ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 124 (1999) 35–40

Journal of Photochemistry and Photobiology A:Chemistry

UV laser induced fluorescence of unirradiated and irradiated low density polyethylene

Y. Badr[a,*], Z.I. Ali[b], R.M. Khafagy[c]

[a]*National Institute Of Laser Enhanced Science (NILES), Cairo University, Cairo, Egypt*
[b]*National Center for Radiation Research and Technology (NCRRT), P.O. Box 29 Madinat Nasr, Cairo, Egypt*
[c]*Faculty of Women for Art, Science, and Education, Ain Shams University, Cairo, Egypt*

Received 9 February 1999; accepted 12 February 1999

Abstract

The auto fluorescence of unirradiated and γ-rays, thermal neutrons, argon ions (Ar^+) irradiated low density polyethylene (LDPE) films was investigated using a spectroscopic system incorporating a pulsed nitrogen (N_2) laser and optical multichannel analyzer (OMA). LDPE film was found to be auto fluorescent in the visible range (639 nm) after being pumped by pulsed N_2 laser in the ultraviolet (UV) range (337 nm). The fluorescence spectra was found to be affected remarkably by the type of irradiation and also on the absorbed dose showing different behavior either in the peak position or height. This behavior showed that LDPE film could be used as a fluorescence solar energy collector in the application of solar energy or laser dyes where it emits in a very important region in the visible region, which is having many applications especially for the photodynamic therapy. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: LDPE films; UV laser; Auto fluorescence

1. Introduction

Laser excited fluorescence (LEF) and fluorescence probes have been used to observe bulk damage in aged crosslinked polyethylene. Striations were observed under a microscope when the aged samples were irradiated by an argon ion laser, and the changes in the bulk fluorescence of samples subjected to various aging conditions were observed as well [1].

The luminescence of LDPE and HDPE films induced by ionizing radiation has been studied. The effect of filling materials, radiation absorbed dose, and dose rate on the luminescence has been investigated [2]. Polymers doped with luminescent materials have potential use in a number of technologies. Various experimental studies have proved that doped polymers might be useful in collecting and concentrating solar energy and as low cost solar photovoltaic materials [3–5]. Also, the emission spectra of unirradiated and γ-irradiated thin film of poly (methylmethacrylate) (PMMA) matrices containing rhodamine B (RhB) or rhodamine 6G (Rh6G) as donor and chlronil (CA) as acceptor have been investigated. The material investigated, particularly Rh6G-CA, proved to be sensitive in absorbing UV light and re-emitting in the visible region, and hence, could be used as a luminescent concentrator for solar cell [5]. The propagation of ultra fast laser pulses through biological tissues were investigated by Feng et al., 1994 [6] using picosecond streak camera method showing a remarkable broadening specially with increasing the thickness of the sample. The transmission of fast laser pulse (fluorescence study) through Nylon 6 film, which is considered as a tissue equivalent material using three types of laser (Nd-YAG, pulsed N_2 laser of wavelength 337.3 nm and Ar^+ ion laser of power up to 25 W) were investigated [7]. In this study an optical multichannel analyser (OMA) was used to investigate the propagated laser pulses in the sample as compared with the incident pulse. Also, a spectroscopic system incorporating a pulsed N_2 laser and OMA was used to record the auto fluorescence spectra of some biological tissues. The resulting spectra could to differentiate histologically normal tissues with a sensitive and positive predictive value of 87, 73 and 74% [8].

Since some polymeric materials are considered as a tissue equivalent materials, it was worthwhile to study the fluorescence spectra of unirradiated, γ-ray and thermal neutrons and Ar^+ ions irradiated low density polyethylene (LDPE) films using a spectroscopic setup which illustrated in the following experimental section.

---

*Corresponding author.

PII: S1010-6030(99)00039-8

2. Experimental

2.1. Materials

Commercial thin films of low density polyethylene (LDPE) were used. LDPE films produced by Al Shreef Company, Egypt (density $\cong 0.92$ gm cm^{-3}, fusion index above 300°C, crystallinity 40%, melt flow index (FI) about 1.35 gm/10 min), having thickness of about 14–17 μm was used.

2.2. Irradiation procedure

2.2.1. Gamma rays irradiation

Gamma irradiation was carried out using NCRRT ^{60}Co Gamma cell 4000A (manufactured at Bhabha Atomic Research Center, India) at a dose rate in the range of 2.35 kGy/h and at ambient temperature about 45°C inside the irradiation chamber. The γ-irradiation of LDPE films has been carried out (atmospheric air) at the central position of the gamma irradiator using a specially designed polymethylmethacrylate holder (5 mm thickness) to insure that the irradiation were performed under condition of electronic equilibrium. The design of the holder ensures that all irradiated films are exposed to the same radiation field in the most homogeneous region of the irradiated chamber. In other words, when the rack holding the LDPE films is fixed inside the irradiation chamber, the LDPE films are on an isodose cylindrical surface concentric with cylindrical irradiation chamber.

2.2.2. Thermal neutrons irradiation

The neutron source used is the ET-RR-1 reactor (located in Anchas, Egypt) which is a 2 MW-WWR-S (Russian type) research reactor. It is a tank type reactor with fuel 10% enriched uranium oxide. Distilled water is used as a moderator, coolant and reflector. The temperature inside the irradiation channel differed along the irradiation time and the average temperature was about 38°C and its maximum was about 42°C (this is the temperature of the water steams coming out after cooling the channel). The samples were irradiated at the exit of the curved neutron guide installed in front of the horizontal channel No. 9. The flux of pure thermal neutrons at the exit of this channel was about 6.7×10^{13} n cm^{-2} s.

2.2.3. Ion bombardment process

A Penning-type cold cathode ion source that had been designed and constructed in our laboratory [9] was used to provide a beam of singly charged argon ions at energy of 4 keV. The argon ions are extracted from a discharge chamber under high electric field. The beam purity is considered as high as extracted directly from the plasma, and also the beam extraction mechanism was previously explained in details by Saad et al., 1989 [10]. The cathode and anticathode were selected to be of stainless steel. An experimental setup to serve the bombardment process was coaxially assembled along the ion beam. The film samples was mounted on a stainless steel holder with a conducting base, keeping it in good contact with the surface of the holder to reduce its surface resistance, and in turn to avoid the charging effect on the insulating polymer film during the bombardment process. The source and the sample are housed in a vacuum chamber with vacuum down to 10^{-6} torr.

To insure the stability of the ion beam intensity, a Faraday cup was, frequently, inserted inside the chamber replacing the sample in order to check the intensity through out the work. The time period for each experimental run was adapted as the required delivered total fluence with energy of 4 keV.

LDPE (14–17 μm) films were cut into square shapes of 1 cm × 1 cm dimensions and the bombardment process using argon gas was carried out in one step (total dose irradiation) as in dosimetry routine work. The fluence measurements of these films were carried out directly after each bombardment, to avoid the introduction of anominals.

2.3. Fluorescence spectroscopy setup

The fluorescence spectroscopy setup used in this study was designed to investigate and record the fluorescence spectra of unirradiated and irradiated LDPE films. This setup consists of the following units as shown in Fig. 1.

Pulsed N_2 laser of power 90 kW, repetition rate 20 Hz, energy of about 450 μJ/pulse, time duration 5 ns and 337.3 nm wavelength.

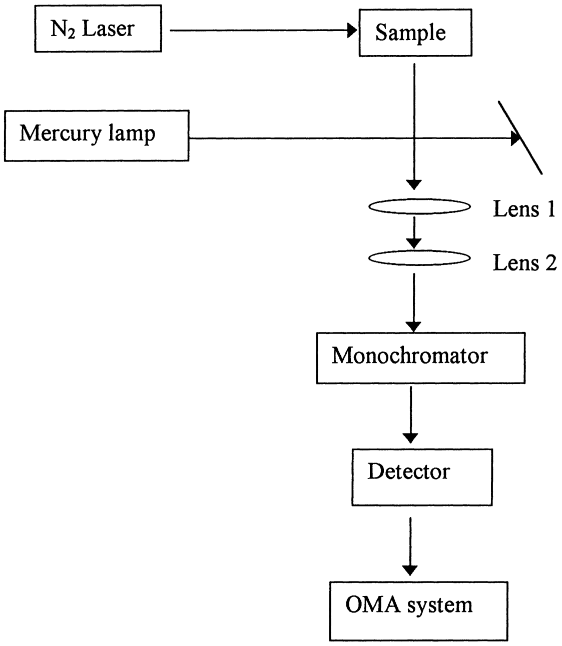

Fig. 1. The fluorescence spectroscopy setup.

Sample compartment.

Mercury lamp was used for wavelength calibration.

Concave and convex lens.

Monochromator of type Spex 500 contain a filter having the same wavelength as the laser beam was used to absorb the line of the laser beam.

Detector controller model 1216 was used to receive the laser beam.

Optical multichannel analyser (OMA) which can detect and analyse a spectrum range (300–650 nm) with a very high resolution.

The sample was inserted in the path of the N_2 laser beam as in the setup and the emission from the sample was focussed into through a monochromater having a filter of the same wavelength of the laser beam. So that, the monochromater filters absorb the line of the laser beam and put it infront of the detector of the OMA system. Before using the OMA system, we calibrate it using a mercury lamp with known wavelength as the laser beam wavelength.

3. Results and discussion

3.1. Laser induced fluorescence of LDPE films

Thin films (14–17 μm) either unirradiated or irradiated LDPE, {(a) different absorbed doses of γ-rays up to about 1.0 MGy, (b) thermal neutrons of flux 6.7×10^{13} n cm^{-2} s, and (c) argon ions source}, were exposed to pulsed N_2 laser at 337.3 nm of power 2.3 mWt. The fluorescence pattern was found to be affected remarkably by irradiation showing different behavior for different types of irradiation either in the peak position or in the peak height. To carry a fluorescence spectral analysis for unirradiated and irradiated LDPE films after being excited by pulsed N_2 laser, a controller was used with the OMA system to perform synchronization between the trigger of the N_2 laser and the OMA system. The pulsed N_2 laser has a line at about 337.3 nm (in the UV range) and the obtained fluorescence pattern was found to be a complex one with a sharp fluorescence peak at 639 nm together with a broad band at about 643 nm (i.e. in the red region). This behavior can be illustrated and discussed as follow:

When the LDPE film giving enough energy to get excited absorbs the laser energy, then it tends to go back to the ground state emitting the excitation energy as fluorescence. The shape of the fluorescence band is related to the number of energy levels which the molecules pass for him when loses the energy back again to the ground state. Each energy level has a fluorescence line, so we obtained a large fluorescence broad band dye to the small difference between energy levels (vibration state) of the molecules.

LDPE was found to be most efficiently excited by 337.3 nm (UV) and emits at about 639 nm (visible); thus this material could be used as fluorescence solar-energy collector in the solar energy technology. Moreover, it could be used with some modification as a laser dye specially it emits in a very important region in the visible range which is having many medical applications especially for the photodynamic therapy.

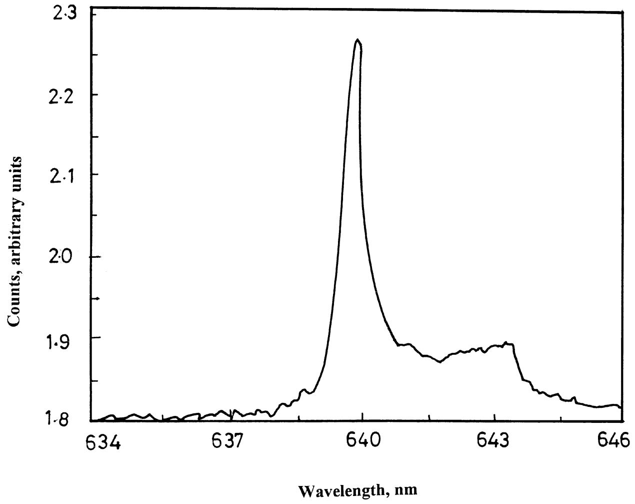

Fig. 2. Fluorescence pattern of unirradiated LDPE films (14–17 μm).

3.2. Auto fluorescence for unirradiated LDPE films

To study the effect of the fluorescence process in unirradiated LDPE film, the background of the fluorescence spectroscopy setup (spectrum detected by the used setup without introducing any sample) was initially recorded where it did not show any specific peaks in the visible range. Thereafter, an unirradiated sample of LDPE film (14–17 μm) was introduced into the setup as shown above yielding the fluorescence spectrum given in Fig. 2 which shows a very clear and sharp fluorescence band at about 639 nm. This means that exciting LDPE film with pulsed N_2 laser having wavelength of 337.3 nm in the UV region resulted in a fluorescence sharp band at 639 nm in the red region. Moreover, this sharp band was found to be associated with another broad fluorescence band at 2.7 nm apart from the original sharp band.

3.3. Auto fluorescence of γ-irradiated LDPE films

It is worthwhile to account for the effect of the γ-irradiation with different radiation absorbed does on the observed fluorescence in LDPE films. Initially three γ-irradiated films by different absorbed does (225, 560 and 934 kGy) were introduced successively in the setup yielding three different fluorescence patterns given in Fig. 3. It was found that γ-irradiation not only caused several changes in the properties of the LDPE film as observed in the FTIR spectrum [11,12], but also it leads to some changes in the fluorescence patterns of the sample. The main effects due to this type of

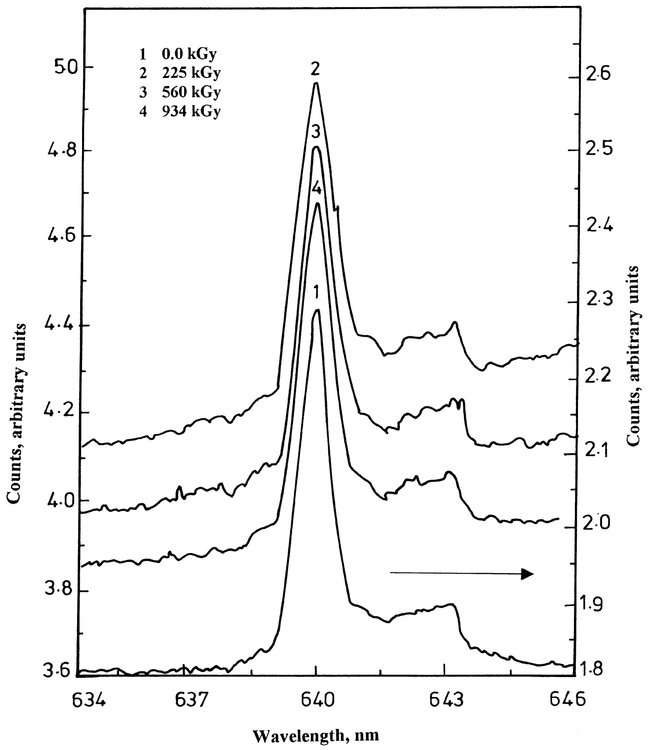

Fig. 3. Fluorescence patterns of unirradiated and γ-irradiated (225, 560 and 934 kGy) LDPE film (14–17 μm).

ionizing radiation on the fluorescence spectra of LDPE films could be summarized as follows:

The integrated intensity of the fluorescence peak at 639 nm was found to increase drastically with γ-rays absorbed dose two or three times the original fluorescence peak of unirradiated LDPE film. Further increase in the radiation absorbed dose led to further increase in the integrated intensity of the fluorescence peak. The increase in the integrated intensity of the main fluorescence peak with the increase of radiation absorbed dose can be attributed to the increase of degree of crosslinking which in consequence increase the disorder behavior of the irradiated films respective to the unirradiated one. So that, when the irradiated film is pulsed with N_2 laser, there are enough exited molecules which lose its energy again as sharp fluorescence peak. Also, the increase the radiation absorbed dose led to a slight decrease in the peak height but it is still higher than the one corresponding to the unirradiated sample.

The peak position of the main fluorescence peak remained constant and was found not to be affected with the γ-irradiation, which is an expected behavior where γ-irradiation does not result in introducing new energy levels for the molecules.

A systematic shift towards lower wavelength and change in the relative intensity of the shoulder (broad fluorescence band) with respect to the sharp fluorescence peak at 639 nm occurred as the γ-irradiation absorbed dose increases.

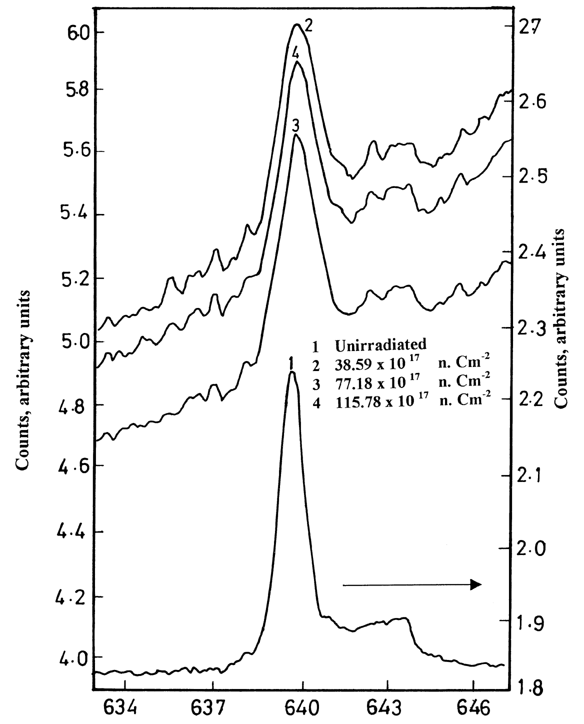

Fig. 4. Fluorescence patterns of unirradiated and thermal neutrons irradiated (16, 32 and 48 h irradiation) LDPE film (14–17 μm).

3.4. Auto fluorescence of thermal neutrons irradiated LDPE films

The fluorescence spectra of three samples exposed to thermal neutrons (flux ≈ 6.7×10^{13} n cm^{-2} s) from the reactor were investigated using the above given setup. The obtained fluorescence spectral as shown in Fig. 4 showed several changes from that obtained for the unirradiated samples, mainly:

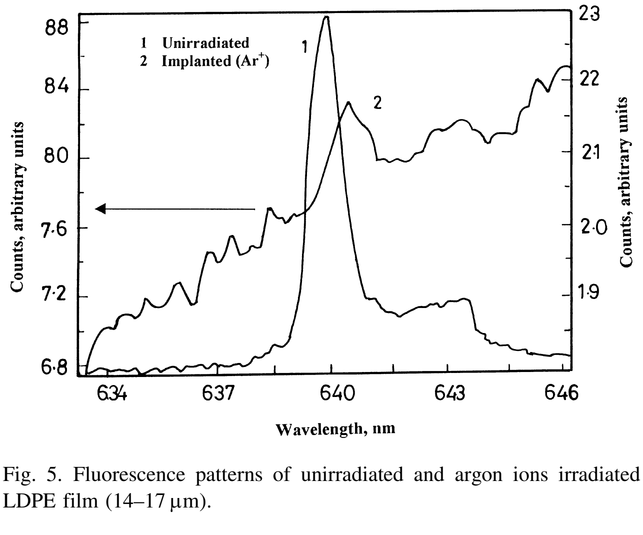

Fig. 5. Fluorescence patterns of unirradiated and argon ions irradiated LDPE film (14–17 μm).

Table 1
Comparison between the effects of different types of radiation on the auto fluorescence pattern of LDPE

	Unirradiated sample	Irradiated sample with gamma rays	Irradiated sample with thermal neutrons	Implanted samples with Ar^+ ions
Background	Low background	Low background	Continuous upward increase of the back-ground towards higher wave-length (higher than that of the unirradiated)	Increase in the level of the background.
Peak at 639 nm	Sharp peak at 639 nm	No shift occurred The integrated intensity $\cong 2$ times that of the unirradiated	Broadening and shift to higher wavelength	Shift towards higher wave-length
Broad band at 643 nm	Broad band at 643 nm.	Systematic shift towards lower wavelength	Systematic shift towards Lower wavelength Appearance of new fine structure (splitting)	Great Shift towards higher wavelength without fine structure.
Relative Intensity between the two bands		No change in the relative intensity	Change in the relative intensity	Great change in the relative intensity

The background of the fluorescence spectra increases remarkably which causes an upward shift in the fluorescence pattern and it did not retain its value again. On the contrary, it continued increasing after the two fluorescence bands.

The main fluorescence peak at 639 nm was found to suffer from a slight broadening in addition to a slight shift in its position.

The broad fluorescence band at higher wavelength was found to show a fine structure of a separation into almost two peaks.

In general the relative intensity between the two fluorescence bands changes remarkably than those obtained for the unirradiated samples.

Once more as observed for γ-irradiated samples, the small broad band was shifted, but in this case it is shifted towards higher wavelength with the increase of the radiation absorbed dose.

3.5. *Auto fluorescence for Ar^+ ions implanted LDPE films*

Finally, the fluorescence of LDPE films implanted by a beam of Ar^+ ions for 15 min from a source of energy 4 keV was recorded. Fig. 5 shows the obtained fluorescence spectra of unimplanted and implanted LDPE films, where it is easily seen that:

An increase in the background level of the implanted sample.

A remarkable shift in the main fluorescence peak towards higher wavelength and also the peak become more broad. The broadening of this peak can be correlated to the mechanism of interaction of Ar^+ ion with the polymer. When the Ar^+ ion is bombarded with the polymer, a fraction of its energy is transferred through the electric field to the electrons of that molecule and as a result these electrons are displaced from their ground state (i.e. excitation) [13].

A drastic decrease in its integrated intensity.

Similar shift in the broad fluorescence band without any fine structure.

The main differences between the three types of radiation on the auto fluorescence patterns are summarized in Table 1.

4. Conclusions

Because some polymeric materials showed good resemblance with the biological tissues, the auto fluorescence, which is characterizing biological tissues, was tested here for thin films of LDPE. Our results showed here for the first time that PE thin film was found to be auto fluorescent as pumped by pulsed N_2 laser ($\lambda = 337.3$ nm in the UV region). The obtained fluorescence spectra was found to have a sharp peak at 639 nm (in the visible region), associated with another broad fluorescence band at 2.7 nm apart from the original sharp peak. Moreover, the fluorescence pattern was found to be affected with different types of irradiation (gamma, neutrons, and Argon ions). Our data showed a very good quality for the obtained fluorescence regions revealing the high resolution and accuracy of our setup used concerning the multichannel analyzer.

References

[1] A.K. Whittaker, Radiat. Phys. Chem. 48(5) (1996) 601–605.
[2] K. Anna, A. Torbjorn, B. Stenberg, J. Polym. Inter. 42(2) (1997) 131–137.
[3] M. Jun Ichiro, H.M. Famito, Phys. Lett. 96A (1982) 101–106.
[4] C.E. Baeks, Sci. Technol. 12 (1975) 1032–1037.
[5] A.M. El Agramy, B.A. Henaish, Polym. Degrad. Stability 40 (1993) 13–17.
[6] L. Feng, K.M. Yoo, R.R. Alfano, Special Personal Publication in the Medical Conference, USA, the City of College and the Graduate Center of the City University of New York, New York, NY 10031, 1994.

[7] A.A. El Dakrory, Interaction of High Power 6W and Pulsed Laser with Nylon 6, M.Sc. Thesis, Faculty of Science, Cairo University, Egypt, 1996.

[8] N.M.S. Raman, M.F. Mitchell, A. Mahadevan, Ginacolgic Oncology, vol. 52, Academy Press, 1994, pp. 31–38.

[9] S. Ebraheem, H.M. Abdel Hamid, Z.I. Ali, Arabian J. Nuclear Sci. and Its Applications, 1998, accepted.

[10] H.M. Saad, A.H. Ashour, H.M. Abdel Hamid, IEEE Transaction on Plasma Science 17 (1989) 555–559.

[11] A.A. Abdel Fattah, S. Ebraheem, Z.I. Ali, F. Abdel Rehim, Appl. Polym. Sci. 67 (1997) 1837–1851.

[12] H. Abou Zeid, Z.I. Ali, T.M. Abdel Maksoud, R.M. Khafagy, Appl. Polym. Sci. (1999), accepted.

[13] A. Chapiro, Radiation Chemistry Systems, Wiley, New York, 1962.