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Evaluation of laser ablation threshold in polymer samples using pulsed photoacoustic technique

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Abstract. The acoustic signals generated in solids due to interaction with pulsed laser beam is used to determine the ablation threshold of bulk polymer samples of teflon (polytetrafluoroethylene) and nylon under the irradiation from a Q-switched Nd:YAG laser at 1·06 μm wavelength. A suitably designed piezoelectric transducer is employed for the detection of photoacoustic (PA) signals generated in this process. It has been observed that an abrupt increase in the amplitude of the PA signal occurs at the ablation threshold. Also there exist distinct values for the threshold corresponding to different mechanisms operative in producing damages like surface morphology, bond breaking and melting processes at different laser energy densities.

Keywords. Polymers; damage threshold; pulsed photoacoustics.

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1. Introduction

High power lasers are becoming increasingly important for controlled removal and etching of organic surfaces in both industrial and medical sectors. In order to obtain the required amount of etching of the sample surface, the laser energy has to be controlled quite accurately, depending on the laser damage threshold of the sample. Removal of polymeric materials under intense laser irradiation can be termed as 'ablative photodecomposition' (Dienstbier *et al* 1990). Some transparent polymeric materials are also widely used in the fabrication of high power laser optical components like prisms, lenses and beam-splitters and also in nonlinear optics while opaque polymers find applications in areas like photolithography. It would therefore be of considerable significance to investigate the optical strength of polymeric materials. The measurement of the optical damage threshold of polymers is thus important for determining the laser energy density required for controlled etching of the material surfaces. There are various methods like surface morphological studies, visual observation of the plasma emission from the target and the reflectivity variation studies from the target to evaluate the ablation threshold of the sample. Most of the data on laser damage are obtained through microscopic visual inspection of the laser damaged surface, which is a tedious and not an *in-situ* process. Techniques based on phenomena like photothermal deflection and photoacoustic effects have also been proven recently to be very effective in evaluating laser ablation thresholds of both

transparent and opaque samples (Srinivasan and Braren 1989; Sell *et al* 1989; Rosencwaig and Willis 1980). The present paper describes the use of pulsed photoacoustic (PA) technique to evaluate the damage threshold of some bulk polymer samples. This method has the added advantage that it can be used as an *in-situ* laser damage monitoring technique for both bulk and thin film samples (Rosencwaig and Willis 1980).

It is well-known that the interaction of laser beam with matter produces acoustic pulses in the target material. At lower laser intensities, acoustic waves are generated essentially by thermo-elastic stress. The analysis of the acoustic pulses produced at comparatively lower laser energies can be used for non-destructive testing (NDT) and evaluation of materials (Harada *et al* 1989). At higher laser energies, where damage of the surface occurs, resulting in plasma formation, the ablation of the material from the surface causes a reactive force which acts as an intense source of acoustic waves (Harada *et al* 1989). IR lasers give rise to multiphoton excitation over the vibrational manifolds of the ground electronic states of the polymeric sample which is then followed by thermal decomposition resulting in the ablation or damage of the target surface. For ablation to take place, there exists a threshold laser energy density beyond which irreversible damage of the sample surface occurs.

The absorption of the incident pulsed radiation gives rise to transient thermal variations due to the heat released through non-radiative channels of de-excitations in the sample (Patel and Tam 1981). Many of the material parameters influencing the thermal balance of the system get significantly altered during ablation. Such sudden heating of the sample also causes pressure waves to be generated in it and these can be detected by an appropriate acoustic transducer. In the case of solids, the sample is placed in firm contact with the transducer for optimum signal amplitude since the acoustic impedance at the sample-transducer interface is minimum in such a configuration.

2. Experimental technique

The schematic diagram of the experimental set-up for evaluation of the damage threshold of bulk polymer samples using PA technique is given in figure 1. The sample, in the shape of a disk of diameter 2·5 cm and thickness 5 mm (sample surface is polished with 400 grade silicon carbide powder) is pressure contacted on to the piezoelectric transducer using silicon grease (Patel and Tam 1981). Since the PZT transducer is mounted inside a steel enclosure, the 1 mm thick steel between sample and the transducer helps in minimizing the acoustic reflection at the interface and gives a delay time limited by the transit time of the longitudinal waves in the transducer casing (Harada *et al* 1989). Also, care is taken to ensure that the laser beam itself does not fall on the transducer casing. The 1·06 μm laser radiation (pulse width $\sim$ 10 ns, single shot) from a Q-switched Nd:YAG laser (Quanta Ray, DCR-11) is focussed to a diameter of $\sim$ 1 mm using a convex lens on to the surface of the sample kept inside a stainless steel irradiation chamber provided with quartz windows. The laser energy was monitored for each laser pulse using an on-line, pulsed laser energy meter (Delta Developments), triggered in synchronization with the laser pulse. Each data point was taken with the laser pulse falling on a fresh surface of the sample by rotating the same about its axis while the distance between the illuminated spot and the centre of the transducer is kept constant.

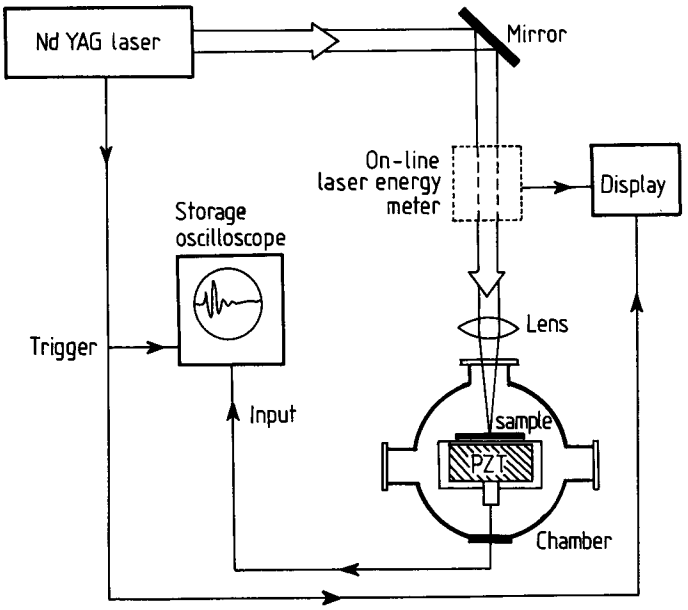

Figure 1. Schematic diagram of the experimental set up.

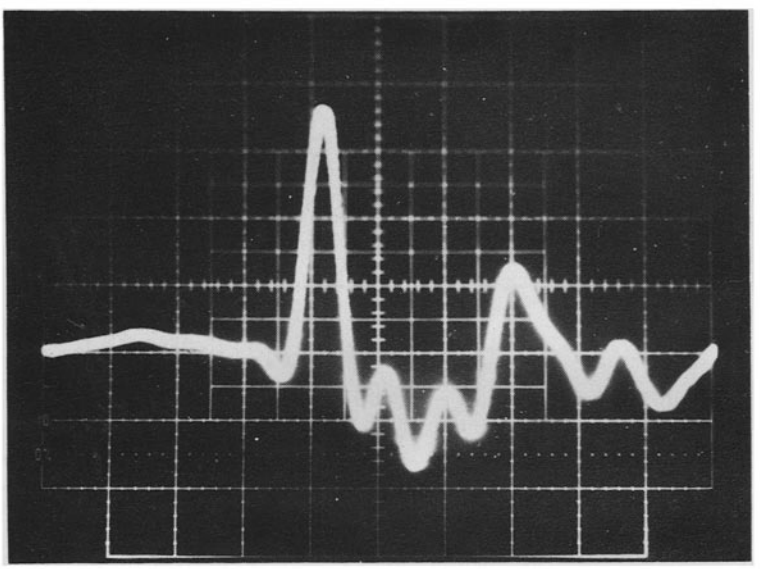

Figure 2. CRO trace of the PA signal from teflon at a laser energy density of $\sim 1{\cdot}8\,J/cm^2$ (50 mV/div., 2 μs/div.).

3. Results and discussion

The resultant PA signal from the PZT transducer is observed on a 100 MHz storage oscilloscope (Tektronix Model 466) using 50 ohm termination. A typical CRO trace of the output signal from the PZT for a laser energy density of $\sim 1{\cdot}8\,J/cm^2$ for teflon sample is shown in figure 2. This PA pulse has a further delay with respect to the laser pulse because of the transit time of the acoustic signal through the sample

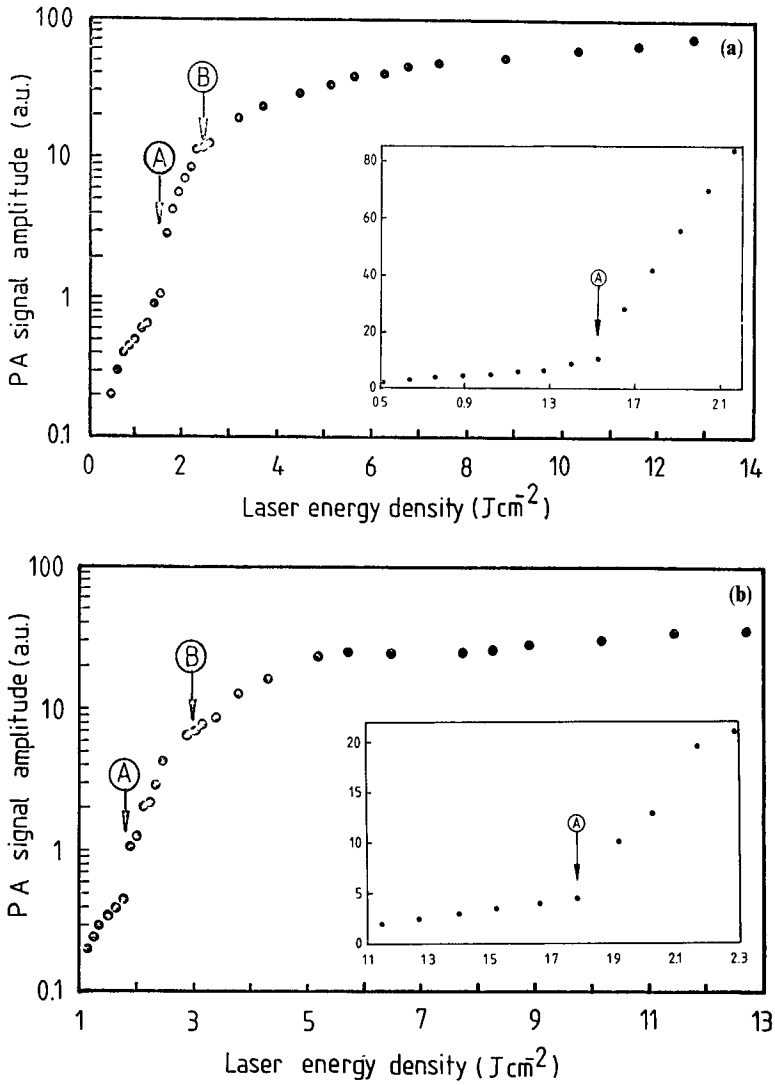

Figure 3. The plot of laser energy density *vs* PA signal amplitude for bulk **(a)** nylon and **(b)** teflon samples in air. Insets: The expanded graph showing region (A) in detail.

material (figure 2). The negative peak observed in the pattern is a result of the rarefaction due to cooling of the sample following the compression wave caused by the heating of the same at laser fluence near damage threshold (Srinivasan and Braren 1989). The amplitude of these peaks is monitored on the CRO. The variation of the PA signal with the laser energy is studied and the plot of laser energy density versus the PA signal for teflon and nylon bulk samples are given in figures 3 (a, b). These show a clear and abrupt increase in the PA signal amplitude in the region of the damage threshold in full agreement with the observations of the previous workers (Srinivasan and Braren 1989; Harada *et al* 1989; Sell *et al* 1989; Rosencwaig and Willis 1980; Dienstbier *et al* 1990). Table 1 shows the values of the ablation thresholds evaluated for the two polymer samples teflon and nylon at 1·06 μm wavelength. At the same wavelength, using multiple beam technique, Milam (1977) determined the

Table 1. Values of laser ablation threshold for polymer samples at 1·06 μm wavelength.

Sample	Region (A) J/cm^2	Region (B) J/cm^2
Teflon#	1·78	2·85
Nylon#	1·53	2·25
PMMA*	1·60	—
Polystyrene*	0·80	—

*Milam (1977), #Present Work (estimated error ~ 20%).

damage thresholds for bulk polymethyl methacrylate (acrylic) and polystyrene samples to be of the order of 1·6 J/cm^2 and 0·8 J/cm^2 respectively which is of the same order of magnitude of damage thresholds for the polymeric materials under the present investigation.

The mechanisms of laser induced damage in polymeric materials have not yet been understood clearly. The damage threshold generally depends on visco-elastic properties of polymers as well as on the molecular structure of the monomers. It has been suggested that (Goldberg *et al* 1983) laser induced damages in low absorbing dielectric materials like polymers are initiated through bond breaking phenomenon which will act as an acoustic source exhibiting the abrupt enhancement of the PA signal near the threshold. A significant fraction of the light energy above the threshold is utilized in the disruption of chemical bonds and also contributes to the thermal and kinetic energy of the ablated fragments (Gorodetsky *et al* 1985). The results for bulk nylon and teflon samples as given in figures 3a and 3b respectively, show that variation in slope occurs at region A (at lower laser energy density), as well as at B (higher laser energy density). Abrupt increase in the amplitude of the PA signal occurs at both these points. This shows the existence of two separate thresholds for the laser induced surface damage occurring apparently due to different causes (Harada *et al* 1989; Dienstbier *et al* 1990). The damage threshold will also depend on possible absorptive inclusions (Goldberg *et al* 1983) and surface polishing of the sample. The laser threshold at A is very sensitive to the sample surface conditions unlike the threshold at B. This observation leads to the conclusion that the threshold at A is determined by the surface morphology of the sample. The threshold A will characterize damage due to inclusions, impurities and surface inhomogeneity, while that at B should correspond to the initiation of bond breaking processes resulting in plasma formation and melting of the sample surface. This observation has been confirmed by recording the PA signal from various points of the sample surface (nylon) at laser energy densities corresponding to threshold A (~ 1·53 J/cm^2) and threshold B (~ 2·25 J/cm^2). As seen from figure 4, the magnitude of the PA signal corresponding to threshold A varies from one point to another on the sample surface while that corresponding to B remains practically constant over the various points on the sample surface which is thus scanned. This implies that the threshold A is sensitive to the surface conditions of the sample while that at B is virtually independent of the nature of the surface. The endothermic phase change occurring at the region of melting can cause a change in the response of the PA signal amplitude (note the change in slope near B). At still higher laser energy densities, the decrease in PA signal is counter-balanced by an increase in the plasma density and corresponding enhancement in the PA signal.

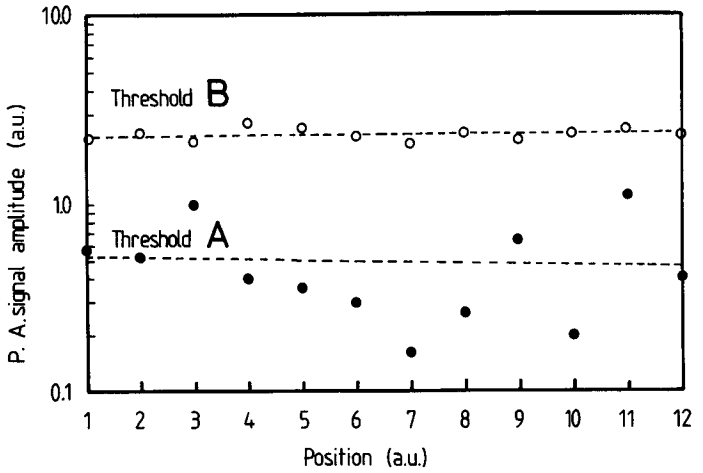

Figure 4. The plot of the variation of the PA signal at various points on the sample (nylon) surface at the two thresholds, A ($\sim 1{\cdot}53\,J/cm^2$) and B ($\sim 2{\cdot}25\,J/cm^2$). The broken lines show average value of the respective PA signals.

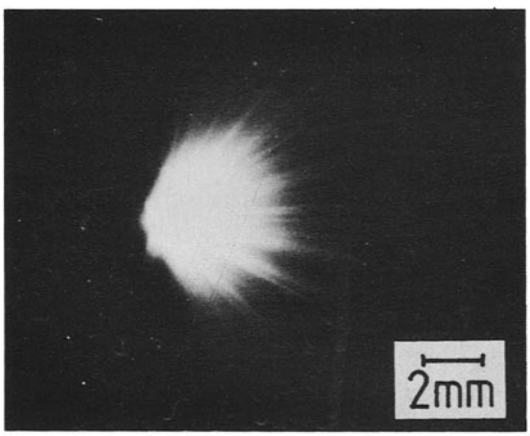

Figure 5. The photograph of the plasma plume from bulk teflon sample at a laser energy density of $\sim 3\,J/cm^2$.

There is also significant absorption of photons by the sample at the damage site or within the plasma produced at this point, this added energy being transferred to the sample *via* electrons. Thus, where laser damage is accompanied by mechanical damage, but with no significant increase in the optical absorption, the PA signal will not increase dramatically (Rosencwaig and Willis 1980). At laser fluences much higher than that at B, the PA signal tend to saturate due to possible absorption of the laser beam by the plasma plume (Harada *et al* 1989). Visually, there is no plasma formation below region A, and as the laser energy crosses the damage threshold, the plasma plume begins to appear and it grows with further increase in laser energy density. Figure 5 shows the plasma plume from a bulk sample of teflon at a laser energy density of $\sim 3\,J/cm^2$. In both nylon and teflon, the profile of the variation of the PA signal with laser energy density is identical. The relatively larger uncertainty in the slopes above region A could be due to the presence of spatial hot spots in the beam

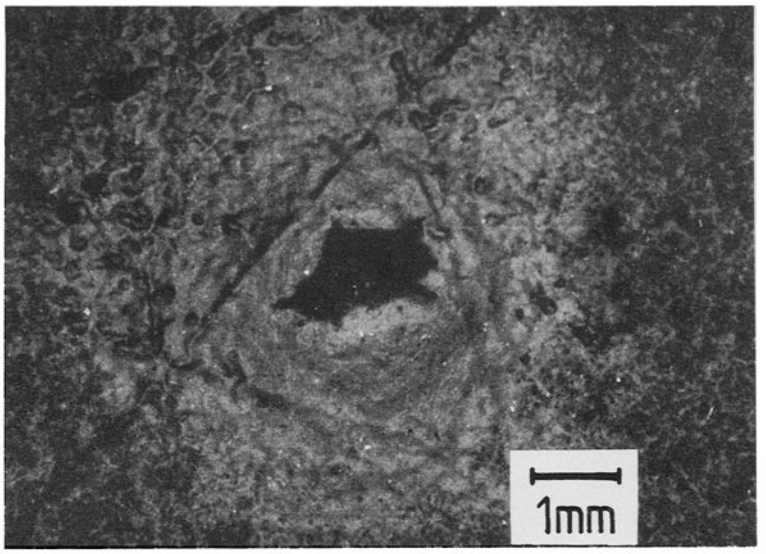

Figure 6. The photograph of the damaged surface of nylon at a laser energy density of $\sim 3\,J/cm^2$ (Photographed in the reflection mode of the microscope).

profile which give rise to scatter in the data points above A. This is a consequence of the strongly non-linear behaviour of the PA signal above threshold A (Rosencwaig and Willis 1980). Figure 6 shows a typical damaged surface of nylon at a laser fluence of $\sim 3\,J/cm^2$.

In conclusion, the laser ablation thresholds of bulk polymer samples were evaluated by pulsed photoacoustic technique using a piezoelectric transducer. The results show two distinct values for thresholds corresponding to damage initiated by surface characteristics and melting and ablative processes in the sample surface.

4. Acknowledgements

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