

# Light-curing polymers for laser plasma generation

E Y Loktionov<sup>1</sup>, Y S Protasov, Y Y Protasov and V D Telekh

State Lab for Photon Energetics, Bauman Moscow State Technical University, 5-1 2<sup>nd</sup>  
Baumanskaya Street, Moscow 105005, Russia

E-mail: stcpe@bmstu.ru

**Abstract.** Solid rather than liquid media are used in pulsed laser plasma generators despite sophisticated transportation and dosing system need for a long-term operation. Liquid media could be more preferable due to transfer and dosing (down to  $10^{-14}$  L) being well developed, but plasma generation of those results in intense droplet formation and kinetic energy losses. Combination of liquids transportation advantages and solids plasma generation efficiency might resolve this trade-off. Liquid-to-solid transition can be induced by cooling down to sublimation temperature, thermo-, photo- or electron induced polymerization (curing). Light cured polymers seem to be very useful as active media for plasma generators, since they can be solidified very fast (ca. 30 ms) just before impact. We considered experimentally several UV-curing polymer and mixtures ablation regimes and supply schemes for laser plasma generation. The best results were obtained for liquid polymer at high-power pulsed irradiation matching curing optimum wavelength.

## 1. Introduction

Application of light-curing polymers (LCP) [1] in laser ablation has a number of advantages for practical applications, which are related to high-intensity laser-matter interaction. Usually laser irradiation of solid surfaces is used to generate plasma flows because of high volumetric energy density in the material, while losses, in most cases, are related only heat dissipation. A specific feature of liquids laser irradiation is related to their linear absorption coefficient being high only within certain spectral intervals. Intense evaporation of liquid causes formation of droplets, as well as part of ablation plume and shock waves kinetic energy dissipation in liquid volume [2]. Although, using liquids is advantageous for working medium supply to the active zone in laser thrusters and technological setups both for arranging transport and precise dosing and for injection of different additives [3]. Liquids solidification just before laser irradiation makes real a combination of the advantages typical of these two aggregation states at different stages of operation. Using LCP for laser plasma generators was first suggested in [4].

It is known that the efficiency of laser ablation can be characterized by mass consumption  $\Delta m/E$ , momentum coupling coefficient  $C_m \approx \Delta m \langle v \rangle / E$ , and other parameters [5]. To eliminate drawbacks of using liquids, which are mainly related to losses of mechanical energy as a result of splashing [6], a number of authors proposed forming thin liquid films [7] and isolated droplets [8], filling porous target matrices with a liquid [9], and increasing viscosity [10]. However, the results of these studies show that the spatial confinement of the evaporation zone and increased liquid viscosity lead to an increase

<sup>1</sup> State Lab for Photon Energetics, Bauman Moscow State Technical University, 5-1 2<sup>nd</sup> Baumanskaya Street, Moscow 105005, Russia. E-mail: stcpe@bmstu.ru.

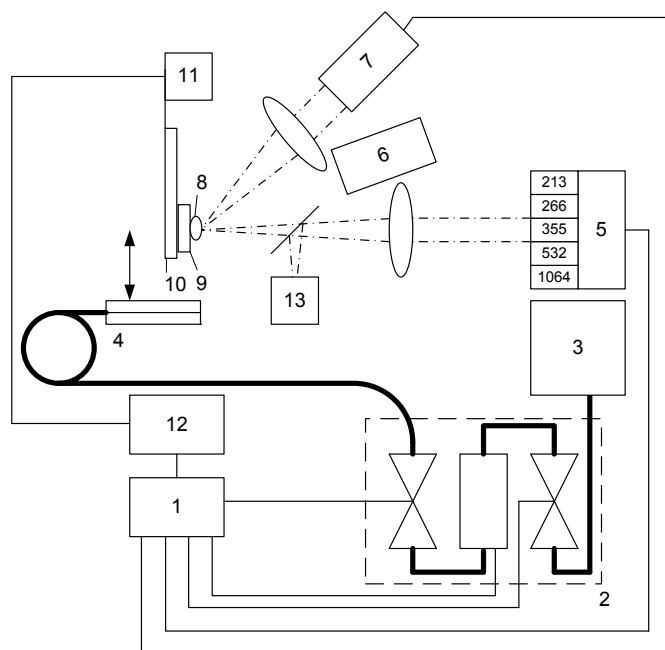


in the laser ablation efficiency by only 1-1.5 orders of magnitude. So, the absolute values of the discussed parameters remain small compared to those in the case of solid targets [11]. For instance, upon the film thickness decrease (or increase in the liquid viscosity), the ablation plume mass averaged velocity increases but remains within the interval  $\langle v \rangle \sim 30-80$  m/s. Although the momentum coupling coefficient is relatively large in the case of liquids,  $C_m \sim (0.2-1) \cdot 10^{-2}$  Ns/J, laser energy conversion efficiency defined as  $\eta = C_m \langle v \rangle / 2$  is small, on the order of  $(1-20) \cdot 10^{-4}$ .

Studies of laser-matter interaction efficiency for both solid and liquid states of the same material have been conducted only for water and ice [12]. It was demonstrated that the momentum coupling coefficient was 6-7 times higher in the case of water. However, due to the opposite ratio of mass averaged velocities of the plume, the energy efficiency was about the same in the both cases (4-6%).

Obviously, cooling a liquid down to the phase transition temperature can be used for its solidification. The latter can also take place as a result of polymerization, wherein photopolymerization occurs faster and is more controllable compared to thermal polymerization. Using special photoinitiators that bleach the reaction products for the incident laser radiation allows achieving UV-IR photopolymerization of layers with a thickness of  $\sim 1$  mm [13]. Processes similar to photopolymerization, which usually takes place in the near-surface layer with a thickness of  $\sim 10^{-6}-10^{-4}$  m, can be initiated at a depth of up to 20 mm by exposing the corresponding substance to an electron beam [14].

Currently, LCPs are used as special optical and dental glues, inks for UV printing, and in stereolithography. The rate of photopolymerization can be regulated by changing the concentration and chemical composition of photoinitiators, or the wavelength and intensity of the radiation initiating the reaction. Solidification time of ca. 30 ms was achieved in UV curing ink jet printing technology at 365 nm irradiation  $\sim 10-30$  mW/cm<sup>2</sup>, which is much lower than the laser ablation threshold.



**Figure 1.** Experimental setup (1 – pulse generator, 2 – piezopump, 3 – reservoir, 4 – ceramic ferrule, 5 – nanosecond laser, 6 – microscope, 7 – diode laser, 8 – LCP droplet, 9 – glass slip, 10 – force sensor, 11 – signal amplifier, 12 – oscilloscope, 13 – calorimeter).

## 2. Experimental setup

We report the results of studying the efficiency of the laser action on acrylic UV-ink films (SPC-0659Y, Mimaki) in the liquid and cured states. The LCP was deposited on a coverslip substrate by means of a dosing dropper (Finnpipette Digital). The droplets had a nominal volume of  $\sim 0.5$   $\mu$ L. The glass substrate was weighed on analytical scales (CAS CAUW-120D) with an accuracy of 10  $\mu$ g at all stages of the investigation. The targets were placed on a PVDF-film calibrated force sensor (Images SI PZ-02) connected to a digital oscilloscope (Tektronix 2024B). The target was cured by exposing it for

ca. 2 s to a 405 nm diode laser (Lasever LSR405NL) 0.8 W/cm<sup>2</sup> radiation, an optimal wavelength for the studied LCP curing is 365±15 nm. For the laser ablation we used five harmonics (1064 nm, 532 nm, 355 nm, 266 nm, and 213 nm) of nanosecond (18 and 12 ns) Nd:YAG lasers (Lotis TII LS-2147 and Solar LQ929 – figure 1). The focal spot size (~0.02 mm<sup>2</sup>) was measured by means of an optical microscope. Optical characteristics of the LCP were studied with an SF-2000 spectrophotometer in the interval from 190 to 1100 nm. The Raman spectra were measured using a Raman Systems R-3000 complex (785 nm, 200–2700 cm<sup>-1</sup>).

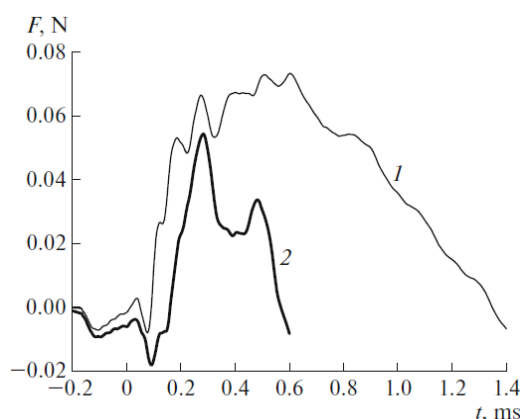
A quasi-continuous LCP supply system sample has been designed using piezo micropump (Burkert 7616), driven by pulse generator (Stanford Research Systems DG645). A ZrO<sub>2</sub> ceramic ferrule for optical fibers (230 μm capillary – Thorlabs CF230) was used to produce LCP droplets at its tip.

### 3. Results

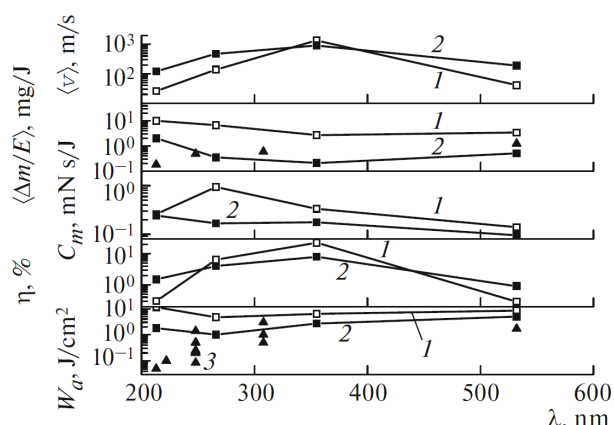
Solidification dynamics of LCPs was investigated in a number of applied studies [15]. The methods of diagnostics used in those studies were based either on light scattering by polymer chains or on the measurement of IR absorption. Our analysis of Raman spectra revealed some differences for the liquid and cured states: the intensity of the Rayleigh scattering was, as expected, higher in cured LCP, and the spectrum contained characteristic peaks at 610, 828, and 913 cm<sup>-1</sup> (similar lines are known for polymethylmethacrylate (PMMA)). The luminescence quantum yields at ~240 nm were also different for the liquid and solidified states.

Characteristic time dependences of the recoil force are presented at figure 2. In contrast to the case of water and ice [12], momentum coupling coefficient for liquid LCP is high not due to an amplitude, but due to a longer duration. Laser irradiation of a liquid produced a large number of droplets with a characteristic size of ~0.2 mm, this substantially increased the mass flow rate and reduced the mass averaged velocity.

Specific characteristics of the laser ablation efficiency averaged over 10–30 pulses are shown in figure 3. Almost all the presented dependences reveal the existence of optimal values. Data for 1064 nm are not shown because they are not representative due to a low value of the spectral absorption coefficient. In this case, either the glass substrate was damaged, or the underlying layer of the force sensor coating was ablated. It should be taken into consideration that the laser ablation thresholds for the liquid and solidified phases at different wavelengths are substantially different; i.e., the relative regimes of laser action  $W/W_a$  [16] ( $W_a$  is the laser ablation threshold) are also different. Since laser irradiation was carried out under the condition  $\ln(W/W_a) \gg 2$ , we assume that the difference of the regimes did not influence the results significantly.



**Figure 2.** Recoil force at liquid (1) and cured (2) LCP.

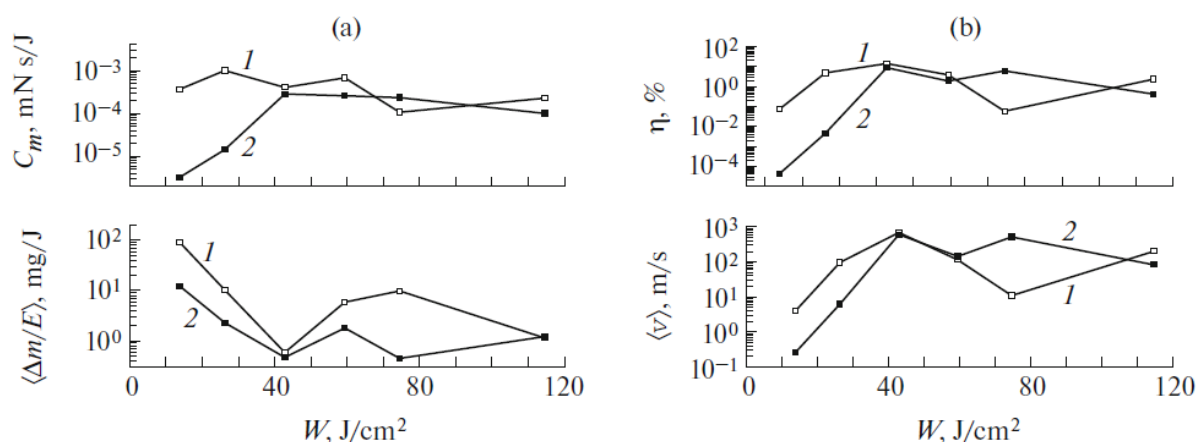


**Figure 3.** Laser ablation efficiency of a LCP ((1) liquid state, (2) cured state, and (3) reference data for nanosecond laser ablation of PMMA under ambient conditions).

Minimum ablation threshold  $W_a$  was observed at 266 nm. In most cases, the ablation thresholds of polymers decrease with increasing photon energy (it can be seen from figure 3 that our data on the laser action on solidified LCP at 266 nm are in good agreement with the data available in the literature for the laser action on PMMA). An increase in the ablation threshold at 213 nm in our experiments could be related to intense luminescence observed in this spectral interval, which leads to large energy losses. For this wavelength, the ablation threshold of liquid LCP reached a maximal value and the difference between the thresholds for the liquid and cured states was the largest.

A minimal specific mass flow was observed under target irradiation at 355 nm - close to the LCP's polymerization optimum wavelength. When a liquid LCP was exposed to such radiation (above a certain threshold, see below), it was cured during the nanosecond pulse (polymerization rate is proportional to light intensity square root), which led to a substantial increase in the mass averaged velocity of ejected plume and laser energy conversion efficiency. The data on momentum coupling coefficient in the case of the laser action on PMMA in the UV-NIR spectral range are not available in the literature (the value of  $\sim 0.04$  mN s/J was obtained for  $10.6 \mu\text{m}$  in [17]; an estimate of  $\langle v \rangle$  from this work yields  $\sim 320$  m/s and  $\eta \sim 0.64\%$ ). The general tendency for polymers is that specific recoil momentum increases inversely proportional to the wavelength, which could be drastic due to the exothermal photochemical reactions initiated when quanta energy exceeds the energies of inter- and intramolecular bonds (usually  $< 345$  nm) [18]. With the exception of the laser action at 355 nm, energy efficiency of laser ablation of solidified LCP was higher than that of liquid LCP, which also agrees with the known data.

We investigated the dependence of the discussed characteristics of the laser ablation efficiency on the energy density of the radiation at 355 nm. Irradiation at this wavelength is of particular interest, because it initiates photochemical processes. It can be seen from figure 4 that there are two regimes of the laser action. One regime leads to macroscopic polymerization of the LCP by pulsed laser radiation, while the other does not. In the region of low energies of the radiation (below  $\sim 40$  J/cm<sup>2</sup>), the discussed characteristics of the laser ablation efficiency of liquid LCP substantially exceed those for cured ones, which is not typical for irradiation at other wavelengths and known tendencies mentioned above. In the region of high energies, this difference becomes much smaller. However, the initially liquid LCP still has an advantage. The dependence of the momentum coupling coefficient on laser fluence reveals two inflection points at which the minimum corresponds to the transition from high-energy regime to a low-energy one [19], while the maximum corresponds to an optimal value for the high-energy regime [20]. Other characteristics of laser ablation efficiency in high-energy region remain approximately equal for material in the initially liquid and cured states.



**Figure 4.** Dependence of LCP ablation efficiency on laser fluence at 355 nm (legend as in figure 3).

At LCP supply system tests irradiation of a ferrule tip and droplets at an intermediate surface were considered. Unlike plastic and metal analogues, been molten or cracked, ceramic ferrules were resistant to thermal and shock loads at laser irradiation. The main issue at tip irradiation is a balance of

added and removed material, if the latter is smaller, supply capillary is blocked by cured LCP. There was no blockage observed at 355 nm (of a liquid) and 1064 nm. We also tested LCP solutions (down to 10% vol.) in ethanol, isopropanol, nitromethane, and those kept curing. Although, polymerization rate decreased proportionally to LCP fraction, this reduces capillary blockage risk.

#### 4. Conclusions

Laser ablation efficiency of the same material was studied in liquid and solidified states. The proposed approach allows combining the advantages of transporting and precisely dosing (down to  $\sim 10^{-12}$  L) liquid working media with a high efficiency of laser action on solid substances. Using liquids allows, if necessary, easily changing chemical composition of the working medium by introducing absorbing, catalytic [21], energy, and ionizing [22] additives, creating heterogeneous [23], multilayer, and spatially structured targets, which may find a broad range of applications in laser and plasma chemistry. Pulsed irradiation with sufficient intensity and at the wavelength corresponding to optimal photopolymerization leads to fast solidification of LCP and increases laser ablation efficiency. LCP solutions could be used as buffers to fix metal nanoparticles solutions been produced by laser ablation at non-curing wavelengths.

#### Acknowledgments

This work was performed at the facility “Beam-M” (RFMEFI59014X0001), supported by the State Task of the Russian Ministry of Education and Science, grant MK-203.2014.8 and the Russian Foundation for Basic Research (grants 13-08-01391 and 14-08-01087).

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