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Effect of GaAs Pulsed Laser on the Structure and Optical Characterization of Makrofol VLG 7-1

Radiyah A. Bahareth

University of Jeddah, College of Science, Department of Physics, Jeddah, Saudi Arabia

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ABSTRACT

Samples of Makrofol films were exposed to different laser fluences (2-18 J/cm^2). X-ray diffraction (XRD) and ultraviolet spectroscopy (UVs) techniques were used to explore the resultant effect of laser radiation on the structure and optical characteristics of the Makrofol polymer. The change of refractive index (n) and the optical band gap (E_g) with the laser fluence was interpreted. A reduction in the E_g values (3.08-2.54 electron volt) was observed when raising the laser fluence up to 18 J/cm^2. This was accompanied by an increase in refractive index from 2.376 to 2.533. This was attributed to the prevalence of crosslinking that damaged the crystalline portion in the Makrofol polymer. The crosslinking created color centers that induced differences in color between the exposed films and the uncolored pristine Makrofol film. The color difference was significant as the values of ΔE were greater than 5. This optimized the Makrofol polymer to be used in dosimetric applications.

1. INTRODUCTION

There are different categories of Makrofol (Mak) (bisphenol-A polycarbonate) nuclear track detectors (NTDs). One of these is the used Mak VLG 7-1 which was fabricated to be used in the applications which require thermoforming. It is an amorphous polymer that possesses excellent properties that allowed it to be brilliant applicant in dosimetry [1-4]. The properties of Mak were found to be dependent on the fabrication environments. Therefore, its characteristics change due to the radiations exposure [1]. One of the distinctive properties of Mak is the existence of carbonyl group which degrades by the act of minor dosages of radiation[5].

Mak is suitable for electronic devices and optical fibers due to its brilliant transparency and low density. These distinctive characteristics allowed it to be used in dosimetry. Besides, Mak is usually used to get track etched films, neutron and alpha radiography, recognitions cosmic radiations, and in the gamma rays and ultraviolet radiation dosimetry [6-8]. Though Mak has a huge practical and marketable rank, some non-expected issues, such as humidity and temperature changes may be established during fabrication. This creates structural deficiencies in the Mak films, leading to variations in its chemical and physical characteristics. Radiation processing can reduce the induced structural defects.

Laser has an important character in materials processing. Laser sintering, for example, is usually applied in several applications [9]. Laser radiation is widely used to alter the properties of material's surface [10]. It creates surface structural properties that have been the attention of research interests [11,12].

Physical and chemical changes in polymeric matter, in the nano and microscales, occur due to laser irradiation. The nonlinear ionization effect of laser causes the elimination of surface atoms in the treated area. This results in alternations of polymer properties [13]. Similarly, the alternations in chemical properties of the polymeric matter are practically appropriate procedures for the manufacture of nanomaterials, 3D photo-polymerization and laser lithography [14].

Characterizing the optical character of polymers represents an energetic part for researchers owing to

Corresponding author: r.bahareth@gmail.com
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their extensive uses in optoelectronic tools [15]. Refractive indices of polymers provide information concerning their essential characteristics [16]. Additionally, the change in color due to irradiation evaluates the optical character of the polymer. It is an important technique that has been used to assess physical changes in polymers due to irradiation. This is important information for their use in marketable applications and dosimetry [17]. Several researches have investigated the importance of color change property of the exposed polymers in dosimetry [18-20]. They investigated that the technique of color changes initiates the foundations which consider the construction of radiation sensors. They attribute the change in color in irradiated Mak to the resultant free radicals that cause the development of conjugated bonds [21]. Additionally, they ascribed the color in irradiated polycarbonate to substituted benzophenones, radical species, highly conjugated compounds or rearranged isopropylidene radicals. The current study aim to tailor the structural and optical properties of Mak VLG 7-1 and enhance its performance in several applications.

2. EXPERIMENTAL

2.1 Materials

Mak VLG 7-1 sheets were manufactured by Farbenfabriken Bayer A.G., Germany. The sheets were 380 μm thick and had a density of 1.2 g/cm^3. They had a light transmission of 90.3%. The chemical formula is $C_{16}H_{14}O_3$.

2.2 Irradiation tool

In the current study, 5 watt pulsated GaAs laser of 904 nm wavelength was utilized. The frequency and pulse duration were 1200 Hz and 200 ns, correspondingly. The diameter of the circular shaped pulse, of a Gaussian profile, was 6 mm and the spot area was 0.28 cm^2.

2.3 Methodology

The XRD analysis was attained by a Shimadzu-6000 diffractometer source (Shimadzu Corporation, Kyoto, Japan) with Cu-K$_\alpha$ rays. The X-rays were of 1.54 Å wavelength and were scanned at speed of 2°.min^{-1}.

A Tomos spectrophotometer, Model No. 1800, was used to record the UV absorbance spectra. The Commission International de E'Claire (CIE) methodology was used to estimate the changes in color in the samples under study. Detailed information concerning the color alternation calculations was given in a previous work [15]. The CIE method is dependent on the explanation of the color as luminance components X, Y and Z. Their spectral weighting curves have been standardized by the CIE based on statistics from trials concerning human viewers. The amounts of the X, Y and Z constituents are proportional to physical energy, but their spectral configuration corresponds to the color matching appearances of human vision. The vision scientists formed a special set of mathematical lights, X, Y and Z, to replace the actual red, green and blue lights known as the color's tristimulus values [22]. Besides, it is often convenient to discuss clean color in the absence of brightness. The CIE defines a normalization method to calculate little x, y and z chromaticity coordinates that specify the saturation.

The 1976 CIE intercepts a^*, b^* and b^* denote the green–red, blue–yellow and dark–white axes, respectively. The accuracy in calculating L^* is ±0.05 and is ±0.01 for both a^* and b^*, correspondingly.

The color intensity (color difference), ΔE is:

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

The subscripts 1 and 2 mention to the exposed and pristine samples.

3. RESULTS AND DISCUSSION

3.1 XRD analysis

We used XRD to demonstrate the change in the amount of the disordered phase owing to laser exposure. The XRD scans of the pristine and exposed samples, scanned in the 2θ array 10-30°, are displayed in Fig. (1).

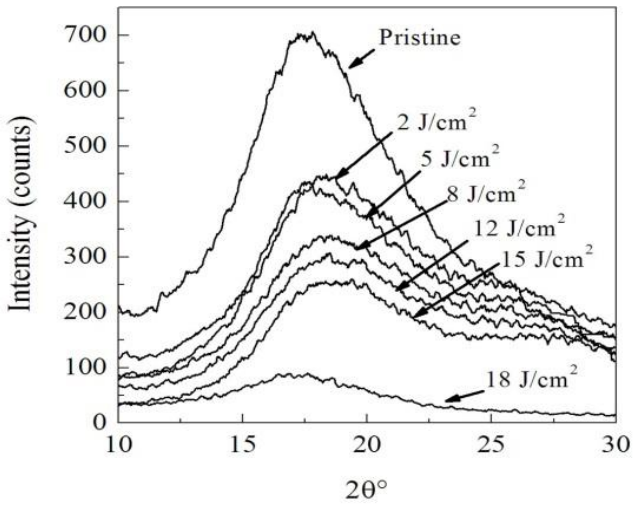

Fig. (1): XRD patterns of the Mak samples

The pristine film exhibited a characteristic amorphous wide peak (halo) at the 2θ range 12-24°, signifying that the Mak was amorphous. When the Mak was irradiated up to 18 J/cm^2, the area under the halo

(integral intensity, I) decreased due to crosslinks. Chemically active free radicals were created in the Mak chains due to the breaking of the carbonate, isopropyl and aromatic groups [23]. The produced hot free radicals formed reactions; hence, forming of covalent bonding through crosslinking. This disturbed the construction of the Mak, so enhancing its flexibility and solidity. Moreover, the Figure shows minor variations in the location of the halo with the laser fluence, signifying the degradation of the Mak molecular structure that altered its chains configuration [24].

3.2 Optical analysis

3.2.1 Absorption analysis

To get knowledge concerning the optical micro-electronic transitions, absorbance study was carried out. This helps to study the construction of the optical bandgap (E_g) and investigate its variation with the laser fluence. The UV absorbance spectra of the pristine and exposed samples are displayed in Fig. (2). The decrease of the absorbance with the increase in the wavelength was attributed to reducing the number of (n– π*) carbonyl group and phenyl group (π– π*) transitions [25].

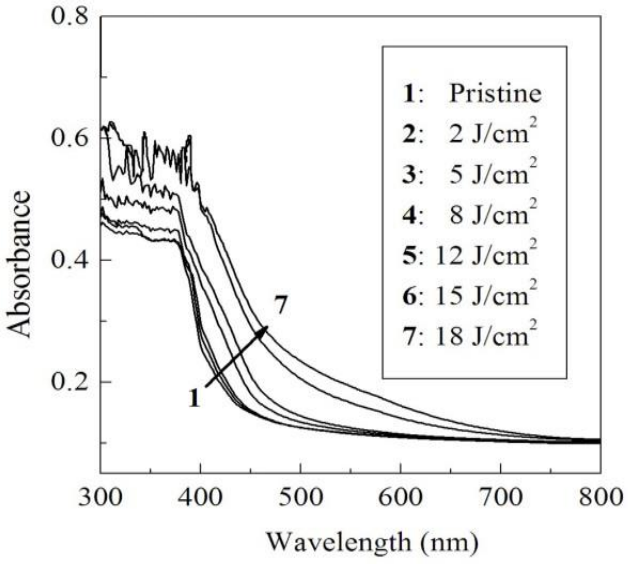

Fig. (2): The UV–Vis absorbance spectra of the Mak samples

Furthermore, the absorbance of the samples was improved with raising the laser fluences up to 18 J/cm^2 due to the development of bonding via crosslinks [26].

One of the essential parameters that supply knowledge about the fractional dispersal of the incident radiation when scattered and absorbed by the penetrated medium is the extinction coefficient (k). The complex refractive index is correlated with k by:

$$n^* = n + ik \quad \textbf{(2)}$$

In this expression, n denotes the real part of the complex refractive index.

We calculated the values of k by means of:

$$k = (\lambda\alpha/4\pi) \quad \textbf{(3)}$$

In which, λ denotes the wavelength and α means the absorption coefficient that can be computed from:

$$\alpha = \text{Absorbance} \times 2.303/\text{thickness of the sample} \quad \textbf{(4)}$$

3.2.2 Analysis of bandgap

The bandgap (E_g) was calculated applying Tauc's principle [27]:

$$\alpha h\nu = B(h\nu - E_g)^n \quad \textbf{(5)}$$

In which, B is a constant, hν denotes the energy of the photon and the n is an index of explores the trend of the micro-electronic transition. If the value of n is 1/2 or 3/2 then the transition is direct, whereas if n is 2 or 3, the transition is allowed or forbidden indirect [28]. The E_g numerical values were calculated by drawing $(\alpha h\nu)^{1/n}$ against hν and extending the linear segment of the plot at the hν axis (Fig. 3).

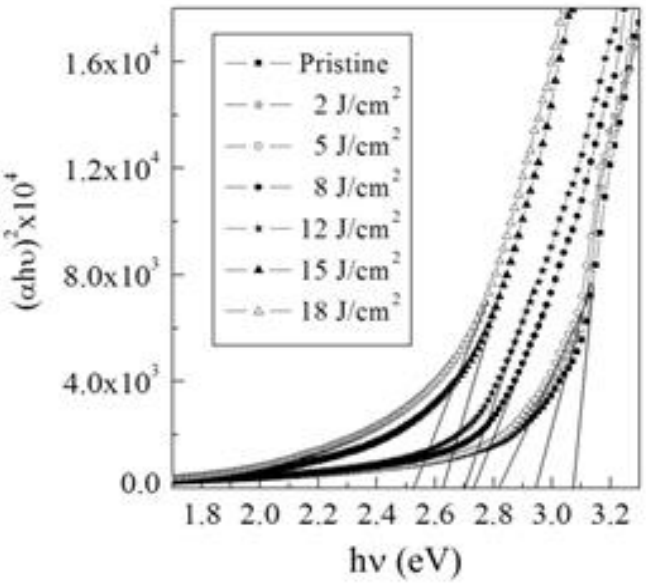

Fig. (3): A Plot of $(\alpha h\nu)^2$ versus hν

The dependence of E_g on the laser fluence is displayed in Fig. (4). The E_g values were reduced (3.08-2.54 electron volt) on raising the fluence up to 18 J/cm^2.

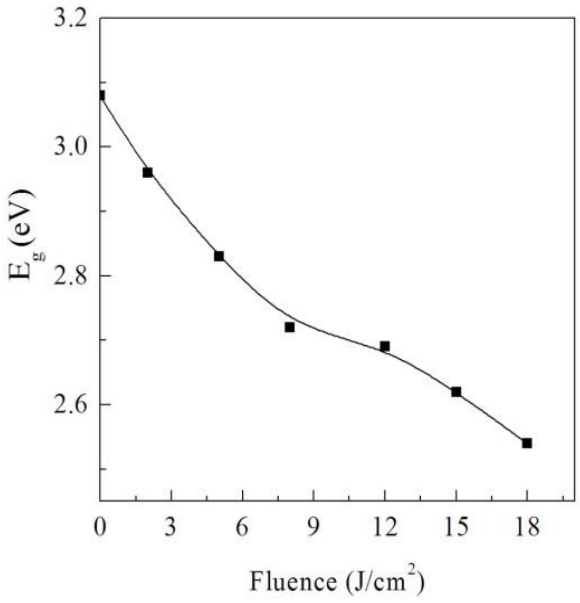

Fig. (4): The change of optical band gap E_g with the laser fluence

The decrease in E_g was attributed to crosslinkins which improves the amorphous phase of the Mak sheets. This creates structural deficiencies, allowing the formation of localized states in the E_g construction initiating lesser energy micro-electronic transitions. Otherwise, the significant act of the laser radiation on the samples was the creation of free radicals which caused the development of the conjugated bonds and hence decreasing the E_g [26].

3.2.4 Refractive index investigation

The refractive index, n, of the Makrofol films is calculated using the following formula [29]:

$$\left(\frac{n^2-1}{n^2+1}\right) = 1 - \sqrt{\frac{E_g}{20}} \qquad (6)$$

The variation of n with the laser fluence is shown in Fig. (5). The values of n increased with increasing fluence up to 18 J/cm^2. The obtained behavior is in agreement with that of E_g, both due to the prevalence of crosslinks. The chain scissions create active free radicals that result in the creation of covalent bonds via crosslinks. This investigation agrees well with that obtained previously [30].

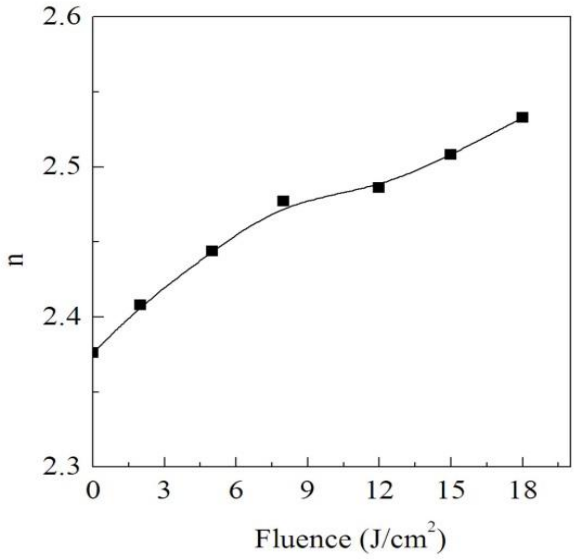

Fig. (5): The change of refractive index with the laser fluence

3.4 Color difference measurements

An essential issue of nuclear track detectors is the assessment of color differences with change in the radiation fluences. The color parameters were calculated by means of the transmission values (370-780 nm) and plotted in Fig. (6). The tristimulus values were estimated and presented in Fig. (7) versus laser fluence. Their values were reduced on raising the laser fluence up to 18 J/cm^2. In addition, the chromaticity coordinates were calculated and displayed in Fig. (8) versus laser fluence. The x and y coordinates were raised on raising the fluence to 18 J/cm^2, whereas, the z coordinate decreased.

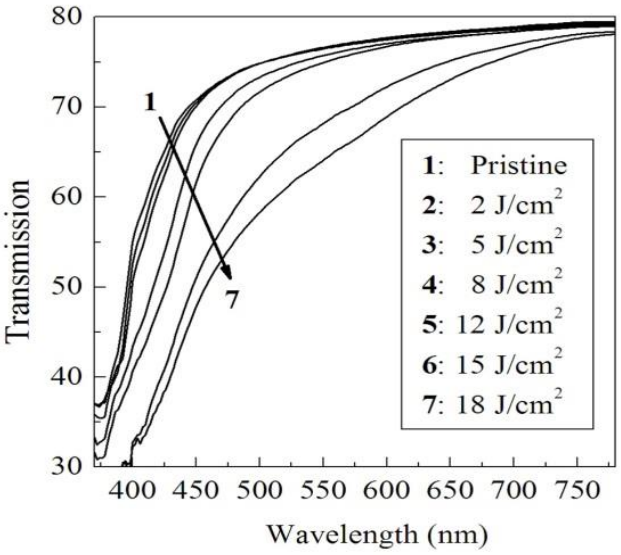

Fig. (6): The UV–Vis transmission spectra of the Mak samples

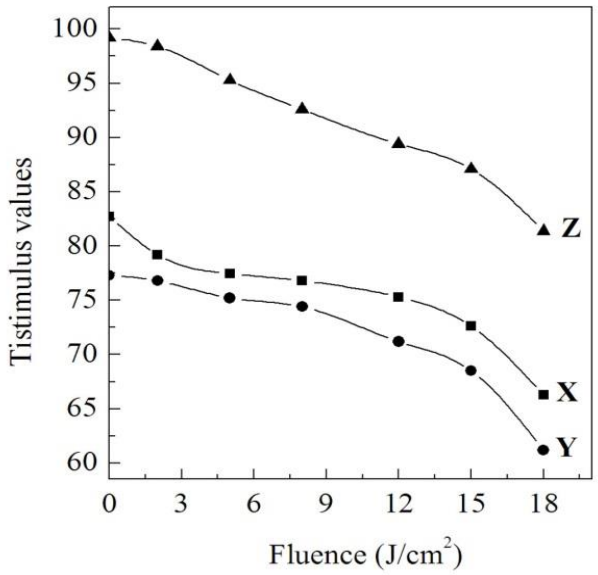

Fig. (7): The change of tristimulus values with the laser fluence

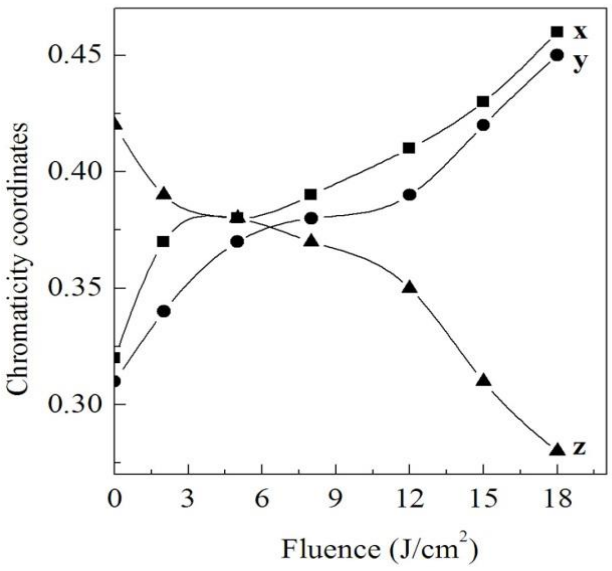

Fig. (8): The change of chromaticity coordinates with the laser fluence

The variations of the color intercepts a^* and b^* with the laser fluence are presented in Fig. (9). The a^* and b^* intercepts displayed negative values that raised on raising the fluence up to 18 J/cm^2, demonstrating the conversion of the green constituent into red and the blue to yellow, respectively. This was correlated to the development of darkness in the Mak ($-L^*$) (Fig. 10).

The color intensity (ΔE) was calculated using equation 1 and is displayed in Fig. (10) against laser fluence. An increase of ΔE was observed on raising the fluence up to 18 J/cm^2. The values of ΔE were more than 5. This indicates a significant color change [31, 32]. The change in the color of Mak due to laser exposure is attributable to the resulting free radicals, re-arranged isopropylidene radicals, formation of strong conjugated bonds and the benzophenones [21]. The resultant free radicals are chemically active and thus take part in the chemical reactions causing crosslinking. This was associated with the creation of the color centers. Additionally, these active free radicals that have electrons with unpaired spin, cause color variations [15].

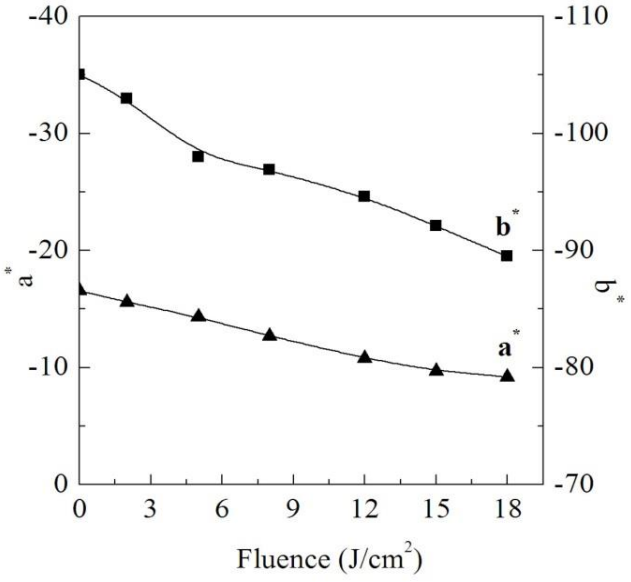

Fig. (9): The change of a^* and b^*color intercepts with the laser fluence

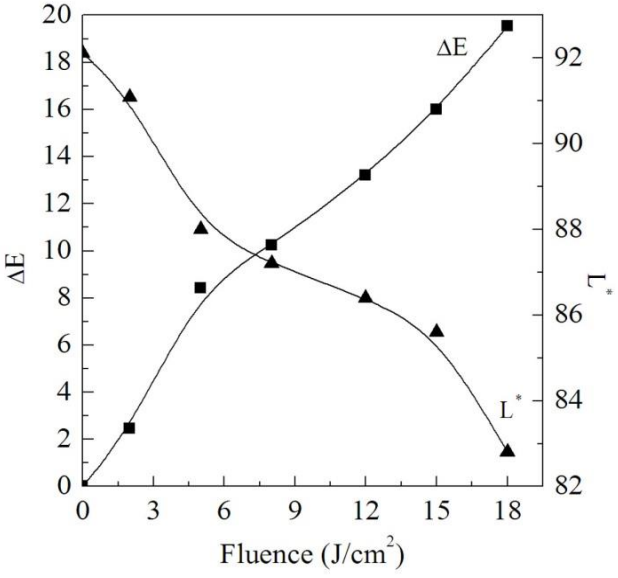

Fig. (10): The change of L^* color intercept and color intensity ΔE with the laser fluence

4. CONCLUSION

The amorphous phase of Makrofol films could be enhanced by laser fluence of 18 J/cm^2 due to crosslinking. This makes the Makrofol more flexible. This was convoyed with changes in the optical character of Makrofol that permitted it to be used as optoelectronic tools. Moreover, the Makrofol displayed a significant color variation due to laser exposure.

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