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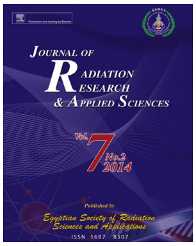

Modified the optical and electrical properties of CR-39 by gamma ray irradiation

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ABSTRACT

The radiation technique is a useful technology technique to induce suitable modifications of the polymeric materials. In the present work, poly allyl diglycol carbonate (CR-39) solid state nuclear track detector samples were irradiated using different doses (150–950 kGy) of gamma ray irradiations. The effect of gamma ray irradiations on the optical and electrical, properties of CR-39 was investigated. The obtained results showed a decrease in the optical energy gap with increasing the gamma dose. Increase in the numbers of carbon atoms (N) in a formed cluster with increasing the irradiation dose was observed. Meanwhile, an increase in the Ac conductivity was obtained with increasing the gamma dose. Also, the variation in the dielectric constant and loss with irradiation dose was studied at the room temperature. The results indicate that the gamma ray irradiations in the dose range 150–950 kGy enhance the optical and electrical properties of the CR-39 polymer samples.

1. Introduction

Poly allyl diglycol carbonate (CR-39) is a class of polymeric solid state nuclear track detector which has many applications in various radiation detections. CR-39 has index of refraction lower than that of crown glass and has also high abrasion. This makes it an advantageous material for eyeglasses and sunglasses (Abdul-Kader, El-Badry, Zaki, Hegazy, & Hashem, 2010). The modification of the polymers is an attractive way to tailor the response of different industrial devices in a wide range of applications. The radiation processing is a useful technology to induce suitable modifications of materials. The interest in radiation treatment of polymers has increased, prompted by the radiations induced modifications of the properties of various polymeric

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materials. The physical and chemical modifications induced in polymers under radiation are triggered by the energy loss by the radiation within the target (Marletta, 1990). In recent years, the optical and electrical properties of polymers have attracted much attention in view of their applications in many optical and electrical devices (Reddy, Zhu, Mai, & Chen, 2006; Radwan, Abdul-Kader, El-Hag Ali, 2008). However polymer at present have many deficiencies, so new methods are required to improve the physical and chemical properties of polymers. Several methods are used to improve the properties of polymers like ion bombardment and electron beam and gamma ray irradiations, UV-light, plasma, … etc. Gamma-ray irradiation of polymers is one method among the physical modification methods, which recently received a lot of attention from the electronic engineering point of view. This is due to their linear energy transfer radiation is lower than that of the ions. Defects induced by irradiation inside the polymeric materials are responsible for changes in the optical (Kumar, Sonkawade, Chakarvarti, Singh, & Dhaliwal, 2012; Siddhartha, Kapil Dev, Raghuvanshi, Krishna, & Wahab, 2012; Rück, 2000; Šiljegović et al., 2011), electrical (Radwan, Abdul-Kader, et al, 2008; Abdel Moez, Aly, & Elshaer, 2012; Qureshi et al., 2009; Radwan, Fawzy, & El-Hag Ali, 2008; Verma, Dhar, Rath, Sarkar, & Dabrowski, 2012), mechanical (Pelagade et al. 2012; Anandha babu, Ramasamy, Vijayan, Kanjilal, Asokan, 2008; Seguchi, Kudoh, Sugimoto, & Hama, 1999) and chemical properties (Abdul-Kader, El-Gendy, & Al-Rashdy, 2012) of the polymer. The breakage of chemical bonds during the irradiation eventually leads to the release of hydrogen atoms as hydrogen molecule (Abdul-Kader, Turos, Grambole, et al., 2005) and the formation of double bonds –C=C– (Mott, 1969). Crosslinking and chain scission also occur. Exposure of the samples during and after the irradiation to the air leads to their oxidation (Abdul-Kader, Turos, Grambole, et al., 2005; Costa, Luda, & Trossarelli, 1997; Costa et al., 1998; Abdul-Kader, Turos, et al., 2005; Premnath, Harris, Jasty, & Merrill, 1996). The hydrogen release and the oxygen uptake cause changes in the physical and chemical properties of the polymeric material (Abdul-Kader, Turos, et al., 2005). The optical absorption method can provide information about the band structure and energy gap in crystalline and non-crystalline materials (Mishra et al., 2000).

The results presented in this work focus on the effect of gamma ray irradiation of CR-39 for use in suitable opto-electronic applications. The principal objective of this work is to improve the optical and electrical properties of CR-39 through gamma ray irradiation induced structural modifications of the polymer surface.

2. Experimental details

2.1. Material

CR-39 polymer is one of the trade names of the family poly allyl diglycol carbonate. The chemical composition of CR-39 is $(C_{12}H_{18}O_7)_n$, where H content is 6.6% wt, C content is 52.6% wt and O content is 40.8% wt. CR-39, sheet used in this study were manufactured by Pershore Mouldings (PM), Ltd, England. It is of thickness 1.5 mm and dimension 20 cm × 20 cm. This sheet was cut into 1cm × 1 cm sized samples.

2.2. Irradiation facility

The CR-39 polymeric samples were placed in polyethylene sachets and the irradiation was carried out with ^{60}Co Gamma source with energies in the order of 1.173 and 1.332 MeV, at a dose rate of 3.5 kGy/h at NCRRT, Atomic Energy Authority, Cairo, Egypt. The samples were irradiated at different absorbed doses ranging from 150 to 950 kGy at the same condition.

2.3. Characterization techniques

2.3.1. Optical measurements

The optical absorption spectra of the pristine and all the irradiated samples were subjected to spectral studies in the Ultraviolet and Visible regions. These studies were carried out by using UV-Visible 8500 Double-Beam Spectrophotometer TECHCOMP in the wavelength range of 190–1100 nm having resolution of 0.1 nm. All the spectra were recorded by mounting the samples in the Integrating Sphere Assembly attached with the Spectrophotometer, keeping air as the reference.

2.3.2. Electrical measurements

The electrical properties of the pristine and gamma irradiated polymer samples were carried out at room temperature by using an LCR Bridge Model Z Hioki-3531, Japan. This bridge is good earthed, and all connected cables are good shielded, and connected to the earth. The two surfaces of each polymer samples were coated with silver paint and checked for good conduction and then kept in between the two cell electrodes for making measurements. The bridge can be used to measure different parameters: resistance, dielectric loss ($D = \tan\delta$) and capacitance in the frequency range of 42 Hz to 5 MHz at room temperature. The AC conductivity was calculated using the relation d/RA ($\Omega^{-1}\ \mathrm{m}^{-1}$) (Singh, Sharma, Shrinet, Rakshit, & Avasthi, 2004). The measured values of capacitance then have been converted into the dielectric constant (ε) by using the formula ($Cd/\varepsilon_o A$) (Singh & Prasher, 2006), where d is the thickness of polymer sample, A is the area of electrode plates and ε_o is the permittivity of free space.

3. Results and discussion

3.1. UV–VIS spectral analysis

Fig. 1 shows the UV-visible spectra recorded for gamma irradiated CR-39 samples at different doses by using the UV-visible spectrophotometer. One notes that with increasing gamma doses, the UV/Vis spectra of the polymers show red shift that indicates a decrease in the band gap (Singh and Prasher, 2004). This shift in absorbance is thought to be caused by the formation of conjugated bonds i.e. possible formation of carbon clusters and/or defects. The visual observation of the irradiated samples indicates change in the colour while the pristine sample is colourless.

3.1.1. *Energy band gap*

The optical band gap of pristine and various irradiated CR-39 samples were determined from the UV–Vis spectra. The optical energy gap E_g, can be obtained by applying the notation given by Tauc equation (Tauc, 1970) as:

$$\alpha(h\upsilon) = B(h\upsilon - E_g)^r / h\upsilon \tag{1}$$

where α is the absorption coefficient and, $h\upsilon$ is the energy of the incident photons, E_g is the value of the optical energy gap between the valence band and the conduction band, and r is an index, which characterizes the electronic transition, whether it is direct or indirect during the absorption process in the K-space. The index r can take the values 1/2, 3/2, 2 and 3 for direct allowed, direct forbidden, indirect allowed and indirect forbidden transitions, respectively. The factor B is constant. The optical absorption coefficient, $\alpha(h\upsilon)$, was calculated from the absorbance, (A) (Fox, 2001):

$$\alpha(h\upsilon) = 2.303A/l \tag{2}$$

where l is the sample thickness in *cm* and A is defined by $A = \log(I_o/I)$ where I_o and I are the intensity of the incident and transmitted beams, respectively. The direct and indirect optical band gap were determined by plot $(\alpha h\upsilon)^2$ and $(\alpha h\upsilon)^{1/2}$ as function of photon energy $h\upsilon$, respectively. Extrapolating the straight parts of these relations to the $h\upsilon$ axis yields the corresponding direct and indirect band gaps. Fig. 2 and Fig. 3 show the relation between $(\alpha h\upsilon)^2$ and $(\alpha h\upsilon)^{1/2}$ for the pristine sample and those irradiated with gamma rays as function of photon energy $h\upsilon$, respectively. The values of direct and indirect band gaps for CR-39 before and after gamma-irradiation have been calculated and are plotted in Fig. 4. The obtained results showed a decrease in both direct and indirect energy gap with increasing the irradiation dose.

The direct band gap in CR-39 decreased from 4.2 eV for pristine sample to 2.75 eV at the highest studied doses of gamma ray irradiation. It was noticed that the indirect band gap in CR-39 reduced from 3.7 eV for pristine sample to 1.73 eV at the highest dose of gamma irradiation. The decrease in band gap after irradiation may be due to the enhanced diffusion rate of π-electrons in the forbidden energy levels of polymer, formation of defects and/or creation of carbonaceous clusters due to partial release of hydrogen molecules. The decrease in the energy gap implies an increase in the electrical conductivity of the irradiated polymers (El-Badry, Zaki, Abdul-Kader, Hegazy, & Morsy, 2009). Upon irradiation, visual changes in the colour of CR-39 samples from milky white, for pristine samples, to yellow are noticed. This change may be due to the formation of carbon clusters. The number of carbon atoms (N) in a carbon cluster is correlated to the optical energy band gap E_g and is given by the following equation (Fink et al., 1995):

$$N = \frac{2\beta\pi}{E_g} \tag{3}$$

Where 2β is the energy of a pair of adjacent π sites and β is taken to be −2.9 eV as it is associated with the $\pi \rightarrow \pi^*$ optical transition in the −C=C− structure (Phukan, Kanjilal, Goswami, & Das, 2003)

Fig.4 shows the change in the number of carbon atoms (N) in carbon clusters as a function of irradiation dose for CR-39 samples. It is clear seen that the number of the carbon atoms in clusters increases with increasing irradiation dose. This is attributed to the breakage of C–H bonds upon irradiation and the escape of hydrogen as hydrogen molecules (Adel, Amir, Kalish, & Feldman, 1989). The carbonaceous clusters are supposed to be rich with charge carriers that enhance the optical properties in radiation bombarded polymers and consequently they also influence the electrical conductivity of such materials (Abdul-Kader, 2009).

3.2. *AC electrical studies*

3.2.1. *The dielectric constant*

Fig. 5 shows the variation of the dielectric constant as a function of gamma dose, within the frequency range from 100 kHz to 3 MHz at room temperature. From the first insight, one can observe the dipole relaxation of all films in the dielectric spectrum. For the pristine sample, as evident from plots, the dielectric constant (ε') remains almost constant over a wide frequency range, followed by a sharp decrease in the relaxation zone. The same behaviour of the dielectric constant, with the frequency, is observed for all irradiated samples. The variation of ε' values with the dose exhibits a direct

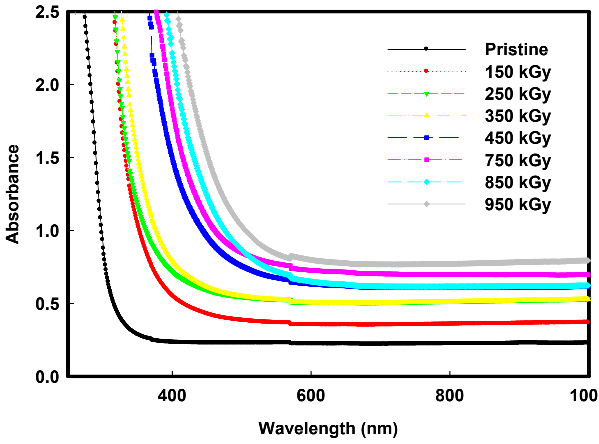

Fig. 1 – UV–visible spectra of the pristine and gamma-irradiated CR-39 polymer.

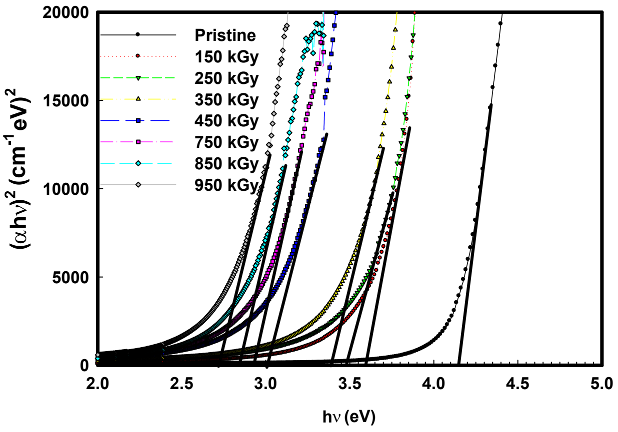

Fig. 2 – The dependence of $(\alpha h\nu)^2$ on photon energy (hν) for pristine and gamma-irradiated CR-39 polymer.

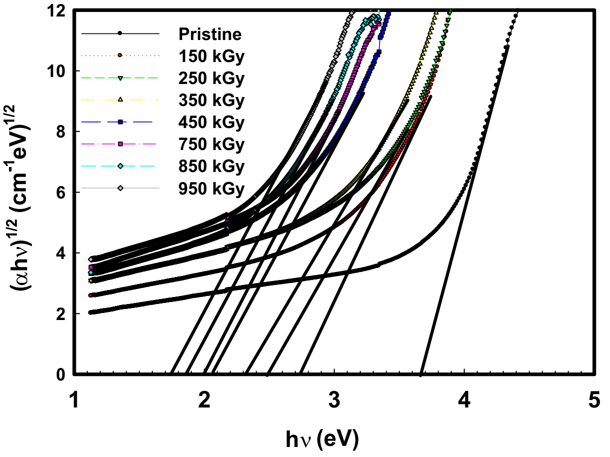

Fig. 3 – The dependence of $(\alpha h\nu)^{1/2}$ on photon energy ($h\nu$) for pristine and gamma irradiated CR-39 polymer.

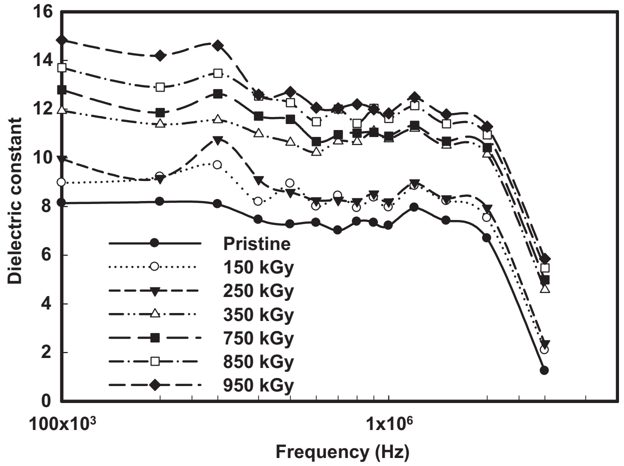

Fig. 5 – Plot of dielectric constant vs. log frequency for pristine and gamma irradiated CR-39 polymer at different doses.

proportional for all doses over the full frequency range. Moreover, a shift in the relaxation towards lower frequencies is shown due to gamma irradiation. Increase in the dielectric constant with the irradiation dose is a characteristic of the conducting polymer (Himanshu et al., 2011). This increase may be attributed to breakage of the chemical bonds that led to formation of –C=C–. The increase in the scissioning of polymer bonds with increasing the irradiation dose leads to increase of the free radical and unsaturation (Singh, Qureshi, Singh, & Avasthi, 2007). The observed decrease in the dielectric constant beyond 1500 kHz (cf. Fig. 5) can be attributed to the fact that the charge carriers migrate get trapped against defect sites, hence induce an opposite charge in its vicinity (Anjum et al., 2009). Generally, these defects may result in the existence of traps of the charge carriers in the band gap of the polymer that can capture the charge carriers (Velitchkova, Krezhov, & Balabanov, 2000; El-Sayed, Abdel-Hamid, & Radwan, 2004). Therefore, the irradiation increases the ability of the polymer to store charge, i.e. the increase of its dielectric constant.

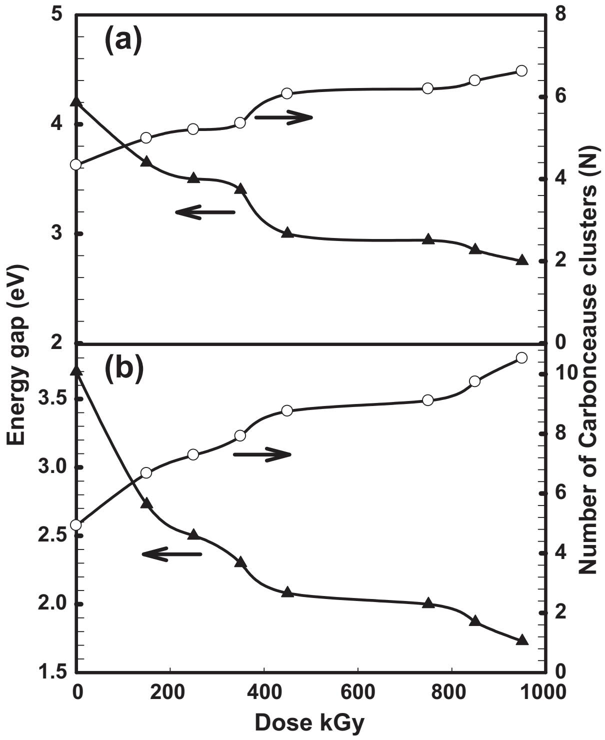

Fig. 4 – Optical energy gap and the number of carbon atoms in cluster of CR-39 as function of gamma irradiation dose (a) direct (b) indirect. The lines are drawn only to guide the eye.

3.2.2. *AC conductivity*

Fig. 6 shows the variation of the AC electrical conductivity with frequency for CR-39 polymer samples as function of gamma irradiation doses. A sharp increase in conductivity was observed at about 100 kHz for CR-39 and the electrical conductivity increases with increasing gamma irradiation dose. Upon irradiation, the increase in the conductivity may

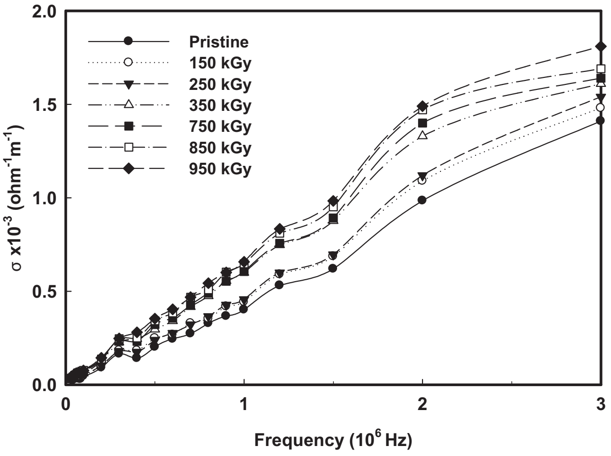

Fig. 6 – AC conductivity vs frequency for pristine and gamma irradiated CR-39 polymer at different doses.

be attributed to scissioning of polymer chains, as mentioned before, resulting in an increase of free radicals, unsaturation, etc. (Singh, Shah, Singh, & Desai, 2005), besides formation of conjugated double bonds (Hussain, Saikia, Singh, Avasthi, & Kumar, 2005). With increasing the irradiation dose the energy deposited in polymer material increases and therefore the number of the conjugated double bonds increases. Increase the conjugated double bonds increase the delocalization of charge carriers, and hence their motion in an applied external electric field. This net polarization produces higher AC conductivity at higher frequency (Jonscher, 1977). The increase in the conductivity with increase the irradiation dose is consistent with UV–Vis measurements. Meanwhile, in the case of operation in high frequency range, a net polarization occurs, which is out of phase with the field. This results in the values of ac conductivity being greater than that at which the traps are filled or emptied (Singh et al., 2005). The slight rise in the electrical conductivity with the frequency, in the high frequency range, is related to the accumulation of charge carriers (Khiar et al., 2006). This may be attributed to the difference in the mobility of the electrons and holes in high frequencies.

4. Conclusion

In this work, the influences of gamma irradiation dose on the optical and electrical properties of CR-39 have been investigated. The gamma irradiation, up to 950 kGy, decreases both direct and indirect energy gap. The direct and indirect energy gap decreases from 4.2 to 3.7 eV for pristine sample, to about 2.75 and 1.73 eV at the highest dose (950 kGy) for samples irradiated with gamma ray, respectively. This modification is attributed to the formation of carbon clusters in the polymer due to the irradiation by gamma rays. The number of carbon atoms in carbon clusters was found to increase with increasing the irradiation dose. The electrical characterization of gamma irradiated CR-39 polymeric material has been investigated. A sharp increase in conductivity has been observed around 100 kHz frequency and conductivity increases as dose increases. The increase in conductivity with increase the irradiation dose is consistent with UV–Vis measurements. The dielectric constant is observed to change significantly with the gamma dose. This might be attributed to breakage of chemical bonds and conversion of the polymeric structure into a hydrogen depleted carbon network due to the escape of hydrogen as hydrogen molecules, which results in the increase of free radicals. Thus irradiation makes the polymer more conductive. Our results also show that the irradiation has changed the dielectric constant without affecting the dielectric loss in the CR-39 polymeric material.

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