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Effect of Laser Treatment on the Optical Properties of Poly(methyl methacrylate) Thin Films

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In this work, the effect of laser pulse treatment on the optical properties of poly(methyl methacrylate) (PMMA) films has been studied experimentally. The second harmonic of a pulsed Nd:YAG laser at 532 nm and 6 ns pulse width with 10 Hz repetition rate was used to modify the surface of red-BS-dye-doped PMMA films. Samples were ablated with 50 and 100 laser pulses. Optical reflectance and transmittance spectra were obtained in the range of 200–2000 nm. The optical properties of the films were influenced by the pulse number significantly. The oscillator and dispersion energies of the films were determined using the Wemple–Didomenico model. The optical band gap energy was extracted using the Tauc method. Results show that the optical parameters of the films were changed significantly after laser treatment.

Keywords: poly(methyl methacrylate), absorption coefficient, extinction coefficient, laser treatment, optical constants, band gap energy

1. Introduction

Recently, the electrical and optical properties of polymers have been extensively investigated owing to their applications in modern optical devices. Polymeric materials have unique properties such as low density, light weight, and high flexibility and are widely used in various industrial sectors.[1,2]

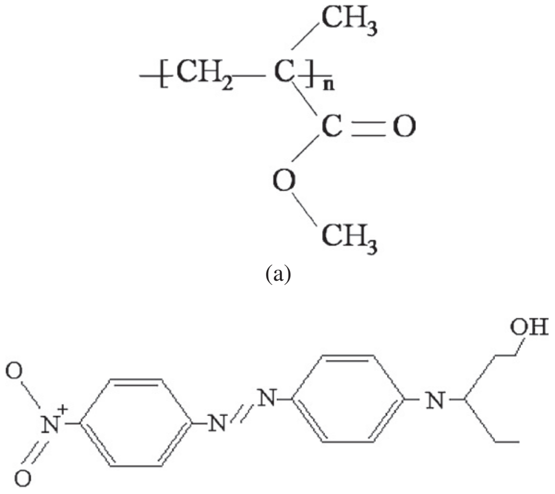
Poly(methyl methacrylate) (PMMA) is an important and interesting polymer because of its attractive physical and optical properties. PMMA contains both hydrophobic (methylene) and hydrophilic (carbonyl) groups in each unit. As a polymer waveguide, PMMA has attracted much attention for use as optical components and in optoelectronic devices owing to its low cost and volume productivity. In addition, it is found that it can produce a large refractive index difference compared with acryl amide-based photopolymers.[3–5]

Most polymeric surfaces as well as PMMA do not possess specific surface properties needed in various applications, and their surfaces need to be treated to obtain polymers with desired surface properties in various instances. One convenient way of treating polymers is laser treatment.[6–10] Therefore it is important to study the effect of treatment on the properties of polymers.

In this manuscript, we present the results of our experimental study on the changes in the optical properties of red-BS-dye-doped PMMA films after laser treatment. Following the introduction in Sect. 1, the experimental detail is presented in Sect. 2. Section 3 is devoted to results and discussion, and the conclusion is presented in Sect. 4.

2. Experimental Methods

PMMA films were prepared by dissolving 30 g of PMMA powder in 300 ml of dichloromethane with 0.08 g of red BS dye. The PMMA powder was provided by Yazd Polymer Talaei (YPT). The viscous solvent was poured on a flat glass in a closed box. The solution was left to dry in air ambient at room temperature for 24 h to obtain 0.21-mm-thick red-BS-dye-doped PMMA films. The chemical structures of PMMA and red BS dye are presented in Figs. 1(a) and 1(b).


(a)

(b)

Fig. 1. Chemical structures of PMMA (a) and red BS dye (b).

Films were cut in $1 \times 1\,\mathrm{cm}^2$ pieces and cleaned in deionized water ultrasonically. The prepared samples were irradiated by the second harmonic of a pulsed Nd:YAG laser at 532 nm wavelength in air. The laser pulse width was 6 ns with 10 Hz repetition rate. Laser beam diameter was 2 mm with an energy density of $20\,\mathrm{J/cm}^2$. The laser beam was focused on the polymer surface with a lens of 8.5 cm focal length. The films were irradiated with 50 and 100 laser pulses which are indicated as samples 2 and 3, respectively. Sample 1 is the pristine sample. A Varian Cary-500

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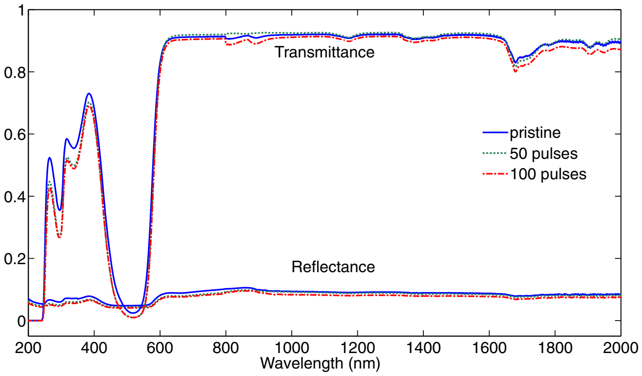

Fig. 2. (Color online) Optical transmittance and reflectance of PMMA films.

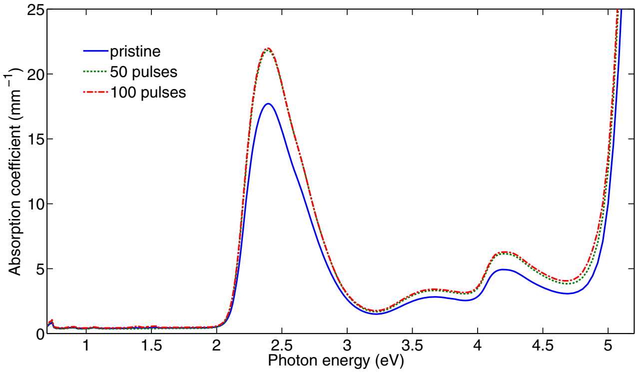

Fig. 3. (Color online) Opticalabsorption coefficient of samples.

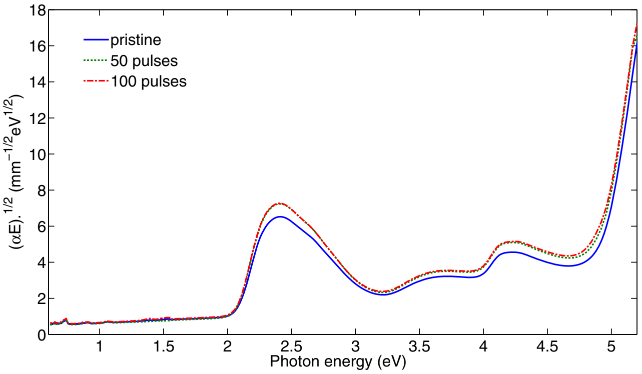

Fig. 4. (Color online) $\alpha E^{1/2}$ vs photon energy to illustrate Tauc method.

spectrophotometer was used for recording UV–vis–NIR transmission and reflection spectrum of the pristine and treated samples.

3. Results and Discussion

3.1 *Transmittance and reflectance spectra*

Pure PMMA is a colorless polymer without any noticeable absorption in the visible range. The optical transmittance T and reflectance R of red-BS-dye-doped PMMA films are shown in Fig. 2. The small changes in the reflectance spectrum of samples after laser treatment can be due to changes in the roughness of the surface of samples. (Laser ablation usually causes many forms of etching on the surface of the target which leads to changes in reflectance.) PMMA transmittance is very large in the range of $\lambda > 256$ nm. Fluctuations of the transmittance spectrum in the range of 250 to 400 nm are due to PMMA, but the large absorption of samples in the range of 400 to 600 nm is due to the red BS dye. In fact, adding the red BS dye to PMMA makes it a good absorber of a 532 nm laser beam. In this case, a 532 nm laser pulse in the treatment process would be more effective for improving the properties of the polymer.

3.2 *Optical absorption coefficient and band gap energy*

The optical absorption coefficients of samples are evaluated from the transmittance data using:[11]

$$\alpha = \frac{1}{d}\ln\left[\frac{(1-R)^2}{2T} + \sqrt{\frac{(1-R)^4}{4T^2} + R^2}\right], \qquad (1)$$

where T and R are the transmittance and reflection respectively, α is the absorption coefficient, and d is the thickness of the polymer. The absorption coefficient of the samples for different photon energies is shown in Fig. 3. The absorption coefficient of the samples increased after laser treatment in the range of the UV–vis spectrum. The increase in the absorption of samples in the UV range is attributed to the C–O and C=O bonds, the number of which decreased owing to the laser irradiation of the samples in air. The peak of the spectrum at about 2.5 eV is the effect of the red BS dye that was doped in PMMA. The red BS dye is known as an absorber in this range because of its chemical structure. The absorption peak at 2.5 eV is attributed to the aromatic π electron system of pyrazine rings of the red BS dye.

The optical energy gap E_g is another important quantity that characterizes semiconductors and dielectric materials since it has a paramount importance in the design and modeling of such materials.[12] The optical energy gap of samples was deduced from the intercept of the extrapolated linear part of the plot of $(\alpha E)^{1/2}$ vs the photon energy E with abscissa (see Fig. 4). This follows by the method of Tauc[13] where

$$\alpha E = B(E - E_g)^p. \qquad (2)$$

In this equation, α is the absorption coefficient, E is the photon energy, and B is a factor that depends on transition probability and can be assumed to be constant within the optical frequency range, and the index p is related to the distribution of the density of states. Taking $p = 2$, which corresponds to indirectly allowed transitions in PMMA films, the band gap energies of films were calculated, which are shown in Table 1. The band gap energies of the samples decreased from 4.842 to 4.826 eV (sample 2) and 4.816 eV (sample 3) after laser treatment. This is also attributed to the increase in the number of C–O and C=O groups in the samples after laser treatment.

Table 1. Sample number and band gap energy of PMMA and red BS dye calculated by Tauc method.

Sample	Number of laser pulses in treatment	Energy gap (eV)
1	Pristine	4.842
2	50	4.826
3	100	4.816

3.3 *Refractive index and extinction coefficient*

Determination of the optical constants n and k is one of the most challenging tasks when studying the optical properties of materials, since this involves complex equations and a great deal of computing. A number of methods and different approaches exist to determine the optical constants of materials.[14,15] The complex refractive index is

$$\hat{n} = n(\omega) + ik(\omega), \tag{3}$$

in which n is the real part and the extinction coefficient k, is the imaginary part. The refractive index n and the extinction coefficient k of the PMMA films studied here were determined using the relation.[16]

$$n = \left(\frac{1+R}{1-R}\right) + \sqrt{\frac{4R}{(1-R)^2} - k^2}, \tag{4}$$

in which $k = \lambda\alpha/4\pi$.

The extinction coefficient k describes the properties of the material with respect to light of a given wavelength and indicates the amount of absorption loss when the electromagnetic wave propagates through the material.[17] The data of refractive index n and the extinction coefficient k as a function of photon energy are shown in Figs. 5 and 6. The extinction coefficients k of the samples have a peak at $E = 2.38\,\text{eV}$, which increases with increasing number of pulses. It can be seen that by increasing the number of pulses, the extinction coefficient k increases while n decreases. These changes are due to the increase in the absorption coefficient of samples. The same results are reported by El-Nasser and Ali[18] that is, when PMMA was illuminated by UV irradiation. These results can be due to several reasons. One of them can be micro structural defects. The dissipation of an incident photon may cause absorption by polymer defects and initiation of cross-linkages, the degradation of polymer molecules, and creation of oxidized groups in PMMA. These processes are facilitated by surface defects, small cracks and micropores. Another reason for the variation of the refractive index of PMMA is carbon–oxygen polarization. Since PMMA contains electronegative oxygen atoms, C–O bonds are polarized, resulting in specific interactions occurring at the inter phase. The dipole–dipole nature, which leads to the rearrangement of polymeric chains and induction of the photochemical processes at the PMMA surface, can also be a reason for the variation of the refractive index of samples.

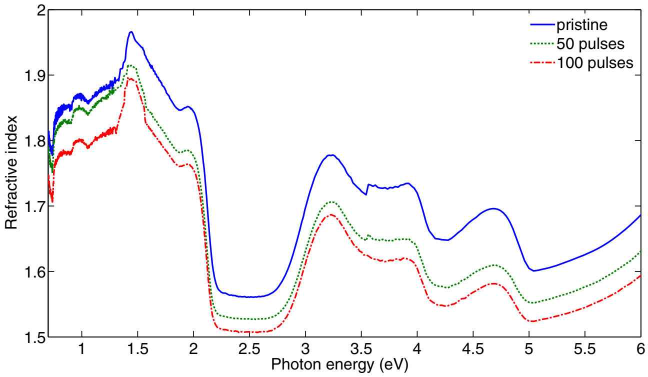

Fig. 5. (Color online) Refractive index of samples.

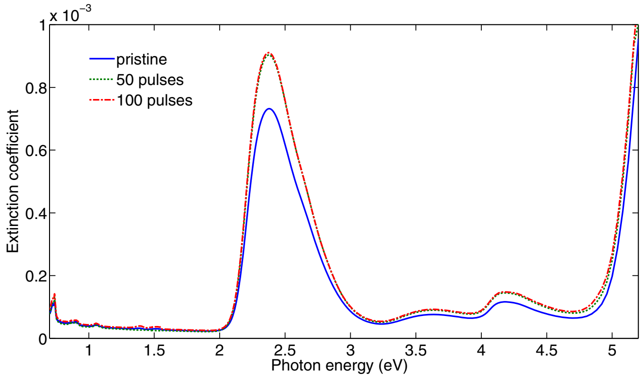

Fig. 6. (Color online) Extinction coefficients of samples.

3.4 *Dielectric properties*

One of the most important basic dielectric parameters that plays a major role in the material properties is permittivity or dielectric constant. This in turn is related to the dipole moment, polarizability, molecular radius, specific and molar refraction, relaxation time, wave impedance, specific and molar dispersivity and dielectric susceptibility. Among others Permittivity is calculated using Maxwell's equation for electromagnetic radiation, $\varepsilon = n^2$. The complex dielectric constant is described by

$$\varepsilon = \varepsilon_\mathrm{r} + i\varepsilon_\mathrm{i}, \tag{5}$$

where ε_r is the real part and ε_i is the imaginary part of dielectric constant. The imaginary and real parts of dielectric constant are expressed as[19]

$$\varepsilon_\mathrm{r} = n^2 - k^2, \tag{6}$$

$$\varepsilon_\mathrm{i} = 2nk. \tag{7}$$

The real part of dielectric constant is related to the dispersion, while the imaginary part provides a measure of the dissipative rate of the wave in the medium. The real and imaginary part dependences of photon energy of samples are shown in Figs. 7 and 8, respectively. Normal dispersion is associated with an increase in ε_r with photon energy, and anomalous dispersion with the decrease in ε_r with photon energy.[20] It is concluded that ε_r is larger than ε_i because

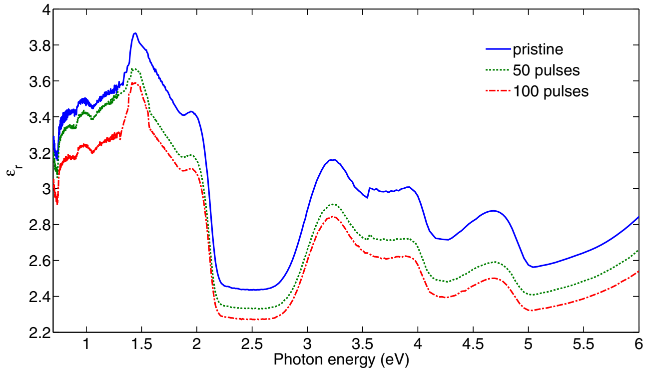

Fig. 7. (Color online) Real part of the dielectric constant of samples.

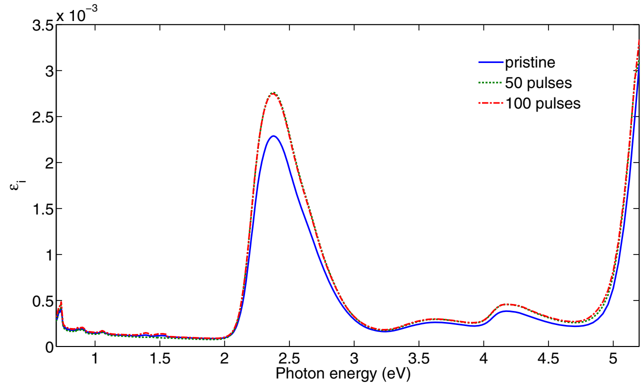

Fig. 8. (Color online) Imaginary part of the dielectric constant of samples.

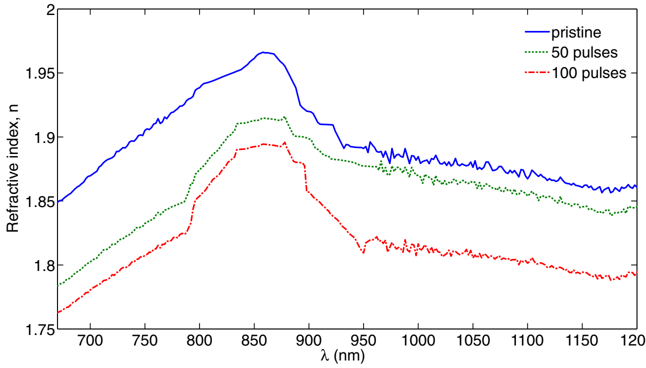

Fig. 9. (Color online) Refractive index vs wavelength.

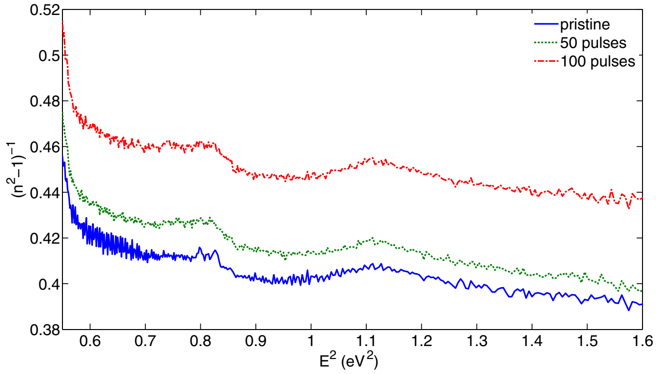

Fig. 10. (Color online) Plot of $(n^2-1)^{-1}$ vs photon energy $(h\nu)^2$ for samples.

Table 2. Dispersion parameters of PMMA films.

Sample	n	ε_∞	ε_L	E_0 (eV)	E_d (eV)
1	1.83	3.34	3.62	4.86	11.42
2	1.805	3.25	3.56	4.60	10.39
3	1.756	3.08	3.35	4.45	9.28

ε_r mainly depends on n^2. The peak appears in Fig. 8 in the range of 2–2.5 eV, which shows the region of resonant absorption.

3.5 Dispersion characteristics

Dispersion of the refractive index can be observed in Fig. 9. There is a small variation in the position of peaks at 1.45 eV from one sample to another. It can be observed that there is anomalous dispersion when $E > 1.45$ eV, as well as normal dispersion when $E < 1.45$ eV. In the normal dispersion region ($E > 1.45$ eV), the refractive index dispersion is analyzed using the single-oscillator model developed by Wemple and DiDomenico.[21] They introduced the energy parameter E_d to describe the dispersion of the refractive index. In terms of the dispersion energy E_d and single oscillator energy E_0, the refractive index can be expressed in the form of

$$\frac{1}{n^2-1} = \frac{E_0}{E_d} - \frac{1}{E_0 E_d}(h\nu)^2. \tag{8}$$

A plot of $(n^2-1)^{-1}$ vs E^2 for PMMA treated with of different numbers laser pulses is shown in Fig. 10. E_0 and E_d are directly determined from the slope of $(E_0 E_d)^{-1}$ and the intersection (E_0/E_d) with the vertical axis, respectively. The calculated values of the dispersion parameters (E_0 and E_d), as well as the corresponding optical dielectric constant ($\varepsilon_\infty = n^2$) for the PMMA films are listed in Table 2.[13,22]

The relationship between the lattice dielectric constant ε_L and the refractive index n is given by[23]

$$n^2 = \varepsilon_L - B\lambda^2, \tag{9}$$

where λ is the light wavelength and B is a constant. Figure 11 shows the dependence of n^2 as a function of λ^2 for different samples. It is observed that the dependence of n^2 on λ^2 is linear at long wavelengths. Extrapolating the linear part towards short wavelengths, the points of interception with the coordinate at $\lambda^2 = 0$ yields the values of ε_L, which are listed in Table 2. As observed, the dielectric constant is in good agreement with the data published by Yadav et al.[24] The disagreement in the dielectric constant and dispersion parameters we obtained with the data published by Caglar

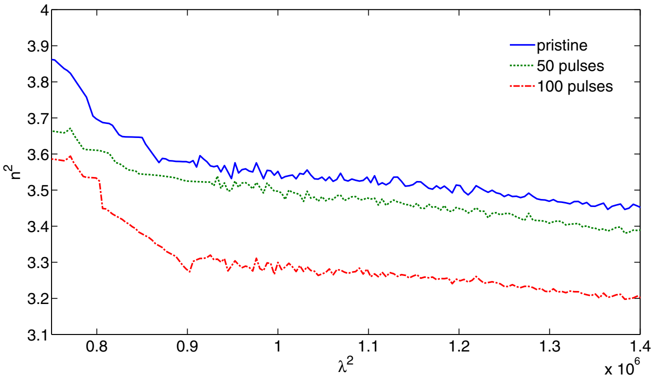

Fig. 11. (Color online) Plot of n^2 vs λ^2 for samples.

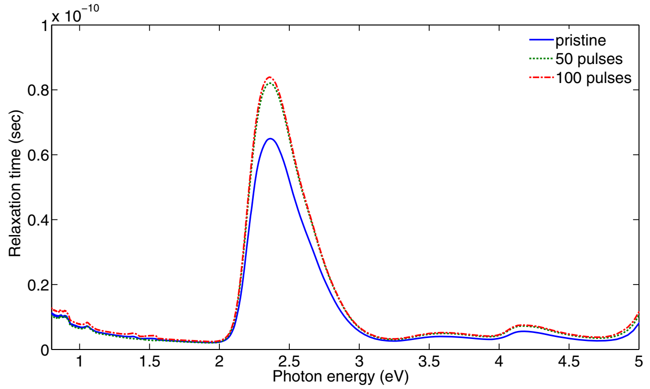

Fig. 12. (Color online) Plot of relaxation time (τ) vs photon energy ($h\nu$) for samples.

et al.[24] may be attributed to the fact that the authors used a different form of polyaniline as well as their samples were prepared under biasing condition. Another parameter can be used to characterize the optical properties of PMMA films, such as the dielectric relaxation time t, which can be evaluated using the relation:[25]

$$\tau = \frac{\varepsilon_\infty - \varepsilon_\mathrm{r}}{\omega\varepsilon_\mathrm{i}}. \tag{10}$$

Figure 12 shows the dielectric relaxation time as a function of photon energy for PMMA films. The peak at $\approx$2.35 eV may be attributed to the band-to-band absorption, because this maximum occurs at $h\nu \approx E_\mathrm{g}$, which corresponds to the onset energy gap for PMMA.

4. Conclusions

In this work the effect of pulsed laser treatment on the optical parameters of red-BS-dye-doped PMMA films was investigated. The linear absorption spectrum of samples has two peaks at 2.5 and 4.45 eV. The magnitude of absorption coefficient at these peaks increased after laser pulse treatment. The band gap energy of samples decreased with increasing the number of laser pulses. The effect of laser pulse irradiation on other optical parameters of films such as refractive index and dielectric constant was also investigated. In all of [them] the real parts of the optical parameter decreased while their imaginary parts increased. It can be claimed that these changes originate from the increase in the peaks of the spectrum of absorption coefficient, which is the effect of the Red BS dye. Results show that with increasing number of laser pulses in the treatment relaxation time increased, which is in good agreement with the decrease in the E_0 and E_d. According to the single-oscillator model, a decrease in the energy of the oscillator leads to an increase in the relaxation time.

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