

Polymer ablation: From fundamentals of polymer design to laser plasma thruster

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Abstract

UV-Laser ablation of polymers is a well-established method to structure and deposit polymers, but the mechanisms of ablation are still controversial, i.e. photothermal or photochemical processes. An approach to probe the ablation mechanisms and to improve ablation is to incorporate photoactive groups into the polymer structure.

The investigation of the ablation behavior of designed triazene polymers showed that the ablation mechanism is always a combination of both photothermal and photochemical processes, but the ratio can be changed by using different polymers and irradiation wavelengths. Also the quality of structures in the triazene polymers is superior at an irradiation wavelength of 308 nm compared to commercially available polymers.

Polymers can be designed not only for UV irradiation, but also for applications in the IR range, but with different requirements. One application for designed polymers in the near-IR range is as fuel for the laser plasma thruster, which is used as propulsion system for small satellites. With commercially available polymers the necessary thrust could not be achieved. A specially designed polymer-absorber system for this application produce more energy in the form of thrust, than the laser delivered.

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1. Introduction

Since laser ablation of polymers was first reported by Srinivasan and Mayne-Banton [1] and Kawamura et al. [2] in 1982, numerous reviews on laser ablation of a large variety of polymers and the according ablation mechanisms have been published [3–7].

There is an ongoing discussion whether the ablation mechanism is dominated by photothermal or photochemical processes. In many studies, a photothermal process has been favored for commercially available polymers such as KaptonTM [8,9]. However, polymers that show a photochemical ablation behavior at the irradiation wavelength are preferable for structuring, as damage to the surrounding material by thermal processes is minimized and there is less surface modification in the irradiated area. Also a conversion of the polymer into gaseous product is advantageous, as the amount of ablation

products that are redeposited on the structured surface is reduced, and additional cleaning procedures are not necessary. One approach to test for photochemical features in the ablation process is to design polymers that contain photochemically active groups. Irradiation with the appropriate wavelength can then lead to photochemical decomposition or bond breaking and energy release in the polymer.

2. Polymer ablation

To understand and discuss ablation data it is important to establish clearly 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 method of measurement.

The ablation process is often described by the following Eqs. [10,11]:

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

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where $d(F)$ represents the ablation rate per pulse, α_{eff} 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 a single pulse at a given fluence, or as the slope of a plot of the ablation depth versus the pulse number for a given fluence. Very different ablation rates can result from these two different analytical methods. This difference is more pronounced for polymers for which “incubation” is observed, implying that ablation begins only after multiple pulses. This phenomenon 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 [12,13], e.g. the formation of double bonds in poly(methylmethacrylate) (PMMA). Incubation is mainly observed for polymers with low absorption coefficients at the irradiation wavelength.

3. Designed polymers for laser ablation

3.1. Approach

Polymer ablation still yields a big potential, even though it has been a research field for over 20 years. One possible reason for this is because commercially available polymers such as polyimide (PI), polymethylmethacrylate (PMMA) and polycarbonate (PC), etc. [14] that are applied in many ablation studies have several characteristics which make them unsuitable for high quality structuring, e.g. low sensitivity, carbonization upon irradiation and redeposition of ablation products on the polymer surface [15]. Therefore, novel photopolymers for laser ablation have been designed [16–19]. The most important criteria for these polymers are:

- High absorption coefficients ($\geq 20,000 \text{ cm}^{-1}$) at the irradiation wavelength.
- Exothermic decomposition at well-defined positions of the polymer backbone.
- Decomposition of the polymer into gaseous products, which do not contaminate the polymer surface [20,21] and carry away solid ablation products from the surface.

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 industrially used for the production of nozzles for inkjet printers [22] and to prepare via-holes in multichip modules through polyimide by IBM [23], and for many other applications.

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 [24–26].

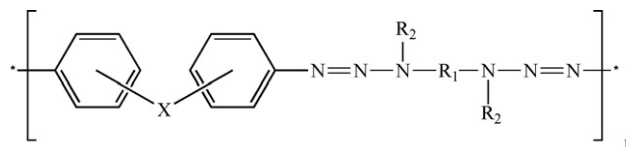


Fig. 1. Chemical structure of the triazene polymers.

3.2. Examples: triazene polymers designed to analyze the ablation mechanisms and for structuring

In order to improve the quality of the ablation process and to understand the ablation mechanisms, new polymers have been developed. One approach was to incorporate a triazene group ($-\text{N}=\text{N}-\text{N}<$) into the polymer main chain. The absorption maximum of these polymers can be varied to certain wavelengths by varying the “X”-component in Fig. 1 [27]. 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 $200,000 \text{ cm}^{-1}$.

In Fig. 2 the chemical structure and the absorption spectra of a selected TP (TP1) are shown. Two absorption maxima can clearly be distinguished in the absorption spectra. The first one around 200 nm can be assigned to the aromatic system, and the second around 330 nm corresponds to the triazene unit [28]. This separation allows excitation of different chromophores and offers the possibility to test their influence on the ablation behavior by using different irradiation wavelengths such as 193, 248 and 308 nm.

Compared to other designed polymers such as polyesters or commercially available polymers such as polyimides, TP showed the highest ablation rate and lowest threshold fluence for selected irradiation wavelengths [29]. Furthermore, no material was redeposited on the structured surface of TP (example in Fig. 3 (right)) compared to polyimide (KaptonTM) (Fig. 3 (left)) after irradiation with 308 nm [30], where substantial contamination of the structured area and the surrounding surface is observed. The structures in TP are also

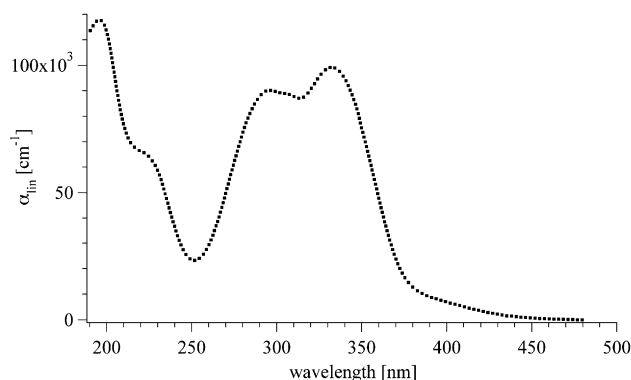
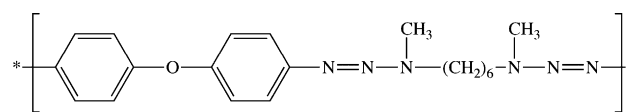


Fig. 2. Chemical structure and linear absorption coefficient of TP1.

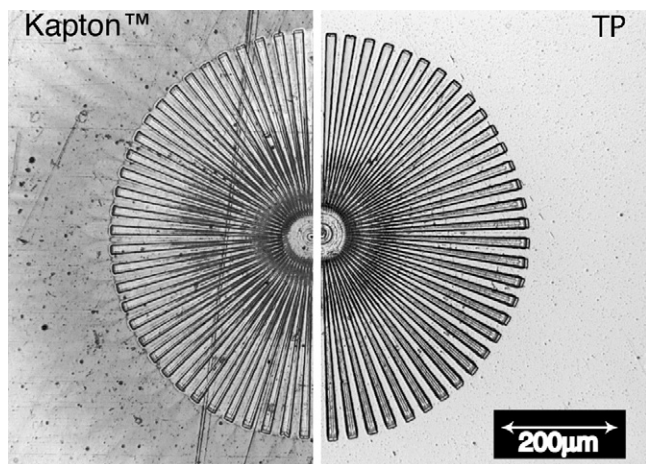


Fig. 3. SEM image of a Siemens Stars in polyimide (Kapton™) (left) and in TP (right), that were produced with five laser pulses at 308 nm.

much sharper than in polyimide, which 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 in Fig. 3 [31].

Another method to gather information about the present ablation mechanisms is ns-interferometry. It has been shown by Furutani et al. [32,33] that pronounced swelling of the polymer surface is initially observed for thermal/photothermal ablation, followed by etching. The etching also 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 observed for TP (see Fig. 4), etching starts and ends with the excitation pulse of the excimer laser [30,31].

Another method that was applied to gain insight in the ablation mechanism was mass spectrometry [21,34,35]. With 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. 5 for 308 nm), but similar products were also observed for a thermal decomposition [36]. An important observation is the presence

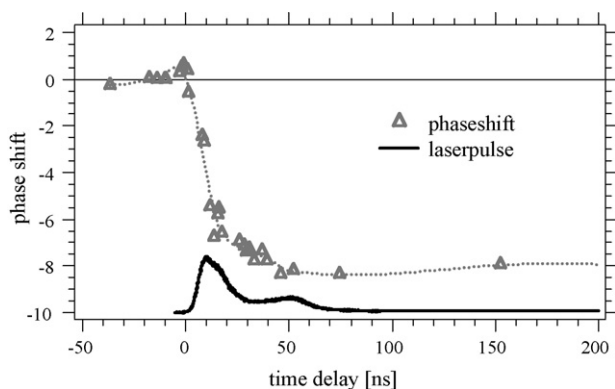


Fig. 4. Interference measurement for TP1 during irradiation with 308 nm. The black curve represents the laser pulse, while the dotted gray line corresponds to the phase shift, which is related to the ablation depth.

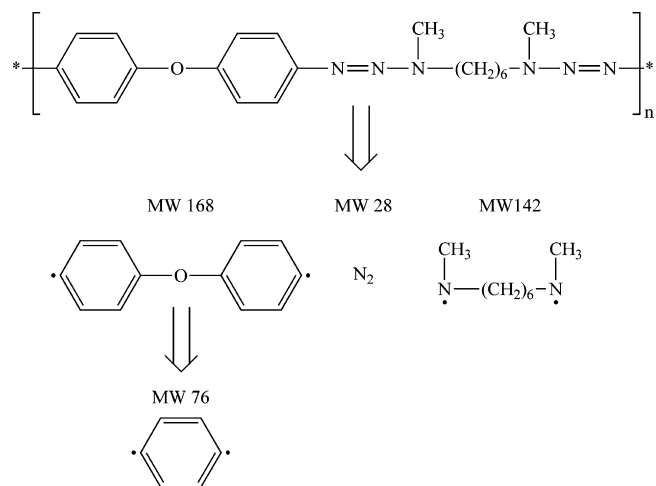


Fig. 5. The decomposition pathway for TP1 after 308 nm irradiation measured by TOF-MS.

of three species of nitrogen in the TOF (time-of-flight)-signal [37], 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 another species which is possibly a *metastable (excited) neutral N₂ species*. This last species could only be created by an electronic excitation [37] (for example by a two photon process), supporting together with the fast species the photochemical part of the mechanism, while the thermal product is a clear indication for the mixed process.

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 N₂ product in the TOF curves. The presence of photothermal features is of course not surprising, as many polymers decompose exothermically during a photochemical decomposition and have a quantum yields of the photochemical reaction which is not equal to one. Therefore, the ablation of polymers will always be a mixture of photochemical and photothermal reactions. The ratio between the two can be modified by using different polymers and irradiation wavelengths.

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.

3.3. Special application of designed polymers: as fuel in the micro laser plasma thruster

The micro laser plasma thruster is a micropropulsion device designed for the steering and propelling of small satellites (1–10 kg) (scheme shown in Fig. 6). A laser is focused onto a polymer layer on a substrate to form a plasma. The thrust

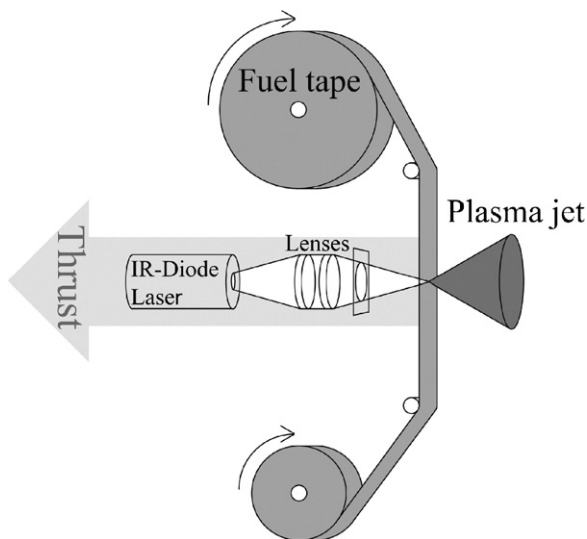


Fig. 6. Scheme of the μ -laser plasma thruster.

produced by this plasma is used to control the satellite motion [38,39]. The μ -LPT is driven by small powerful diode lasers (due to the specific demands on weight and power), which emit in the near IR (920–980 nm) with an available power of 1–15 W and a pulse duration from 100 μ s to the millisecond range [40]. This pulse duration and wavelength require the utilization of materials for the fuel with low thermal conductivity, i.e. polymers [15,41].

As most polymers are not absorbing in the near-IR range, it is necessary to add absorbers, such as carbon nanoparticles or IR-dyes. Carbon nanoparticles were selected as they showed the best results in thrust experiments, even though they tend to agglomerate in suspensions to form particles of 10–20 μ m diameter [42]. 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 as exothermic decomposition, gas formation and a well-defined decomposition temperature are the most important factor for the LPT application, the photochemical properties are only of minor importance, as the main demand on the polymer for LPT

application is sufficient energy release during the ablation process. The concept of the LPT contemplates that chemically stored energy can be transferred into thrust. Therefore, other even more energetic polymers were utilized, as exothermic decomposition seems to be a key element in generation of thrust. The absorption of the polymer at the irradiation wavelength is less important, as it can be achieved by utilizing the dopants as primary absorbers.

To understand the influence of the specific properties of the fuel polymers, three 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 [43].
- Glycidyl azide polymer (GAP) and poly(vinyl nitrate) (PVN) as high-energetic polymers (chemical structure in Fig. 7).

GAP was originally developed as binder for solid propellant rockets [44,45] 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 and GAP (see Table 1).

Carbon nanoparticles were used as absorbers in all three polymers. For GAP, also an IR-dye was tested as absorber, to investigate its influence on the thrust performance. The polymers will be referred to in this paper with the abbreviation of the polymer and by indicating the dopant by “+C” for carbon and “+IR” for the IR-dye.

The target momentum of the polymers was measured with a torsion balance as described in Ref. [43] to evaluate their performance in a μ -LPT. From the target momentum, the momentum coupling coefficient, C_m , was calculated according to:

$$C_m = \frac{m\Delta v}{W} = \frac{F}{P} \text{ (dyn/W)} \quad (2)$$

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

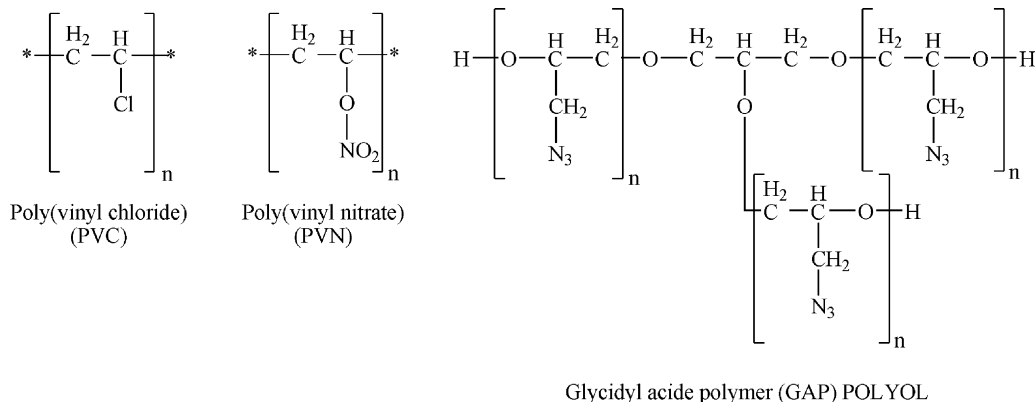


Fig. 7. Chemical structures of PVC, PVN and GAP-POLYOL.

Table 1
Decomposition properties of GAP, PVN and PVC [47]

Polymer	Decomposition temperature (°C)	Decomposition enthalpy (J/g) ^a
GAP	249	−2053
PVN	204	−3829
PVC	241,288,383	−418

^a Measured by DSC, using carbon doped samples of the polymer.

thrusters and is defined as:

$$I_{sp}g = v_E = C_m Q^* \quad (\text{cm/s}) \quad (3)$$

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

The ablation efficiency parameter η_{AB} is defined as the efficiency of the conversion of the laser energy into exhaust kinetic energy:

$$2\eta_{AB} = C_m \cdot v_E (\%) \quad (4)$$

The thrust measurements reveal the best performance for GAP + C as fuel polymer with η_{AB} of up to 368%. GAP + IR reveals also a η_{AB} value, which exceeds 100% (see Table 3). This means that more energy is released in the form of thrust than deposited in the polymer by the incident laser pulse, suggesting that the μ -LPT with GAP as fuel can be described as a hybrid thruster utilizing chemical-stored and laser energy. Significant lower η_{AB} values are observed for PVC + C and PVN + C. For PVC + C this was expected, as only a small amount of energy is stored in the polymer.

The worst performance in the thrust measurements was observed for PVN, which has the highest decomposition enthalpy of −3829 J/g. One possible explanation for this surprising behavior could be related to the material properties of PVN, as it is a thermoplast with a softening temperature of 30–45 °C. When this temperature is reached during the decomposition process, the polymer starts to flow and later to melt. For the evaluation of the thrust measurements, the ablated mass has to be determined. Thermal effects such as melting or the formation of fibers on the surface [46] may result in an overestimation of the ablated mass, which will yield a lower momentum coupling coefficients and efficiencies (Eqs. (2) and (4)). The mass spectra presented in Ref. [46] also reveal the presence of solvent in the polymers film. The

Table 2
Thrust data for all for polymer-absorber systems at optimized experimental conditions, i.e. maximum η_{AB} value [48]

Polymer	I_{sp} (s)	C_m ($\mu\text{N/W}$)	v_E (m/s)	η_{AB} (%)
GAP + C	867	865	8502	368
GAP + IR	256	1574	2510	198
PVN + C	137	310	1343	21
PVC + C	159	635	1559	49

remaining solvent acts as inert mass during the ablation process, which will not contribute to the thrust.

For the spectroscopy and shadowgraphy experiments the fundamental wavelength ($\lambda = 1064$ nm, $\tau = 6$ ns) of a Nd:YAG laser (Brillant B from Quantel) with some hotspots was utilized.

Shadowgraphy is a fast, non-vacuum method to test the different polymers. The shockwave velocity is used as indicator for the thrust performance of the polymer (see [47]). The main difference to the thrust measurements is that the experiments were performed under ambient conditions at a fluence below the plasma formation threshold. The experimental setup is described in detail in Ref. [47].

The expansion velocity of the shockwave has been calculated 1 μs after the laser pulse (see Table 3). The highest expansion velocity was observed for PVN + C, followed by GAP + IR, GAP + C and PVC + C. This result corresponds well to the decomposition enthalpies of the polymers (see Table 1), but not to the measured thrust data (Table 2), where the best performance was observed for GAP with both dopants. PVN, the polymer with the highest decomposition enthalpy, has the fastest shockwave, while for PVC the lowest shockwave velocity and decomposition enthalpy was measured.

The mass- and plasma emission spectroscopy were performed in a UHV chamber at a pressure of 8×10^{-8} mbar (for experimental details see [46] and [48]).

Time and space resolved plasma emission spectra of the Balmer H_{α} line at 656.6 nm were recorded for an irradiation fluence of 25 J cm^{-2} . The temporal position of the maximum intensity for each distance from the sample surface was used to calculate the propagation velocity of the excited neutral hydrogen along the central axis of the plasma plume. The fastest hydrogen was observed for GAP + C and PVC + C, followed by GAP + IR and PVN + C. The expansion velocities are compared in Table 3.

More fragmentation for the energetic polymers was observed by mass spectrometry [46]. The kinetic energies of the C^+ -ions were measured with the mass spectrometer for an

Table 3
Expansion velocities for the shockwave, C^+ -ions and hydrogen from the Balmer H_{α} line [48]

Polymer	Shadowgraphy (from shockwave) (m/s)	Mass spectrometry (from C^+ -ions)(m/s)	Plasma emission (from Balmer H_{α}) (m/s)
GAP + C	710	28600	46000
GAP + IR	850	29300	36700
PVN + C	1080	25100	31100
PVC + C	630	25900	48300

irradiation fluence of 23 J cm^{-2} , as for all polymers one of the main decomposition products was positively charged carbon (C^+). The expansion velocity of ionic carbon was determined from the energy with the highest intensity.

The highest velocity was observed for GAP + IR, followed by GAP + C. For PVN + C and PVC + C a similar lower velocity for the C^+ was observed (see Table 3). In comparison to the velocities from the emission measurements, the propagation was slower by a factor of 1.2–1.8. A possible explanation for this is the experimental design: The emission spectroscopy is a non-invasive measurement method, whereas the nozzle of the mass spectrometer can have an influence on the plasma and its expansion. Another possible reason could be that in the energy measurements with the mass spectrometer, ions are measured, while the Balmer H_α line corresponds to excited neutral hydrogen.

No quantitative correlation could until now be established between thrust and the results of the different measurement methods. GAP + C shows a good performance in all experiments, while GAP + IR reveals good results in the thrust and mass spectrometry measurements, but the velocity of the hydrogen measured by plasma emission spectroscopy is much lower compared to GAP + C and PVC + C. Until now, only a single line in the emission spectra (Balmer H_α) and only one mass in the mass spectrometer (C^+) have been investigated in detail. It is possible that thrust, which is the sum of different effects, can only be explained by a combination of different measurements.

For GAP, 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.

The longer pulse lengths and possibly the shorter irradiation wavelength (980 nm versus 1064 nm) in the thrust measurements may also have a significant influence on the ablation process. The longer pulse length could increase the influence of the thermal side effects, such as melt ejection, and may therefore result in the worse performances of the thermoplasts, PVN and PVC.

For a quantitative correlation the thrust measurements have to be performed with the same experimental conditions, i.e. pulse length and irradiation wavelength.

4. Conclusions

Designed triazene polymers were investigated to determine the mechanisms that are present in the ablation process of polymers with UV irradiation. The measurements with different methods (i.e. mass spectrometry, ns-interferometry and ns-shadowgraphy) revealed that always a combination of photothermal and photochemical processes are taking place during laser ablation, and that the ratio between the two mechanisms can be influenced by the polymer structure and the irradiation wavelengths. A photochemical decomposition is preferable for structuring, as less contamination of the sample surface and sharper structures are resulting. The designed

triazene polymers are therefore better suited for micro structuring from a strict performance aspect compared to commercially available polymers.

The triazene polymers were also tested as fuel for the laser plasma thruster. Satisfying results were obtained, but as the most important material property for this application the exothermic decomposition was identified. Therefore, polymers with higher decomposition enthalpies were investigated additionally.

In the thrust measurements, an azide polymer, i.e. GAP doped with carbon reached the highest values, followed by GAP doped with an IR-dye, PVC + C and PVN + C. The worst result for PVN + C with respect to thrust for the polymer with the highest decomposition enthalpy, can be explained by thermal effects that take place during the polymer decomposition and by solvent that is trapped in the polymers film.

A correlation of the thrust measurements with other measurement methods could only be established qualitatively. Shadowgraphy measurements the fastest shockwaves were observed for the more energetic polymers, but a quantitative correlation with the thrust measurements is difficult, as the experimental parameters are different (i.e. pulse length, laser fluence and surrounding pressure). In mass and emission spectroscopy measurements, the best results with respect to the expansion velocity of selected species in the ablation plume (C^+ for mass- and H for emission spectroscopy) were obtained for GAP, followed by PVC and PVN.

References

- [1] R. Srinivasan, V. Mayne-Banton, *Appl. Phys. Lett.* 41 (1982) 576–578.
- [2] Y. Kawamura, K. Toyoda, S. Namba, *Appl. Phys. Lett.* 40 (1982) 374–375.
- [3] R. Srinivasan, B. Braren, *Chem. Rev.* 89 (1989) 1303–1316.
- [4] D. Bäuerle, *Laser Processing and Chemistry*, Springer Verlag, Berlin, 2000.
- [5] S. Lazare, V. Granier, *Laser Chem.* 10 (1989) 25–40.
- [6] T. Lippert, J.T. Dickinson, *Chem. Rev.* 103 (2003) 453–485.
- [7] T. Lippert, *Laser application of polymers*, in: *Polymers and Light*, Springer-Verlag Berlin, Berlin, 2004, pp. 51–246.
- [8] N. Arnold, N. Biturin, *Appl. Phys. A-Mater. Sci. Process.* 68 (1999) 615–625.
- [9] N. Biturin, B.S. Luk'yanchuk, M.H. Hong, T.C. Chong, *Chem. Rev.* 103 (2003) 519–552.
- [10] J.E. Andrew, P.E. Dyer, D. Forster, P.H. Key, *Appl. Phys. Lett.* 43 (1983) 717–719.
- [11] R. Srinivasan, B. Braren, *J. Polym. Sci. Polym. Chem.* 22 (1984) 2601–2609.
- [12] R. Srinivasan, B. Braren, K.G. Casey, *J. Appl. Phys.* 68 (1990) 1842–1847.
- [13] S. Küper, M. Stuke, *Appl. Phys. A-Mater. Sci. Process.* 49 (1989) 211–215.
- [14] K. Suzuki, M. Matsuda, T. Ogino, N. Hayashi, T. Terabayashi, K. Amemiya, *SPIE* 2992 (1997) 98–107.
- [15] T. Lippert, M. Hauer, C.R. Phipps, A. Wokaun, *Appl. Phys. A-Mater. Sci. Process.* 77 (2003) 259–264.
- [16] T. Lippert, A. Wokaun, J. Stebani, O. Nuyken, J. Ihlemann, *Angew. Makromol. Chem.* 206 (1993) 97–110.
- [17] K. Suzuki, M. Matsuda, N. Hayashi, *Appl. Surf. Sci.* 129 (1998) 905–910.
- [18] T. Buruiana, A. Airinei, E.C. Buruiana, G. Robila, *J. Macromol. Sci.-Pure Appl. Chem.* A32 (1995) 1397–1404.
- [19] T. Buruiana, A. Airinei, E.C. Buruiana, G. Robila, *Angew. Makromol. Chem.* 226 (1995) 205–212.

- [20] L.S. Bennett, T. Lippert, H. Furutani, H. Fukumura, H. Masuhara, Appl. Phys. A-Mater. Sci. Process. 63 (1996) 327–332.
- [21] T. Lippert, S.C. Langford, A. Wokaun, G. Savas, J.T. Dickinson, J. Appl. Phys. 86 (1999) 7116–7122.
- [22] H. Aoki, Laser processing method to form an ink jet nozzle plate, U.S. Patent 5736999, April 7, 1998.
- [23] R.S. Patel, T.A. Wassick, SPIE 2991 (1997) 217.
- [24] A. Pique, P. Wu, B.R. Ringeisen, D.M. Bubb, J.S. Melinger, R.A. McGill, D.B. Chrisey, Appl. Surf. Sci. 186 (2002) 408–415.
- [25] D.B. Chrisey, A. Pique, R.A. McGill, J.S. Horwitz, B.R. Ringeisen, D.M. Bubb, P.K. Wu, Chem. Rev. 103 (2003) 553–576.
- [26] D.M. Bubb, R.F. Haglund Jr., Resonant infrared pulsed laser ablation and deposition of thin polymer films, in: R. Eason (Ed.), Pulsed Laser Deposition of Thin Films: Applications-Led Growth of Functional Materials, John Wiley and Sons, Inc., New York, 2006, pp. 35–61.
- [27] O. Nuyken, J. Stebani, T. Lippert, A. Wokaun, A. Stasko, Macromol. Chem. Phys. 196 (1995) 739–749.
- [28] T. Lippert, L.S. Bennett, T. Nakamura, H. Niino, A. Ouchi, A. Yabe, Appl. Phys. A-Mater. Sci. Process. 63 (1996) 257–265.
- [29] J. Wei, N. Hoogen, T. Lippert, O. Nuyken, A. Wokaun, J. Phys. Chem. B 105 (2001) 1267–1275.
- [30] T. Lippert, J.T. Dickinson, M. Hauer, G. Kopitkovas, S.C. Langford, H. Masuhara, O. Nuyken, J. Robert, H. Salmio, T. Tada, K. Tomita, A. Wokaun, Appl. Surf. Sci. 197 (2002) 746–756.
- [31] M. Hauer, D.J. Funk, T. Lippert, A. Wokaun, Appl. Surf. Sci. 208 (2003) 107–112.
- [32] H. Furutani, H. Fukumura, H. Masuhara, J. Phys. Chem. 100 (1996) 6871–6875.
- [33] H. Furutani, H. Fukumura, H. Masuhara, S. Kambara, T. Kitaguchi, H. Tsukada, T. Ozawa, J. Phys. Chem. B 102 (1998) 3395–3401.
- [34] T. Lippert, C. David, J.T. Dickinson, M. Hauer, U. Kogelschatz, S.C. Langford, O. Nuyken, C. Phipps, J. Robert, A. Wokaun, J. Photochem. Photobiol. A-Chem. 145 (2001) 145–157.
- [35] T. Lippert, A. Wokaun, S.C. Langford, J.T. Dickinson, Appl. Phys. A-Mater. Sci. Process. 69 (1999) S655–S658.
- [36] O. Nuyken, J. Stebani, T. Lippert, A. Wokaun, A. Stasko, Macromol. Chem. Phys. 196 (1995) 751–761.
- [37] M. Hauer, T. Dickinson, S. Langford, T. Lippert, A. Wokaun, Appl. Surf. Sci. 197 (2002) 791–795.
- [38] C. Phipps, J. Luke, T. Lippert, Thin Solid Films 453–54 (2004) 573–583.
- [39] C.R. Phipps, J.R. Luke, G.G. McDuff, T. Lippert, Appl. Phys. A-Mater. Sci. Process. 77 (2003) 193–201.
- [40] C. Phipps, J. Luke, T. Lippert, M. Hauer, A. Wokaun, J. Propul. Power 20 (2004) 1000–1011.
- [41] T. Lippert, C. David, M. Hauer, T. Masubuchi, H. Masuhara, K. Nomura, O. Nuyken, C. Phipps, J. Robert, T. Tada, K. Tomita, A. Wokaun, Appl. Surf. Sci. 186 (2002) 14–23.
- [42] R.P. Richner, *Entwicklung neuartig gebundener Kohlenstoffmaterialien für elektrische Doppelschichtkondensatorelektroden*, Diss. ETH, 2001.
- [43] C. Phipps, J. Luke, J. Marquis, Diode laser-based microthrusters: a new departure in high isp, long-life engines, in: 36th AIAA/ASME/SAE/ASEE—Joint Propulsion Conference, Huntsville, Alabama, 2000.
- [44] J. Köhler, R. Meyer, Explosivstoffe, Wiley-VCH, Weinheim, 1998.
- [45] M.B. Frankel, L.R. Grant, J.E. Flanagan, J. Propul. Power 8 (1992) 560–563.
- [46] L. Urech, T. Lippert, C. Phipps, A. Wokaun, SPIE 6261 (2006) 626114.
- [47] L. Urech, M. Hauer, T. Lippert, C.R. Phipps, E. Schmid, A. Wokaun, I. Wysong, SPIE 5448 (2004) 52–64.
- [48] L. Urech, T. Lippert, C. Phipps, A. Wokaun, Appl. Surf. Sci., (in press).