Molecular and Optical Investigations of Laser Radiation Influence in Makrofol LS 1-1 Polycarbonate

Ali A. S. Alhazmi

Physics Department, Faculty of Science, Taibah University, P.O. Box 30002, Al-Madinah Al-Munawarah 41411, Saudi Arabia

Abstract: Polymeric sheets of Makrofol material LS 1-1 were irradiated with IR-laser fluence ranges from 1.5 to 18.0 J/cm^2. The impact of laser radiation on optical and molecular features of Makrofol was studied by using various methods as intrinsic viscosity to measure average molecular mass, refractive index, UV spectroscopy and color difference measurements. The results ensure that the laser radiation cause rupture of bonds of the Makrofol samples when irradiated with fluences up to 7 J/cm^2. The irradiation of laser in the range of fluences 7 - 18 J/cm^2 results in more compact structures of Makrofol, which led to enhancement the molecular mass and raise the refractive index. Furthermore, the optical energy gap decreases from 6.28 to 3.11 eV with increasing laser fluences to 18 J/cm^2, and related with the increase the Urbach energy from 0.58 to 0.98 eV. Further, we investigated the transmission and color changes of the samples in the range of wavelengths of 370-780 nm. The non-irradiated Makrofol sample is almost colorless. It exhibited respectable color sensitivity to laser irradiation that improvement in green and blue color components.

Keywords: laser, Makrofol LS 1-1, viscosity, optical properties, color

1 Introduction

The amorphous polymer of polycarbonate Makrofol becomes one of the attractive engineering properties [1]. Laser radiation interacting with Makrofol leads to bond rupture, chain aggregation and double bonds developments that improved Makrofol properties [2,3,4, 5,6,7]. The result chemical system has new electronic structures, functional groups, different backbone with different new physical characteristics [8].

This is considered as a valuable technology to persuade appropriate modifications of Makrofol polymer [9]. Moreover, intrinsic viscosity evaluation helps in molecular identity of Makrofol. Also, the processing and applicability of it depend strongly on molecular structure [10]. The refractive indices of Makrofol offer valuable information on its structural characteristics [9]. Moreover, light-induced color changes of polymers influence their applications of commercial in processing for polymeric materials radiation and applying polymers as sensors for radiation dosimetry.

A lot of work studied the change of color in polymer and its uses in nuclear tracks detector (NTDs) [11,12,13, 14]. It was reported that remarkable color change is observed even at a small radiation dose in some NTDs.

These changes can be applied effectively in dosimetry. Factor *et al.* [15] found that polycarbonate (PC) color changes to a moderate intense yellow because of gamma irradiation. Whereas, it attains a green color when it is exposed to an electron beam. Many authors have attributed the colororation of irradiated PC to highly conjugated compounds and radical species [16]. Modifications in polycarbonate due to radiation have been widely studied [17,18,19,20,21,22]. Despite the severe use of PC in several fields, the light-induced modifications in Makrofol LS 1-1 have not received such expected attention. Therefore, we focus in the present work on laser-induced modifications in the molecular and optical properties of Makrofol LS 1-1. His would be valuable in getting information on the interaction of laser with Makrofol LS 1-1 and to investigate the possibility of improving its characteristics and achievements in several applications.

* Corresponding author e-mail: ahazime@taibahu.edu.sa

2 Experimental procedures

2.1 Samples

Makrofol LS 1-1 film is a polycarbonate that has superior impact and clarity. It is superior to standard polycarbonate films in terms of excellent registration on formed parts. It has a gloss surface on both sides. Its chemical composition is $C16H14O3$ and produced by Farbenfabriken Bayer A.G., Leverkusen (Germany) with density 1.2 g/cm^3 and an average thickness of 300 μm.

2.2 Irradiation Facilities

Sample exposed to laser at different fluences. We used an IR-pulsed laser of 5-W power and wavelength 904 nm (Model No. SSL3, USA). The laser is able to produce 2000 puls/sec, but we operated it at one pulse per second at a pulse duration of 200 ns. Diameter of the laser beam is 1.8 cm. The laser was focused on sample surface.

2.3 Irradiation Analysis

Viscosity measurements conducted in Oswald viscometer, manufactured by Poulten, self, and LEE, LTD, England, type pinkevitch Size 0 No. 2106. It was regulated according to the standard methods specified in ASTM D 445-IP 71.

The measurements of refractive index were done by using Abbe refractometer (Type-Reichert; mark-II, Model-10480, New York). The refractive indices values have an accuracy of ±0.0001 at 22-24 °C and 5893 °A.e. We usually measure the refractive index many times, but we considered only the average value.

The transmittance and absorbance measurements were done by means of a Shimadzu UV-Vis-Nir scanning spectrophotometer, type 3101 PC To describe the color of samples, we used the methodology of the Commission International de E'Claire (CIE units x, y and z).

2.4 Calculation and determination of the tristimulus values

A special mathematical sets of lights, X,Y and Z are usually used to exchange the actual lights. The functions of color matching are positive numbers and termed, and. Each color can be matched using the appropriate amount of X, Y and Z light. The required amount lights to match a color are called the color's tristimulus amounts.

The values of CIE tristimulus values are usually calculated by summing up the products of the spectral power distributions of illuminant, color matching functions of observer and transmittance factor of sample at each wavelength in visible spectrum. For more information on tristimulus values see Ref. [16].

2.5 The 1976 CIE L* a* b*(CIELAB) color space

A weakness of the CIE X, Y and Z color space points to its lack of visual uniformity. Creating a uniform color space would permit plots presenting the perceptually relative positions of two or more colors in color space. This helps in forming formation a good color difference ruler between two samples.

The 1976 CIE L* a** b** (CIELAB) color space is generally used in industries of plastic, textile, and paint. L* is connected with perceived lightness in CIELAB color space. The CIELAB coordinate a* connected with red (a*) and green (-a*), whereas the coordinate b* correlates with yellow (+b*) and blue (-b*). The CIELAB L*, a* and b* coordinates are determined from the tristimulus values, for more details see Ref. [16].

The CIELAB color difference, ΔE is given by

$$\Delta E = \left[(a_1^* - a_2^*)^2 + (L_1^* - L_2^*)^2 + (b_1^* - b_2^*)^2\right]^{1/2} (1) \quad (1)$$

Here, the subscripts 1 point to irradiated and 2 to non-irradiated samples.
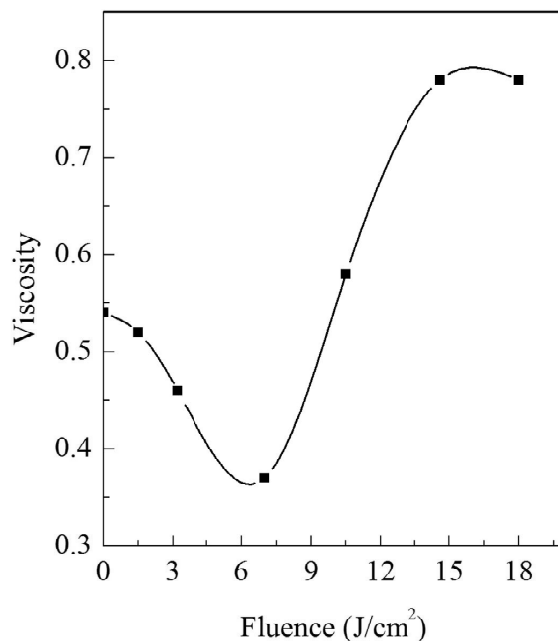

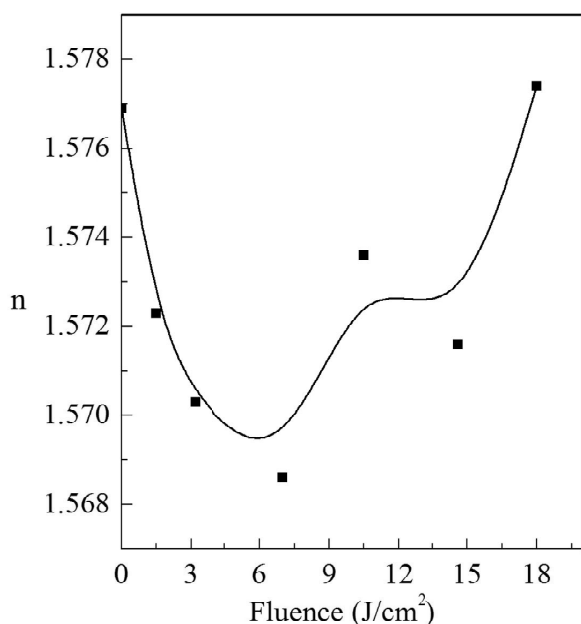**Fig. 1:** The intrinsic viscosity of Makrofol polymer against laser fluence.

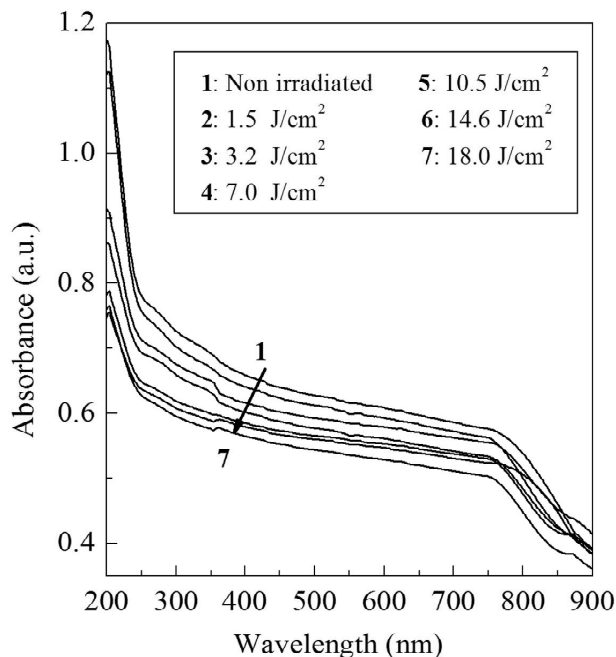**Fig. 2:** Refractive index as a function of laser fluence.

Fig. 3: The UVVisabsorption spectra of irradiated and non-irradiated Makrofol samples.

3 Results and Discussions

3.1 Intrinsic Viscosity

Using chloroform as a solvent, we prepared concentrations of (0.2, 0.4, 0.6 and 0.8%) from the non-irradiated and irradiated samples. We used the dilute solutions in order to avert any probable attractive secondary interactions between solvent molecules and the polymer that can affect the accuracy of measurements.

The flow time (t) was measured five times at 32 °C for each sample solution. The samples viscosity kinematic (ηk) were determined as the product of t and the capillary constant of the viscometer (C) ($\eta k = t \times C$). The obtained result is expressed as relative viscosity (η_{rel}); the ratio of the viscosities of solutions to that of the pure solvent. We calculate the values of specific viscosity ($\eta_{spc} = \eta_{rel} - 1$), reduced viscosity ($\eta_{red} = \eta_{spc}$ / concentration) and intrinsic viscosity. We calculated also the limiting viscosity number ($\eta_{in} = \lim \eta_{red}$) when concentration tends to zero.

Figure 1 inspects the intrinsic viscosity versus laser fluence. It decreases up to minimum value at fluence up to 7 J/cm^2. Then, it increase with the increases up to 18 J/cm^2. The decrease of intrinsic viscosity at a certain fluence range may be caused by the generation of shorter molecules due to bond rupture that causes randomly breaking in bonds and creation of stable lower molecular weight molecules [23]. Whereas increasing intrinsic viscosity in the 20-150 kGy, refers to free radicals that

produced from bond rupture were chemically active. They took part in chemical reactions and thus new covalent bonds were formed.

3.2 Refractive index

Figure 2 shows the change of refractive index of solid sheets with laser fluence. Refractive index decreases until minimum value at a laser fluence around 7 J/cm^2, escorted by an increase when the fluence is increased to 18 J/cm^2. This behavior is in agreement with the results of intrinsic viscosity and may be demonstrated by bond rupture and cross-linking induced by laser radiation. This behavior enables the production of free radicals. This leads to the generation of covalent bonds between different chains which in turn minimize the anisotropic behavior of the Makrofoland the increase in refractive index.

3.3 Optical analysis

Makrofol samples were investigated by spectral absorption measurements which investigated in the spectral range UV-Vis and noted in Figure 3. This varies with change laser fluence to 18 J/cm^2. It founded those levels at energy band influenced by laser fluences. In
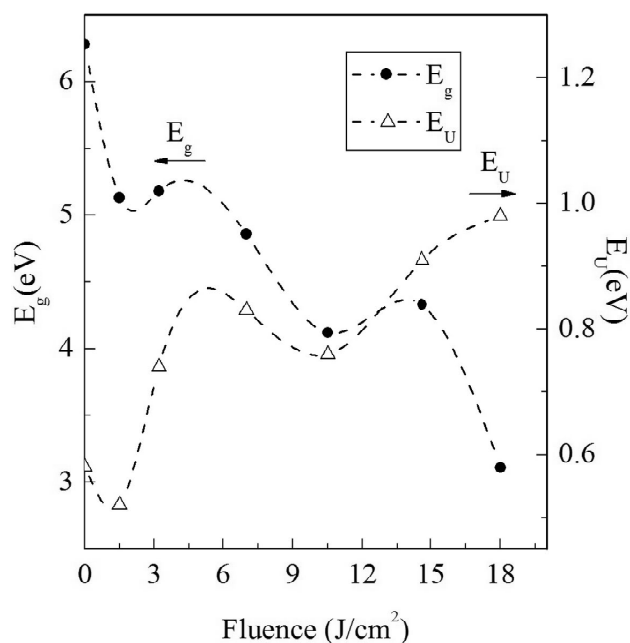
Fig. 4: The Urbachs energy and the energy band gap versus laser fluence.

Fig. 5: The UVVis transmission spectra of the irradiated and non-irradiated Makrofol samples.

amorphous phase, tail states are observed in gap region below the fundamental absorption edge that obtained by absorption coefficient (α). The latter obeys the Urbach rule [24]:

$$\alpha = \alpha_0 \left(\frac{h\nu}{E_U} \right) \qquad (2)$$

where α_0 is a constant characterized the investigated material and E_U is the Urbach energy that gives the tail states width. The E_U is obtained by reciprocal of straight line slope when $\ln \alpha$ is plotted against $h\nu$ for irradiated and non-irradiated samples. E_U increases with laser fluence, see (Figure 4) which indicate that the laser radiation forms a defects in the Makrofol samples [25]. E_g is calculated using the UV/Vis absorption spectra and the Taucs relation [26]:

$$\alpha h\nu = B(h\nu - E_g)^n, \qquad (3)$$

where $h\nu$ is the incident energy, B is a constant and n equals $3/2$ and $1/2$ for direct forbidden and allowed transitions, respectively, whereas $n = 2$ and 3 for indirect allowed and forbidden transitions, respectively. The change of the optical band gap with laser fluence is presented in Figure 4. E_g decreases with fluence. It showed the laser radiation leads to crosslinking. It is due to formation of a new covalent bonds and different chains are formed that is in turn resist the molecules motion which reduces activity and decreases optical band gap [27].
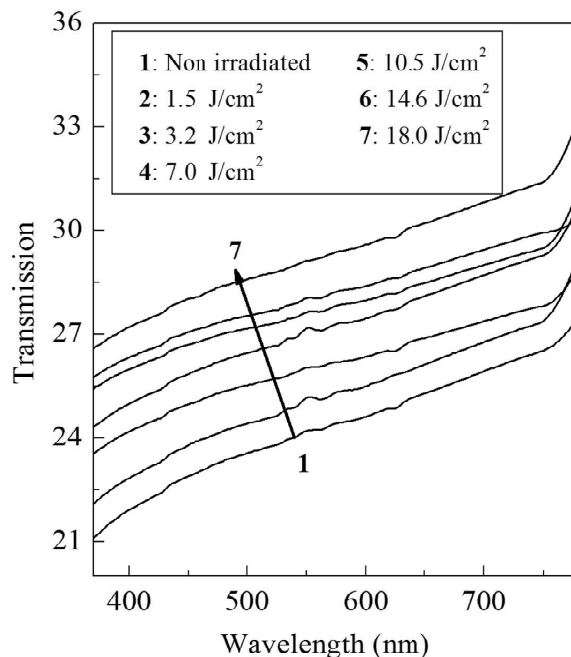
3.4 Color measurements

In figure 5, transmission spectra of both non-irradiated (irradiated) samples. We analyzed the chromatic coordinates and values of tristimulus via transmission data. Figure 6 shows the change of trismus (X, Y, Z) values with laser fluences. X, Y and Z displayed same tendency for increasing with laser fluence up to 18 J/cm^2. Figure 7 shows the change of (x, y and z) with the laser fluences. The values of x and y increases with the fluence up to 18 J/cm^2 whereas, z has a reverse tendency. The change of (a*, b* and L*) with the laser fluence is given in Figure 8. The values of L* has an accuracy of ± 0.05, but the accuracy is ± 0.01 for a* (b*). The yellow (+b*) color is converted to blue (-b*) after laser exposure up to 18 J/cm^2 (Figure 8a). Also, (+a*) converted to green (-a*) (Figure 8b). This was escorted by a decreasing in (+L*) (Figure 8c).

The intensity of color ΔE that refers to difference in color between the irradiated (non-irradiated) samples, it can be determined by CIELAB equation [28]. In Figure 9, ΔE varies with laser fluences. It was noted that ΔE increases by the laser fluence up 18 J/cm^2.

The color changes may be caused by trapped excited free radicals by ionization. This trapping break molecules of polymer with unpaired spin and produce optical coloration [28].
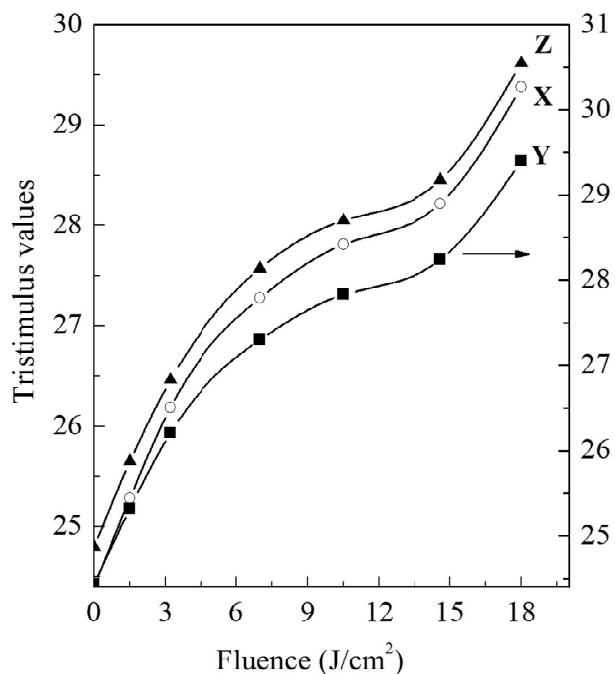
Fig. 6: The tristimulus values (X, Y, Z) of Makrofol polymer as a function of laser fluence.
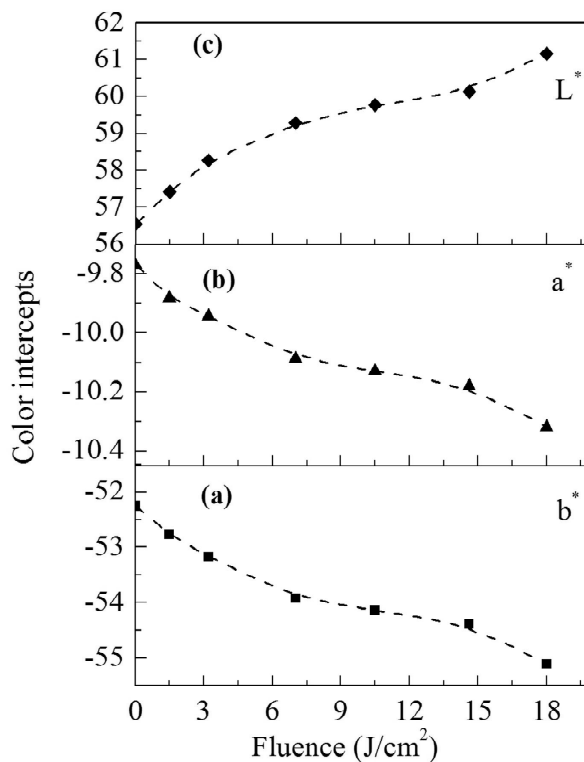

Fig. 7: Chromaticity coordinates (x, y, z) of Makrofol polymer against laser fluence.

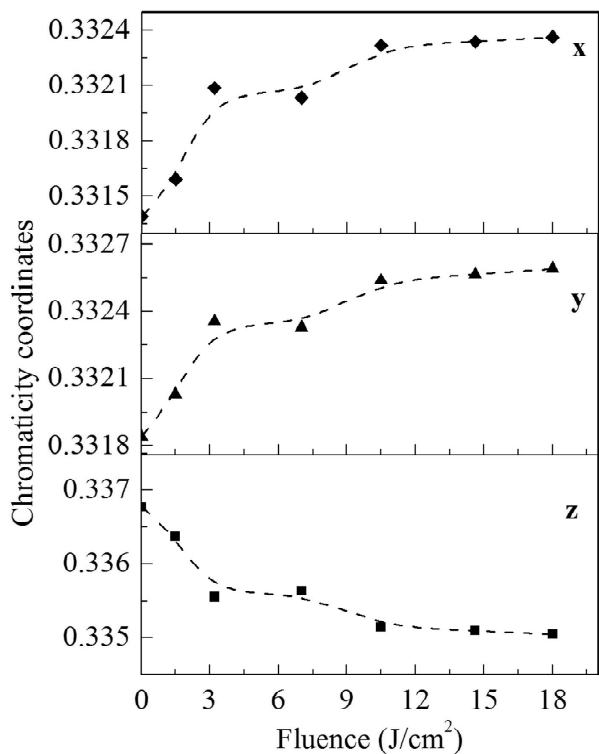**Fig. 8:** The color intercepts a^*, b^* and L^* of Makrofol polymer versus laser fluence.
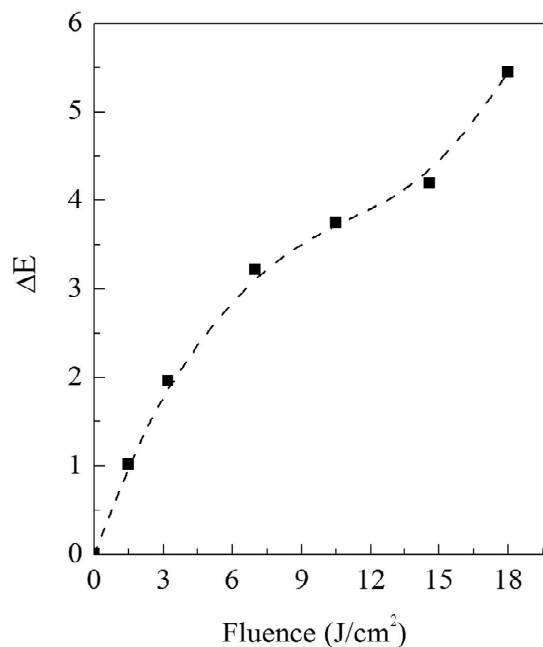

Fig. 9: Variation of color intensity ΔE of Makrofol polymer with laser fluence.

4 Conclusion

Laser irradiation in the fluence range 7 - 18 J/cm^2 results in a Makrofol polymer with more compact that led to increasing the refractive index and average molecular mass. The optical properties reveal that the laser irradiation in fluence range 1.5 - 18 J/cm^2 diminishes the optical energy gap. This effect may be caused by increasing in structural of irradiated samples disorder. The samples of non-irradiated Makrofol exhibit respectable color sensitivity to laser dose. The color intensity ΔE increases with laser influence up to 18 J/cm^2 and is convoyed by increases in green and blue color components.

References

[1] N. L. Singh, S. Nilam, and K. P. Singh, *Bull. Mater. Sci.* **28**, 599-602 (2005).

[2] D. Sinha, G. K. Sarker, S. Ghosh, A. Kulshreshthta, K. K. Dwivedi, and D. Fink, *Radiat. Meas.* **29**, 599-604 (1997).

[3] D. Sinha and K. K. Dwivedi, *Radiat. Phys. Chem.* **53**, 99-105 (1998).

[4] T. Phukan, D. Kanjilal, T. Goswami, and H. Das, *Nucl. Instrum. Methods B* **155**, 116-119 (1999).

[5] R. Mishra, S. P. Tripathy, D. Sinda, K. K. Dwivedi, S. Ghosh, D. T. Khathing, M. Muller, D. Fink, and W. H. Chung, *Nucl. Instrum. Methods B* **168**, 59-64 (2000).

[6] R. Mishra, S. P. Tripathy, K. K. Dwivedi, D. T. Khathing, S. Ghosh, M. Muller, and D. Fink, *Radiat. Eff. Def. Solids* **153**, 257-269 (2001).

[7] T. Yamauchi, H. Nakai, Y. Somaki, and K. Oda, *Radiat. Meas.* **36**, 99-103 (2003).

[8] Z. Lounis, M. Fromm, R. Barillon, A. Chambaudet, and X. Allab, *Radiat. Meas.* **36**, 615-620 (2003).

[9] S. A. Nouh, *Radiat. Meas.* **38**, 167-172 (2004).

[10] T. Rushing, and R. J. Hester, *Appl. Polym. Sci.* **89**, 2831-2835 (2003).

[11] R. Clough, K. Gillen, G. Malon, and J. S. Wallace, *Radiat. Phys. Chem.* **48**, 583-594 (1996).

[12] R. F. Khan, N. Ahmed, and M. Aslam, *Radiat. Meas.* **33**, 129-137 (2001).

[13] R. Shweikani, G. Raja, and A. Sawaf, *Radiat. Meas.* **35**, 281-285 (2002).

[14] B. Dörschel, D. Hermsdorf, and K. Kadner, *Radiat. Meas.* **35**, 183-187 (2002).

[15] A. Factor, J. C. Carnahan, S. B. Dorn, and P. C. Van Dort, *Polym. Degrad. Stab.* **45**, 127-137 (1994).

[16] M. Hossam, A. Ali, and E. Hussein, *J. Appl. Polym. Sci.* **101**, 4358-4365 (2006).

[17] B. Bodmann, and U. Hoim, *Nucl. Instrum. Methods B* **185**, 299-304 (2001).

[18] A. Belafrites, A. Nourreddine, D. Mouhssine, A. Nachab, and A. Boucenna, *Radiat. Meas.* **39**, 241-244 (2005).

[19] M. Janez, *J. Nucl. Mater.* **245**, 185-190 (1997).

[20] A. K. Srivastava and H. S. Virk, *J. Pure Appl. Phys.* **37**, 713-717 (1997).

[21] K. O. Harling, E. G. Kohse, and J. K. Riley, *J. Nucl. Mater.* **304**, 83-85 (2002).

[22] P.C. Kalsi and C. Agarwal, *Radiat. Eff. Def. Solids* **162**, 25-30 (2007).

[23] S. A. Nouh, M. Amal, H. EL Hussieny, and T. M. Hegazy, *J. Applied polymer science* **109**, 3447-3451 (2008).

[24] F. Urbach, *Phys. Rev.* **92**, 1324-1324 (1953).

[25] P.C. Rishi, M. Suman, A. K. Tomar, and K. Shyam, *J. Alloys Compd.* **538**, 212-219 (2012).

[26] J. Tauc, in *Optical Properties of Solids*; edited by F. Abeles; North-Holland: Amsterdam, p. 77 (1972).

[27] E. Sayeda, E. Seif, M. Nehad, *Open J. Polym. Chem.* **4**, 21-30 (2014).

[28] S. A. Nouh, A. Mohamed, R. Bahareth, M. Abutalib, and K. Benthami, *Eur. Phys. J. Appl. Phys.* **65**, 1-5 (2014).