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RESEARCH ARTICLE

Investigation of the physical properties of polymeric materials induced by alpha radiation

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Abstract

CR-39 is an ideal solid-state detector of nuclear radiation, which is frequently used to learn more about cosmic rays, long-standing radioactive elements, radon concentration in houses, and the age of geological samples. The effects of α-particles on the physical properties (optical properties, electrical properties and the structure) of CR-39 polymer were investigated. The irradiations were performed by using ^{241}Am at constant alpha particle energy 4.86 MeV at normal incident for different irradiation times (6-96) hours. A variation in the optical energy band gap (E_g) values was appeared. This variation suggested formation of defects (radicals and organic species). Moreover, X- ray diffractions were performed on irradiated and non –irradiated CR-39 samples to study the structure of samples. Positron Annihilation Doppler- Broadening technique was used to study the effect of irradiation α-particles emitted from ^{241}Am (4.86Mev) source on the line shape S- and w- parameters for CR-39 samples. The results showed formation of defects in CR-39 samples after irradiations, and good correlation between S and W parameters with R=0.99 for the sample at irradiation times (6, 24 and72 hrs). In addition a correlation is exists with R=0.72 between the E_g and S-parameter .Extended system of conjugated bonds due to irradiation was noticed. The obtained results were discussed and compared with other literature data; it showed an agreement with these results to some extent.

Introduction

The ionizing radiation cause electronic ionization in the material which leads to break molecular bonds and formation of free radicals. The free radicals associate with scission and cross linking for the molecular chains. This, turn on, change the optical and electrical properties of polymer .The optical and electrical properties of polymers have much attention due to their applications in optical and electrical devices. The optical properties of CR-39 irradiated with different doses of gamma rays and different ions fluencies were studied previous by different authors **[Abdelrazek et al, 2010and Ramola et al, 2009].** They found that the optical energy band gap was reduced with increasing gamma-absorbed dose or ions fluencies, also the cluster size increases with increase of electronic stopping power and the reduction in the optical energy band gaps **[Mujahid et al, 2005].** The overlapping tracks formed by irradiation with low light particles are known to produce cluster **[Negi et al, 2011].** These clusters supposed to be carriers of electrical conductivity in ion irradiated polymers and influence the optical properties **[Fink et al, 1988]** Cluster size is inversely proportional to the optical energy band gap **[Fink et al, 1995]**.

The relation between the band gap (E_g) and the number of carbon atoms per cluster (N) can be determined according to the following formula **[Rajesh et al, 2008]:**

$$E_g=34.3/\sqrt{N}\ eV \qquad (1)$$

Electrical properties are studied by calculating the dielectric constant and dielectric loss by using the following relations **[Eissa et al, 2007]**,

$$\varepsilon'=Cd/\varepsilon_o A \qquad (2)$$

$$\varepsilon''=\varepsilon' \tan\delta \qquad (3)$$

where ω is the angular frequency (ω =2πF) F is the frequency, ε_o is the permittivity of vacuum, A is the area of the sample and d is the sample thickness. The angle δ is the phase difference between the applied electric field and the induced current.

Positron annihilation spectroscopies are used to study voids and defects in solids **[Jean et al, 2003]**, there are several techniques of positron annihilation such as Positron Annihilation lifetime Spectroscopy (PALTS), Positron Annihilation Doppler Broadening Spectroscopy (PADBS) and Positron annihilation Age-Momentum Correlation Spectroscopy (AMOC). Doppler- Broadening spectroscopy is used to measure open volume defect concentration in polymers, two parameters (S&W) have been often used to characterize the annihilation peak in Doppler Broadening spectroscopy. The S-parameter is the fraction of annihilation with low momentum valence and unbound electrons and is defined as the ratio of the integration over the central part of the annihilation line to the total area of the line. The W-parameter is the fraction of annihilation with high momentum core electrons and it is defined as the ratio of counts in the wing regions of the peak to the total counts in the peak. Doppler- Broadening allows us to measure the energy of the gamma rays using a high-purity Germanium detector (HPGe). The two gammas emitted from Positron annihilation should have energy of 511 keV.

The present work aims to study the effect of irradiation time on optical properties, dielectrical properties and Doppler- Broadening of CR-39 polymer irradiated with alpha particles at constant energy (4.86±0.22 MeV) ,but different irradiation times .

2. Experimental methodology

2.1. Irradiation of CR-39 by alpha particle

CR-39samples (1.00×1.00 cm^2 ×1.50 mm) detectors were normally irradiated by alpha particles emitted from a ^{241}Am source in air through a holder collimator shown in figure 1.The energy of α-particles emerging from the collimator was determined by using a surface-barrier semiconductor detector and a calibrated multichannel analyzer **[Eissa, 2011].**The heights of the collimator would reduce energy of 5.486 MeV α-particles from ^{241}Am-source to 4.86±0.22 MeV. The incident flux (φ) **[Enge, 1980]** was calculated using the following equation:

$$\varphi=A/4\pi r^2 \qquad (4)$$

Where A is the activity of the ^{241}Am- source in Bq and r is the source-detector distance in centimeter. The total number of α- particles (Φ) emitted from the collimator and incident on CR-39 per unit area in a certain irradiation time (t) is given by:

$$\Phi=\phi t \qquad (5)$$

The optical properties of the CR-39 samples before and after irradiations were investigated using double beam UV-Vis spectrophotometer "**Shimadzu UV 3101 PC**" in the wavelength range of 200-900 nm. The resultant data obtained were used to calculate the energy band gap (E_g).

Dielectric properties of the samples were measured using "**INSTEK LCR-METER LCR-819**" at frequency range from 60 Hz - 10^5 Hz at room temperature. The capacitance (C) and displacement (D= tanδ) were measured as a function of frequency. Dielectric constant (ε') and dielectric loss (ε'') can be calculated using relations (2-3).

The structural studies were carried out using "**X-Ray Diffraction –Panalytical X, pert, PRO, Holland**" Cu (k_α λ=1.54 Å) for a range of Bragg's angle 2θ (4≤θ≤80).

Positron Annihilation Doppler- Broadening technique was used to study the effect of irradiation α-particles emitted from ^{241}Am (4.86Mev) source on the line shape S and w parameters for CR-39 samples. In this technique, two parameters (S&W) have been used to characterize the annihilation peak due to the damage induced by α-particles radiation of CR-39.The positron source of 1mCi free carrier $^{22}NaCl$ is evaporated from an aqueous solution of sodium chloride and deposited on a thin kapton foil of 7.5 µm in thickness. The source has to be very thin so that only small fractions of the positron annihilate in the source. A sandwich configuration has been used to guide the positron into the CR-39 samples. The detail of the system, used in the present work is similar to that used in **figure 2**. All samples spectra are collected for 30 min.

3. Results and discussions

3.1 Energy band gap and cluster size variation with irradiation time.

Energy band gap is calculated using the data by UV- Vis spectrophotometer for virgin and irradiated CR-39 samples. These data were calculated using Tauc's plot **[Tauc J, 1968],** for the absorption spectra to calculate the band gap (E_g) of the CR-39 samples in direct allowed transition **[Eissa, 2014].** The values of energy gap (E_g) and cluster size for different irradiation times are reported in **table 1**. The maximum value for cluster size was found at 72 hrs whereas the minimum value for the band gap, this data is in agreement with previous studies **[Zhao et al, 1999]**. The variations in the E_g values suggested the formation of defects (radicals and organic species) after alpha particles irradiations and/or the presence of carbon enriched clusters. It is observed that, the optical energy gap and the corresponding cluster size has maximum impact at irradiation times from about 20-45 hrs. A shift in the absorption edge towards the higher wavelength indicates the decrease in band gap energy of the polymer samples. One of the possibilities behind this behavior is interpreted as the formation of extended system of conjugated bonds or in other words the formation of carbon cluster **[Kumar et al, 2009].**

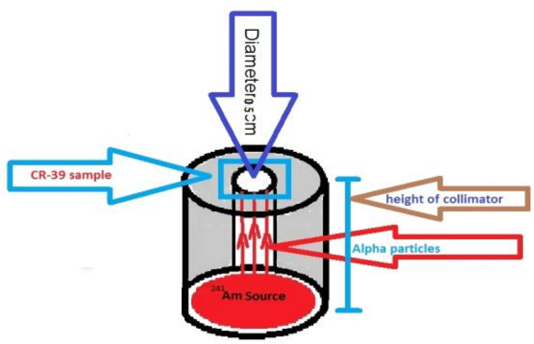


Figure 1: Sketch of irradiation of CR-39 by α- particles (^{241}Am) using collimator.

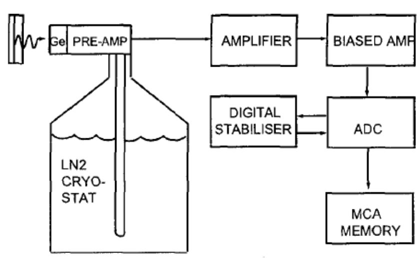


Figure 2: Doppler- Broadening spectrometer.

3.2. Dielectric constant

The relation between the frequency (0.1-100 kHz) and dielectric constant for CR-39 samples before and after irradiations is showed in **figure 3.** Dielectric constant for whole samples decreases sharply in the low frequency and has constant value in the high frequency. The dipoles have sufficient time to align with the applied field so the dielectric constant has higher values. At high frequency, the dipole does not have time to align before the field change direction so the dielectric constant has constant value. Therefore, the dielectric constant is insensitive to the fluence variations in this frequency region.

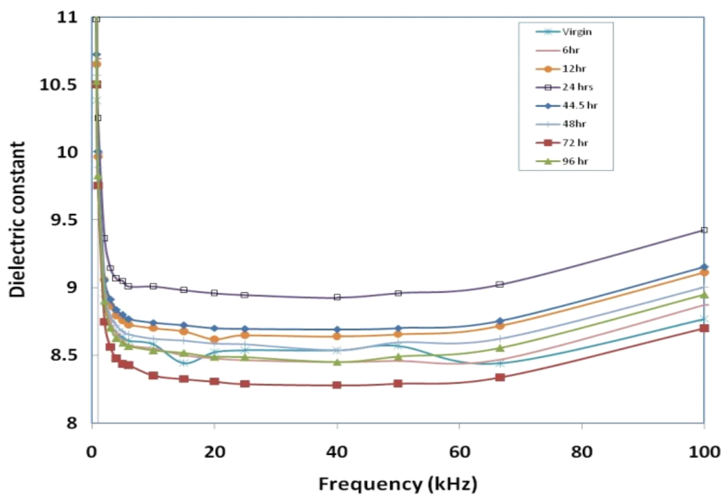
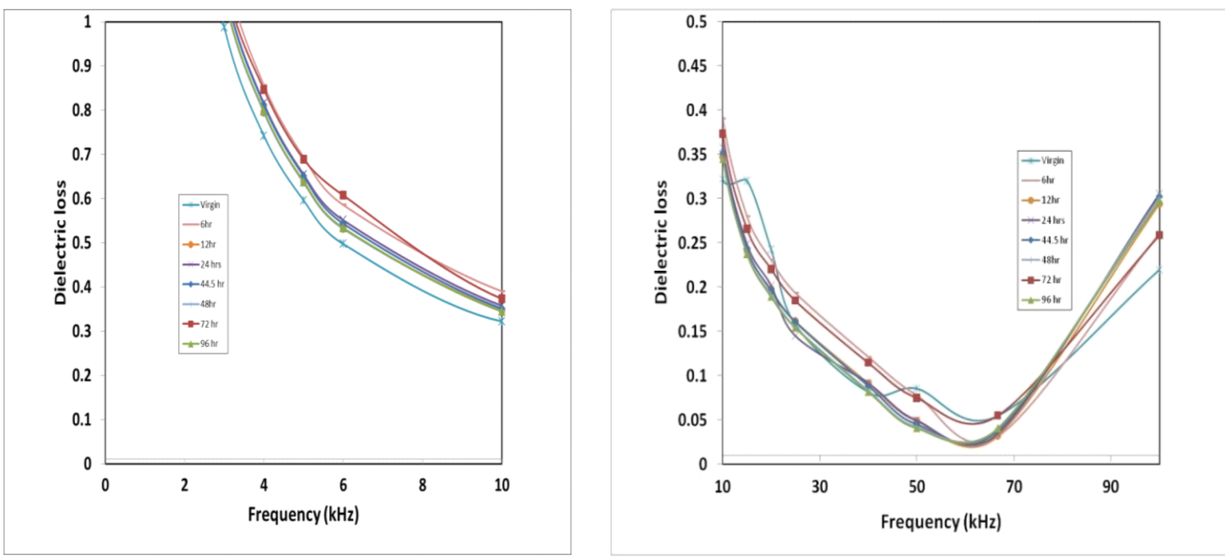


Figure 3: The variations of the dielectric constant with frequency for different irradiation times of alpha particle energy 4.86 MeV.

The dependence of dielectric loss on the frequency for virgin and irradiated CR-39 samples is shown in **figure 4**. The results showed that the dielectric loss decreases with increasing frequency up to 50 kHz and then slightly increases. The loss factor has positive values so the inductive behavior dominated.



(a) (b)

Figure 4: The variations of the dielectric loss with frequency {a. (0-10) KHz and b. (10-100) KHz} for different irradiation times of alpha particle energy 4.86 MeV.

3.3. X-ray diffraction

(XRD) patterns of the virgin and irradiated CR-39 are shown in **figure 5**. It has been observed that polymers contain both crystalline as well as amorphous regions. Crystalline polymer has two components, the crystalline portion and the amorphous portion. It is found that the presence of an amorphous region leads to the appearance of characteristic halo in diffraction pattern **[Nouh et al 2005 and Kumar et al, 2012].**The change in intensity of XRD spectra due to irradiatios may be due to the destruction of original structure of CR-39 **[Ramola et al, 2009].**

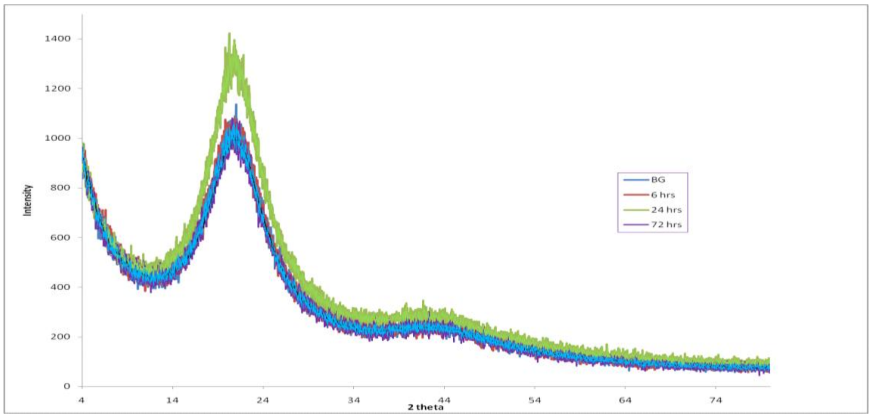


Figure 5. X-Ray diffraction of virgin and irradiated CR-39 at different times.

The prominent peak at 2θ ~21.5 as in **figure 5** is the characteristics peak of CR-39. The intensity of the irradiated CR-39 sample at 24hrs irradiation time is the largest value. The virgin sample shows a semi-crystalline (i.e., a mixture of small crystalline and amorphous states within the material) with dominating amorphous content on it **[Singh and Prasher, 2006].** The degree of crystallinity was calculated by separating intensities due to amorphous and crystalline phase on diffraction pattern. Percentage of crystallinity (X_c %) is measured as the ratio of crystalline area to total area **[Ramola et al, 2009].**

$$X_c(\%) = \left\{\frac{A_c}{A_{a+A_c}}\right\} x100\% \qquad (6)$$

Where A_c = area of crystalline phase and A_a = area of amorphous phase. The degree of crystallinity of (0, 6, 24 and 72) hours is (71.28%, 70.99%, 72.88% and 71.03%), respectively. An appreciable change in the diffraction pattern of CR-39 after irradiation up to the fluence level of 1.04x10^8 /cm^2 is observed, showing its structural stability

Table 1. Variations of the irradiation time with the present physical behaviors for vertical alpha irradiations at 4.86 MeV.

Alpha particle irradiation time (hrs)	Total normal fluence /cm^2(Φ=φt)	Optical energy gap E_g(eV)	Cluster size	peak area of X-ray	S- parameter	W- parameter
0	0	3.96	75	0.98	0.42681±0.0011	0.2465±0.000545
6	6.5x 10^6	3.933	76	88.36	0.43044±0.0011	0.2522±0.000539
12	1.3x 10^7	3.96	75			
24	2.6x 10^7	4.002	73	196.69	0.43575±0.0011	0.1889±0.000461
44.5		4.005	73			

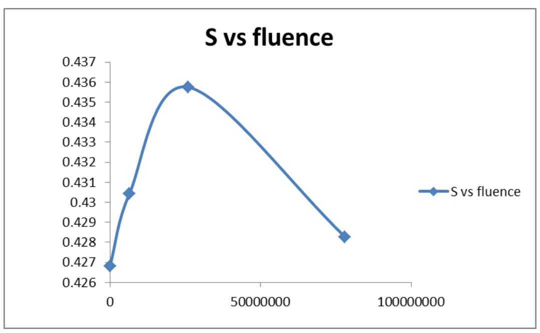
48	5.2x 10^7	3.96	75			
72	7.8x 10^7	3.934	76	543.75	0.42828±0.0011	0.2792±0.000567
96	1.04 x10^8	3.986	74			

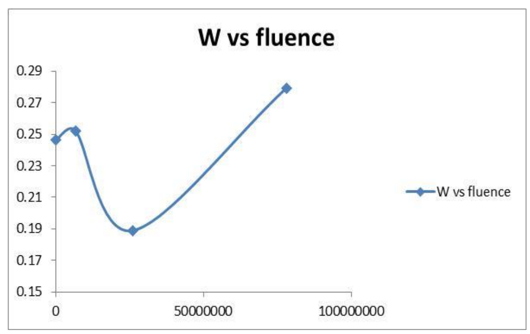
3.4. Positron annihilation technique {Doppler- Broadening spectroscopy (PADB)}.

When the positron is trapped in an open-volume defect, the annihilation parameters are changed in a characteristic way. The positron lifetime increases in an open-volume defect due to the lower electron density. Momentum conservation during gamma-annihilation leads to a small angular spread of the Doppler shift of the annihilation energy. Both properties, the density and the momentum distribution of electrons participating in the annihilation, result in observables to be detected in a positron experiment. The analysis of the annihilation radiation thus gives the possibility of defect detection. Clustering of vacancies as a typical defect reaction may be observed as the increase in the defect-related lifetime due to the further decrease in the electron density.

Two parameters S (for shape), and W (for wings) are usually used to characterize the 511 keV annihilation peak of Doppler- Broadening. The S parameter represents annihilation with low momentum valence or unbound electrons and the W parameter with high momentum core electrons. Figure.6 shows Doppler- Broadening line shape from which the S and W parameters are calculated. The measurements of S- and W- parameters were estimated using **SP ver. 1.0 program [**http://www.ifj.edu.pl/~mdryzek**]**; this program was designed to automatically analyze the 511 keV line of the positron annihilation shown in **figure 7**. The channel numbers (input data) for this program are fixed for all measurements. These numbers are chosen until the values of S- and W- parameters must not exceed 0.50 and 0.30 respectively.

The calculated values of S- and W- parameters at different irradiation times are shown in **table 1 and figure 6**.





a. S-parameter vs fluence **b. W-parameter vs fluence**

Figure 6: (**a**) Variation of S-parameter with alpha particle fluence, (**b**) variation of W-parameter with alpha particle fluence.

It is obvious that S-parameter increases with irradiation time until maximum value at 24 hrs irradiation time. The S-parameter at irradiation time of 72 hrs has small value. The values of W-parameter show different behavior with the irradiation times. An abrupt change definitely is observed at fluence =2.6x10^7 /cm^2 for both S- and W- parameters. At this value of fluence a rapid decrease in the S- parameter comparable with a rapid increase in W parameter occurred. An increase and decrease in the values of S- and W-parameters, respectively is due to the Positron trapping in vacancies, since annihilation with low momentum valence electrons increased at vacancies.

In addition there are a good correlation between S-parameter and W-parameter with r =0.99 for the samples at irradiation times (6, 24 and 72 hrs). This means that a one type defect was existed in these samples.

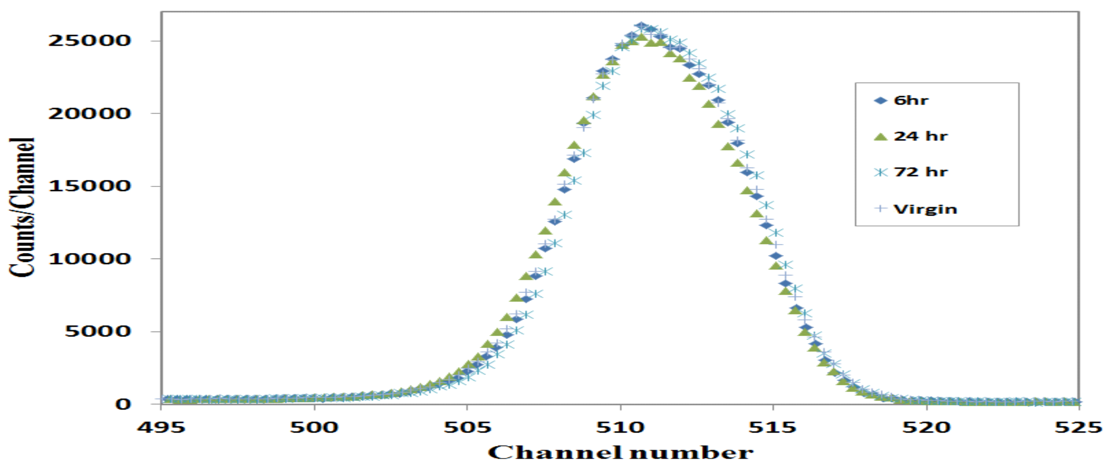


Figure 7: Doppler- Broadening spectra for different irradiation times.

Figure7 shows the variation of S- and W- parameters of Doppler-Broadening for normal position irradiation.
Since the Eg values of irradiated samples at 12 and 24 hrs is greater than that at irradiation time 72 hrs, so, the cross linking is dominant in the two irradiated samples. The cross linking in the polymeric chain causes reduction in the free volume, while its increase in case of chain scission **[Mandal et al, 2013a, Mandal et al, 2013b and Wang et al , 2005].** Consequently, the positrons in small free volume (12 and 24 hrs) have higher probability of interaction with valence electron than the large free volume (72 hrs). Therefore, the value of S- parameter increases with decreasing free volume. This concurrently the existence of the correlation (R=0.72) between the E_g and S-parameter as shown in **figure 8** and **table 1**.

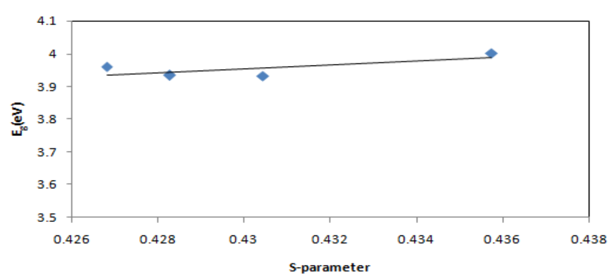


Figure 8: Correlation between energy band gap and S- parameter.

4. Conclusion

In the present paper the effect of alpha particles irradiations on the optical, electrical and structural properties of CR-39 SSNTD has been investigated. The UV–visible spectroscopic showed that there is a chain scission in the polymer backbone at low fluence. The chain scission increased at high fluence. A shift in the absorption edge towards the higher wavelength indicates the decrease in band gap energy of the polymer samples. The variations in the E_g suggested formation of defects (radicals and organic species).The maximum value for cluster size was found at 72 hrs whereas the minimum value for the band gap. There is positive correlation between the E_g and S-parameter. Accordingly, the annihilation of the low momentum valence electron depends on the defect formation.

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