ABLATION ON POLYMETHYLMETHACRYLATE BY ARGON FLOURIDE EXCIMER LASER[*]

Aishah Zarzali Shah, Noriah Bidin and Yaacob Mat Daud

Laser Technology Laboratory, Physics Department
Faculty of Science, University Teknologi Malaysia, 81310 UTM Skudai, Johor, Malaysia
Email: aishahzarzalishah@yahoo.com

ABSTRACT

Laser ablation with pulsed UV laser such as excimer laser enables fine micromachining of a variety of optical materials, including organic material. Polymer (organic material) is always been the subject of interest in laser ablation research field. The aim of the research is to analyze the ablation effect on the organic material. UV light from ArF excimer laser was utilized as a source of ablation. The fundamental wavelength of UV light is 193 nm with pulse duration of 12 ns. PMMA was employed as polymer specimen. The target was exposed at variable time of exposure in the range of 5 s to 50 s. The exposed material was analysed using ATR-FTIR spectrometer. The results obtained showed that the chemical bonding of PMMA have been weakened due to the photochemical mechanism. Consequently, this results increases the refractive index of PMMA. However, at longer exposure or large number of exposure the physical changes become unstable.

Keywords: ablation, excimer laser, PMMA, chemical bonding, photochemical, refractive index

INTRODUCTION

Research and development in excimer laser polymer ablation have been actively pursued for some twenty years, as its application in micromachining had emerged high revolution technique for material removal [1]. A number of reviews have appeared over the years charting progress made in this field at various stages of its development, for example, during 1980's by Srinivasan [2], and the early 1990's by Dyer [3]. The UV radiation performs electronic excitation of some organic bonds and so initiates photochemical reaction [4]. These modify the polymeric structure in a controllable way to obtain specific functional properties of the irradiated area [5]. In general, two typical mechanism of material ejection by UV laser ablation of polymers are thought to exist: *Photochemical and photothermal*. Bond breaking and material ejection are believed to occur directly from the excited electronic state in the photochemical mechanism.

Among many polymeric materials, PMMA has been the most intensively examined target material to elucidate ablation mechanisms [6] as it is known that PMMA will undergo unzipping, e.g photo-initiated scission followed by thermal unzipping might be important [3]. In this present paper, the effect of ablation on PMMA is discussed. The changes in chemical bonding is investigated using ATR spectroscopy while the refractive index changes is determined using Brewster angle method.

THEORY

A photochemical process is a chemical reaction which takes place under the influence of light. Only light which is absorbed can result in a photochemical effect. The primary

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interaction is an interaction between one molecule and one photon [7]. Any photo-chemical events start with the absorption of a photon by a molecule M, with production of an excited molecule M*

$$(a) \qquad M + h\nu \rightarrow M^* \text{ (absorption)}$$
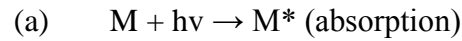
The excited molecule M* may now react chemically, either by rearrangement or, for instance, by reaction with another species N:

$$(b) \qquad M^* + N \rightarrow P$$

The steps (b) which involves chemical, the excited molecule M* is the primary photo-chemical process. Thereafter the products P may undergo further reactions which are the secondary processes.

Hooke's law was used to describe the behaviour of springs and the force involved. An alternate form of Hooke's law involves the period of oscillation of the spring. Hooke's law also can be used to estimate the frequency of the vibration, such as

$$\nu = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \qquad (1)$$

where ν is vibrational frequency of the chemical bonding, in wavenumber (cm^{-1}), c is velocity of light = 3 x 10^{10} cm/sec, k is force constant, indicating the strength of the chemical bond (dynes/cm) and μ is reduced mass, which is given by

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \qquad (2)$$

where m_1 and m_2 are the masses of the two atoms (in kilograms per molecule) Hooke's law can be used to calculate the strength of the bonding (N/m) by knowing the wavenumber of chemical bonding.

METHODOLOGY

Polymethylmethacrylate (PMMA) has been chosen to be a polymer specimen. Polymer surface is always smooth and chemically unreactive. PMMA was chosen as the sample material because of the good ablation uniformity under UV irradiation. PMMA is an amorphous thermoplastics which is optically transparent with a refractive index of 1.62, unaffected by moisture, and offers a high strength-to-weight ratio. In this study, PMMA with dimension of 5 cm × 4 cm was ablated with UV lights from ArF excimer laser (EX5-/200-110) production of GAMlaser. The laser is controlled via a personal computer. The duration of exposure can be varied according to the experimental requirement. The output laser wavelength was 193 nm with the pulse duration of 12 ns. The polymer specimen was ablated at various time of exposure ranging from 5 s to 50 s. ATR-FTIR Model Nicolet Avatar 370 DTS was utilized to analyze the photochemical effect on ablated PMMA. The whole experiment set-up is shown in Figure 1.
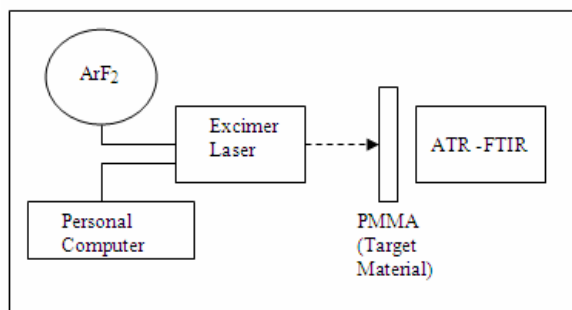
**Figure 1** : The experimental arrangement

Following the examination under FTIR-ATR, the refractive index was measured in order to check any optical property changes due to photochemical reaction. In this experiment, the same ablated sample was employed. The refractive index of ablated material is measured using Brewster angle method (Figure 2). In this experiment, He-Ne laser was utilized as a source of light. The sample is placed on a rotating table. The laser beam is incident at an angle and the power of reflection beam was detected using photodiode which coupled to digital power meter. The Brewster angle is identified when the reflection power is minimum or zero. The refractive index is computed as a tangent of Brewster angle.
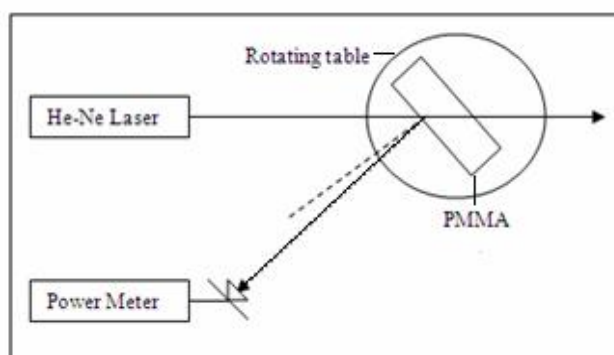
**Figure 2** : Schematic diagram for Brewster angle measurement

RESULT AND DISCUSSION

Typical spectrum obtained from ATR-FTIR analysis is shown in Figure 3. The spectrum is plotted in reflectance percentage against the wavenumber (cm^{-1}). However, the reflectance value of the ATR is equal with the transmission value in FTIR, thus the reflectance percentage was considered as its transmission value. From the gained spectrum, there are several peaks appeared corresponding to the wavenumber. Every peak represents the bonding existed in ablated PMMA. Three major peaks were chosen from the spectrum in order to determine the bonding changes due to the variation in exposure. The peaks chosen are identified as C-O bonding (wavenumber = $1147 cm^{-1}$ and $1241 cm^{-1}$) and C=O bonding (wavenumber $1726 cm^{-1}$) since these bondings show the most intense transmission in the spectrum.
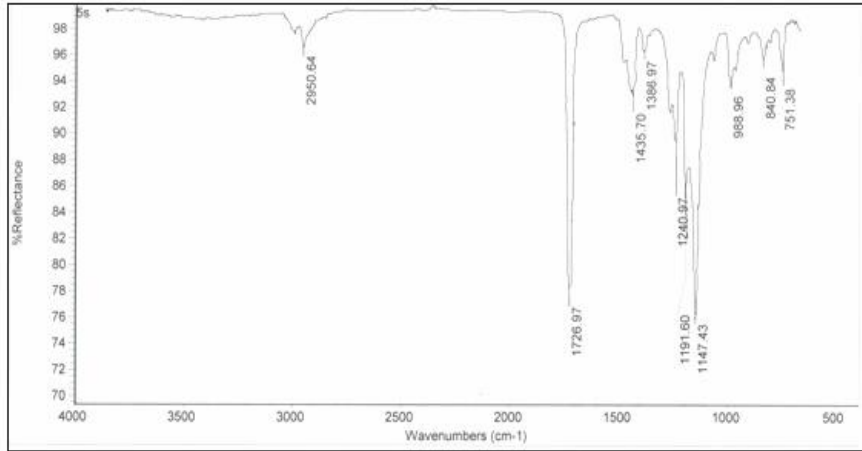
Figure 3 : The ATR Spectrum of ablated PMMA

Frequency each of chosen peak indicates the vibrational frequency of the chemical bonding. This frequency is utilized to estimate the force of the chemical bonding. The bonding strength (N/m) was calculated using Equation (1). It is convenient to use relative bonding strength rather than absolute value. This can be obtained by dividing the bonding strength of ablated sample k, with pure or nonablated sample k_o. The calculated data of relative bonding strength (N/m) are plotted against the time of exposure (Figure 4).
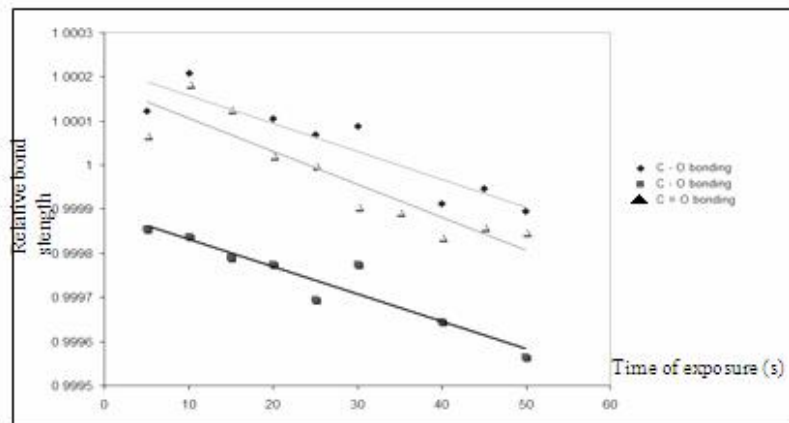

Figure 4 : Relative bonding strength against time of exposure

The graphs in Figure 4 show that the strength of the chosen bondings are found inversely proportional as the time progress. These indicate that the chemical bonding of C-O and C=O are getting weaker. The weakness are due to the UV light absorption during ablation using excimer laser. However, no chemical bonding was broken in this experiment since no new peaks appear or vanish from the ATR spectrum. This is due to the weak energy delivered by the ArF excimer laser. The transparency of PMMA material is sustained even after been exposed by 1000 number of pulses. Hence, this type of material is suitable to be coating optical component. Its transparent property is maintained after

ablating the material. The weakening of the chemical bonding is due to the photochemical mechanism which lead to bleach and crosslinked in polymer [4].

The refractive index of the ablated PMMA was measured using Brewster angle method. The results of the measurement are plotted such as shown in Figure 3. The bell shape curve is obtained. The optimum refractive index achieved was 1.70 which corresponding to the exposed time of 35 seconds. Greater than 40 seconds time of exposure, the refractive index is decreased. This suggested that the ablation on PMMA cannot be longer than 40 seconds, it transparency is concerned.
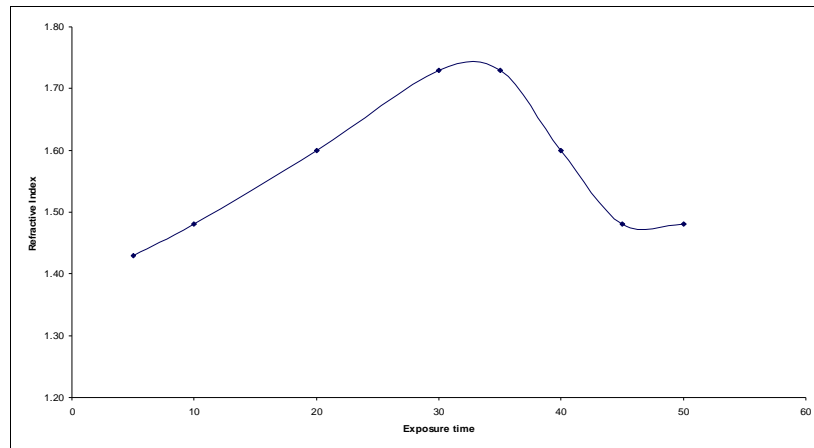
Figure 5 : Refractive Index upon the time of exposure

The increase of the refractive index is due to the partial separation of the side chain from the PMMA molecule. This implies a volume contraction by Van der Waals interaction, leading to a local increase of the mechanical density and consequently of the refractive index. The change of refractive index shows that the effect of UV ablation can also modify the optical property of PMMA. Since the refractive index of the ablated material is increased, this indicates that, the PMMA become more harden. However the ablation period is limited up to 40 seconds. Greater than that periods the refractive index suddenly drop. The drop of the refractive index can be explained due to the degradation of the main polymer structure.

CONCLUSION

PMMA was ablated by ArF excimer laser. When laser beam interact with PMMA sample, a photoluminescence of violet colour was observed. When photoinduced on such material, this leads to optical and chemical alteration as its chemical bonding and its refractive index. The effect of ablation was analyzed using ATR – FTIR spectrometer and Brewster angle method. Two major chemical bondings had been affected they are C-O and C=O. The strength of the chemical bonding have been reduced. In constrast the refractie index of the ablated material is found increasing. This showed that the ablated PMMA become more harden. However, that is only true if the ablation time is not more than 40 second. When photoinduced on such material, it will lead to optical and chemical alteration such as its chemical bonding and its refractive index.

ACKNOWLEDGEMENT

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