CHAPTER IV

EVALUATION OF LASER DAMAGE THRESHOLD IN POLYMER SAMPLES

Abstract

The characterization of the laser interaction with polymers like polymethyl methacrylate and polyacrylamide was done using photothermal phase shift spectroscopy. The optical damage threshold of samples were measured using this technique.
4.1 Introduction

The interaction of intense laser pulses with solid materials is currently of considerable interest in view of the development of new techniques and devices involving nonlinear effects. For example, laser ablation of polymeric materials is being used in photolithography and in the fabrication of micro electronic systems\(^1\). Some of the transparent polymers are being used as optical components as well as non-linear optical materials\(^2\). Very good optical transparency of polymethyl methacrylate (PMMA) in the visible range of the electromagnetic spectrum helps them to be useful in optics. PMMA is also suitable for the fabrication of optical fibre core as well as cladding.

When pulsed laser radiation falls on the surface of an organic material, the surface layer is spontaneously etched away and the resultant molecular fragments get rapidly ablated from the target surface and the photochemistry is more or less simplified as explosive thermal decomposition. Materials used in high power applications should have high damage threshold under laser irradiation. Polyacrylamide is being used as polymeric hosts for dye molecules which can be used in tunable solid state dye lasers\(^5\)\(^-\)\(^10\). The use of dye doped polymer matrices in high power dye lasers demands the accurate knowledge of its laser damage threshold at different doping concentrations.

When a low power laser beam is passed through a material, no irreversible effects are observed, but at sufficiently high power or energy density, transient or permanent effects like refractive index changes, removal of material from the surface, production of internal voids, melting, vaporization and even ablation occur. There is a threshold value for the power density of laser beam so as to produce such irreversible damage effects and this value is called Laser Damage Threshold (LDT) for the particular material. The mechanism of LDT is not yet fully understood and moreover, since there are numerous parameters that determine the LDT of a material, a technique that can be used to determine this quantity accurately for different kinds of samples is highly useful.

The effect of high power lasers on transparent polymeric materials is different from that of transparent dielectrics. The polymer has a lower laser damage threshold as compared to the dielectric crystals, a strong dependence of the optical strength on the micro-elastic properties and temperature, a wide range of radiation intensities below
damage threshold in which cumulative effects are observed, the occurrence of micro
damage of dimensions 10 μm, not accompanied by bright spark and the absence of
formation of soot during damage process6–10. Another feature of the polymer materials
is their higher surface optical strength as compared to their bulk optical strength6,11.
The actual measurement of LDT involves three steps, viz.,

1. to irradiate the samples at several laser energy densities,

2. to measure the absolute characteristics of the laser pulse and

3. to determine which of the laser pulses caused the damage to the target.

Though the steps described are quite simple, the process of an absolute measurement
of this quantity is beset with various problems. Some of these problems faced are
discussed below12.

Since the laser pulse energy varies with the pulse width and the beam profile,
these parameters must also be measured accurately. Sophisticated instruments like
the streak camera, recticon13 or pyroelectric or photodiode arrays are often required
for these measurements. In such cases, the serious problem is that regardless of how
the image is recorded, there is a background noise level which greatly complicates the
interpretation of the low-intensity wings of the profile. This can be eliminated to an
extent by placing an aperture, the diameter of which is approximately equal to the
spot size of the profile. For such a setup with laser pulse width of about 1 ns, the
uncertainties in LDT measurements due to the laser energy, flux and intensity are
±3, ±5-7 and ±10-15% respectively. The absolute accuracy in the energy density
measurements, however depends on the accuracy of the calorimeter used to determine
the pulse energy, which, using commercial energy meters, can be measured with good
precision within an error margin of 1%. Since it is the measurement of beam profile
that involves serious problems, often, only the results of LDT measurements without
shot-to-shot determination of the beam profile are reported. Obviously, the margin of
the experimental error is enlarged in these cases. Even the ability to determine the
laser flux within a 5% error does not imply that the laser damage threshold can be
measured with the same degree of accuracy since uncertainties can be introduced by
the large step-sizes in flux during the sequence of shots used for irradiation or due to
the indecision as to which particular shot has caused the damage. The laser spot size

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must be big so as to ensure that the worst-case defects have been encountered.

The test area must be illuminated uniformly to within the desired precision of the LDT measurement. Since damage is a cumulative effect, multiple shots at the same site will lower the LDT. It is better to expose a new site to each shot so that the surface morphology is uniform within the measurement error. For testing of laser optics, it is needed to know as to how many shots the surface can endure before damage sets in. For such studies multiple exposure is ideal, so long as the pulse-to-pulse stability of the shots are ensured. The work in this chapter has followed the method of single shot laser damage threshold measurements. Moreover, there is no a-priori guarantee that different sites will respond alike to the same flux level.

The total energy \( Q \) in terms of energy density \( E(r) \) at the focal plane can be expressed as

\[
Q = E(r) \int_0^\infty 2\pi r^2 dr
\]  

and \( E_0 = \frac{2Q}{\pi r_0^2} \) where \( E_0 \) is the peak on-axis energy and \( r_0 \) the radius at which the intensity has fallen to \( 1/e^2 \) of its original value. In terms of the peak on-axis intensity, the damage threshold, \( I \) is given by

\[
I = \frac{2Q}{\pi r_0^2 \eta L}
\]

The r.m.s electric field associated with this intensity is,

\[
E = 19.41 \left[ \frac{I}{7} \right]^{1/2}
\]

where \( \eta L \) is the laser pulse width and \( \eta \) is the refractive index of the material. The total energy \( Q \) is related to the incident energy on the focusing lens (\( Q_{in} \)) as,

\[
Q = Q_{in} T_L T_S
\]

\( T_L \) and \( T_S \) are the transmittance of the focusing lens and the sample respectively.

The sample surface must be polished carefully cleaned with organic solvents since dust or other minute inclusions at the focal sites reduce the LDT at those sites. Scratches and residue on the surface as a result of cleaning can also cause lower LDT.
Even then there is no guarantee that each point on the sample surface can give an absolute average value of the damage threshold.

Even though many methods have been reported for the detection of LDT, none of them can be acclaimed as accurate and fool proof for all kinds of samples. It is seen that LDT measurements are influenced by many parameters relating to the experimental conditions like pulse width, repetition rate, beam diameter, beam focussing, temperature, laser frequency, optical pumping conditions etc. And the different techniques used are (a) Emission of spark/ light, (b) Change in scattering/reflection, (c) Particulate plume, (d) Microscopy (e) Breath-fogging etc. to mention a few. This chapter describes how the photothermal phase shift spectroscopy\textsuperscript{13,14} (PTPS) can be used for the measurement of the laser damage threshold of PMMA and dye doped polyacrylamide when irradiated with a pulsed high power Nd:YAG laser beam.

4.2 Photothermal phase shift spectroscopy

Photothermal spectroscopy is an active area of research at recent times\textsuperscript{17-19}. A wide range of applications of this technique has been developed. The basic idea underlying this technique is well known. A laser beam (pump beam) passes through the medium of interest. The laser is tuned to an absorption line of the medium and the optical energy is absorbed by the medium. If the collisional quenching rate in the medium is much higher than the radiative rate, most of this energy appears in the rotational-transitional modes (heating) of the molecules. The heating of the medium modifies the refractive index of the laser irradiated region. The change in refractive index of the medium is detected by a second laser beam (probe beam). There are three different methods of measuring this refractive index change, viz., namely photothermal phase shift spectroscopy, photothermal deflection spectroscopy and photothermal lensing spectroscopy. In photothermal phase shift spectroscopy, the refractive index change is measured directly by placing the sample in one of the arms of the Michelson interferometer or inside a Fabry-Perot cavity. The refractive index change produces a change in the optical path length which is detected as a fringe-shift.

In photothermal deflection spectroscopy (PTDS) the pump beam has a spatial profile (generally assumed to be Gaussian) and hence, the refractive index of the pump beam irradiated region also acquires a similar spatial profile. This non-uniform re-
fractive index causes a deflection of the probe beam, which can easily be detected by a position sensitive optical detector. The signal is proportional to the gradient of refractive index.

In photothermal lensing spectroscopy (PTLS) the non-uniform refractive index also produces a lensing effect in the medium. A probe beam passing through the medium changes shape, resulting in a change in the intensity of the probe beam passing through a pin-hole. In this technique the signal is proportional to the second derivative of refractive index. These techniques were discovered and developed separately by various workers. PTPS was developed by Stone and by Davis\textsuperscript{20,21} and has found applications in analytical chemistry. PTDS was developed by Amer, Boccara, Fourier and collaborators\textsuperscript{22-25} and is used as a diagnostic tool. PTLS is the used in the measurement of the collisional relaxation rates of molecules as well as in analytical chemistry\textsuperscript{26-28}.

Among the above mentioned three different methods in photothermal spectroscopy we have used PTPS as the diagnostic tool for the present measurements. A detailed theoretical treatment of PTPS in fluid medium is considered. The temperature distribution created by the absorption of the pump beam is given by the solution of the differential equation\textsuperscript{16}

\[
\frac{\partial T(r,t)}{\partial t} = D \nabla^2 T(r,t) - v_x \frac{\partial T(r,t)}{\partial x} + \frac{1}{\rho C_p} Q(r,t)
\]

where \(T(r,t)\) is the temperature above the ambient, \(D\) is the thermal diffusivity, \(\rho\) is the density, and \(C_p\) is the specific heat at constant pressure of the medium. \(v_x\) is the flow velocity of the medium which is assumed to be in the \(x\)-direction, and \(Q(r,t)\) is the source term. The first, second and third terms on the right in hand side of eq.5 represent, respectively the effects of the thermal diffusion, flow and heating due to the pump beam absorption. If a pulsed laser is used, the heat produced per second per unit volume by the absorption of laser energy \(Q(r,t)\) is given by

\[
Q(r,t) = \alpha I(r,t) = \left(\frac{2\alpha E_0}{\pi a^2 t_0}\right) \exp\left(-\frac{2r^2}{a^2}\right) \text{ for } 0 \leq t \leq t_0
\]

\[
= 0 \text{ for } t > t_0
\]

Here \(\alpha\) is the absorption coefficient of the medium and the medium is assumed to be optically thin (weakly absorbing). \(I(r,t)\) is the intensity of the beam and the total
energy per pulse is $E_0$.

We assume that the pump beam propagates in the $z$-direction. If there are no inhomogeneity in the medium along the pump beam, eq.5 may be solved in two dimension ($x$ and $y$). The boundary conditions given by

$$T(x,y,t)|_{t=0} = 0; \ T'(x,y,t)|_{k=0} = 0$$

$$T(x,y,t)|_{x=\pm\infty} = 0; \ T(x,y,t)|_{y=\pm\infty} = 0$$

(7)

where the laser is turned on at $t = 0$ and $T'$ represents the gradient of the temperature. With the boundary condition one may obtain the to the desired temperature distributions due to the pulsed laser irradiation as

$$T(x,y,t) = \frac{(2\alpha E_0/\pi t_0 \rho C_p) \int_0^1 \left\{ \frac{1}{8D(t-\tau)} \right\} \exp\left\{-2\left[\frac{x - v_z(t - \tau)}{t_0} + \frac{y^2}{\sigma^2}\right]\right\} d\tau}{[8D(t - \tau) + a^2]} \text{ for } t > t_0$$

(8)

In order to measure the laser damage threshold of polymeric samples, the variation of the fringe shift is measured as a function of laser power density. At a point where the damage occurs to the polymer matrix electrons, atoms and ions will be ejected out of the target and the measurement of electron density as a function of laser power density near the ablated surface will directly give the damage threshold. We have used eq.11 to derive the expression for the refractive index variation and hence the electron density of plasma generated in one of the arms of the Michelson interferometer. The intensity distribution of the fringe pattern of a Michelson Interferometer is given by,

$$I(t) = A^2 + B^2 + 2AB\cos[(\phi_A - \phi_B) - \gamma(t)]$$

(9)

where $A$ and $B$ are the amplitudes, and $\phi_A$ and $\phi_B$ the phases of the two interfering beams respectively and $\gamma(t)$ is the phase difference introduced due to the presence of the plasma. This derivation is made in accordance with the arguments given in Monson et al.16,17.

The shift in the fringe pattern resulting from this time dependent phase factor can be measured as voltage change in the output of the photodiode. For the intensity
to be very sensitive to small changes in $\gamma(t)$, the operating point is chosen such that $(\phi_A - \phi_B) = (m + \frac{1}{2})\pi$. Then the change in the output voltage of the photodetector $\delta V(t)$ is,

$$\delta V(t) \propto 2AB \sin \left[ \frac{4\pi}{\lambda} \int_0^1 \Delta \mu(t) \, dt \right]$$  \hspace{1cm} (10)

where $\lambda$ is the wavelength of the probe laser beam, $l$ the lateral extension of the plasma and $\Delta \mu(t)$ is the change in refractive index due to the presence of the plasma. When the phase difference $(\phi_A - \phi_B)$ is taken through a phase change of $\pi$, i.e., the operating point is moved from the bright to the dark fringe center the corresponding difference in intensities $(I_{\text{max}} - I_{\text{min}})$ will be proportional to $4AB$ in the absence of plasma. With a linear response for the photodetector, the corresponding voltage difference $V_{\text{max}} - V_{\text{min}}$ denoted by $V$ is proportional to $4AB$. Therefore from eq. 13,

$$\gamma(t) = \sin^{-1} \left[ \frac{2\delta V}{V} \right]$$  \hspace{1cm} (11)

Assuming negligible absorption and light scattering at the probe wavelength, the index of refraction $\mu$ of the plasma is given by $\mu^2 \approx n_e/n_c$ where $n_e$ is the plasma electron density and $n_c$ the critical plasma electron density given by $n_c = (\omega^2 \varepsilon_0 m e^2)/e^3$ where $\varepsilon_0$ is the permittivity of free space, $m$ the electron mass, $e$ the electron charge and $\omega$ the angular frequency of the pump laser radiation. $n_c$ has a typical value $9.92 \times 10^{20}$ cm$^{-3}$ when the Nd:YAG laser of wavelength 1.06 $\mu$m is used as the pump beam. When the critical density $n_e/n_c << 1$, we get

$$\gamma(t) \approx \frac{e^2}{mc^2 \varepsilon_0} \int_0^l n_e \, dl$$  \hspace{1cm} (12)

for a path length $l$ in the plasma. One can write the line averaged electron density from eq.15 as,

$$n_e \approx \frac{k \gamma(t)}{\lambda}$$  \hspace{1cm} (13)

where $k = 1.778 \times 10^{12}$ cm$^{-1}$. The phase factor $\gamma(t)$ in eq.16 is experimentally found out using eq.14.
4.3 Characterization of polymeric samples

With the advent of the use of the so called 'organic glasses' i.e., transparent polymeric materials for laser optics, laser damage threshold measurements in various bulk and thin films of polymeric materials such as those in the methacrylate series like polymethyl methacrylate (PMMA) and their co-polymers as well as polymers containing additives in the form of various plastics like dimethylphthalate have gained great importance. Many of these materials are now being used as laser optical elements and thus the need exists to study the laser induced damage process in these polymeric materials.

The laser induced damage in polymeric materials has been attributed to various mechanisms depending on the kind of results obtained. Multiphoton photo-destruction of the polymer chains is one of the major causes leading to damage in these materials. Another possibility for damage to occur in polymers is due to the mechanisms involving the formation of highly absorbing products and inclusions resulting from chemical changes at high temperatures produced following irradiation by laser beam.

 Irradiation of a polymethyl methacrylate target using a pulsed Nd:YAG laser causes plasma formation in the vicinity of the target. The refractive index gradient due to the presence of the plasma is probed using phaseshift detection technique. The phaseshift technique is a simple but sensitive technique for the determination of laser ablation threshold of solids. The number density of laser generated plasma above the ablation threshold from polymethyl methacrylate is calculated as a function of laser fluence. The number density varies from $2 \times 10^{16} \text{cm}^{-3}$ to $2 \times 10^{17} \text{cm}^{-3}$ in the fluence interval 2.8 - 13 J cm$^{-2}$.

4.3.1 Experimental setup

The experimental setup is as shown in Fig.2.8. The basic element in PTPS technique is a Michelson interferometer. Laser radiation from an intensity stabilized 5 mW He-Ne laser source (Spectra Physics) is used to construct the Michelson interferometer (MI). Optical setup is aligned so as to get well defined straight fringe pattern. The beam in one of the arms of MI passes parallel and very close to the target surface. High power laser radiation from a pulsed Nd:YAG (Quanta ray DCR 11) laser at wavelength 1.06 $\mu$m with pulse duration 10 ns is focused on to the target in order to produce plasma.

The sample chosen for our study is a disc of PMMA having diameter 15 mm and
thickness 4 mm. The point of irradiation is shifted by mechanically rotating the target after each measurement so that a fresh location is available on the target surface for each pulse. The probe beam passes grazing to the sample surface so that the length of the plasma near the target is taken as equal to the pump laser spot size. The shift in fringe pattern is measured as a voltage change using a PIN photo diode (HP - 4207) and it is displayed on a digital storage oscilloscope (Iwatsu, 200 MHz). The whole setup has been properly vibration isolated by using an indigenously built vibration isolated table. Measurements were taken for different laser pulse repetition frequencies.

The presence of the plasma on one of the arms of the interferometer changes the effective path length on that arm and the corresponding phase change $\gamma(x,t)$ will shift the fringe pattern which is proportional to the change in refractive index. This shift in fringe pattern can be measured as a voltage change $\delta V(x,t)$ in the output of a photodiode from which $\gamma$ can be calculated using eq.15 and the line averaged electron density can then be obtained by using the eq.16. The electron density was calculated for varying laser fluence using this equation.

4.3.2 Results and discussion

The oscilloscope trace of the signal obtained corresponding to the interference fringe shift is shown in Fig.4.1. Variation of electron density with laser intensity is given in Fig.4.2 which shows that electron density varies nonlinearly with respect to laser fluence. The graph exhibits regions of different slopes corresponding to different mechanisms for laser beam interaction with the target surface. At the point A, there is an abrupt change in the electron density of the plasma. It can be explained in terms of surface damage. For the values of the energy densities near the point A, the surface temperature is very high so as to produce intense ionization, thereby causing rapid ionic and electronic emission from the surface. This rapid ionization causes an abrupt change in the electron density which marks the surface damage threshold of PMMA at the laser fluence of $\approx 3.5 \text{ Jcm}^{-2}$. Above the damage threshold there is a marked increase in the plasma electron density for a fluence up to about $\approx 7.5 \text{ Jcm}^{-2}$. Above this fluence the slow increase in electron density can be attributed partly to the increased electron-ion recombination forming a quasi-stable state and partly to the absorption of the incident laser radiation by the plasma plume.34
Fig. 4.1. Signal observed in the oscilloscope, fringe shift was detected as voltage variation.

Fig. 4.3 shows the dependence of the damage threshold on the pulse repetition frequency. At 16 Hz repetition frequency the ablation threshold comes down to 2.8 Jcm\(^{-2}\) compared to 3.5 Jcm\(^{-2}\) at 2.5 Hz. That is, the damage threshold decreases linearly with increasing laser pulse repetition frequency. At higher laser pulse repetition rate, damage threshold is low due to the influence of the thermal energy contribution from the previous pulse. This indicates that the process of ablation is thermal in nature. Similar studies were done on dye doped polyacrylamide, undoped polyacrylamide is transparent in the visible region. The studies on dye doped polyacrylamide were done at 532 nm instead of 1.06 \(\mu\)m since it is the pumping wavelength for the dye emission. The measurement of damage threshold in this wavelength is important in understanding the utility of the polymer as a solid matrix for dyes. The samples used were of size (20x10x1) mm\(^3\), with varying rhodamine 6G concentrations. (The preparation and impregnation method of rhodamine 6G doped polyacrylamide is described in Chapter III). The experimental details are same as that for PMMA.
Fig. 4.2 Electron density of laser produced plasma as a function of laser fluence at a pulse repetition rate of 2.5 Hz.

Fig. 4.3 Variation of damage threshold with laser pulse repetition frequency. The solid line gives a linear fit to the observed data.
Fig. 4.4 shows the variation of damage threshold with the concentration of dye molecules. As the dye concentration is increased, the damage threshold intensity decreases. This is because of the higher absorption of the laser radiation by the highly concentrated samples. But the damage threshold is fairly high when compared to other materials.

The determination of LDT is a purely destructive testing process and permanent damage to the sample studied occurs. It would be appropriate to divide the damage occurring in polymers under laser radiation as that occurring in ideally pure media and that caused by impurities. The mechanisms causing damage are different. In pure media, it is optical rupture, which is qualitatively similar to gas rupture: in media containing impurities, it is damage caused by the superheating of impurities35,36.

In dye doped polymers photo-destruction of dyes take place at higher laser fluences. Detailed studies are needed to understand the role played by this decomposed dyes on photoablation of the samples. They may act as absorbing inclusions in the matrix. The
anomalous micro-elastic properties of polymers can lead to damage in these materials even when the heating of absorbing inclusions is negligible. A mechanism of non-linear absorption of the incident laser radiation associated with triboprocesses in the matrix surrounding the inclusion accompanied by the formation of micro cracks in the matrix has been proposed by Danileiko et al. This mechanism could explain the visible damage of dimensions >1 μm initiated by small inclusions (0.1 μm). This essentially involves surface electronic states being formed during micro crack formation process, and these are capable of absorbing the incident energy to cause damage. The existence of such states have been shown by the sub-threshold luminescence in the Vis-near-UV regions due to radiative de-excitations. In this analysis, the damage mechanism for a spherically symmetric absorbing defect comprising of a small region of dimension (smaller than the wavelength) and having an absorption coefficient appreciably larger than the surroundings, under irradiation for a short pulse is considered. This induced thermo-elastic stresses increase with time in the matrix. At the damage threshold, these stresses reach micro-breaking magnitudes leading to micro cracks. A further increase in the laser energy causes the increased density of these micro cracks and thus the concentration of electronic states capable of further absorption of the laser energy increases. Assuming the thermo-elastic stress near an inclusion to be proportional to its temperature, the process of non-linear heating in the matrix can be described in terms of a heat conductive equation which describes the absorption of laser energy by the inclusion and possibly by the electronic states formed at the damage sites, the solution of which gives the expression for the temperature at the centre of the defect. The LDT can be estimated from the conditions of loss of stability of the steady state solution of the equation for the temperature with respect to time. This mechanism accounts for damage mechanisms like micro-cracks and micro-damages.

4.4 Methods for improving laser resistance in polymeric media

An increase in the ambient temperature to the level at which the matrix passes from the glassy into the highly elastic state leads to a significant increase in the damage threshold. This effect is dependent on the intensity as well as the wavelength of the radiation.

It has been found that introduction of plasticizers increases the damage threshold.
Low molecular dopants improve the optical transparency and reduces the mechochemical reactions and hence responsible for the suppression of the accumulation effect. The influence of plasticizers on the rate of destruction of polymeric samples is associated with the transfer of energy by hot radicals to the dopant. For example, a significant improvement in the laser resistance of PMMA was observed by the addition of the plasticizer viz. ethanol.

Another method of enhancing the laser resistance of polymeric matrices used in active laser media, along with the technological uniformity (absence of dust particles, bubbles etc.) and the introduction of plasticizers, is a significant improvement of the structural uniformity of the polymeric systems and a more uniform distribution of the dye in the matrix.

4.5 Conclusions
The various aspects of laser induced damage process have been discussed in detail. Photothermal phase shift technique was used to characterize the laser polymer interaction. The photothermal phase shift effect has been applied to the estimation of the laser damage threshold in PMMA and polyacrylamide. There exists abrupt change in the PTPS signal in the region of laser damage threshold. Also, the method of determination of electron density in experimental plasma studies using interferometric technique has some advantages compared to other methods like spectroscopic methods and electronic probing. Spectroscopic determination of electron density requires absolute calibration of the detector in the entire spectral range of interest and in electronic probing, the flow pattern of the plasma is perturbed due to probe insertion. PTPS technique that we have described offers a simple, sensitive technique for determining the laser plasma densities and avoids the use of complex detection systems and painstaking calibration procedures.
References


[37] Danileiko et al., 'Proceedings of the 4th All Union Conference on Non-linear Interaction of Optical Radiation'.


