Military Technical College
Kobry El-Kobbah,
Cairo, Egypt

6th International Conference
on
Chemical & Environmental
Engineering
29 -31 May, 2012.

ABSORBANCE AND CONDUCTIVITY OF ANILINE HYDROCHLORIDE/ POLYVINYL ALCOHOL FILMS (AN/PVA) FOR GAMMA RADIATION DOSIMETRY IN THE RANGE 0 – 10 KGY

Ahmed Omar*, Ahmad Baraka*, Ahmed H.Zaki* and Karam A.Sharshar**

Abstract

The changes of optical and electrical properties of aniline hydrochloride/polyvinyl alcohol films (AN/PVA) influenced by gamma radiation for the purpose of gamma dosimetry are presented in this work. Optically, by exposing films to doses of gamma radiation from 0 to 10 kGy, films showed visually apparent gradual change in color from violet to yellow green with increase of absorbance at 424 nm. Electrical, conductivity also was increased regularly in the same dose range. It can be suggested that aniline hydrochloride in the AN/PVA form may be used for dosimetry for the mentioned dose range.

Keywords: Aniline hydrochloride, PVA, Gamma radiation, Gamma Dosimetry.

* Egyptian Armed Forces
** Egyptian Atomic Energy Authority

Introduction

A radiation dosimeter is a system that either directly or indirectly determines the absorbed dose of ionizing radiation. The dosimeter has to possess a physical property (or more) that changes with radiation dose with proper manner to be calibrated. In order to be useful, radiation dosimeters must exhibit several desirable characteristics. Radiation dosimeters are important for many applications including environmental safety and remediation, medical imaging, industrial process monitoring, national security, military surveillance and even basic science. However, environmental and personal protection are the most increasing concern due to wide civil application of radiation sources and this needs new or improved dosimeter. Accuracy, simplicity, ease of use and cost-effectiveness are some demands that dosimeter should meet.

Aniline hydrochloride is an organic monomer salt which upon exposure to gamma radiation polymerize to polyaniline[1],[3][4] . Polyaniline has two oxidation states. One of these states is conductive while the other is not. Also, conductive polyaniline has a distinctive greenish color. Polyaniline can be thought as electrochromic material that exhibit redox property. Spectral investigation of its UV-visible absorption can determine the switching between its redox states and the change in redox state can be carried out by gamma radiation. Both of these physical properties (color and conductivity) can be used for dosimetry of gamma radiation.

Aniline hydrochloride was previously used as dosimeter for detection of gamma radiation. Ali *et al* used aniline hydrochloride in polyvinyl alcohol as host films. The prepared films were irradiated with dose 10 – 50 kGy and showed that absorbance at 790 nm increased exponentially with dose [2]. Laranjeira *et al* synthesized polyaniline as nano films on glass substrate using spin coating technique. The films were irradiated by ^{60}Co gamma cell (dose rate of 0.2 Gy/min), with doses from 0 to 8 kGy. Formation of polyemeraldine base was characterized using UV-visible spectrophotometry [5].

Khoury *et al* studied the optical change of polyaniline nano films deposited on glass substrate. Films of polyaniline in the emeraldine base form were exposed to different gamma radiation doses. The characteristic deep blue color of the films becomes green by irradiation [6]. Pacheco *et al* prepared polyaniline/polyacrylic acid (PAA) thin film composites. The four-point conductivity measurements showed that composite exhibits a linear response for the dose range from 0 to 5 kGy [7].

Lasta *et al* investigated polyaniline pellets as radiation sensor. The pellets were formed by hydraulic press. The electrical conductivity before and during radiation exposure (using alpha, beta, gamma radiation sources) was measured and evaluated[8]. Olgun Guven blended polyaniline with chlorine-containing polymers, copolymers and HCl-releasing compounds to determine their radiation response in terms of induced conductivities. The results showed that ionizing radiation induced controllable conductivity in these blends [9].

Ali *et al* prepared nano-polyaniline hosted by polyvinyl alcohol in a form of films by γ-irradiation technique (10 – 50 kGy). The effect of radiation on the conductivity of the prepared films with different concentrations of aniline hydrochloride monomer was evaluated [1]. Ali *et al* obtained polyaniline nanoparticles in films prepared from aniline-HCl/polyvinyl alcohol blend with gamma rays under ambient conditions. The conductivity measurement

showed that the initial electrical insulating PVA/AniHCl blend has been transformed into the electrically conducting PVA/nano-polyaniline nanocomposites. The conductivity increased by 5 orders of magnitude after exposure to 50 kGy [10].
In this work, (PVA) is used as a host for colored polymeric material (AN) which is polymerized by gamma radiation. The polyaniline in AN/PVA films is produced in its conductive state which is yellow greenish. This was estimated visually by observing the step wise change of light violet color of AN to yellow greenish color following the radiation doses. This conveys simple useful information to an observer. Also, this change was tracked by UV-visible absorption spectroscopy at 424 nm where absorbance increases as a function of gamma dose in the range 0 – 10 kGy. In a similar manner, the conductivity of these films was found to increase regularly as a function of gamma dose in the same dose range. The most important property is the evaluation of this composition (AN/PVA) for gamma dosimetry in the range 0 – 10 kGy either optically or electrically. Several AN/PVA compositions were pre-synthesized and comparison of these was performed to select the best composition that is sensitive to apply for gamma dosimetry in the investigated lower range of dose (0-10 kGy). This work presents the results of this best composition.

Experimental

Materials

Aniline hydrochloride as a monomer (AN, Mw = 129.59 g/mol, Aldrich), polyvinyl alcohol as a substrate (PVA, Mw = 145,000 g/mol, Merck) were used to prepare AN/PVA films on a cleaned glass substrate. Bi-distilled water was used to prepare primary PVA solutions.

Preparation of AN/PVA films

Five solutions of AN/PVA were prepared by dissolving certain amounts of AN (0.2, 0.4, 0.6, 0.8 and 1 g) in 100 ml of 4% PVA aqueous solution. For homogeneity, solutions were continuously stirred in caped 250-ml volumetric flasks overnight at reasonable rate to avoid bubbling effect and to reduce oxygen solvation. After forming a clear solution samples, 50 ml of each solution was then poured on cleaned glass substrate (30 × 30 cm) and allowed to dry for two days under ambient conditions to form the required films. After complete dryness, all films were violet in color with different intensities. These films were carefully detached from glass substrates and each was cut into several piece-films (3 × 6 cm) then each film was covered using plastic cover for subsequent radiation exposures.

Gamma irradiation of AN/PVA films

The AN/PVA piece-films were exposed to gamma radiation using ^{60}Co radiation facility (Gamma Chamber 5000) at a constant dose rate (26.66 Gy/min) at room temperature. The samples were irradiated by a linearly increased dose with 2 kGy step from 0 to 10 kGy.

Results and discussion

Optical UV-Vis Spectra

Figure 1 shows the variation of color of different AN/PVA films with gamma dose. Change of color from light yellow green to dark yellow green appears following the radiation dose from 0 to 10 kGy. Such coloration indicates the polymerization of AN into polyaniline.

Absorption spectra of all films were determined by UV-visible absorption spectrometer. Figure 2 shows the spectra of films containing 0.2 and 1 g of AN in the mixture as an example. From the figure, it is clear that film has a wavelength maximum at 424 nm which is corresponding to the greenish yellow color. Also, from figure, the absorbance increases with dose suggesting the increase formation of conductive polyaniline form.

Figure 3 shows the absorbance change (at λ = 424 nm) of different AN/PVA films with respect to gamma radiation dose. For all doses, absorbance increases with AN content in AN/PVA. For example, the absorbance increases from 0.092 to 0.12 as AN content increases from 0.2 to 1g for dose 2 kGy. Also for all AN contents, the absorbance increases with dose. For example, the absorbance increases from 0.092 to 0.135 as dose increases from 2 to 10 kGy for AN content 0.2 g. For each AN content sample, linear fitting of absorbance against dose was determined. Table 1 shows the best equations, regarding correlation factor, to be assigned for 0.8 and 1 g AN contents. Accordingly, if absorbance is to be used for dosimetry in this range of dose, these samples are recommended. However, the small slope values may limit this application.

Table. 1. The fitted linear equations for different AN content.

No	AN content (g)	Fitted linear equations	Correlation factor (R^2)
4	0.8	$A = 0.009D + 0.100$	0.997
5	1.0	$A = 0.010D + 0.104$	0.974

A is the absorbance of film and *D* is the gamma radiation dose (kGy).

Gamma–induced electrical current (conductivity) of AN/PVA films (0.2, 0.4, 0.6, 0.8 and 1.0 g / 4% PVA solution)

Polyaniline has two forms; nonconductive emeraldine-base and conductive polyaniline (emeraldine-HCl). Upon exposing aniline to gamma radiation, it polymerizes into the conductive form; PANI-emiraldine-HCl [1],[2],[10]. The conductivity originates from the free electrons and charge carriers (Cl–) that present on its structure as shown in figure 4.

The conductivity of the prepared films was determined by measuring the induced current by applying different voltages in the range 0-25 V. In this work, the conductivity is represented by induced current. A (Meterman 37XR) was used to measure the current induced in the sample due to voltage applied by (DC power supply HY3010E) voltage source. For current measurement, samples irradiated with different doses (0-10 kGy) were attached to a simple electrical measurement circuit as shown in figure 5 in which the films placed between two aluminum pieces as connectors.

Figures 6-10 show the effect of gamma radiation doses on the induced electrical current of AN/PVA films (for contents: 0.2, 0.4, 0.6, 0.8 and 1.0 g / 4% PVA). For all samples, the current increases with voltage (0 – 25 V) and dose (0 – 10 kGy).

For each sample, linear fitting of current against dose was determined considering AN content and applied volt. Table 2 shows the best equations, regarding correlation factor, to be assigned for 1 g AN content at bios values of 5 and 10 V. Accordingly, if current is to be used for dosimetry, this sample at these two volt values are recommended for application. Besides, both equations have suitable slope values to account on when considering sensitivity.

In general, this increment of induced current with dose strongly suggests the increase of the conductive polyaniline formation in the film because of exposure to gamma radiation. This is in agreement with the conclusion of absorbance measurement. Also, the initial content of AN in AN/PVA film is another factor affecting conductivity. At a selected dose, as this content increases, the conductivity increases. The increase of induced current is attributed to more increase of free electrons and charge carrier in the film[10].

Table.2. The best fitted equation of 1.0 g AN at 5 and 10 V.

No	Volt (V)	Fitted linear equations	Correlation factor (R^2)
1	5	$I = 0.5107\,D - 0.1019$	0.975
2	10	$I = 0.9186\,D - 0.0429$	0.976

I is the induced current (µA) and *D* is the gamma radiation dose (kGy).

A comparison between optical and induced electrical current measurements for dosimetry:

Considering optical and electrical response to dose, it is highly suggested using conductivity change with dose for dosimetry in the range of 0 – 10 kGy of gamma radiation. This is because of higher slope value of the fitted equations of conductivity measurements compared to fitted equations of absorbance measurements.

Conclusion

Samples of AN/PVA were prepared, having gradually varied AN content. These samples were exposed to varying gamma radiation in the range of 0 – 10 kGy. It was found that both absorbance (at 424 nm) and conductivity (induced current) have a regular change with dose that could be represented linearly. For linear fitted equations, dose can be determined from both absorbance and current. However, conductivity is more recommended to rely on as it gives better recognition between applied doses. Although this composition (AN/PVA) was previously applied for gamma dosimetry, preparation of it in this work was designed to be sensitive in the lower range of dose (0-10 kGy).

References

[1] Mohammed Ahmed Ali *et al*. Synthesis of conducting polyaniline nanocomposites by radiation doping. J of Engineering Science and Technology. Vol. 2, No. 1 (2007) 111-118.

[2] Mohammed Ahmed Ali, *et al*. Optical radio-chromic properties of polyaniline Film irradiated with gamma radiation. J Engineering Science and Technology. Vol. 5, No. 2 (2010) 244 – 250.

[3] J. STEJSKAL. Polyaniline. Preparation of a conducting polymer. Pure Appl. Chem., Vol. 74, No. 5, pp. 857–867, 2002.

[4] Narendra V. Bhat et al. Interaction of gamma radiation with PVA/PANi composite films: Structural and morphological studies. J of Applied Polymer Science Volume 110, Issue 4, pages 2243–2252, 15 November 2008.

[5] J.M.G. Laranjeira, *et al*. Polyaniline nano films as a sensing device for ionizing radiation. Physica E 17 (2003) 666 – 667.

[6] H.J. Khoury, *et al*. Polyaniline nanofilms as a monitoring label and dosimetric device for gamma radiation. Materials Characterization 50 (2003) 127– 130.

[7] Ana P. Lima Pacheco, *et al*. Polyaniline/poly acid acrylic thin film composites: a new gamma radiation detector. Materials Characterization 50 (2003) 245– 248.
[8] Neal Alfie Y. Lasta, *et al*. Polyaniline pellets: radiation sensor. 8th SPVM National Physics Conference.
[9] Olgun Guven. Radiation-induced conductivity control in polyaniline blends/composites. Radiation Physics and Chemistry 76 (2007) 1302–1307.
[10] M.A. Ali, *et al*. Chemical modification and control of polyaniline nanocomposites conductivity by radiation technique in PVA matrix. J Engineering Science and Technology. Vol. 2, No. 3 (2007) 280- 289.

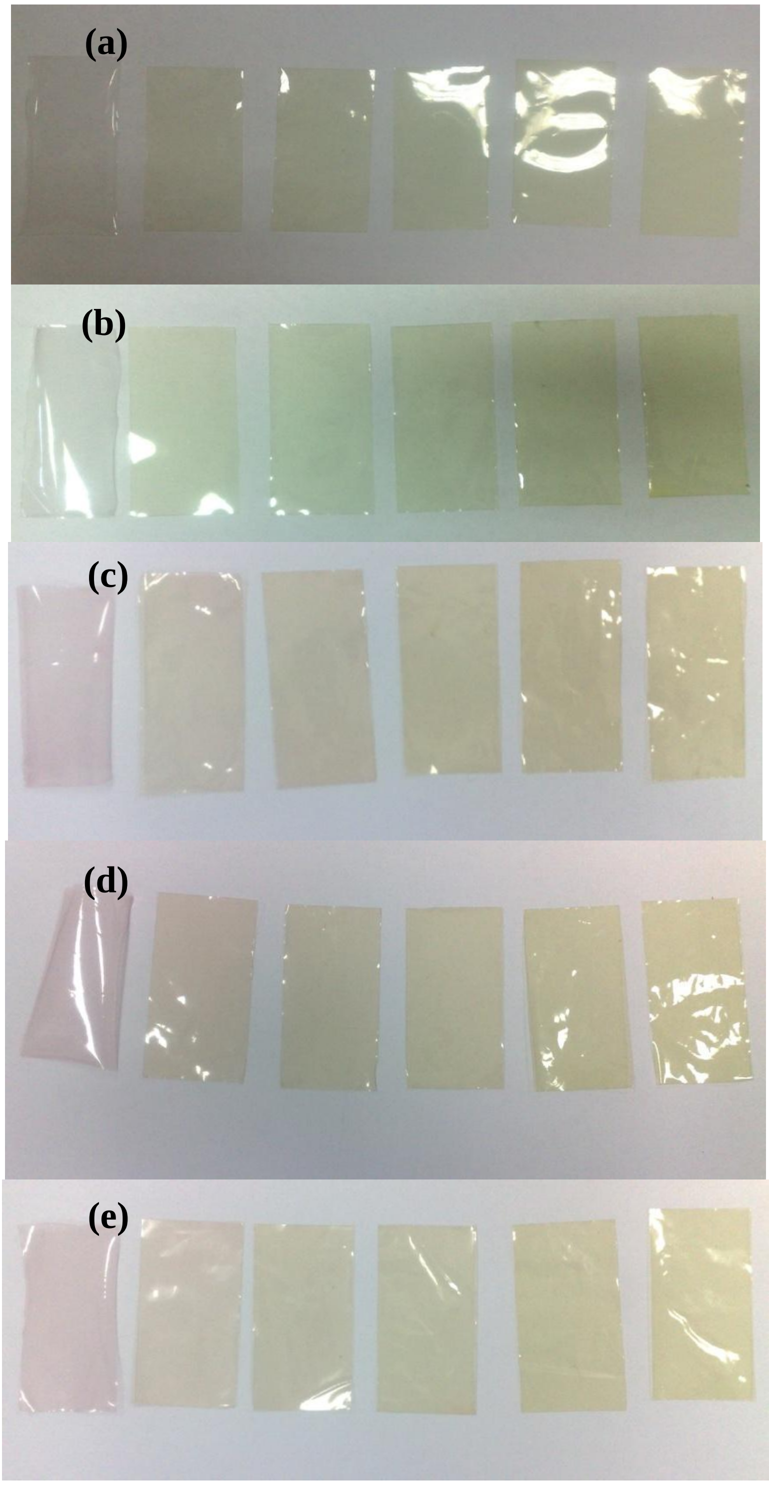

Fig.1. Response of (AN/PVA) composite to gamma irradiation from 0 to 10 kGy. (a) 0.2g AN, (b)0.4g AN, (c)0.6g AN, (d) 0.8g AN and (e) 1.0g AN.

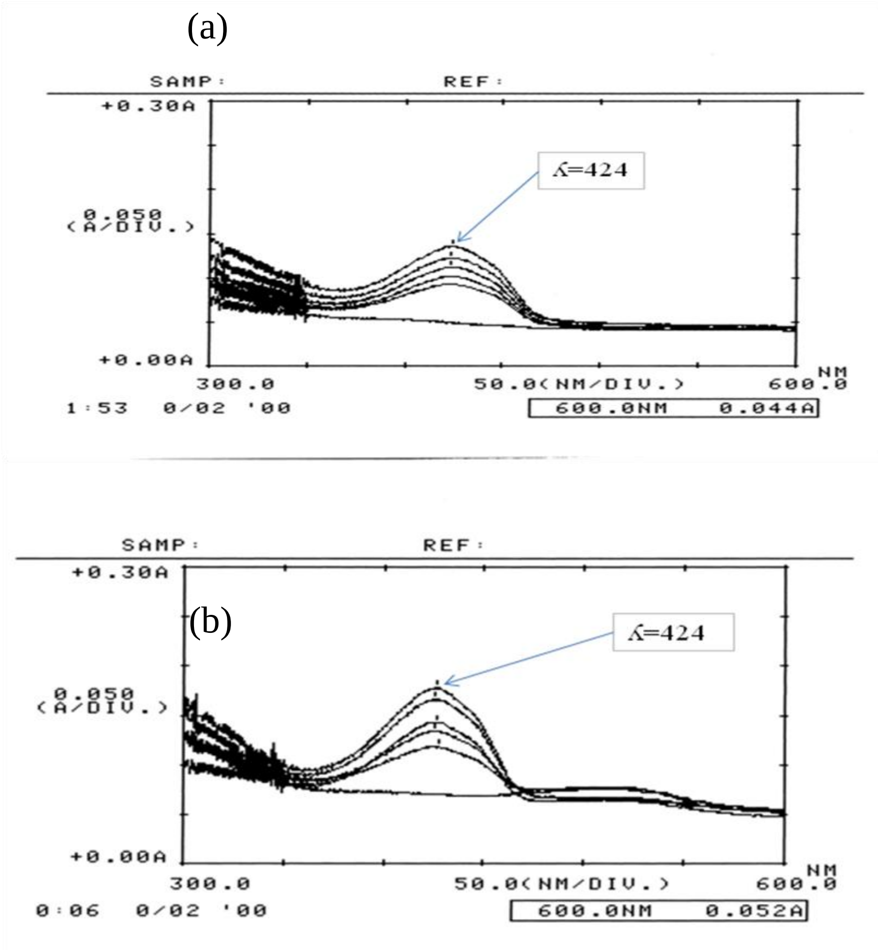

Fig.2. Absorbance of films at 424 nm: (a) 0.2 g AN, (b) 1.0g AN.

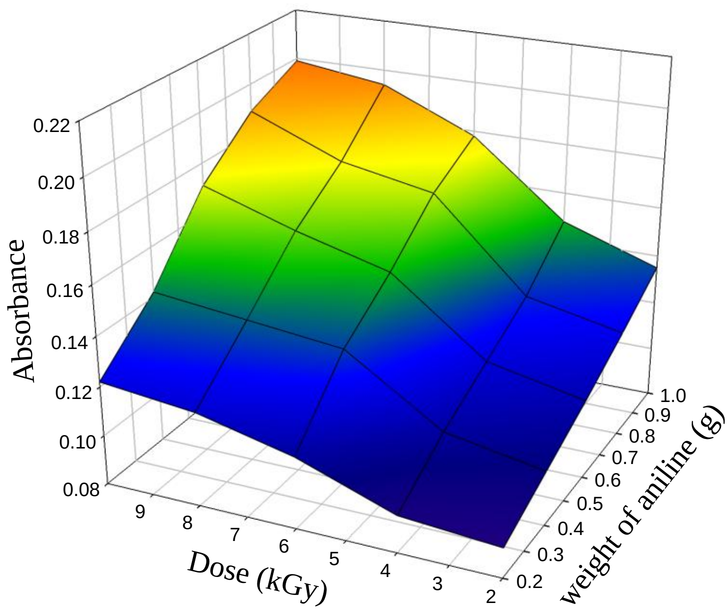

Fig.3. Absorbance variation against gamma radiation absorbed dose (different AN content).

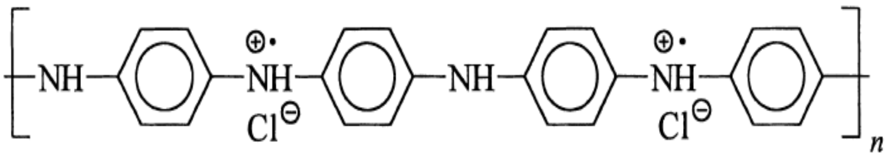

Fig. 4. Structure of conductive polyaniline (emeraldine) hydrochloride.

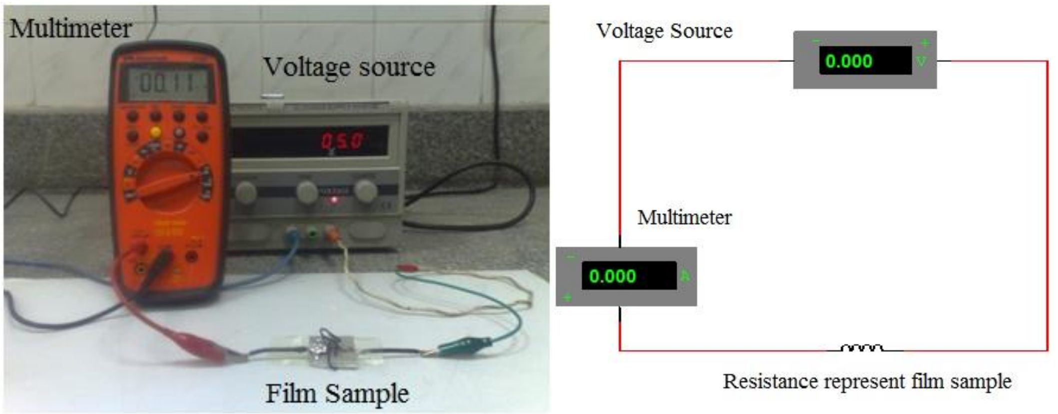

Fig.5. Electrical measurement circuit
(Conductivity determination of AN/PVA films).

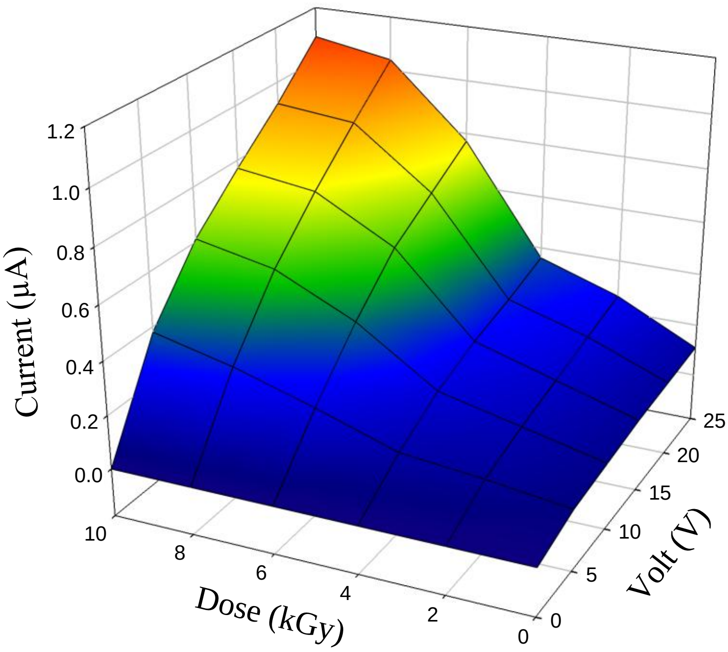

Fig.6. Induced current variation against gamma radiation absorbed dose
(0.2 g AN/PVA film).

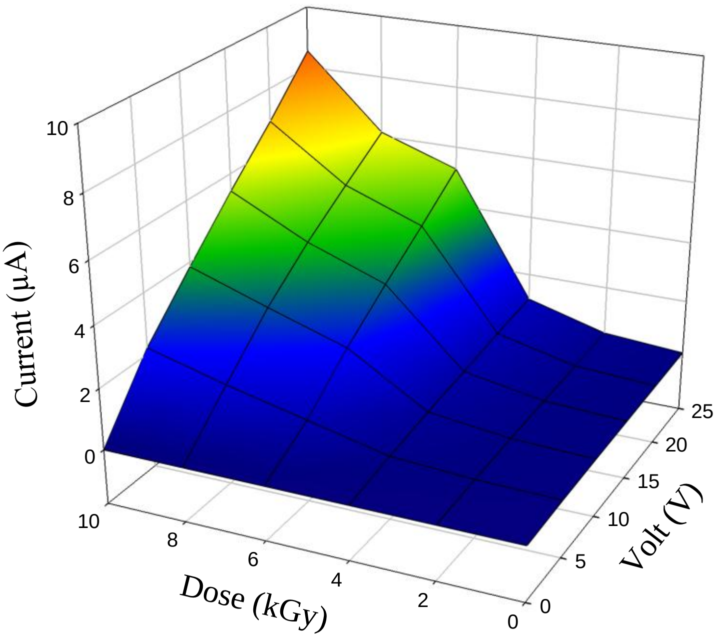

Fig.7. Induced current variation against gamma radiation absorbed dose (0.4 g AN/PVA film).

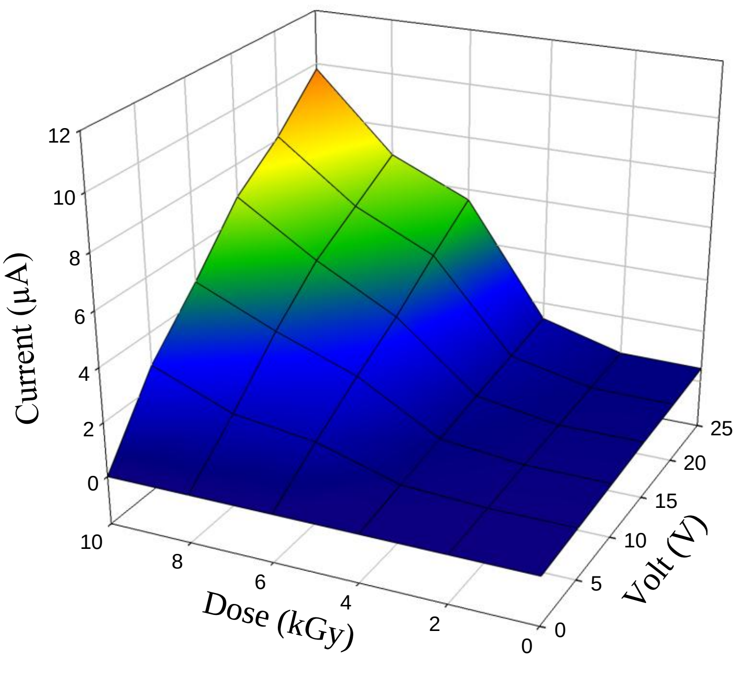

Fig.8. Induced current variation against gamma radiation absorbed dose (0.6 g AN/PVA film).

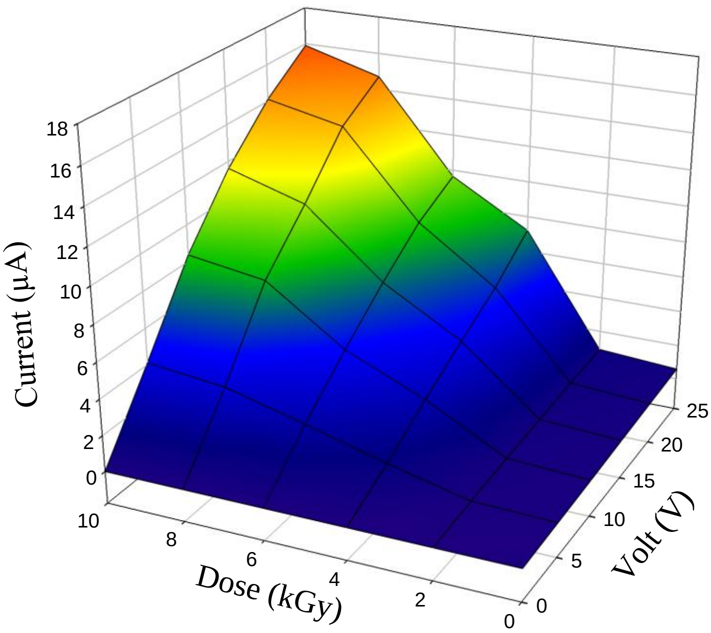

Fig.9. Induced current variation against gamma radiation absorbed dose (0.8 g AN/PVA film).

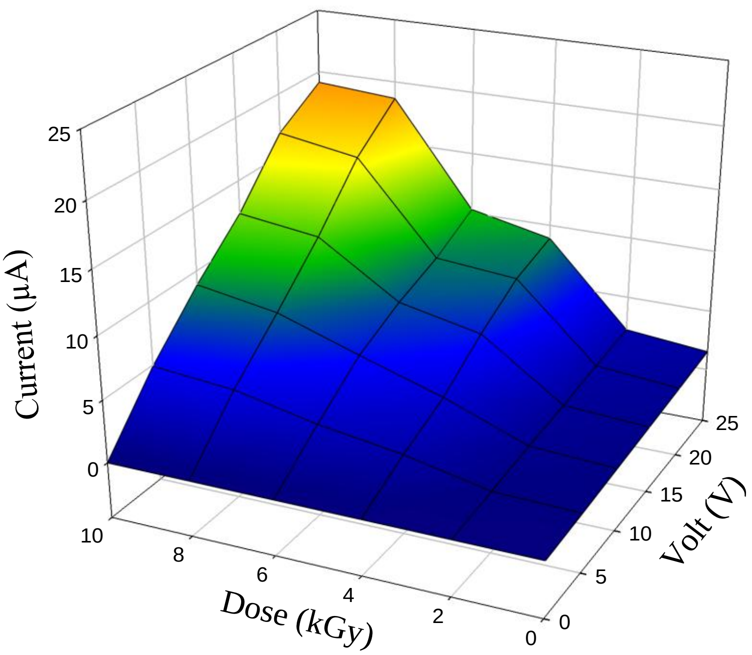

Fig.10. Induced current variation against gamma radiation absorbed dose (1 g AN/PVA film).