Influence of Laser Irradiation on the Optical and the Mechanical Properties of Makrofol-DE Polycarbonate

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ABSTRACT: The effect of IR laser irradiation on the optical and the mechanical properties of Makrofol-DE 1-1 CC polycarbonate films were investigated. Three hundred microns-thick films of Makrofol-DE 1-1 CC polycarbonate were irradiated with 0.00–10.40 J/cm^2 of Ga-As laser pulses, 904 nm, 5 W, and 200-ns pulse duration. Fourier transform infrared spectroscopy measurements showed that (C=O) groups degrade under laser irradiation at the studied fluence range. The aliphatic and aromatic (C—H) groups exhibited the same behavior, which can be attributed to nature of laser interaction with matter. The Makrofol samples exhibited degradation under the effect of laser irradiation up to 0.94 J/cm^2, where crosslinking mechanism started and continued until 7.07 J/cm^2. The refractive index had a minimum value at 0.94 J/cm^2 and maximum value at 7.07 J/cm^2 due to the degradation and crosslinking formation inside the sample, respectively. The decrease in elastic modulus, E, of Makrofol irradiated with 0.47–0.94 and 7.07–10.40 J/cm^2 indicates that the sample becomes more flexible, which results from the decrease in interatomic force constants. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 4620–4627, 2012

Key words: mechanical properties; FT-IR; refractive index; polycarbonates

INTRODUCTION

Makrofol-DE 1-1-CC polycarbonate is a class of polymeric solid state nuclear track detectors, which have many applications in various radiation detection fields. Radiation-induced modification of polymers is a promising technique for the production of new polymeric materials, which can be engineered with specific physical and optical properties. The interaction of radiations with polymers leads to specific changes in the polymer properties due to induced chain scissions and crosslinking.[1–5] Crosslinking generally improves the physical properties of polymers, reduces crystallinity, and increases the light transmission of the polymer. Degradation has the opposite effect and can be considered as a prompt way to study the aging of polymers and their radiation stability. The primary product of the absorbed laser light is not heat, but free electrons or phonons. The degradation of the ordered and localized primary excitation energy into uniform heat could be related as follows; the first step is spatial and temporal randomization of the motion of excited particles, proceeding with the collision time of the particles in question. The next step, energy equipartition tends to involve a large number of elementary collisions and intermediate states.[6,7]

Hot carriers in polymer matrix lose their energy by phonons emission in the conduction band or may recombine again to form crosslinking. The particular bonds that are broken, may be identified by Fourier transform infrared spectroscopy (FTIR) analysis of the virgin and irradiated samples.[8] In addition, refractive indices of polymers provide information about their structural characteristics.[9] Several investigations have been introduced to study the change in physical as well as optical properties of polymers due to irradiation.[10–12] The results indicated that the changes in the optical properties of the polymer depend on whether crosslinking or degradation dominates during the irradiation. The refractive index and the anisotropic characteristics of the nuclear track detector were found to be dose-dependent. Also, the optical absorption of the Makrofol detector was found to be connected to the morphological changes induced as a result of irradiation.

The mechanical properties of polymers depend on a variety of parameters. They depend on the forces between atoms of neighboring molecules, and on the mobility of segments of molecules. The intermolecular forces are largely determined by the nature of the atoms and are only slightly changed by the crosslinking and scission induced by radiation. The most common way of recording mechanical

properties is to carry out stress–strain behavior that is sensitive to some parameters, as molecular weight, reflecting in many cases the method of polymerization of the polymer and its origin. The lower the average molecular weight, the softer the polymer is. Crosslinking will further influence mechanical properties.

The present work investigates the effect of IR laser pulses on the optical and the mechanical properties of Makrofol DE 1-1 CC sample. This study aimed not only to give evidence about the physical and chemical changes in the investigated sample but also to improve its properties to make it more applicable.

EXPERIMENTAL

Samples

Makrofol-DE 1-1 CC is a bisphenol-A polycarbonate of chemical composition ($C_{16}H_{14}O_3$). It is manufactured by Farbenfabriken Bayer A. G., Leverkusen (Germany), with an average thickness of 300 μm and density 1.23 g/cm^3.

Irradiation facilities

Makrofol polycarbonate samples were exposed to laser pulses for different exposure doses between 0.00 and 10.4 J/cm^2, using an infrared pulsed laser of 5-W power (Model No. SSL3, USA). The unit is capable of producing 2000 pulses per second with pulse duration of 200 ns at 904 nm. The laser beam was in the form of a circle 1.8 cm in diameter, of Gaussian intensity profile across the circle.

Fourier transform infrared spectroscopy (FTIR)

Fourier transforms infrared spectra of nonirradiated and the irradiated Makrofol samples were recorded using model Shimadzu 8201 PC. All the measurements were done in the range of 4000–400 cm^{-1}. The spectra were obtained for the absorbance of the polymer as a function of wave number with resolution 1 cm^{-1}. The accuracy of the spectra is better than ± 4 cm^{-1}.

Refractive index measurements

The refractive index measurements were carried out using an Abbe refractometer (Type Reichert; mark II, Model-10480, New York). The surface temperature of the prism and the wavelength of the light were 18.3–20.5°C and 5893 Å, respectively. The accuracy of the measuring values of the refractive indices was ± 0.0001.

Color difference measurements

The transmission measurements were carried out at room temperature using a Shimadzu UV–vis-NIR scanning spectrophotometer, type 3101 PC. This unit measures in the wavelength range from 200 to 3200 nm, with wavelength accuracy better than ± 3 nm over 200–2000 nm and better than ± 9 nm over 2000–3000. The Commission Internationale de l'Eclairage (CIE) approach was used in the present work for the description of colored samples. The color difference (ΔE) of the irradiated samples, with respect to the nonirradiated samples, was calculated using the CIELAB color-difference equation[13]:

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

where

$$L* = 116 f(Y/Y_s) - 16, \quad (2)$$
$$a* = 500[f(X/X_s) - f(Y/Y_s)], \quad (3)$$

and

$$b* = 200[f(Y/Y_s) - f(Z/Z_s)]. \quad (4)$$

The subscripts 1 and 2 refer to the irradiated and nonirradiated samples, while the subscript s refers to the tristimulus values of the perfect diffuser for the given illuminant and standard observer. The accuracy in measuring L*, a*, and b* is ± 0.05, ± 0.01, and ± 0.01, respectively.

Mechanical measurements

Mechanical measurements were carried out using Testometric M350-5Ax with 5-kN load cell, at room temperature. Dumbbell-shaped samples of standard dimensions (50-mm long with a neck of 27 mm and width of 3 mm) were placed between the jaws and the load was applied at a rate of 50 mm/min until failure occurred. Three pieces of the same sample were used and results were averaged for each data point. The accuracy of the tensile measurements was ± 0.5%.

RESULTS AND DISCUSSION

Fourier transform infrared (FTIR)

FTIR spectral analysis has been performed to investigate the structural changes in the Makrofol polymer due to laser irradiation. These changes have been estimated from the relative increase or decrease in the intensity of the peaks associated to the functional groups present in the polymers. These studies may be helpful in analyzing the changes in the properties of the investigated sample. Figure 1 shows the IR
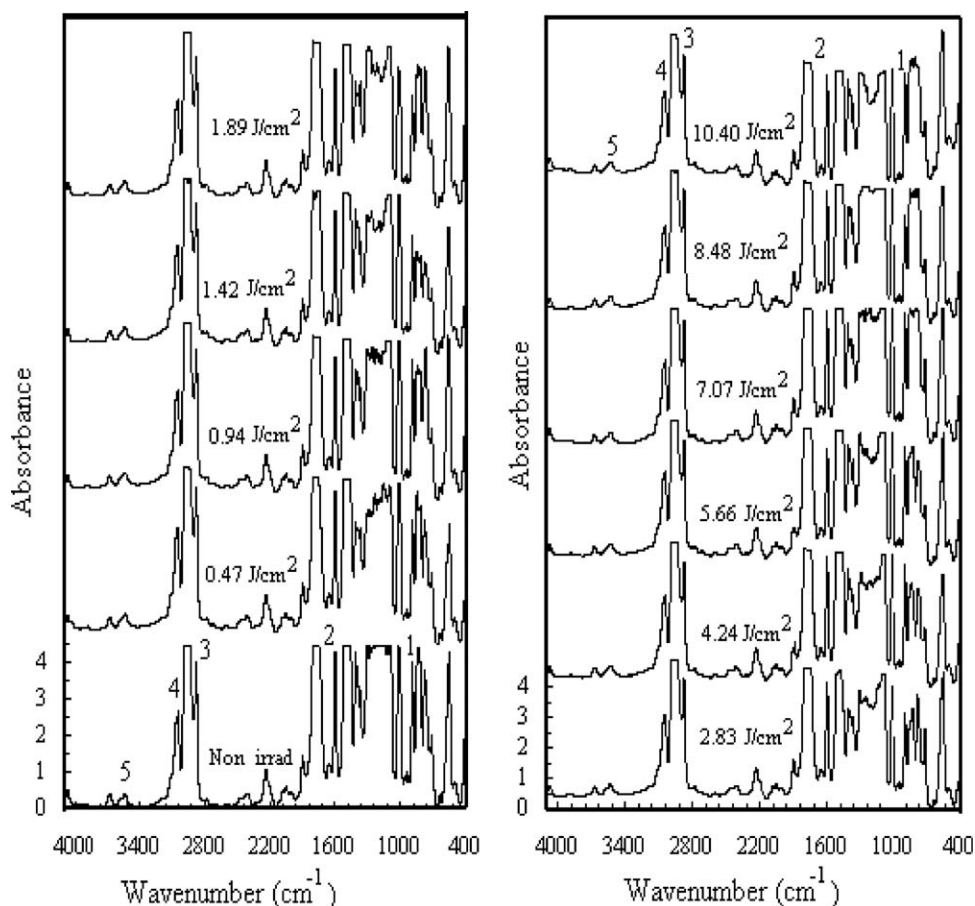
Figure 1 FTIR Spectra of nonirradiated and irradiated Makrofol samples with the characteristic bands of: 889 cm^{-1} (1), 1778 cm^{-1} (2), 2877 cm^{-1} (3), 3047 cm^{-1} (4), and 3533 cm^{-1} (5).

absorption spectra for the nonirradiated and irradiated samples. The material used in this study is aromatic polycarbonate. Its functional groups include methyl, phenyl ring, C=O, C—O, and OH ones. The absorbance of different bands coming from the function group, exhibits the same trend with the laser fluence. So, each characteristic group of polycarbonate is represented by only one wave number.

Figure 2 shows the variation of the absorbance with the laser fluence. It is clear that the absorbance at 1778 and 889 cm^{-1}, decreases with the increase of the laser fluence up to 10.40 J/cm^2. This indicates that the breaking of the C=O and C—O—C bonds is achieved. The absorbance at the wave number 2877 and 3047 cm^{-1} shows lower values of the intensity of aromatic C—H and CH$_3$ bond, respectively, until a minimum one for the irradiated sample with 0.94 J/cm^2. The intensity of CH$_3$ bond is proportional to the laser fluence within the range of 1.42–7.07 J/cm^2. However, the increase of the laser fluence above 7.07 J/cm^2 leads to reduction in the intensity of this bond.

The intensity of the peak corresponding to OH group, at 3533 cm^{-1}, exhibits an opposite trend to that of C—H bond. These results indicate that scission takes place at the carbonate site with probable elimi-

nation of carbon dioxide/carbon monoxide and formation of hydroxyl groups. The increase of hydroxyl groups in the fluence ranges of 0.47–0.94 J/cm^2 and of 7.07–10.40 J/cm^2, which means an increase in the end groups of macromolecules. This indicates that the degradation process prevails at these fluence ranges. At the fluence range 0.94–7.07 J/cm^2, an opposite trend has been observed due to the formation of bonds through crosslinking mechanism.

Optical properties

Refractive index

The refractive indices of solid sheets of Makrofol, which were exposed to laser irradiation up to 10.40 J/cm^2, were measured. Figure 3 illustrates the variation of the refractive index (n) with laser fluence. From this figure, it is observed that the values of n show a reduction in magnitude until a minimum value at around 0.94 J/cm^2. Moreover, the higher values of n were found to be accompanied with the laser fluence range of 0.94–7.007 J/cm^2. Above 7.07 J/cm^2, it decreases again. This behavior can be explained in terms of degradation and crosslinking
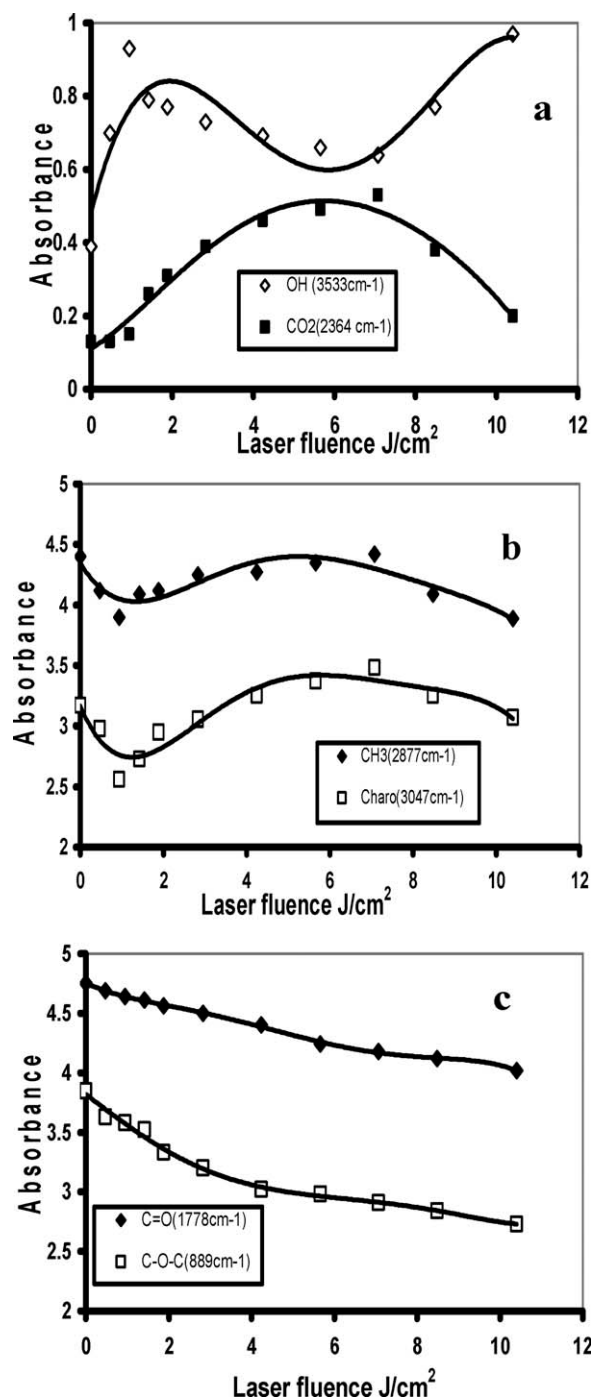
Figure 2 The absorbance bands of Makrofol sample with the IR laser fluence.

induced by laser irradiation. The reduction of the refractive index may be assigned to the degradation process as a result of the random breaking of the bonds of the backbone structure of the investigated sample. In other words, the effect of the random breaking of Makrofol bonds that takes place through the degradation mechanism and the free radicals produce a steric strain that weakens the backbone bonds. So, the reduction of the refractive can be expected. At the laser fluence range of 1.42–7.07 J/cm^2, the active

sites or branching points that were created by scission lead to intermolecular crosslinking. Thus, the minimizing of the anisotropic character of the investigated sample is obtained. This is responsible for the increase of the refractive index.[10,14,15]

In addition, the scission of chains and crosslinking may cause variations in chain orientation, which may lead to the observed changes in the refractive index.[16] Moreover, the laser photons lose their energy within the polymer structure by phonon emission that leads to enhancement of the heat of the Makrofol sample. This causes chain scission and consequently the formation of low molecular weight fragments. All these fractured molecules are trapped somewhere causing deficient regions and disordered structure of the Makrofol sample that leads to the reduction of the electronic polarization due to the scattering between these fragments and the steric effect of the polar groups of the investigated sample. So, the decrease of the refractive index can be expected. With the increase of the laser fluence from 0.94 to 7.07 J/cm^2, these radicals can recombine again to form crosslinking. This will be accompanied by the enhancement of the order state between the polymer main chains. Consequently, the electronic polarization may be increased and the increment of the refractive index is obtained.[17] These results are in good agreement with those obtained by Shams-Eldin et al.[18] They illustrate that, the incident photons activate the main polymer chain implying a main chain scission that results in a decrease of the refractive index. However, they interpret the increase of the refractive index as a result of the crosslinking formation within the polymer structure. The same effect was also investigated by Ranby and Rebek.[19]

Color difference measurements

Figure 4 shows the absorption spectra of the nonirradiated and irradiated Makrofol samples in the wavelength range 200–3200 nm. The variation of L*, a*, and b* with laser fluence is shown in Figure 5. It can be seen that the color parameters were significantly changed after exposure to laser irradiation. The green (−a*) and blue (−b*) color components of the nonirradiated sample were changed to red (+a*) and yellow (+b*), after exposure to laser, respectively, up to 10.40 J/cm^2. This is accompanied by an increase in the darkness of the samples (−L*).

The color difference between the nonirradiated sample and those irradiated ΔE were calculated and are plotted in Figure 6 as a function of laser fluence. It can be noticed that, the color intensity $\Delta E*$ increased with the laser fluence and was accompanied by a significant increase in the red and yellow color components (+a*), (+b*). This indicates that the color change of Makrofol sample has a response to the laser irradiation. These changes in color can
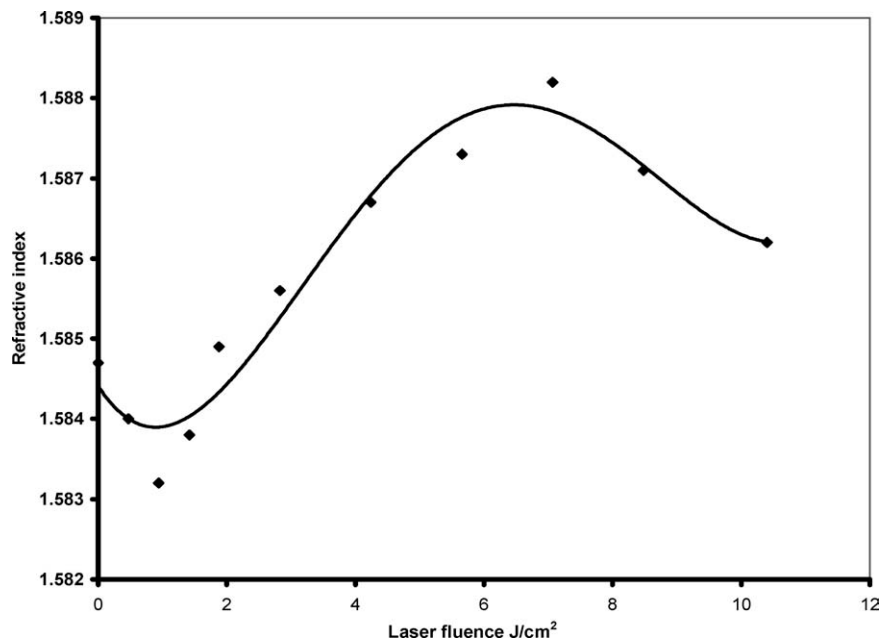
Figure 3 The change of the refractive index (n) with the IR laser fluence.
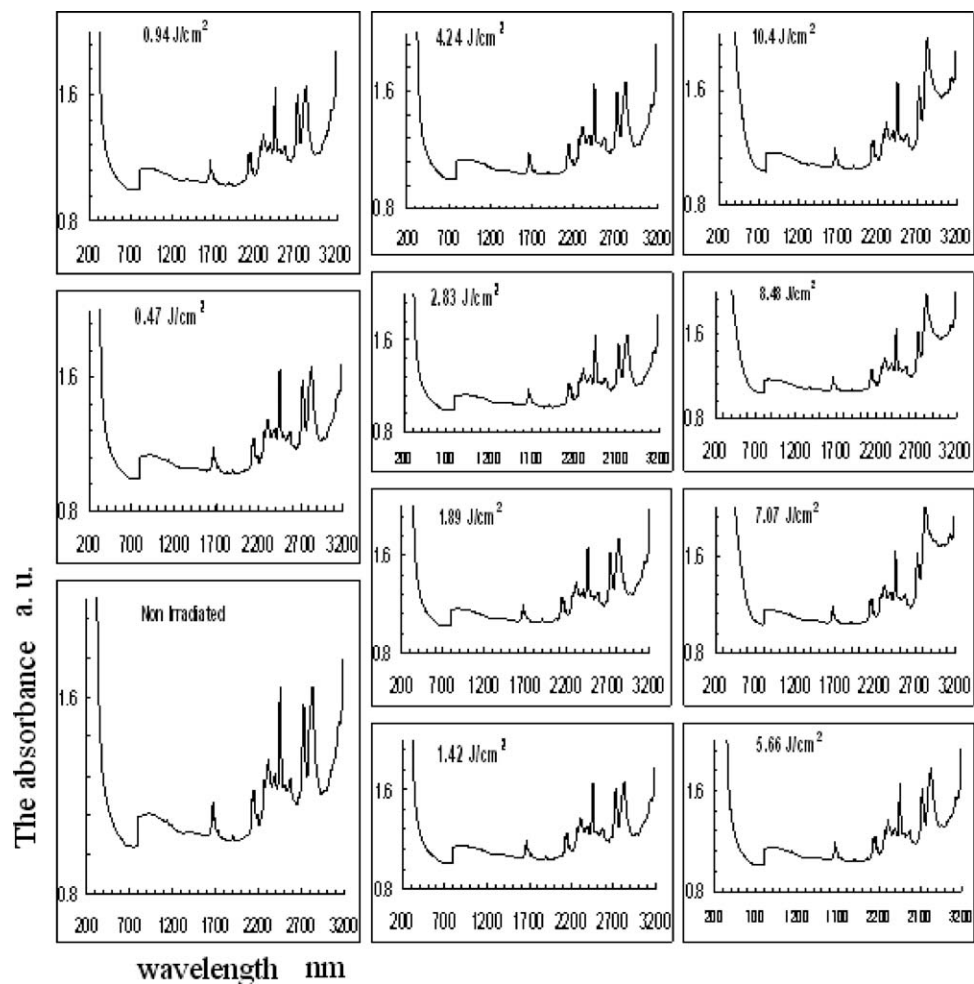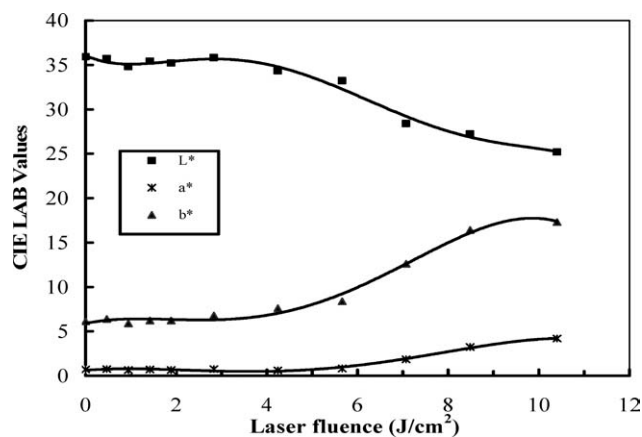

Figure 4 The absorption spectra measured in the wavelength range 200–3200 nm of irradiated and nonirradiated Makrofol samples.

**Figure 5** The plot of L*, a*, and b* as a function of the IR laser fluence.

be attributed to the trapping of the excited free radicals that are formed by ionization.[20] In other words, the trapped free radicals resulting from radiation-induced rupture of polymer molecules have electrons with unpaired spin. Such species may also give optical coloration.[11,21]

Mechanical properties

The stress–strain curves for the irradiated and nonirradiated Makrofol samples were measured. These curves were obtained by continuously measuring the force that developed as the sample was elongated at a constant rate of extension. Generally, the strain increases with the increase of the stress due to the increase in the flexibility of the chain in the macromolecules. The stress–strain curves serve to calculate several useful quantities including yield strength σ_y, tensile strength σ_f, and fracture strain ε_f or elongation at the break.
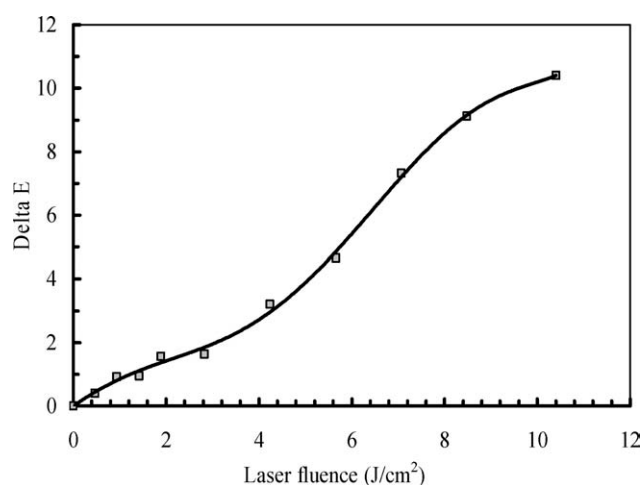

Figure 6 The calculated values of color intensity ΔE as a function of the IR laser fluence.
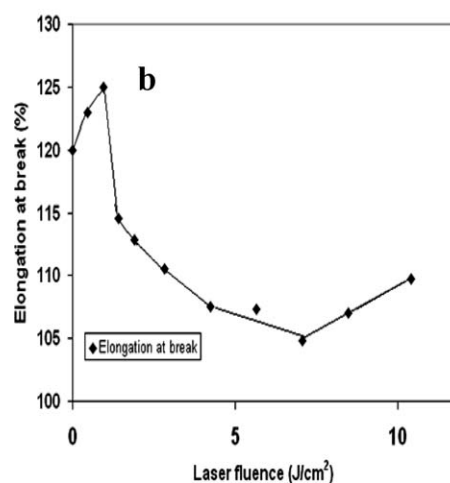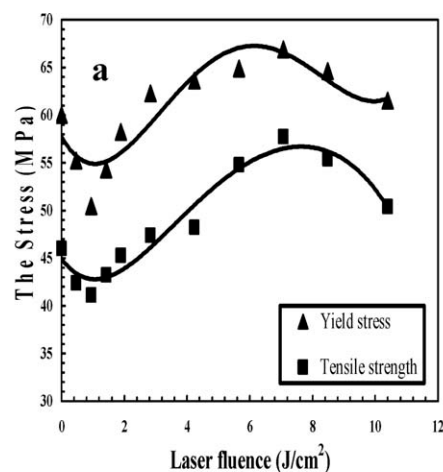
Figure 7 The relation of (a) σ_y and σ_f as a function of the IR laser fluence (b) ε_f as a function of the IR laser fluence.

The variation of σ_y, σ_f, and ε_f with the laser fluence is shown in Figure 7. It is clear that, σ_y and σ_f exhibit the same trend with the laser fluence. They reduce gradually within the laser fluence range of 0.47–0.94 J/cm^2, and then they exhibit higher values with the increase of the fluence from 0.94 up to 7.07 J/cm^2. Above 7.07 J/cm^2 the values of σ_y and σ_f decrease again. The opposite trend could be observed by ε_f. The higher values of the yield stress may be due to the fact that high stresses enhance the flow mechanism by increasing the mobility of the macromolecular chains. Also, at the fluence range 0.47–0.94 J/cm^2 in which σ_f decreases, the changes can be assigned to the initial scission in the chains.

On increasing the fluence above 0.94 and up to 7.07 J/cm^2, the free radicals produced from scission can recombine again to form crosslinking. Above 7.07 J/cm^2, degradation process predominates and thus the standard chains and a great number of chain ends weaken and the material may become softer. The dose ranges at which the degradation process predominates, the elongation at break increases (i.e., the higher toughness) due to the increment of the
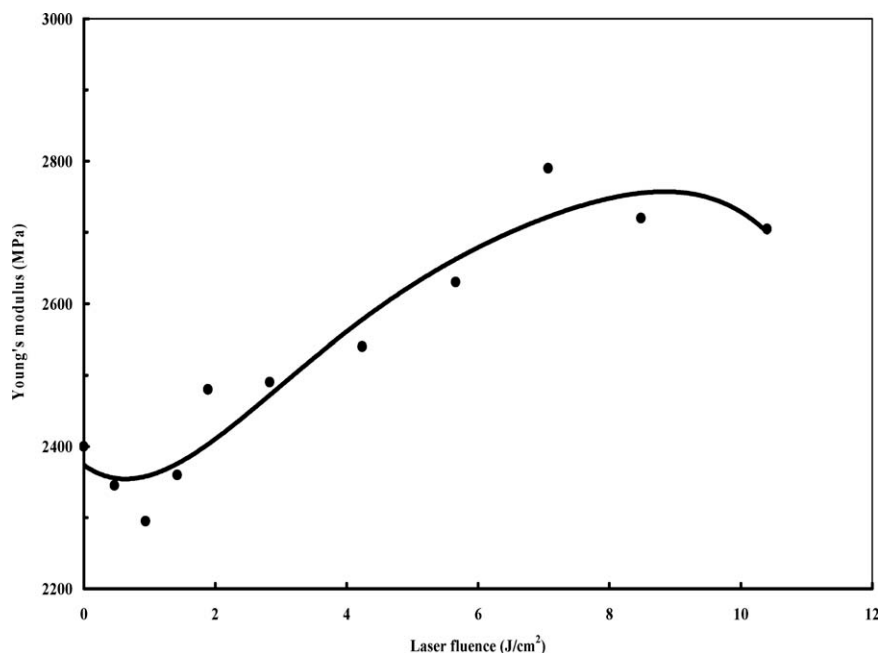
Figure 8 The variation of the Young's modulus of the Makrofol sample with the IR laser fluence.

crystallinity inside the Makrofol samples, where the crystalline regions formed act as reinforcement.[22] Also, in the laser fluence range 0.94–7.07 J/cm^2, where the crosslinking is the dominant process, the elongation at break was found to be decreased. So, the hardness of the investigated sample is achieved.

The variation of Young's modulus, E, with the laser fluence is shown in Figure 8. The Young's modulus shows lower values until it reaches a minimum value for the irradiated sample with 0.94 J/cm^2, followed by an increase in its values within the laser fluence range of 0.94–7.07 J/cm^2. Above 7.07 J/cm^2, it decreases again. The reduction in the elastic modulus indicates that the sample has become more flexible that simply results from the decrease in interatomic force constants. The increment in yield stress may be due to the crosslinking density, which restricted the polymer chain mobility. This leads to formation of an immobilized polymer nodes, and threatens the rigidity of chain increases within the polymer matrix as confirmed by the mechanical properties.[23] The effect of IR laser, at the fluence range 7.07–10.40 J/cm^2, tends to allow the onset of rather localized rotational or fluctuation motions in many parts of the polymer molecules. These motions altered the crosslinking formation inside the sample as a result of the decrease of the elastic modulus.[24–26]

CONCLUSION

IR laser irradiations of Makrofol-DE 1-1 CC polycarbonate lead to chain scission followed by crosslinking, and as a result there are changes in its optional and mechanical properties. Refractive indices measurements provided information about the structural properties of Makrofol samples. At the fluence range 0.94–7.07 J/cm^2, the branching points created by scission led to intermolecular crosslinking and allowed the formation of covalent bonds between different chains, so there was an increase in the refractive index.

The nonirradiated Makrofol polymer is nearly colorless. However, it showed significant color sensitivity toward laser irradiation. The sensitivity in color change toward laser irradiation appeared clearly in the change in the green and blue color components to red and yellow, accompanied by an increase in the darkness of the polymer samples.

Mechanical properties measurements of Makrofol indicated that, at the fluence ranges 0.47–0.94 and 7.07–10.40 J/cm^2, the standard chains and a great number of chain ends weaken and the material may become softer. Also the decrease in elastic modulus indicates that the sample has become more flexible, which results from the decrease in interatomic force constants. This enhances the mechanical properties of Makrofol for different applications.

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