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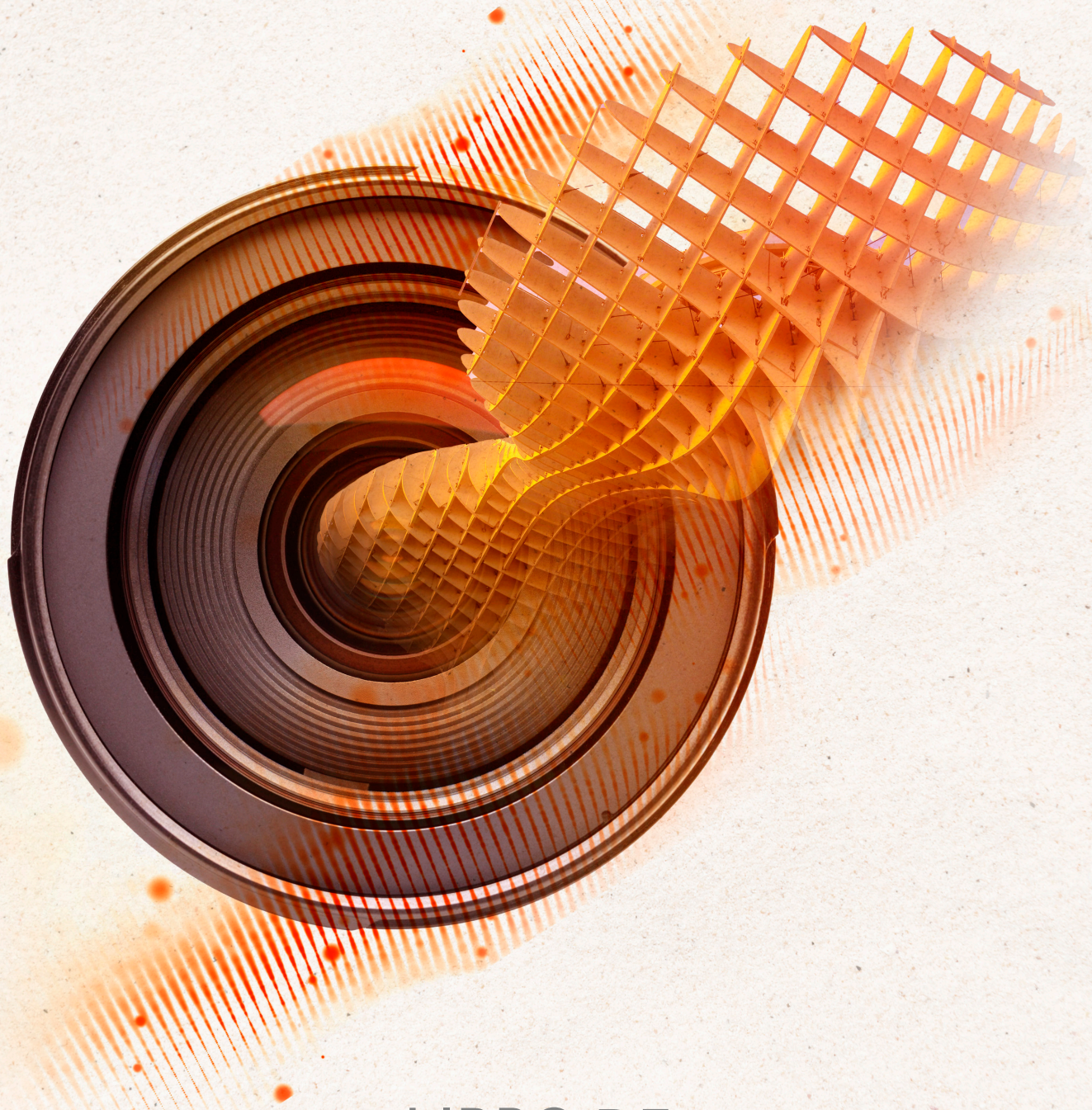

LIBRO DE ACTAS

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High-frequency photothermal processing of commercial polymers under femtosecond laser irradiation for waveguide writing

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ABSTRACT

The processing of three commonly used commercial polymer films (poly(vinyl chloride) (PVC), poly(ethylene terephthalate) (PET) and polypropylene (PP)) with different thermal properties under femtosecond (450 fs) irradiations at high frequency (1 kHz-1 MHz) multi-pulse (N=10-18000) laser at λ=515 (1.34 J/cm^2, radius 9 μm) is analysed in order to have knowledge of which material and laser conditions are more suitable to write waveguides. Thermal and ablative effects are observed after laser irradiations. Heat accumulation effects of successive pulses impinging are simulated through a photothermal model in order to explain the results of irradiating these materials. Thermal analyses (Modulated Differential Scanning Calorimetry (MDSC) and Thermogravimetry (TG)) are performed and used to explain the different behaviour of each polymer. Three different regimes (non-thermal, thermal and saturation) are identified and explained from the model and experimental results. A connection between ablation depth and simulated reached temperature is established. A study of which number of pulses/spot area and frequency are appropriate for a better shape and ablation depth for writing waveguides on these polymers is performed.

Key words: Femtosecond laser processing, ablation, waveguides, thermal effects, photothermal model, thermal regimes, polymers.

1.- Introduction

The importance of polymers has risen up in the last decades. Because of their remarkable properties and their low economical cost, these materials have been introduced in a vast number of fields, such as electronics, technological devices, vehicle industry, aeronautics, domestic appliances, medical devices or biomedicine [1-3].

The advantages of femtosecond lasers to process materials has attracted much attention in the latter decades [4].Because of their short pulse time, high intensities are produced, and non-linear absorption processes are induced. Consequently, absorption is restricted to the focal volume for femtosecond lasers, unlike pico or nanosecond sources [4-7]. The use of high-frequency lasers allows considerably shorter processing times, which is an advantage for processing and device fabrication [8-9].

Nevertheless, after a succession of ultra-short pulses, the temperature increases and starts to diffuse, enlarging the damaged area. This effect increases when the time between pulses is small (i.e. high repetition rates) and depends on the thermal diffusivity of the processed material [7]. Therefore, fine control of these processes is key for the industrial use of high repetition rate lasers, as it would allow the mass production of these devices to be envisaged.

2.- Thermal model and regimes

A photothermal model [8,10] is used to simulate the heat accumulation effects that are produced after the femtosecond laser processing of three polymers at a wide range of repetition rate frequencies (up to 1 MHz).

This model is based on the heat diffusion equation:

$$\frac{\partial T(x,t)}{\partial t} = D\frac{\partial^2 T(x,t)}{\partial x^2}, \qquad (1)$$

where T is the reached temperature after a given number of laser pulses, x is de distance from the laser spot center, t is the time coordinate, and D is the heat diffusion (about 1-2$\times 10^{-7}$ m^2/s at 25ºC for these three polymers).

The resulting temperature increases instantly each time a pulse arrives as

$$\Delta T(x,t) = AE(x,t)/(C_p\rho), \qquad (2)$$

where A is the estimated energy fraction absorbed by each polymer, $E(x,t)$ is the gaussian laser energy density distribution, ρ is the material density and C_p is the heat capacity of the material.

Thermal parameters (heat capacity, thermal conductivity and heat diffusion) and phase changes (glass-rubbery, crystalline-amorphous, crystallizations and decomposition temperatures) of each polymer are measured through thermal analyses including MDSC and TG. The characteristic glass-rubbery, crystalline-amorphous and decomposition temperatures for each material are presented in Table 1.

Polymer	T_g (ºC)	T_m (ºC)	T_d (ºC)
PVC	72.29	-	225
PET	75.55	245.45	349
PP	< 0	157.96	320

Table 1: Glass-rubbery transition temperatures (Tg), crystalline-amorphous transition temperatures (Tm) and decomposition temperatures (Td) obtained from MDSC and TG for PVC, PET and PP.

Thermal parameters are implemented in the model up to 350ºC. The absorbed energy fraction of each polymer (A) is estimated from the transmittance of each material. Material density (ρ) is also measured.

Simulated temperature profiles at the center of the laser spot for a given number of static irradiations and three different frequency values are shown in Figure 1.

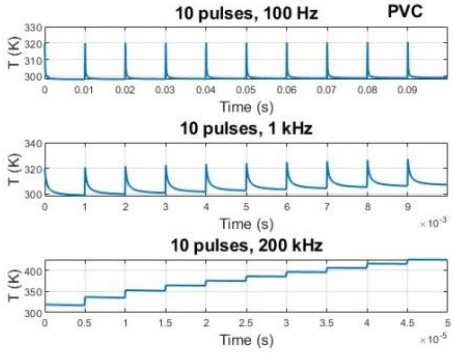

Fig. 1: Simulations of PVC temperature profiles at the center of the laser spot for 10 pulses and 100 Hz, 1 kHz and 200 kHz for λ=515 nm conditions.

Three different regimes are observed in Figure 1. For lower frequencies (100 Hz) the time between two pulses is large enough, so the material cools down to ambient temperature before the next pulse arrives (non-thermal regime). If frequency is raised up (1 kHz) time between pulses is shorter and the material is not able to decrease its temperature to the ambient one. Thus, heat accumulation effect begins (thermal regime).

The critical frequency that indicates the beginning of the thermal regime can be estimated as [3]

$$f_{CR} = \frac{D}{4\omega^2}, \qquad (3)$$

where D is the thermal diffusion and ω is the radius of the laser beam. For λ=515 nm the

critical frequency is about 600 Hz for the three materials.

For higher frequencies (200 kHz) heat diffusion is practically non-existent and temperature remains essentially constant until the next pulse impinges the material. Therefore, the reached temperature will not rise up for higher frequencies (saturation).

A saturation frequency can be estimated from the model. The frequency value that guarantees that the temperature will not rise more than a 5% for higher repetition rates is about 132 kHz, 197 kHz and 160 kHz for PVC, PET and PP, respectively, for λ=515. At the working frequencies (1 kHz-1 MHz) we are between thermal and saturation regimes.

3.- Frequency saturation regime determination

A procedure to verify whether the polymers present this saturation behavior is to perform series of irradiations with a wide range of frequencies and measure the ablated depth of each one. From a photothermal point of view, ablated depth must be related to the reached temperature produced by irradiations and present a saturation for the same range of frequencies.

To confirm this hypothesis, series of irradiations with different number of pulses per spot are (30, 75 and 150) and frequencies (from 1 kHz to 1 MHz) are performed on the three materials surfaces in a single irradiation step, as it is shown in Figure 2.

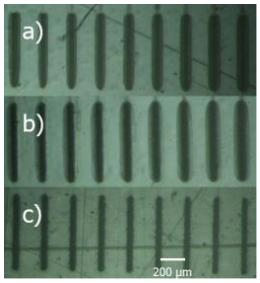

Fig. 2: PVC (a), PET (b) and PP (c) 0.5 mm length irradiations at 515 nm with 150 pulses/spot area and frequency increasing from right to left.

It must be noted that ablation is achieved for the three materials with these conditions. In addition, PVC and PET present greater ablations widths and reflectivity changes at the surroundings of the processed surfaces than in the PP case. These effects are labeled as extended thermal effects.

This might be attributed to two facts. On the one hand, glass-rubbery transition that occurs for PVC and PET and is not produced for PP, according to MDSC results (see Table 1). For points outside the focal volume, reached temperatures could be high enough to produce this phase transitions, increasing the volume of the material. After heat diffusion, rubbery state solidifies and causes this refractive index change [7,8,11,12]. Thermal analyses also show that PET presents a recrystallization process and a second phase change from semi-crystalline to amorphous state at 245ºC (see Table 1) that might increase these effects compared to PVC.

On the other hand, MDSC indicates that heat capacity for PP is greater than for PVC and PP (at least up to 300ºC). If this tendency is maintained for higher temperatures, it would mean that greater energies are needed to produce an increase of temperature in the case of PP than in the case of PVC and PET.

The ablation depth is measured experimentally for each irradiation and it is compared to the reached temperatures obtained from the model. The results show that ablated depth also saturates for frequencies about 150 kHz, as the simulated temperatures.

Ablated depths at 1 MHz are higher for PVC (40 µm) and PET (40 µm) than for PP (22 µm) for 150 pulses per spot size. As in the case of the ablation width, this might be attributed to the different values of thermal parameters at high temperatures (as the case of specific heat for PP). The glass-rubbery transitions, that only occur for PVC and PET could enhance these effects.

The importance of this part of the study is to have knowledge of the optimal frequency range for writing waveguides. The most efficient procedure is to induce ablation at the saturation regime frequencies. This ensures that maximum ablation depth is

reached for a given number of pulses and fluence, since ablation depth does not increase for higher frequencies. In addition, the processing time is much smaller than for low frequencies, so it becomes more suitable for industrial purposes.

However, extended thermal effects could be huge and difficult the light transmission. For that reason, several irradiations with different laser conditions have been done for the three materials in order to get the best processing conditions and to find out which polymer is more appropriate to write waveguides as it will be described in the next section.

4.- Study of waveguide writing laser conditions

The maximum ablation depths reached in the previous study (40 µm for PVC and PET; 22 µm for PP) might not be enough for writing waveguides. Higher number of pulses are required to produce larger ablation depths. Ideally, the maximum ablated depth is wanted, considering that the thickness of the three polymer films is 300 µm.

For this reason, irradiation lines with 2 mm length with a high number of pulses/spot area at a frequency value of 1 MHz (above saturation threshold for the three materials) were performed.

For PVC and PET, 5000 pulses/spot area were enough to ensure an adequate ablation, in a single irradiation step, i.e. the ablated depth is high enough to bend the material beyond the backside surface. However, the extended thermal effects become massive for both materials at these conditions, as it is presented in Figure 3 (a-b).

In contrast, PP requires a larger number of pulses to produce this ablation. More than 18000 pulses/spot area (the maximum allowed of our system at 1 MHz and the minimum scan velocity) are needed. Therefore, the number of rescans was increased and 8 rescans were necessary to bend the backside surface. This implies 144000 effective pulses/spot area. In addition, the damaged area is considerably smaller compared to both previous materials as it can be seen in Figure 3 (c). As it was explained above, the difference between the responses of the three materials is attributable to the glass-rubbery transition present in PVC and PET and to their different thermal parameters at high temperatures (as specific heat for PP).

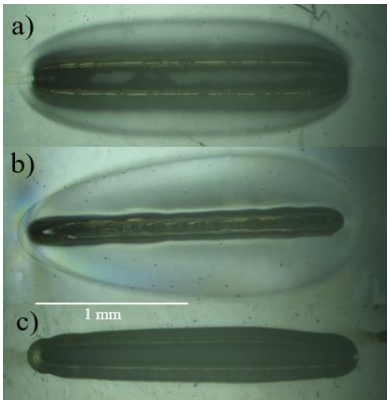

Fig. 3: Irradiated lines with 2 mm length at λ=515 nm, 1 MHz and 5000 pulses/spot are for PVC (a) and PET (b) and 18000 pulses/spot area and 8 rescans (144000 effective pulses/spot area) for PP (c).

In order to relieve the extended thermal effects issue, irradiation series with lower frequencies were also performed for PVC and PET. This attempt is performed because when frequency is reduced, time between pulses is increased and the material could cool down before the next pulse arrives, so temperature of the surrounding areas of the focal volume could be small enough for not presenting the phase change. This also implies that ablation is not so efficient (not saturation regime), so a greater number of pulses are needed to reach the desired ablated depth. Furthermore, decreasing frequency also means to reduce the maximum number of pulses that impinge the material per spot area allowed for our system in a single irradiation step. Therefore, in order to get high effective number of pulses, a great number of rescans is required.

For frequencies above the saturation threshold but lower than 1 MHz, thermal effects are huge. For frequencies near below 100 kHz thermal effects are still important. Even for small frequencies (compared to 1 MHz) as 10 kHz, thermal effects are still present, as it can be seen in Figure 4.

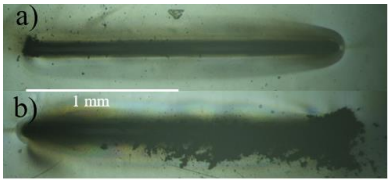

Fig. 4: Irradiated lines with 2 mm length at λ=515 nm, 10 kHz, 180 pulses/spot area and 300 rescans (54000 effective pulses) for PVC (a) and PET (b).

Despite the extended thermal effects are considerably reduced (although not eliminated), the high number of rescans (300) and effective pulses (54000) and the low frequency result in a very large processing time compared (about 5 minutes for processing a single line) to 1 MHz frequency irradiated lines (about 5 seconds per line).

Regarding the effective number of pulses, more than 54000 effective pulses at 10 kHz are required to obtain the maximum ablation for PVC and PET. For PP, 144000 effective pulses are enough to ensure maximum ablation at 1MHz. Even so, the size of the extended thermal effects at low frequencies for PVC and PET is similar to the damaged area produced for PP at high frequencies.

Considering the high processing time and the size of the extended thermal effects, low frequency processing with huge number of rescans for PVC and PET would not be appropriate for industrial purposes.

5.- Further studies

Additional studies related to the behavior and the consequences of irradiating these materials are also currently being developed. Micro-Raman spectra analyses on the processed surfaces are compared to the spectra of the non-irradiated materials. In the case of PVC, an increase on the fluorescence and a decrease of the peak intensities (especially for the C-Cl bond peaks) are observed, indicating chemical bond degradation.

6.- Conclusions

The response of three different commercial polymers under femtosecond laser irradiation at λ=515 nm is studied.

Three different thermal regimes that depend on the laser repetition rate frequency are identified and simulated from a photothermal model. A connection between heat accumulation effects and ablated depth is established, leading to a saturation frequency that supposes an optimal minimum frequency that is needed to obtain the maximum depth for a given number of pules and fluence.

A study of which values of the frequency and number of pulses are more suitable to write waveguides on these polymers is performed.

PVC and PET need about 5000 pulses on a single scan processing at 1 MHz to get high ablation depths. However, these materials present huge extended thermal effects associated to their phase change transitions at high frequencies, which could increase the guiding losses. Only at lower frequencies (10 kHz) these effects can be considerably reduced, but the processing time becomes massive.

On the other hand, for PP, 144000 effective pulses at 1 MHz are required to obtain huge ablation depths. The damaged area is much smaller than for PVC and PET, so this fact makes PP a better candidate for writing waveguides by femtosecond laser processing techniques.

Acknowledgements

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