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Study of Changes in Optical Properties of PMMA Film before and after Irradiation by Laser

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Abstract In this work the effects of Nd: YAG laser 1064 nm on optical properties of pure Poly Methyl Methacrylate (PMMA) were investigated .The absorption and transmission spectra have been recorded in the wavelength range (190-890) nm using UV-Vis spectroscopy. The results show that Egopt of the films decreases with increasing time of irradiation .The absorbance, absorption coefficient, extinction coefficient and refraction index of pure and irradiated PMMA increase with increasing the time of irradiation.

Keywords Laser Irradiation, Optical Properties, Polymer

1. Introduction

Polymers are widely used in diverse fields of everyday life starting from household goods to delicate bio-medical devices . Molding and extrusion are common processes for manufacturing parts from polymers [1]. Micro-parts are produced by different etching techniques. Lithography requires use of masks and is acceptable for mass-production. Excimer lasers are usually used for processing polymers. Their usage is also related to the mask technique. Because of specific features of the excimer lasers there is an overall tendency to replace them by solid-state lasers with the laser-direct-write possibility. The technique offers flexibility, which is especially important at the development stage of micro-devices. The wavelength of the laser is an important parameter for micromachining of polymers. Special care should be taken to minimize the thermal damage of the device when fabricating devices for biomedical applications. UV radiation is able to break chemical bonds directly without significant heat transfer to the surrounding material [2]. Most of the lasers used today for polymer processing are with nanosecond pulse duration. Another way in clean processing of polymers is an application of femtosecond lasers, especially to biodegradable materials [3]. Short pulses inspire rapid evaporation of the material by a high energy input rate, preventing dissipation of excitation in the form of heat. New challenges in real-world applications of the laser micro-fabrication induce the picoseconds lasers with UV radiation. The pulse duration of the lasers is comparable to the time of electron-phonon relaxation and is short enough for "cold" ablation. Easy and effective conversion to UV radiation [4] offers a cost- effective source for photochemical ablation of polymers. Ablation of organic materials, such as polymers, is quite different from that of metals and other inorganic materials. Vaporization and melting are the main methods of material removal for inorganic materials. Most of polymers tend to decompose before evaporation. Long chains of molecules are cut into fragments before they are able to leave bulk of the material. Some fragments are volatile. The ablation rate is closely related to a number of broken bonds in a polymeric chain [5, 6]. Volume of the fragments and monomers is bigger than that of the polymer. Volume explosion is the force for expelling of the material [7]. Below the ablation threshold, swelling of the polymer surface was observed in the laser irradiated areas [8]. Thermal activation of material removal appears as a typical "Arrhenius tail" instead of the definite ablation threshold.

There was no detailed investigation on behavior of different polymeric materials under laser irradiation.

2. Materials and Methods

Poly Methyl Methacrylate **(PMMA)** films were prepared by using casting technique, it was dissolved in glass beaker (30 ml) by chloroform using magnetic stirrer and placed in Petri dish 5cm diameter to prepare the film . Sample was poured in 25 cm^2 glass basin after being cleaned with water using ultrasonic device .The thickness of the sample are (0.05) cm.The spectra of absorption and transmittance were recorded for wavelengths (190 to 890) nm by using double beam spectrophometer UV-Vis- CECIL 2700, provided by optima 300 plus company at room temperature before irradiation by Nd YAG laser, after this the film is irradiated by pulse laser (50and100 pulse) and recorded the absorption

spectra. The extinction coefficient (k) is calculated by using the following equation [9]:

$$k = \alpha\lambda / 4\pi \quad (1)$$

Where α is absorption coefficient and λ is wave length.

The absorption coefficient (α) is calculated by using the following equation:

$$\alpha = 2.303(A/t) \quad (2)$$

Where A is absorption and t is the thickness of films

The refractive index (n) is calculated by using the following equation:

$$n = \sqrt{\frac{4R}{(R-1)^2}} - \frac{R+1}{R-1} \quad (3)$$

The allowed indirect transition energy gap is calculated by using the following equation [9]:

$$\alpha h\upsilon = A(h\upsilon - E_g)^m \quad (4)$$

3. Results and Discussion

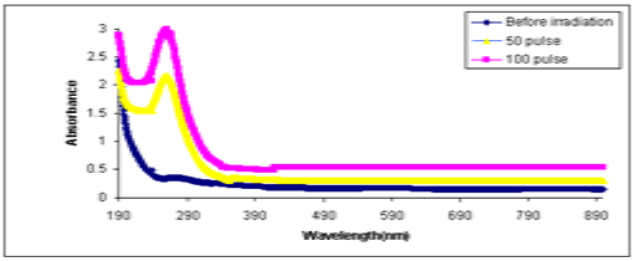

Figure 1. the absorbance spectra as function of incident wavelength

Figure (1) shows the absorbance spectra as function of the wavelength of the incident light. The figure shows that the intensity of the peak increased with increasing of number of pulses but no shift in the peak position, i.e. applied of laser on the polymer do not change the chemical structure of the material but new physical properties is formed

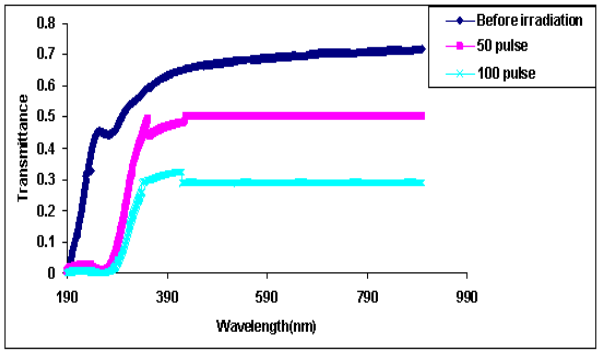

Figure 2. the transmittance spectrum as function of incident wavelength

Figure (2) shows the behavior of optical transmittance of polymer with wavelength. The figure shows that the transmittance decreases with increase the number of laser pulses.

The absorption coefficient (α) is calculated by using the equation (2) .Figure (3) shows that the absorption coefficient (α) as a function of the photon energy, it can be noted that absorption is little at low energy. This means that the possibility of electron transition is little because the energy of the incident photon is not sufficient to move the electron from the valence band to the conduction band ($h\upsilon < E_g$).

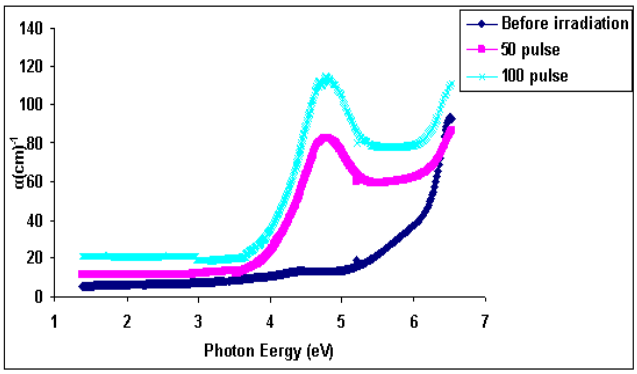

Figure 3. the absorption coefficient as a funtion of photon energy

At high energies, absorption is greater ,this shows that there is great possibility for electron transitions consequently, the energy of incident photon is enough to move the electron from the valence band to conduction band ,this means that the energy of the incident photon is greater than the forbidden energy gap[10] .This shows that the absorption coefficient assists in figuring out the nature of electron transition ,when the values of the absorption coefficient is high ($\alpha > 10^4$) cm^{-1} at high energies, it is expected that direct transition of electron occur ,the energy and moment are maintained by the electrons and photons ,on the other hand when the values of the absorption coefficient is low ($\alpha < 10^4$)cm^{-1} at low energies ,it is expected that indirect transition of electron occur ,and the electronic momentum is maintained with the assistance of the photon .Among other results is that the coefficient of absorption for the PS-$FeCl_2$ composites is less than 10^4 cm^{-1} ,this explains that the electron transition is indirect.

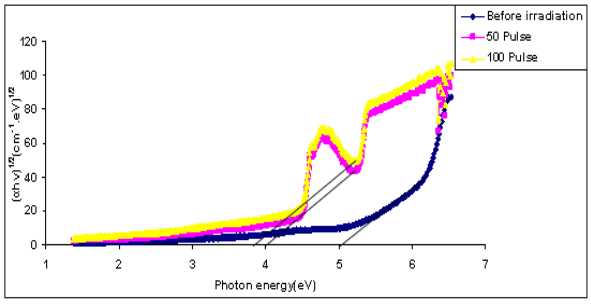

Figure 4. $(\alpha h\upsilon)^{1/2}$ as a function of photon energy

Figure (4) shows the relationship between absorption edge as a function of photon energy .At extension of the

curve to the values of ,we get indirect allowed gap transition .

From Figure (5),we see that the values of energy gap decrease with increase of the pulses of laser .These attributes to the creation of the site levels in forbidden indirect energy gap lead to facilitate the crossing of electron from the valence band to the local levels to conduction band [7].

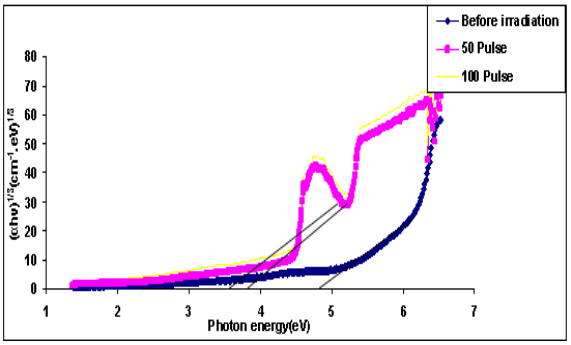

Figure 5. $(\alpha h\upsilon)^{1/3}$ as a function of photon energy

The change of extinction coefficient as a function of wavelength is shown in Figure (6). It was noted that k is increasing with increase of number of laser pulses .The extinction coefficient is high at the longest wavelengths.

Figure (7) describes the change in refraction index for (PMMA) before and after irradiation by laser as a function of wavelength that has occurred due to an increase in with increasing the number of laser pulses. The refraction index decreases at the greatest wavelengths and increases at greatest laser pulse, because the transmission of the longest wavelength is more.

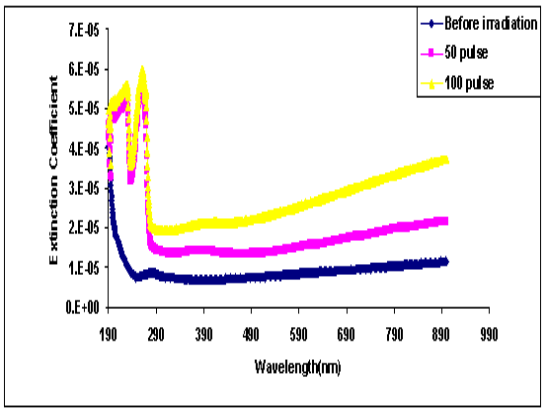

Figure 6. the extinction coefficient as a function wavelength

4. Conclusions

The absorbance, absorption coefficient, extinction coefficient and refraction index increase with increasing the number of laser pulses, except the transmittance. This treatment of polymer by laser (1064nm) leads to decrease the dielectric properties of polymer which leads to guide and develop the use of the polymers in the areas of conductive polymers. The energy gap of indirect transition decreases with increasing the number of laser pulses. The allowed indirect transition optical energy gap is greater than the forbidden indirect transition.

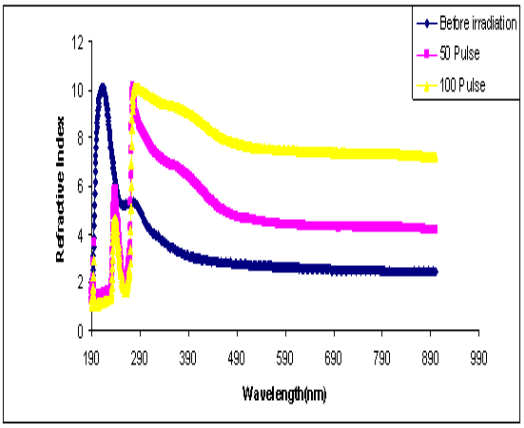

Figure 7. the refractive index as a function wavelength

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