Controlled photothermal ablative processing of commercial polymers minimizing undesired thermal effects under high frequency femtosecond laser irradiation

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Supplementary material

1. Fluence value motivation

The value of the working fluence has been chosen according to the results of a fluence test that has been performed for the three materials (PVC, PET and PP). Single pulse series and 1 MHz scanning lines with 150 pulses/spot area (maximum number of pulses for the repetition rate analysis) with different values of fluence (0.03 - 3.43 J/cm^2) have been irradiated and the width of the modified surface areas has been measured in order to determine the fluence threshold that allows to induce changes on the materials. The results of the fluence test can be seen in Figure S1.

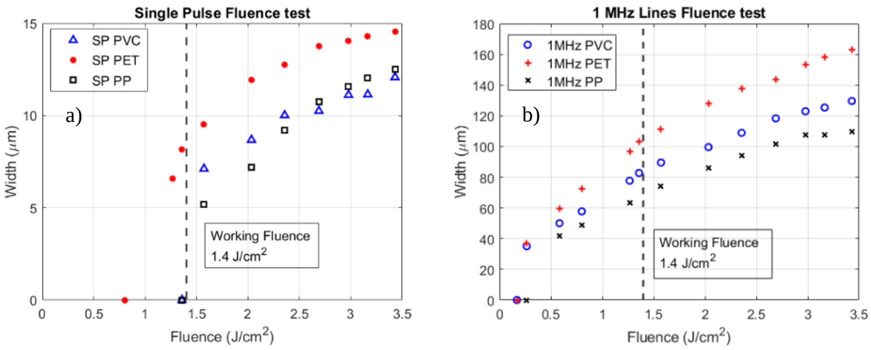

Fig. S1. (a) Modified region width as a function of fluence for single pulse irradiations and PVC (blue triangles), PET (red asterisks) and PP (black squares). (b) Modified region width as a function of fluence for 1 MHz scanning lines (150 pulses/spot area) irradiations and PVC (blue circles), PET (red plus signs) and PP (black crosses). Several irradiation series are produced on the surface of the three materials with different fluence values. Only the results between the modification threshold and 3.43 J/cm^2 are presented. The modified width for fluence values lower than the threshold is zero for all the cases. The vertical black dashed line represents the chosen working value for fluence (1.4 J/cm^2).

As it can be seen in Figure S1 (a), the modification threshold for single pulse irradiation is produced for 0.80 J/cm^2 for PET and 1.36 J/cm^2 for PVC and PP. The lower single pulse threshold for PET can be related to its lower bandgap compared to PVC and PP. For the 1 MHz lines case (Figure S1 (b)), the threshold values are 0.17 J/cm^2 for PVC and PET and 0.26 J/cm^2 for PP. Therefore, the working fluence has been selected in order to be higher than the single pulse fluence threshold. In this way, we ensure that all the emitted pulses are able to modify the material surface. Regarding the 1 MHz fluence test, a fluence value that minimizes the extended thermal effects that are produced around the irradiation area is required. Therefore, a fluence value that fulfills these both conditions has been chosen (1.4 J/cm^2).

2. Thermal model

2.1 Saturation frequency determination

The model used to understand the heat accumulation and repetition rate frequency effects is a simple and phenomenological model that offers an analytical solution for the heat diffusion equation (equation S1) on the surface of the materials as a function of time:

$$\frac{\partial T(x,t)}{\partial t} = D\frac{\partial^2 T(x,t)}{\partial x^2}, \qquad \text{(S1)}$$

where T is the temperature in the spatial coordinate x at the time t and D is the thermal diffusivity of the material. Each time a pulse arrives to the surface of the material temperature in x is increased as $\Delta T_0(x,t) = AE(x,t)/(C_p\rho)$, 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.

Most of these parameters vary with temperature. To obtain more accurate temperature distributions, diffusivity and heat capacity dependence on the temperature up to the decomposition temperature (T_d) of each polymer are included in the model. Beyond this temperature these values are implemented as constants, taking their value at T_d. These dependences are obtained from Modulated Differential Scanning Calorimetry (MDSC) analyses for the three materials and the values of T_d are determined from Thermogravimetry (TG).

The analytical solution to equation (S1) is based on the Shimizu et al. proposal to heat diffusion equation for high frequencies laser irradiation [1], adapting it to 2D surface diffusion:

$$\Delta T(t,r) = \Delta T_0 \frac{(\omega/2)^2}{(\omega/2)^2+4Dt} \exp\left[-\frac{r^2}{(\omega/2)^2+4Dt}\right], \quad \text{(S2)}$$

Where ω is the laser spot radius at $1/e^2$ and t is the diffusion time after a pulse arrives. To calculate the temperature of the material surface at the time when the next pulse arrives t must be set to the inverse of the repetition rate frequency ($t = 1/f$).

Considering the thermal parameters dependence on temperature complicates the analytical estimation of the saturation frequency (f_{sat}) because solving the model equation becomes iterative. However, a reasonable approximation can be done in order to get a simple and accurate enough f_{sat} estimation. We are interested in calculating the saturation frequency for 30, 75 and 150 pulses. According to the results of the model implemented with temperature dependent parameters, the reached temperature for static irradiations at the central point are above T_d for all the cases. This means that a significant part of the simulation is performed with the thermal parameters set to their values at T_d. Therefore, it seems feasible to calculate f_{sat} from the model equations using the thermal parameters values at T_d, and that is what we have done in the following development.

If we focus on static irradiations, the maximum allowed temperature after N pulses is expressed as

$$T_{max} = N\Delta T_0 + T_a, \quad \text{(S3)}$$

where T_a is the ambient temperature. Therefore, the saturation frequency can be defined as the frequency for which the temperature reached at the center of the spot point represents the 90% of the T_{max} value.

On the other hand, the achieved temperature at the center of the spot point after N pulses can be determined from the model too:

$$T_N = \frac{(N-1)\Delta T_0 f\omega^2}{f(\omega^2-16Ddt)+16D} + T_a + \Delta T_0, \quad \text{(S4)}$$

where dt is the temporal differential increase. Setting equation (S4) equal to the 90% of the value of equation (S3) f_{sat} can be solved:

$$f_{sat} = \frac{16D[0.9(N\Delta T_0+T_a)-T_a-\Delta T_0]}{(N-1)\Delta T_0\omega^2-(\omega^2-16Ddt)[0.9(N\Delta T_0+T_a)-T_a-\Delta T_0]}. \quad \text{(S5)}$$

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References

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