Chapter 11

DESIGNED POLYMERS FOR ABLATION

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1. INTRODUCTION

Since laser ablation of polymers was first reported by Srinivasan, et al., (Srinivasan and Mayne-Banton 1982) and Kawamura, et al., (Kawamura, et al., 1982) in 1982, numerous reviews on laser ablation of a large variety of polymers and the according ablation mechanisms have been published (Lazare and Granier, 1989; Srinivasan and Braren, 1989; Bäuerle, 2000; Lippert and Dickinson, 2003; Lippert, 2004). There is still ongoing discussion about the ablation mechanism, e.g. whether it is dominated by photothermal or photochemical processes. In many studies, a photothermal process was favored for commercially available polymers such as Kapton™ (Arnold and Bityurin, 1999; Bityurin, et al., 2003). However, polymers that show a photochemical ablation behavior at the irradiation wavelength are preferable for structuring, as damage to the surrounding material via thermal processes is minimized. In addition, a conversion of the polymer into gaseous product is advantageous, as minimal amounts of ablation products are redeposited on the structured surface, and additional cleaning procedures are not necessary. One approach to test for photochemical features in the ablation process is the design of polymers that contain photochemically active groups. An irradiation with the appropriate wavelength can then lead to photochemical decomposition or bond-breaking in the polymer.

Even though polymer ablation has been a research field for over 20 years, its potential has not yet been fully explored. One possible reason for this is because commercially available polymers such as polyimide (PI), polymethylmethacrylate (PMMA), and polycarbonate (PC), etc. (Suzuki, et al., 1997) that are applied in many ablation studies have several characteristics which make them unsuitable for high quality structuring. These include low sensitivity, carbonization upon irradiation, and redeposition of ablation products on the polymer surface (Lippert, et al., 2003). Therefore, novel photopolymers for laser ablation have been designed. The most important criteria for these polymers are:

1. High absorption coefficients ($\geq$ 20000 cm^{-1}) at the irradiation wavelength.
2. Exothermic decomposition at well-defined positions of the polymer backbone.
3. Decomposition of the polymer into gaseous products, which do not contaminate the polymer surface (Bennett, et al., 1996; Lippert, et al., 1999a).

The applications for polymers in laser ablation can be separated into two main fields. In the first one, a structure is produced in the polymer, whereas in the second field, it is the ablation products, which are of specific interest. Structuring of polymers today is used industrially for the production of nozzles for inkjet printers (Aoki, 1998) and to prepare via holes in multichip modules through polyimide by IBM (Patel and Wassick, 1997), and for many other applications, e.g. fabrication of microoptical devices.

Examples for the second group are polymers as fuel in the micro laser plasma thruster (μ-LPT), pulsed laser deposition (PLD) of polymers, or matrix assisted pulsed laser evaporation (MAPLE), which is a deposition technique that can be used to deposit highly uniform thin-films (Pique, et al., 2002).

POLYMER ABLATION

In the context of comparing ablation data it is important to clearly establish the method by which the usual ablation parameters (ablation rate, threshold fluence, and effective absorption coefficient) are defined as these values can vary considerably depending on the approach taken.

The ablation process is often described by the following equation (Andrew, et al., 1983; Srinivasan and Braren, 1984):

$$d(F)=\frac{1}{\alpha_{eff}}\ln\left(\frac{F}{F_{th}}\right), \qquad (1)$$

where $d(F)$ represents the ablation rate per pulse, α_{eff} is the effective absorption coefficient, and F is the irradiation fluence. F_{th} is the ablation threshold fluence and is defined as the minimum fluence where the onset of ablation can be observed.

It is important to specify how the ablation rate is defined, either as the ablation depth after one pulse at a given fluence, or as the slope of a plot of the ablation depth versus the pulse number for a given fluence. These two different analytical methods can result in very different ablation rates, especially in the case of polymers where ablation does not start with the first pulse, but after multiple pulses. This phenomena is known as "incubation" and is related to a chemical or physical modification of the polymer by the first few laser pulses, which increases the absorption at the irradiation wavelength (Küper and Stuke, 1989; Srinivasan, et al., 1990), e.g. the formation of double bonds in poly(methylmethacrylate) (PMMA). Incubation is normally only observed for polymers with low absorption coefficients at the irradiation wavelength.

Nevertheless, even taking into account these approaches, it is often the case that this dependence of the ablation rate cannot be described by a single set of parameters. In Fig. 1 the ablation rate versus irradiation fluence is schematically shown. Fig. 1 is a generic representation of polymer ablation rates indicating three fluence regions, which can be categorized as follows:

- Low fluence range, from which F_{th} can be defined. Incubation phenomena are also observed at these low fluences.
- Intermediate fluence range in which an increase of the slope of the ablation rate is often observed, which may be due to additional or more effective decomposition of the polymer by energy that has been gained from decomposing the polymer.
- High fluence range where the ablation rates of many polymers are similar, as the incident laser light is screened by ablation products and the plasma which are created during the ablation process (Lazare and Granier, 1989).

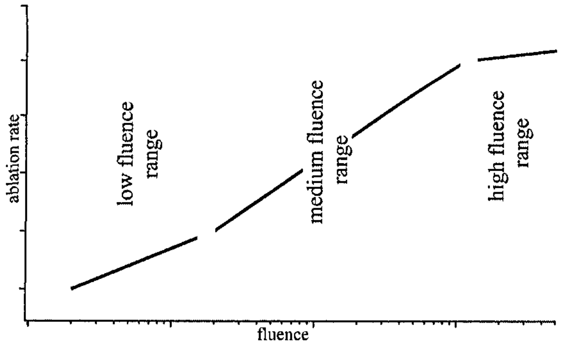


Figure 1. Schematic view of the three fluence regimes observed for most polymers.

It is worth mentioning in this context that "polyimide" (PI) is probably the most studied polymer in laser ablation and is also the material for which most ablation models are applied, but great care has to be taken for which type of polyimide the data has been obtained. Polyimide is not a single polymer, but describes a class of polymers, which contain at least one cyclic imide group per repetition unit. PI ranges from soluble polymers, to films and even photosensitive polymers which can all have very different properties (Lippert, 2005). Even products with the same name, such as Kapton™ are not one polymer, but there are also many different types of Kapton™ which are defined with additional letters, e.g. HN.

DOPED POLYMERS

In order to investigate the ablation mechanism on PMMA, various dopants have been added to the polymer ranging from polyaromatic compounds to compounds that contained photochemical active groups (Lippert, et al., 1997). Dopants based on the triazene group (-N=N-N<) have been tested, as they are photochemically well studied (Stasko, et al., 1993; Lippert, et al., 1994; Nuyken, et al., 1995a) and release a large amount of nitrogen during photochemical decomposition. The formation of gaseous products by photolabile dopants has been confirmed with a SEM analysis of the ablation craters of doped PMMA, which showed a pronounced swelling at low fluences. This swelling is caused by the decomposition of the dopants into gaseous products (Lippert and Dickinson, 2003). These authors have suggested that the released nitrogen and other gaseous ablation products act as carriers for larger ablation fragments.

At higher fluence an ablation rate of up to 80 μm can be achieved, but pronounced signs of surface melting are always visible (Lippert, et al., 1993), indicating the presence of a photothermal mechanism. One reason for this could be the limited amount of dopant (maximum of ≈10 %) that can be added to the polymer.

DESIGNED POLYMERS

In order to improve the quality of the ablation process, new polymers have been developed, where the triazene group was incorporated into the polymer main chain. One of the unique features of these polymers is the possibility to tune the absorption maximum to certain wavelengths by varying the "X" component in Fig. 2 (Nuyken, et al., 1995b). The absorption maximum of these triazene polymers (TP) can be tuned from 290 to 360 nm with a maximum linear absorption coefficient of up to almost 200000 cm^{-1}.

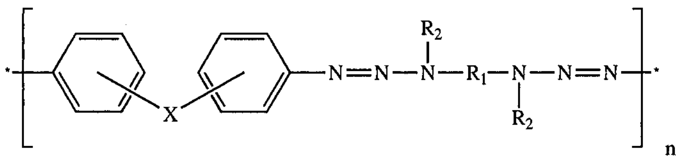


Figure 2. Chemical structure of the triazene polymers.

In Fig. 3, the chemical structure and the absorption spectra of a selected TP are shown. Two absorption maxima can clearly be distinguished in the absorption spectra, one around 200 nm which can be assigned to the aromatic system, and one around 330 nm, corresponding to the triazene unit. This allows excitation of different chromophores and the possibility to test their influence on the ablation behavior by using different irradiation wavelengths such as 193, 248, and 308 nm. A clear and well-defined F_{th} of 25 mJ cm^{-2} (± 5 mJ cm^{-2}) is observed for TP1 at an irradiation wavelength of 308 nm, while for irradiation with 248 nm a much broader range for F_{th} of 16 – 28 mJ cm^{-2} has been measured (Lippert, et al., 1996). The ablation rates measured for different wavelengths ranging from 193 to 351 nm also showed much higher ablation rates for the wavelengths that excite the triazene system, i.e. 266, 308, and also 351 nm (Lippert and Dickinson, 2003).

Another indication for different ablation mechanisms is the detection of carbonization for 248 nm irradiation, whereas the chemical composition remained unchanged after several pulses with 308 nm.

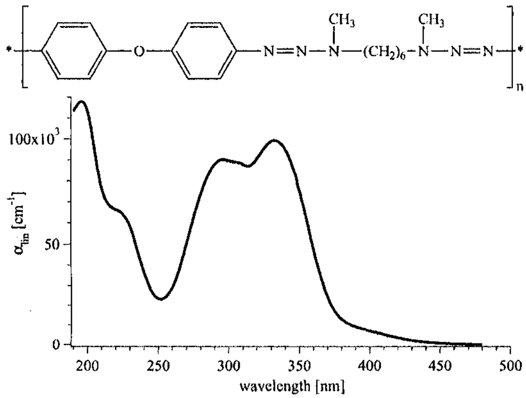


Figure 3. Chemical structure and linear absorption coefficient of TP1.

The ablation products have been studied by mass spectrometry to gain an insight into the ablation mechanism (Lippert, et al., 1999a; Lippert, et al., 1999b; Lippert, et al., 2001a). With the time-resolved mass spectrometry measurements at 248 and 308 nm irradiation wavelengths, all decomposition products for the decomposition of TP1 were identified (shown in Fig. 4 for irradiation with 308 nm), but for a thermal decomposition similar products were also observed (Nuyken, et al., 1995a). An important observation is the presence of three different species of nitrogen in the TOF (time-of-flight) signal, i.e. a very fast ground state neutral with up to 6 eV of kinetic energy, a slower neutral ground state species with a broad energy distribution, which is probably a thermal product, and possibly a metastable (excited) neutral N_2

species, that can only be created by an electronic excitation (Hauer, et al., 2002).

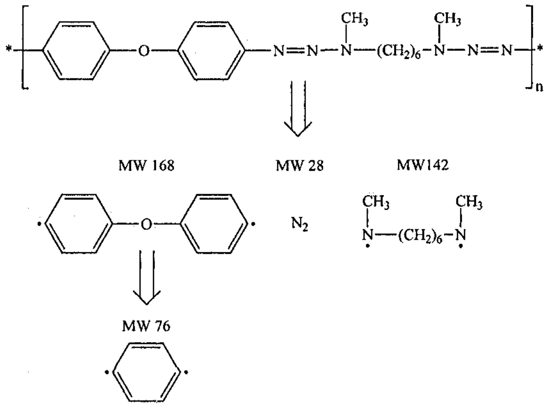


Figure 4. Decomposition pathway for TP1 measured by TOF-MS after irradiation with 308 nm.

The photochemical activity of the triazene group was also confirmed by irradiation with excimer lamps at low fluences, where linear photochemistry is expected (Lippert, et al., 2001a). At irradiation wavelengths of 308 nm and 222 nm, decomposition of the triazene chromophore was observed below F_{th}. In the case of the irradiation with 222 nm, a decomposition of the aromatic chrompohores has also been detected (Lippert, et al., 2002b) suggesting that decomposition of the aromatic part is related to carbonization. This indicates that the triazene group is clearly the most sensitive unit in the triazene polymer and that a photochemical part in the ablation mechanism is likely.

Another method to determine the present ablation mechanisms is ns-interferometry. It has been shown that thermal/photothermal ablation first results in pronounced swelling of the polymer surface, followed by etching (Furutani, et al., 1996; Furutani, et al., 1998). The etching takes place on time scales much longer than the pulse length of the excimer laser (up to the μs range).

However, for a photochemical process, as was observed for TP (see Fig. 5), etching starts and ends with the excitation pulse of the excimer laser (Lippert, et al., 2002b; Hauer, et al., 2003).

The triazene polymers were also tested for 157 nm irradiation and mass spectrometry measurements showed a higher fragmentation of the polymer than for 308 or 248 nm. At this shorter wavelength, even fragmentation of the aromatic groups was observed (Kuhnke, et al., 2003).

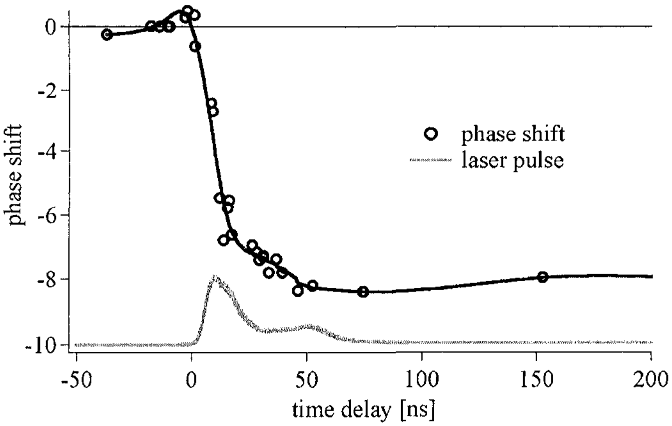


Figure 5. Interference measurement for TP1 during irradiation with 308 nm. The gray curve represents the laser pulse, while the black line corresponds to the phase shift, which is related to the ablation depth.

Irradiation with pulses in the pico and femtosecond range were performed in the near-IR at 800 nm. A lower ablation threshold fluence was found for the femtosecond pulse than for picosecond pulse indicating the presence of a thermal mechanism (Bonse, et al., 2005a). A clean removal of a thin TP film from a glass substrate was impossible with a 100 fs pulse. Therefore the structuring of TP with ultrashort pulses in the near-IR range is not an alternative to UV ablation (Bonse, et al., 2005b).

Compared to other designed polymers like polyesters or commercially available polymers such as polyimides, TP showed the highest ablation rate and lowest threshold fluence for selected irradiation wavelengths. Furthermore, structures obtained in TP (example in Fig. 6 (left)) are much sharper than in Kapton™ (see Fig. 6 (right)) and no redeposited carbon material is visible in the case of TP irradiated at 308 nm (Lippert, et al., 2002b). For comparison, Kapton™ was selected as a commercially available reference with a similar α_{lin} at 308 nm.

With ns-shadowgraphy measurements, it was shown that no solid products are produced for 308 nm irradiation of TP, which correlates well with the absence of redeposited material (Hauer, et al., 2003).

To summarize, the data obtained for the photochemical active TP strongly suggest that photochemical mechanisms play a significant role during laser ablation of polymers, but it is also clear that photothermal processes also take place. This is, for example, confirmed by the presence of a thermal N_2 product in the TOF curves. Photothermal processes will also always be present if the polymer decomposes exothermically during a photochemical decomposition and if the quantum yields of the photochemical reaction is not equal to one.

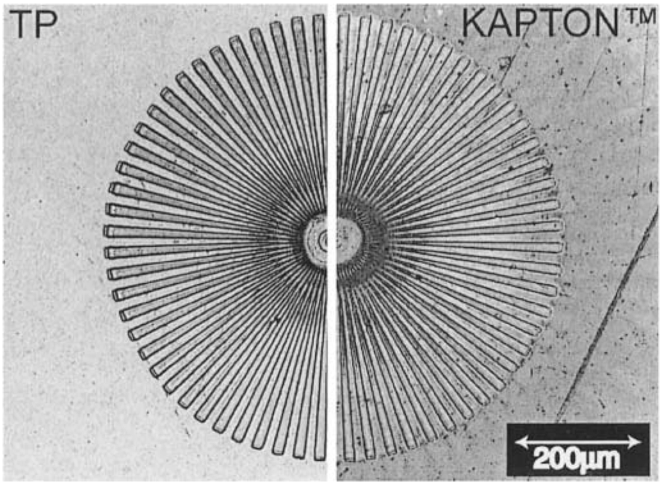


Figure 6. SEM of Siemens Stars in TP (left) and Kapton™ (right), both produced with five laser pulses at 308 nm.

Therefore, the ablation of polymers will always be a mixture of photochemical and photothermal reactions, where the ratio between the two is a function of the polymer and the irradiation wavelength.

Finally, from a material structuring point of view, it is worth noting that a photochemical mechanism leads to a more uniform decomposition of the polymer into small fragments. Furthermore, greater quantities of gaseous product are produced in the ablation plume and less material is redeposited. Therefore, the designed polymers of the TP group show clear advantages over commercially available polymers.

Selected novel applications

One of the novel applications for the designed polymers is the production of microoptical elements.

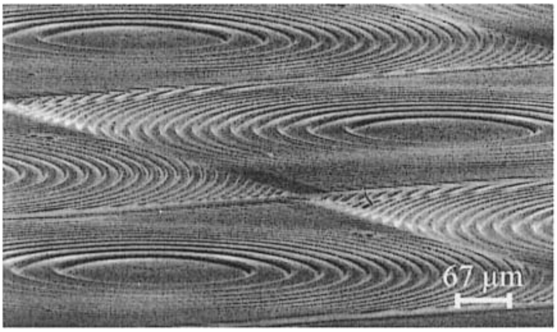


Figure 7. Fresnel lens array in photosensitive PI.

Complicated structures such as a Fresnel lens array (shown in Fig. 7) can be created with only a few pulses (Lippert, et al., 2001b), by using a specially designed diffractive gray tone phase mask that modulates the laser beam intensity (David, et al., 2001). The high sensitivity and etch rate of the TP or photosensitive PI allows the application of larger phase masks compared to other polymers such as polyimide. Alternatively, less pulses are necessary to fabricate an optical element with a given depth of the structure.

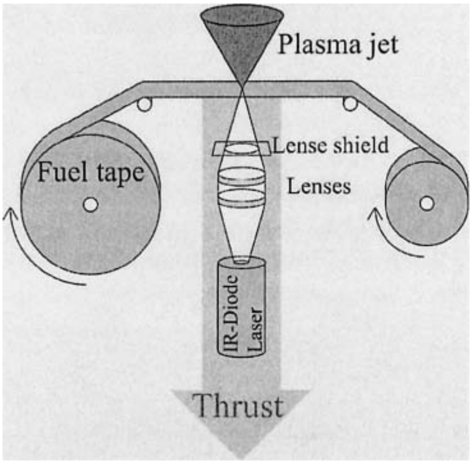


Figure 8. Scheme of the laser plasma thruster.

Another quite different application utilizes near-IR irradiation from diode lasers. The plasma created by laser ablation of the polymer acts as a micro thruster for small satellites (operating principle and setup are described in detail elsewhere (Lippert, et al., 2001b; Phipps, et al., 2002)).

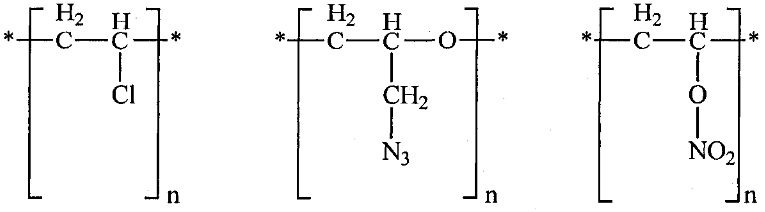
The micro laser plasma thruster (μ-LPT) is a micropropulsion device designed for the steering and propelling of small satellites (1 to 10 kg) (scheme shown in Fig. 8). A laser is focused on to a polymer layer on a substrate to form a plasma. The thrust produced by this plasma is used to control the satellite motion (Phipps, et al., 2003; Phipps, et al., 2004a). Due to the specific demands (weight and power), the μ-LPT is driven by small powerful diode lasers, which emit in the near-IR (920-980 nm) with an available power of 1 to 15 W, and a pulse length from 100 μs to the millisecond range (Phipps, et al., 2004b). This pulse duration and wavelength require the utilization of materials for the fuel with low thermal conductivity, i.e. polymers (Lippert, et al., 2002a; Lippert, et al., 2003).

As most polymers are not absorbing in the near-IR range, it was necessary to add dopants, such as carbon or IR-dyes. Carbon nanopearls were selected as they showed the best results in thrust experiments, even though they tend to agglomerate in suspensions to form particles of 10 to 20 μm diameter (Richner, 2001). The IR-dye, on the other hand, is distributed on a molecular level. A different concentration for both dopants was selected to reach the same linear absorption coefficient at the irradiation wavelength of 1064 nm.

TP's also revealed good properties for this application, but the photochemical properties are only of minor importance, since exothermic decomposition, gas formation, and a well-defined decomposition temperature are more important for the LPT application. As exothermic decomposition seems to be a key element in generation of thrust, new higher energetic polymers were developed. Absorption of the polymer at the irradiation wavelength is less important, as the dopants are the primary absorbers.

To understand the influence of the specific properties of the fuel polymers, four different "high" and "low"energetic polymers were tested:

- Poly(vinyl chloride) (PVC) as a low-energetic reference polymer that showed the best properties among commercial polymers (Phipps and Luke, 2002),
- A triazene polymer (TP1), that was designed for laser ablation in the UV range, and
- Glycidyl azide polymer (GAP) and Poly(vinyl nitrate) (PVN) as high-energetic polymers (chemical structure in Fig. 9).



Poly(vinyl chloride) (PVC) Glycidyl azide polymer (GAP) Poly(vinyl nitrate) (PVN)

Figure 9. Chemical structure of PVC, GAP, and PVN.

GAP was originally developed as binder for solid propellant rockets (Frankel, et al., 1992; Köhler and Meyer, 1998) but it meets the demands for the LPT, such as easy handling, exothermic decomposition and well defined decomposition temperature. PVN is a thermoplastic polymer with a similar decomposition temperature but a much higher decomposition enthalpy than PVC, TP1, and GAP (see Table 1).

Table 1. Properties of polymers (Urech, et al., 2004)

Polymer	Decomposition temperature [°C]	Decomposition Enthalpy [J/g]
PVC	241, 288, 383	-418
TP1	227	-700
GAP	249	-2053
PVN	204	-3829

All polymers were doped with carbon (nanoparticles) and, in the case of GAP, also with an IR-dye (Epolight 2057), to achieve absorption in the near-IR (λ=1064 nm). In this section polymers will be referred to with the abbreviation of the polymer, and by indicating the dopant by "+ C" for carbon and "+ IR" for IR-dye.

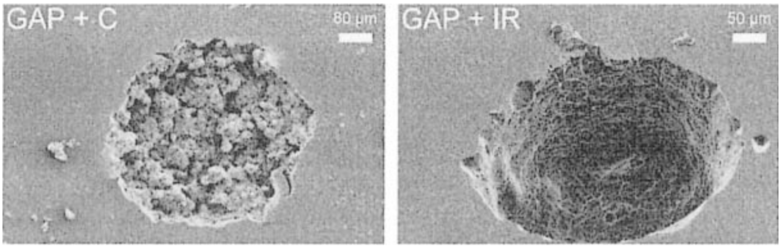


Figure 10. SEM images of the ablation spots of GAP + C (left) and GAP + IR (right).

The different dopants for GAP seem to have only a small influence on the ablation properties, such as ablation rate and threshold fluence (Urech, et al., 2004). The most pronounced differences are observed in the ejected fragments detected in the shadowgraphy measurements and the ablation crater appearance. An SEM investigation of the ablation crater confirmed these results, by showing an ablation crater with steep, smooth walls for GAP + IR, whereas the crater of GAP + C is quite rough, with deep holes and a very uneven bottom (see Fig. 10). Large fragments of solid and liquid ablation products are observed for GAP + C in the ns-shadowgraphy image (see Fig. 11 (left)), while almost no solid fragments are ejected by GAP + IR (see Fig. 11 (right)). It seems that the ablated material is transformed completely into gaseous products. This is a desired effect, as more energy is gained by decomposing more polymer.

The more homogeneous and non-agglomerating IR-dye leads to a more homogeneous decomposition, whereas the big carbon clusters produce local hotspots (Wen, et al., 1994). In the near surrounding of these clusters, the material is decomposed. This decomposition leads to the formation of gaseous products and the ejection of polymer fragments between the ablation spots. Energy gained by decomposing the polymer is lost by the ejection of solid or liquid polymer fragments.

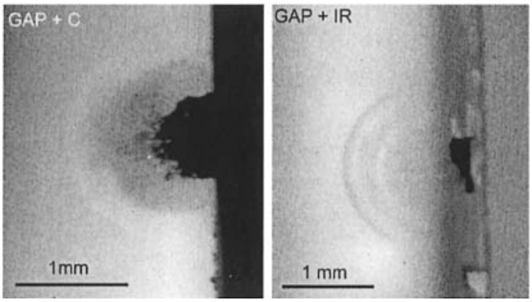


Figure 11. Shadowgraphy images of carbon (left) and IR-dye (right) doped GAP. The image was taken 1 μs after the laser pulse.

A pronounced difference has been observed in the shockwave and ejected products for the different polymers. In all cases, large polymer fragments are ejected. The largest fragments are observed when using PVC + C and PVN + C (see Fig. 12). The trajectory of these fragments is strongly directed towards the normal to the polymer surface, much more so than in the case of GAP + C and TP1 + C. The fragments also overtake the shockwave after ~500 ns in the case of PVN, and after 3 μs in the case of PVC. For GAP + C and TP + C, the product plume can be separated into two parts. The first part consists of small (gaseous) products, whereas the second part is formed by much larger polymer fragments. The particle plume in both cases expands almost hemispherical and is slower than the shockwave.

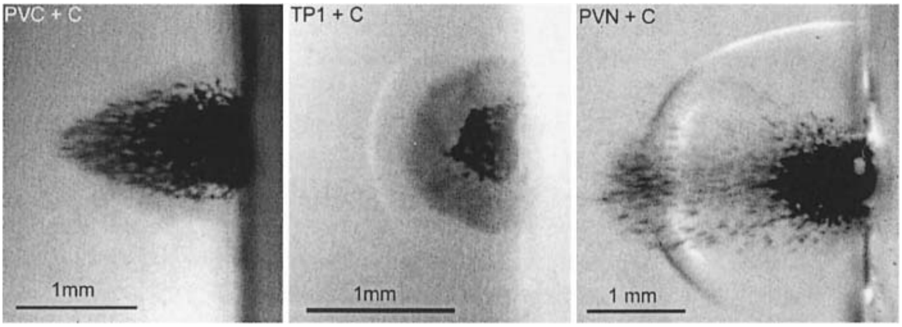


Figure 12. Ns-shadowgraphy images for carbon doped PVC, TP1, and PVN. The images were taken 1 μ s after the laser pulse.

The fastest shockwave was observed for PVN, followed by GAP, where only a small difference between the two dopants could be observed, and then TP and PVC (Hauer, et al., 2004; Urech, et al., 2004) (shown in Fig. 13). The slowest shockwave velocity was measured for PVC. This order correlates well with the decomposition enthalpy of the polymers, where the largest amount of chemically stored energy leads to the highest shockwave velocity.

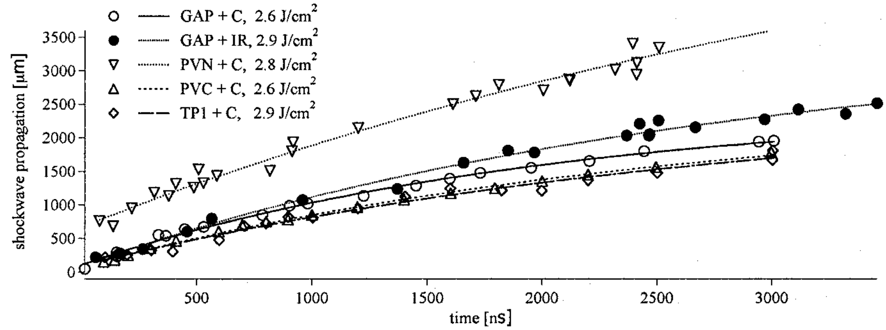


Figure 13. Shockwave front propagation versus time for GAP, PNV, TP1, and PVC doped with carbon, and for GAP doped with IR-dye

To analyze the performance of the polymers as fuel for the LPT, the target momentum was measured on a torsion balance as described in (Phipps and Luke, 2002). The target momentum was then used to calculate the momentum coupling coefficient C_m:

$$C_m = \frac{m\Delta v}{W} = \frac{F}{P} , \qquad (2)$$

where $m\,\Delta v$ is the target momentum produced during the ejection of laser ablated material. W is the incident laser pulse energy, F is the thrust, and P the incident power. The second important parameter for thrusters is the specific impulse I_{sp}, which is defined as:

$$I_{sp}g = v_E = C_m Q^* \ . \qquad (3)$$

Q^* is the specific ablation energy (incident power/mass ablation rate), v_E is the exhaust velocity, and g is the acceleration due to gravity.

As Eq. (3) demonstrates, I_{sp} and C_m are not independent. If, for example, a significant amount of incident energy is absorbed as heat in the target rather than producing material ejection, Q^* will be higher and C_m will be proportionally lower. This results in the same exhaust velocity and I_{sp} for both cases.

The thrust measurements revealed the highest I_{sp} for PVN + C (2320 s), whereas the other polymers showed much lower values (200 to 650 s) (dark grey in Fig. 14). The highest values for C_m were obtained for GAP + IR (2000 μN/W), followed by GAP + C, PVN + C, TP + C, and PVC + C (1170 to 120 μN/W) (light gray in Fig. 14). The high C_m value for the IR-doped polymer indicates a high transformation of polymer into the gaseous state, as also observed in the shadowgraphy and SEM measurements.

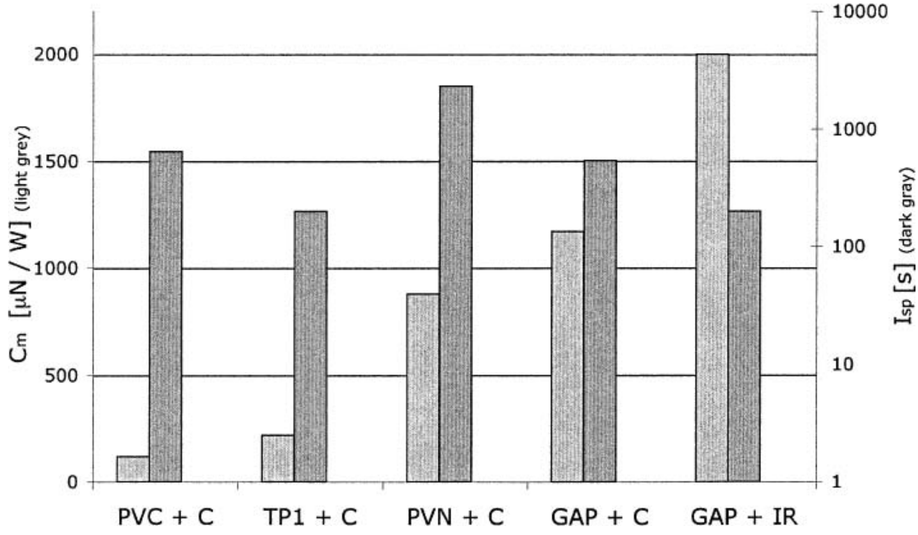


Figure 14. Coupling momentum coefficient (light grey) and the specific impulse (dark gray) for PVC, TP1, PVN, and GAP doped with carbon, and for GAP doped with IR-dye.

Surprisingly, the same order for the performance was observed for thrust and shadowgraphy measurements, even though the measurements were performed under totally different conditions, i.e. ambient conditions and low fluences for the shadowgraphy measurements and vacuum and high fluences for the thrust measurements. This allows evaluation of polymers under ambient conditions instead of vacuum.

For energetic polymers, a transformation of induced laser energy to measured thrust of more than 100% was observed. This indicates that energy gained from decomposing the polymer can be transferred into thrust, and that the ablation mechanism plays only a minor role.

These experiments demonstrate that the main demand on polymers as fuel for the μ-LPT is a high decomposition enthalpy. Furthermore, a high transition rate of the polymer into gaseous products is favorable, as more energy can be gained. As the influence of the dopant also needs to be considered, future developments may have to concentrate on polymer-dopant systems, not just on polymers.

ACKNOWLEDGMENTS

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