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Investigation of pulsed laser effects on the structure of poly methyl methacrylate polymer

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ABSTRACT

In this work the second harmonic of Nd:YAG laser with 6 ns pulse width and 10 Hz repetition rate was used to modify the surface of red BS dye doped poly methyl methacrylate (PMMA) films. Samples were ablated with 30, 50, and 100 pulses of laser beam. Results show noticeable changes in Fourier transform infrared spectrum of samples, confirms that treatment has made noticeable changes in functional groups of samples surface. According to AFM micrographs there are significant modification in morphology of samples surface. Laser treatment in this range has increased the surface energy of samples. From different measured data it can be claimed that properties of the samples treated with 30 laser pulse is closer to the properties of pristine sample while properties of treated samples with 50 and 100 pulses are very similar to each other.

KEYWORDS

Poly methyl methacrylate;
Laser treatment;
AFM;
FTIR;
Surface energy;
Contact angle;
Hydrophilic;
Hydrophobic.

INTRODUCTION

Recently modification of polymer surface to obtain desired surface properties has attracted much interests. Polymers have become the fastest growing segment of materials with hundreds of polymers being used in an increasing number of applications[1]. Comparability of physical and chemical characteristics of polymers to those of conventional materials and their relatively low cost are the primary reasons for this increased trend[2]. Polymeric materials have unique properties such as low density, light weight, and high flexibility[1,2]. About two decays ago, application of polymers was limited to food packaging, water tubes and so on but in the recent five years they are widely used for much important applications such as producing the artificial parts of body (biopolymers), or electrical insulator, or high resolution optical elements[3,4].

PMMA is an important and interesting polymer because of attractive physical and optical properties decisive about its broad application. This is the thermoplastic material with the good tensile strength and hardness, high rigidity, transparency, good insulation properties and thermal stability dependent on tactility. PMMA have some disadvantages such as brittleness and low chemical resistance which can be eliminated by chemical or physical modification. PMMA contains both hydrophobic (methylene) and hydrophilic (carbonyl) groups in each unit[3]. In addition, it is found that it can produce a large refractive index difference with acryl amide-based photopolymer[5].

There are several methods for modification of poly-

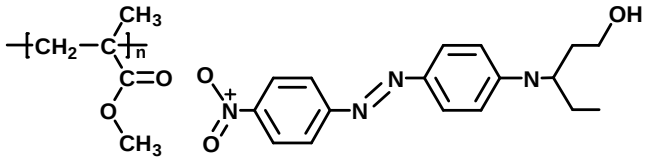
meric surfaces. Physical surface modification methods range from simple flame and corona treatments to more complicated and advanced techniques such as UV, gamma-ray, electron beam irradiations, ion beam, plasma, and laser treatments[2,3,6-10]. These treatments lead the breakage of covalent bonds, promotion of cross linkages, formation of carbon clusters, liberation of volatile species and in certain cases creation of new chemical bonds[11]. Effect of these changes will be appeared in modification of surface energy of polymer, its surface roughness, the hydrophilicity of polymer, and its optical properties. Laser treatment is a convenient way to obtain modifications without affecting the overall quality of the material.

In this work effect of pulsed laser treatment on the structure and optical properties of PMMA polymer is studied experimentally as a function of laser pulse number. To avoid thermal effects, a short pulsed laser was employed at 532 nm wavelength. Red BS dye doped PMMA has high absorption at this wavelength.

This manuscript is organized as follow. After introduction in Sec. 1, experimental details are presented in Sec.2. Sec.3 is devoted to results and discussion, and conclusion can be read in Sec.4.

EXPERIMENTAL

PMMA films were prepared by solving 30 gr PMMA geranol in 300 ml dichloromethane with 0.08 gr red BS dye. PMMA granol was provided by Yazd Polymer Talaei (YPT) Co., Tehran, Iran. A schematic of PMMA molecular structure and red BS dye are presented in Figures 1 (a) and (b). The viscous solvent was poured on a flat glass in a closed box. Solution was left to dry in a atmosphere at room temperature for 24 hours to obtain 0.21 mm thickness red BS dye doped PMMA film. Samples were cut in 1×1 cm pieces and cleaned in deionized water ultrasonically. Prepared films were irradiated by the second harmonic of a pulsed Nd:YAG laser beam at 532 nm wavelength in air. Laser pulse width was 6 ns with 10 Hz repetition rate and was focused with a 8.5 cm focal length lens on target. Laser energy density was 1.6×10^4 J/cm^2 on target surface. Independent variable in this experiment was the pulse number of the treatment. Three red BS dye doped PMMA films were irradiated with 30, 50 and 100 described laser pulses and results are compared.



(a) (b)

Figure 1 : Chemical structure of PMMA (a) and red BS dye (b).

Different analysis were used to study the effect of laser treatment of samples. Total reflectance Fourier transform infrared (ATR –FTIR) analysis was performed using BRUKER FTIR instrument to study the intermolecular interactions between laser pulse energy and molecules of polymer surface. The surface morphology of PMMA films was studied by atomic force microscope (AFM) micrographs, using a Park Scientific Instrument microscope. Static water and diodo-methane drop contact angle measurement was carried out using the sessile drop method on a Kruss G10 contact angle measurement device. All contact angles are the mean value of five measurement on different parts of the films. Varian Cary 500 spectrometer was employed for recording UV-Vis-NIR transmission and reflection spectrum of the pristine and treated red BS dye doped PMMA films.

RESULTS AND DISCUSSION

The most important change in polymer treatments is variation of fundamental groups and molecular binding of polymer surfaces which can be studied by means of ATR-FTIR spectrum. ATR-FTIR spectrum of pristine and treated samples are presented in Figure 2. The wavelengths correspond to FTIR main peaks with their molecular bindings and transmission magnitudes are shown in TABLE 1. Transmission of several peaks belong to C-H bindings on the surface of samples are all increased confirms that incident of photons of laser pulse of 2.33 eV energy with the surface can break these binds. The same is occurred for O-H (2850 and 3030 cm^{-1}), C-O (1060 cm^{-1}), C=O (1760 cm^{-1}) and CH_3 (1670 cm^{-1}) bindings. According to FTIR spectrum, the amount of N-H (3440 and 3550 cm^{-1}) and O-H (3630 cm^{-1}) bindings on the surface of samples are increased which is due to irradiation of PMMA polymers

in air. In their cases carbon atoms are substituted with N_2 and O_2 of air. Although changes are not so much but they have caused noticeable modification in different Physical characteristics of films. It can be seen that spectrum of 30 pulses treated sample is very close to pristine one while spectrum of 50 pulses and 100 pulses treated samples are very similar together. It may be due to existence of a threshold number for the pulses (energy magnitude) to create noticeable changes on polymer surfaces and modification of polymer surfaces for the magnitudes of pulse number smaller than this threshold and larger than it are very similar.

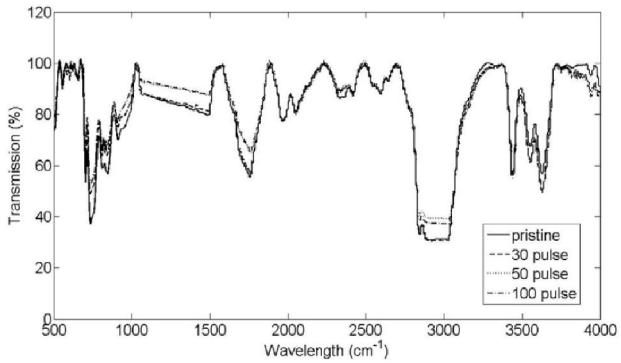


Figure 2 : ATR-FTIR spectrum of pristine and pulse laser treated samples.

TABLE 1 : The wavelengths correspond to FTIR main peaks with their molecular bindings and transmission magnitudes.

Functional group	λ(cm^{-1})	pristine	30 pulse	50 pulse	100 pulse
C – H	735	37.1	49.3	53.8	52.4
C – H	800	63.8	70.8	71.2	70
C – H	910	69.9	74.9	78	78.2
C – H	2840	33.5	32.7	40.5	38.5
C – H	2890	31.5	30.8	39.5	37.6
C – H	3030	32.6	30.7	39.4	37.4
O – H	2850	33.2	33.3	40.7	38.7
O – H	3030	32.6	30.7	39.4	37.4
O – H	3630	56.9	50.6	49.5	49.2
C – O	1060	88.3	89.8	92.6	93.2
C = O	1760	55.5	57.5	65.3	65.9
N – H	3440	57.4	57	56	55
N – H	3550	67.9	62.9	61.7	61.3
CH_3	1670	71.3	72.4	77.4	77.8

Images of the surface of samples with resolution in the order of nanometer taking by atomic force microscope can be seen in Figures 3(a-d), and the plot of surface roughness of samples extracting from these images are presented in Figure 4. Effect of laser pulse impact is clear. Size of nodule like structures on the surface of pristine sample are reduced by the impact of laser pulse and roughness of surface of samples is decreases by increasing the number of incident laser pulses. In fact laser pulse etch polymeric sample surface, and this is an important effect in adhesion and printability of polymer surfaces. After laser pulse irradiation the remain structure of samples surface have very strong binding to bulk material leads to strong adhesion of irradiated sample.

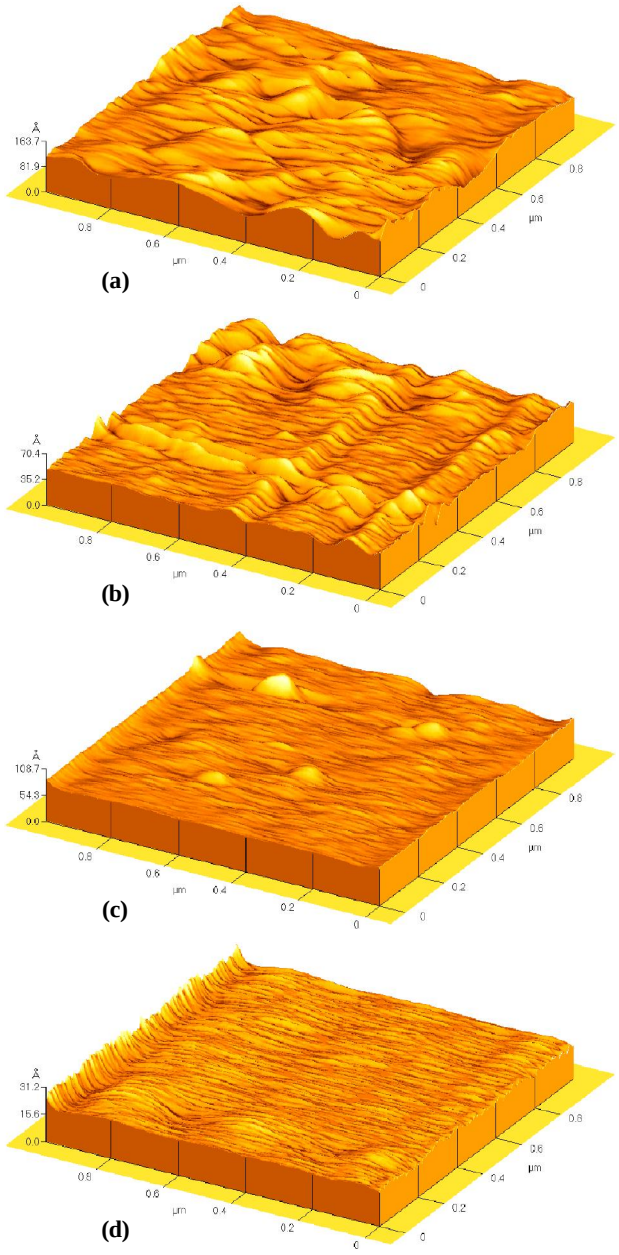


Figure 3 : AFM micrographs of (a) pristine sample, (b) 30 pulses, (c) 50 pulses and (d) 100 pulses treated samples.

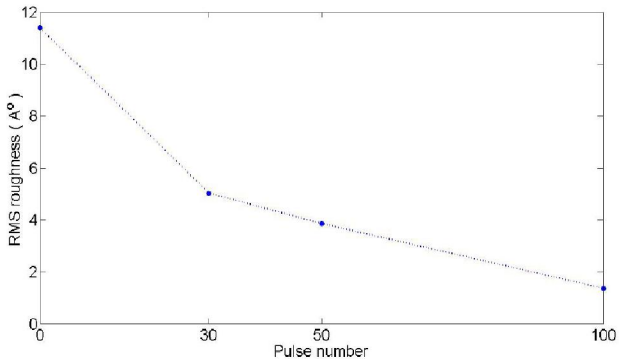


Figure 4 : RMS roughness of the surface of samples after pulsed laser treatment versus pulse number.

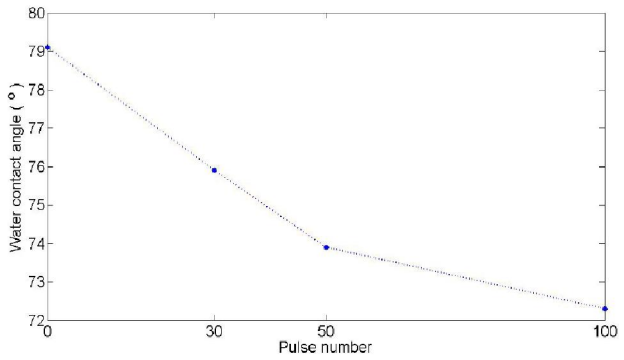


Figure 5 : The water contact angle with the surface of pristine and laser treated red BS dye doped PMMA films versus pulse number.

Another important parameter in the treatment process is surface energy. Surface energy of samples can be calculated by measuring the water (a polar liquid) and diiodomethane (a disperse liquid) contact angle with the surface of PMMA samples which are presented in TABLE 2. Furthermore water contact angle is a scale for hydrophilic or hydrophobic characterization of polymers. Change of water contact angle of treated samples versus pulse number in treatment is plotted in Figure 5. Using contact angle magnitudes, the polar and disperse parts of surface energy of samples is calculated by Owens-Wendt method[12] which is presented in Figure 6. Extracted magnitudes for these three quantities are also written in TABLE 2. Because most of molecular structure of PMMA surface have polar bindings, diiodomethane contact angle and disperse part of surface energy are not changed noticeably in this experiment. In contrast the water contact angle is decreased with increasing the laser pulse number in the treatment, shows an increase in the polar part of surface energy. However after adding these two magnitudes to find total surface energy one can see that with pulse laser treatment of PMMA surface the surface energy has not been changed so much in comparison with other methods of surface treatment. Especially in

TABLE 2 : Water and diiodomethane contact angle with target surface. The magnitudes for surface energy is extracted from contact angles using Owens-Wendt method.

Pulse number	Contact angle (°)		Surface energy (mN/m)		
	Water	Diiodomethane	Polar	Disperse	Total
0	79.1	39.8	3.78	39.73	43.51
30	75.9	40.3	4.96	39.46	44.42
50	73.9	36.7	5.36	41.22	46.58
100	72.3	38.3	6.18	40.45	46.63

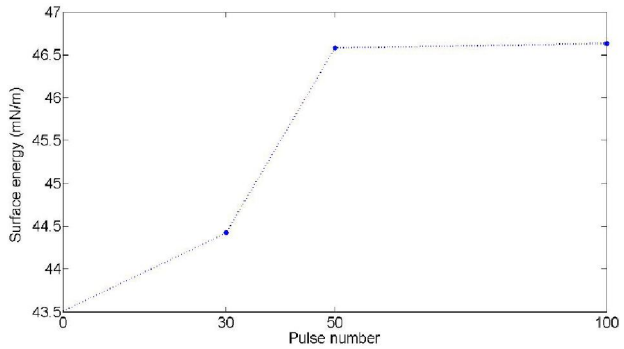


Figure 6 : Variation of surface energy of samples after pulsed laser treatment.

the treatment experiments of PMMA with UV water contact angle changes is larger[3,12].

The optical transmittance of red BS dye doped PMMA treated by different laser pulse number are presented in Figure 7. Transmittance of different samples are very close but noticeable changes can be observed at peaks of spectrum. The same is occurred for absorption coefficient spectrum of samples which are plotted in Figure 8. The optical absorption coefficients of samples are evaluated from the transmittance data using the following relation;

$$\alpha = -\frac{1}{d}\ln\left[\frac{1}{T}\right] \qquad (1)$$

in which α is the absorption coefficient, d=0.21 mm is the thickness of PMMA films and T is transmittance. Similar to other results the transmittance and absorption coefficient of sample 1 treated by 30 laser pulses is very close to the pristine sample while for sample 2 and 3 treated by 50 and 100 laser pulses data are close to each other. Absorption coefficient of samples 2 and 3 show an increase at the absorption peak, confirms that the optical band gap energy of samples are changed due to treatment.

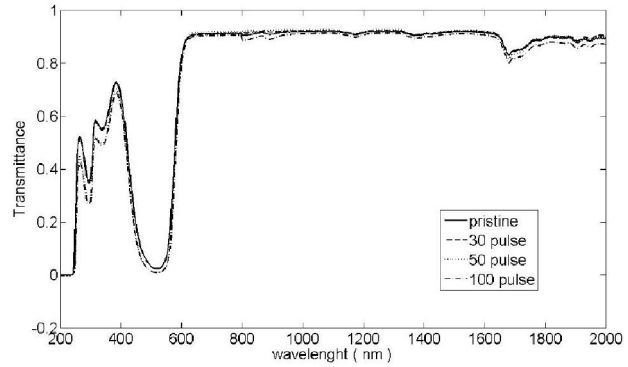


Figure 7 : The transmittance spectrum of samples.

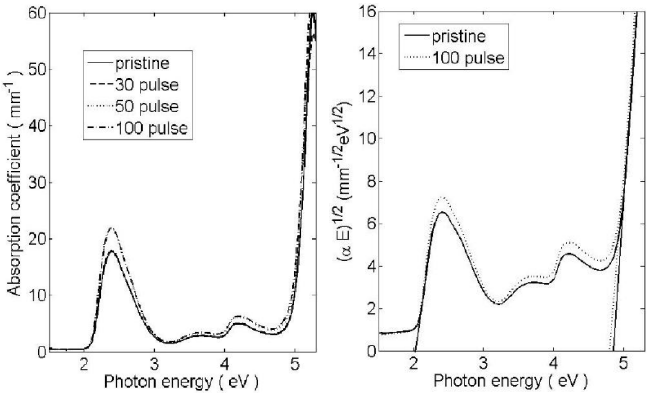


Figure 8 : (a) Absorption coefficient of four samples before treatment and after treatment by different number of laser pulses. (b) $\alpha E^{1/2}$ versus photon energy to illustrate Tauc method. The interpolation of linear part of the curve with photon energy axis indicates the magnitude of band gap energy.

The optical energy gap of PMMA films are deduced from the intercept of the extrapolated liner part of the plot of $(\alpha E)^{1/2}$ versus the photon energy E with abscissa which is illustrated in Figure 8 (b) for pristine and 100 pulses treated sample. This followed from the method of Tauc et al.[13] where:

$$\alpha E = B(E - E_g)^P \quad (2)$$

In this equation α is the absorption coefficient, E is the photon energy, and B is a factor depends on the 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. The index p has discrete values like 1/2, 3/2, 2, more depending on whether the transition is direct or indirect and allowed or forbidden. In the direct and allowed cases, the index p = 1/2 whereas for the direct but forbidden cases it is 3/2. But for the indirect and allowed cases p = 2 and for the forbidden cases it is 3 or more. Taking p = 2 corresponds to indirect allowed transitions[13] the band energy of films are calculated using Tauc relation. Figure 8(b) displays plots of $(\alpha E)^{1/2}$ versus the photon energy E for pristine sample based on Tauc method. Two linear parts of this plot extrapolate the photon energy axis at 2.039 eV and 4.8611 eV. The first point indicates the energy gap of Red BS dye while the second point belongs to PMMA band gap energy. The same is done for all samples and results are written in TABLE 3. Variation of PMMA band gap energy versus pulse number in treatment is plotted in Figure 9(a). The change of band gap energy of dye is too small to calculate. What can be say is that this magnitude is 2.039 eV for pristine and 30 pulses treated samples and is increased to 2.040 eV for samples 2 and 3. But changes of band gap energy of PMMA can be calculated. Results show that this parameter is decreased with increasing the pulse number in the treatment.

TABLE 3 : Band gap energy of PMMA and red BS dye calculated by Tauc method.

Energy gap (eV)	pristine	30 pulse	50 pulse	100 pulse
Red BS dye	2.039	2.039	2.040	2.040
PMMA	4.842	4.831	4.826	4.816

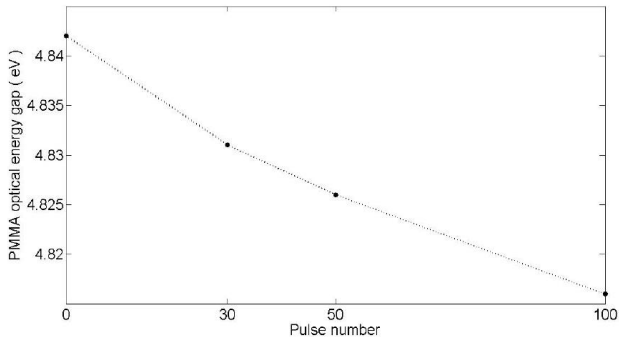


Figure 9 : The variation of band gap energy of PMMA polymer after laser treatment.

COCLUSION

Effect of 532 nm pulsed laser beam on the structural properties of PMMA thin film is investigated experimentally. The photon energy of laser pulse is 2.33 eV smaller than the band gap energy of PMMA film which is about 4.8 eV. In this case the target is transparent against the beam. But adding red BS dye to PMMA film with energy gap of 2.039 eV has changed the scenario. Red BS dye can absorb the energy from the laser beam due to it smaller band gap energy in comparison with photon energy and the thermal effects

caused by this absorption can modify the polymer structure. Of course this modification is not so strong because of small amount of doped dye in polymer. FTIR spectrum of irradiated samples confirm that the chemical structure of polymer film is changed. 30 number of laser pulse at this range do not cause noticeable changes and the properties of irradiated film with 30 laser pulse is close to pristine film but for the samples irradiated with 50 and 100 number of laser pulse these are more noticeable. Results of structural modifications are appeared in the surface energy of samples. It can be seen that the 532 nm wavelength laser pulse can increase the surface energy red BS dye doped PMMA sample specially its polar part make it a more hydrophilic polymer.

In the processes of modification the optical band gap energy of red BS dye doped PMMA films is also decreased. It may be due to the fact that energy of laser beam in sample generates molecules with perturbation in their valance or conduction energy levels leads to formation of defect levels in the material. Decreasing the band gap energy is due to formation of defect levels.

Modification of polymer surface morphology is more noticeable because of impact effect of laser pulse on the surface. This impact may etch the impurities and particles with weak bonding energy from the surface of PMMA, leads to decreasing the surface roughness. So in the case of surface morphology the intensity of laser pulse is more effective parameter than photon energy. Clearly larger number of laser pulse has decreased the roughness of surface more effectively.

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