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Changes in the fundamental absorption edge of cellulose nitrate and its possible use for radiation dosimetry

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The induced changes in the absorption edge and optical density by γ-irradiation was measured for cellulose nitrate (CN). The optical absorption edge of CN is accurately determined as a function of absorbed dose up to 67.5 kGy. The results obtained show that the absorption edge and the optical density at a 520 nm wavelength were changed to a lower value by γ-irradiation. The post-irradiation stability of the films under different conditions were studied. The results suggest the possible use of a cellulose nitrate film as a dosimeter for absorbed doses up to 67.5 kGy.

1. Introduction

The spectrophotometric measurement of optical density changes in dyed and undyed plastic films is the most widely used routine methods of high-dose dosimetry (Abdel-Rehim and Abdel-Fattah [1]; Abdel-Rehim *et al.* [2–5]; McLaughlin *et al.* [6–9]; Tamura *et al.* [10]; Tanaka *et al.* [11].

Cellulose nitrate is widely used in track etching for neutron dosimetry and charged particle field (Attix [12]; Fadel *et al.* [13]; Fain *et al.* [14, 15]). The study of optical absorption and particularly the absorption edge is a useful method for the investigation of optically-induced transitions and for the provision of information about the band structure and energy gap in both crystalline semiconductors and non-crystalline materials. The absorption edge in many disordered materials follows the Urbach rule. It was of interest to see how the absorption edge and the optical energy gap changed as the absorbed dose was varied as it seemed that the higher value of resistivity of the complex dielectric material should be associated with an increased value of E_{opt} (Ilyas and Hogarth [16]; Mott and Davis [17]; Farag and Edmond [18].)

2. Experimental procedures

Cellulose nitrate plastic film detectors type CA80–15, thickness = 0.1 mm (manufactured by Kodak Pathé-France) were used in this study. The dimensions of each individual film were chosen to fit into the standard 1 cm cuvette holder of most spectrophotometers.

The irradiations of the cellulose nitrate films were carried out with a series of absorbed doses (in water), in the range up to 67.5 kGy, using gamma radiation from the standard ^{60}Co gamma chamber 4000A. The absorbed dose rate was measured to be 6.425 kGy h^{-1} using Fricke dosimetry [$G(\mathrm{Fe}^{3+}) = 1.62\ \mu\mathrm{mol\,J}^{-1} = 1.56 \times 10^{-2}/\mathrm{eV}$] (Sehested, [19]). The films were held between electron equilibrium layers (5 mm thick polystyrene). The irradiations were carried out without temperature control, but the temperature was measured before and after irradiation and the average was found to be about 25 °C.

A UV/VIS lambda 3B Perkin-Elmer spectrophotometer was used for measuring the absorption spectra of unirradiated and irradiated films throughout the wavelength range 300–700 nm. During spectrophotometry, the films were held in matt-black metal holders, with 1 cm × 1 cm openings for transmitting the object-beam slit image through the centre of the film, while the reference beam passed through a matched film holder with only air in the beam path.

3. Results and discussion

3.1. Absorption spectra and absorbed dose response

The absorption spectra of the cellulose nitrate films recorded before and after irradiation to different doses are shown in Fig. 1. The absorption spectrum of the unirradiated film shows a main absorption band in the visible region peaking at 515 nm (Fig. 1, curve 1). The irradiation of the film to a minor dose (6.4 kGy) produces a bathochromic shift by about 12 nm and a small increase in optical density (Fig. 1, curve 2). After that the amplitude of the absorption band decreases gradually with the increase in the dose of gamma ray photons. A new absorption band in the visible region (380–420 nm) is developed due to irradiation to doses higher than 20 kGy (Fig. 1, curves 4–9). These results explain the visual observation of a change in colour of the original plastic film from pink to light yellow upon irradiation. This change in

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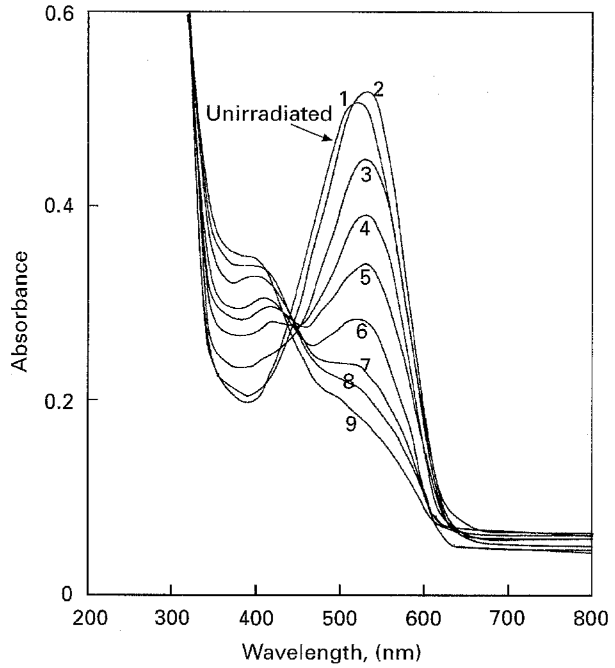

Figure 1 The absorption of cellulose nitrate films unirradiated and irradiated to different doses. The doses being (1) 0 kGy, (2) 6.40 kGy, (3) 12.85 kGy, (4) 19.27 kGy, (5) 25.70 kGy, (6) 33.73 kGy, (7) 43.37 kGy, (8) 54.62 kGy and (9) 64.47 kGy.

colour takes place through the formation of an isobestic point at about 440 nm. The change in absorbance of the films which were irradiated to a series of different absorbed doses, were measured spectrophotometrically at a fixed wavelength (520 nm). Fig. 2 shows the response curve of the film in terms of the change in absorbance per unit thickness (ΔA mm^{-1}) versus absorbed dose in water ($\Delta A = A_0 - A_i$, where A_0 and A_i are values of optical absorbance at 520 nm wavelength for the unirradiated and irradiated films, respectively).

Electronic transitions between the valence and conduction bands in the crystalline and non-crystalline materials start at the absorption edge which corresponds to the minimum energy difference E_g between the lowest minimum of the conduction band and the highest maximum of the valence band. If these extremes lie at the same point in K-space, then the transitions are called direct. If this is not the case, then transitions are possible only when phonon-assisted and are called indirect. The rule governing these transitions is the conservation of quasimomentum during the transitions, either of the electron alone in direct transitions, or the sum of the electron and phonon quasimomento in indirect transitions.

The value of the energy gap E_g depends in a rather subtle way on the structure and actual values of the pseudopotential in the crystal. It is to be distinguished from the energy gap E_g, which is characteristic of the whole absorption band and is connected with the basic chemical properties of the material.

For a semiconductor material in which the minimum of the conduction band and the maximum of the valence band occur at the same value of K, absorption begins at $h\nu = E_g$ and the electron is transferred vertically between the two bands without a change in momentum. Non vertical transitions are normally forbidden in this case. The optical absorption coefficient for a direct transition is given by (Fahrenbruch and Bube [20]):

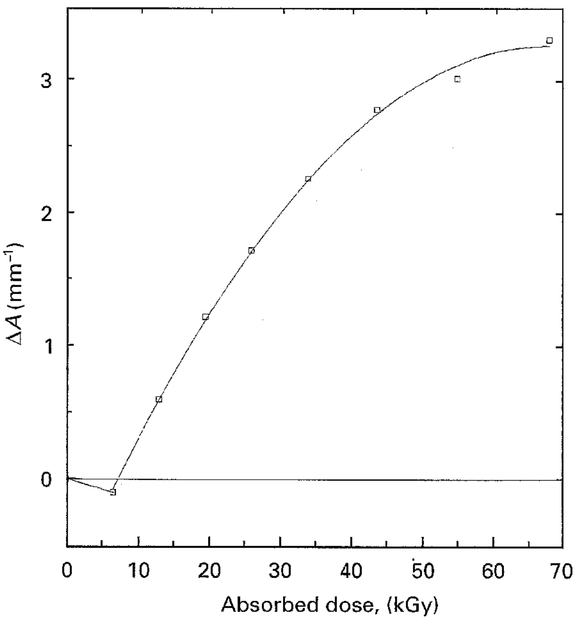

Figure 2 The response (ΔA mm^{-1}) of cellulose nitrate films versus absorbed dose, when measured at a wavelength of 520 nm.

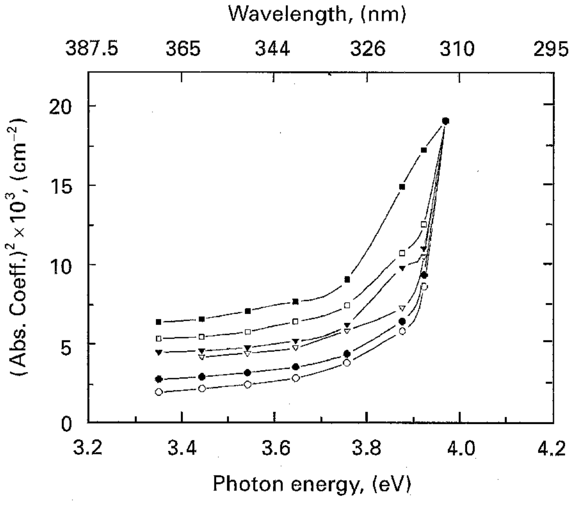

Figure 3 Optical absorption coefficient versus photon energy of cellulose nitrate at different doses of γ-radiation. The doses being (○) 0.0 kGy (●) 12.85 kGy, (▽) 25.70 kGy, (▼) 33.73 kGy, (□) 43.37 kGy and (■) 67.47 kGy.

$$\alpha = A(h\nu - E_g)^{1/2}$$

where; A is a constant. h is Plank's constant. ν is the frequency of the radiation. E_g is the optical energy gap.

From the results obtained in the present work, it was found that the absorption edge of cellulose nitrate under investigation changed with different doses (Fig. 3). Fig. 4 shows that the absorption edge (estimated by extrapolation of the linear part of the curves in Fig. 3) decreases slightly in the range 0–43 kGy and sharply in the range 43–67.5 kGy with increasing doses of γ-radiation. The experimental results can be explained on the basis that the irradiation may cause electrons to be exerted to an essentially free state (in the conduction band). These electrons may become loosely bound at trapping sites within the plastics. Previous studies on the effect of γ-radiation on lithium–potassium silicate glass and cabal glass resulted

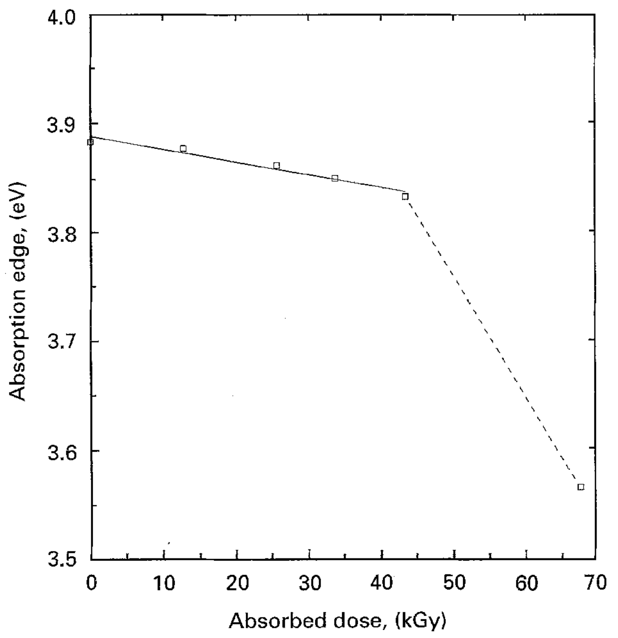

Figure 4 Absorption edge versus the absorbed dose for cellulose nitrate.

in E_{opt} values that vary between 1.0–1.68 and 0.55–3.35 eV respectively (Maged *et al.* [21]; Maged and Abdel-Rehim [22]; Hogarth *et al.* [23]).

3.2. Post-irradiation stability

Cellulose nitrate films irradiated to a dose of 25 kGy were stored for different periods after irradiation in different conditions, in the dark and at $\sim 35\%$ relative humidity (r.h.) at three different temperatures (0, 25, 40 °C), in the dark and 25 °C at relative humidities 0 and 100% and in direct day-light at ambient temperature (25 °C) and $\sim 35\%$ r.h. These films were read out spectrophotometrically at 520 nm wavelength at different intervals of time during the post-irradiation storage period of 63 days. The representative results are shown in Fig. 5. The results reveal that, the film which was stored in the dark at 0 °C and 35% r.h., has the best post-irradiation stability. In all other cases, the optical density decreases sharply by a per cent range of 11–35% within 3 days, however after that, the decrease becomes less pronounced.

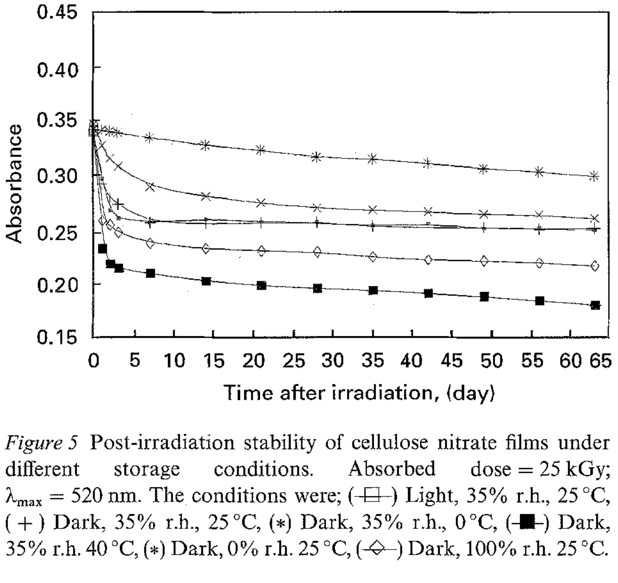

Figure 5 Post-irradiation stability of cellulose nitrate films under different storage conditions. Absorbed dose = 25 kGy; $\lambda_{\max} = 520$ nm. The conditions were; (⊟) Light, 35% r.h., 25 °C, (+) Dark, 35% r.h., 25 °C, (∗) Dark, 35% r.h., 0 °C, (■) Dark, 35% r.h. 40 °C, (∗) Dark, 0% r.h. 25 °C, (◇) Dark, 100% r.h. 25 °C.

4. Conclusions

From the experimental results it may be concluded that:

1. The absorption edge (E_g) for CN decreases with increasing the radiation dose.
2. In the dose range up to 67.5 kGy, the original absorption band was decreased gradually and a new absorption band (380–420 nm) is developed with an increase in the γ-ray doses.
3. The results suggest the possible use of cellulose nitrate films as a dosimeter for γ-ray doses up to 67.5 kGy. For practical use of a cellulose nitrate dosimeter, all films must be pre-irradiated to a dose of about 10 kGy. Irradiated films should be measured immediately after irradiation, or after waiting for 3 days.

References

1. F. ABDEL-REHIM and A. A. ABDEL-FATTAH, *Appl. Radiat. Isotopes* **44** (1993) 1047.
2. F. ABDEL-REHIM, F. SOLIMAN, S. IBRAHIM and N. SOUKA, *ibid.* **41** (1990) 700.
3. F. ABDEL-REHIM, S. EBRAHEEM, BA WEI-ZHEN and W. L. McLAUGHIN, *ibid.* **43** (1992) 1503.
4. F. ABDEL-REHIM, S. EBRAHEEM and N. SOUKA, *Radiat. Phys. Chem.* **39** (1992) 191.
5. F. ABDEL-REHIM, N. M. EL-SAWY and A. A. ABDEL-FATTAH, *Appl. Radiat. Isotopes* **44** (1993) 1055.
6. W. L. McLAUGHLIN, R. M. URIBE and A. MILLER, *Radiat. Phys. Chem.* **25** (1983) 729.
7. W. L. McLAUGHLIN, T. PREISINGER, A. MILLER and F. ABDEL-REHIM *ibid.* **25** (1985) 729.
8. W. L. McLAUGHLIN, BA WEI-ZHEN and W. J. CHAPPAS, *ibid.* **31** (1988) 481.
9. W. L. McLAUGHLIN, J. C. HUMPHREYS, D. HOCKEN and W. J. CHAPPAS, *ibid.* **31** (1988) 505.
10. N. TAMURA, R. M. TANAKA, S. MITOMO, K. MALSUDA and S. NAGAI, *ibid.* **18**, (1981) 947.
11. R. TANAKA, S. MITOMO and N. TAMURA, *Int. J. Appl. Radiat. Isot.* **35** (1984) 875.
12. F. H. ATTIX, "Introduction to Radiological Physics and Radiation Dosimetry". (John Wiley, New York, 1986) p. 487.
13. M. A. FADEL, A. A. ABDULLA and N. R. ADNAN, *Nuclear Instruments and Methods* **161** (1979) 339.
14. J. FAIN, M. MONNIN and M. MONTRET, Proc. Third Tihany Symp. on Radiation Chemistry, Hungary edited by J. Dobo and P. Hedjig (Academia Kiado, Budapest, 1972), p. 883.
15. *Idem* Proc. Int. Conference Nuclear Photography and Solid-State Track Detectors, Bucharest, 10–15 July 1972 (Institute of Atomic Physics, Bucharest, 1972) p. 34.
16. M. ILYAS and C. A. HOGARTH, *J. Mater. Sci. Lett.* **2** (1983) 535.
17. N. F. MOTT and E. A. DAVIS, "Electronic Processes In Non-crystalline Materials", second edition (Claredon Press, Oxford, 1979) Chap. 6.
18. A. FARAG and J. T. EDMOND, *Phil. Mag. B.* **53** (1986) 413.
19. K. SEHESTED, In "Manual on Radiation Dosimetry", edited by N. W. Holm and R. J. Berry (Marcel-Dekker: New York, 1970) p. 313.
20. A. L. FAHRENBRUCH and R. H. BUDE, "Fundamentals of Solar Cells" (Academic Press, New York, 1983) p. 49.
21. A. F. MAGED, F. ABDEL-REHIM, M. A. MORSY and A. M. HASHAD, In Lithium–Potassium Silicate Glass, St. Katherine, Sinai, Egypt, Proc. Special Issue in *Egyptian Journal of Solids* **12** (1989) 109.
22. A. F. MAGED and F. ABDEL-REHIM *Appl. Radiat. Isot.* **42** (1991) 763.
23. C. A. HOGARTH and A. A. HOSSEINI, *J. Mater. Sci.* **18** (1983) 2697.

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