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ABSTRACT

The effects of He-Ne laser on the optical characteristics of Cellulose nitrate, CN-85, and Poly allyl diglycole carbonate, CR-39, nuclear track detectors have been studied by using photoluminescence (PL) and UV-visible spectroscopic techniques. The polymers irradiated with alpha particles with close contact to²⁴¹Am and then exposed to He-Ne laser with different doses. The laser energy intensities ranged between 0 and 217 J/cm². The change in the PL spectra may be explained by chain conformational disorders as well as chain scission. From the UV-visible spectra, it is found that a shift in the absorption edge towards a longer wavelength with increasing laser doses can be readily observed. The absorption peak with increasing dose is seen to change into a broad one. The optical band gaps determined from the UV-visible spectra were found to decrease with the increase of energy intensities of He-Ne laser. These results have been explained on the basis of scission of the polymers due to laser irradiation. The UV absorption tail formation in both polymers was related to the diminution of optical band gap. Results show good correlation with the applied doses.

Key Words: CN-85/ CR-39/ Photoluminescence spectra/ UV–Vis absorption.

INTRODUCTION

Polymeric materials find several applications in different fields from everyday life to high technology engineering, especially Solid State Nuclear Track Detectors (SSNTDs) which are used in different applications and many articles are studied to understand and modify these polymers¹⁷. Since radiation is one of the major factors that change the structural properties of polymers, in particular solid state nuclear track detectors (SSNTDs), it would be worthwhile to study the modifications on their properties due to irradiation. The lower LET radiations (X-ray, electrons, gamma and laser) produce the bulk changes in the form of many broken molecular chains, leading to the change in bulk etch rate and optical response. These changed also find widespread applications in different scientific and technological fields⁹. It is well documented that Low Linear Energy Transfer (LLET) radiation has significant effect on the properties of track detectors. The modification in registration characteristics of track detectors is caused by radiation as a result of structure changes. The irradiation in track detectors yields (i) cross-linking which increases the molecular weight and decreases the etch rates, (ii) chain scission which decreases the molecular weight and subsequently increases the etch rates, in addition to emission of atoms and molecules (CO, CO₂ and H₂) which is resulting from cut in the long chain. During simultaneous chain scission and cross-linking reactions, if the probability of cross-linking reaction is larger than the other one, the polymer would become hardened, otherwise the polymer softening occurs. The laser effect on the SSNTDs depends on laser properties (laser wavelength, laser repetition rate and energy density) and on the detector properties density, thickness, etc.⁹. In general, infrared (IR) laser interaction with SSNTDs can induce thermal effects¹⁰, while
ultraviolet (UV) laser will give rise to photo-ablation or photodecomposition\(^{(11)}\). Recently, some studies\(^{(12-14)}\) on the effects of gamma irradiation on the track registration and optical characteristics of some nuclear track detectors such as CR-39, Makrofol and polyester have been reported. A recent review article in 2004\(^{(15)}\) has also summarized the influence of radiations on various SSNTDs. Investigations include those on the effects of irradiation to gamma rays, electrons, protons, ultraviolet and infrared radiations. The common finding in all these studies is increase in bulk etch rate with the increase in dose of radiation. Moreover, no work on He-Ne laser irradiation effects on photoluminescence and UV-visible spectroscopic for the polymers under investigation.

In the present work, we have, therefore, studied the effects of He-Ne laser irradiation in the dose range of 0 to 217 J/cm\(^2\) by measuring the optical properties of two detectors, CR-39 and CN-85, using UV-visible and photoluminescence spectroscopic techniques. The modification in the absorption and optical band gap of irradiated and pristine samples was studied by UV-Vis spectroscopy. This study is not only obtaining information concerning the interaction and effects of He-Ne laser with CR-39 and CN-85, but also to study the feasibility of enhancing their properties, improving its performance in different fields.

**EXPERIMENTAL STUDY**

1. **Samples**:

   The first type of polymer is CN-85 samples, used in this study were cut from 100 µm thickness sheets manufactured by Eastman Kodak Company, Rochester, New York, with density is 1.42 gm/cm\(^3\) and the chemical formula is C\(_6\)H\(_8\)O\(_9\)N\(_2\). The second type is CR-39 detector (1 cm×1 cm) of thickness 1 mm and density 1.32 gm/cm\(^3\) and the chemical formula is C\(_{12}\)H\(_{18}\)O\(_7\) manufactured by TASTRAK type (Track Analysis System Ltd., UK).

2. **Irradiation facilities**:

   The samples for the two types was exposed to alpha radiation using \(^{241}\)Am source at normal incidence and then exposed to He-Ne laser source by different energy densities varying from 0 to 217 J/cm\(^2\). All the samples were etched in 5N NaOH solution at 60 °C for 4 h.

3. **Photoluminescence (PL) Spectroscopy**:

   Photoluminescence spectra were recorded with spectrofluorophotometer (RF-1501 SHIMADZU, Ltd.) The measurement setup of the photoluminescence consists of two monochromators, the excitation monochromator selects the excitation a single wavelength that emitted from light of high-pressure xenon lamp while the emission monochromator allows a fixed emission wavelength to strick a photomultiplier detector. All spectra were measured in reflection geometry and a special attention was taken to avoid stray light. This measuring setup made it possible to excite and detect luminescence in a 200–900 nm wavelength region. In order to choose suitable excitation wavelength that gives the maximum response of the sample, we scanned the sample in successive steps in which the emission monochromator is adjusted to detect different wavelength in each step. The 346 nm exciting wavelength of a xenon lamp was used as a result of excitation scan for the samples. To prevent the spectrometer detector to reach its saturation value, the opening slit of the excitation was covered by a dark paper with a small pinhole of diameter 2 mm. All measurements were performed at room temperature.
4. **UV-VIS spectrometry** :

The UV–Vis spectra of the different laser doses irradiated CN-85 and CR-39 polymers have been recorded using double beam monochromator UV–Vis spectrophotometer (UV-8500), TECHCOMP, in the wavelength range of 190–1100 nm. All the spectra were taken with the pristine one as reference.

**RESULTS AND DISCUSSION**

1. **Photoluminescence Analysis** :

The photoluminescence features of CR-39 and CN-85 polymers are scarcely studied. The PL spectra obtained for He-Ne laser irradiation CR-39 and CN-85 polymers under excitation wavelength of 346 nm are shown in Figs. 1, and 2, respectively. PL spectra for both polymers showed a decrease in the broadband intensity as the laser dose increase and in the case of CN-85 the decrease is more prominent than CR-39. This behavior may be attributed to laser irradiation induced defects and clusters in the both polymers which serves as non-radiative centers\(^{(16)}\). The emission bands in the investigated range of wavelength are associated to the less energetic \(\pi^*–\pi\) and \(\pi^*–\pi^*\) electronic transitions\(^{(17)}\). This type of transition occurs in the unsaturated centers of the molecules, i.e. in compounds containing multiple (double or triple) bonds or aromatic species, which seems to be more likely process responsible for the decrease in the PL intensity.

![Fig. (1) PL spectra of CR-39 irradiated with different doses of He-Ne laser.](image-url)
Fig. (2) PL spectra of CN-85 irradiated with different doses of He-Ne laser.

Fig. (3). Linear correlation between the laser irradiation dose and the PL peak for CR-39.
Fig. (4). Linear correlation between the laser irradiation dose and the PL peak for CN-85.

Fig. 3 and 4 show the dosimetric relation between the PL peak and laser doses for CR-39 and CN-85 polymer track detectors, respectively. This relation represents a linear fit to the experimental data. Therefore, these graphs serve as the standard calibration to determine the laser dose provided that the PL peak is determined for samples.

2. UV–vis spectral analysis:

Figs. 5 and 6 show the UV–vis spectra of pristine and irradiated CR-39 and CN-85 polymers with different doses of He-Ne laser, respectively. From these optical spectra, it is clear that the pristine sample has a sharp decrease in absorption with increasing wavelength up to certain value, followed by a plateau region in its UV–vis spectrum. The optical spectra of all samples show shifting in the absorption edge towards longer wavelength with increasing laser doses. This behavior is generally interpreted as caused by the formation of extended systems of conjugate bonds, i.e., possible formation of carbon clusters and/or defects. The absorption bands in the investigated range of wavelength are associated to the $\pi$–$\pi^*$ electronic transitions (18-21). This type of transitions occurs in the unsaturated centers of the molecules, i.e., in compounds containing double or triple bonds and also in aromatics. The excitation of $\pi$ electron requires smaller energy and hence, transition of this type occurs at longer wavelengths.

3. Energy band gap:

The optical absorption method can provide information about the band structure and energy gap in crystalline and non-crystalline materials (22). The optical gap $E_g$, could be obtained by applying the notation given by Tauc’s equation (23) as:

$$\alpha(h\nu) = \beta(h\nu - E_g)^n / h\nu$$

(1)
where $\alpha$ is the absorption coefficient, $h\nu$ 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 $n$ is the power, which characterizes the electronic transition, whether it is direct or indirect during the absorption process in the $K$-space. Specially, $n$ is 1/2, 3/2, 2 and 3 for direct allowed, direct forbidden, indirect allowed and indirect forbidden transitions, respectively. The factor $\beta$ depends on the transition probability and can be assumed to be constant within the optical frequency range. The usual method for the determination of the value of $E_g$ involves plotting $(\alpha h\nu)^{1/n}$ against $(h\nu)$. In the present study the most satisfactory fit is obtained by plotting $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^2$ as a function of photon energy $(h\nu)$, taking into account the linear portion of the fundamental absorption edge of the UV–visible spectra. The method to draw such plots is presented in previous work(1).

The indirect and direct band gaps have been determined for pristine and irradiated CR-39 and CN-85 samples. The values of $E_g$ for different laser doses are presented in table 1. One notes that the value of $E_g$ decreases with increasing laser doses for CR-39 and CN-85 irradiated with He-Ne laser beam. This result confirms that the irradiation with He-Ne laser produces defects in the polymers structure (band rupture, free radical, etc.), which increases the electronic disorder inducing the creation of a permitted state in the forbidden band gap or the deformation of the valence band. Furthermore, the values of energy gaps in the case of indirect transitions are lower than the energy gaps of direct transition, due to the presence of delocalized states between valence band and conduction band(24).

![Graph](image_url)

**Fig. (5)** UV–visible spectra of CR-39 irradiated with different doses of He-Ne laser.
4. Urbach’s energy:

The absorption coefficient $\alpha(hv)$ near the band edge for non-crystalline materials shows an exponential dependence on the photon energy $(hv)$ which follows the Urbach’s formula(25):

$$\alpha(hv) = \alpha_o \exp(hv/E_u)$$  \hspace{1cm} (2)

where $\alpha_o$ is a constant, $E_u$ is an energy that represents the width of the tail of localized states in the forbidden band gap and it is equal an inverse logarithmic slope of the absorption coefficient, $v$ is the frequency of radiation and $h$ is Planck’s constant. The origin of $E_u$ is considered as thermal vibrations in the lattice(26). Figs. 7 and 8 show the logarithm of the absorption coefficient $\alpha(v)$ as a function of the photon energy $(hv)$ for CR-39 and CN-85 irradiated with different doses of He-Ne laser. The values of the Urbach’s energy ($E_u$) were calculated by taking the reciprocal of the slopes of the linear portion in the lower photon energy region of these curves and listed in Table 1. The decrease in the Urbach’s energy may be due to the decrease in the crystalline nature of the polymers(1).

The number of carbon atoms per conjugated length $N$ for a linear structure is given by Robertson relation(25):

$$E_g = \frac{2\beta}{\sqrt{N}eV}$$  \hspace{1cm} (3)

where $N$ is the number of carbon atoms per conjugated length, $2\beta$ gives the band structure energy of a pair of adjacent $\pi$ sites. The value of $\beta$ is taken to be $\sim 2.9$ eV as it is associated with $\pi-\pi^*$ optical transition in the $\text{C}=\text{C}$ structure. The value of carbon atoms $(N)$ per conjugated length are given in Table 1 for CR-39 and CN-85, respectively. From the Robertson's relation cluster size can be calculated and then the following relation can be used to calculate the number of carbon atoms per cluster:

$$E_g = \frac{34.3}{\sqrt{N}eV}$$  \hspace{1cm} (4)
Table 1. The variation of band gap energy \( (E_g) \), the number of carbon atoms \( (N) \) and Urbach’s energy \( (E_u) \) for pristine and CR-39 and CN-85 irradiated with He-Ne laser.

<table>
<thead>
<tr>
<th>Laser doses ((J/cm^2))</th>
<th>CR-39</th>
<th>CN-85</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>indirect ( E_g ) (eV)</td>
<td>( N )</td>
</tr>
<tr>
<td>Pristine</td>
<td>3.83</td>
<td>80</td>
</tr>
<tr>
<td>36</td>
<td>3.70</td>
<td>86</td>
</tr>
<tr>
<td>72</td>
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<tr>
<td>109</td>
<td>3.50</td>
<td>96</td>
</tr>
<tr>
<td>145</td>
<td>3.43</td>
<td>100</td>
</tr>
<tr>
<td>181</td>
<td>3.32</td>
<td>107</td>
</tr>
<tr>
<td>217</td>
<td>3.22</td>
<td>113</td>
</tr>
</tbody>
</table>

Fig. (7) The linear part of the curve between \( \ln (\alpha) \) and \( h\nu \) (eV) for pristine and irradiated CR-39 polymer at different doses of He-Ne laser.
Fig. (8) The linear part of the curve between $L_n$ (§) and $h\nu$ (eV) for pristine and irradiated CN-85 polymer at different doses of He-Ne laser.

CONCLUSIONS

The effect of He-Ne laser irradiation on the optical properties of the two types of polymers CR-39 and CN-85 was investigated. It is found that, the PL spectra show that the intensity of PL decreased with increase in doses of He-Ne laser, which may be due to the disordered system via creation of defects in the irradiated polymers. From this experimental study of pristine and He-Ne laser irradiated CR-39 and CN-85, the values of the optical band gap ($E_g$) are affected with He-Ne laser doses as determined from the linear portion of optical spectra, while the number of carbon atoms (N) per conjugated length increases with the increase in He-Ne laser doses. Whereas the Urbach's energy ($E_u$) decreases significantly, this may be due to the amorphisation of these polymers after He-Ne laser irradiation. Using regression analysis, a linear correlation is found between the laser irradiation doses and the PL emission peak for CR-39 and CN-85. Thus, these types of polymer track detectors can be used as a dosimeter for laser beam.

REFERENCES