

Structure and Optical Investigation of the Effect of Electron Beam-Irradiation in Poly-Allyl-Diglycol-Carbonate

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ABSTRACT: The effect of electron beam irradiation on the structural and optical properties of Poly-Allyl-Diglycol-Carbonate CR-39 solid state nuclear track detector was investigated. Samples from CR-39 detector were irradiated with electron beam with doses at levels between 10 and 140 kGy. The structural and optical modifications in the electron beam irradiated CR-39 samples have been studied as a function of dose using different characterization techniques such as FTIR spectroscopy, Vickers hardness, re-

fractive index and color difference measurements. The electron beam irradiation in the dose range 25–140 kGy led to a more compact structure of CR-39 polymer, which resulted in an improvement in its hardness with an increase in the refractive index. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 3552–3557, 2010

Key words: electron beam irradiation; FTIR spectra; Vickers hardness; refractive index; color changes; CR-39

INTRODUCTION

Electron beam irradiation is a suitable tool to modify the physical properties of polymers. Poly-Allyl-Diglycol-Carbonate (CR-39) is a solid state nuclear track detector that is used in nuclear particles detection. CR-39 is transparent in visible spectrum and almost completely opaque in infrared and ultraviolet range. Irradiation of CR-39 is always accompanied by a gradual increase in absorbance,¹ generation of chromophoric groups, loss of crystallinity,² formation of carbonized inclusions along with a gradual phase transition,³ as well as creation of three-dimensional network and triple bonds.^{4,5} These effects depend on the amount of energy deposited in the polymer.

Nowadays, the modification of polymers by radiation whether to achieve crosslinking or chain scission is a significant industrial process throughout the world. Extensive studies have been undertaken to understand this technology and thus the effects of radiation on the most significant classes of polymers are reasonably well catalogued and understood.^{6–10} Many widely used polymers suffer main chain scission and loss in mechanical strength;¹¹ such polymers are known as degrading polymers. On the other hand, many polymers possess enhanced physical properties due to irradiation. Both crosslinking and degradation are the consequences of irradiation

but the one which predominates determine the net effect.

Refractive indices of polymers provide information about their structural characteristics.¹² Additionally, the study of color change in irradiated polymers is an important technique that has been used to assess the physical and chemical changes in polymers. This phenomenon has important commercial applications in the radiation processing of polymeric materials and the use of polymers in certain optical devices in radiation environments. In our previous work we studied the color changes in CR-39 nuclear track detector due to neutron irradiation¹³ and gamma irradiation.¹⁴ The results indicated that the CR-39 detector acquires color under neutron or gamma irradiation, but it has more response to color changes by gamma irradiation. This study deals with the investigation of the effect of electron beam irradiation on the structural and optical properties of CR-39 detector not only to obtain information concerning the interaction of electrons with CR-39, but also to study the feasibility of enhancing its properties, improving its performance in different applications.

EXPERIMENTAL

Samples

Poly-Allyl-Diglycol-Carbonate, CR-39, sheets manufactured by Pershore, England, are used in this study. They are of density 1.32 g/cm³ (composition C₁₂H₁₈O₇, molecular weight 274 a.m.u.) and thickness 0.5 mm.

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Irradiation facilities

The irradiation process was performed in air, at room temperature 25°C, using 1.5 MeV electron beam accelerator of the ICT-type operating with insulating core transformer, with a beam current of 25 mA. The conveyer was attached with a cooling system to avoid heating of the samples. The dose was adjusted frequently using FWT'60-00 dosimeter that was calibrated by irradiation in gamma facility against Ceric/Cerous dosimeter supplied by Nordion, Canada. It is recognized that transfer of the calibration from gamma to 1.5 MeV electron beam irradiation involves an added uncertainty. We estimate this uncertainty to be no more than 5%.

Analysis of irradiated samples

Fourier transform infrared spectroscopic measurements were carried out using a spectrophotometer Type Shimadzu, Model 8201 PC. This instrument measures in the wavenumber range 400–4000 cm^{-1} , with an accuracy better than $\pm 4 \text{ cm}^{-1}$.

The hardness measurements were performed with Shimadzu H MV-2000 microhardness tester which uses a Vickers diamond pyramid indenter having a square base and 136° pyramid angle to measure the Vickers hardness (Hv). The harness indentations were carried out on the surfaces of the pristine and irradiated CR-39 at room temperature at the load range 50–700 mN. For each load, 5 indentations were performed at several points of the sample and the average values were considered. The duration of the indentations was 10 seconds.

The refractive index measurements were carried out using an Abbe refractometer (Type Reichert; mark II, Model-10480, NY). The accuracy of measuring the values of refractive indices, surface temperature of the prism and the wavelength of the light used were ± 0.0001 , 18.3–20.5°C and 5893 Å, respectively. Several values were measured to the same sample and the average values were considered.

The transmission measurements were carried out at room temperature using a Shimadzu UV-Vis-NIR scanning spectrophotometer, Type 3101 PC. This unit measures in the wavelength range from 200 to 3200 nm, with wavelength accuracy better than $\pm 3 \text{ nm}$ over 200–2000 nm and better than $\pm 9 \text{ nm}$ over 2000–3000.

Determination and calculation of the tristimulus values

The vision scientists created a special set of mathematical lights, X, Y, and Z, to replace actual red, green and blue lights. The color matching functions for the X, Y, and Z lights are all positive numbers

and are labeled \bar{x} , \bar{y} , and \bar{z} . Every color can be matched using the appropriate amount of X, Y, and Z light. The amount of X, Y, and Z light needed to match a color are called the color's tristimulus values.

The CIE tristimulus values for a transmitting sample are calculated by adding the product of the spectral power distribution of illuminant, the transmittance factor of the sample and the color matching functions of the observer at each wavelength of the visible spectrum, as shown in the following equations:

$$\begin{aligned} X &= k \sum P(\lambda) \times (\lambda) T(\lambda) \\ Y &= k \sum P(\lambda) y(\lambda) T(\lambda) \\ Z &= k \sum P(\lambda) z(\lambda) T(\lambda) \\ k &= 100 / \sum P(\lambda) y(\lambda) \end{aligned}$$

where $P(\lambda)$ is the value of the spectral power distribution of the illuminant at the wavelength λ . $T(\lambda)$ is the transmittance factor of the sample at the wavelength λ and $x(\lambda)$, $y(\lambda)$, and $z(\lambda)$ are the CIE color matching functions for the standard observer at the wavelength λ . The factor k normalizes the tristimulus value so that Y will have a value of 100 for a perfect white diffuser.

The 1976 CIE L* a* b* (Cielab) color space

A weakness of the CIE X, Y, and Z color space is its lack of visual uniformity. Creating a uniform color space would have two major advantages. It would allow plots showing the perceptually relative positions of two or more colors in color space, and it would facilitate the creation of a good color difference ruler between two samples. The 1976 CIE L* a* b* (CIELAB) color space is widely used in the paint, plastic and textile industries, while the 1976 CIE L* u* v* (CIELUV) color space is widely used in the television and video display industries. L* correlates with perceived lightness in CIELAB color space. A perfect white would have an L* of 100, and a perfect black would have an L* of 0. The coordinates a* and b* have their history in the opponent color theory. It was proposed that three pairs of opposing color sensations produce all colors: red and green; yellow and blue; and black and white. The CIELAB coordinate a* correlates with red (+a*) and green (−a*), while the coordinate b* correlates with yellow (+b*) and blue (−b*). The CIELAB L*, a* and b* coordinates are calculated from the tristimulus values according to the following equations

$$\begin{aligned} L^* &= 116 f(Y/Y_n) - 16 \\ a^* &= 500[f(X/X_n) - f(Y/Y_n)] \\ b^* &= 200[f(Y/Y_n) - f(Z/Z_n)] \end{aligned}$$

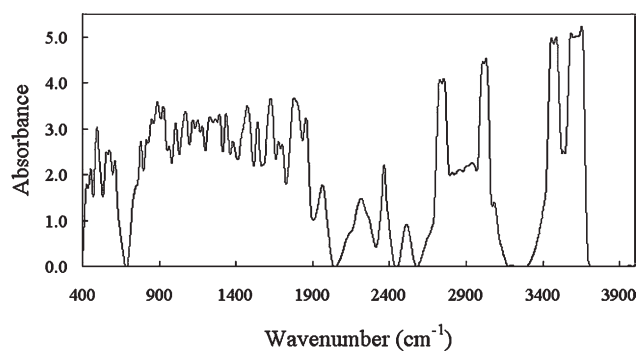


Figure 1 FTIR spectrum of the nonirradiated CR-39 sample.

In which X , Y , and Z are the tristimulus values and the subscript n refers to the tristimulus values of the perfect diffuser for the given illuminant and standard observer; $f(X/X_n) = (X/X_n)^{1/3}$ for values of (X/X_n) greater than 0.008856 and $f(X/X_n) = 7.787(X/X_n) + 16/116$ for values of (X/X_n) equal to or less than 0.008856; and the same with Y and Z replacing X in turn.

The CIELAB color difference, ΔE is given by^{15,16}

$$\Delta E = [(L_1^* - L_2^*) + (a_1^* - a_2^*) + (b_1^* - b_2^*)]^2$$

The subscripts 1 and 2 refer to the irradiated and nonirradiated samples.

RESULTS AND DISCUSSION

Fourier-transform infrared spectroscopy

The FTIR spectral analysis has been performed to investigate the structural changes induced in CR-39 polymer due to electron beam irradiation. The changes have been estimated from the relative increase or decrease in the intensity of the peak associated to the functional groups present in the polymer. Figure 1 shows the infrared absorption spectra for the nonirradiated CR-39 sample as an example. The strong bands at wavenumbers 1723 cm^{-1} , 1234 cm^{-1} and 2930 cm^{-1} have been assigned as C=O stretching in carbonate groups, C—O—C groups and C—H stretching, respectively. These strong IR bands were saturated because the used detector is thick. So, it is not possible to obtain accurate quantitative information about the absorbance of these groups from it, but the absorption band at wavenumber 2340 cm^{-1} corresponding to CO_2 was clearly observed. The break up of the content of the carbonate group leads to the evolution of CO_2 gas that is trapped in the material.¹⁷ Another absorption band around 3500 cm^{-1} has been identified as hydroxyl group OH. The abstraction of —H from the polymer backbone besides the breaking in the car-

bonate group, leads to the formation of —OH groups.⁸ These results are in agreement with that obtained by Saad et al.,¹⁷ who studied the effect of gamma irradiation on the FTIR spectroscopy of CR-39 polymeric detector.

Hardness measurements

The Vickers hardness H_v is calculated from the relation:

$$H_v = 1.854 F/d^2$$

where F is the applied load (mN) obtained as the product of the load (g) and the acceleration due to gravity (ms^{-2}) and d is the diameter of the indentation (μm). The variation of Vickers hardness with the applied load for the pristine and irradiated CR-39 samples is shown in Figure 2. From the figure it is seen that the hardness increases with the load up to 700 mN becomes saturated beyond 500 mN. The increase of hardness with load could be explained on the basis of the strain hardening phenomenon.¹⁸ The variation of hardness with the electron beam dose is shown in Figure 3. The hardness shows a decrease until a minimum value around the 25 kGy irradiated sample followed by an increase with increasing the dose up to 140 kGy due to crosslinking.

Refractive index measurements

The refractive indices of solid sheets of CR-39 of 0.5 mm thickness, exposed to electron beam irradiation up to 140 kGy were measured. The accuracy of

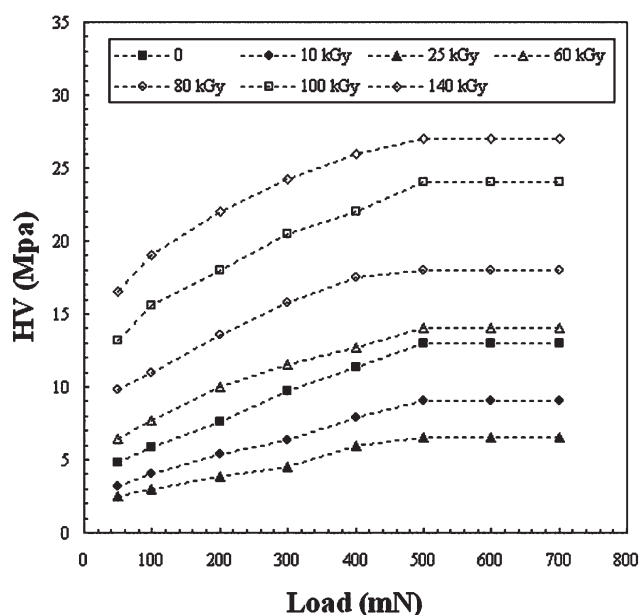


Figure 2 The variation of the Vickers hardness of the nonirradiated and irradiated CR-39 samples with the applied load.

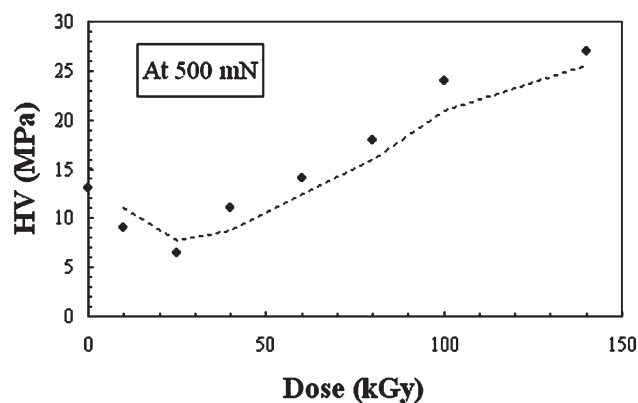


Figure 3 The variation of the Vickers hardness of CR-39 samples with the electron beam dose.

measuring the values of refractive indices, surface temperature of the prism and the wavelength of the light used were ± 0.0001 , $18.3\text{--}20 : 5^\circ\text{C}$ and 5893 \AA , respectively. Figure 4 illustrates the variation of the refractive index with the dose. The refractive index showed a decrease in magnitude until a minimum value at around 25 kGy followed by an increase on increasing the dose up to 140 kGy. This behavior can be explained in terms of degradation and cross-linking induced by electron irradiation. Such behavior facilitates the formation of free radicals that are chemically active. This allows the formation of covalent bonds between different chains (crosslinking), and in turn minimizes the anisotropic character of the CR-39 polymer, leading to the increase in refractive index.

Color changes

Figure 5 shows the transmittance of the nonirradiated and the 140 kGy as an example for the irradiated CR-39 samples, measured in the wavelength range 200–2500 nm. The transmission values in the wavelength range 370–780 nm (Fig. 6) were used to in computing the color intercepts L^* , a^* , and b^* . The

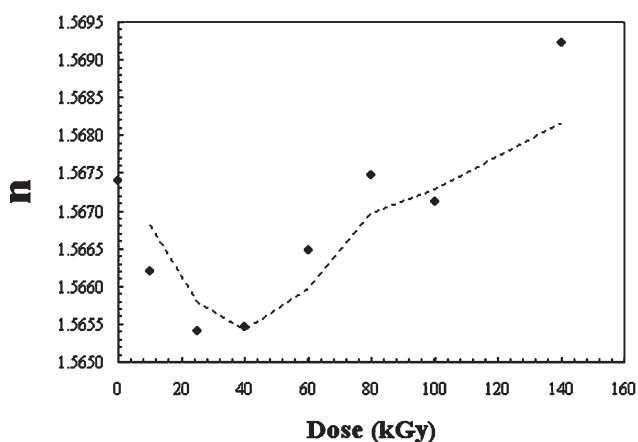


Figure 4 The variation of the refractive index of CR-39 samples with the electron beam dose.

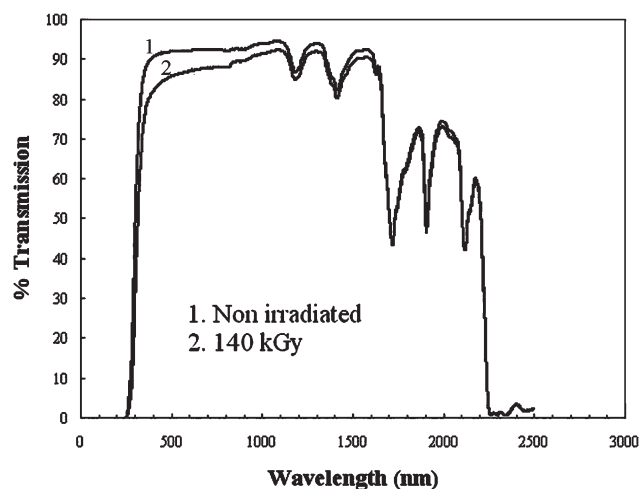


Figure 5 The transmittance spectra of nonirradiated and the 140 kGy as an example for the irradiated CR-39 samples, measured in the wavelength 200–2500 nm.

accuracy in measuring L^* is $+0.05$ and $+0.01$ for a^* and b^* . The variation of color intercepts (L^* and b^*) with dose is shown in Figure 7. It can be seen that the color parameters were significantly changed after exposure to electron beam irradiation. The blue ($-b^*$) color components of the nonirradiated film was changed to yellow ($+b^*$) after exposure to electrons in the dose range from 10 to 140 kGy. This is accompanied by an increase in the darkness of the samples ($-L^*$). The green color component ($-a^*$) is not affected by electron beam irradiation at the dose range under study.

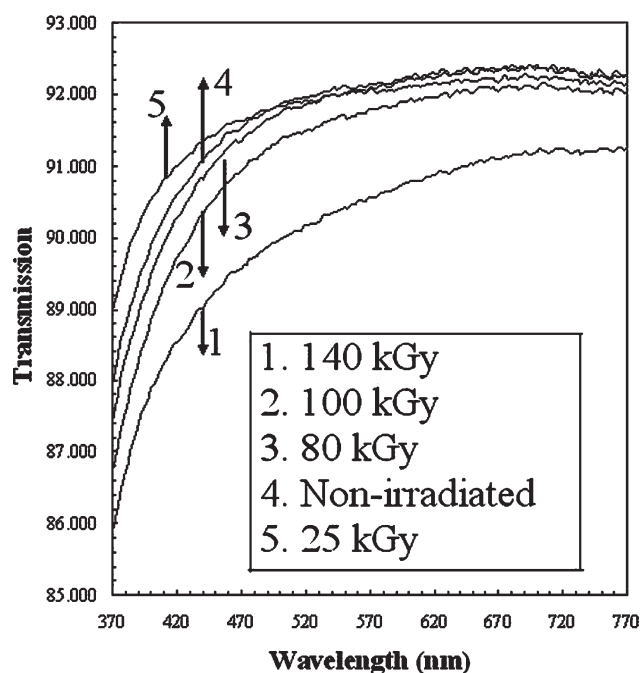


Figure 6 The transmittance spectra of nonirradiated and some irradiated CR-39 samples, measured in the wavelength 370–780 nm.

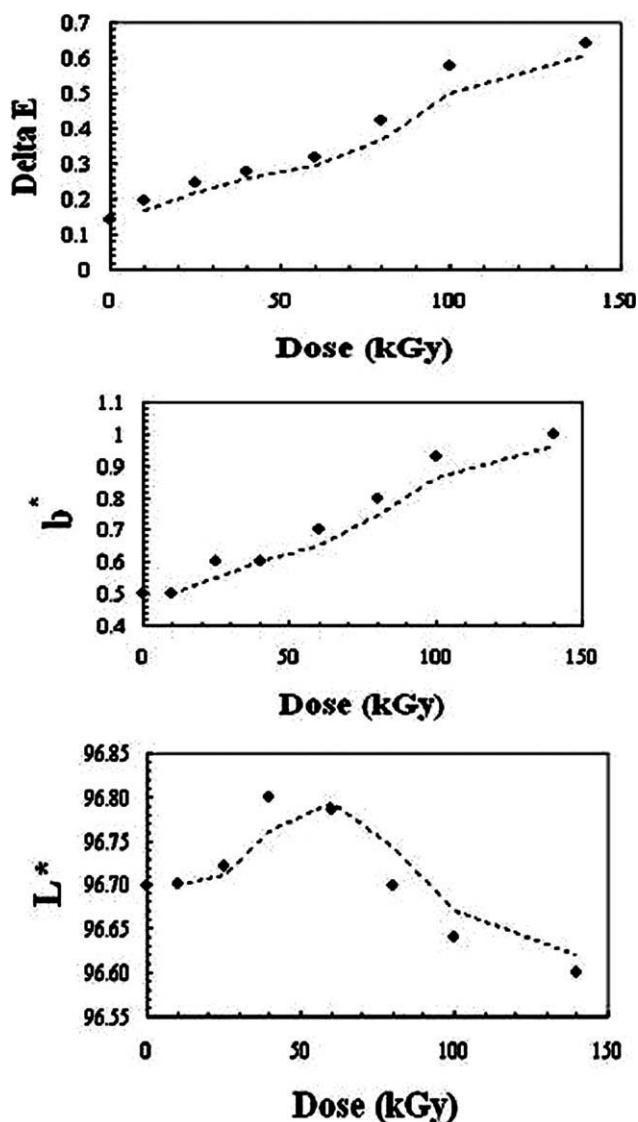


Figure 7 Variation of the color intercepts (L^* and b^*) and the color intensity ΔE with the electron beam dose.

The color intensity ΔE , which is the difference between the nonirradiated sample and those irradiated with different electron beam doses was calculated and is plotted in Figure 7 as a function of dose. The color intensity ΔE was greatly increased with increasing the dose, and accompanied by a significant increase in the yellow color component ($+b^*$). This indicates that the CR-39 polymer has more response to color change by electron beam irradiation. These changes in color can be attributed to the trapping of the excited free radicals that are formed by ionization.¹⁹ Also, the trapped free radicals resulting from radiation-induced rupture of polymer molecules have electrons with unpaired spin. Such species may also give optical coloration.

In addition, it can be observed that the color changes in irradiated CR-39 depends on the type of radiation, since in our previous work¹³ it is found

that the color intensity ΔE decreased with increasing the neutron dose which indicated that the response of CR-39 to color changes by neutron irradiation is weak. In another previous work¹⁴ we found that the CR-39 polymer has a response to color changes by gamma irradiation, but the main color component which is responsible for coloration was the blue that changed into yellow ($+b^*$), a^* and L^* were not affected by gamma irradiation at the studied dose range. In this study, as it is mentioned above the blue color component has changed into yellow ($+b^*$) by electron beam irradiation, accompanied by an increase in the darkness of the samples ($-L^*$). Only a^* is not affected by electron beam irradiation at the dose range under study.

CONCLUSION

The electron beam irradiations of CR-39 polymer lead to chain scission followed by crosslinking and as a result there are changes in its structural and optical properties.

Optical absorbance of the CR-39 detector appears to be connected to the morphological changes induced due to electron beam irradiation, where, the degradation process predominates below 25 kGy. At the dose range 25–140 kGy, the free radicals produced from scission can be used in reactions that lead to the enhancement of crosslinking.

The electron beam irradiation in the dose range 25–140 kGy led to a more compact structure of CR-39 polymer, which resulted in an improvement in its Vickers hardness.

The nonirradiated CR-39 polymer is nearly colorless; however, it showed significant color sensitivity towards electron beam irradiation. The sensitivity in color change towards electron irradiation appeared clearly in the change in the blue color components to yellow, accompanied by an increase in the darkness of the polymer samples.

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