PROCESSING OF POLYMERS BY UV PICOSECOND LASERS

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Abstract

Laser micromachining has been proven an excellent technique for patterning many engineering materials. The emitted photon energy from a UV laser is high enough to break the chemical bonds of the target reducing the heat effects on surrounding material. We present the results obtained by investigation of the laser ablation processes with picosecond pulses in about 20 different organic materials. Micro-drilling and cutting of polymers were performed by the 266-nm radiation. The effect of laser fluence on the ablation rate and drilling depth was investigated.

Most of the materials showed two ablation thresholds. One of them was below 1 J/cm^2 with a low material removal rate. Another threshold was spread in the range of 3 – 30 J/cm^2 and the rapid increase in the ablation rate was found above it. The results are discussed in connection with optical ant thermal properties of the materials. The thermal activation of the ablation plays an important role at low fluences.

The processing regimes of polymers were proved at formation of microstructures. UV laser radiation with the picosecond pulse duration can be useful in manufacturing micro-systems for diverse technical applications.

Introduction

Polymers are widely used in diverse fields of everyday life starting from household goods to delicate bio-medical devices and MEMS. Molding and extrusion are common processes for manufacturing parts from polymers [1].

Micro-parts are produced by different etching techniques. Lithography requires use of masks and is acceptable for mass-production. Excimer lasers are usually used for processing polymers. Their usage is also related to the mask technique. Because of specific features of the excimer lasers there is an overall tendency to replace them by solid-state lasers with the laser-direct-write possibility. The technique offers flexibility, which is especially important at the development stage of micro-devices.

The wavelength of the laser is an important parameter for micromachining of polymers. Special care should be taken to minimize the thermal damage of the device when fabricating devices for biomedical applications. UV radiation is able to break chemical bonds directly without significant heat transfer to the surrounding material [2]. Most of the lasers used today for polymer processing are with nanosecond pulse duration.

Another way in clean processing of polymers is an application of femtosecond lasers, especially to biodegradable materials [3]. Short pulses inspire rapid evaporation of the material by a high energy input rate, preventing dissipation of excitation in the form of heat.

New challenges in real-world applications of the laser micro-fabrication induce the picosecond lasers with UV radiation. The pulse duration of the lasers is comparable to the time of electron-phonon relaxation and is short enough for “cold” ablation. Easy and effective conversion to UV radiation [4] offers a cost-effective source for photochemical ablation of polymers.

Ablation of organic materials, such as polymers, is quite different from that of metals and other inorganic materials. Vaporisation and melting are the main methods of material removal for inorganic materials. Most of polymers tend to decompose before evaporation. Long chains of molecules are cut into fragments before they are able to leave bulk of the material. Some fragments are volatile. The ablation rate is closely related to a number of broken bonds in a polymeric chain [5, 6]. Volume of the fragments and monomers is bigger than that of the polymer. Volume explosion is the force for expelling of the material [7]. Below the ablation threshold, swelling of the polymer surface was observed in the laser irradiated areas [8]. Thermal activation of

material removal appears as a typical "Arrhenius tail" instead of the definite ablation threshold.

There was no detailed investigation on behaviour of different polymeric materials under laser irradiation. Research of this work was dedicated to estimation of some relationships between polymer properties and the ablation threshold as well as ablation rate by using picosecond and nanosecond UV lasers.

Experimental set-up

Laser ablation experiments were performed on the workstation that included a laser, the beam delivery system with harmonics generation, focusing head and XY and Z stages [9]. Two different lasers were used in experiments. The picosecond laser with a lamp-pumped regenerative amplifier PL2241 (Ekspla) generated pulses of 60 ps duration at 1064 nm wavelength and 250 Hz repetition rate. The frequency-converted radiations of 266 nm and 355 nm were used in experiments. The nanosecond laser NL640 (Ekspla) with third harmonics (355 nm) was used in some experiments.

An attenuator made of a half-wave plate and polarizer was used to change laser pulse energy. Single plano-convex lens made of fused silica with the focal length of 50 mm finally focused the beam on samples. The spot diameter was 25 μm. The pulse energy was varied between 4 μJ and 280 μJ at 266 nm, which corresponded to laser fluences 0.4-50 J/cm^2 on a workpiece. The range of laser fluences used in experiments was limited at the lower end by the sensitivity of a powermeter below 1 mW. On the other hand, the higher fluences are more attractive for real applications while they enable higher processing efficiency.

Samples were mounted on a two-coordinate linear step motor with the air-bearing. The programmable step was 0.5 μm and repeatability not worse than 5 μm. The Z-axis was controlled by moving the focusing lens up to down.

Commercially available sheet materials of various polymers were used in the investigation. A list of the materials is presented in table 1. Thickness of the samples varied from 0.85 mm to 6.88 mm. The thickest samples (> 6 mm) were separated from a bulk by milling. No special preparation was performed to make the surface of samples smooth. The as-grown surfaces varied from even as a glass of the extruded PMMA to a "goose-skin" like surface. Extruded PMMA was clear, polyester and both PTFE were of white color, acetal Derlin™ filled with PTFE was brown and fiberglass was of light brown color. All other materials were of black color.

Table 1. Polymers used in the ablation experiments. Thickness of the samples and initial glassing as well as decomposition temperatures of polymers are indicated.

#	Material	d, mm	T_{glas} ^oC	T_{dec} ^oC
1.	ABS	1,54	95	350
2.	ABS/PVC	3,22	85	270
3.	PVC	3,27	70	200
4.	Acrylic PVC	3,18	90	185
5.	Extruded PMMA	1,42	90	200
6.	Cast PMMA (black)	2,91	90	200
7.	Polyester	6,55	150	350
8.	Polycarbonate	6,88	150	350
9.	Nylon™ (polyamide)	1,6	170	300
10.	UHMWPE	6,9	105	340
11.	Acetal copolymer	3,18	165	
12.	Derlin™ acetal	1,59	165	
13.	PTFE filled Derlin™	3,3		
14.	Teflon™ PTFE	1,04	320	510
15.	Virgin™ PTFE	0,85	320	510
16.	Polypropylene	1,05	155	330
17.	Polypropylene oxide	6,45		
18.	Fiberglass	3,74		
19.	Carbon fiber	1,74		

The experiments included single-pulse ablation, percussion drilling, cutting trenches and milling cylindrical as well as rectangular holes. Optical microscopes were used for analysis of the samples. Geometrical parameters of holes and trenches were measured. Quality of the processing was evaluated by sharpness of edges, presence of melt and deposition.

Results and Discussion

266 nm versus 355 nm

In all cases with the picosecond laser, the use of 266 nm radiation provided better processing quality and higher ablation rate compared to the 355 nm radiation. Pictures of the lines cut in the fiberglass with 266 nm and 355 nm at the same fluence are shown in figure 1.

Vertical and horizontal lines were cut by 1, 10 and 100 passes. Distance between lines was 300 μm. Signs of burning and deposition were found after the ablation of the fibreglass with 355 nm radiation. Nanosecond pulses at 355 nm led to poor processing quality, compared to picosecond pulses.

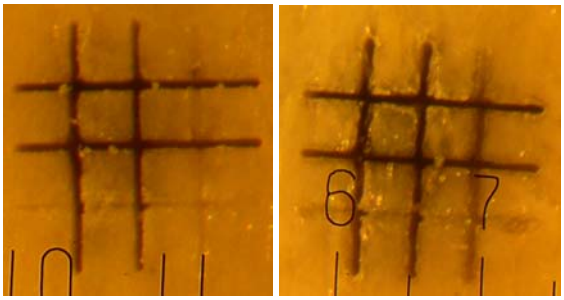

Figure 1. Vertical and horizontal lines cut in fiberglass (30 J/cm^2, 60 ps; left - 266 nm; right – 355 nm).

Nylon™ can be machined by laser radiation of both wavelengths with acceptable quality (figure 2) because the polyamide chain includes C-N bonds with the lowest bonding energy of 3.04 eV [3] less than the quanta energy of the 355 nm radiation. Nevertheless, more deposit was generated by using the 355 nm radiation. The latter was true for all materials. We assume that the reason was a photo-thermal nature of the ablation with the low-photon-energy quanta.

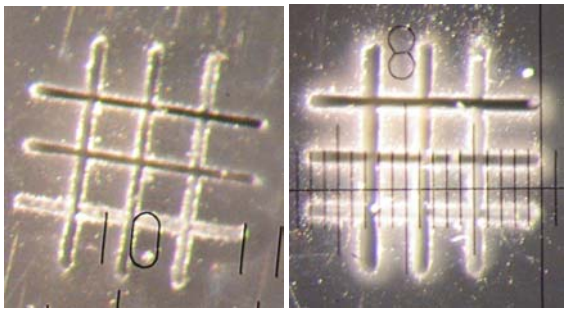

Figure 2. Vertical and horizontal lines cut in Nylon™ polyamide (30 J/cm^2, 60 ps; left -266 nm; right - 355 nm).

Besides the strong bonds along a molecule, the chains in linear polymers, such as polyethylene, are linked together by weak bonds (Van-der-Walse etc.) [6]. Breaking of the long chains does not lead directly to removal of fragments. Contribution of the weak forces is proportional to the length of the fragment. The chain has to be sliced into small pieces before evaporation occurs. Therefore, the energy of photons exceeding binding energy of monomers is not a sufficient warranty for clean ablation because more energy is required for releasing a lot of weak covalent links.

In case of polyethylene, the chain is formed exceptionally by the C-C bonds with the energy of 3.62 eV. The 355 nm radiation (3.50 eV) cannot break the bonds directly, while this is feasible with the 266 nm radiation (4.66 eV). Poor edge quality was found by cutting the ultra-high molecular weight polyethylene (UHMWPE) with both 355 nm and 266 nm radiation (figure 3). The weak bonds in polyethylene comprise significant portion of the attractive force between atoms.

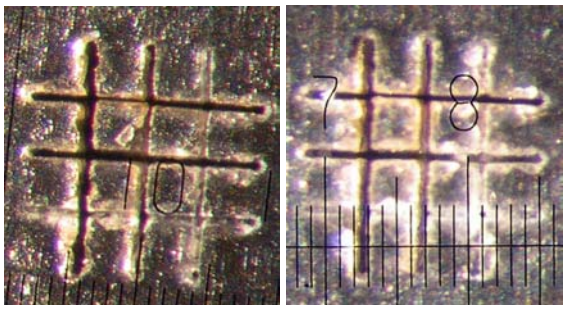

Figure 3. Vertical and horizontal lines cut in the ultra-high molecular weight polyethylene (UHMWPE) (30 J/cm^2, 60 ps; left -266 nm; right - 355 nm).

The clear extruded polymethylmetacrylate (PMMA) showed poor machining ability at the used wavelengths. The reason was a small absorption of PMMA. The material requires shorter wavelength of 193 nm for reasonable quality of laser ablation [2]. Dopants, that coloured in black the cast PMMA, increased the absorbivity of the material at 266 nm and 355 nm. The ablation of the cast PMMA was efficient and provided sharp edges with little deposition (figure 4).

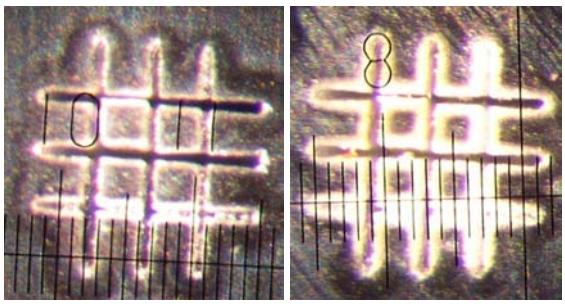

Figure 4. Vertical and horizontal lines cut in the black cast PMMA (30 J/cm^2, 60 ps; left -266 nm; right - 355 nm).

Ablation rate versus laser fluence

The 266 nm radiation of the picosecond laser was used to mill cylindrical and rectangular holes in polymers. The holes were formed by scanning 1, 2, 5, 10, 50 passes at the same pulse and line overlap in

the layer. Two of the holes with excellent edge quality are shown in figure 5.

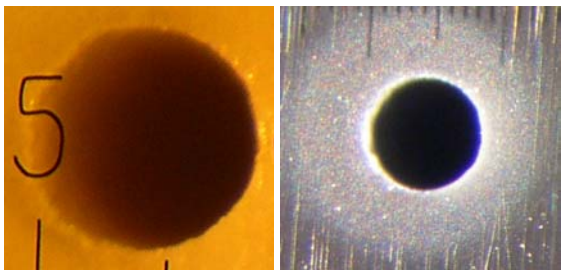

Figure 5. The 400 µm diameter holes milled in fiberglass (left) and Derlin™ acetal (30 J/cm^2, 60 ps).

The laser pulse energy of the wide range was chosen to get a relationship between the laser fluence and the ablation rate. Some holes went through all thickness of the sheet material (2-6 mm). Depth of the holes was measured and their volume was divided by the number of laser pulses used to mill a hole. The average ablation rate in µm per pulse was calculated for all the holes. Dimensions of the holes were much bigger than the beam diameter.

Two different graphical representations were used for analysis of the experimental results. The first one is typically used for laser ablation of inorganic materials: the ablation rate versus logarithm of the laser fluence. Figure 6 shows the relationship between the laser fluence and the ablation rate for the Acrylic PVC. The lines in figure 6 show results of approximations made for two different models.

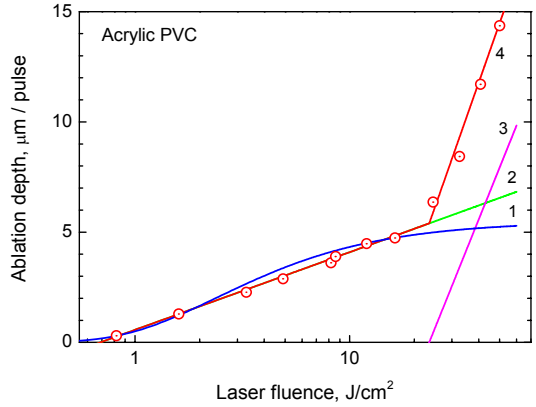

Figure 6. Ablation rate versus laser fluence in Acrylic PVC polymer: circles – experiment; lines - approximations: 1 – exponential thermal activation of Arrhenius-type (2); 2, 3 – logarithmic Beer's law (1); 4 – the sum of 2 and 3 (266 nm, 60 ps).

A linear approximation in the representation of figure 6 allowed an estimation of the ablation threshold and the effective absorption length, according to the equation for the general phenomenological Beer's model of laser ablation:

$$L = \alpha^{-1} \cdot \ln(\frac{F}{F_{th}}) \qquad (1),$$

where L – the ablation depth, α^{-1} – the absorption length, F – the laser fluence and F_{th} - the ablation threshold.

Most of the materials exhibited two nearly linear segments in the investigated range of laser fluences. The existence of two different ablation thresholds related to photo-chemical and photo-thermal decomposition of polymers was supposed. Therefore, equation (1) was used twice in the approximation with different threshold energies and later they were summed.

Thermal activation of laser ablation in polymers is a well known fact. The "Arrhenius tails" were observed at polymer ablation for long enough wavelengths which cannot cause the direct photochemical decomposition [10]. Therefore, the low-fluence segment of the relationship was approximated to the Arrhenius law, also:

$$L_a = L_\infty \cdot \exp(-\frac{E_a}{kT}) \qquad (2),$$

where L_a – the ablation depth, L_∞ - a constant, E_a – the thermal activation energy, k – the Boltzmann constant, T- temperature. The activation energy is related to bond energy of polymers.

The linearization of the data for the Arrhenius-law approximation was performed by representing them in the form of $\ln(L_a) \sim f(1/F)$ (figure 7).

In case of PVC, the Arrhenius approximation (curve 1) was in better agreement with the experiment. The same was with some other polymers: polycarbonate, polyester. A clear Arrhenius tail was observed for ultra high molecular weight polyethylene. More detailed investigations at a lower fluence range are required in other materials.

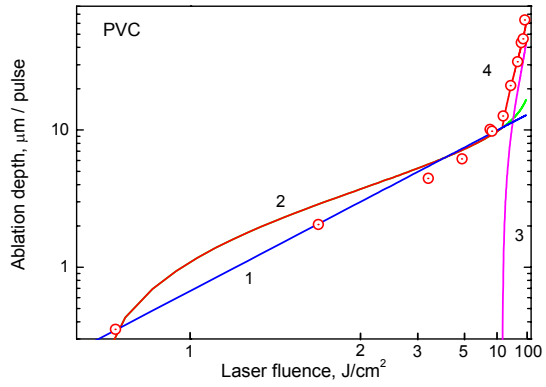

Figure 7. Ablation rate versus laser fluence in PVC polymer: circles – experiment; lines - approximations: 1 – exponential thermal activation of Arrhenius-type (2); 2, 3 – logarithmic Beer's law (1); 4 – the sum of 2 and 3 (266 nm, 60 ps).

The critical fluence was converted to the Arrhenius activation energy according to (2). It was suggested that all absorbed energy is distributed equally in the absorption length, raising the temperature of the absorbing volume by ΔT.

$$Q = \rho\alpha^{-1}C_p\Delta T \qquad (3),$$

where ρ – the density, C_p – the thermal capacity and Q – the absorbed energy

$$Q = F \cdot S \qquad (4),$$

where S – the irradiated area, 1 cm^2 for simplicity.

The temperature in the absorbing volume at the end of laser pulse can be written as

$$T = \frac{F}{\rho\alpha^{-1}C_p} + RT \qquad (5),$$

where RT – the room temperature.

The relationship between the ablation depth and laser fluence for all polymers investigated in this work is presented in figures 8-13. Picosecond pulses (60 ps) of UV radiation at 266 nm were used in experiments. The sum of two approximations, made according to the logarithmic Beer's law (1) with different threshold values, where applicable, is shown for visualization of non-even nature of the ablation process.

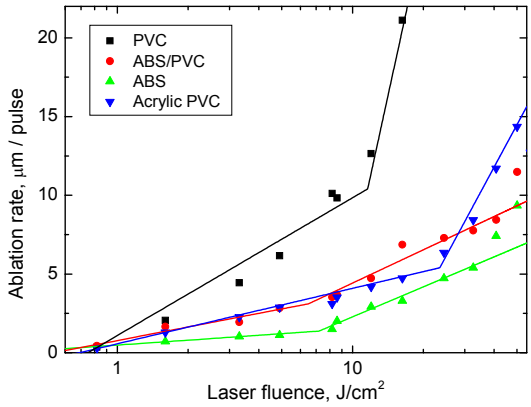

Figure 8. Ablation rate versus laser fluence in ABS and PVC and their derivative: points – experiment; lines – two-threshold approximations according to equation (1).

The PVC polymer possessed the highest ablation rate between all tested materials. An especially rapid rise in the ablation rate was observed above the laser fluence of 10 J/cm^2. The ablation rate of ABS was low enough. Addition of chlorine-vinyl groups into polymer (ABS/PVC) led to the increase of the ablation. All three materials showed the turning-point at the same fluence around 10 J/cm^2.

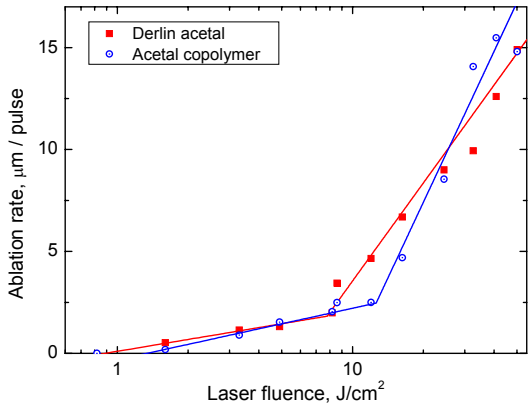

Figure 9. Ablation rate versus laser fluence in acetal polymers -Derlin™ and copolymer: Points – experiment; lines – two-threshold approximations according to equation (1).

Different forms of the acetal polymers showed nearly the same behavior in the ablation rate versus laser fluence (figure 9). The difference in position of the

second threshold can be attributed to various densities of the polymers.

The fluoropolymers (PTFE) are stable to laser radiation and only slight decomposition is initiated by 266 nm radiation (figure 10). Doping of the acetal Derlin™ with tetrafluoroethylene makes the material more resistant to the ablative as well as mechanical impact.

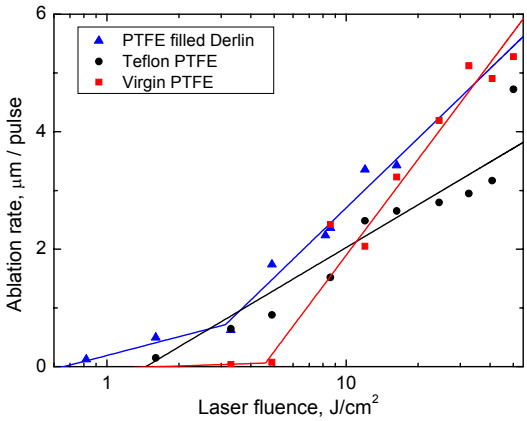

Figure 10. Ablation rate versus laser fluence in polytetrafluoroethylenes: points – experiment; lines – two-threshold approximations according to equation (1).

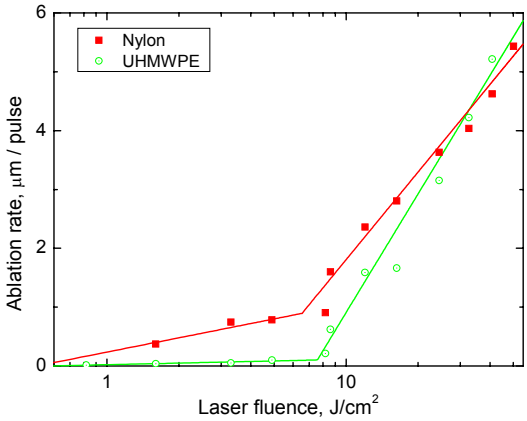

Figure 11. Ablation rate versus laser fluence in Nylon™ and UHMWPE: points – experiment; lines – two-threshold approximations according to equation (1).

Nylon™ and ultra high molecular weight polyethylene experienced drastic changes of their ablation rate starting from the fluence of 7-8 J/cm^2 (figure 11). Polyethylene showed extremely weak ablation below the threshold.

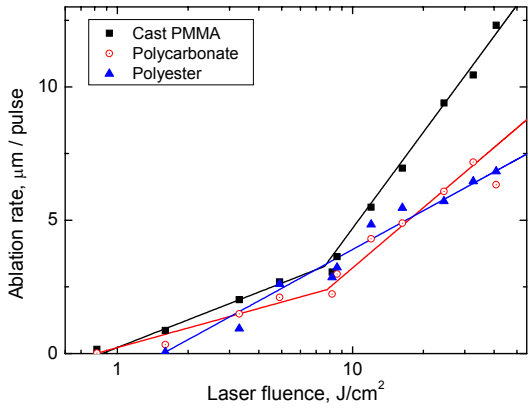

Figure 12. Ablation rate versus laser fluence in the black cast PMMA, polycarbonate and polyester: points – experiment; lines – two-threshold approximations to according (1).

Polyester was one of a few investigated polymers that did not revealed a second threshold in the range of laser fluences from 0.5 to 60 J/cm^2 (figure12). The Arrhenius type approximation better fitted for the ablation rate in polyester. Clear extruded PMMA could be ablated by 266 nm, but the quality was poor and breaks occurred near the ablation edge. Black cast PMMA was successfully processed by 266 nm and 355 nm radiation with high ablation rate. Clean ablation of polycarbonate was possible with UV.

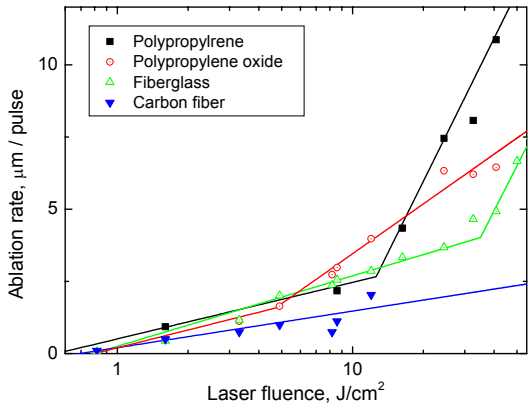

Figure 13. Ablation rate versus laser fluence in propylene and fiber filled polymers: points – experiment; lines – two-threshold approximations to equation (1).

Table 2. Parameters of polymers established from the results on laser ablation with the 266 nm picosecond laser radiation: the ablation thresholds for two segments of laser fluences and the Arrhenius activation energy.

#	Material	F_{th1} J/cm^2	F_{th2} J/cm^2	E_a eV
1.	ABS	0.34	7.20	0.72
2.	ABS/PVC	0.54	6.50	1.00
3.	PVC	0.75	11.60	1.67
4.	Acrylic PVC	0.69	23.50	1.34
5.	Extruded PMMA	0.42	-	0.72
6.	Cast PMMA (black)	0.86	7.60	1.39
7.	Polyester	1.56	-	4.46
8.	Polycarbonate	0.81	7.80	2.45
9.	Nylon™ (polyamide)	0.51	6.54	1.00
10	UHMWPE	0.60	7.58	1.00
11	Acetal copolymer	1.34	12.60	2.56
12	Derlin™ acetal	0.89	7.80	1.34
13	PTFE filled Derlin™	0.66	3.13	1.12
14	Teflon™ PTFE	1.45	-	3.12
15	Virgin™ PTFE	1.63	4.60	3.07
16	Polypropylene	0.55	12.60	0.95
17	Polypropylene oxide	0.81	4.70	2.29
18	Fiberglass	0.79	37.00	1.90
19	Carbon fiber	0.69	-	1.34

By employing approximations (1) and (2), the parameters describing reaction of the materials to laser irradiation were established. The ablation threshold and activation energy are presented in table 2. It is worth to notice that F_{th1} and E_a correspond to different approximations of the results in the same segment of laser fluences. As the low-fluence threshold was in most cases outside the actual range, its value is based on extrapolation. It was difficult to compare the results with those of other authors because of lack of information about most of the polymers and the materials can differ significantly by chemical composition and structure. Typical values for the excimer laser at 193 nm are less than those found in this work, in the range of 20-150 mJ/cm^2 [2, 11]. The Arrhenius activation energy for polyimide Kapton™ was found to be 1.5 eV at 248 nm [5]. The activation energies of our materials are close to this value.

The absorption length α^{-1} in (1) was found to be from 40 nm to 2 µm for the low-fluence segment and 2-25 µm at high fluences. The absorption length is related not only to optical absorption near the surface. It reflects the depth where density of the deposited energy exceeds the limit of polymer decomposition. Thermal conductivity plays essential role, especially at high fluences increasing an excited area.

Manipulation with the results and material parameters (absorption coefficient, glass transition and decomposition temperatures) did not highlight any unambiguous relationship between the parameters. The only exception is shown in figure 14.

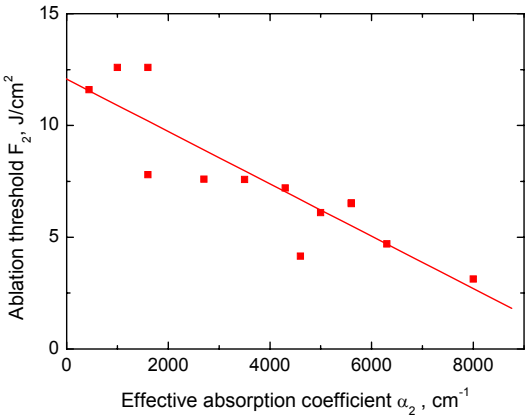

Figure 14. Relationship between ablation threshold and effective absorption coefficient.

The higher absorption coefficient the less volume was involved in reaction. The smaller volume required less energy input for decomposition. This could be a reason for the observed relationship between the ablation threshold and effective absorption.

Most of the investigated polymers had a chain with the C-C bonds and small side groups (polyethylene, PVC, polypropylene, polystyrene (in ABS), PMMA). The main chain could be photo-chemically broken by 266 nm radiation because photon energy exceeds the bond energy . However, properties of the material are determined by the side groups, a tangle of the chains and plenty of weak bonds between chains. The differences make the material unique. More detailed information about structure of the polymers is required for further analysis of the result on laser ablation.

Applications

The polymers were tested in fabrication of cavities, relevant to different microdevices. Examples are shown in figures 16-17. Combined cavities for the ink-jet printer head and a micro-fluidic set were formed by laser etching. Dimension of the micro-fluidic system was 0.5x 1 mm^2, and width of channels was 30 µm.

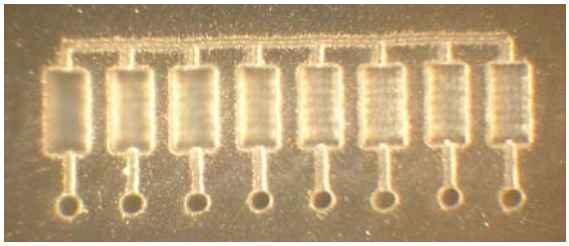

Figure 16. Combined cavities of the ink-jet prototype (Nylon™, 266 nm, 30 J/cm^2).

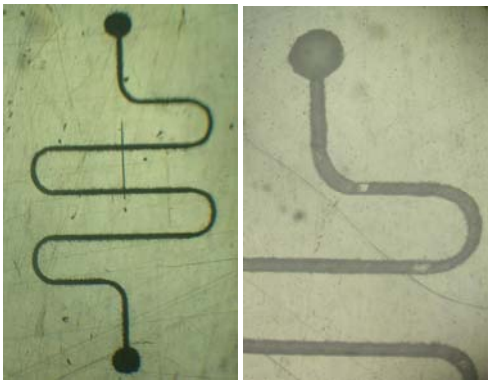

Figure 17. Micro-fluidic devices (left- acetal; right - Nylon™; 266 nm, 1.6 J/cm^2).

Surface of trenches in Nylon™ was smoother than in acetal. High fluences produced melting on edges of the trenches in acetal (figure 18).

Figure. 18. Tranches at high fluence (acetal copolymer, 266 nm, 41 J/cm^2).

Conclusions

A set of diverse polymers was used for comparative study of laser ablation with the pulsed UV radiation.

UV picosecond lasers can be good alternative to excimer lasers in processing of polymers. UV radiation with shorter wavelength (266 nm) produces better quality of machining and extends the number of polymers that can be processed by a laser.

The ablation rate as a function of laser fluence was investigated. Most of the materials possessed two ablation thresholds. One of them was below 1 J/cm^2 with the low material removal rate. Another threshold was above 3 J/cm^2 with a rapid increase in the ablation rate. The logarithmic model predicting the well-defined ablation threshold and the thermal activation model of Arrhenius –type were used for approximation of the results. The ablation thresholds, activation energy and effective absorption length were estimated. More detailed information about structure of the polymers is required for further analysis of the result on laser ablation in relation with material parameters.

The processing regimes of polymers were proved at formation of microstructures. UV laser radiation with the picosecond pulse duration can be useful in manufacturing micro-systems for diverse technical applications.

Acknowledgment

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