



# Gravimetric and profilometric measurements of the ablation rates of photosensitive polymers at different wavelengths

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## Abstract

The ablation rates of two polyimides (PMDA and Durimid<sup>TM</sup>) and one triazene polymer were studied by gravimetric (quartz microbalance) and profilometric (profilometer) methods at irradiation wavelengths of 193, 248 and 308 nm. The ablation rates determined by the two methods are discussed in the context of the absorption behavior of the materials. Furthermore, the consistence of the two experimental methods is discussed for the ablation rates of Durimid<sup>TM</sup> and the triazene polymer. The gravimetric measurements revealed a good correlation between the ablation rate and the absorption properties of the examined materials. The comparison of the gravimetric and the profilometric measurements suggest a significant mass removal, e.g. by formation of gaseous products, prior to the detection of changes in the surface morphology.

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## 1. Introduction

UV laser ablation of polymers is the objective of intense experimental and theoretical research due to the potential applications in many fields (chemistry, physics, biology, and electronics) [1–3]. Studies of the laser-induced decomposition or transformation of polymers with single pulses and laser fluences close to the threshold of ablation require very sensitive

techniques, such as a quartz crystal microbalance (QMB), atomic force microscopy (AFM) or profilometry. One important question in polymer ablation is related to the ablation mechanism, i.e., photochemical versus photothermal. The understanding of these mechanisms is important for the design of new materials (e.g. photosensitive polymers) or the optimization of existing industrial processes. Models also play an important role in the understanding of these mechanisms. The mass loss during laser irradiation is one important parameter for the development of theoretical models that describe ablation.

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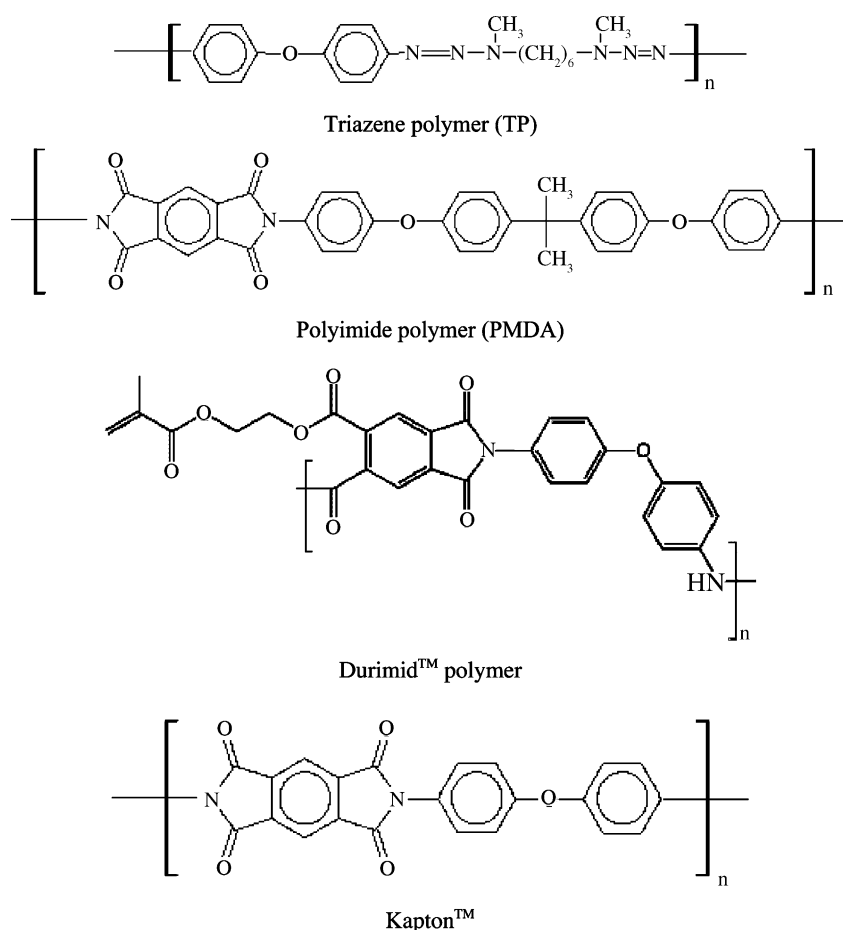
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A mass loss (e.g. by QMB) due to photochemical reactions is expected for photosensitive polymers before a change in the surface morphology (e.g. by AFM or profilometry) can be measured. Another important parameter that may influence the ablation data is the role of solvent that remains in the polymer film (e.g. from the film preparation). Since QMB was first introduced as a gravimetric tool by Sauerbrey in 1959 [4], it has not only been used in many fields as sensor and thickness monitor, but also as a gravimetric tool to study the ablation process of polymers [5–10]. The basis of the QMB is the fundamental vibration frequency of an AT-cut quartz plate, which is directly proportional to its thickness. The frequency of the quartz decreases according to the amount of added mass, e.g. by coating the surface with a polymer or a

metal. The change can be directly converted to a mass load per unit area. If the density of the material is known, the film thickness of the material can be calculated. This method is very sensitive even to small variations of the mass load. For a 5 MHz quartz plate, a variation of 1 Hz corresponds to a mass variation of  $17 \text{ ng cm}^{-2}$ . This corresponds, for example, to a thickness variation of  $1.3 \text{ \AA}$  in the case of a polymer, such as polyethylenterephthalat (PET). Such high precision is especially useful for studies of the ablation behavior of photosensitive polymers near the ablation threshold.

Two polyimide polymers, i.e., PMDA and Durimid<sup>TM</sup>, and a triazene (TP) polymer (chemical structures shown in Scheme 1) were studied gravimetrically and profilometrically after irradiation with



Scheme 1. Chemical structure of TP, PMDA, Durimid<sup>TM</sup> and Kapton<sup>TM</sup>.

fluences below and above the threshold of ablation at irradiation wavelengths of 193, 248 and 308 nm. The triazene polymer is a specially designed photosensitive polymer for microstructuring, while Durimid<sup>TM</sup> is a photosensitive polyimide, which is comparable to Pyralin<sup>TM</sup> that has been utilized in previous QMB study of the ablation process [6]. PMDA is another polyimide that is not especially photosensitive but may be used as a model for the most studied polymer in ablation, i.e., Kapton<sup>TM</sup>. These experiments extend the previous work with PMDA and TP at irradiation wavelengths of 248 and 308 nm.

## 2. Experimental

Commercial quartz plates with silver electrodes and a fundamental frequency of 4.9152 MHz were utilized as substrates in the QMB measurements. The samples were prepared by spin coating of several polymer layers on one side of the quartz plate. The polymer films were dried at 40 °C under nitrogen atmosphere for at least 2 h for the triazene polymer or at 250 °C for 1 h for PMDA and at 250 °C for 3 h for Durimid<sup>TM</sup>. The chemical structures of the polymers are shown in Scheme 1. The total film thickness of the polymers was in the range of several  $\mu\text{m}$  and was chosen in a way that the frequency change of the quartz did not exceed 2% of the initial value to ensure the linearity of the Sauerbrey Eq. (1):

$$\Delta F = -\Delta m \frac{F^2}{(\mu\rho)^{1/2}} A \quad (1)$$

where  $\Delta F$  is the resonant frequency shift,  $F$  the resonant frequency of the quartz,  $\Delta m$  the mass change on the surface,  $\mu$  the shear modulus,  $\rho$  the density of the quartz, and  $A$  is the surface of the piezoelectrically active surface [9].

The aperture of the irradiation setup exceeded slightly the surface of the silver electrodes to assure that the complete sensitivity of the vibrating area is used. The laser fluence was varied by an attenuator and the beam energy was measured online via a beam splitter and a power meter. The frequency change over time was determined by a frequency counter connected to a computer.

The polymers were ablated at irradiation wavelengths of 193, 248 and 308 nm. Each sample was

ablated at a constant fluence with 1–5 pulses. The frequency change was measured after every pulse for at least 30 s at a rate of 1 Hz. The profilometric measurements were carried out on a DEKTAK 8000 Profilometer. All experiments were performed at ambient conditions. The samples for the profilometric measurements were prepared by spin coating of the polymer on glass substrates and dried with the same procedure as for the QMB samples. The densities of the polymers applied in the calculations are: 1.12 g/ml for TP, 1.27 g/ml for PMDA and 1.12 g/ml for Durimid<sup>TM</sup>. The densities were measured experimentally by floating a small piece of the polymer film in a solution of defined density.

## 3. Results and discussion

### 3.1. Gravimetric measurements of TP, PMDA and Durimid<sup>TM</sup>

Pronounced differences between the ablation rate for single-pulse and multi-pulse experiments have been observed in previous experiments [11]. It has been shown that the ablation rates decrease strongly after the first pulse for TP at an irradiation wavelength of 248 nm and for PMDA for all applied wavelengths, i.e., 248 and 308 nm due to the partial carbonization of the material. Almost no changes of the ablation rate for succeeding pulses were detected for an irradiation wavelength of 308 nm for the triazene polymer. In this study, we analyze only the ablation rates determined for the first pulse, i.e., each data point represents an untreated sample. The measurements were carried out for fluences near the threshold of ablation. The ablation rates of the triazene polymer (TP) are shown in Fig. 1 for irradiation wavelengths of 193, 248 and 308 nm. A clear dependence of the ablation rate on the applied irradiation wavelength can be observed. The highest rates at low fluences are found for an irradiation wavelength of 193 nm followed by 308 nm. The lowest ablation rates are detected for an irradiation wavelength of 248 nm. These data suggest a direct relation to the UV–vis absorption spectrum of the triazene polymer at these wavelengths (see Fig. 2 top), i.e., high ablation rates for high absorption coefficients. The intense band at 196 nm corresponds mainly to the aromatic and aliphatic

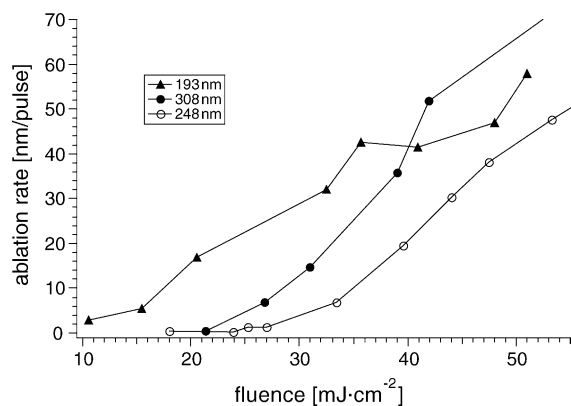


Fig. 1. Ablation rates of TP at irradiation wavelengths of 193, 248 and 308 nm measured with a QMB.

groups of the polymer, whereas the band at 322 nm corresponds to the triazene chromophore ( $>N=N=N-$ ; see also structure of the polymer in Scheme 1) [12,13]. The laser wavelength of 248 nm can directly excite both groups. The absorption reaches a minimum at 250 nm, but still exhibits a quite high absorption coefficient ( $24340 \text{ cm}^{-1}$ ). The etch rate can, therefore, be divided roughly into two groups, i.e., the wavelengths which directly excite the triazene system (e.g. 308 nm) and 193 nm that is in resonance with the aromatic system. The weakest functional group in the molecule, however, is the triazene group (bond energy 1.5–3 eV), which can be broken directly with a single photon at all irradiation wavelengths applied in this work. Aromatic fragments also absorb the shorter wavelength (especially 193 nm) in the gas phase, which limits the number of photons reaching the surface. Furthermore, the products remaining in the polymer film may also be strongly absorbing at a wavelength of 193 nm, thus limiting the penetration depth of the photons. An increase of the photon energy should result in an increase of directly broken chemical bonds, which should result in a decrease of the ablation threshold (as shown in Table 1). The photon energy of the three applied wavelengths are also included in Table 1. The ablation rate is also strongly related to the absorption coefficient of the material at a given wavelength. The photon penetration depth decreases with increasing values of  $\alpha$ , if the linear absorption coefficient ( $\alpha_{\text{linear}}$ ) is considered. High absorption coefficient should, therefore, result in lower ablation rates. The ablation rates measured by

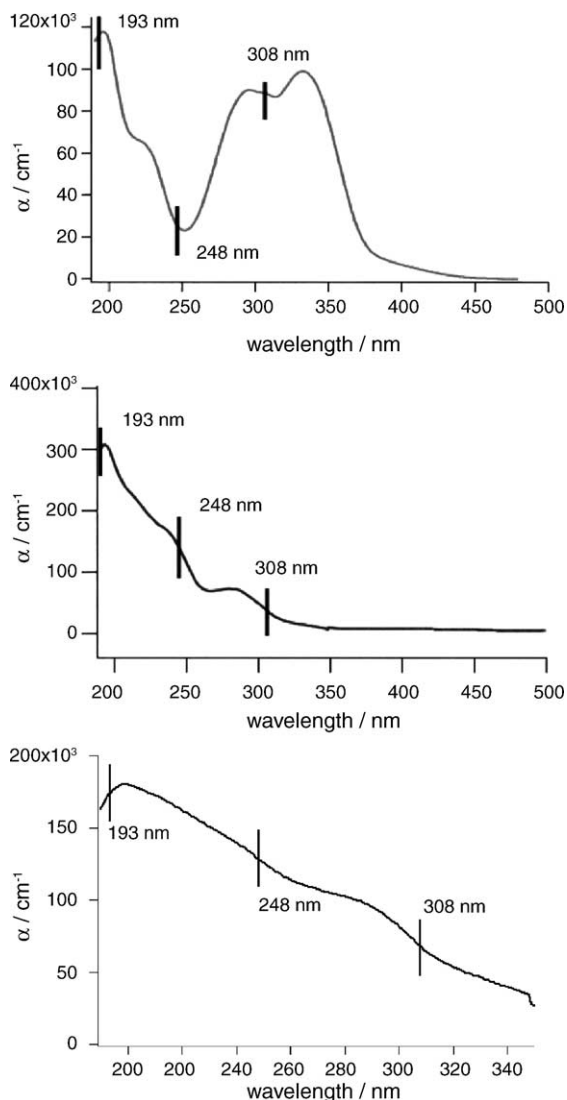


Fig. 2. UV-vis absorption spectra of TP (top), PMDA (middle) and Durimid™ (bottom).

QMB for the triazene polymer, however, do not exhibit this behavior at the low laser fluences applied. It is noteworthy to mention that bleaching of the triazene band at 330 nm occurs in TP during the laser pulses, especially at the irradiation wavelength of 308 nm [13]. The photon penetration depth is, therefore, increasing by this process, resulting in a lower effective absorption coefficient ( $\alpha_{\text{eff}}$ ). This can explain the crossing of the curves for 193 and 308 nm around  $40 \text{ mJ/cm}^2$  in Fig. 1. Another

Table 1  
Photon energies corresponding to the applied irradiation wavelengths

Wavelength (nm)	Photon energy (eV)	Linear absorption coefficient (cm <sup>-1</sup> )	Ablation threshold (mJ/cm <sup>2</sup> )
193	6.41	116,500	13
248	4.99	24,340	22.5
308	4.02	88,455	27.7

Physical parameters of TP at these wavelengths as retrieved from the absorption spectra in Fig. 2. The ablation thresholds were calculated fitting the function  $d(F) = 1/\alpha_{\text{eff}} \ln(F/F_{\text{th}})$ , where  $d(F)$  is the crater depth,  $F$  the applied fluence and  $F_{\text{th}}$  the threshold of ablation.

important factor is the above-discussed absorption of the laser photon (especially at 193 nm) by decomposition products. This will result in an increase of the  $\alpha_{\text{eff}}$ , which is experimentally observed for TP at 193 nm [12]. No Arrhenius tail could be found for TP at irradiation wavelengths of 193 and 308 nm. As already discussed in our previous paper [11], this is contradicting the results obtained by Küper et al.

The ablation rates for PMDA show even stronger differences for the different irradiation wavelengths (see Fig. 3). The data are again quite consistent with the considerations from the absorption spectra (see Fig. 2, middle). The spectrum exhibits a strong absorption at 193 nm, which is constantly decreasing towards higher wavelengths. The removal rates suggest a possible crossing of the curves at a fluence of around 55 mJ/cm<sup>2</sup> for the irradiation wavelengths of 193 and 248 nm (fluences above 50 mJ/cm<sup>2</sup> were not available for the 0.326 cm<sup>2</sup> area of the QMB

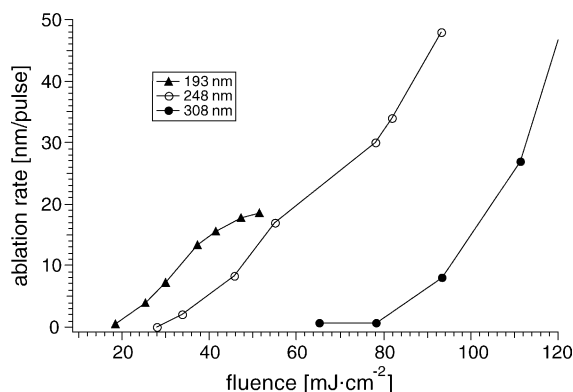


Fig. 3. Ablation rates of PMDA at irradiation wavelengths of 193, 248 and 308 nm measured with a QMB.

target). The absorption of fragments created by the decomposition of the polymer is more pronounced at 193 nm than at 248 nm, resulting in a reduction of the photon penetration depth (or number of the photons reaching the surface) of the polymer. Furthermore, the complete volume that is decomposed is not only a function of the penetration depth (absorption coefficient), but also of the applied fluence (a larger volume is decomposed for higher fluences). From all these considerations, it is possible to predict a crossing of the curves. The ablation starts at much higher fluences for the irradiation wavelength of 308 nm, which is probably the reason that no crossing is observed in the applied fluence range.

The ablation rates for Durimid<sup>TM</sup> (see Fig. 4) are much higher at all applied wavelengths than for PMDA. Durimid<sup>TM</sup> is, as discussed above, a photosensitive polyimide, which is probably comparable to Pyralin<sup>TM</sup> that has been used by Küper et al. [6]. The ablation rates determined by QMB for single pulses do not exhibit an Arrhenius tail for all applied irradiation wavelengths as shown by Küper et al. for the ablation of Pyralin<sup>TM</sup>. Küper detected Arrhenius tails for Pyralin<sup>TM</sup> for irradiation wavelengths of 248, 308 and 351 nm but not at 193 nm. The main difference between our experiments and the experiments by Küper et al. is the data collection sequence and the usage of a high vacuum chamber (10<sup>-6</sup> Torr). They started at the highest fluences and measured the removal rates with decreasing fluences for a single sample, which means that multiple pulses are applied for each sample. However, carbonization of photo-

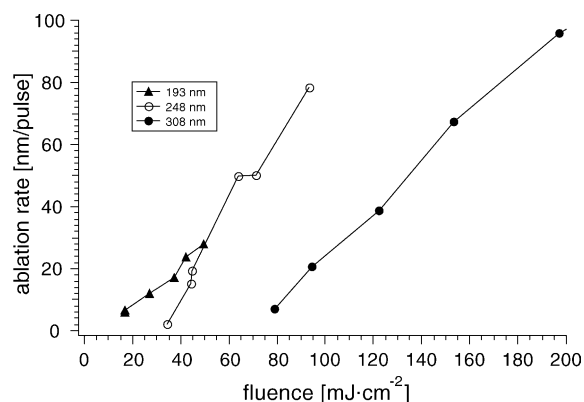


Fig. 4. Ablation rates of Durimid<sup>TM</sup> at irradiation wavelengths of 193, 248 and 308 nm measured with a QMB.

sensitive polymers [14] and polyimide [15] was reported in QMB measurements [11] and we could show that this chemical modification lowered the removal rates. It is also noteworthy to point out that the data of Küper et al. are often used as experimental reference data for models of the ablation of Kapton<sup>TM</sup> [16,17]. Our data suggest strongly that the removal rates are quite different for true single-pulse experiments and that the Arrhenius tail is related to surface carbonization upon multi-pulse irradiation. Another important fact to consider is the difference between the photosensitive Pyralin<sup>TM</sup> (or in our case Durimid<sup>TM</sup>) to Kapton<sup>TM</sup>. Ablation experiments of Kapton<sup>TM</sup>, Durimid<sup>TM</sup> and PMDA reveal strong differences between Durimid<sup>TM</sup> and the other two polyimides, which behave quite similar (also the chemical structure is slightly different, shown in Scheme 1). This suggests that PMDA might be the better choice if QMB reference data for Kapton<sup>TM</sup> are needed.

### 3.2. Profilometric measurements of TP and Durimid<sup>TM</sup>

Fig. 5 shows a comparison of the gravimetric and profilometric measurements of the ablation rates of TP at irradiation wavelengths of 308 and 248 nm for single-pulse experiments. The ablation rates obtained with the QMB correlate quite well with the profilometer data. The removal rates for an irradiation wavelength of 248 nm (inset in Fig. 5) measured with

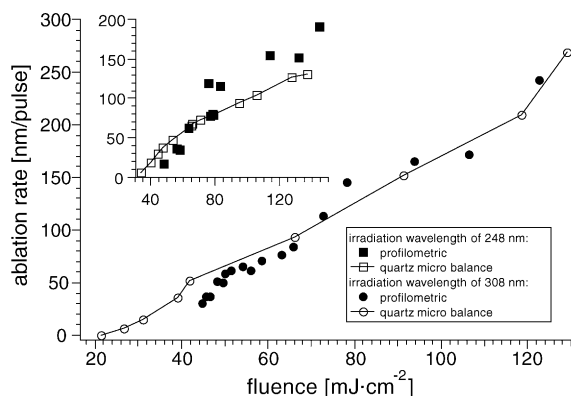


Fig. 5. Profilometric (●, ■) and gravimetric (○, □) measurement of the ablation rates of TP at irradiation wavelengths of 248 (■, □) and 308 nm (○, ●).

the profilometer are slightly higher relative to the data obtained by QMB at fluences above 80 mJ/cm<sup>2</sup>. A possible explanation could be the carbonization of the polymer surface for higher fluences, i.e., decomposition of the aromatic rings [14]. This carbonization was observed in our experiments for all applied polymers and is more pronounced for higher fluences. However, carbon reveals a much higher density than the original polymer leading to a loss in volume without significant mass loss. Therefore, the craters can be found to be deeper when measured with the profilometer than calculated from the QMB data. In TP, this decomposition is more pronounced for shorter wavelengths (larger absorption of aromatic ring at shorter wavelengths). This could explain why this shift is not found at an irradiation wavelength of 308 nm. For fluences below 50 mJ/cm<sup>2</sup>, profilometric measurements reveal a slightly lower ablation rate than calculated from the QMB data. This suggests that a mass loss, e.g. by formation of nitrogen from the photodecomposition of the triazene group or by evaporation of remaining solvent, occurs before any change in the surface morphology of the polymer can be detected. The ablation rates calculated for an irradiation wavelength of 308 nm, however, reveal a quite good agreement. For fluences below 45 mJ/cm<sup>2</sup>, no significant ablation of the material could be measured by profilometry, which is also close to the reliable detection limit of this method. However, the data calculated from QMB exhibits clear mass removal for fluences well below 45 mJ/cm<sup>2</sup>. Again, this suggests, as expected for a photolabile material, the formation of gaseous products in the bulk and/or at the surface of the polymer prior to ablation.

Fig. 6 shows the ablation rates for Durimid<sup>TM</sup> for irradiation wavelengths of 193 and 308 nm. For an irradiation wavelength of 193 nm again, clear mass removal is detected gravimetrically for fluences where the profilometric measurements reveal only clear ablation above a fluence of 100 mJ/cm<sup>2</sup>. However, for an irradiation wavelength of 308 nm, the gravimetric measurements reveal a clearly higher ablation rate than calculated from QMB data. The values for the crater depths measured by profilometry are about 1.7 times higher than the values calculated by QMB for fluences above 200 mJ/cm<sup>2</sup>. Even a different value for the density of the polymer cannot explain this shift, which suggests that above 150 mJ/cm<sup>2</sup>, a higher

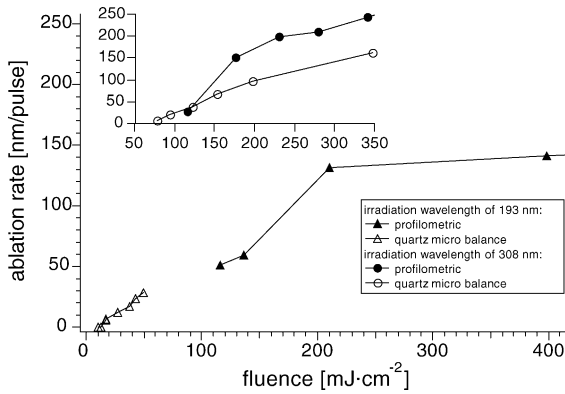


Fig. 6. Profilometric (●, ▲) and gravimetric (○, △) measurements of the ablation rates of Durimid™ at irradiation wavelengths of 193 (▲, △) and 308 nm (●, ○).

volume of material is removed from the surface than is calculated from the QMB data. One possible explanation could be the partial carbonization of the material surface as in the experiments with TP (see above). Another possible explanation is pushing of polymer material from the crater into a rim surrounding the crater, which has been observed previously [18,19]. This will result in a deeper crater without truly removing the whole volume of the crater and therefore a lower mass, which is detected by the QMB.

### 3.3. Influence of ambient conditions

During the ablation experiments with PMDA at an irradiation wavelength of 308 nm, it was discovered that the increasing frequency due to the loss of mass was slightly decreasing again to a constant value, which suggests an increase of the layer mass. This phenomenon can easily be overlooked for higher fluences. Nevertheless, this change in mass is very pronounced for fluences slightly above the threshold of ablation relative to the frequency change due to true removal of the polymer. It can even be observed when the sample is irradiated with fluences below the threshold of ablation (see Fig. 7) without any overall mass removal of the polymer. A QMB crystal was coated with PMDA and irradiated at a wavelength of 308 nm and fluences below the threshold of ablation, i.e., of permanent mass removal in a closed environmental chamber, which could be purged by dry nitrogen. In air, a pronounced increase of the frequency is detected, which is followed by a relatively slow decrease to the initial value. In nitrogen, the frequency does not drop back to its initial value in spite of the fact that the sample was irradiated with the same fluence. This suggests that an adsorbed species (most probably water) is removed by the laser and is reabsorbed to the surface after the laser pulse in ambient conditions, but not in dry nitrogen.

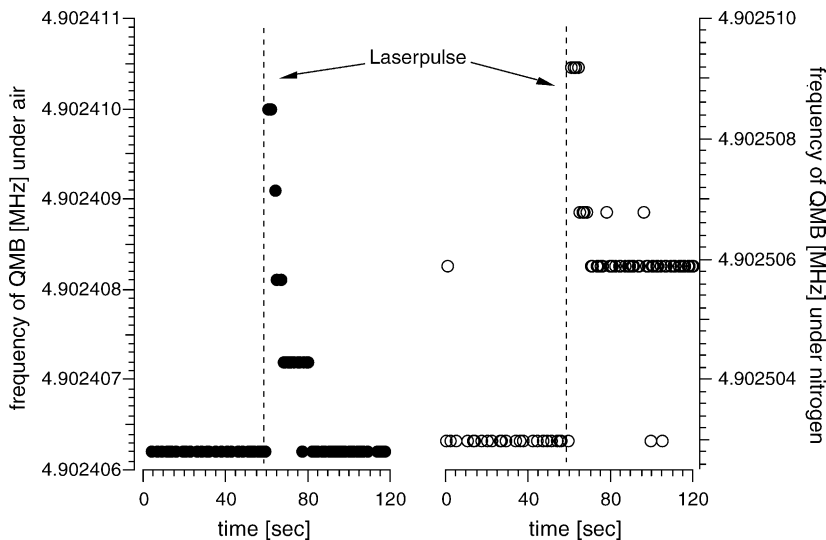


Fig. 7. Frequency measurement of PMDA. Irradiated with 1 pulse below the threshold of ablation in air (left) and under nitrogen (right). The irradiation wavelength was 308 nm. The scattered line indicates the laser pulse.



The difference in frequency corresponds to a mass load of  $50 \text{ ng/cm}^2$ , which corresponds to a monolayer of water.

#### 4. Conclusion

Three polymers were studied at three different irradiation wavelengths (193, 248 and 308 nm) using a Quartz microbalance and a profilometer. The gravimetric measurements exhibit a strong correlation between the ablation rates and the absorption coefficients of the applied polymers, but revealed a strong contradiction to the results obtained by Küper et al. who studied the ablation of Pyralin<sup>TM</sup>. In fact, the results, which clearly exhibit Arrhenius tails for irradiation wavelengths of 248, 308 and 351 nm, could not be reproduced in our setup with a triazene polymer and Durimid<sup>TM</sup> for irradiation wavelengths of 193, 248 and 308 nm. The main reason for this is that Küper et al. utilized the same sample for a whole sequence of different fluences which results in an altering the polymer surface by partial carbonization. The comparison of the ablation rates obtained by gravimetric and profilometric methods revealed a significant mass removal prior to ablation for the triazene polymer and Durimid<sup>TM</sup> at irradiation wavelengths of 248 and 308 nm in the case of TP, and 193 nm in the case of Durimid<sup>TM</sup>, and a clear offset between the ablation rates obtained from profilometry and from QMB. Partial carbonization of the material at the polymer surface may be the main reason for this difference.

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