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Femtosecond laser micromachining in the conjugated polymer MEH–PPV

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Abstract

Femtosecond-laser micromachining of poly[2-methoxy-5-(2′-ethylhexyloxy)-p-phenylene vinylene] films is investigated using 130 fs pulses at 800 nm from a laser oscillator operating at 76 MHz repetition rate. We investigate the effect of pulse energy and translation speed on the depth and morphology of the micromachined regions. We quantified the MEH–PPV photobleaching induced by the fs-laser, and the conditions in which the emission of MEH–PPV is preserved after the micromaching.
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1. Introduction

Polymeric materials are promising candidates for fabricating micro- and nano-photonic devices in optical communications and sensing [1–5]. Several methods exist to structure polymeric materials in an inexpensive and reproducible manner, but most of these methods—standard photolithography, electron beam writing, or photopatterning in photosensitive polymers [6–11]—are limited to structuring surfaces. Femtosecond laser micromachining has received considerable attention due to its precision and ability to structure in three-dimensions.

When femtosecond laser pulses are focused into a material, the light intensity at the focal volume is sufficient to induce multi-photon absorption, leading to permanent structural changes in the material [12,13]. Such changes can be used to fabricate devices; for example, modification of the refractive index enables the direct integration of photonic devices in three-dimensions [14,15]. Several studies have been reported on the micromachining of polymers, most of them transparent, with laser light, exploiting fundamental aspects of the micromachining process as well as devices fabrication [1–3,5,16–19].

In this paper, we investigate femtosecond laser micromachining in poly[2-methoxy-5-(2′-ethylhexy-loxy)-p-phenylene vinylene] (MEH–PPV) [20], whose chemical structure is presented in Fig. 1. MEH–PPV is a conjugated polymer with photo- and electro-luminescent properties desirable for fabricating optoelectronic devices such as organic light-emitting diodes, chemical sensors, semiconductors and flexible displays [21,22].

We studied the influence of pulse energy and translation speed on MEH–PPV micromachining using optical and atomic force microscopy. We determined the energy threshold for polymer removal, and distinguished polymer removal from surface modification or photobleaching. We quantified polymer photobleaching during microfabrication via measurements of the absorption spectrum before and after laser irradiation. Finally, fluorescence microscopy of the microstructures reveals that the characteristic MEH–PPV emission persists after fabrication under appropriate micromachining conditions.
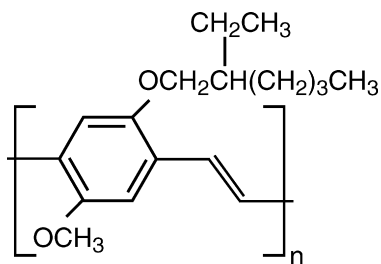
$$CH_2CH_3$$
$$|$$
$$OCH_2CH(CH_2)_3CH_3$$

Fig. 1. Chemical structure of MEH–PPV.

2. Experimental

MEH–PPV was dissolved in chloroform with a concentration of 5 mg/ml. This solution was spin-coated on a glass substrate at 700 rpm, yielding films with thicknesses of approximately 350 nm. The films were stored at room temperature and protected from light to avoid photodegradation.

The MEH–PPV films were micromachined using 130 fs, 800 nm laser pulses from an oscillator at a 76 MHz repetition rate. The pulses were focused through 0.65 NA microscope objective onto the sample surface, which was translated at a constant speed with respect to the laser beam. The speed was maintained by a computer controlled translation stage.

The micromachined samples were analyzed by atomic force microscopy (Asylum Research MFP-3D), transmission optical microscopy (Nikon Eclipse ME600L), and fluorescence microscopy (Nikon Eclipse TE2000-E). To evaluate the optical properties of the samples, we measured their UV and visible absorbance with a spectrophotometer.

3. Results

Fig. 2 shows optical microscope images of microstructures produced in MEH–PPV at a translation speed of 20 μm/s and various pulse energies. The transmission of visible light by the micromachined lines clearly increases with the pulse energy. At an energy of 0.07 nJ, the smallest pulse energy employed, little contrast is obtained, whereas at higher pulse energies a much higher contrast is observed (cf. Fig. 2a and d). The widths of the microstructured lines varies from 2 to 4 μm when the pulse energy is increased from 0.07 to 2.4 nJ. For a translation
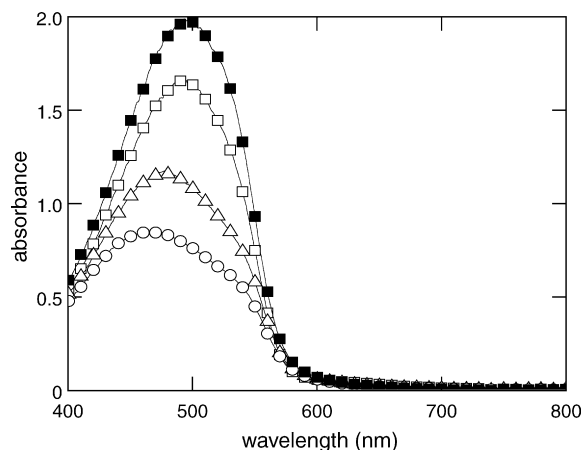

Fig. 3. Absorbance spectra for a MEH–PPV films not irradiated (solid squares), and after irradiation with 0.27 nJ (open squares), 0.55 nJ (open triangles) and 0.89 nJ (open circles) laser pulses.

speed of 20 μm/s, the threshold energy for inducing visible modification in the MEH–PPV sample was measured to be 0.05 nJ.

To evaluate the optical properties of the micromachined samples, we measured the absorbance of 3 mm × 3 mm areas, fabricated at various pulse energies with a translation speed of 20 μm/s. Fig. 3 (open symbols) shows the absorption spectra of such areas. For comparison, the solid squares in Fig. 3 show the absorption spectrum of a sample that has not been irradiated. The absorption band around 500 nm, which corresponds to the $\pi \rightarrow \pi^*$ electronic transition of MEH–PPV [21], decreases with the pulse energy used for the micromachining. This decrease indicates that the MEH–PPV photobleaches during the micromachining.

In order to determine the effect of the laser pulse energy on the depth and morphology of the micromachining, we micromachined a set of lines for pulse energies ranging from 0.07 to 2.4 nJ and a fixed translation speed of 20 μm/s. Fig. 4 shows two representative atomic force micrographs of grooves machined at pulse energies of 0.3 and 2.0 nJ. The depths of the grooves were determined from the atomic force micrographs, and are plotted as a function of pulse energy in Fig. 5.

As seen in Fig. 5, there are two distinct regimes for the depths of the grooves as a function of pulse energy. For energies
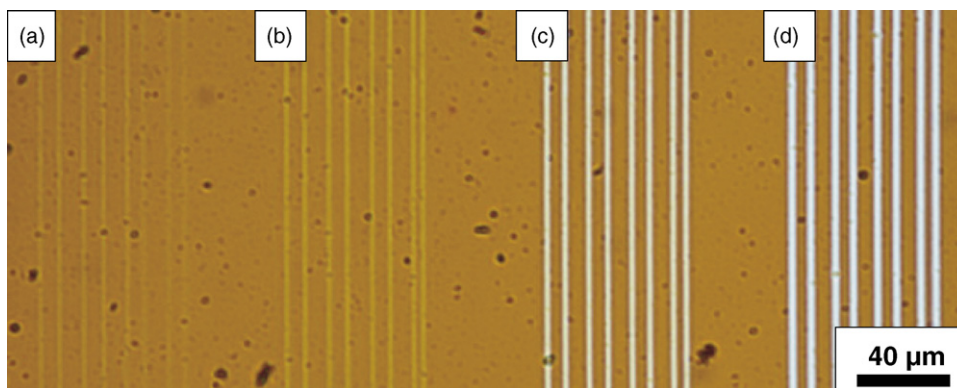

Fig. 2. Transmission optical microcopy of lines micromachined in MEH–PPV with pulse energies of (a) 0.07 nJ, (b) 0.14 nJ, (c) 0.34 nJ and (d) 0.68 nJ.
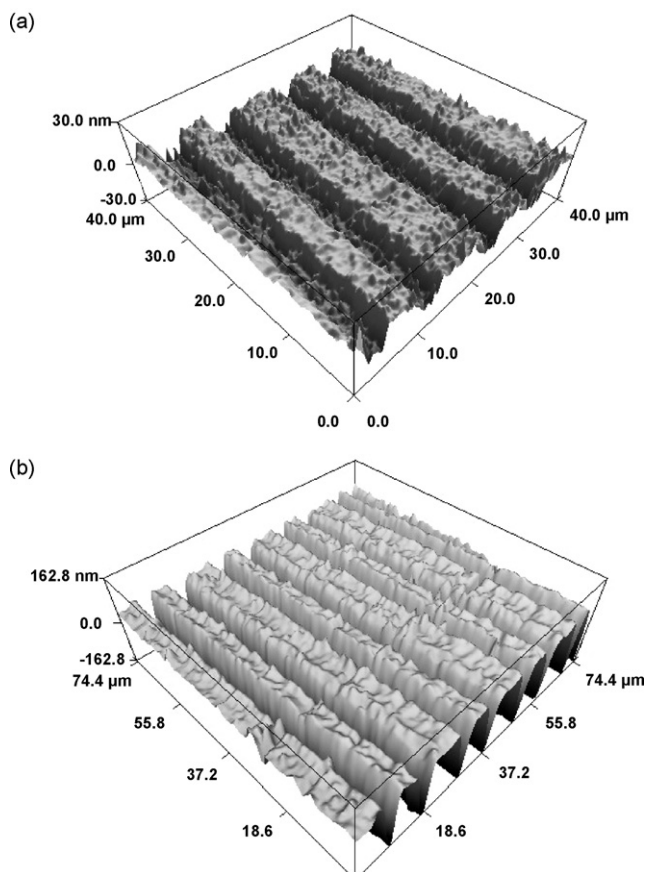
(a)

(b)

Fig. 4. Atomic force micrograph of grooves micromachined in the MEH–PPV films with (a) 0.3 nJ and (b) 2.0 nJ laser pulses.

up to 1 nJ, the groove depths varies from 7 to 30 nm, indicating only slight material removal from the polymer surface. For energies higher than 1.4 nJ, however, the groove depth becomes comparable to the 240 nm films thickness. The mid-point between the two regimes observed in Fig. 5 at 1.2 nJ defines the threshold between slight surface removal and material ablation.

From the atomic force micrographs (Fig. 4) we also observed an increase in the average surface roughness of the
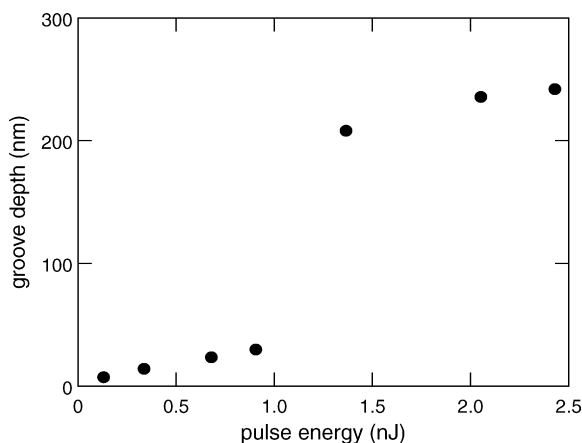

Fig. 5. Depth of the grooves as a function of the pulse energy for a translation speed of 20 μm/s.
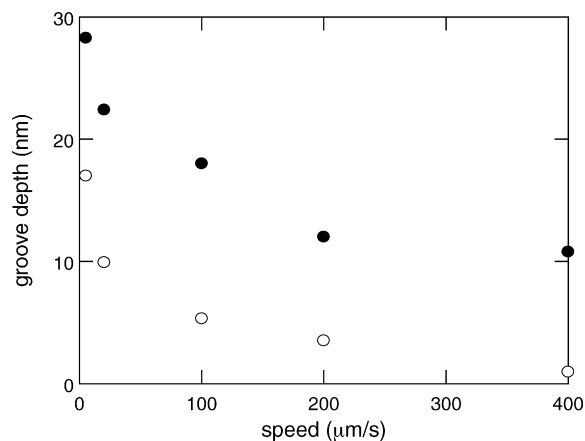

Fig. 6. Depth of the grooves versus translation speed for two different pulse energies: 0.7 nJ (solid circles) and 0.14 nJ (open circles).

irradiated regions. Below the ablation threshold RMS roughness increases from 4 to 10 nm; above threshold surface roughnesses up to 50 nm are observed.

To study the effect of the translation speed on the fs-laser micromachining of MEH–PPV, we prepared two sets of grooves with different pulse energies, for speeds ranging from 5 to 400 μm/s. As before, the morphology of such grooves was analyzed through atomic force microscopy. In Fig. 6, we show the depth of the grooves as a function of the translation speed and energies of 0.7 nJ (solid circles) and 0.14 nJ (open circles). The groove depth decreases with increasing translation speed. We also found that for fixed pulse energy the translation speed has little effect on the width of the groove.

We also carried out fluorescence microscopy measurements of the micromachined MEH–PPV films. As shown in Fig. 7, the MEH–PPV film (not exposed to the fs laser) exhibits fluorescence at approximately 600 nm when excited at 540 nm. The inset in this figure corresponds to the fluorescence microscopy image, obtained with excitation at 540 nm, for the sample micromachined at an energy of 0.07 nJ. As can be seen, the micromachined lines present the characteristic fluorescent emission of MEH–PPV, although with smaller intensity in
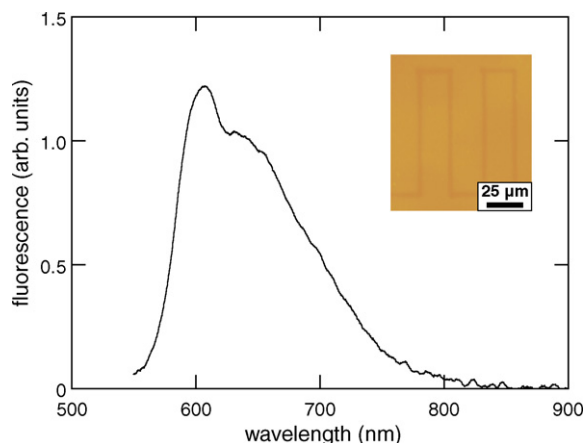

Fig. 7. Fluorescence spectrum of a MEH–PPV film obtained under excitation at 540 nm. The inset shows an image obtained through fluorescence microscopy (excitation at 540 nm) of lines micromachined with an pulse energy of 0.07 nJ.

comparison to the not irradiated region. Similar fluorescence microscopy images were obtained for samples micromachined with energies upto 0.2 nJ, indicating that the conjugated polymer emission is preserved after the fs-laser micromaching under appropriate conditions.

4. Discussion

Our results indicate that the interaction of fs laser pulses with the conjugated polymer MEH–PPV falls into two regimes, depending on the pulse energy [18,23]. For pulses energies up to the ablation threshold of 1.2 nJ, only slight material removal from the film surface occurs, and the maximum observed groove depth is approximately 30 nm, which corresponds to less than 10% of the total film thickness. Above the ablation threshold, we observe groove depths equal to the thickness of the films. Below threshold the depth of the micromachined groove can also be controlled by changing the translation speed, as revealed by the results of Fig. 6.

The increase we observe in the average surface roughness after micromachining has also been reported for poly(methylmethacrylate) [5,19]. However, as shown in Refs. [5,19], thermal annealing can be used to reduce the laser-machining-induced surface roughness. Therefore, if applications require smooth surfaces, micromachined MEH–PPV samples could be thermally annealed.

As observed in the optical transmission microscopy image (Fig. 2), a decrease in the absorption of MEH–PPV occurs for pulse energies below the ablation threshold. The decrease in MEH–PPV absorbance with pulse energy shown in Fig. 3 cannot be accounted for by the decrease in film thickness. The maximum decrease in the film thickness is 10%, while at the same pulse energy the absorption drops by 62%. Furthermore, the absorbance spectrum observed in Fig. 3 after micromachining with a pulse energy of 0.89 nJ (open circles) is very distinct from the other ones, indicating that photochemical changes to the MEH–PPV structure start to take place around this pulse energy.

A similar response to light exposure (a decrease of MEH–PPV absorbance peak, followed by a change in the spectrum shape) has been reported in the literature [24,25]. Such changes in MEH–PPV absorption was attributed to photo-oxidation induced by one-photon absorption (photobleaching) [24,25]. As the same general features were observed in our results, we attribute the photobleaching observed after the fs-laser micromachining to a two-photon induced oxidation of MEH–PPV. This polymer is completely transparent in the near infrared region (as seen in Fig. 3), but exhibits a large two-photon absorption cross-section at 800 nm (the wavelength employed in the micromachining) [26,27]. These facts support the two-photon induced oxidation hypothesis.

The fluorescence exhibited by MEH–PPV films micromachined with pulse energies below 1.2 nJ (Fig. 7) reveal that the sample preserves its characteristic emission. Although the emission intensity of the micromachined region is diminished due to photobleaching, Fig. 3 shows that an appreciable amount of unbleached MEH–PPV remains in the sample provided the right pulse energy is used. These results suggest that the polymer's conductive properties may also be preserved after the fs-laser micromachining if the right energy regime is used.

It has been demonstrated that the photo-oxidation of MEH–PPV can be diminished, or even eliminated, when the sample is irradiated in an inert atmosphere [24,25,28]. Although this procedure, irradiation in an inert atmosphere, has been performed only with visible continuum-wave light sources, we believe it also could be employed during fs-laser micromachining (near infra-red irradiation) of MEH–PPV to minimize photobleaching and, consequently, providing samples with a stronger photoluminescence and larger electrical conductivity.

5. Conclusion

In conclusion, we studied the role of pulse energy and translation speed in the resulting morphology of femtosecond laser micromachined MEH–PPV. For pulse energies higher than 1.2 nJ, film removal from the glass substrate occurs. Below 1.2 nJ only superficial material removal occurs, with a maximum groove depth of 30 nm. Furthermore, we demonstrated that although photobleaching occurs during the micromachining process, for the energy regime up to 1.2 nJ, the optical properties of the polymer remain unchanged. The results presented in this paper provide the optimum parameters for fs-laser micromachining of MEH–PPV for applications in polymeric-based photonic devices.

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