



# Photoluminescence, optical band gap and surface wettability of some polymeric track detectors modified by electron beam



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## ABSTRACT

In the present study, modifications have been performed on two polymeric track detectors (PTDs), CR-39 and Makrofol. The samples were irradiated with 1.5 MeV electron beam at different doses ranging from 0 to 500 kGy. Changes in photoluminescence (PL) and ultraviolet–visible (UV–vis) spectrophotometry as well as surface properties have been carried out for all PTD samples. The PL spectra indicate noticeable decrease of the integrated intensity for both types of irradiated PTDs with the increase of electron beam doses. This may be due to the creation of defects in the irradiated PTDs polymers. UV–vis spectra reveal that the optical absorption was shifted towards higher wavelength region after irradiation with electron beam. The optical band gap energy and Urbach's energy are decreased with increasing electron beam doses. Contact angle measurements show that the wettability and surface free energy are increased for irradiated samples with increasing electron irradiation doses. The change in roughness is also investigated.

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## 1. Introduction

During the last decades, the polymeric materials have a rapidly growing interest in their properties. The improvement of polymeric materials becomes an important subject to use in different technology applications [1,2]. Polymeric track detectors (PTDs) are polymeric material that currently used as a detector due to its ability to record the charged particles. Scientists and engineers give a great attentiveness to PTDs due to their extensive use in different applications [3–5]. However, it is found that PTDs are limited in use for some applications. Therefore, new methods must be used to modify the properties of such materials. One of these methods is the irradiation of polymeric materials that attributed to the production of new polymeric materials.

The electron beam irradiation technique is one of the important irradiation tools which used to modify the surface properties of polymeric material such as dielectric, electrical, structural, and optical

properties [6,7]. The modification of polymeric material by electron beam depends upon the irradiation dose rate and material characteristics. Therefore, the modified polymers are prognathous to be used in a wide range of potential applications such as light-emitting diode [8], electronic device [9,10] optical display and solid state battery [11]. Penetration depth of the electron beam within the polymer will be limited compared to the gamma ray and this gives preference to absorb the electron energy falling on the material [12]. Overall, the passage of charged particles through polymeric materials causes improvements in the physical and chemical properties due to the energy deposition of these particles within the material [13]. These improvements have been attributed to the processes of ionization, scission, cross-linking in the polymer chain and the creation of carbon clusters [14–21].

Furthermore, during the irradiation process, the volatile species may be liberated and the contact of polymers after irradiation with the air leads to their rapid oxidation. The volatile species released from the irradiated polymer materials and the oxidation process of the treated surface leads to variations in the polymer properties such as optical, electrical, mechanical, wettability and photoluminescence.

In the present study, two commercially important polymer track detectors, CR-39 and Makrofol have been considered as a point of

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interest. The main objective of this investigation is to improve the optical, wettability and surface free energy of the polymer track detectors after electron beam irradiation in order to use them in the appropriate applications.

## 2. Materials and methods

Polymeric track detectors (PTDs), CR-39 and Makrofol are used with chemical composition  $C_{12}H_{18}O_7$  and  $C_{16}H_{14}O_3$ , and thickness 1000 and 300  $\mu\text{m}$ , respectively. Fig. 1 shows the structure of CR-39 and Makrofol.

Electron beam bombardment of all samples was carried out at room temperature using 1.5 MeV electron beam accelerator of ICT, at National Center for Radiation Research and Technology (NCRRT), Atomic Energy Authority (AEA), Cairo, Egypt. The beam current was 0.001 A with a maximum power of 5  $\text{W}/\text{mm}^2$ . The electron irradiation doses were 100, 300, 500 kGy.

The induced defects of the irradiated samples have been observed by measuring the photoluminescence spectra. The photoluminescence measurements were carried out with RF-1501 SHIMADZU double monochromator spectrometer at Nuclear Research Center, Atomic Energy Authority, Cairo, Egypt. The excitation wavelength of the photoluminescence emission spectra of pristine and irradiated samples was 350 nm.

To study the nature of the changes induced by the electron beam bombardment and the variation in the optical energy gap,  $E_g$ , the optical absorption spectra of the electron bombarded samples were carried out using TECHCOMP 8500 Double-Beam UV–vis spectrophotometer with wavelength range from 200 to 900 nm at Nuclear Research Center, Atomic Energy Authority, Cairo, Egypt. During measurements, the air has been kept as a reference, and the samples have been held in a metal holder after cleaning with distilled water.

The wettability and surface free energy of the bombarded samples were determined by measuring the contact angle for two liquids, namely water and dimethyl-formamide. The liquid on the surface material takes the shape of semi-sphere and this is due to the surface energy equilibrium. Therefore, the liquid drop volume, height, and contact area can be estimated. For each liquid, three drops were placed on the sample surface using micropipette. The drops are captured using CCD camera attached with computer and the images were obtained for the contact angle measurements. The contact angle can be measured by establishing the tangent (angle) of a liquid drop using the formula [22]:

$$\theta = \arcsin(4bh / (4h^2 + b^2)) \quad (1)$$

where  $h$  is the height and  $b$  is the baseline length.

Surface roughness  $R_a$  of the pristine and bombarded samples was measured using the instrument stylus-profiler type Surtronic + 3. Average roughness values are determined by using three measurements. Wettability and roughness measurements were carried out at Helwan University, Cairo, Egypt.

## 3. Results and discussions

### 3.1. Photoluminescence analysis

The common method to investigate the induced defects in polymer is photoluminescence spectroscopy. In this process, the radiative recombination of the thermalized pairs of electron–hole ( $e-h$ ) takes place due to the excitation by source of energy that transfer the energy to the chromophoric sites [23]. The PL spectra of pristine and irradiated CR-39 and Makrofol samples are shown in Fig. 2a and b, respectively.

PL intensity of irradiated samples of CR-39 and Makrofol decreases (hyper-chromatic effect) with increasing the electron beam doses [24, 25]. This decrease may be due to the increase of energy deposited by the electron beam within the samples and this leads to the increase of the defect concentrations after irradiation [26]. As well, decreasing PL intensity confirms the creation of new radiative recombination levels [27]. Thus, with increasing irradiation doses, the rate of radiative transfer is reduced, and consequently decreasing PL intensity of irradiated samples.

It can be seen that the PL intensity of CR-39 decreases with 87% at the highest dose compared with the pristine sample. While, the PL intensity of Makrofol decreases with 61% at the highest dose compared with the pristine sample. This means that CR-39 is more affected by the electron irradiation dose compared with Makrofol. This is because CR-39 is more sensitive to irradiation than the Makrofol [28]. Moreover, it is notice that the peak wavelength  $\lambda_{\text{peak}}$  were 711 nm, 708 nm 706 nm and 703 nm of pristine, 100, 300 and 500 kGy respectively for CR-39. While in the case of Makrofol, the heights PL intensity at the peak wavelength  $\lambda_{\text{peak}}$  were 718 nm, 717 nm 715 nm and 713 nm of pristine, 100, 300 and 500 kGy. This change may be attributed to the changes in molecular structure.

In addition, the PL spectra were placed in the red region and are shifted towards lower wavelengths with increasing the electron dose. This shift represents the bathochromic effect. Furthermore, the Stokes' shift represents the difference between positions of the band maxima of absorption and fluorescence of the same electronic transition [29] and it is tabulated in Table 1. These changes in Stokes' shift may be attributed to the emission band that associated with the less energetic  $\pi^*-\pi$  and  $\pi^*-n$  electronic transitions. The Stokes' shift can be used to separate strong excitation light from weak emitted luminescence using suitable optics [30].

### 3.2. UV–visible analysis

Polymeric materials absorb light leads to the acquisition of electrons of energy, allowing them to move from ground level to the highest level and these electronic transitions in the UV and visual regions are  $\sigma-\sigma^*$ ,  $\pi-\pi^*$  and  $n-\pi^*$  [31]. Fig. 3a and b shows the UV visible spectra of pristine and electron irradiated PTDs. We can notice that the absorbance edges were shifted towards the higher wavelength for all samples with the increase of the electron irradiation dose. This shift may be due to the creation of unsaturated species formed and/or formation of multiple conjugated bonds during irradiation [32,33].

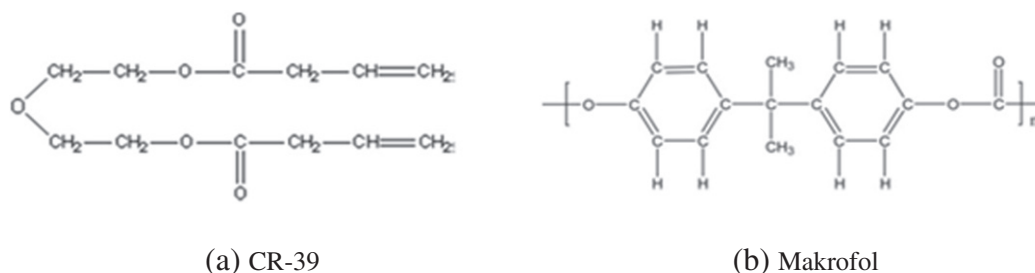


Fig. 1. The chemical structure of (a) CR-39 and (b) Makrofol polymers.

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