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Radiation-induced modifications on spectroscopic and thermal properties of CR-39 and SR-90 nuclear track detectors

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Abstract

CR-39 and SR-90 polymer samples were irradiated with γ-rays at high doses ranging from 5×10^4 to 4×10^5 Gy. Irradiation effects were studied using Fourier Transform IR spectroscopy (FT-IR) in transmission mode, ultraviolet-visible spectroscopy and thermo-gravimetric analysis. Besides production of carbon dioxide due to polymerization and irradiation processes observed by FT-IR spectrometer, the IR absorption spectra of the fresh (non-aged) and irradiated samples also show the presence of a strong new absorption band at 2273 cm^{-1} which is attributed to the gaseous products inside the plastic. Moreover, the IR spectra indicate that on irradiation there is a change in the intensity and the shape of the OH group absorption bands relative to the unexposed sample. Optical absorption of CR-39 is influenced by the irradiation dose, while for SR-90 it was found to be an inverse function of higher doses. The thermal stability of these polymeric detectors shows considerable changes due to irradiation. The present study reveals that γ-ray irradiation is more effective in the build up of new structures in SR-90 than CR-39 due to the damage that depends on the radiation fluences.

Keywords: Track detectors; Gamma irradiation; CO; CO_2; Thermal stability

1. Introduction

Irradiation of polymeric track detectors by high-energy ionizing radiation causes modifications in the chemical, physical and mechanical properties in the polymer material. Among these effects, degradation of polymers (Sinha and Dwivedi, 1998; El-Shahawy et al., 1992; Tripathy et al., 2001) and production of CO_2 gas (Chong et al., 1997; Saad et al., 2001; Malek, 2000; Malek and Chong, 2002) should be noticed.

In our previous study (Saad et al., 2001), the amount of created free radicals, ionic species, water molecules and gaseous products such as CO and CO_2 were small, because the linear energy transfer due to gamma irradiation to polymeric detectors was by far so small. In the present investigation, we propose to study modifications of the structure induced by γ-rays of different high doses. For this purpose, several standard experimental techniques of spectroscopic and thermal analysis of polymeric materials are used.

2. Experimental

2.1. Materials

The polymer detectors used for this study are CR-39 (IC: Intercast) fabricated by the Intercast Europe Company

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of Parma Italy, CR-39 (HM: Homemade) and SR-90 (HM: Homemade) polymerized in Fujii laboratory at Faculty of Engineering, Aomori University, Japan (Fujii et al., 1993). The thicknesses of Intercast CR-39 (IC) and both of homemade detectors CR-39 (HM) and SR-90 (HM) were about 660 and 930 μm, respectively. The size of detector samples was 1 cm × 2 cm.

2.2. Irradiation conditions

The CR-39 (IC) and SR-90 (HM) track detectors were irradiated by the ^{60}Co gamma cell irradiation facility (ISSLE-DOVATEL) manufactured by the Russian Atomic Energy dated January 16th, 1998. The dose rate was 6 kGy/h. The activity of this cell is 5.97×10^{14} Bq. The samples were always positioned at the center of the driving belt and the irradiation process was achieved automatically. The samples were irradiated at different gamma doses ranging from 5×10^4 to 4×10^5 Gy. These gamma irradiations were performed at the Gamma Division, Atomic Energy Authority, Cairo. While for the case of low dose γ-ray irradiation, a sample of CR-39 (IC) was exposed to a ^{60}Co radioactive source for 14 d at Aomori University, Japan. The nominal activity of this source was calculated to be 3.7 MBq and the corresponding dose rate was found to be 0.114 ± 0.003 mGy/h.

2.3. Measurements

The detector samples were mainly analyzed using a FT-IR spectrometer of Bruker Vector 22, Germany, at Cairo University, Egypt, while fresh (non-aged) samples just after polymerization were analyzed by a Jasco-5300 FT-IR spectrometer at the Faculty of Engineering, Aomori University, Japan. The transmitted IR spectra analyzed at Cairo were obtained by averaging 64 scans at a resolution of 16 cm^{-1}.

Moreover, each detector sample was analyzed using an UV-vis spectrophotometer of Perkin Elmer 4B, made in Germany, at our laboratory in Zagazig. The UV-spectra were obtained for wavelengths from 190 to 900 nm.

Thermo-gravimetric analysis (TGA) was carried out under a nitrogen stream at a flow rate of 20 ml min^{-1} on a Shimadzu 50 H thermal analyzer fabricated in Japan. The temperature range employed was 30–600 °C. The thermal analyses for detectors exposed to high dose γ-rays were performed in the Microanalysis Centre at Cairo University, while a sample exposed to very low dose was measured at the Institute of Space and Astronautical Science (ISAS), Tokyo, Japan.

3. Results and discussion

A new band at wave number 2273 cm^{-1}, which could be identified as CO gas, was found in the FT-IR spectra for fresh unexposed samples of CR-39 (HM) and SR-90 (HM). The FT-IR spectra of these fresh samples of CR-39 (HM) and SR-90 (HM) have been found to be identical (Saad et al., 2001). The very strong bands at wave numbers 2950, 1745, 1250 and 875 cm^{-1} have been assigned as C–H stretching, C═O stretching in carbonate groups, C–O–C groups and ether groups, respectively (Saad et al., 2001; Yamauchi et al., 2001). These strong IR bands were saturated because these detectors were too thick, but the bands at wave numbers 2515, 2217 (CO) and 1960 cm^{-1} were clearly detected. In addition, the absorption bands of CO_2 at wave numbers 2340 and 657 cm^{-1} were also observed. The first band of CO_2 was very large and it seemed to be saturated, while the other band was weakly resolved. Another broad absorption band around 3500 cm^{-1} has been identified as OH group and/or adsorbed water (Gagandre et al., 1993; Malek and Chong, 2000).

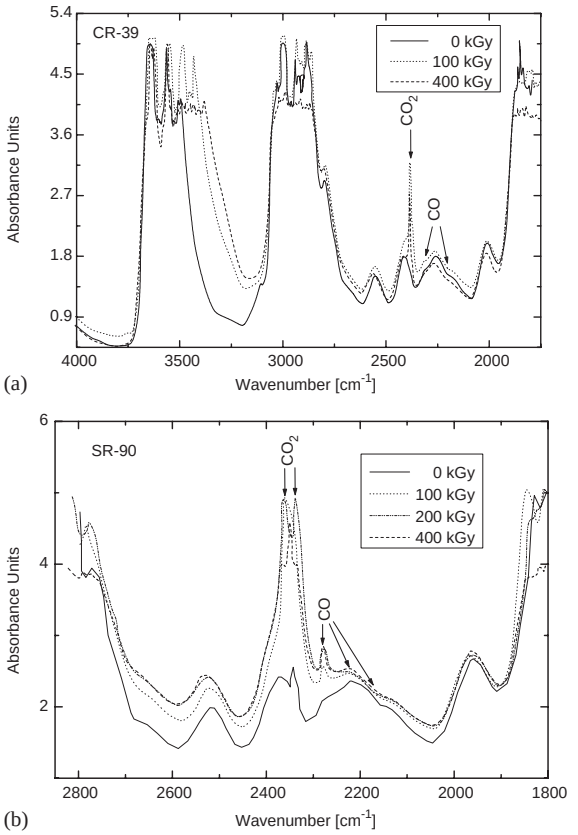

Fig. 1. FT-IR spectra in transmission mode. (a) CR-39 (IC) unirradiated and irradiated with γ-rays at absorbed dose 100 and 400 kGy. (b) SR-90 (HM) unirradiated and irradiated with γ-rays at absorbed doses 100, 200 and 400 kGy.

Fig. 1(a) shows the FT-IR spectra of unirradiated and irradiated samples of CR-39 (IC) at different gamma doses. At the first glance, it can be seen that many absorption bands are strongly affected by gamma irradiation in their shapes and/or intensities. The band area of CO_2 at 2340 cm^{-1} is a function of irradiation dose. The irradiation dose is also a

function of irradiation time. The band area of CO_2 quickly enhances with increasing dose (short irradiation time) and then gradually decreases with higher dose (long irradiation time). It is well known that the CO_2 gas diffuses out from the polymeric detector material if it is aged in the air at room temperature (Malek and Chong, 1999; Saad et al., 2001), while the amount of CO_2 does not suffer any decrease if the detector is stored in the freezer (Saad et al., 2001). Consequently, this is the main reason why the amount of CO_2 is not in proportion with the intensity of γ-ray exposure during the long irradiation time in air.

It is also observed that there is no significant change of the broad band of CO at 2214 cm^{-1} after gamma irradiation. In addition, Fig. 1(a) shows that the broad band of OH group contains three component peaks. The wave number of these peaks are 3470, 3550 and 3635 cm^{-1} and their assignments have been attributed to be the first over tone of carbonyl group, the symmetric stretching of OH bond water and the anti-symmetric vibration of water, respectively (Gagandre et al., 1993; Malek and Chong, 2000). In general, the shape and size of OH group absorption are affected by gamma irradiation. But, specifically the intensity of absorption bands of OH group is found to vary irregularly with absorbed dose, while the broad absorption increases at lower wave number. This irregularity is attributed most likely to the humidity of the environment during and after irradiation.

The FT-IR spectra of SR-90 (HM) before and after irradiation are shown in Fig. 1(b). In order to detect absorption signal of CO_2 produced by irradiation in CR-39 (HM) and SR-90 (HM), these plastic detectors should be sufficiently aged in the air before exposure. In the case of SR-90 (HM) samples that were exposed to γ-rays at doses 100, 200 and 400 kGy, it was easy to recognize the large amount of CO_2 produced by irradiation from the relatively small amount of CO_2 originally produced by polymerization. As mentioned above, it is clear that the absorbance of CO_2 bands in SR-90 (HM) increases by increasing the absorbed dose during the short time irradiation. Furthermore, this increase of absorbance of CO_2 was attributed to the break-up of the content of carbonate groups, in the vicinity of 1738 cm^{-1}, which corresponds to C═O stretching of –OCOO– groups. This leads to evolution of carbon dioxide gas that is trapped in the detector material (Gagandre et al., 1993; Malek and Chong, 2000).

It is worth mentioning that a new sharp absorption peak at 2273 cm^{-1} was seen in Fig. 1(b) due to high dose irradiation, which could be assigned to the CO gas. The original assignment of the CO is at wave number 2160 cm^{-1}. Generally, the broad bands at 2273, 2215 and 2160 cm^{-1} would be identified as the CO gas. The absorption at the first peak at 2273 cm^{-1} strongly increases with absorbed dose, as well as the main peak at 2215 cm^{-1} slightly increases, while no change in the third peak (as a shoulder).

In order to investigate the aging effect on the amount of CO in the detector, we measured IR spectra at different aging times for the unexposed SR-90 (HM) and CR-39 (HM)

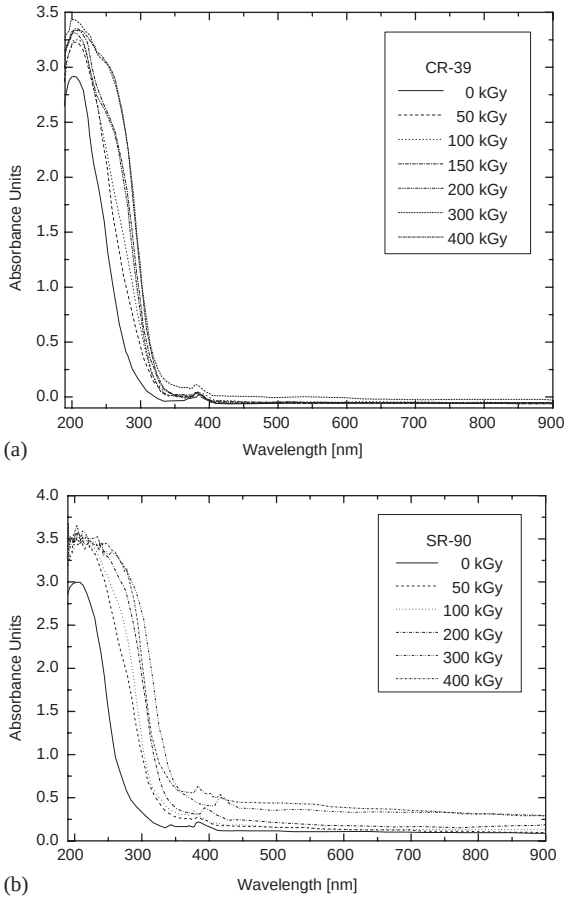

Fig. 2. UV-visible spectra. (a) CR-39 (IC) unirradiated and irradiated. (b) SR-90 (HM) unirradiated and irradiated. Irradiations were performed with γ-rays at different doses up to 400 kGy.

samples. From these IR measurements we have found that both detectors contain a relatively large amount of CO gas just after polymerization and that CO escapes from the detector material by diffusion, similar to behavior of CO_2 gas, if the detector is stored in air at room temperature.

The optical absorption measurements with UV-visible spectrophotometer carried out on unirradiated and irradiated samples of CR-39 (IC) and SR-90 (HM) are shown in Fig. 2(a) and (b). We notice that the optical absorbance spectra for CR-39 (IC) shift from UV towards the visible at higher wavelengths with the increase of gamma dose, while for SR-90 (HM) is inverted at higher doses. The samples become gradually opaque to the visible light and the material of these detectors changes from very high transparent to yellowish with the increase of the gamma dose. Moreover, the transmittance of the irradiated SR-90 (HM) samples is much lower than that of the irradiated CR-39 (IC) samples at the same dose.

The decrease in the transmittance at 385 nm wavelength with gamma dose was plotted on a graph. Thus, it was

found that the gamma doses used in our experiment seem to be sufficient to induce a considerable change in the optical band-width of both kinds of polymeric track detectors CR-39 and SR-90. Our results are similar to those of who investigated the polymers CA 80-15 and Lexan (Akber et al., 1980) and CR-39 (Chong et al., 1997). The change in optical transmittance of both CR-39 and SR-90 detectors may be attributed to the generation of some chromophoric groups (Lounis-Mokrani et al., 2003) and /or scattering due to new complex compounds formed.

The results of TGA show a decrease in thermal stability of the polymeric track detectors CR-39 and SR-90 with increasing the absorbed dose of γ-rays. Fig. 3(a) shows TGA thermograms of the unirradiated CR-39 and the one irradiated at very low dose 0.038 Gy. The blank CR-39 remained stable up to 296 °C that was named a stable zone, followed by a considerable decrease in the weight of the sample with increasing the temperature up to 487 °C that was named a major decomposition zone and finally followed by the residual decomposition zone up to the end of temperature range. In Fig. 3(a), a small decrease in thermal stability of the irradiated sample can be seen even at very low dose.

In the case of high doses, there is a significant decrease in the thermal stability of the irradiated samples of CR-39 and SR-90 dependent on the gamma dose. Fig. 3(b) shows the thermograms of CR-39 for gamma dose from 0 to 400 kGy. It should be mentioned that there is an irregular decrease in thermal stability of the irradiated SR-90 (HM) at higher doses.

Fig. 3(c) shows the TGA thermograms of the blank SR-90 and the one irradiated at 300 kGy dose. The thermograms indicate that the stable, major decomposition and residual decomposition zones are ranging from 30 °C to 295 °C, from 295 °C to 385 °C and from 385 °C to 600 °C for unirradiated samples of SR-90 and that from 30 °C to 259 °C, from 259 °C to 481 °C and from 481 °C to 600 °C for irradiated samples of SR-90, respectively. It should be noticed that the CR-39 decomposes through three steps for both unirradiated and irradiated samples, while SR-90 decomposes through two steps for the unirradiated samples and three steps in the case of the irradiated one.

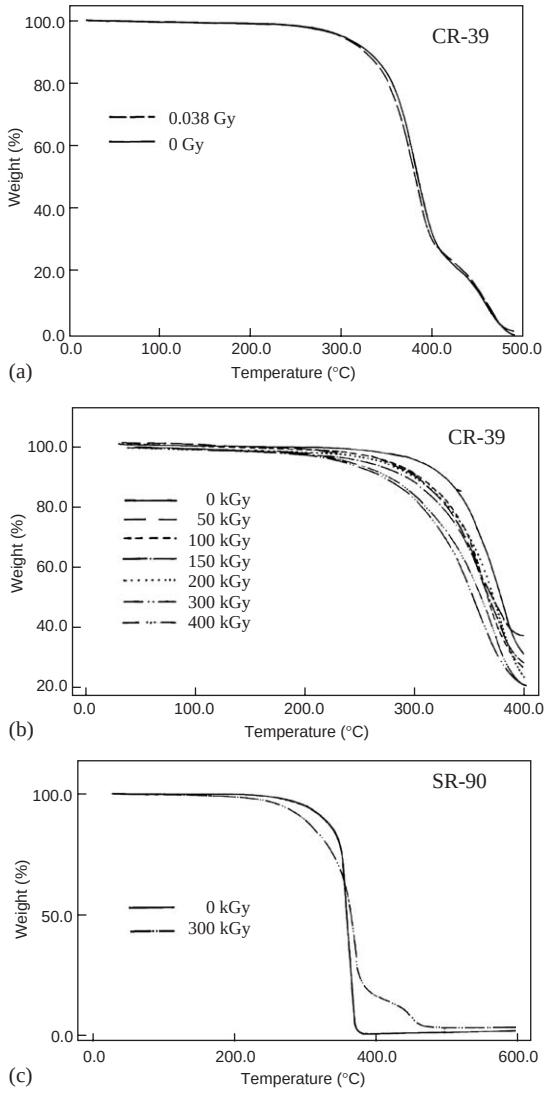

Fig. 3. TGA thermograms. (a) CR-39 (IC) unirradiated and irradiated with γ-rays at absorbed dose 0.038 Gy. (b) CR-39 (IC) unirradiated and irradiated with γ-rays at different doses up to 400 kGy. (c) SR-90 unirradiated and irradiated with γ-rays at absorbed dose 300 kGy.

4. Conclusion

From the results obtained by the gamma irradiation on CR-39 and SR-90 polymeric detectors, our conclusions can be summarized as follows.

The FT-IR spectroscopy proves: (i) gaseous products such as CO and CO_2 are formed in both detectors through the polymerization process; (ii) additional CO and CO_2 are produced through the irradiation process; (iii) both the amounts of CO and CO_2 are dose dependent at lower doses till 2×10^5 Gy or during the short irradiation time.

The UV-visible analysis proves the following: (i) complex compounds are created resultantly by the break of the main chain of the polymer material; (ii) the break increases with increasing dose level for CR-39, whereas for SR-90 the break is irregular at higher doses; (iii) a shift in the absorption edge towards the higher wavelength indicates the decrease in the energy band gap of the irradiated detectors.

The thermogravimetric analysis proves the following: (i) a measurable effect on the thermal stability can be seen even at very low dose 0.038 Gy; (ii) the decrease in the thermal stability is significant in both of the polymeric detectors at high gamma doses from 5×10^4 to 4×10^5 Gy.

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References

Akber, R.A., Nadeem, K., Majid, C.A., Zaman, N., Chaudhary, M.A, Khan, H.A, 1980. Studies of structural changes produced by high doses of gamma rays in some plastic track detectors. Nucl. Instrum. Methods 173, 217–221.

Chong, C.S., Ishak, I., Mahat, R.H., Amin, Y.M., 1997. UV-VIS and FTIR spectral studies of CR-39 plastics irradiated with X-rays. Radiat. Meas. 28, 119–122.

El-Shahawy, M., Hussein, A., Tawansi, A., 1992. CR-39 as a gamma dosimeter: dielectric and infrared studies. J. Mater. Sci. 27, 6605–6608.

Fujii, M., Asari, T., Yokota, R., Kobayashi, T., Hasegawa, H., 1993. Aging effects on a new polymeric track detector SR-90 and a model of the nuclear track formation. Nucl. Tracks Radiat. Meas. 22, 199–204.

Gagandre, C., Decossas, J.L., Vareille, J.C., 1993. IR spectroscopy studies of polycarbonate irradiated by H^+ and Li^+ ions. Nucl. Instrum. Methods B 73, 48–52.

Lounis-Mokrani, Z., Fromm, M., Barillon, R., Chambaudet, A., Allab, M., 2003. Characterization of chemical and optical modifications induced by 22.5 MeV proton beams in CR-39 detectors. Radiat. Meas. 36, 615–620.

Malek, A., 2000. Study of the effects of X-ray and gamma-ray irradiation on CR-39 plastic track detector. Ph.D. Thesis, University Sains Malaysia, Penang, Malaysia.

Malek, M.A., Chong, C.S.,1999. Diffusion of CO_2 gas from X-ray and γ-ray irradiated CR-39 plastic. In: Proceedings, The Symposium on Nuclear and Related Techniques in Agriculture, Industry and Environmental Studies (NURT'99), Havana, Cuba, 26–29 October, 1999.

Malek, M.A., Chong, C.S., 2000. FTIR study of H_2O in polyallyldiglycol carbonate. Vib. Spectrosc. 24, 181–184.

Malek, M.A., Chong, C.S., 2002. Gerenration of CO_2 in γ-ray-irradicated CR-39 plastic. Radiat. Meas. 35, 109–112.

Saad, A.F., Atwa, S.T., Yasuda, N., Fujii, M., 2001. FT-IR spectroscopy of carbon dioxide in CR-39 and SR-90 track detectors irradiated with ions and gamma rays at different energies and fluences. Radiat. Meas. 34, 51–54.

Sinha, D., Dwivedi, K.K., 1998. Modifications of radiation detection response of PADC track detectors by photons. Radiat. Phys. Chem. 53, 99–105.

Tripathy, S.P., Mishra, R., Dwivedi, K.K., Khathing, D.T., Ghosh, S., Fink, D., 2001. Modification induced by proton irradiation in polyallyldiglycol carbonate (PADC). Radiat. Meas. 34, 15–17.

Yamauchi, T., Takada, S., Ichijo, H., Oda, K., 2001. Raman and near-IR study on proton irradiated CR-39 detector and the effect of air-leak on damage formation. Radiat. Meas. 34, 69–73.