# Laser Induced Damage Study of Dye Doped Polystyrene Films deposited in Glass Substrate by Dip Coating Technique

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*Volume 1, Issue 2, March 2024*
*Received: 18 January, 2024; Accepted: 1 March, 2024*
*DOI: https://doi.org/10.63015/5c-2415.1.2*

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**Abstract:** In the present work, the Laser-induced Damage Morphology of Dye-doped Polystyrene films is investigated. The focus is on the Front and Rear side Damage Morphology at two different Pulse Repetition Frequencies, namely 1 pps and 20 pps. For this experiment, films were deposited on both sides of Borosilicate Glass. It was found that at 1 pps, the front side film is damaged without affecting the glass, while the modified beam propagates through the glass to damage the rear side film. Dendrimer-like microstructures are found on both the front and rear sides of the damaged spots, along with pits and craters. At 20 pps frequency, the front side film is damaged, including damage to the glass, resulting in a large crater on the front surface. The morphological features were studied using Fresnel equations. Polymeric films were fabricated using the Dip Coating Technique, and Film thickness was evaluated using the Prism Coupling technique.

**Keywords:** Laser Induced Damage; Polymeric Films; Dendrimer; Prism Coupling; Dip Coating.

## 1. Introduction

The microprocessing of Polymers using High power lasers has great importance as it provides good precision and control at micron and nano level. The laser-matter interaction not only depend upon the materials composition but also depend upon the various laser parameters e.g. laser wavelength, pulse repetition frequency and pulse duration (in case of pulsed laser), energy of the laser beam etc. Recently, laser based various methods were reported by different research groups. For example, Rybaltovskii et al has created linear periodic structure in poly-2,20-poxydiphenylene-5,50-bis-benzimidazole (OPBI) by laser drawing process (Rybaltovskii et al.2021). Similarly polymeric surface were modified using Excimer laser based ablation technique for the fabrication of microfluidic systems (Hsieh et al. 2017). Laser ablation studies were performed on poly(dimethyl siloxane) (PDMS), poly(glycerol sebacate) (PGS) and poly(1,3-diamino-2-hydroxypropane-co-polyol sebacate) (APS) polymers. Laser ablation technique was employed (Tazdidzadeh et al, 2017) to synthesize gold nanoparticle in polyethylene glycol and chitosan solutions. Q switched Nd:YAG pulsed laser were used for the synthesis. Ultrathin Polymeric films on Quartz substrate were ablated using Femtosecond laser by (Jun et al. 2016) to study thin film patterning process. Depending upon the pulse energy it was reported that films can be ablated with or without substrate. The mechanism of ablation was reported to be non-thermal. Photothermal ablation of polymers were analyzed (Kappes et al. 2014) using the temperature measurement setup based on spectral pyrometry. They performed their experiment on Polystyrene, poly (α-methylstyrene), a polyimide and triazene polymer using μs laser. Surface patterning in doped polymers were also studied

(J.Vapaavuori et al. 2013). Surface Relief Gratings were inscribed in Polymers using laser irradiation. These reported works suggest that Laser-materials processing has great prospect in the area of Polymer synthesis and microprocessing technology. Polymeric materials are cost effective and easy to process. But the unique features offered by Laser beam provides a new dimension in Materials Processing. One such finding of laser microprocessing is reported in the present work in which polymeric films were converted into micron to nano level dendrimers. Absorbing dyes were doped in the polymeric chemistry and used as a catalyst to initiate damage in the polymeric films.

The present work reports the front and rear side damage morphology of Dye doped Polystyrene films fabricated on Borosilicate Glass. Damage morphology is studied using two different pulse repetition frequency-1pps and 20pps. The experiments were performed with Nd:YAG Laser (Wavelength 1.06µm, pulse duration 20 ns). Polystyrene films are transparent at 1.06 µm, but doping of Methyl red dye makes polymeric film absorbing.

**2. Experimental Details:** In the present experiment, the damage was performed using Q-switched Nd:YAG laser (wavelength 1.06 µm, pulse duration 20ns). The pulse repetition frequency was used in two modes: 1pps (pulse per second) and 20pps mode. 1 pps was controlled manually while 20 pps was set in automatic mode. The pulse repetition frequency was changed by changing the fringe rate of flash lamp. The output laser beam has Gaussian profile. The beam diameter was determined using slit scan technique. The laser beam in TEM00 mode was focused by a lens of 45cm focal length. The incident energy was adjusted using Neutral Density Filters. He:Ne laser beam (frequency stabilized) was used as a probe beam. It was set to the spot to be damaged and reflected beam was collected by Si photodiode as shown in figure. The He:Ne laser beam size was kept smaller than the Nd:YAG laser spot size. The reflected intensity from damaged spot is decreased and this decrease is always permanent. The present experiment was performed in air, at room temperature and under normal atmosphere. As shown in Fig.1 laser beam interacts with dye doped polystyrene film deposited on both sides of Borosilicate glass.

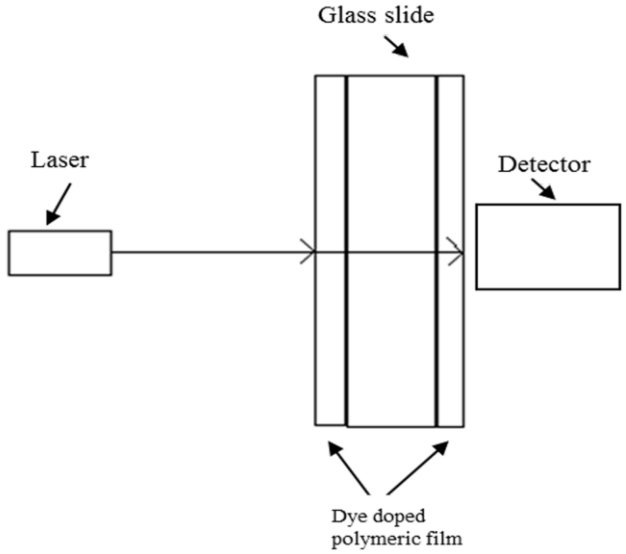


**Figure 1. showing the setup of front and rear side Damage experiment**

Energy levels in both 1pps and 20pps were fixed to single pulse damage threshold. Single shot damage was first observed using the energy of 0.13 J/cm$^2$ while the beam diameter was about 1mm. Then damage was also produced using double the energy value of the damage threshold. With reference to fig.1, the film facing to the laser is called herewith front-side film and the film deposited in the other side of the glass slide is called herewith rear-side film.

To define the damage threshold, the film surface was irradiated by laser beam by varying the fluence gradually. For each fluence level data were collected from different places of the film. Damage threshold values were found to be the same at each site. Irradiated spots were studied using SEM to make sure if any modification occurred.

The dye doped films were fabricated on the Borosilicate Glass by Dip Coating technique in clean room environment. The details about the technique can be found in the reference (Kumar et al 2005) Polystyrene was dissolved in Chlorobenzine (10% wt./vol) and Methyl Red dye was mixed in such a manner that its percentage was maintained at 0.3 %. Films were dried in the vacuum oven overnight at room temperature to evaporate the excess solvent in the film. The refractive index and extinction coefficient of polystyrene films at 1.06 μm were found to be 1.57 and $9.5x10^{-7}$ respectively. To correlate the different physical and optical parameters of polymer films same sample was first characterized for refractive index evaluation and then sample was placed into laser damage experimental setup for damage experiments.

Film thickness was evaluated using Prism Coupling technique (Kumar et al 2005). Since these films have waveguiding capabilities, thickness of the film can be found using Prism Coupling technique. The He:Ne Laser beam (0.6329 μm) enters into the film with the help of input prism (refractive index 1.756 at laser wavelength). The m-line spectroscopy was performed and waveguiding modes were observed using output prism (refractive index 1.756 at laser wavelength).

## 3. Results and Discussion

**3.1 Damage Morphology in 20 pps regime:** Fig.2(a) shows the damaged spot using 20pps pulse at the energy of 1mJ. The depth of the spot is around 100 μm. The film thickness was evaluated by Prism Coupling Technique and is found to be 20 μm. That means Damage involved Glass as well. Comparatively larger values of Damage threshold of Borosilicate Glass in the similar conditions were reported by other groups (Kimmel et al. 2011). In this work the lesser value of Damage may be due to absorbing film (the presence of absorbing dyes in transparent polymer chemistry) fabricated on glass.

In the damaged spot a big crater is formed. Surface removal, Striations (Fig.2b), crack (Fig.2c) are some of the noticeable feature that defines damage morphology in 20pps regime. In the back side of the system no damage in the film is formed that was concluded by SEM studies. This may be due to damage in Bulk Glass that results in no further propagation of laser pulse in the system. The periphery of the damaged spot in Fig.2a shows that mixed type of damage morphology which involves melting, crack, burning etc.

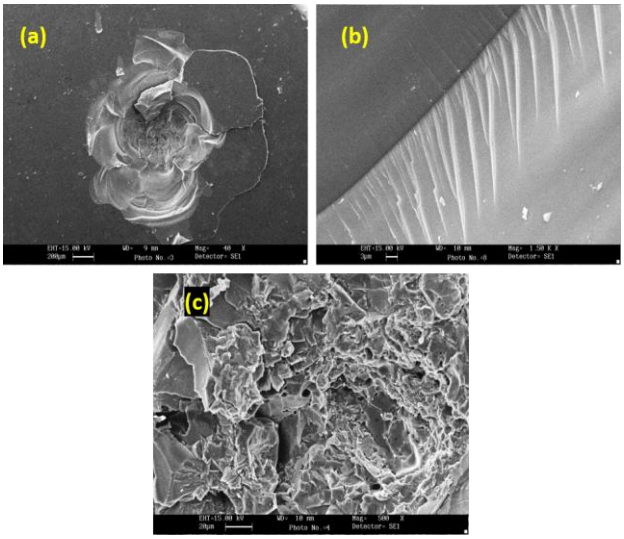


**Figure 2. (a) showing the damaged spot with 20pps laser pulse, (b) showing the formation of striations in the damaged spot shown in fig.2a, (c) showing the central portion of damaged spot. Ablation and cracks are clear in the figure.**

**3.2 Damage Morphology in 1 pps regime**

Fig.3a shows the damaged spot at the front end of the film. In this regime the complete film removal can be observed that not involves the glass. The periphery of the damaged spot shows the clear boundaries that are absent in the 20 pps regime. The enlarged view of the periphery (Fig.3b) shows the layered structure that suggests the surface removal through melting.

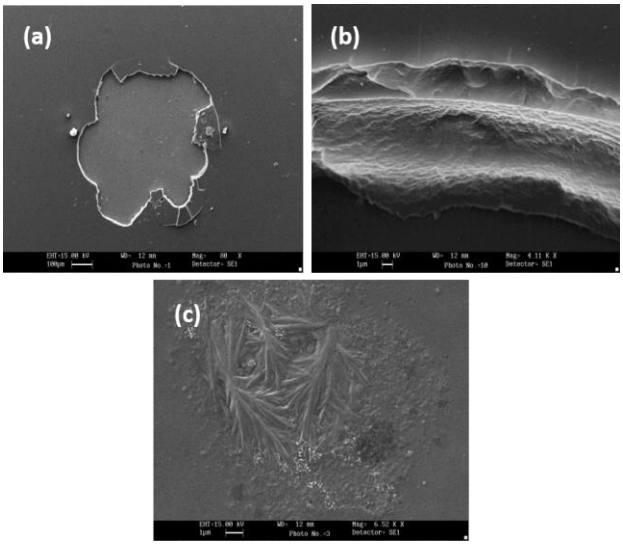


**Figure 3. (a) showing the damaged spot using the 1pps pulse at threshold fluence, (b) showing the periphery of the damaged spot shown in fig.3a, (c) showing the dendrimer structure deposited in the glass in the damaged regionig.3**

In the damaged spot, the glass surface is filled with some micro-particles (Fig.3c) whose enlarged view suggests the formation of dendrimer like structure (Folgado et al 2016).
When the energy is increased to two times, the similar kind of morphology was found in the form of film removal in both sides of the glass without any damage to Glass (Fig.4a). But in the periphery (Fig.4b), layered structure is absent suggesting that film removal does not involve melting.

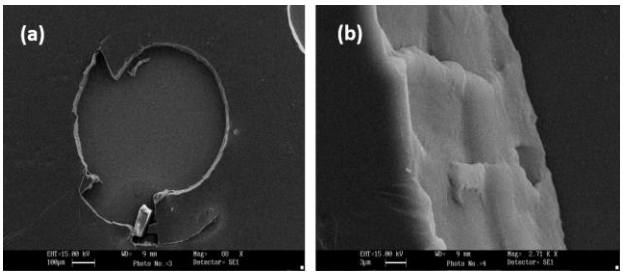


**Figure 4. (a) showing the damaged spot using two times energy of damage threshold, (b) showing the periphery of the damaged spot.**

Fig.5a shows the rear side damage morphology at the damage threshold value. The complete damaged spot is made of pits and cracks. Dendrimers exists also in the rear side of damage morphology (Fig.5b). Complete film removal in rear side is absent that may be due to modification in the beam profile after crossing the front side damaged spot. When the energy is increased the similar trend can be seen in rear side film in the form of pits and cracks. But at higher energy level, more area is covered by this morphology, in the form of pits and cracks (Fig.5c and 5d).

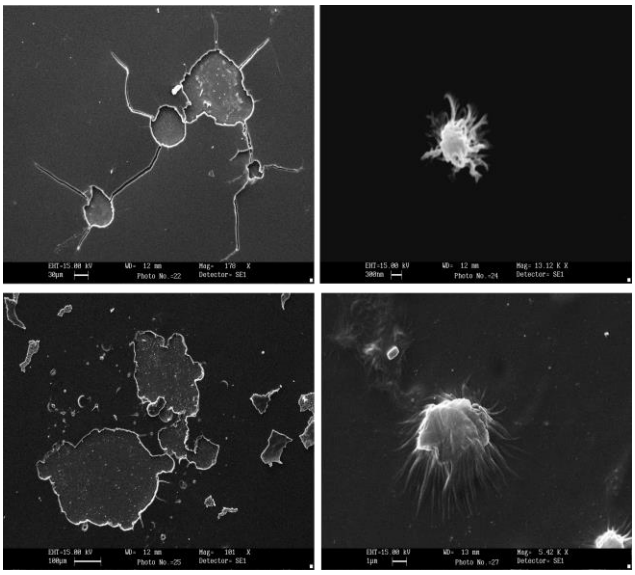

**Figure 5. (a) showing the rear side damage at damage threshold value, (b) dendrimer structure in rear side damage shown in fig.5a, (c) rear side damaged spot at two times the damage threshold value, (d) showing the dendrimer in the damaged spot shown in fig 5c.**

The difference in the damage morphology of entrance and exit face can be understood as follows:
In fig.1, when light enters into the films (side I), it suffers $180^0$ phase shift (Crisp et al 1972). Therefore, due to partial destructive interference, the electric field strength at the film surface (side I), $E_{ent}^{fl}$ can be related to the electric field of incident light $E_i$, by the following relation

$$E_{ent}^{fl} = E_{R1} + E_i = \frac{2}{n_1 + n_2} \text{.....(1)}$$

Here $E_{R1}$ is the electric field of reflected light from the film (side I), $n_1$ is the refractive index

of film, $n_2$ is the refractive index of cover (in the present experiment the cover is air therefore the value of $n_2$ is 1). Now the light with reduced electric field will transmit through the film and incident into the glass surface. At the film-glass interface there will be no phase shift (Boling et al. 1972). Therefore, due to constructive interference at film-glass interface, the electric field becomes

$$E_{fI}^{g} = E_{R2} + E_{ent}^{fI} = \frac{n_2 - n_3}{n_2 + n_3} E_{ent}^{fI} + E_{ent}^{fI}$$
$$= \left(\frac{2n_2}{n_2 + n_3}\right)\left(\frac{2}{n_2 + 1}\right) E_i$$
$$= \frac{4n_2}{(1+n_2)(n_2 + n_3)} E_i = E_g \text{.....(2)}$$

Here $E_{R2}$ is the electric field of reflected beam from the glass surface. This transmitted beam through the glass slide will again incident into the film (side II). Again due to $180^0$ phase shift there will be destructive interference at the glass-film interface. The electric field will take the form

$$E_g^{fII} = E_{R3} + E_g$$
$$= \left(\frac{n_3 - n_2}{n_3 + n_2}\right) E_g + E_g = \frac{2n_3}{n_3 + n_2} E_g$$
$$= \left(\frac{2n_3}{n_3 + n_2}\right)\left(\frac{4n_2}{(1+n_2)(n_3 + n_2)}\right) E_i$$
$$= \frac{8n_2 n_3}{(1+n_2)(n_2 + n_3)^2} E_i = E_{fII} \text{.....(3)}$$

here $E_{R3}$ is the electric field of reflected beam from the film (side II). This electric field transmit through the film and exit the surface. Therefore, at the exit face, the electric field due to constructive interference (Boling et al. 1972) will be

$$E_{fII}^{exit} = E_{R4} + E_{fII}$$
$$= \left(\frac{n_2 - 1}{n_2 + 1}\right) E_{fII} + E_{fII} = \left(\frac{2n_2}{1 + n_2}\right) E_{fII}$$
$$= \left(\frac{2n_2}{1 + n_2}\right)\left(\frac{8n_2 n_3}{(1+n_2)(n_2 + n_3)^2}\right) E_i$$
$$= \left(\frac{16 n_2^2 n_3}{(1+n_2)^2 (n_2 + n_3)^2}\right) E_i \text{.....(4)}$$

from the above analysis, it is clear that the ratio of electric field at entrance face to that of exit face $\left(E_{ent}^{fI} \Big/ E_{fII}^{exit}\right)$ depends upon the refractive index of both film ($n_2$) and substrate material ($n_3$). Using the value of film ($n_2$) as 1.59 glass ($n_3$) as 1.52, the ratio of electric field at entrance and exit face found to be 0.95. This difference in the electric field in the entrance and exit face is the reason for morphology asymmetry (Boling et al 1972). The sufficiently strong laser beam can create plasma in the surface of polymer film at the entrance face. As the plasma density increased, a standing wave can be formed through the film-glass interface. The electric field at the antinodes can become twice as large as the electric field in the incident beam. This strong electric field can create the pits in the film at side II. Therefore this pits formation in the exit face is due to internal damage rather than surface damage. In case of entrance surface there is no standing wave formation. The plasma at the entrance surface can be heated by the laser so that thermal shock can be created causing the complete surface removal at the exposed surface.

## 4. Conclusions:

Laser induced damage morphology study has been performed on dye doped polystyrene films that were deposited in both side of glass substrates. The morphological features has been studied in two different prf regime i.e. 1 pps and 20 pps. The study reveals distinct damage morphologies in different pulse regimes when interacting with transparent polymer films on

glass substrates. In the 20 pps regime, a complex interplay of surface removal, striations, and cracks results in a crater formation, influenced by the presence of absorbing dyes in the film. Conversely, the 1 pps regime shows complete film removal at the front end with minimal damage to the glass, indicating localized melting effects. Rear side damage morphology highlights the influence of beam profile modifications on damage patterns. The observed morphology asymmetry is attributed to differences in the electric field at the entrance and exit faces, leading to internal damage mechanisms such as plasma formation and standing wave effects. The presence of dendrimer-like microstructures in both front and rear side films suggests avenues for further research into their characteristics, potentially yielding insights applicable in biophysics. These findings underscore the importance of considering pulse frequency, energy levels, and internal dynamics in understanding laser-induced damage mechanisms and guiding the development of tailored mitigation strategies and the exploration of novel applications in diverse fields.

**Acknowledgements**

We are grateful to Dr. S. Pal, Laser Science and Technology Center (LASTEC), Metcalfe House, Delhi-110054, for allowing us to conduct experiments in his lab and for providing the necessary experimental facilities for the present research.

**Conflict of Interest**

Authors declare there is no conflict of interest.

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