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Surface Structuring of Synthetic Fibers by UV Laser Irradiation Simulation of the Temperature Profile at the Polymer Surface

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An investigation of the mechanism of the UV laser induced temperature field in a PETP-polymer is presented. We discuss a specific mathematical solution of the heat equation for large-area (uniform) irradiation on the PETP-substrate in relation to laser and substrate parameters.

Depending on the order of magnitude of the absorption coefficient of the polymer for different UV-light surface temperatures of approx. 16,000 °C (193 nm), 11,000 °C (248 nm) and 520 °C (308 nm) are calculated by simulation at the end of the laser pulse. The temperature input within the polymer layer is limited to only a very small penetration depth (< 0.4 μm at 193 nm, 248 nm and < 8 μm for 308 nm).

Besides the effect of surface structuring, material ablation processes also occur simultaneously during laser irradiation. Theoretically calculated results of the material removal depth on the PETP-polymer agree largely with the experiments.

Keywords: UV laser; surface structuring; temperature field modeling; poly(ethyleneterephthalate); laser ablation

INTRODUCTION

During the irradiation of fibrous polymers with pulsed UV-Excimer lasers under suitable conditions at first Bossmann et. al. [1-2] found regular, strictly aligned structures on a micrometer scale which are formed by both the temperature input into the polymer surface during the irradiation and internal frozen stress fields in the polymer.

For the investigation of the influence of the temperature or the UV laser wavelength on the structure formation PETP monofilaments were irradiated at different laser wavelengths (157 nm, 193 nm, 248 nm, 308 nm) with a constant pulse energy density and pulse number [3-7].

A summary of the experimental results is presented by D. Knittel et. al. [7].

The results of the investigation depicted in Fig. 1 clearly show the significant influence of the laser wavelength and the resulting absorption coefficient on structure formation.

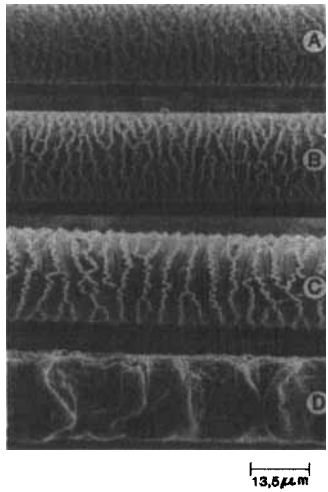

FIGURE 1 Influence of the laser wavelength on the surface structuring of a PETP monofilament after Kesting [5], irradiation parameters; laser frequency 2 Hz, laser pulse number 20, pulse intensity 150 mJ/cm^2, wavelength A) 157 nm, B) 193 nm, C) 248 nm, D) 308 nm.

The temperature input by laser irradiation leads to roll shaped structures (A-C), whereby the elevations are almost aligned vertically to the axis of drawing. The mean distance between the elevations becomes larger at higher irradiation wavelengths when the pulse number and pulse energy density remain constant. UV laser irradiation at a wavelength of 308 nm results in deep fusing and destruction of the fibers (D).

For the formation of such structures several fundamental preconditions have to be met [5-7] . These include a sufficiently high UV absorption coefficient of the polymer towards the laser beam. A number of highly absorbing synthetic fibers, such as poly(ethyleneterephthalate) (PETP), polyether ether ketone (PEEK), meet these conditions, so that in this case surface structures are formed on the polymer. On the other hand, with other materials, such as polyethylene (PE) and polypropylene (PP) etc., the irradiation does not produce surface structuring when laser wavelengths of 193 nm and 248 nm are used. The reason for this lies in the fact that the absorption coefficients of these polymers are too low [5-7].

On elastomers and PETP-fibers it was also shown that the orientation of the chain molecules and the resulting internal stress of the polymer has to be considered as another necessary condition for structure formation [2,5,6-7].

In PETP-fibers the structures are formed only in the case of stretched fibers (internal or external stress field) or in elastomer fibers in an expanded state (tension applied externally) [2,5,6-7]. So the surface structuring is thus influenced by both the temperature field and the internal stress fields in the polymer.

Furthermore, if the UV absorption coefficient of the polymer is sufficiently high at the laser wavelength used and the UV laser pulse during the irradiation is intense enough, a thin layer of material is removed up to a certain depth (etching depth) [5-10].

This laser-induced removal is called "ablative photodecomposition" or, in short, "ablation". The removal is strictly limited to the surface without thermal damage in the surroundings or in deeper layers.

From experimental IR-measurements by Dyer et. al. of the surface heating generated by the laser-induced surface removal of PETP and polyimide (PI) foils during laser irradiation at the wavelengths of 193 nm, 248 nm and 308 nm it was possible from the experimental data to estimate temperatures far above 1000 °C on the irradiated polymer surface [10].

For the calculation of the temperature field $\Delta T(z,t)$ within the irradiated material surface in relation to time (t), irradiation intensity (I_a), wavelength (λ), pulse shape (single rectangular pulse), pulse time (ι_i) and depth (z) a one-dimensional function was derived from the general heat differential equation assuming constant material parameters (heat diffusion coefficient (D), heat conductivity (κ) and absorption coefficient (α)) [11-13].

The solution of the heat equation requires boundary conditions. The temperature rise in the z-direction during the heating cycle is described by Eq. (1)

$$\Delta T(z,t)=\frac{I_s}{\kappa}\cdot\left\{2\sqrt{Dt}\cdot ierfc\left(\frac{z}{2\sqrt{Dt}}\right)-\frac{1}{\alpha}\exp(-\alpha z)+\frac{1}{2\alpha}\exp\left(\frac{\alpha\cdot 2\sqrt{Dt}}{2}\right)^2\cdot\right.$$
$$\left.\left(\exp(\alpha z)\cdot erfc\left(\frac{\alpha\cdot 2\sqrt{Dt}}{2}+\frac{z}{2\sqrt{Dt}}\right)+\left(\exp(-\alpha z)\cdot erfc\left(\frac{\alpha\cdot 2\sqrt{Dt}}{2}-\frac{z}{2\sqrt{Dt}}\right)\right)\right)\right\} \quad (1)$$

whereby erf(x) is the error function and erfc(x) and ierfc(x) are the complementary error functions

$$erf(x)=-erf(-x)=\frac{2}{\sqrt{\pi}}\int_0^x\exp(-\zeta^2)d\zeta \qquad erfc(x)=(1-erfx)=\frac{2}{\sqrt{\pi}}\int_x^\infty\exp(-\zeta^2)d\zeta$$

$$ierfc(x)=\frac{\exp(-x^2)}{\sqrt{\pi}}-x\cdot erfc(x)$$

Using this equation and the assumptions above it is possible to calculate the temperature in relation to pulse time and depth of penetration. At the end of the laser pulse for $t=\tau_1$ the temperature

$$\Delta T_{max}=\Delta T(z,t=\tau_1) \quad (2)$$

is obtained.

Subsequently there is cooling for $t>\tau_1$. This is calculated by Eq. (3)

$$\Delta T(z,t)=\frac{2I_0D^{1/2}}{\kappa}\left[t^{1/2}ierfc\left(\frac{z}{2(Dt)^{1/2}}\right)-(t-\tau_1)^{1/2}\cdot ierfc\left(\frac{z}{2D^{1/2}(t-\tau_1)^{1/2}}\right)\right] \quad (3)$$

with the additional condition

$$I_0 = \Delta T_{max} \cdot \kappa \cdot \frac{1}{2 \cdot \sqrt{D\tau_l} \cdot \text{ierfc}\left(\frac{z}{2 \cdot \sqrt{D\tau_l}}\right)}$$

For a better understanding of the surface structuring and the laser ablation of polymers, at first model calculations of the temperature fields in relation to laser irradiation- and polymer parameters are presented in this paper, using PETP polymers as an example, and compared with experimental results.

SIMULATION OF THE TEMPERATURE PROFILE AT THE POLYMER SURFACE

On the basis of the experimental findings described for the UV laser-induced structuring of polymers and the given model for the calculation of the temperature field on the polymer surface, the simulation results of the temperature profile of PETP polymers are presented with temperature-independent material parameters known from literature (see Table 1).

TABLE 1 Simulation parameters [11]

Laser parameters				Material parameters of PETP		
Laser wavelength [nm]	Gas mixture	Pulse time [ns]	Pulse density [J/cm^2]	Absorption coefficient [1/cm]	Heat conductivity [W/cmK]	Heat diffusivity [cm^2/s]
193 (UV-Excimer-Laser, LPX-210, Lambda Physic)	F_2	23	0.01-1	$3*10^5$	0.0015	0.0013
248 (UV-Excimer-Laser, LPX-210 Lambda Physic)	KrF	34	0.01-1	$1.6*10^5$	0.0015	0.0013
308 (UV-Excimer-Laser, EMG 101 MSC, Lambda Physic)	XeCl	17	0.01-1	$4*10^3$	0.0015	0.0013

At first the influence of the UV laser wavelength on the temperature flow or distribution in the PETP-polymer at a constant pulse energy density (150 mJ/cm^2) of different laser wavelength irradiation (193 nm, 248 nm, 308 nm) is calculated.

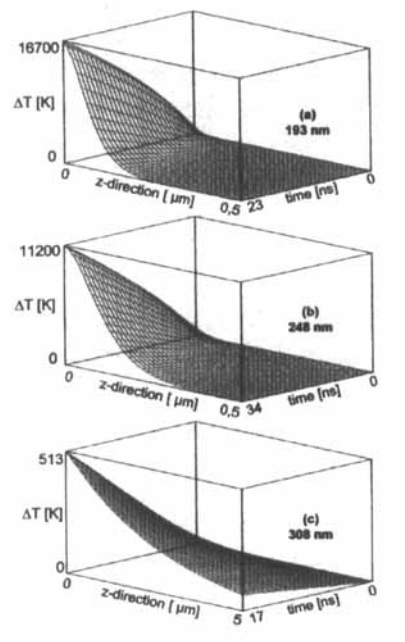

FIGURE 2 Temperature difference ($\Delta T = (T - T_\infty)$) of the PETP surface in relation to the laser pulse duration and the penetration depth (z) in the PETP-polymer at different laser wavelengths and / or optical absorption coefficient.
((a), 193 nm $\alpha=3*10^5$ 1/cm, (b) 248 nm $\alpha=1{,}6*10^5$ 1/cm, (c) 308 nm $\alpha=4*10^3$ 1/cm, absorbed laser light 150 mJ/cm^2, thermal conductivity 0.0015 W/cmK, heat diffusivity 0.0013cm^2/s, note the different z-scale).

The experimental results for these irradiation parameters are shown in Fig. 1. For the laser wavelength irradiation at 157 nm there are no data for the absorption coefficient known from literature. The results presented in Fig. 2 demon-

strate the influence of the laser wavelength on the temperature profile in the polymer (note the different z-scale).

For the irradiation at wavelengths of 193 nm and 248 nm the energy input remains limited to a short depth of penetration (< 0.4 μm). In contrast to this the UV laser irradiation at a wavelength of 308 nm penetrates much deeper into the polymer (< 8 μm) and leads to melting without structuring (see Fig. 1).

For the irradiation at the wavelengths of 193 nm and 248 nm the temperatures are significantly higher in comparison to the wavelength at 308 nm. At these high temperatures there is not only a melting of the polymer surface with structuring in the fibers with an internal stress field (PETP, PEEK), but also decomposition of the chain molecules on the polymer surface. In the form of a volume explosion the fragments formed are emitted and burn under atmospheric conditions in a hot exothermic cloud of material. In contrast to this, there is only melting without structuring of the polymer surface during irradiation at a wavelength of 308 nm. This is also demonstrated by the calculation. The penetration depth of the temperature at a wavelength of 308 nm is approx. 20 times higher and is at considerably lower temperatures (< 520 °C) than at the wavelengths of 193 nm and 248 nm.

MODEL CALCULATION FOR ABLATION BEHAVIOR

The ablation behavior of various types of PETP-polymers was tested experimentally in relation to the pulse energy density and characterized by suitable constants such as etching depth and threshold energy [5-10]. This is presented schematically in Fig. 3.

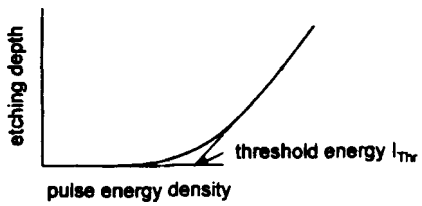

FIGURE 3 Schematic presentation of an etching diagram for the determination of the threshold energy density.

By extrapolation of the linear range to the etching depth zero the threshold fluence is determined from the experimental data. The energy densities determined experimentally for PETP-polymers above which ablation occur are shown in Table 2.

TABLE 2 Thermal threshold energy densities for PETP-materials

Material	Threshold energy density I_{Thr} [mJ/cm²]	
	193 nm	248 nm
PETP foil	51 [6]	63.6 [6], 37 [10], 45 [8]
PETP fabric	121 [6]	78 [6], 67 [6]
PETP multi-filament fiber	27 [6]	39 [6], 65 [6]
Mean value	66.3	56.4

The values determined experimentally are of the same order of magnitude, but depending on the composition of the PETP polymer (foil, fabric, fiber), various values result due to experimental uncertainties. For this reason a mean value is used for the theoretical considerations of the ablation behavior for the threshold energy at the laser wavelengths tested.

There are no experimental data concerning the ablation threshold energy of laser irradiation at the wavelength of 308 nm. The simulation of the temperature profile at this wavelength shows a significantly lower increase in temperature below 520 °C in comparison to irradiation at 196 nm and 248 nm. Evidently no measurable decomposition of the PETP-polymers takes place in this temperature range. This is also indicated by dynamic heat flow difference measurements carried out in conjunction with this work, whereby only above approximately 375 °C under atmospheric conditions and above 385 °C under a nitrogen atmosphere was exothermic decomposition observed experimentally.

Using Eq. (6) the penetration depth (etching depth per laser pulse) can also be calculated and its evaluation clearly depicted in Fig. 4.

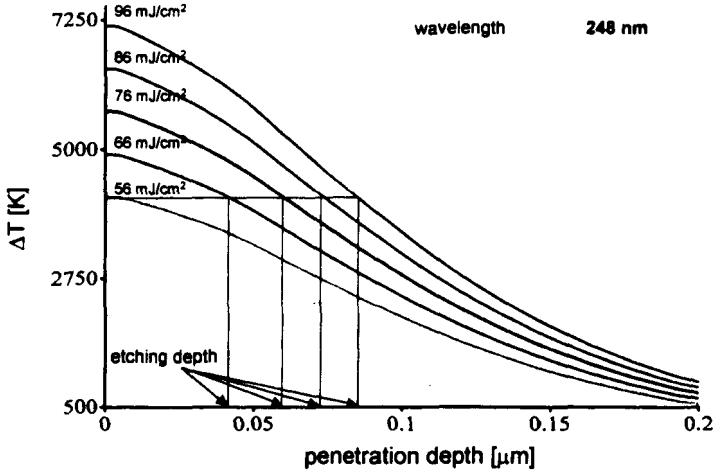

FIGURE 4 Temperature profile in the PETP-polymer at the end of the laser pulse ($t = \tau_l$) for determining the etching depth in relation to the penetration depth and the pulse energy density.

Initially, with the mean threshold energy density above which ablation occurs, the temperature profile in the polymer at time ($t = \tau_l$) is calculated in relation to the penetration depth (lower red curve). The calculation results in an ablation temperature of 4,100 °C directly on the polymer surface for z = 0. For each calculated temperature curve with a pulse fluence above the threshold fluence the etching depth (z) is determined using the equation

$$\Delta T(z, I_a > I_{Thr}, t = \tau_l) = \Delta T(I_a = I_{Thr}, z = 0, t = \tau_l) = 4{,}100\ ^\circ C \qquad (4)$$

at 248 nm.

For this purpose the non-linear equation is solved iteratively and the etching depth (z) solved according to the Newton method. This procedure is also depicted schematically in Fig. 4.

A summary of the calculated results for the wavelengths of 193 nm and 248 nm is shown in Fig. 5.

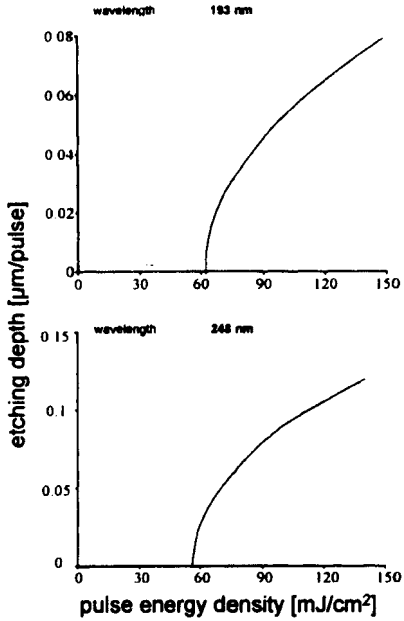

FIGURE 5 Calculated etching depth per pulse in the PETP-polymer for the laser wavelengths of 193 nm and 248 nm for different pulse energy densities.

Above the threshold fluence there is a significant thermically-induced layer ablation of the polymer surface. Here, the ablation rates achieved increase significantly with higher energy density increasing amounts of molecular polymer fragments removed from the polymer surface. In the case of irradiation at a wavelength of 193 nm the etching depth is less at the same pulse energy density compared to the wavelength of 248 nm. Furthermore, extremely small etching depths are achieved with sufficiently small pulse energy densities (< 0.05 µm). The etching depth calculated in this work per pulse in relation to the pulse energy density agrees with the values found experimentally at the laser wavelength of 248 nm [8], which was determined by a very accurate weighing of the loss of weight of the sample during ablation.

CLOSING REMARKS AND OUTLOOK

In this work, a way is presented to explain the laser-induced surface structuring. Although for the calculation of the temperature field in the polymer during and after laser irradiation from the general heat differential equation many simplifications were assumed (temperature-independent material parameters, closed boundary conditions), there is nevertheless a very good agreement of the experimental results with the values calculated by the model concerning temperature and ablation behavior of PETP fibers during and after irradiation with pulsed UV lasers. For a comprehensive understanding of the structure formation further theoretical and experimental trials have to be carried out. In particular, the question has to be clarified concerning to what extent the temperature field in the local limited surface influences the thermo-mechanical behavior of the polymers and the viscosity of a molten surface layer.

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