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Incubation behaviour in triazenepolymer thin films upon near-infrared femtosecond laser pulse irradiation

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Abstract. The effects of laser radiation induced by a sequence of ultrashort (130 fs), near-infrared (800 nm) Ti:sapphire laser pulses in ~1 μm thick triazenepolymer films on glass substrates have been investigated by means of *in-situ* real-time reflectivity measurements featuring a ps-resolution streak camera and a ns-resolution photodiode set-up. The polymer films show incubation effects when each laser pulse in the sequence has a fluence below the single-pulse damage threshold. Non-damage conditions are maintained for several incubation pulses such that the reflectivity of the film shows a rapid decrease of up to 30% within 1 ns but subsequently recovers to its initial value on a ms timescale. Additional pulses lead to a permanent film damage. The critical number of laser pulses needed to generate a permanent damage of the film has been studied as a function of the laser fluence. Once damage is created, further laser pulses cause a partial removal of the film material from the glass substrate. Scanning force microscopy has been used to characterise *ex-situ* the irradiated surface areas. Based on these complementary measurements possible incubation mechanisms are discussed.

1. Introduction

Laser processing of polymers is an area of great research interest owing to its large number of potential applications in the material and biomedical sciences [1-4]. Most of the research has been related to the nature of the laser-matter interaction mechanisms [4-6] while possible applications of laser ablation have mainly been concentrated on the UV regime where many polymers of interest are highly absorbing. One polymer group of particular interest is that of the triazenepolymers [7] which are photochemically very active upon UV irradiation and feature superior ablation properties for irradiation at a wavelength of 308 nm [8]. These polymers have recently attracted numerous applications, e.g., as a photoresist material in laser lithography and also for laser plasma thrusters in micro-/nanosatellites [3].

In two previous studies [9,10], we broadened the scope of triazenepolymer film research by investigating their behaviour upon irradiation with single near-infrared femtosecond laser pulses. The first work [9] utilised real-time reflectivity (RTR) measurements to determine the physical mechanisms which act during the irradiation for different pulse durations in the range 130 fs - 2.6 ps and at fluences below and slightly above the ablation threshold fluence. A model based on optical interference effects was proposed to explain the observed transient reflectivity changes, the basis of

which is the decomposition of the polymer *within* the film material. This model was then further supported by the second study [10] employing both *in-situ* (RTR) and *ex-situ* (scanning force microscopy, modulated lateral force microscopy) techniques for fluences in the ablative regime.

An additional characteristic exhibited by many polymers is that of incubation behaviour. This is particularly the case for irradiation at wavelengths where they are essentially transparent [2]. Under multiple near-infrared fs laser pulse irradiation, such behaviour has been previously observed for commercial polymers such as polymethylmethacrylate (PMMA) [11], polycarbonate (PC) [11], and polyimide (PI) [12]. The phenomenon manifests itself in the fact that many low-intensity laser pulses have to be applied to the same irradiation area before a permanent damage occurs. In most cases it is associated with an increase in the absorption coefficient due to chemical alterations of the polymer induced by the repetitive illuminations.

In the present study, we have extended our previous work [9,10] on the irradiation of triazenepolymer thin films by single near-infrared fs laser pulses, i.e., in the transparency region of this polymer, with a detailed investigation of multi-pulse irradiation effects (incubation) at laser fluences below the single-pulse damage threshold. RTR measurements with sub-ns resolution have diagnosed the transient behaviour of the laser-heated films and post-irradiation scanning force microscopy studies have imaged the irradiated spots. These complementary techniques have allowed the incubation effects in these triazenepolymer thin films to be better understood.

2. Experimental details

The polymer film, with a chemical structure as shown in figure 1(a), has been synthesised according to a procedure described elsewhere [13]. The samples for the experiments have been prepared on glass substrates by solvent casting or spin coating of a 10% wt. solution of the polymer in a 1:1 mixture of cyclohexanone / chlorobenzene with one additional drop of a surfactant (Pluronic L-62), resulting in a final film thickness of ~1 μm.

A commercial chirped pulse amplification (CPA) Ti:sapphire laser system (Spectra Physics, Spitfire), providing linearly polarised pulses of 130 fs duration at a wavelength of 800 nm, was used for irradiation in air at atmospheric pressure. The polymer film is essentially transparent at the irradiation wavelength (photon energy ~1.55 eV) such that, in the linear absorption regime, the optical penetration depth $1/\alpha$ exceeds the film thickness by several orders of magnitude.

In the irradiation set-up, the sample was placed at normal incidence close to the focal plane of a lens with 150 mm focal length, resulting in an almost circular laser spot on the surface that corresponds approximately to a spatial Gaussian distribution with a ($1/e^2$) diameter of the order of 100 μm.

The temporal evolution of the surface reflectivity upon irradiation has been monitored using a single-mode Ar^+ laser operating at 514.5 nm. This probe beam was focused at the centre of the fs-laser irradiated region to a spot diameter ($1/e^2$) of ~30 μm, at an angle of incidence of ~18°. The intensity evolution of the reflected probe beam was then recorded by a streak camera (Hamamatsu Model C5680, equipped with a single sweep unit Model M5676; time-resolution of 350 ps in a time window of 50 ns) and by a photodiode/oscilloscope detection system (a few ns temporal resolution in a 2 μs time window). Further details regarding this RTR set-up can be found elsewhere [14].

Scanning force microscopy (SFM) in the contact mode has been used to probe the surface topography of the laser irradiated spots with a high lateral and vertical precision in the nm range. The basic instrumentation of the employed scanning force microscope (type “Explorer”) was supplied by Thermo-Microscopes/TopoMetrix. Additional details of the SFM measurements are given in Ref. [10].

3. Results and discussion

3.1. *Time-Resolved Reflectivity measurements (RTR).* Figure 1 shows the transient surface reflectivity (normalised to the non-irradiated level) upon exposure of the non-irradiated triazenepolymer film with a single 130-fs laser pulse at a fluence level of ~0.8 times the single-pulse damage threshold fluence

ϕ_{th}. A rapid reflectivity decrease of up to 30% within the first ns has been observed by the streak camera [figure 1(b)], followed by some rapid oscillations which have previously been reported in Ref. [9]. These oscillations are not resolved by the photodiode detection system, which is monitoring the reflectivity on longer timescales up to 2 µs [figure 1(c)]. The reflectivity decrease is then followed by a recovery towards the initial level on a ms timescale [9].

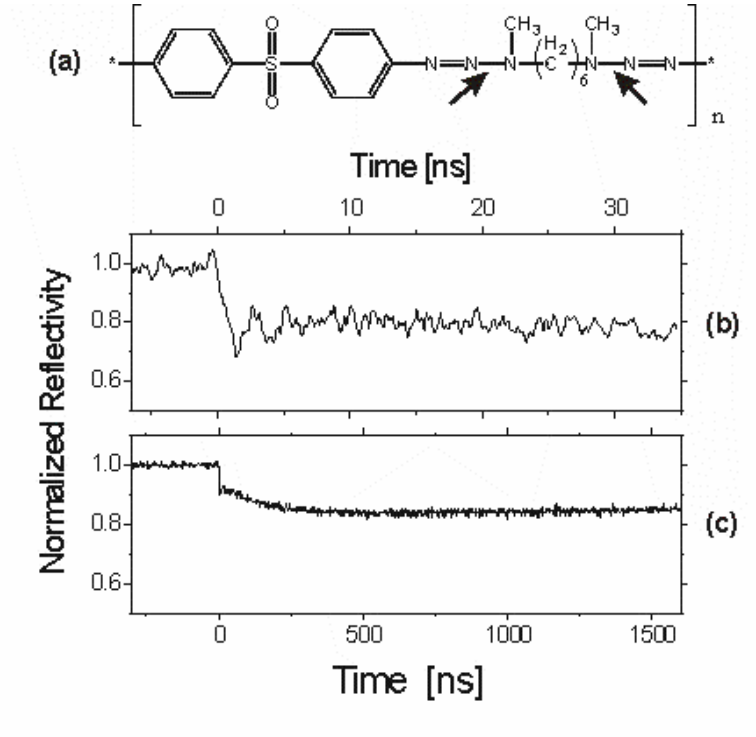

Figure 1. Chemical structure of the triazenepolymer (a). The two arrows mark the weakest bonds in the polymer chain. The two lower graphs show simultaneously recorded surface reflectivity transients for the unexposed polymer film upon irradiation with a single fs laser pulse (~390 mJ/cm^2, 130 fs, 800 nm). Streak camera: 50 ns time window (b), Photodiode: 2 µs time window (c). Both reflectivity curves have been normalised to the reflectivity of the non-irradiated film.

Figure 2 shows some selected surface reflectivity transients out of an irradiation sequence consisting of 20 consecutive single-pulse irradiation events to the same spot at a fluence around 400 ± 20 mJ/cm^2 (~80% of the single-pulse damage threshold fluence). All transient reflectivities have been measured by a photodiode and have been normalised to the initial reflectivity of the non-irradiated film.

The first eight laser pulses did not lead to any permanent change of the film reflectivity, i.e., the reflectivity recovered its initial level on a ms timescale (a time much longer than the probed time span shown here). In this regime, the reflectivity dropped rapidly by up to 25% and started to increase afterwards [see figures 2(a) and 1(b) for the first and the fifth laser pulse, respectively]. The complete recovery of the reflectivity is also visible in the initial normalised reflectivity level of ~1.0 before the arrival of the subsequent pulses, e.g., in figure 2(b).

At this fluence level, the ninth laser pulse caused a permanent damage of the polymer film [figure 2(c)]. Apart from a more significant initial drop in the surface reflectivity (~42% decrease) and a decreased final reflectivity at the end of the measured time window, it is also possible to observe a strong scattering of the probe beam radiation by the naked eye after the irradiation. This is indicative of a decrease in the final reflectivity that is mainly caused by topographical effects (a roughened surface).

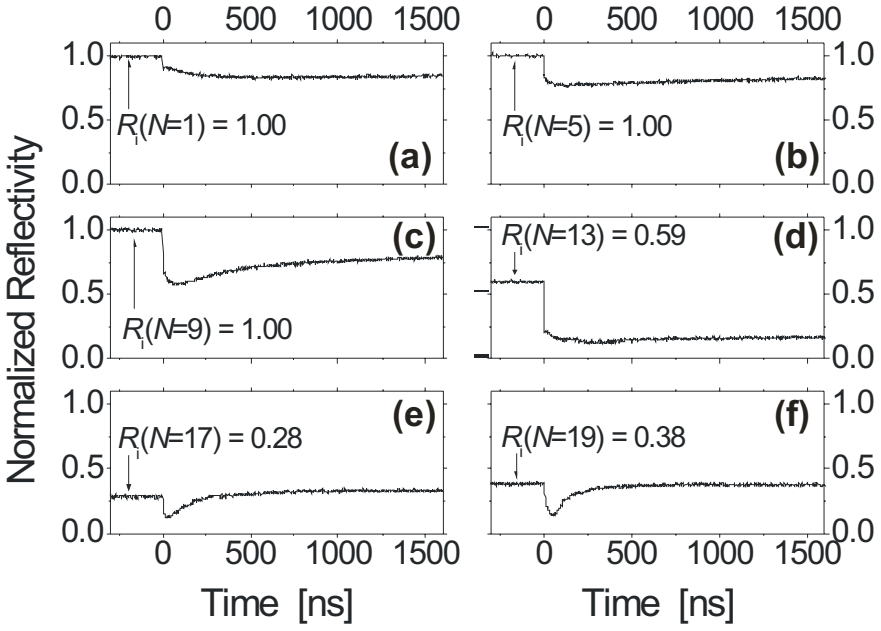

Figure 2. Selected surface reflectivity transients for a single laser pulse irradiation sequence (400±20 mJ/cm^2, 130 fs, 800 nm) on the same spot where N denotes the nth laser pulse. All transient reflectivities (a)-(f) were measured by a photodiode and have been normalised to the initial reflectivity of the non-irradiated film. The labelled arrows indicate the reflectivity R_i before the arrival of each laser pulse to the surface (at the time $t = 0$).

For all subsequent laser pulses, the initial surface reflectivity was now different from that of the non-irradiated polymer film and the irradiation always led to a permanent variation in the final reflectivity [figures 2(d)-(f)]. Interestingly, a small increase of the final reflectivity level when compared to the initial one has also been observed [see figure 2(e) after $N = 17$].

Figure 3(a) shows the initial surface reflectivity of all 20 consecutive reflectivity transients as a function of the pulse number. As already noted, during the first 8 laser pulses, the reflectivity has always recovered to its initial level. After the 9th laser pulse, permanent damage of the film has been observed as indicated by an increased optical scattering of the probe beam and, hence, a reduced initial reflectivity for the next laser pulse. Consequently, for pulse numbers between 9 and 15, the initial reflectivity significantly decreases to normalised values of ~0.25. Along with the increased surface roughness, modifications like the formation of dark pits in the polymer film have also been observed in this pulse number regime. These are probably caused by a local carbonisation of the triazenepolymer as has been observed previously in the case of fs laser pulse irradiation of polycarbonate samples under similar irradiation conditions [11]. For pulse numbers higher than 15, the initial reflectivity starts to increase again which is caused by the removal of the already modified and rough polymer film from the underlying glass substrate. This finally leads to a smoothening of the irradiated surface when approaching the flat interface of the glass substrate. All these observations are consistent with *incubation effects* which have been previously observed in polymers such as PMMA, PC, and PI for near-infrared fs laser pulse irradiation [11,12]. The incubation generally manifests itself in (i) a certain number of laser pulses (fluence dependent) which are necessary to induce irreversible changes in the irradiated material and (ii) a damage threshold fluence which decreases with the

number of pulses applied to the irradiated spot. In the present case of triazenepolymer films, the incubation might be caused by the local release of gaseous nitrogen at the weakest bond of the polymer [9] [marked by arrows in figure 1(a)] which, under multiple-pulse irradiation, successively shortens the polymer chains until local carbonisation or chemical alteration occur in the film. These material modifications then lead to a locally increased optical energy deposition for the subsequent laser pulses which reinforces the damage for the subsequent laser pulses.

The same qualitative behaviour as seen in figure 3(a) has been observed when increasing the laser fluence to a value of 455 ± 15 mJ/cm^2 (~0.9×ϕ_{th}) that is still clearly below the single-pulse damage threshold [figure 3(b)]. In that case, the number of laser pulses needed to induce a permanent damage of the film was observed to be lower (only 4 pulses per spot). This observation is consistent with the proposed damage mechanism since the amount of released nitrogen should increase with increasing laser fluence. Hence, higher laser fluences will be more effective in shortening the polymer chains and, consequently, less laser pulses are needed to reach the carbonisation stage.

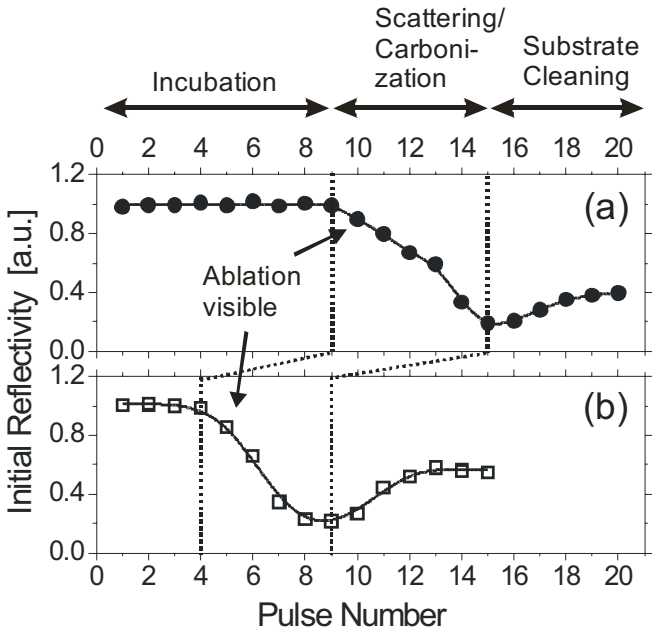

Figure 3. Initial film reflectivity (normalised to the value of the non-irradiated polymer surface) as a function of the pulse number applied to the same respective spot for fluence levels of (a) 400±20 mJ/cm^2 and (b) 455±15 mJ/cm^2 [130 fs, 800 nm]. The dashed vertical lines separate three characteristic regimes.

Assuming the validity of an incubation model which already has been successfully applied to polymers [11,12], the degree of incubation can be characterised from the data shown in figure 3, i.e., from the laser fluence applied and the respective number of pulses needed to induce damage at those fluence values. In this incubation model, as was first introduced for metals [15], the multi (N-) pulse damage threshold is related to the single-pulse threshold by a power law $\phi_{th}(N) = \phi_{th}(1)\times N^{\xi-1}$, where $\phi_{th}(1)$ = 495 mJ/cm^2 is the single-pulse threshold [9] and $0 \le \xi \le 1$ is a coefficient characterising the degree of incubation [15]. From the two observations $\phi_{th}(N=9)$ = 400 ± 20 mJ/cm^2 and $\phi_{th}(N=4)$ = 455 ± 15 mJ/cm^2, the incubation coefficient of the triazenepolymer is calculated to be ξ = 0.92 ± 0.06 which is similar to the value reported for PI (ξ = 0.87, [12]) but significantly larger than that for both PMMA (ξ = 0.67, [11]) and PC (ξ = 0.74, [11]) under near-infrared fs laser irradiation. This indicates that incubation effects are less important in triazenepolymer films than in other polymers such as PMMA and PC.

3.2. *Scanning Force Microscopy.* Figure 4 shows complementary SFM topography images of the surface after the irradiation sequence with 20 laser pulses (corresponding to the results given in figures

1 to 3). In figure 4(a), a large area overview of the irradiated spot is given whereas, in figure 4(b), a detailed magnification of the upper part of the central illuminated region is shown.

Upon the irradiation, a crater with a depth of ~900 nm and a diameter of ~50 µm has been formed on the surface [figure 4(a)]. It is surrounded by some irregular protrusions of polymeric material exhibiting heights up to 1.2 µm above the original surface plane. Even after irradiation with 20 laser pulses, the film has not been completely removed and some organic material has remained in the crater region as evidenced by the irregularly arranged structures with sizes between 250 nm and 1.5 µm [figure 4(b)]. Simultaneously, the surface roughness (as evaluated by the SFM software SPMLab NT, Ver. 5.01) is increased in this central crater area (R_a~35 nm) when compared to the non-irradiated film surface (R_a~ 19 nm).

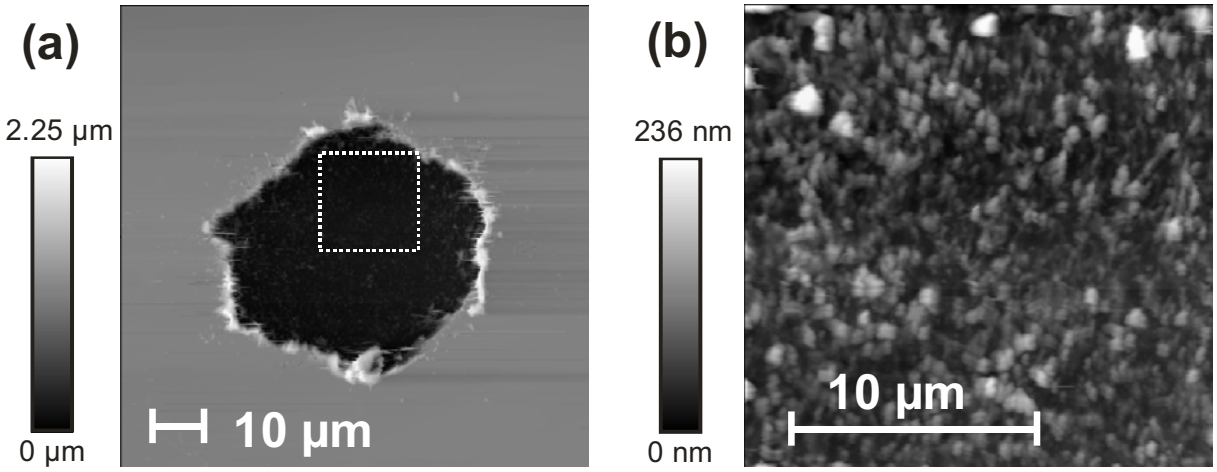

Figure 4. Surface topography of the triazenepolymer film after the irradiation with 20 laser pulses (130 fs, 800 nm, 400±20 mJ/cm^2). (a) Overview over the irradiated area (90×90 µm^2) and (b) detailed magnification (19×19 µm^2), as indicated by the white dashed frame in (a).

These observations are consistent with the evolution of the optical surface properties shown in figure 2, where a decrease of the initial reflectivity has been observed due to scattering and carbonisation. Interestingly, no laser induced periodic surface structures (LIPSS, ripples) have been detected inside the ablated areas. This is in contrast to the femtosecond laser irradiation of bulk polymers such as PI, where ripples with a period of ~800 nm oriented parallel to the electric field vector of the laser radiation has been reported for similar irradiation conditions [12,16]. This latter observation is also consistent with our previous studies, where we have proposed that the damage occurs within the film material close to the polymer/glass interface [9,10]. Obviously, then, no topographical features (such as ripples) are expected to be formed at the surface, in agreement with the SFM topography images shown in figure 4.

4. Conclusions

The irradiation of ~1µm thin triazenepolymer films on glass substrates upon multiple near-infrared femtosecond laser pulses (130 fs, 800 nm) has been investigated by complementary *in-situ* and *ex-situ* analysis techniques (ns-resolution reflectivity measurements and scanning force microscopy respectively). Below the single-pulse ablation threshold, incubation behaviour upon irradiation with multiple laser pulses has been observed. At a fluence of ~0.8 times the single-pulse damage threshold fluence, 9 laser pulses were needed to cause irreversible damage of the film. At higher fluences, less pulses are needed to create the film damage. This damage may be associated with the fragmentation of the polymer at its weakest chemical bond leading to the release of nitrogen and a successive shortening of the polymer chains, which might be accompanied by carbonisation or oxidation. The

calculated value of the incubation coefficient ($\xi_{TP} = 0.92 \pm 0.06$) demonstrates that incubation effects, under near-infrared fs laser irradiation, are less pronounced in these films when compared with polymers such as PMMA and PC.

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