

High-frequency processing effects on three commercial polymers with different thermal properties under femtosecond laser irradiation.

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Abstract. The response of three of the most used commercial polymers (poly(vinyl chloride) (PVC), poly(ethylene terephthalate) (PET) and polypropylene (PP)) with different thermal properties under irradiation with high frequency (1 kHz-1 MHz) femtosecond (450 fs) multi-pulse (N=10-1500) laser at $\lambda=515$ (1.34 J/cm²) and 1030 (1.70 J/cm²) is reported. Thermal and ablative effects are observed after laser irradiations. The results are compared to a photothermal model that pretends to explain the heat accumulation effect of successive pulses irradiation. Thermal analyses (Modulated Differential Scanning Calorimetry (MDSC) and Thermogravimetry (TG)) are performed and utilized 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. Further studies as micro-Raman analyses on the irradiated area and the dependence of damaged area on the repetition rate are being performed.

1. Thermal model and thermal regimes

A photothermal model [1, 2] is used to understand the behaviour of the three polymers under femtosecond laser irradiation at a wide range of repetition rate frequencies. The model is built by solving the Flick's heat diffusion equation. Measured thermal and mechanical parameters of the three polymers up to 300°C are implemented in the model. Simulated temperature profiles for a given number of pulses and a frequency value, are shown in Figure 1.

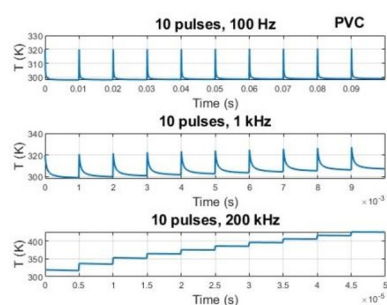


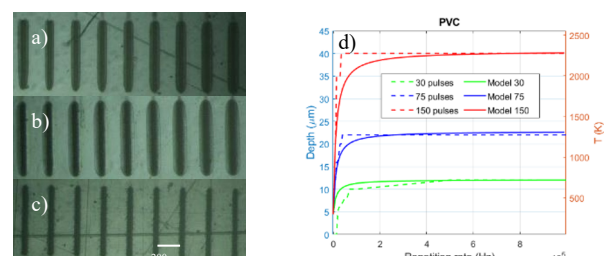
Figure 1. Simulations of PVC temperature profile for 10 pulses and 100 Hz, 1 kHz and 200 kHz for $\lambda=515$ nm conditions.

Three different regimes are observed in Figure 1. For low frequencies (100 Hz) time between pulses is high enough, and the material cools down before the next

pulse arrives (non-thermal regime). If frequency is increased (1 kHz) heat accumulation begins [3]. For higher frequencies (200 kHz) heat diffusion is practically non-existent and temperature remains almost constant until the next pulse arrives. So, no matter how much frequency is increased, the reached temperature will be the same (saturation). At the working frequencies, we are between the thermal and saturation regimes.

2. Results for 515 nm

Series of irradiations for different number of pulses per spot area (30, 75 and 150) and frequencies (swept from 1 kHz to 1 MHz) are produced for the three materials (Figure 2 (a-c)). Ablation depths of each irradiation are measured experimentally and the temperature profile is simulated through the model. Both results are represented as a function of the frequency in Figure 2 (d-f).



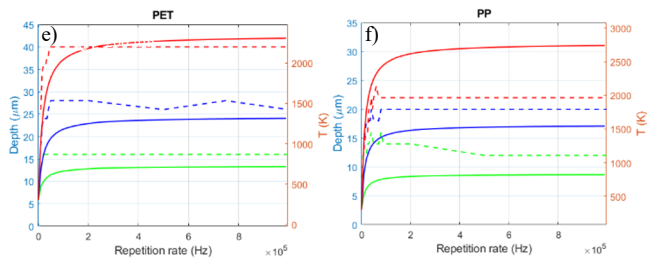


Figure 2. PVC (a), PET (b) and PP (c) irradiations at 515 nm with $N=150$ pulses and frequency increasing from right to left. (d-f) Measured irradiated lines depth (dashed lines, left axis) and temperature simulations at the centre of the spot (continuous lines, right axis) for 30 pulses (green), 75 pulses (blue) and 150 pulses (red)/spot area as functions of repetition rate for PVC (d), PET (e) and PP (f).

Figure 2 (d-f) indicates an increase of depth with repetition rate while this parameter is under 100-150 kHz (dashed lines) for any number of pulses. For higher frequencies, a saturation is produced and depth does not rise up. Modelled temperatures have the same behavior, saturating at the same range of frequencies. Ablated depth is higher for PVC and PET than for PP at 150 pulses per spot size. The differences in ablated shape and depth are attributable to the different thermal parameters at high temperatures (especially specific heat for PP) and glass-rubbery transitions (also determined through MDSC), that only take place in PVC and PET.

3. Results for 1030 nm

For 1030 nm ablation is not the dominant process because absorption is lower, so temperatures must be smaller too. PVC and PET present analogous effects at this wavelength. For lower number of pulses/spot area (about 25 for PVC and 50 for PET) and frequencies above 40 kHz, only reflectivity changes are observed on the material surface (see Figure 3 (a, c)). Above these values, thermal effects extended outside the irradiation area emerge. As the number of pulses increases (50-65 for PVC and 100-125 for PET) ablation appears and mixes with those extended thermal effects (see Figure 3 (b, d)). For higher number of pulses (65 for PVC and 125 for PET) and frequencies (60 kHz for PVC and 100 kHz for PET) ablation dominates as it can be seen for the left lines in Figure 3 (b, d).

The extended thermal effects can be explained by the glass-rubbery phase transitions that suffer PVC and PET when temperature is above 72° C and 76° C (results obtained from MDSC), respectively. These phase changes increase the volume of the material and when rubbery state resolidifies causes a change in the refractive index [2-5], extending these effects.

PP shows a different behaviour. A high number of pulses and frequency (1100 pulses and 100 kHz or 625 pulses and 500 kHz) is needed to ensure ablation. A possible explanation is that its specific heat might increase drastically at high temperatures, leading to a low heat transfer efficiency. In addition, PP does not present extended thermal effects. This is attributable to its negative glass-rubbery transition temperature. Therefore, PP is already at rubbery state at ambient temperature, and this transition does not occur.

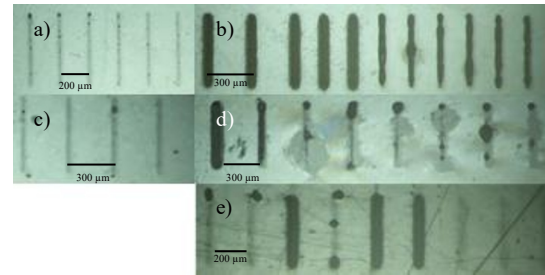


Figure 3. (a) Images of reflectivity changes for PVC at 1030nm with $N=30$ pulses/spot area and $f=10-40$ kHz increasing from right to left. (b) PVC irradiations at 1030nm with $N=65$ pulses and $f=15-100$ kHz increasing from right to left. (c) Images of PET at 1030 nm with $N=65$ pulses/spot area and $f=2.5-10$ kHz increasing from right to left. (d) PET irradiations at 1030 nm with $N=75-125$ pulses increasing from right to left and $f=100$ kHz. (e) PP irradiations at 1030 nm with $N=375$ pulses and $f=150-700$ kHz increasing from right to left.

Further studies, as micro-Raman spectra analyses on the non-irradiated areas and processed surfaces are performed too. An increase on the fluorescence and a decrease of the peak intensities are observed for the irradiation zone in PVC, indicating chemical bonds degradation. The dependence of the ablated width on the repetition rate, the simulation of the damaged area after irradiations and the use of these processed polymers as waveguides are currently being developed.

4. Conclusions

Different thermal regimes that depend on the laser repetition rate frequency are experimentally identified and simulated from a photothermal model on three commercial polymers under femtosecond laser irradiations. The different behavior of each polymer for high frequency irradiation is attributable to their different thermal parameters and phase transitions.

Acknowledgements

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References

- [1] M. Shimizu, M. Sakakura, M. Ohnishi, Y. Shimotsuna, T. Nakaya, K. Miura, K. Hirao, *J. Appl. Phys.* **108**, 073533 (2010).
- [2] S. M. Eaton, H. Zhang, P. R. Herman, F. Yoshino, L. Shah, J. Bovatsek, A. Y. Arai, *Opt. Exp.* **13**, 4708-4716 (2005).
- [3] H. Misawa, S. Juodkakis, *3D Laser Microfabrication*, Weinheim, Germany: Wiley-VCH Verlag, 2006.
- [4] D. Sola, J. R. Vázquez de Aldana, P. Artal, *Polym.* **12**, 2965 (2020).
- [5] C. B. Schaffer, J. F. García, E. Mazur, *Appl. Phys. A* **76**, 351-354 (2003).