

Femtosecond laser waveguide micromachining of PMMA films with azaromatic chromophores

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Abstract: We report on the femtosecond-laser micromachining of poly(methyl methacrylate) (PMMA) films doped with nonlinear azaromatic chromophores: Disperse Red 1, Disperse Red 13 and Disperse Orange 3. We study the conditions for controlling chromophore degradation during the micromachining of PMMA doped with each chromophore. Furthermore, we successfully used fs-micromachining to fabricate optical waveguides within a bulk sample of PMMA doped with these azochromophores.

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1. Introduction

Femtosecond micromachining of transparent materials allow the fabrication of waveguides within a material volume without damaging its surface [1-7]. Femtosecond laser micromachining has been used in a wide variety of glasses to fabricate waveguide-based photonic devices, including interferometers, amplifiers, resonators, waveguide couplers, and switches [1, 3-19]. In the last five years, this technique has been used to fabricate devices in polymers [20-26]. Polymers are of interest for photonic components because they are cheaper and easier to manufacture than glass, and the optical properties of polymers can be tailored by chemical synthesis or by doping, allowing easy customization for specific applications.

Because of its high transmission in the visible and near-infrared [27], poly(methyl methacrylate) (PMMA) is one of the most widely used polymers for optical components. Previous work has shown fabrication of waveguides in pure PMMA via femtosecond micromachining [20-23, 25, 26] and structural modifications in azo-doped polymers by amplified femtosecond laser pulses [28-31]. However, there is no work on oscillator-only micromachining of waveguides in PMMA doped with optically active organic molecules. In this paper, we investigate femtosecond laser micromachining in PMMA doped with chromophores Disperse Red 1 (DR1), Disperse Red 13 (DR13) and Disperse Orange 3 (DO3). Because of the molecular structures of these chromophores (Fig. 1), these molecules are often referred to as azoaromatic chromophores, or azochromophores. These azochromophores possess interesting linear and nonlinear optical properties, which can be exploited for electro-optic modulators [32], second-harmonic generation [33], and birefringent devices [34, 35]. We determine the threshold energy for polymer modification, and demonstrated that the micromachining results from two-photon absorption. We also quantify the azochromophore photobleaching during microfabrication by measuring the sample absorption spectrum before and after laser irradiation. Finally, we present the first demonstration of waveguide fabrication within the bulk of PMMA doped with azochromophores.

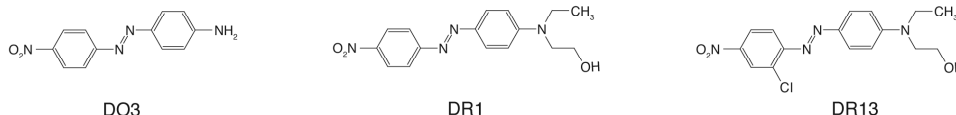


Fig. 1. Molecular structure of (a) DO3, (b) DR1, and (c) DR13.

2. Experimental

The DR1 (4-nitro-4'-[N-ethyl-N-(2-hydroxyethyl)-amino]azobenzene), DR13 (4-nitro-1-chloro-4'-[N-ethyl-N-(2-hydroxyethyl)-amino]azobenzene) and DO3 (4-(4-nitrophenylazo)aniline) were purchased from Aldrich and used as received. PMMA with a molecular weight of 350,000 g/mol was used for sample preparation without further purification.

We spin-coated films of 5% (by weight) PMMA chloroform solution containing the dissolved azochromophores onto glass slides. The concentration of the azochromophores in the polymer films ranged from 1% to 20%. The resulting film thicknesses were measured with a profilometer and ranged between 3 to 5 mm. For the waveguide fabrication, we prepared thicker samples (2 mm) by casting multiple layers of chloroform solution containing both the polymer and the azochromophores. To determine the optical properties of the doped films, we measured their absorbance from 350 nm to 800 nm with a spectrophotometer.

The PMMA-doped sample was micromachined using 130-fs, 800-nm laser pulses with pulse energies ranging from 0.01 nJ to 0.2 nJ from a Kerr-lens mode-locked oscillator operating at a 76-MHz repetition rate. The pulses were focused through a 0.65-NA microscope objective into the doped films, which were translated at speeds ranging from 5 $\mu\text{m/s}$ to 75 $\mu\text{m/s}$ with respect to the laser beam. Waveguides were written along the entire 5-mm length of the sample, and spaced by 200 μm to prevent crosstalk between them. After micromachining, the ends of the sample were polished to allow coupling of light into the

waveguides. HeNe laser light at 632.8 nm was coupled into and out of the waveguide using two 10× microscope objectives and an iris blocked any scattered light at the exit of the second objective lens. The resulting structures were imaged by transmission optical microscopy to determine their size and shape.

3. Results

The solid lines in Fig. 2 show the absorption spectra of 3- μm thick PMMA films containing 3.5% of DO3, DR1, and DR13. The spectra exhibit absorption bands centered between 440 nm and 515 nm, which correspond to the $\pi \rightarrow \pi^*$ electronic transition of the azochromophores. The samples are completely transparent in the near infrared region, where the micromachining is carried out.

For each sample, we determined the threshold energy at which a change occurs in the PMMA films containing various % of DO3, DR1, and DR13 as a result of the focusing of the Ti:sapphire laser beam into the sample. We used a CCD camera to monitor the sample transmission in real time as we micromachined the material. Figure 3 shows the threshold energy as we vary the concentration of each azochromophore in the sample. For all samples, we see that the threshold energy decreases as the azochromophore concentration increases. We also observe that the threshold energy is highest for DO3, followed by DR1, and DR13 respectively. For instance, with an azochromophore concentration of 1.0%, the sample doped with DO3 has the highest modification energy at 0.17 nJ, DR1 has the next highest energy at 0.11 nJ, and DR13 requires the least energy at 0.05 nJ. This trend is most pronounced for azochromophore concentrations up to 4%. At higher concentrations, the threshold energy is so small that it is hard to distinguish the value from experimental noise. The threshold energy for each sample of a fixed concentration scales very well with the two-photon photon absorption cross-section of the azochromophores; DO3, DR1 and DR13 present two-photon absorption cross-section of 35, 75 and 130 GM, respectively, at 800 nm [36-38]. This result indicates that micromachining in the doped polymers is a two-photon induced process. We also determined the threshold for pure PMMA to be 0.54 nJ. Above this threshold, micromachining of the doped samples results in carbonization of the sample.

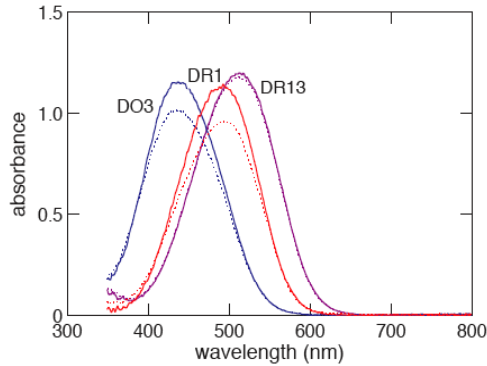


Fig. 2. Absorbance spectrum of PMMA films containing 3.5% by weight of (a) DO3, (b) DR1, and (c) DR13. The dashed lines show the absorbance after micromachining the films.

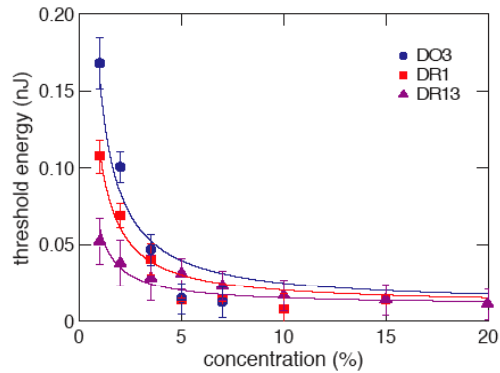


Fig. 3. Threshold energy of PMMA films doped with DO3, DR1 and DR13 as a function of the azochromophore concentration. The solid lines are drawn to guide the eye.

To fabricate waveguides and to study the optical properties of the samples after micromachining, we chose to work exclusively with samples containing 3.5% of azochromophores. Samples with 3.5% doping contain sufficient azochromophores to be useful for applications. We chose not to use samples with higher azochromophore

concentrations because the azochromophores in the highly doped samples tend to aggregate, inhibiting switching of the material, making those samples ineffective for device applications.

To evaluate the optical properties of the micromachined samples, we measured the absorbance of $2\text{ mm} \times 2\text{ mm}$ micromachined areas of each sample. The areas were micromachined at a speed of $20\text{ }\mu\text{m/s}$ with laser pulse energies at the threshold energy of each sample. The dashed lines in Fig. 2 show the absorption spectrum of the microfabricated areas for each sample, while the solid lines show the absorption spectrum of samples that have not been irradiated. The $\pi \rightarrow \pi^*$ electronic transition of the azochromophores decreases after irradiation, indicating photobleaching of the chromophores during the micromachining. The decrease in absorbance is highest for DR1, followed by DO3 and DR13, which has the smallest decrease in the absorption.

Figure 4 shows the decrease in absorbance for each sample at the peak of its absorbance band as function of the writing speed. For this experiment we used energies of 0.29, 0.14 and 0.08 nJ for DO3, DR1 and DR13, respectively, such that the product of the pulse energies and the two photon absorption cross-section is constant. Figure 4, shows that the order of greatest to least drop in absorption is from DR1 to DO3 to DR13, in agreement with the result shown in Fig. 2. The drop in absorption decreases with increasing translation speed, showing that less azochromophore photobleaching occurs at higher micromachining speeds, as expected.

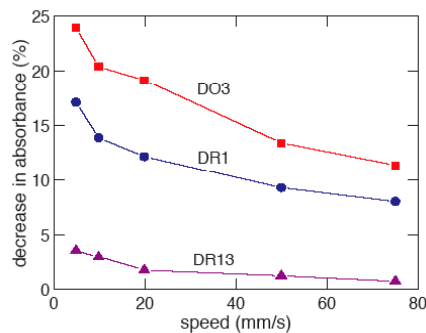


Fig. 4. Decrease in absorbance of PMMA films doped with DO3, DR1 and DR13 as a function of the writing speed of the waveguides.

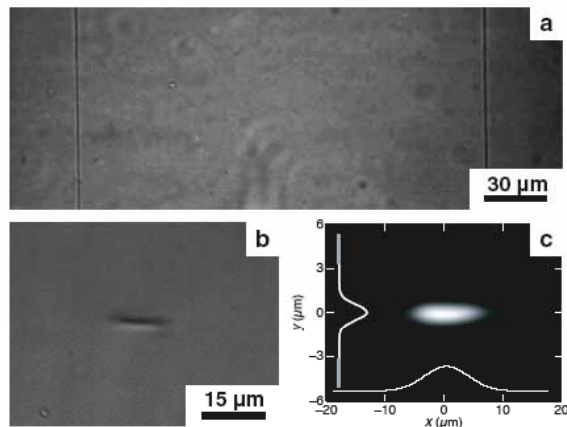


Fig. 5. (a). Optical microscope image of the waveguides micromachined in PMMA doped with DR1 written at a speed of $20\text{ }\mu\text{m/s}$, spaced by $200\text{ }\mu\text{m}$ to prevent crosstalk. (b) Cross-sectional view of the waveguides. (c) Output image of the single-mode profile of 632.8-nm light coupled through the waveguide, along with a graphical representation of the spatial intensity distribution of the profile along the two major axes.

Figure 5(a) shows a transmission optical microscopy image of the femtosecond laser micromachined waveguides in DR1-doped PMMA. These waveguides are visible only in transmission and not in reflection, indicating that the waveguides are inside the bulk. The threshold energies determined for waveguide fabrication inside the bulk are approximately 15% higher than the threshold energies for surface micromachining (Fig. 3) [39]. Figure 5(b) shows a transverse image of a waveguide. As can be seen, the waveguide profile is oblong because the voxel in which modification occurs has elliptical symmetry, due to the two-photon-absorption nature of micromachining in azo-doped PMMA. This is in contrast to the more spherical voxels produced by multi-photon absorption in undoped materials [23]. We

also looked at the output of the waveguide (Fig. 5(c)), confirming that the guided mode is single mode at 632.8 nm. By measuring the numerical aperture (NA) of the waveguide output [23], we estimate the magnitude of the refractive index change to be about 1×10^{-4} .

4. Discussion

In contrast to fs-laser micromachining in undoped transparent materials, where the optical breakdown is a multi-photon process, the results in Fig. 3 show that micromachining in doped polymers is driven by two-photon absorption of the azochromophores. The doping yields a threshold energy that is an order of magnitude smaller than pure PMMA and of glasses [5].

The absorption spectra of the samples (Fig. 2) show that a decrease in absorbance of the PMMA samples doped with the azochromophores occurs after fs-laser micromachining. A similar decrease in the absorption has been reported in the literature when samples containing azochromophores are exposed to light whose wavelengths are within the azochromophores absorption band [40-42]. The observed decrease in absorbance has been attributed to photo-oxidation induced by one-photon absorption (photobleaching) [40-42]. The azochromophore-containing samples we studied, however, are completely transparent and exhibit a large two-photon absorption cross-section at our excitation wavelength of 800 nm, as shown in Fig. 2. This leads us to attribute the photobleaching after fs-laser micromachining to two-photon induced photo-oxidation of the azochromophores. The smaller photobleaching observed for DR13 in Figs. 2 and 4 can be explained by the smaller photo-oxidation potential of DR13 compared to the other two azochromophores. This interpretation is in agreement with photodegradation studies reported for azocompounds under one-photon excitation [40-42].

Photodegradation of azochromophores is a complex subject, and depends on the host polymer, irradiation wavelength, temperature, atmospheric environment and azochromophore structure [40-42]. Systematic studies have demonstrated that photo-induced oxidation is the dominant mechanism for photodegradation of azobenzenes [40-42]. There is a strong correlation between the oxidation potential and the azodye degradation; molecules that have largest oxidation potentials are the most stable, meaning that they photobleach the least [40]. This correlation may explain the observed photobleaching for different azochromophores as observed in Fig. 2. Because DR13 possesses a higher oxidation potential than DO3 and DR1 [40], the observed photobleaching in DR13 is negligible for the range of irradiances we used.

The pulse energy for fs-laser micromachining of doped polymers should be minimized to avoid carbonization and photobleaching. Although the samples show some photobleaching (Fig. 2), the results in Fig. 4 show that significant amounts of unbleached azochromophores remain in the sample. In a previous study, the one-photon-induced photo-oxidation of azochromophores was reduced when the sample was irradiated in an inert atmosphere [40-42]. Similarly, we could micromachine azo-doped PMMA samples in an inert atmosphere to minimize the observed two-photon induced photobleaching, preserving a higher azochromophore concentration after micromachining, and enabling device fabrication.

In Fig. 5, we use a high-repetition laser to micromachine waveguides in the DR1-doped PMMA. Because the interval between successive pulses is shorter than the thermal diffusion time (approximately 1 μ s) in the polymer, the volume around the focal point is heated above the glass transition temperature. After the exposed area is translated out of the focus, the polymer resolidifies producing an index change. The resulting difference in index of refraction yields a waveguide inside the azochromophore-doped PMMA that guides light at 632.8 nm in single mode (Fig. 5(c)). This demonstration opens the doors for new applications of fs-laser micromachined polymeric waveguides containing nonlinear chromophores.

5. Conclusion

In summary, we show that fs-laser waveguide micromachining is possible in azochromophore doped PMMA. The micromachining results from two-photon absorption by the azochromophores at 800 nm. We determined the laser and sample parameters for micromachining PMMA samples doped with the azochromophores DO3, DR1 and DR13. Although we observe photobleaching of the azochromophores during micromachining, our

results show that a significant amount of azochromophores remains unbleached. Finally, we fabricated optical waveguides in bulk PMMA doped with DR1, demonstrating single-mode wave guiding in doped polymers.

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