Journal of Materials Processing Tech. 252 (2018) 813–820

Contents lists available at ScienceDirect

Journal of Materials Processing Tech.

journal homepage: www.elsevier.com/locate/jmatprotec

Research Paper

Resonant polymer ablation using a compact 3.44 μm fiber laser

Clément Frayssinous[a,*], Vincent Fortin[a], Jean-Philippe Bérubé[a], Alex Fraser[b], Réal Vallée[a]

[a] Center for Optics, Photonics and Lasers (COPL), Université Laval, 2375, rue de la Terrasse, Québec, QC, G1 V 0A6, Canada
[b] Laserax Inc., 2811 Ave Watt, local 101, Québec, QC, G1X 4S8, Canada

ARTICLE INFO

Keywords:
Laser materials processing
Polymers
Fiber lasers
Infrared and far-infrared lasers

ABSTRACT

In this experimental study, we investigate polymer ablation with a novel fiber laser source emitting at 3.44 μm, a wavelength resonant with the C—H bond fundamental stretching frequency of widespread polymer materials. The wavelength of the laser and the heating regime in the material are found to play key roles in the ablation process of polymers. We compare the results from two series of experiments performed, with both the 3.44 μm fiber laser and a CO_2 laser at 10.6 μm, on three common polymers: poly(methyl methacrylate), polypropylene and polyethylene. The ablation thresholds, its efficiency as well as the morphology of laser-induced grooves are evaluated experimentally. Polymer processing with mid-IR fiber lasers could be applied to a wide variety of compositions and has a strong potential for applications.

1. Introduction

In the last twenty years, the industry of laser processing was subjected to an exponential growth, primarily fueled by the versatility, high efficiency and low cost of laser-based processes compared to other technologies, as presented by Ready et al. (2001). These processes can be applied to a wide range of materials, notably polymers which are used in many application fields ranging from electronics to biomedical. Santo et al. (2014) made a review of laser processing experiments conducted with a 10.6 μm CO_2 laser, which is currently the most common source for processing polymeric materials. However, other laser technologies, such as fiber lasers, could help achieving a better accuracy and a greater efficiency for the most challenging applications.

It is well known that the wavelength of the laser source plays a critical role during polymer ablation, as first observed by Srinivasan and Mayne-Banton (1982) with an ArF excimer laser and Dyer et al. (1989) with a pulsed TEA CO_2 laser on PET films. Both groups reported an enhancement of the ablation when the wavelength is tuned near a strong absorption peak. In another experiment, Braun et al. (1989) investigated the differences observed in the ablation process resulting from UV and IR absorption on polyimide films. It was demonstrated that UV photons have the shortest penetration depth which reduced the energy needed to produce ablation by a factor of 100, nevertheless, no specific ablation mechanisms were identified in these experiments. However, since UV photons are energetic enough to directly break the polymer bonds, it was shown by Lippert (2005) that the resulting photochemical interaction can deteriorate the structure of the material. On the other hand, Bauerle (2011) pointed out that the mid-infrared (mid-IR) photons do not carry sufficient energy to cause a direct rupture of the polymers bonds and their interaction with the material is primarily photothermal. Remarkably, the mid-IR absorption spectrum of polymers contains a large number of strong absorption bands caused by vibrational resonances, in particular around 3.4 μm (C—H bonds stretching), as shown by Koenig (1999). In mid-infrared resonant laser ablation, light is strongly absorbed by the polymer bonds, resulting in a fast ablation rate with reduced laser power requirements.

To date, the lack of mid-IR laser sources restricted most demonstrations to non-resonant regimes, for instance near 10.6 μm. The few studies that were performed in mid-infrared resonant laser ablation regimes were conducted with complex laser systems: Bubb et al. (2001) used a free-electron laser source and Naithani et al. (2014) used an OPO laser source. In the demonstration reported by Naithani et al. (2014), resonant laser ablation near the C—H bands was realized on PMMA with an OPO that emitted ~15 ns pulses at wavelengths from 3.20 to 3.39 μm at a repetition rate of 20 kHz and an average power of 165 mW. The results showed an improved ablation rate as the emission wavelength was tuned on the strongest absorption peak. Recently, significant progress was made in the field of mid-IR fiber lasers operating around 3.5 μm. Henderson-Sapir et al. (2014) showed that erbium-doped fluoride glasses fiber lasers could achieve high powers and high efficiencies under dual-wavelength pumping. Based on this approach, Fortin et al. (2016) achieved more than 1.5 W of continuous (CW) power at a wavelength of 3.44 μm. These sources possess attractive features for polymeric material processing: a high quality beam profile (M^2 close to one), an excellent reliability and a relatively narrow linewidth (< 1 nm).

* Corresponding author at: Center for Optics, Photonics and Lasers (COPL), Université Laval, 2375, rue de la Terrasse, Québec, QC, G1 V 0A6, Canada.
E-mail address: clement.frayssinous.1@ulaval.ca (C. Frayssinous).

http://dx.doi.org/10.1016/j.jmatprotec.2017.10.051
Received 6 April 2017; Received in revised form 25 October 2017; Accepted 28 October 2017
Available online 31 October 2017
0924-0136/

The aim of this study is to evaluate the performances of a 3.44 μm CW fiber laser in polymer processing applications. We begin by reviewing the basic concepts associated to photothermal polymer ablation. Three polymer compositions are selected for the experiment: poly (methyl methacrylate) (PMMA), polypropylene (PP) and polyethylene (PE). Optical characterizations are first carried out to evaluate the absorption coefficient of these materials. We also review their thermal properties and explain how they influence the ablation dynamics. Then, we perform two series of ablation experiments, one with the fiber laser and the second with a commercial CO_2 laser (at 10.6 μm). The results obtained allow us to underline the major impact of increased optical absorption on polymer processing using the fiber laser operating at near-resonant wavelength. This study also aims at establishing a clear link between the laser ablation characteristics and the thermal properties of the polymer materials.

2. Basic concepts in polymer processing

2.1. Photothermal mechanism

A photothermal laser-induced process occurs when the thermalization of the absorbed energy is fast compared to the excitation rate of the process. In the case of mid-IR photons, the reaction is clearly photothermal since the absorption of photons will activate the polymer bonds vibrations and thus directly contribute to the rapid thermalization of the material on a picosecond time scale, as exposed by Bauerle (2011). In these conditions, Berrie and Birkett (1980) demonstrated that the laser radiation can be approximated as a heat source and the thermal energy diffusion in the system is governed by the heat equation. As such, the main ablation mechanism is phase change followed by vaporization of the material, as shown by Zhang et al. (2006).

As stated earlier, the 3.44 μm emission wavelength of our fiber laser is nearly resonant with the fundamental stretching frequency of C—H bonds within polymer materials. However, Bubb et al. (2001) explained that it is only possible to induce resonant ablation of polymers when strict conditions on wavelength, fluence and time-scale of irradiation are met. These combined conditions provoke the absorption of multiple photons before the energy can be transferred to the polymer lattice. Johnson et al. (2010) demonstrated that since the heating is local and fast enough to break the polymers bonds, ablation can take place through spinodal decomposition, which causes the ejection of melted material while preserving the structure of the polymer.

In the experiment performed with our mid-IR fiber laser, although the resonant ablation conditions are not fully met, we still benefit from an enhanced absorption coefficient when compared to the absorption of 10.6 μm radiation. It will be assumed that the excitation and ablation mechanisms are the same as in the CO_2 laser experiment.

2.2. Characteristic lengths and heating regimes

The attenuation of light in the material is governed by the Beer-Lambert law. From this relation, it is possible to derive an optical penetration length in the material, L_α i.e. the length at which 63% (i.e. 1 − 1/e) of the energy is absorbed:

$$L_\alpha = \frac{1}{\alpha}, \tag{1}$$

where α (cm^{-1}) is the absorption coefficient at a given wavelength and temperature.

To describe the propagation of the thermal flux during irradiation, Bauerle (2011) defined a heat diffusion length L_{th} as follows:

$$L_{th} = 2 \times \sqrt{Dt_i}, \tag{2}$$

where D is the thermal diffusivity of the material and t_i the laser beam dwell time. This length, which, strictly speaking, represents the exponential decay of heat from a point source, provides an estimation of the dimensionality of the heat flow. Clearly though, the actual dimensionality of the heat flow may significantly vary as a function of the boundary-value irradiation problem considered. Accordingly, various patterns of propagation of the heat in 3-D may occur depending on the value of L_{th} with respect to the optical penetration depth, L_α, and the beam size, *w*. Bauerle (2011) used the characteristic lengths defined above to identify two limiting cases of heating, each with their associated temperature and energy distribution. Brygo (2005) investigated theoretically and experimentally the two heating regimes while conducting a study of the laser removal efficiency of epoxy resin with Nd:YAG and CO_2 lasers. For $\mathbf{L_\alpha << L_{th}}$, the light is rapidly absorbed at the surface ("Surface absorption") and the propagation of thermal energy is driven only by the thermal properties of the material. In this regime, the highest temperature is reached at the surface and the thermic flux decays exponentially in the volume. When $\mathbf{L_\alpha >> L_{th}}$, the regime is rather called "Volume absorption" and the deposition of thermal energy is mostly related to the laser beam intensity profile. Several parameters may affect the temperature distribution in the material, notably the irradiation time, the wavelength of the source, the incident average power, and the material properties (especially the absorption coefficient and the heat diffusivity). Note that in practice, intermediate cases ranging between surface and volume absorptions are generally encountered.

3. Experimental procedure

3.1. Samples preparation and characterization

This study was conducted on three types of common polymers, more specifically poly(methyl methacrylate) (PMMA), high density polyethylene (HDPE) and polypropylene (PP). All samples were obtained from an industrial supplier (Plastiver Inc.) and had dimensions of 30 mm (height) × 60 mm (width) × 1.5 mm (thickness).

In order to measure the absorption coefficient of PMMA, we deposited a thin film (~2.2 μm thickness) on KBr substrates. This was achieved by dissolving a 3.4 g piece of PMMA in a solution containing 25 mL of dichloromethane that we diluted eight times to obtain a density of ρ = 0.017 g/mL. Thin films were obtained using a spin-coater rotating at a speed of 2000 rpm during 50 s. The samples were finally dried at 140 °C during 15 min and at 70 °C for 24 h to ensure all the solvent was removed. We estimated the thickness of the films using a surface profiler (Dektak 150, Bruker).

The optical characterization of the three types of polymers was performed with a Fourier transform spectrometer (Frontier IR Dual-Range Systems, Perkin Elmer) equipped with an attenuated total reflectance (ATR) accessory based on a ZnSe crystal at 45° and a linear polarizer used in parallel polarization to the axis of beam propagation.

3.2. Polymer ablation setups

Considering the large wavelength difference between the two laser sources, the experiments were conducted using two distinct setups. The parameters of both sources are summarized in Table 1.

The CO_2 laser is a Diamond G-150 system from Coherent and emits at λ = 10.6 μm. Its beam is sent into a galvanometric scanner (MiniScan 2, Raylase) positioned above the polymer sample. The fiber laser operating at λ = 3.44 μm was described in a previous publication by Fortin et al. (2016). Its output beam is collimated with a ZnSe aspheric lens (f = 50 mm) and is also directed into a galvanometric scanner (MiniScan 2, Raylase). ZnSe f-theta lenses (SL1-10.6-F75Z-48, Wavelength Opto-Electronic) with a focal length of f = 75 mm are mounted on each scanner head. They are coated with antireflection coatings optimized for each laser wavelength. At the output of the scanners, the beams waist was measured with a beam analyzer (NanoScan NS-Pyro/9/5, Ophir), we found w_0 = 28.5 μm for the fiber laser setup and w_0 = 55 μm for the CO_2 laser setup.