

Laser micro-engineering of functionalized cyclic olefin polymers for microfluidic applications

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ABSTRACT

Direct-write laser processing has been demonstrated to be capable of both surface patterning of micro- and nanoscale structures on polymer surfaces without significant modification of the surface chemistry or optical transmission of the laser processed area. In this work, the creation of microchannels via direct-write laser processing of 188 μm thickness cyclic olefin polymers is demonstrated, along with a route towards channel functionalization. Cyclic olefin polymers (COP) are an emerging class of polymers noted for their high chemical resistance, biocompatibility and higher optical transparency when compared to other common polymers. These properties make them excellent substrates for the fabrication of microfluidic devices. This paper presents the first investigation into infrared laser processing of COP using a 1064 nm Nd:YAG laser. Scanning electron microscopy and Raman spectroscopy were utilized to investigate the morphology and composition of these laser textured surfaces.

A route for functionalization of these substrates for chemical and biological speciation and separation was examined using carbon nanoparticles. The nanoparticles were produced using pulsed laser ablation in liquid (PLAL) which has been reported as a fast and adaptable method for nanoparticle production. The nanoparticles produced were using transmission electron microscopy while the coating of substrates with these CNPs was examined using SEM. These results are discussed in the context of development of a new route for achieving surfaces optimized for microfluidic-based separations and speciation.

Keywords: Cyclic olefin polymer, pulsed laser ablation, carbon nanoparticles, functionalization, microfluidics, Nd:YAG,

1. INTRODUCTION

Cyclic olefin polymer (COP), and its co-polymer variant (COC), are promising classes of polymers noted for their exceptional properties such as high optical transparency from mid-UV to near-IR wavelengths, low cost, biocompatibility, strong chemical resistance to polar solvents, and high mechanical and dimensional stability when in contact with liquids¹. To date, COPs have been demonstrated in a wide range of applications such as IR-waveguide coatings², IR lenses³ as well as lithographic photoresist⁴. Another area of application which takes advantage of COPs excellent properties is the field of microfluidics. Typically, these microfluidic platforms would be fabricated from glass or polymers such as poly(methyl methacrylate) (PMMA), polycarbonate (PC) or polydimethylsiloxane (PDMS). Though these polymeric materials have good mechanical and thermal properties, thus allowing for easy processing, they tend to lack the optical transparency in the UV range necessary for the optical analysis of aromatics, proteins and nucleic acids. COPs remarkable optical and mechanical properties make them extremely suitable replacements for fabrication of microfluidic devices.

Polymeric microfluidic device fabrication can be done via techniques such as xurography⁵, micromilling⁶, UV-polymerisation⁷ and more recently, 3D printing^{8,9}. These processes, while allowing for rapid prototyping and device optimization, are difficult or are not conventionally utilized for mass production. Laser processing however, allows for both rapid device creation and high-throughput. Though laser processing of other polymers for microfluidic device

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creation have been studied^{10,11}, few studies to date have investigated the possibility of laser processing either COP or COC. Sabbert et al. studied ablation of COC using an ArF excimer laser¹² and showed the ability of this system to engineer high precision, micron size square holes was shown. The Ablation depth per pulse for COC was found 3.4 times smaller than for PMMA, a property which could be exploited for the fabrication of microchannel structures. In another study by Suriano et al. explored the use of a femtosecond titanium sapphire laser (800 nm) for microchannel fabrication on COP, PMMA and polystyrene (PS) substrates. V-shaped microchannels on COP ranging in depth from 10 μm up to 80 μm were created, with channel roughness comparable to those created through micromilling. No study has yet examined the use of Nd:YAG infrared lasers, which are widely used in industry for material processing¹³, for the processing of COPs.

Though COP based substrates offer excellent platforms for microfluidic devices, additional functionalization is required for use in chemical and biological speciation applications. Nanoparticle (NP) coatings offer the capability of providing novel and adaptable substrate functionalization. The use of Pulsed Laser Ablation in Liquid (PLAL), unlike other forms methods of NP production, allows for the synthesis of chemically highly pure NPs. Furthermore, similarly to laser processing, PLAL is a fast process allowing for rapid production and optimization of the produced NP suspensions. In this work, IR 1064nm laser processing of 188 μm thick COP using a 1064nm laser as a potential route to create microfluidic devices was investigated. Additionally, the production of carbon nanoparticles through PLAL and their potential use for functionalization of laser produced microchannels was also examined with an aim to develop a route for rapid creation fabrication of chemical or biological speciation platforms.

2. EXPERIMENTAL

2.1. 1064 nm laser processing system

The laser system used (shown in Figure 1) consisted of a Q-switched diode-pumped solid state (DPSS) 1064 nm neodymium-doped yttrium aluminum garnet (Nd:YAG). The laser had a maximum average power output of 4 W, a pulse width of 750 ps and a pulse repetition frequency of 7.5 kHz. A 2-dimensional galvanometer (SS-12, Raylase) provided x- and y-positioning of the laser beam and a movable z-stage (M-404 4PD, Physik Instrumente) controlled the sample position in the laser focal plane.

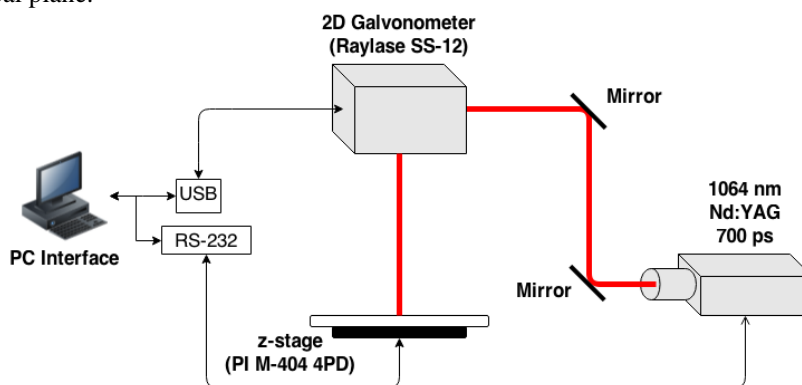


Figure 1. Schematic of the 1064 nm Nd:YAG laser processing system used for the experiment.

2.2. Laser texturing of substrates

The cyclic olefin polymer substrates used had a thickness of 188 μm (ZF14-188 ZeonorFilm®, Zeon Chemical, Japan) with a thickness of 188 μm . The polymer substrates were cut, cleaned, washed with isopropanol (>70%) and rinsed with deionized water (DI water) and dried with compressed clean dry air to ensure the substrate was pristine prior to laser processing. The laser beam was focused to a spot diameter of 140 μm and scanned unidirectionally across the sample at a speed of 1.2 mm/s to form channels separated by 200 μm . For the whole duration of the processing, the sample was mechanically clamped. The substrates were processed in two phases. During the first phase, a high fluence pass was applied to ablate the substrate surface and form the microchannel. This was then followed by a number of low fluence passes to remove condensed melt and ablated particulates from the microchannel. The fluence was set at 0.51 J/cm² and 0.34 J/cm² for the high and low passes, respectively.

2.3. Synthesis of nanoparticles and substrate coating

Synthesis of the carbon nanoparticles was conducted via PLAL using the 1064 nm Nd:YAG as described previously by Bagga et al.¹⁴ using the same laser used to produce the substrates. A cylindrical graphite target (>99.999%, Sigma) with a diameter of 6 mm and height of 8 mm was placed on the bottom of a glass cuvette (10 × 10 × 50 mm). The cuvette was filled with 2 mL of DI water, corresponding to 1 cm of liquid above the surface of the target. The target was polished mechanically and washed with DI water to ensure it was pristine prior to ablation. The laser ablation was conducted using a laser fluence ranging from 0.02 J/cm² to 0.71 J/cm².

Substrate coating was conducted by first activating the surface of as-received COP substrates using 20 μL of toluene applied using a micropipette for around 10 seconds. Though COP exhibits high chemical resistance to acids, bases and alcohols, it is easily attacked by non-polar solvents such as toluene. After activation, a CNP suspension was drop cast onto COP substrates with a micropipette. The CNP-coated substrates were then left in an oven at 36.5 °C for 24 hours to completely evaporate the toluene and isopropanol present on the substrate surface. Finally, these COP substrates were rinsed three times using deionized water and dried with compressed clean dry air, which was repeated three times per substrate. The substrates were sealed in petri dishes at room temperature for storage until analysis.

2.4. Characterization

Characterization of both the nanoparticles and the polymer substrates was performed using a number of techniques. Scanning electron microscopy (SEM) was performed to examine the microchannel morphology and nanoparticle coating using a Zeiss EVO LS15 (Carl Zeiss AG, Germany) at an accelerating voltage of 15 kV and a beam intensity of 15 pA. The substrates were gold coated using a ScanCost Six (Edwards, UK) for 80 s at a sputter current of 25 mA, with a resultant coating of 34 nm. The surface was imaged at a 52° tilt with respect to the normal to the electron beam emission direction.

Micro-Raman spectroscopy was performed on the CNPs with a Jobin-Yvon Horiba LabRam® HR800 at 20 mW and 1 μm² spot size (using Ar+ 488 nm air cooled laser and an accumulation time of 20 s) in backscatter configuration with a resolution of approximately 1.1 cm⁻¹. Transmission electron microscopy (TEM) was employed to examine the nanoparticle morphology using a FEI Titan instrument, operating at 300 kV. Samples were prepared by drop casting onto a carbon coated 300 mesh copper grid and left to evaporate at room temperature.

3. RESULTS

3.1. Substrate characterization

For single laser passes, SEM imaging showed the formation microchannels with deep V-shaped profiles however the presence of localized ablation holes were seen at the bottom of the microchannels. For multiple laser passes, the microchannels became deeper with surface roughness along the channel base being reduced. This suggests suggested that both further material removal and a localized melting or annealing took place during successive passes. Though the localized ablation holes were still present on the base of the microchannels after multiple passes, the relative size was less when compared with the channel depths. Depths for the microchannels ranged from 22 μm for a single high fluence pass, up to 77 μm which resulted from one high fluence pass, in combination with eight low fluence passes.

Raman spectroscopy was performed to study the chemical composition after laser processing. The base of the microchannel was examined for changes, while the measurements from the interchannel areas (which were not processed, were used as a reference, see Figure 3. No significant differences in location were seen between the channel and interchannel peak positions.

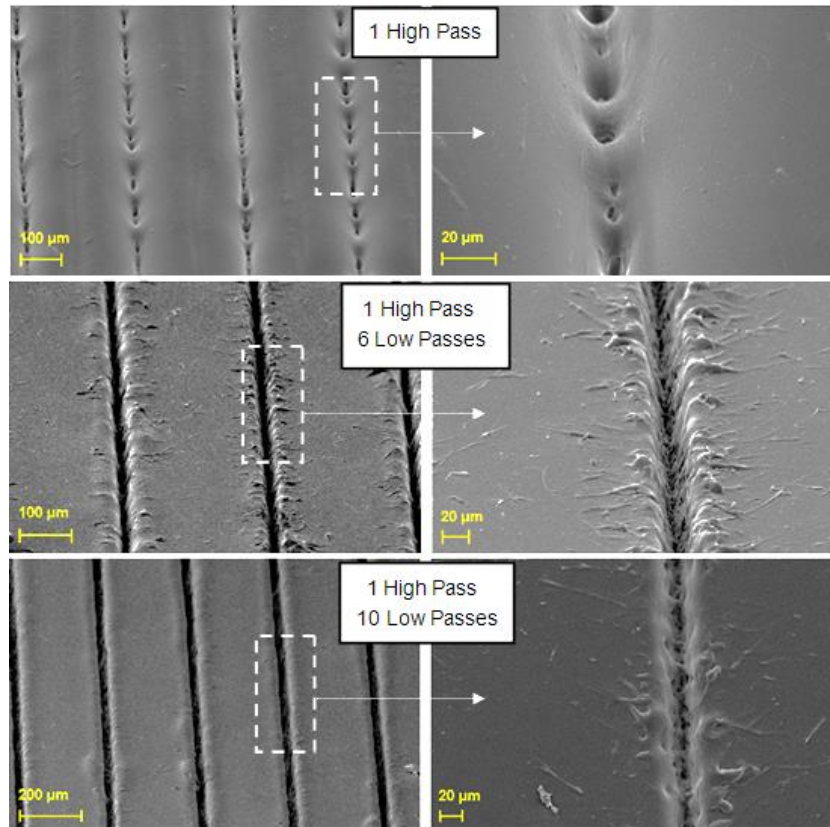


Figure 2. SEM images of the COP substrate after (top) 1 pass, (middle) 7 passes (1 high, 6 low), and (bottom) 11 passes (1 high, 10 low).

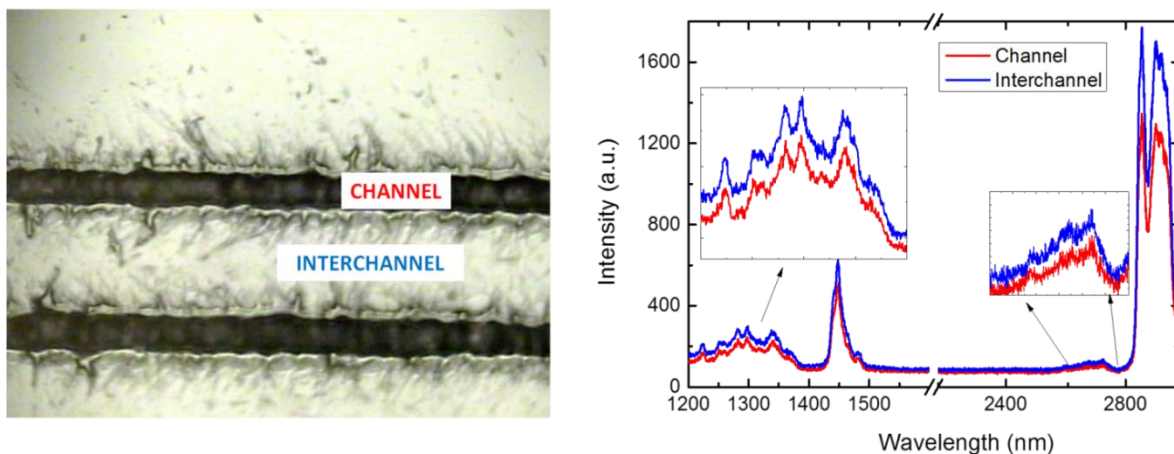


Figure 3: Micro-Raman spectroscopic analysis of the laser processed COP substrates. No significant compositional change was seen between the laser processed (channel) and reference (interchannel) areas.

3.2. Nanoparticle morphology and substrate coating

Figure 4 shows TEM images of the produced CNPs with a scale bar of (a) 100 nm and (b) 5 nm. The nanoparticle size distribution was seen to be Gaussian in nature and ranged from 5 nm to 50 nm with a mean value of 18 nm. The CNP nanoparticle colloid was drop cast onto the pristine COP and examined via SEM, see Figure 5. It can be seen that post

coating, aligned CNP structures (< 200 nm) formed. Larger CNPs clusters were also evident at discrete locations. Due to the cellular alignment of the smaller CNPs it is postulated that this CNP distribution originated mainly from the evaporation process. At lower concentrations, only the larger clusters formation was observed, demonstrating the need for optimization of the nanoparticle colloid concentration when performing substrate coating.

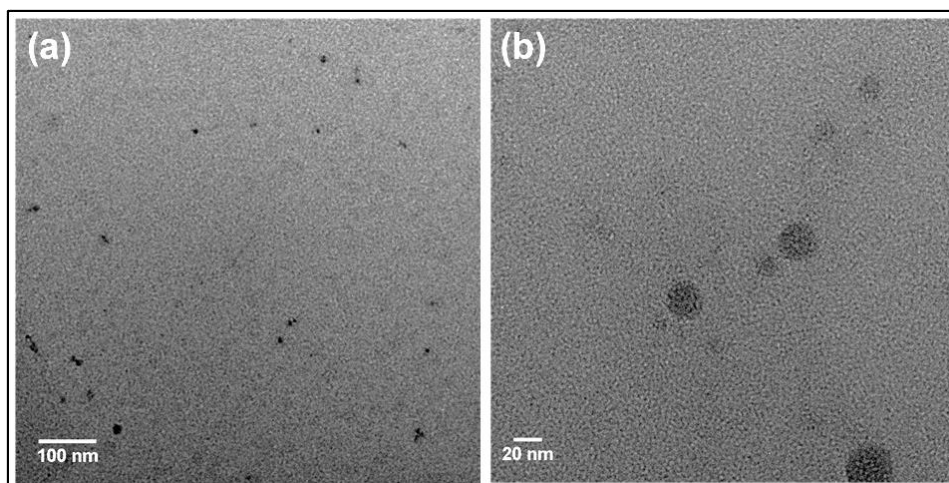


Figure 4. TEM analysis of CNPs produced via pulsed laser ablation in liquid in DI water at laser fluence of 0.40 J/cm^2 .

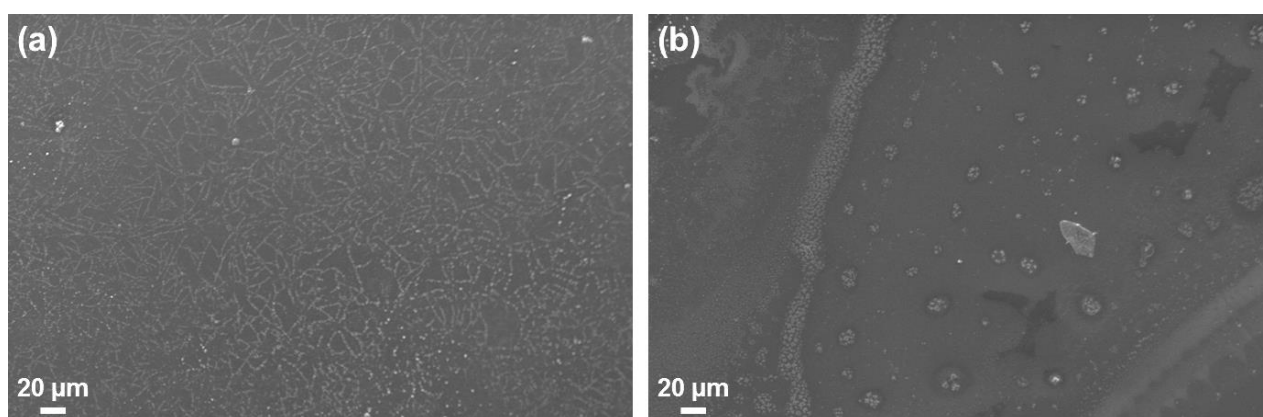


Figure 5. Carbon nanoparticles deposited on untextured COP. For higher CNP concentrations (a), the formation of structures was seen along with some larger nanoparticles clusters, while at lower concentrations (b) the formation of isolated clusters was apparent.

4. DISCUSSION

Laser processing was demonstrated to be capable of generating of micron sized channels on the surface of the thin polymer substrates. This capability, coupled with the speed and adaptability of laser processing, makes it an excellent route for the fabrication of microfluidic platforms. Raman spectroscopy confirmed the microchannels were not chemically altered by laser processing, thus the laser processed channels will presumably have the chemical resistance and biocompatibility of the unprocessed COP. This demonstrates that laser processing of COP is a viable route to generate substrates and devices suitable for microfluidics, where the chemistry of the surface in contact with the liquid plays a crucial role. Though the presence of localized ablation sites along the bottom surface of the microchannels was seen, further optimization of the laser processing parameters may allow for the creation of smoother and more uniform bottom surfaces of the microchannels.

Furthermore, COP's chemical resistance and biocompatibility make it extremely suitable for microfluidic applications once functionalized. To this end, carbon nanoparticles were produced via PLAL. The CNPs produced were seen to have

a uniform Gaussian distribution, which demonstrates that PLAL is an excellent route for the fabrication of CNPs. Furthermore, the chemical purity of the CNPs produced via the PLAL method, as discussed in Section 1, could allow for a wide range of possible functionalization routes such as tosyl attachment¹⁵ which can be employed for the speciation of aromatic compounds. The drop cast coated substrates showed good coverage at higher CNP colloid concentrations, though lower concentrations only saw the presence of clusters. This demonstrates the need for optimization of the nanoparticle colloid concentration prior to drop casting. These nanoparticles, if coupled with the laser-processed COP substrates could allow for the fabrication of platforms with a wide range of applications in both chemical and biological speciation.

5. CONCLUSIONS

This article presents the first investigation into infrared laser processing of cyclic olefin polymers which was applied for the fabrication of microchannels or microfluidic applications. The novel use of an IR laser will allow for this fabrication technique to be used in both research and industrial environments. The ability to create microchannels ranging in depth from 22 μm to 77 μm was demonstrated using a 1064 nm Nd:YAG laser. The chemical composition of the polymer post-processing was not significantly changed, thereby leaving preserving COPs the high chemical resistance and biocompatibility which are necessary for many sensing and assay related applications. Functionalization by way of drop casting carbon nanoparticles produced via PLAL was also examined. PLAL was used as a fast and adaptable route to for CNP production, with the coated substrates showing good coverage of nanoparticles when produced with colloid of high concentration. In conclusion, both laser fabrication of the polymer substrates along with functionalization using CNPs provides a route to rapidly create functional surfaces for chemical and biological speciation and separation.

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