

T. LIPPERT^{1,✉}
M. HAUER¹
C.R. PHIPPS²
A. WOKAUN²

Fundamentals and applications of polymers designed for laser ablation

¹ Paul Scherrer Institut, 5232 Villigen PSI, Switzerland

² Photonic Associates, 200A Ojo de la Vaca Road, Santa Fe, NM 87508, USA

Received: 21 October 2002/Accepted: 20 January 2003
Published online: 28 May 2003 • © Springer-Verlag 2003

ABSTRACT The ablation characteristics of various polymers were studied at low and high fluences for an irradiation wavelength of 308 nm. The polymers can be divided into three groups, i.e. polymers containing triazene groups, designed ester groups, and reference polymers, such as polyimide. The polymers containing the photochemically most active group (triazene) exhibit the lowest thresholds of ablation (as low as 25 mJ cm^{-2}) and the highest etch rates (e.g. 250 nm/pulse at 100 mJ cm^{-2}), followed by the designed polyesters and then polyimide. Neither the linear nor the effective absorption coefficients have a clear influence on the ablation characteristics. The different behavior of polyimide might be explained by a pronounced thermal part in the ablation mechanism. The laser-induced decomposition of the designed polymers was studied by nanosecond interferometry and shadowgraphy. The etching of the triazene polymer starts and ends with the laser pulse, indicating photochemical ablation. Shadowgraphy reveals mainly gaseous products and a pronounced shockwave in air. The designed polymers were tested for an application as the polymer fuel in laser plasma thrusters.

PACS 52.38.Mf; 82.50; 61.82.Pv

1 Introduction

Laser ablation of polymers was first reported in 1982 [1, 2] and fast became an important research area [3]. Laser ablation was originally envisioned as a possible alternative or complementary technique to conventional photolithography, due to the lower number of processing steps; but up to now, this potential could not be exploited with commercially available polymers, such as polymethylmethacrylate (PMMA), polyimide (PI), and polycarbonate (PC), etc. [4]. These polymers have severe drawbacks, such as low sensitivity, carbonization upon irradiation, or ablation debris contaminating the surface and optics. Therefore, novel photopolymers were developed to overcome these limitations [5–8].

Photochemical considerations have been applied to the design of these polymers. They were designed for an irradiation wavelength of 308 nm, because not all photolithographic processes require a resolution in the sub-micrometer range, and it

is possible to de-couple the absorption of the photochemically active groups from the absorption of other parts of the polymer structure. This concept can be used to test whether the incorporation of photochemically active groups into the polymer chain improves the ablation characteristics. The XeCl excimer laser (308 nm) is a technically interesting tool, due to the long lifetime of gas fills and laser optics. The most promising approach for the design of these ‘laser ablation polymers’ is the incorporation of the photochemically active chromophore into the main polymer chain. Other criteria for the laser ablation polymers are:

- High absorptivity at the irradiation wavelength.
- Exothermic decomposition at well-defined positions of the polymer backbone.
- Mostly gaseous ablation products [9, 10].

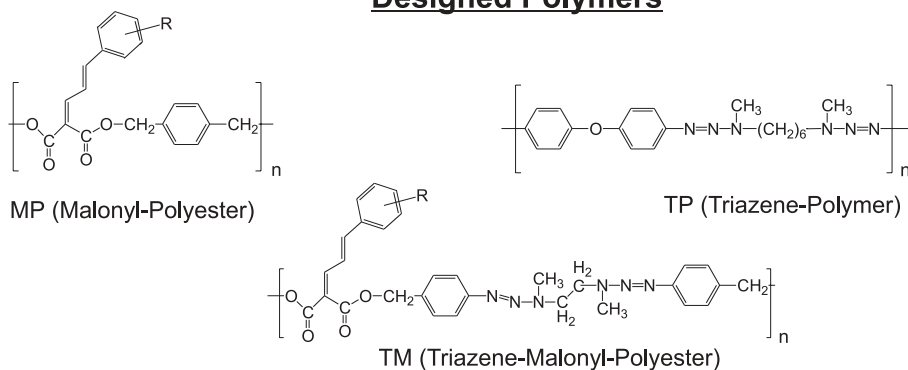
The gaseous products do not contaminate the surface and carry (by entrainment) larger fragments, which could otherwise contaminate the surface, perpendicular to and away from the surface. The polymers are therefore ablated without major modifications of the residual polymer surface, thus allowing a reproducible ablation [11].

From the standpoint of ablation properties, i.e. high etch rates, low threshold fluence, no surface contamination, and a low heat affected zone (high ablation quality), triazene group ($-\text{N}=\text{N}-\text{N}<$) containing laser-resists (TP) have been identified as the most promising candidates. Unfortunately problems associated with stability, e.g., during processes such as oxidation of the substrate [12], encountered during a complete processing cycle. Selected polyesters (PE) and polyestercarbonates (PEC) have also been found to exhibit good ablation behavior [13]. The sensitivities of the PE’s and PEC’s are lower than those of the triazene-based polymers, but they exhibit higher chemical stabilities. These polymers also produce small gaseous products (CO_2 , CO) upon decomposition.

Novel polymers were synthesized to test whether it is possible to combine the sensitivity of the triazene polymers with the stability of the polyesters. These polyesters contain cinnamylidenemalonyl groups and the triazene functional group. To compare the influence of these two chromophores (triazene vs. ester), polymers containing the same ester group but with (TM) and without (MP) the triazene groups were synthesized. The chemical structures of the polymers TM and MP

✉ Fax: +41-56/3104-412, E-mail: thomas.lippert@psi.ch

Designed Polymers



Reference Polymers

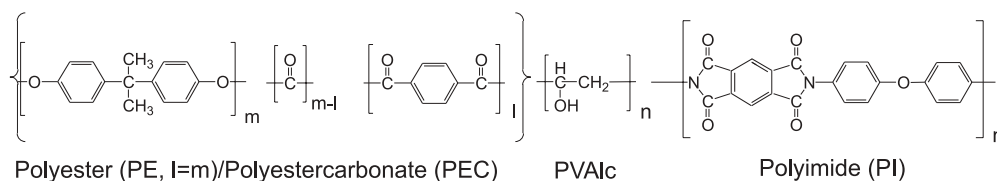


FIGURE 1 Chemical structures of the designed and reference polymers

are shown in Scheme 1. To compare the ablation properties of the new polymers, several other polymers were included as references in this study: polyimide (PI, KaptonTM from Goodfellow) as representative of a highly absorbing ‘standard’ polymer, a commercial polyester (PE, Bayer AG) as representative of standard ester polymers, and TP as representative of the original triazene polymers.

Previous studies have shown [12], that laser ablation will not replace optical microlithography with photoresists, but may find applications in microstructuring and as a fast prototyping tool.

A very different application of laser ablation of polymers can be found in aerospace science. With the advent of microsattellites (> 10 kg), nanosatellites (1–10 kg), and even picosatellites (< 1 kg), it has become necessary to develop steering engines that have a small mass (≤ 200 g) and size, produce a high specific impulse, and are inexpensive. One promising candidate for this application are laser plasma thrusters (LPT’s) [14, 15], which have some advantages over more common candidates for microthrusters, such as pulsed plasma thrusters or resistojets. The performance of the LPT’s is to a large extent dependent on the properties of the polymers

used in these devices. The well-defined exothermic decomposition of the above mentioned photopolymers was an attractive feature for testing these polymers also for an application with near-IR irradiation. Additional polymers, such as polyvinylalcohol and other designed polymers, were also tested for this application (see scheme 1).

2 Experimental

The synthesis of the triazene polymer (structure shown in scheme 1) has been described in detail elsewhere [16]. The polymers TM and MP were synthesized using a standard polycondensation reaction [17]. The polyimide (Kapton) was obtained from Goodfellow, while Bayer AG supplied the polyester, and BASF the polyvinylalcohol. The linear absorption coefficients, α_{lin} , of the polymers used for ablation are compiled in Table 1.

A XeCl excimer laser (Lambda Physik, Compex 205; $\lambda = 308$ nm, $\tau = 20$ ns), was used as the irradiation source for most experiments, with the exception of the interference experiments (see below). The polymer films (50 to 250 μm thick) for the ablation experiments, i.e. to determine the

	α_{308}^a (cm^{-1})	$\alpha_{\text{eff}}^b \text{LF}^b$ (cm^{-1})	$F_{\text{th}} \text{LF}^c$ (mJ cm^{-2})	T_{dec} (K)	Relevant bond energy (eV)
MP1 (R=H)	102 000	$50\,700 \pm 2100$	63 ± 3	594	[O=]C–O (≤ 3.7)
MP2 (R=OCH ₃)	32 000	$57\,000 \pm 2000$	48 ± 3	600	[O=]C–O (≤ 3.7)
TM1 (R=H)	69 000	$56\,100 \pm 3400$	27 ± 2	554	[N=]N–N (≤ 1.7)
TP	100 000	$49\,800 \pm 2900$	27 ± 2	555	[N=]N–N (≤ 1.7)
TM2 (R=OCH ₃)	92 000	$53\,300 \pm 2500$	28 ± 2	553	[N=]N–N (≤ 1.7)
PI	95 000	$83\,300 \pm 3400$	60 ± 3	773	[O=]C–N (≤ 3.2)
PE	8000	$51\,500 \pm 3200$	73 ± 4	n.m. ^d	[C=]C–O (≤ 3.7)

^a linear absorption coefficient at 308 nm determined by UV-spectroscopy and profilometry

^b effective absorption coefficient calculated from (1) at low fluences (LF)

^c threshold fluence calculated from (1) at low fluences

^d not measured

TABLE 1 Chemical properties and ablation parameters of the polymers

threshold and ablation rates, and to measure time-of-flight mass spectra, were prepared by solvent casting with THF as the solvent. The ablation rates, $d(F)$, were determined by analyzing the ablation depth as a function of the pulse number (typically between 2 and 500) at various fluences (described in detail elsewhere [18]). Linear plots of pulse number vs. ablation depth were obtained for all polymers, and were used to determine the ablation rate. The threshold for one polymer (TP) was also measured by single pulse experiments [19] and coincides very well with the value obtained from the multiple pulse experiments. For all polymers, multiple pulses were applied to determine the ablation rate, because, especially in the case of solvent cast films, skin layers (e.g. detected for PMMA [20]) and surface contamination may alter the ablation rates in single pulse experiments. All ablation experiments were performed in air. The depth of the ablated craters was measured with a surface profiler (Dektak 8000). The ablation experiments were performed at low (10–400 mJ cm⁻²) and high fluences (0.5–10 J cm⁻²) to investigate the ablation behavior of the polymers over a broad fluence range. The experimental set-up for the time-resolved (ns) surface interference fringes and shadowgraphy has been described in detail elsewhere [21]. We used a modified version of this setup, described in detail elsewhere [22].

For the IR irradiation experiments (LPT application), carbon-doped polymer films (designed polymers and polyvinylalcohol, PVAIc, as reference polymer) were prepared onto polymer substrates (PET or PI or Acetate) with a thickness of 60 to 260 μm. The performance of the films was determined by irradiation with a diode laser (SDL, Inc. XC30) and measurement with a specially developed torsion balance (sensitivity as low as 10⁻¹⁰ N s) (described in detail elsewhere [15]).

3 Results and discussion

3.1 Ablation characteristics

All polymers in this study can be classified as highly absorbing polymers (α_{lin} larger than 8000 cm⁻¹ at the irradiation wavelength of 308 nm), as shown in Table 1. The absorbance of the designed polymers (MP and TM) can be tuned by varying the substituent R. We selected R to obtain a similar (and different) α_{lin} that would allow a direct comparison of the polymers. This could be accomplished for the high end of absorptivity for four different polymers, i.e. TP, TM2, MP1, and PI. The polymers were studied at low fluences, which offers the opportunity to study the influence of structural parameters on the ablation rates. In Fig. 2 the ablation rate (on a logarithmic fluence scale) is shown for TP. The high fluence range is mainly interesting for applications in which high ablation rates in small areas are important, e.g. drilling or cutting. The ablation rates at very high fluences are often governed by plasma processes, such as inverse Bremsstrahlung, but etch rates of up to 3 μm/pulse could still be achieved for TP. At shorter wavelengths, smaller maximum ablation rates are observed (e.g. 1 μm for 248 nm irradiation). The low fluence range is also important for lithographic applications, in which the cost of photons is important. Low fluences may be defined from 10 to 400 mJ cm⁻². The ablation rates of the designed polymers (MP's, TM's and TP)

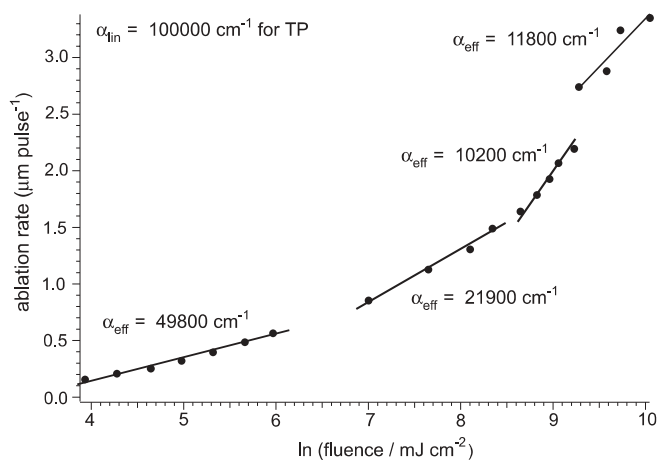


FIGURE 2 Ablation rate as a function of the laser fluence for 308 nm irradiation of the triazene polymer (TP). The effective absorption coefficients, α_{eff} , were calculated from (1) for different fluence ranges

could be divided into two groups with respect to the etch rates. All triazene-containing polymers had significantly higher ablation rates than the other polymers. The designed polyesters (MP's), as well as PE, had a higher etch rate than PI. The ablation rate was independent of α_{lin} (see Table 1 and Fig. 3) and is determined by the chemical structure. The ablation rates of non-triazene-containing polymers, MP's, were approximately 100 nm/pulse, which is about half the value for the triazene-containing polymers, TM's and TP. A slightly higher ablation rate was obtained for TP, which has the highest triazene density per polymer chain. The ablation rates of the polyester (PE) and polyimide were about 60 nm/pulse, which is again about half of the value for the designed polyesters. This is remarkable because the linear absorption coefficients of the designed polyesters cover the same broad range as those of PE and PI.

The ablation parameters, α_{eff} (effective absorption coefficient) and F_{th} (threshold fluence), were calculated according to [23, 24]

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

where $d(F)$ is the ablation rate (ablation depth per pulse). The resulting ablation parameters are summarized in Table 1.

The expression (1) was originally obtained from a fit to experimental curves (such as the different regions in Fig. 2), and is only used to derive the ablation parameters, α_{eff} and F_{th} here. This equation is not sensitive to the underlying ablation mechanism, but was used because more advanced models, which describe laser ablation very well with a photothermal mechanism (i.e. for PI) [3], require various material constants, such as the heat diffusivity, specific heat, heat of vaporization, etc., which are not known for the special polymers.

The effective absorption coefficient, α_{eff} , decreased with increasing fluence, as shown for TP in Fig. 2. The ablation rate may be divided into 4 different regions. For lower fluences, an increasing ablation rate (decreasing α_{eff}) was observed, and only at the very high fluences was a decrease of the ablation rate (expected for plasma shielding) clearly visible. This is probably due to the low absorption of the ablation products (and plasma) at the irradiation wavelength of 308 nm.

The increasing ablation rates may be due to a temperature increase from the exothermic decomposition (255 kJ mol^{-1}) of the polymer, or due to plasma–polymer interactions (plasma is only observed for fluences $\geq 1 \text{ J cm}^{-2}$). The effective absorption coefficients do not correlate with the linear absorption coefficients (Table 1), with the possible exception of PI. A difference between the values of α_{eff} and α_{lin} was observed for most polymers. An important feature is the similarity of α_{eff} for all designed polymers, including PE ($\approx 54\,000 \pm 5\,000 \text{ cm}^{-1}$), while PI has a much higher value (Table 1).

From an economic point-of-view, a polymer with a threshold fluence as low as possible is most desirable. The threshold fluences of the triazene-containing polymers, TM's and TP, were about 30 mJ cm^{-2} , which is much lower than those for the non-triazene-containing polymers, MP's ($\approx 60 \text{ mJ cm}^{-2}$). These values are, to our knowledge, the lowest threshold fluences reported for laser ablation of polymers at 308 nm. The threshold fluence of TP obtained from this study is in good agreement with the value determined previously by UV-spectroscopy for single pulse experiments [19]. A comparison of all polymers is shown in Fig. 3 (from plots such as Fig. 2). The linear absorption coefficients of the polymers are plotted against the ablation rate at a fluence of 100 mJ cm^{-2} (Fig. 3a) and against the threshold fluence (Fig. 3b). TP had the highest activity among the triazene-containing polymers, probably due to the highest density of triazene groups in the polymer chain, resulting in larger amounts of nitrogen as a product. The same order of activity is also confirmed by other experimental techniques, i.e. irradiation of the polymer in solution and mass spectrometry. The triazene-containing polymers decomposed much faster during irradiation in solution [18], where thermal effects should be of only minor importance. In the mass spectrometry studies, a much higher amount of gaseous products was detected for the triazene-containing polymers, confirming of course the higher etch rates, but also the role and importance of the gaseous species. These very pronounced differences are even more remarkably if we consider that the polymers were selected for similar absorption properties. At least one polymer out of each group has a comparable, linear absorption coefficient ($97\,000 \pm 5\,000 \text{ cm}^{-1}$), i.e. TP and TM for the triazene-containing polymers, MP for the designed polyesters, and PI for the reference polymers (see Fig. 3). This ensures that a direct comparison of these polymers is possible, due to the deposition of the laser energy within the same volume of the polymer. If the effective absorption coefficient is considered, then the triazene polymers can still be compared with the polyesters because their values are again quite similar ($54\,000 \pm 5\,000 \text{ cm}^{-1}$). Only PI has a quite different effective absorption coefficient, similar to the value of the linear absorption coefficient. Whereas the effective absorption coefficients are comparable, very pronounced differences between the triazene-containing polymers and the polyesters were obtained for the ablation activity. This suggests that α_{eff} is of only minor importance for the ablation performance. The same is true for the linear absorption coefficients, because a variation of α_{lin} within one group of polymers again had no pronounced influence, as seen when comparing MP1 and MP2 (see Fig. 3). It is probably more important for its value to lie above a certain threshold

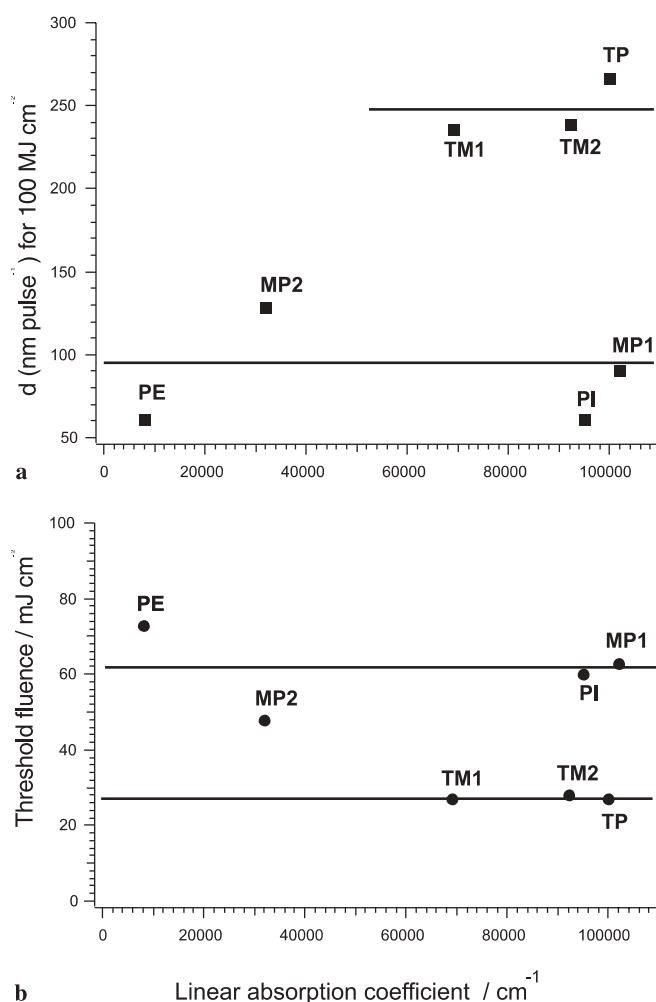


FIGURE 3 Influence of the linear absorption coefficients at the laser wavelength on a the ablation rates at 100 mJ cm^{-2} and on b the threshold fluences. The lines in the figure are just for guiding the eyes

($\approx 10\,000 \text{ cm}^{-1}$), for which direct ablation without incubation is observed.

The similar ablation rates and threshold fluences for the different polymers may be explained by analyzing the functional groups and bonds that are part of the polymers. TP and the TM's contain a $-\text{N}-\text{N}-$ group, which has the lowest energy ($\leq 1.7 \text{ eV}$, see Table 1), followed by the $-\text{C}-\text{N}-$, and $-\text{C}-\text{O}-$ bonds of the other polymers (see Table 1). The same order was obtained for the ablation rates (highest for TP and TM) and threshold fluences (lowest for TP and TM). The $\text{N}-\text{N}$ bond (if not all bonds mentioned) can be broken directly by a single photon of the XeCl excimer laser ($308 \text{ nm} = 4.02 \text{ eV}$), suggesting that photochemical decomposition is at least a possibility.

Of course one might argue that the same order of activity is also obtained if only the decomposition temperatures (T_{dec} in Table 1) are considered, i.e. the lowest T_{dec} for the TP and TM polymers, followed by MP and the PI. However, a comparison reveals that the largest difference in thermal stability ($170 \text{ }^\circ\text{C}$) between polymers of different groups (PI and MP) corresponds to the smallest difference in ablation activity ($d(F)$ and F_{th}). This suggests that thermal considerations are less important for this comparison, but only an in-depth analy-

sis, e.g. applying the models developed for PI, could validate this hypothesis.

3.2 Time-resolved measurements

Various time-resolved measurements were performed to probe the ablation mechanisms for selected polymers, i.e. TP. Time-resolved transmission studies have shown that bleaching of the triazene chromophore takes place during the laser pulse [19]. Nanosecond shadowgraphy revealed that only gaseous products were formed and that the decomposition enthalpy of the polymer supported the resulting shock wave in air. The speed of the shock wave was fastest for the designed polymers and energetic polymers, probably due to the higher amount of gaseous products and energy released upon decomposition [22]. Nanosecond interferometry revealed that etching of TP starts and ends with the laser pulse. A very different behavior, i.e. pronounced swelling and delayed etching, has been detected for PI [25] and polymethylmethacrylate (PMMA) [21, 26], and has been interpreted as an indication of a thermal ablation mechanism. We also performed time-of-flight mass spectrometry (TOF-MS) measurements for the TP polymer at two irradiation wavelengths (248 and 308 nm). N_2 was identified as the main decomposition product. A detailed analysis of the TOF curves shows that there were 3 different species of N_2 originating from TP:

- A metastable (excited) N_2 , with kinetic energies between 1 and 2 eV.
- A very fast ground state N_2 , with kinetic energies of up to 6 eV.
- A slow N_2 , with a very broad kinetic energy distribution that can be described by a decaying Maxwell–Boltzmann function.

The metastable and fast ground state N_2 species are hard to explain by a thermal mechanism. Details of these measurements are described elsewhere [10, 27].

3.3 Applications: laser plasma thruster

To analyze the performance of the various polymer films for LPT's, the target momentum was measured by the torsion balance and used to calculate the momentum coupling coefficient, C_m . This quantity is defined as

$$C_m = \frac{m \Delta v}{W}, \quad (2)$$

with $m \Delta v$ as the target momentum produced during the ejection of laser-ablated material. W is the incident laser pulse energy. Another important parameter for thrusters is the specific impulse I_{sp} , which is defined as

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

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.

The measurements were performed in the transmission mode, which is the most probable candidate for LPT's. The laser passed through an IR-transparent substrate to initiate

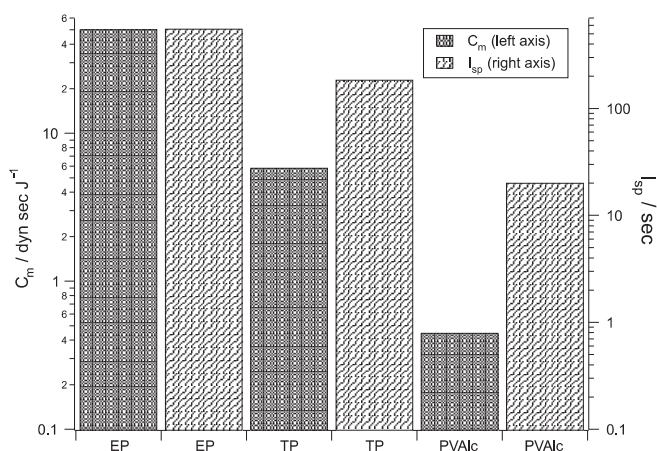


FIGURE 4 Comparison of the maximum momentum coupling coefficient, C_m , and the specific impulse, I_{sp} (for three selected polymers)

ablation at the polymer–substrate interface. Three polymers were selected for the tests, i.e. a polymer designed for laser ablation in the UV (triazene polymer, TP), a highly energetic polymer (EP), and a commercial polymer (polyvinylalcohol, PVALc). All polymers pass the fundamental requirements for LPT's. The polymers give homogenous films with good adhesion to the substrates; they do not stick to each other; they are elastic over a broad temperature range (-50 to $+60$ °C) and have optical densities of about 1. Most polymers have to be doped to accomplish an effective absorption in the near-IR. Carbon was chosen as the dopant due to the broad homogeneous absorption over the whole near-IR range.

In Fig. 4 the maximum values of the momentum coupling coefficients (C_m) and specific impulse (I_{sp}) are compared on a logarithmic scale. The PVALc reveals the lowest values for C_m and I_{sp} , followed by TP and the energetic polymer. The values for the EP are among the highest values obtained for a non-confined material [28]. Improvements of one order of magnitude were obtained for C_m from PVALc to TP and EP. The improvements correlate quite well with the increase of the decomposition enthalpy of the polymers. The EP is a highly exothermic material, which releases a large amount of energy (around 3100 Jg^{-1}) that may support the action of the laser plasma thruster.

4 Conclusions

The ablation characteristics of various polymers were studied. The polymers can be divided into three groups: polymers containing triazene groups, designed polyesters, and polyimide as a reference polymer. The polymers containing the photochemically most active group (triazene) are also the polymers with the lowest thresholds of ablation and the highest etch rates, followed by the designed polyesters, and then polyimide. No pronounced influences of the absorption coefficients, α_{lin} and α_{eff} , on the ablation characteristics were detected. The clear difference between PI and the designed polymers might be explained by a pronounced thermal part in the ablation mechanism of PI, while photochemical activities are more important for the triazene polymer. The time-resolved measurements also support a pronounced photochemical part in the ablation mechanism.

The designed polymers also display superior properties for LPT applications, in which IR wavelengths are applied during irradiation. The energetic polymer has exceptionally high momentum coupling coefficients, followed by the designed photopolymer and a commercial polymer.

ACKNOWLEDGEMENTS This work has been supported by the Swiss National Science Foundation and by the U.S. Air Force Office of Scientific Research. Nitrochemie Wimmis, BASF, and BAYER have made some materials available.

REFERENCES

- 1 R. Srinivasan, V. Mayne-Banton: *Appl. Phys. Lett.* **41**, 576 (1982)
- 2 Y. Kawamura, K. Toyoda, S. Namba: *Appl. Phys. Lett.* **40**, 374 (1982)
- 3 D. Bäuerle: *Laser Processing and Chemistry*, 3rd edn. (Springer-Verlag, Berlin 2000)
- 4 K. Suzuki, M. Matsuda, T. Ogino, N. Hayashi, T. Terabayashi, K. Amemiya: *Proc. SPIE* **2992**, 98 (1997)
- 5 T. Lippert, J. Stebani, J. Ihlemann, O. Nuyken, A. Wokaun: *Angew. Makromol. Chem.* **206**, 97 (1993)
- 6 T. Lippert, J. Stebani, J. Ihlemann, O. Nuyken, A. Wokaun: *J. Phys. Chem.* **97**, 12296 (1993)
- 7 T. Lippert, T. Kunz, C. Hahn, A. Wokaun: *Recent Res. Dev. Macromol. Res.* **2**, 121 (1997)
- 8 O. Nuyken, U. Dahn, N. Hoogen, D. Marquis, M.N. Nobis, C. Scherer, J. Stebani, A. Wokaun, C. Hahn, T. Kunz, T. Lippert: *Polym. News* **24**, 257 (1999)
- 9 L.S. Bennett, T. Lippert, H. Furutani, H. Fukumura, H. Masuhara: *Appl. Phys. A* **63**, 327 (1996)
- 10 T. Lippert, S.C. Langford, A. Wokaun, S. Georgiou, J.T. Dickinson: *J. Appl. Phys.* **86**, 7116 (1999)
- 11 T. Lippert, T. Nakamura, H. Niino, A. Yabe: *Macromolecules* **29**, 6301 (1996)
- 12 T. Lippert, J. Wei, A. Wokaun, N. Hoogen, O. Nuyken: *Appl. Surf. Sci.* **168**, 270 (2000)
- 13 T. Kunz, J. Stebani, J. Ihlemann, A. Wokaun: *Appl. Phys. A* **67**, 347 (1998)
- 14 C.R. Phipps, J. Luke: *Proc. SPIE* **4065**, 801 (2000)
- 15 C.R. Phipps, J. Luke: *AIAA J.* **40**, 310 (2002)
- 16 J. Stebani, O. Nuyken, T. Lippert, A. Wokaun: *Makromol. Chem. Rapid Commun.* **14**, 365 (1993)
- 17 N. Hoogen, O. Nuyken: *J. Polym. Sci., Part A: Polym. Chem.* **38**, 1903 (2000)
- 18 J. Wei, N. Hoogen, T. Lippert, O. Nuyken, A. Wokaun: *J. Phys. Chem. B* **105**, 1267 (2001)
- 19 T. Lippert, L.S. Bennett, T. Nakamura, H. Niino, A. Ouchi, A. Yabe: *Appl. Phys. A* **63**, 257 (1996)
- 20 T. Lippert, R.L. Webb, S.C. Langford, J.T. Dickinson: *J. Appl. Phys.* **85**, 1838 (1999)
- 21 H. Furutani, H. Fukumura, H. Masuhara: *Appl. Phys. Lett.* **65**, 3413 (1994)
- 22 M. Hauer, D.J. Funk, T. Lippert, A. Wokaun: *Proc. SPIE* **4760**, 259 (2002)
- 23 J.E. Andrews, P.E. Dyer, D. Forster, P.H. Key: *Appl. Phys. Lett.* **43**, 717 (1983)
- 24 R. Srinivasan, B. Braren: *J. Polym. Sci.* **22**, 2601 (1984)
- 25 T. Masabuchi, T. Tada, E. Nomura, K. Hatanaka, H. Fukumura, H. Masuhara: *J. Phys. Chem A* **106**, 2180 (2002)
- 26 H. Furutani, H. Fukumura, H. Masuhara: *J. Phys. Chem.* **100**, 6871 (1996)
- 27 T. Dickinson: private communication
- 28 C.R. Phipps, J. Luke, G. McDuff, T. Lippert: *Proc. SPIE* **4760**, 833 (2002)