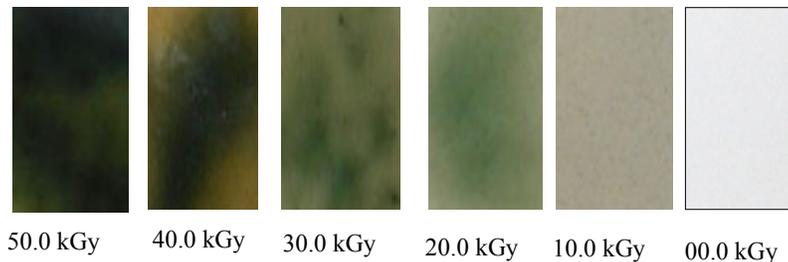


Fig. 1. Response of PVA/AniHCl Composite to γ -Irradiation, Indicating the Electro-Chromic and Polymerization of Aniline Monomer.

Figure 2 (a)-(d) illustrates the UV-visible spectroscopy of PVA/AniHCl at 9.0, 16.7, 23.0 and 28.6 wt. % of AniHCl concentrations. The composites UV-spectrum 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 color. This result is in agreement with previous study carried out by Rao et al. [9]. The absorbance increases with the increase of dose and AniHCl concentration and both peaks become sharper with dose increase, indicating the amount of Cl⁻ and polarons formed (represented by C=N) have increased with dose increment.

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 $y = y_0 \exp(D/D_0)$, as well as the increasing of imines group C=N which response for the green color (electrochromic response), where y is the absorbance at dose D , y_0 is the absorbance at zero doses and D_0 is the dose sensitivity parameter of the composite.

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 some where by Devi et al. [10], The absorption edge decreases with increasing monomer concentration and also decreases with increasing dose as more C=N polaron species were formed by γ -irradiation.

The Raman intensity versus Raman shift spectrogram of the irradiated PVA/AniHCl up to 50 kGy (Fig. 4). The spectrum revealed the formed new bond C=N at 1637 cm^{-1} together with other bonds due to PVA radiolysis. It was observed that the formation of imines group C=N intensity has been increased following the radiation dose and the relation between formation of imines group C=N intensity and the dose can be govern by the following relation $y = y_0 \exp(D/D_0)$. The intense formation of C=N leading to increase the intensity and hue of green color up to dark green color.

4. Conclusions

Polyaniline is a typical electrochromic material that has been prepared by γ -irradiation in a dose range of 10–50 kGy, the obvious response as electrochromic material has been shown by naked eye as stepwise green color and confirmed by UV-visible spectroscopy. The cause of chromatic green color appearance was due to formation of polaron within the imines group C=N which confirmed by Raman spectroscopy.

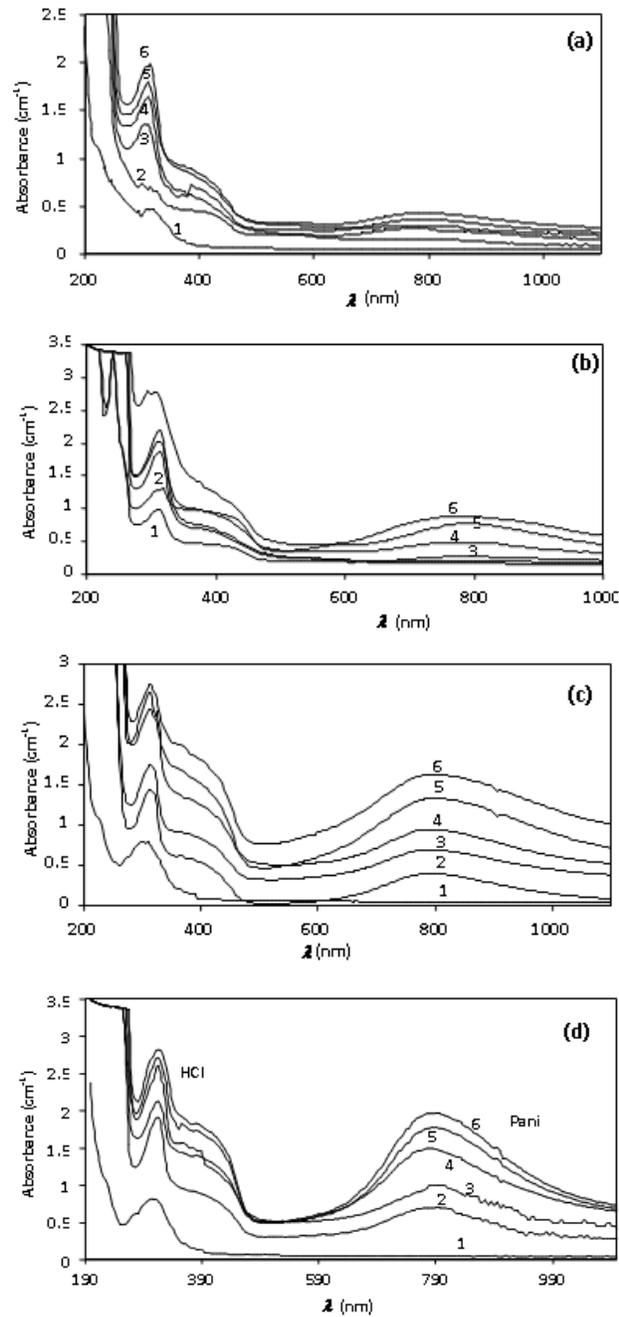


Fig. 2. UV-Visible Spectroscopy of PVA/AniHCl at Different Concentration of AniHCl (a) 9.0, (b) 16.7, (c) 23.0 and (d) 28.6 wt% and Radiation Dose up to 50 kGy.

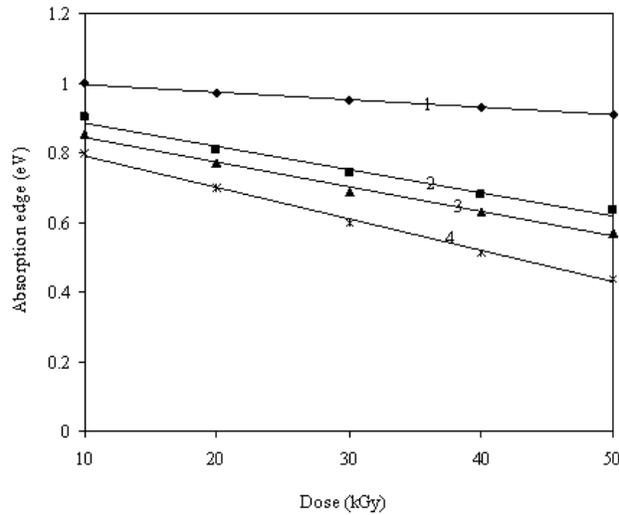


Fig. 3. Dependence of the Absorbance Band at 790 nm on Radiation Dose and the Monomer Concentration.

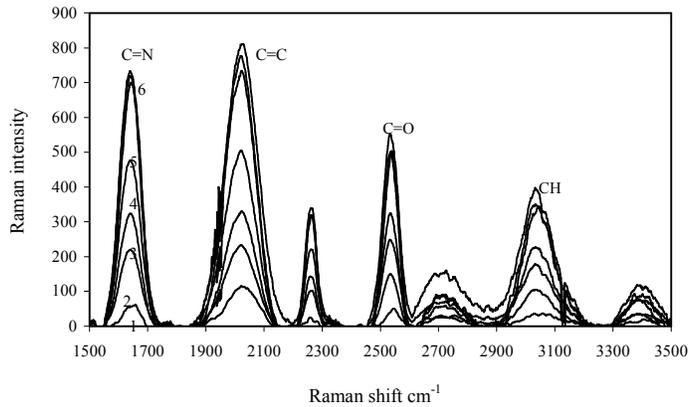


Fig. 4. The Raman Intensity versus Raman Shift Spectrogram of the Irradiated PVA/AniHCl up to 50 kGy, Revealing the Formed New Chemical Bonds by Radiation.

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