

Ultraviolet laser ablation and decomposition of organic materials

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ABSTRACT - Pulsed, ultraviolet radiation from an excimer laser with wavelengths of 193nm or 248nm, a pulse width of about 20ns, and fluences above a threshold value causes the ablation and etching of the surface of solid polymethyl methacrylate. The reaction which is termed 'ablative photodecomposition' results in the break up of the polymer chains to oligomers of much lower molecular weight along with the production of gases such as C₂, CO, CO₂, and the monomer, methyl methacrylate. The gaseous products are ejected from the surface at supersonic velocities and carry the solid particles of the polymer along. In recent work, the ablation process has been probed by imaging the surface of the polymer as well as the plume by a second laser which produced short, visible pulses and which was fired at a preset time interval after the first laser.

INTRODUCTION

The advent of the excimer laser has made it easy to study the action of pulsed, ultraviolet radiation of power densities of 1 - 100 Mw/cm² on a variety of organic solids. The resulting phenomenon of ablative photodecomposition has attracted wide attention over the past decade (ref. 1,2). Scientific studies have dealt with the products of the decomposition and the chemical physics of the ablation process. Technological processes which use the excimer laser to pattern polymeric films as well as living tissue such as the cornea in the human eye are beginning to find commercial acceptance. We describe here the action of pulsed, UV laser radiation on one polymer, polymethyl methacrylate (= PMMA), a system in which there are sufficient data to provide some understanding of the nature of the laser-polymer interaction.

CHARACTERISTICS OF UV LASER ABLATION

Fig. 1 shows the UV absorption spectrum of commercial PMMA with a molecular weight of 10⁶. At the three principal wavelengths of the excimer laser which are noted in this figure, both the absorption and etching characteristics of the material vary significantly. The ablation of the surface of a polymer by a UV laser pulse

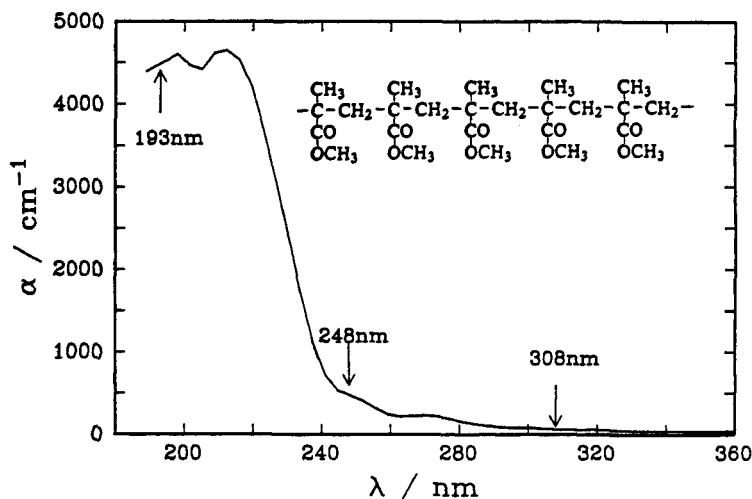


Fig. 1. Ultraviolet absorption spectrum of PMMA. The arrows point to the wavelengths of the strong emission lines from an excimer laser

is a function of the energy deposited in the solid in unit time. If a typical UV pulse has a full width at half-maximum (FWHM) of 20ns and an energy of 450 mJ and the size of the beam at the polymer surface is 1.5 cm², the fluence at the surface will be 300 mJ/cm² and the power density will be 1.5×10^7 W/cm². When this pulse strikes the surface a loud audible report will be heard and, depending upon the wavelength, 0.01-0.1 μ m of the material would have been etched away with a geometry that is defined by the light beam. Typically, UV laser ablation is carried out with a succession of pulses. The depth etched is a linear function of the number of pulses but, at wavelengths at which the polymer absorbs weakly (absorptivities of < 4000 cm⁻¹), the first few pulses do not cause any etching. This phenomenon which is called 'incubation' will be discussed in some detail later. Fig. 2 shows a plot of the average etch depth per pulse vs fluence in the ablation

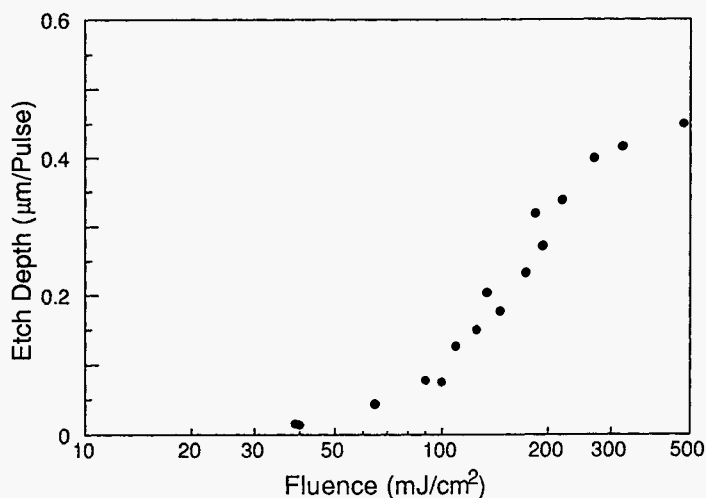
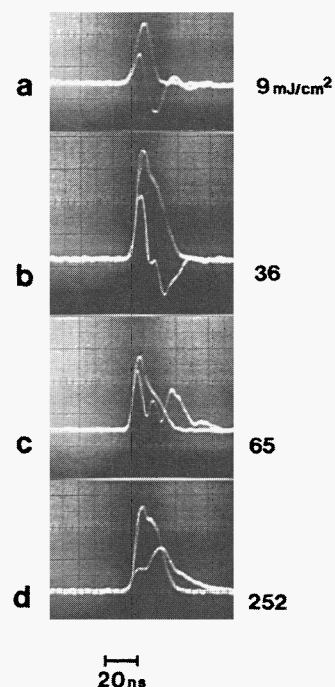


Fig. 2. Plot of etch depth vs log (fluence) in the laser ablation of PMMA at 193nm.

Fig. 3. Time synchronized laser and stress waveforms for laser-irradiated PMMA at 193nm. The larger amplitude signal is the laser pulse which varies slightly in shape due to different operating voltages being used.



of PMMA with 193nm pulses. In this and all subsequent discussion, although the fluence (number of joules per pulse/ unit surface area of sample) is quoted, it is important to remember that it is the power density (power/unit area) that matters and discussions based on fluence are acceptable only so long as the pulse width is constant. However, the major portion of the data that are currently in the literature is based on pulse widths of 15-30ns so that this imprecision is not serious. The profile of the etch plot in Fig. 2 is the typical "lazy S" form of a polymer with a moderate or weak absorption at the laser wavelength. There is always a threshold value for the fluence for the onset of etching and it is difficult to pinpoint this value exactly because the etch curve approaches the abscissa asymptotically. This initial region of slight etching is followed by a steeply rising region in which the etch depth/pulse is linear with the fluence when the latter is plotted on a logarithmic scale. This linear region terminates in a third region in which the sensitivity of the polymer to etching rises more gradually or even decreases with increasing fluence. In comparison to the behavior at 193nm, the etching of PMMA by 248nm pulses has a higher fluence threshold, a steeply rising middle region and an abrupt flattening in the third region. The etch depths per pulse can be as large as 4 μ m. It should be strongly emphasized that at an ultraviolet wavelength (e.g., 308nm) at which PMMA has a negligible absorption, etching does not decrease to zero. Instead, as the fluence is increased steadily, etching does set in but the two characteristics which are readily seen in UV laser ablation are no longer to be observed. These are the control that can be exercised over the depth of etching in a reproducible manner and the lack of thermal damage to the substrate. It is reasonable to say that at 308nm, the characteristics of the etching change from photoablation to the thermal ablation that is observed at visible and infrared wavelengths.

At the laser wavelength of 248nm, the principal product of the ablation of PMMA is an oligomer of much lower molecular weight (ref. 3). The number average molecular weight of the product is 2500 and the weight

average molecular weight, 4500. In addition there are gaseous products such as C_2 , CO, and CO_2 but $< 1\%$ of the monomer. The composition of the products is different when a laser wavelength of 193nm is used. In addition to the gases mentioned above, the monomer accounts for 18% of the polymer that is decomposed. A polymer of low (*ca.* 1000) weight is also formed.

The dynamics of the ablation process has been followed in several ways. Dyer and Srinivasan (ref. 4) glued a strip of polyvinylidene fluoride, a piezo-electric detector, to a thin sample of PMMA and measured the electrical voltage that was generated in the detector when a UV laser pulse was directed at the free surface of the PMMA. Fig. 3 shows traces of the output of the UV laser at 193nm as a function of time superimposed on the electrical signal from the piezo-electric detector. In each frame the unidirectional trace is the output from the laser and the scale of the ordinate was changed from frame 'a' to 'd' to accommodate the increase in the fluence. At 9 mJ/cm^2 the threshold for the ablation of PMMA at this wavelength is not exceeded and the laser pulse causes very little decomposition. The absorbed photon energy transiently heats the surface which expands but immediately thereafter cools to regain its original volume. This rapid expansion and contraction are recorded as a sinusoidal signal in Fig. 3a. At 36 mJ/cm^2 (Fig. 3b) ablation barely begins and a unidirectional signal is seen to be superimposed on the sinusoidal signal. At 252 mJ/cm^2 , there is strong ablation and the piezo-electric detector records (Fig. 3d) only a strong unidirectional signal which begins almost at the same time as the laser pulse and ends soon after the laser pulse ends. A calibration of the magnitude of the detector signal showed that pressures as large as a 1000 atmospheres were developed inside the polymer film and this would account for the ejection of the products with considerable velocity. The ejecta which are usually referred to as a 'plume' have been studied by mass spectrometry (ref 5,6), emission spectroscopy (ref. 7), and laser-induced fluorescence (ref. 8). All of these methods give information about products from a single pulse but do not resolve the events that occur within that time.

Recently, several groups have reported (ref. 9-12) the results of laser ablation studies in which pulsed, visible radiation from a second laser has been used to probe the nature of the ablation phenomenon. In one such study (ref. 10), a dye laser with a pulse of $< 200\text{ps}$ was electronically coupled to the pulse from an excimer laser so that either the polymer surface that is ablated or the plume that emerged from the surface could be photographed at a preset time delay after the start of the UV pulse. A typical set of results from the ablation of PMMA at 248nm in an air atmosphere is shown in Fig. 4. The polymer surface is seen in profile in these frames so that it appears as a horizontal line near the bottom of each picture. The first indication of ablation is a blast wave which appears above the surface and travels at velocities $> 10^5 \text{ cm/sec}$. The blast wave is undoubtedly driven by the expansion of gaseous products which escape from the irradiated volume and

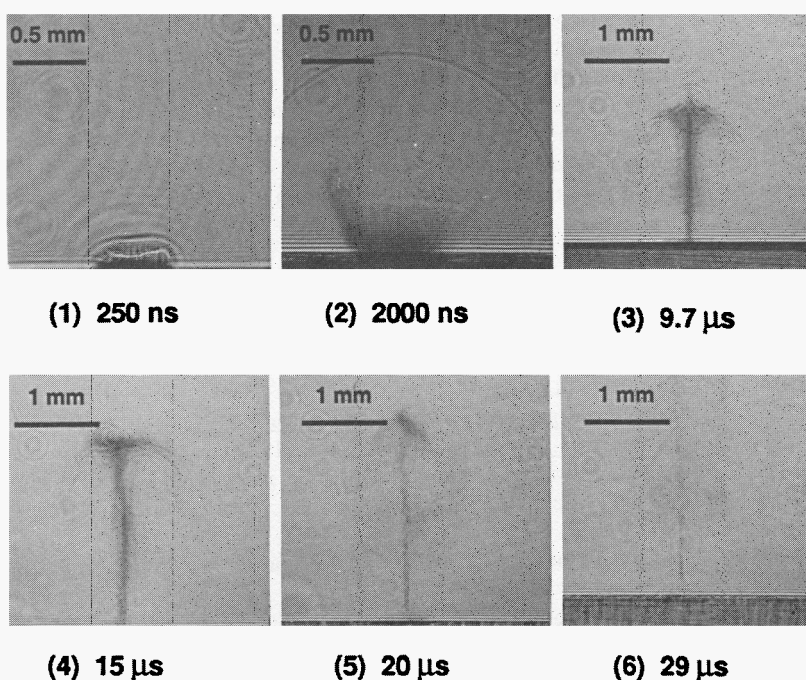


Fig. 4. Photographs of plume from ablation of PMMA with 248nm, 2.1 J/cm^2 pulses. The edge of the polymer sample which is seen in profile lies parallel to the bottom of each frame. Note change in the scale from the top row to the bottom row. The width of the ultraviolet beam is $600 \mu\text{m}$.

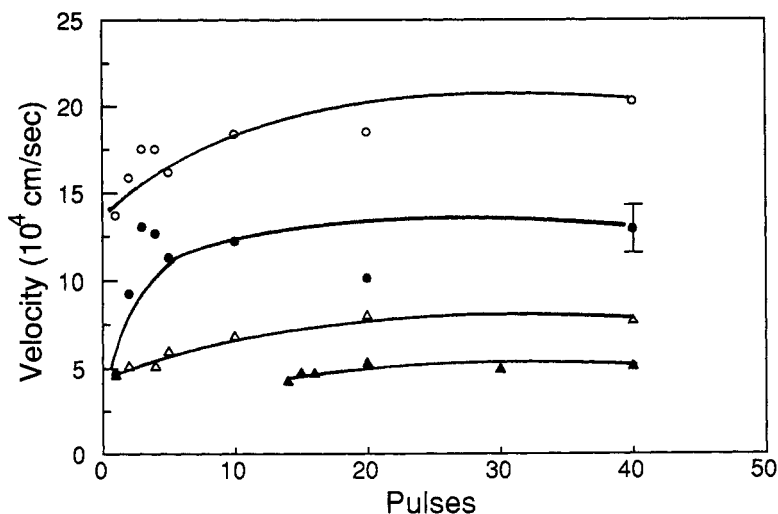


Fig. 5. The velocity of the blast wave at a constant delay (500ns) plotted against the number of the pulse in the ablation of PMMA at 193nm and 248nm at different fluences. open circles: 193nm, 0.67 J/cm²; open triangles: 193nm, 0.16 J/cm² Filled circles, 248nm, 2.1 J/cm²; Filled triangles, 248nm, 0.9 J/cm²

spread hemispherically. The gaseous material is followed by a plume of solid material which travels at subsonic velocity and maintains a direction that is normal to the polymer surface. The pattern is similar to that of a mixture of low and high-molecular weight materials that flow at high-velocity through a nozzle.

It was mentioned earlier that PMMA displays the phenomenon of incubation, i.e., a need for several initial pulses before the etch depth/pulse settles to a steady value at a given fluence and wavelength. When the ablation plume was probed by high-speed photography, it was discovered (ref. 13) that during the incubation period, the polymer did undergo decomposition by the laser pulse(s) but a minimum of material was ejected and there was no net etching of the surface. Instead, the exposed area of the surface was filled with a voluminous, friable mass which was readily dissolved out by a solvent such as a mixture of methyl isobutyl ketone and isopropyl alcohol (3:1). The reason that this material was not ejected can be understood by the data in Fig. 5 which shows a plot of the velocity of the blast wave as a function of the number of the pulse in the sequence of ablation pulses. It is seen that the velocity of the blast wave which, in turn, reflects the velocity of the gaseous products that drive it does not reach its maximum value at a given fluence and wavelength until a succession of pulses have irradiated the polymer surface. If UV ablation of polymers is viewed as a volume explosion (ref. 14), a combination of gas production and break-up of the long chains of the polymer molecules is necessary to cause ablation. The phenomenon of incubation is consistent with this picture.

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