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Femto- and nanosecond laser treatment of doped polymethylmethacrylate

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Abstract

Femto- and nanosecond laser ablation of polymethylmethacrylate (PMMA) and PMMA doped with a linear absorber was investigated in the infrared spectral region. Ablation thresholds were determined and incubation phenomena were identified. The 'degree' of incubation was calculated employing a phenomenological model. The influence of the pulse duration on the machining quality of the polymers was examined. The presence of an absorbing chromophore is not a prerequisite for a controllable fs-laser structuring in contrast to the ns-treatment. Surface swelling always accompanied ablation.

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Keywords: Laser ablation; Laser beam machining; Doping thin films; Polymers-radiation effects

1. Introduction

The micromachining of polymers with ultraviolet (nanosecond) laser radiation has reached an advanced status. More than 20 years ago, it was demonstrated that a polymer could be etched in a controlled manner employing an ArF excimer laser [1]. Advantages of that laser type are good focusability of the radiation and a significant absorption of most polymers due to the shortness of the wavelength [2]. Examples of technical applications include via-hole drilling on multi-chip modules or drilling of inkjet printer nozzles.

A large variety of polymers can be processed with excimer lasers successfully, but the involvement of thermal processes can lead to unwanted deviations from the targeted quality. Therefore, photopolymers were designed employing photolabile chromophores

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to achieve a pure photochemical ablation with a minimum of thermal side effects and a well-defined decomposition pathway yielding only gaseous ablation products. A high contour sharpness with practically no surface contamination could be achieved [3–5].

A number of studies have been concerned with femtosecond laser processing of polymers [6–20]. An open issue remains the influence of a dopant on the ablation behaviour of polymethylmethacrylate (PMMA) employing femtosecond laser pulses in comparison to nanosecond pulses. The fs- and ns-lasers have different wavelengths (790 and 1064 nm, respectively), but this drawback is compensated by the doping level of the PMMA samples achieving equal linear absorption coefficients for 790 and 1064 nm radiation. Therefore, the effect of the pulse duration could be elucidated.

2. Experimental

Samples were prepared by dissolving PMMA (Aldrich) in a solvent mixture (50 wt.% methyl ethyl ketone, 15 wt.% *n*-butylacetate, 15 wt.% cyclohexanone and 20 wt.% 4-methyl-2-pentanone) by stirring for 12 h to obtain a 10 wt.% polymer solution. An IR-dye (IR165) was dispersed in the same solvent and added to the polymer solution by stirring with a magnetic stirrer for 30 min. Then, the solution was cast in a Teflon form. The samples were dried under ambient conditions for 24 h, before they were heated to 40 °C to remove leftover solvent.

Linear absorption spectra of the samples were acquired from spin-coated films on fused silica substrates with a UV–vis spectrometer (Carry 500, Varian). Dopant concentrations were selected to yield a linear absorption coefficient of 750 cm^{-1} at 790 (5% IR165) and 1064 nm wavelengths (1% IR165).

A femtosecond Ti:sapphire laser (Femtopower Compact Pro, Femtolasers) and a nanosecond Nd:YAG laser (Brilliant B, Quantel) were utilized for the ablation experiments in air. The fs-laser emitted 790 nm-central-wavelength pulses with a bandwidth-limited duration of 30 fs at a repetition rate of 1 kHz. The pulse duration was determined by means of a dispersion-minimised autocorrelator (Femtolasers). Laser pulse energies were varied using a rotatable half-wave plate in front of the compressor unit. The Brewster prisms of the compressor acted as analyser. The pulse energy was measured employing a pyroelectric detector (J25LP series with a display unit 3Sigma, Molectron). The beam profile was Gaussian. The ns-laser yielded 6 ns pulses at 1064 nm wavelength and 10 Hz repetition rate. The beam profile showed some hotspots.

In both cases, the target was mounted on a motorized *x*–*y*–*z*-translation stage. The surface of the sample was positioned perpendicular to the direction of the incident laser beam. The laser beams were focused to spot diameters of approximately 200 μm. The number of laser pulses per spot was controlled between 1 and 1000.

For the femtosecond experiments, the measurement of the diameter, D, of the laser-damaged area was done with an optical microscope (Eclipse L200, Nikon). The ablation threshold fluences, F_{th}, were determined by a plot of D^2 versus maximum laser fluence, F_0, for a fixed pulse duration, τ, and number of pulses per spot, N [21].

For the nanosecond laser investigations, the laser-ablated area was analysed with an optical microscope (SZH10, Olympus) and a surface profilometer (Dektak 8000, Sloan). To determine F_{th}, it was assumed that ablation takes place only if a clear removal of material was observed with both methods.

A detailed characterization of morphological changes of the laser-modified areas was performed by means of a scanning electron microscope (Cambridge Stereoscan 180, accelerating voltage 10–20 kV).

3. Results and discussion

The ablation threshold fluence, F_{th}, of PMMA and PMMA doped with 5% IR165 in dependence on the number of 30 fs laser pulses per spot N is depicted in Fig. 1. A strong incubation behaviour was found for pure PMMA. The single-pulse ablation threshold, $F_{th}(1) = 0.9$ J cm^{-2} is one order of magnitude higher than that for $N = 1000$ pulses. To quantify the 'degree' of incubation, a phenomenological model describing a relation between the single-pulse ablation threshold $F_{th}(1)$ and the multi-pulse ablation threshold $F_{th}(N)$ in the form

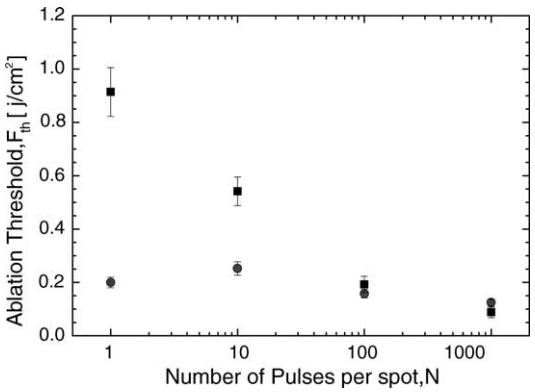

Fig. 1. Ablation threshold fluence, F_{th}, vs. number of pulses per spot N for the ablation of PMMA (■) and PMMA doped with 5% IR165 (●) with 30 fs laser pulses.

$$F_{th}(N) = F_{th}(1)N^{\xi-1}, \quad (1)$$

with a material-dependent incubation parameter, ξ, was established [22]. $\xi = 1$ would mean that no incubation is found. In the present case, $\xi = 0.67$ was calculated according to Eq. (1). This is the same value as reported before for a 150 fs laser treatment of PMMA [23]. The single-pulse threshold, $F_{th}(1)$, at 30 fs pulse duration, however, is by a factor of 3 lower than $F_{th}(1) = 2.6$ J cm^{-2} for $\tau = 150$ fs [23]. Single-pulse ablation in transparent dielectrics was explained by laser-induced breakdown in such a manner that a critical electron density in the conduction band has to be reached for damage [24]. Actually, both avalanche and multiphoton ionisation cause this accumulation of electrons [25]. A shorter pulse duration, i.e. a higher intensity, results in an enhanced probability for the multiphoton absorption process. Therefore, the seed electrons for the avalanche ionisation are generated more deterministically resulting in a lower ablation threshold [26].

The relation between F_{th} and N for PMMA doped with 5% IR165 also shows an incubation effect with $\xi = 0.92$, but much less pronounced. For $N < 100$, F_{th}

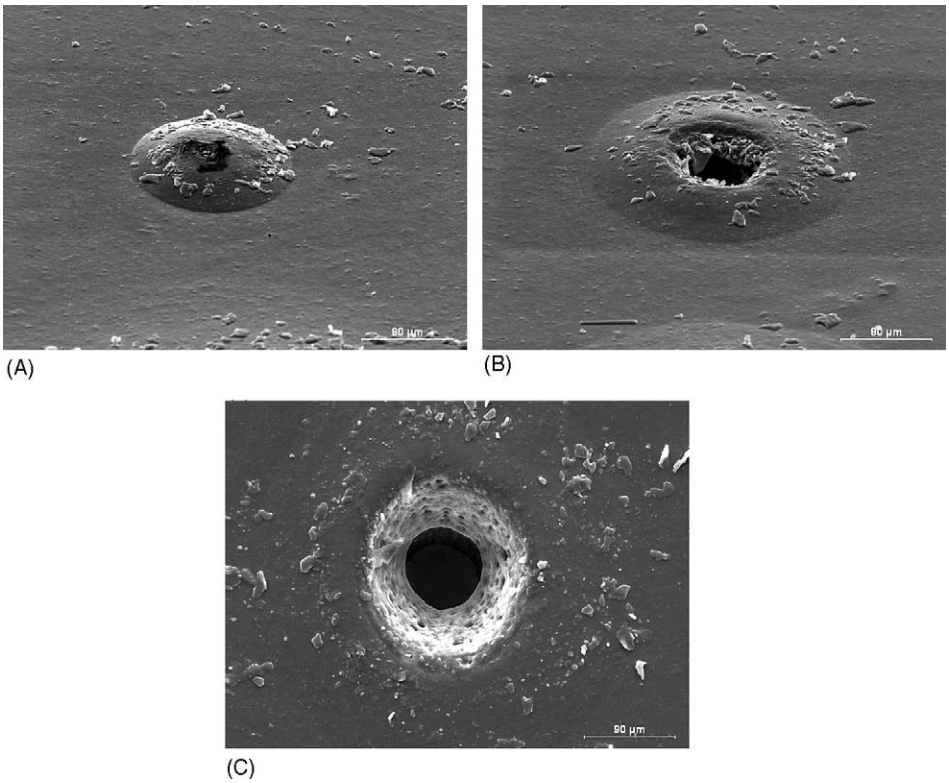

Fig. 2. Scanning electron microscope (SEM) pictures of PMMA after treatment with 30 fs laser pulses, $N = 1000$ and F_0: (a) 0.18 J cm^{-2}; (b) 0.23 J cm^{-2}; (c) 0.48 J cm^{-2}. The black area in the centre of the hump (a) is SEM artefact.

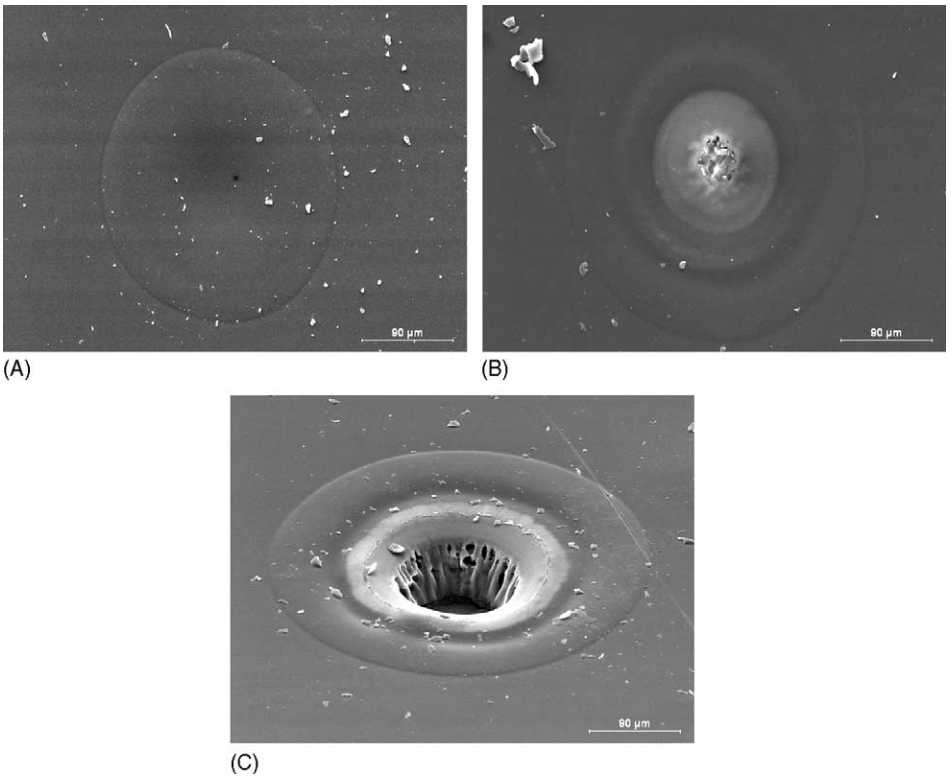

Fig. 3. SEM pictures of PMMA doped with 5% IR165 after illumination with 30 fs laser pulses, $N = 1000$ and F_0: (a) 0.14 J cm^{-2}; (b) 0.27 J cm^{-2}; (c) 0.45 J cm^{-2}.

of undoped PMMA is higher than for the doped one. The single-pulse thresholds differ by a factor of 4.5. Interestingly, undoped and doped PMMA exhibit the same ablation thresholds for $N \geq 100$ due to the distinct incubation of pure PMMA.

Scanning electron microscope (SEM) pictures of the surfaces after laser illumination allow statements about the quality of the machining process. Fig. 2 represents the evolution of a crater in PMMA in dependence on the maximum laser fluence, F_0, for a fixed N. Clearly, swelling can be observed (Fig. 2a and b). This phenomenon was interpreted in terms of a fractionation of the polymer and the formation of gaseous products (e.g. CO_2) [16,27]. The application of 1000 pulses with $F_0 = 2 \times F_{th}$ leads to the generation of a comparatively clear-cut hole with debris deposited around (Fig. 2c). Fig. 3 shows the formation of a cavity in PMMA doped with 5% IR165 for an increasing laser fluence. The multi-pulse behaviour of doped PMMA is similar to that observed for the pure type. Swelling of the surface occurred close to the ablation threshold (Fig. 3a). A cavity started to evolve in the centre of the hump for fluences slightly above the threshold (Fig. 3b). A fluence of

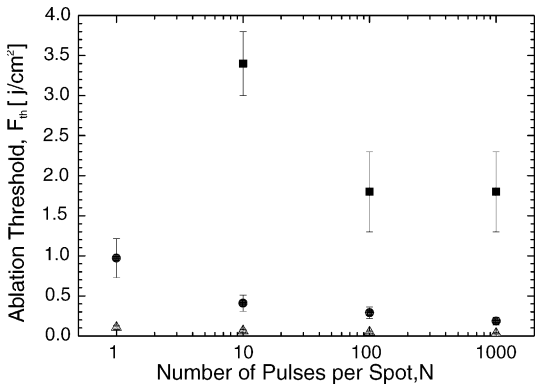

Fig. 4. Ablation threshold fluence, F_{th}, vs. number of pulses per spot N for the ablation of PMMA (■), PMMA doped with 1% IR165 (●) and PMMA doped with 5% IR165 (▲) with 6 ns laser pulses.

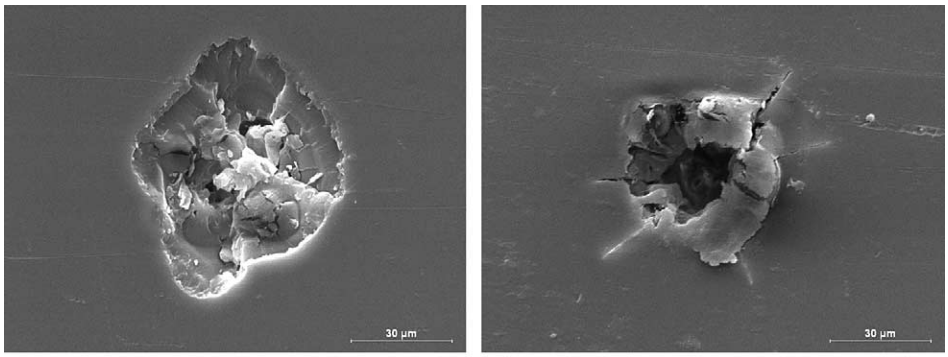

Fig. 5. SEM pictures of PMMA after treatment with 6 ns laser pulses, $N = 100$ and F_0: (a) 1.87 J cm^{-2}; (b) 3.84 J cm^{-2}.

$F_0 = 2 \times F_{th}$ results in a laser-induced cavity surrounded by a rim of swollen material (Fig. 3c), but less debris compared to the pure PMMA is observed (Fig. 2c).

Combining Figs. 2 and 3, it can be stated that the presence of an absorbing chromophore is not a prerequisite for a structuring process with a satisfying quality. This is in contrast to the machining result of doped PMMA with a 100 ps laser (1064 nm) [4].

Fig. 4 displays the F_{th} versus N relation for the ablation of PMMA, PMMA doped with 1% IR165, and PMMA doped with 5% IR165 with 6 ns laser pulses. Fluences up to 5 J cm^{-2} were not sufficient to ablate pure PMMA with a single laser pulse. Even for $N = 100$, the F_{th} values differ by one order of magnitude between 6 ns and 30 fs pulses (compare Fig. 1). The reason for this finding is the large difference of the laser intensities resulting in a much lower probability for a nonlinear absorption mechanism in the nanosecond case.

The morphology of the ns-laser-treated surface appeared more disrupted than ablated (Fig. 5a). It is impossible to control the structuring process precisely. The utilization of pulses with an increasing F_0 for a constant N gives rise to cracks (Fig. 5b).

A completely different behaviour can be seen for the doped polymer (Fig. 6). No cracks are found and, ignoring the inhomogeneous beam profile, a smooth ablation can be achieved.

Further, the relation of the ablation thresholds of femto- and nanosecond laser treatment changes if doped PMMA with a linear absorption coefficient of 750 cm^{-1} is investigated. In the nanosecond case, the multi-pulse ablation thresholds are only about 50% higher (Figs. 1 and 4), which is a dramatic alteration in comparison to pure PMMA. The difference of the F_{th} values can be attributed to a stronger energy 'confinement' for the femtosecond laser coupling and higher dissipation losses for the application of the Nd:YAG laser.

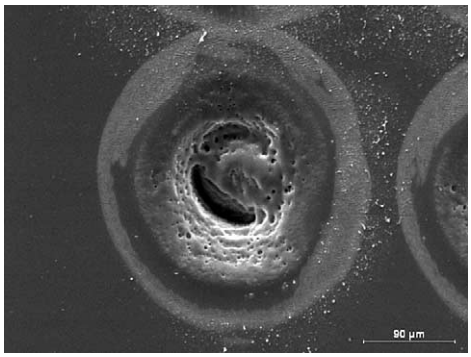

Fig. 6. SEM picture of PMMA doped with 1% IR165 after illumination with 6 ns laser pulses, $N = 1000$ and $F_0 = 0.41$ J cm^{-2}.

4. Conclusions

Ablation experiments with Ti:sapphire (30 fs, 790 nm) and Nd:YAG laser pulses (6 ns, 1064 nm) on PMMA and doped PMMA were conducted in air. The dopant concentration was chosen for an equal linear absorption coefficient of about 750 cm^{-1} at 790 and 1064 nm. The ablation thresholds for nanosecond laser treatment are higher than those observed for

femtosecond laser illumination for all number of pulses per spot applied. The difference is about one order of magnitude for pure PMMA and reaches only 50% in the case of the doped polymer.

For both materials and pulse durations, the ablation threshold fluences decrease with an increasing number of pulses per spot (incubation). In the 30 fs case, the incubation behaviour of pure PMMA is much more pronounced than that of PMMA doped with 5% IR165 resulting in incubation parameters of 0.67 and 0.92, respectively. The single-pulse thresholds differ by a factor of 4.5, but the multi-pulse ablation thresholds ($N \geq 100$) are identical.

Ablation of the polymers is accompanied by a surface swelling due to the fractionation of the materials and the formation of gaseous products. Pure PMMA can only be processed successfully with fs-laser pulses in the near-IR wavelength range while doped PMMA can also be machined with the nano-second laser with a sufficient quality.

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References

[1] R. Srinivasan, V. Mayne-Banton, Appl. Phys. Lett. 41 (1982) 576.
[2] D. Bäuerle, Laser Processing and Chemistry, 3rd ed. Springer-Verlag, Berlin, 2000.
[3] T. Lippert, J.T. Dickinson, S.C. Langford, H. Furutani, H. Fukumura, H. Masuhara, T. Kunz, A. Wokaun, Appl. Surf. Sci. 127-129 (1998) 117.
[4] C. Hahn, T. Lippert, A. Wokaun, J. Phys. Chem. B 103 (1999) 1287.
[5] T. Lippert, Laser application of polymers, in: T. Lippert (Ed.), Springer Review Series Advances in Polymer Science, Special Issue Polymers and Light, vol. 168, 2004, p. 51.
[6] S. Küper, M. Stuke, Appl. Phys. B 44 (1987) 199.
[7] R. Srinivasan, E. Sutcliffe, B. Braren, Appl. Phys. Lett. 51 (1987) 1285.
[8] H. Kumagai, K. Midorikawa, K. Toyoda, S. Nakamura, T. Okamoto, M. Obara, Appl. Phys. Lett. 65 (1994) 1850.
[9] J. Heitz, E. Arenholz, D. Bäuerle, R. Sauerbrey, H.M. Phillips, Appl. Phys. A 59 (1994) 289.
[10] S. Nakamura, K. Midorikawa, H. Kumagai, M. Obara, K. Toyoda, Jpn. J. Appl. Phys. 35 (1996) 101.
[11] J. Krüger, W. Kautek, Appl. Surf. Sci. 96–98 (1996) 430.
[12] T. von Woedtke, P. Abel, J. Krüger, W. Kautek, Sens. Actuators B 42 (1997) 151.
[13] A.A. Serafetinidis, C.D. Skordoulis, M.I. Makropoulou, A.K. Kar, Appl. Surf. Sci. 135 (1998) 276.
[14] B. Hopp, Z. Toth, K. Gal, A. Mechler, Z. Bor, S.D. Moustaizis, S. Georgiou, C. Fotakis, Appl. Phys. A 69 (1999) 191.
[15] S. Baudach, J. Bonse, W. Kautek, Appl. Phys. A 69 (1999) 395.
[16] S. Baudach, J. Bonse, J. Krüger, W. Kautek, Appl. Surf. Sci. 154–155 (2000) 555.
[17] H. Niino, J. Ihlemann, S. Ono, A. Yabe, J. Photopolym. Sci. Technol. 13 (2000) 167.
[18] H. Niino, A. Yabe, J. Photopolym. Sci. Technol. 14 (2001) 197.
[19] Y. Zhang, R.M. Lowe, E. Harvey, P. Hannaford, A. Endo, Appl. Surf. Sci. 186 (2002) 345.
[20] J. Krüger, W. Kautek, Ultrashort pulse laser interaction with dielectrics and polymers, in: T. Lippert (Ed.), Springer Review Series Advances in Polymer Science, Special Issue Polymers and Light, vol. 168, 2004, p. 247.
[21] J.M. Liu, Opt. Lett. 7 (1982) 196.
[22] Y. Jee, M.F. Becker, R.M. Walser, J. Opt. Soc. Am. B 5 (1988) 648.
[23] S. Baudach, J. Krüger, W. Kautek, Rev. Laser Eng. 29 (2001) 705.
[24] N. Bloembergen, IEEE J. Quant. Electr. QE-10 (1974) 375.
[25] B.C. Stuart, M.D. Feit, A.M. Rubenchik, B.W. Shore, M.D. Perry, Phys. Rev. Lett. 74 (1995) 2248.
[26] M. Lenzner, J. Krüger, W. Kautek, F. Krausz, Appl. Phys. A 68 (1999) 369.
[27] T. Kunz, J. Stebani, J. Ihlemann, A. Wokaun, Appl. Phys. A 67 (1989) 347.