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Fabrication of microstructured planar chromatography platforms via laser ablation

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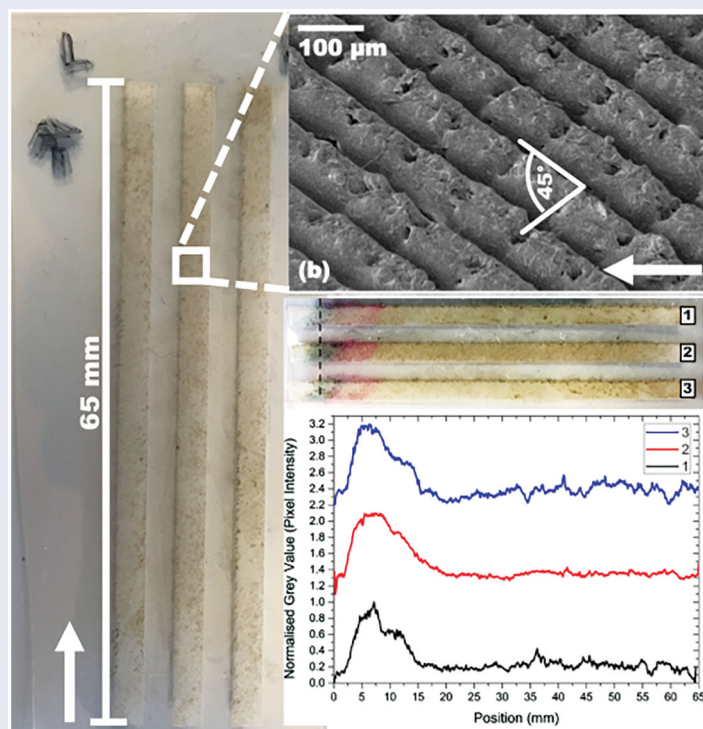
ABSTRACT

The field of planar chromatography has seen a resurgence due to interest in novel fabrication techniques for sorbent (stationary phase) layers. These novel sorbents must have high surface areas and achieve separations over short distances. Here, we present the first attempt to fabricate a planar chromatographic platform via laser ablation. Microchannels of $24\ \mu\text{m} \times 68\ \mu\text{m}$ depth were produced using an Nd:YAG laser on cyclic olefin polymer substrates which act as the stationary phase. These plates were then applied to a proof-of-concept organic dye separation and were able to resolve a binary dye mixture over 11 mm of plate length. Results showed promising potential for laser ablation as a new fabrication technique for planar chromatographic substrates.

KEYWORDS

Cyclic olefin polymer; laser ablation; microchannel; microfluidic; microstructuring; Nd:YAG; planar chromatography; thin layer chromatography; ultra-thin layer chromatography; zeonor film

GRAPHICAL ABSTRACT



Introduction

Recent years have seen a resurgence of interest in planar chromatographic methods, driven in-part by the move toward novel materials such as monolithic and nanomaterial

stationary phase layers. These materials achieve layer heights and porosities far smaller than that of existing stationary phases used in High-Performance Thin Layer Chromatography (HP-TLC) plates resulting in faster

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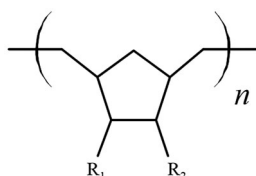


Figure 1. Structure of cyclic olefin polymer, an amorphous polyolefin.

separations and higher sensitivities.^[1,2] Furthermore, nano-material-based stationary phases can incorporate novel or highly targeted functionalities allowing separation of specific analytes not possible using traditional silica or alumina sorbent materials. These next-generation of “Ultra TLC” (UTLC) stationary phase layers have been fabricated using a number of techniques including Atomic Layer Deposition,^[1] Chemical Vapor Deposition,^[3] Polymer Electrospinning,^[4] sol-gel coating^[5] or through deposition of silicon or silver nanoparticle thin films.^[5,6]

One technique heretofore not explored for the fabrication of UTLC platforms is laser micromachining which is commonly used for the creation of micro- and nanoscale features and is adaptable to suit a range of polymers and glasses and has also been frequently applied for the fabrication of low-cost devices such as microfluidic chips.^[7,8]

Substrate choice has a significant impact on the performance analytical platforms. Low-cost polymers such as Cyclic Olefin Polymer (COP) are noted for their excellence in analytical applications, owing to their superior optical and chemical properties such as resistance to common acids, bases and polar solvents.^[9,10] This has resulted in COPs being applied in lab-on-a-chip systems,^[11] as substrates for capillary electrophoresis,^[12] and in DNA microarrays.^[13] COP has also been applied as a stationary phase and substrate material for electrochemical separations making it an ideal candidate material for planar separation plates.^[14]

In this work, we present the laser fabrication of open capillary microchannels on COP substrates which were applied as a stationary phase for a proof-of-concept separation. The solvent flow capabilities of three different COP plate morphologies were examined and the fabricated plates were applied to the separation of a mixture of organic dyes with the results benchmarked against a commercial reversed-phase (RP) TLC plate.

Experimental methods

Materials

The chosen substrate material was COP, an amorphous polyolefin with a bulky ring structure, is shown in Figure 1.^[15] The COP used was 188 μm thick ZeonorFilm ZF14-188 (ZeonChemical, Japan) sourced from Ibidi (Germany).

Given the hydrophobic nature of COP, the laser-fabricated polymer UTLC plates were benchmarked against commercial RP-TLC plates (C18-modified silica gel with F254s fluorescent indicator, Merck Millipore) which had a pore size of 60 \AA , and layer thickness of 200 μm .

The sample for separation tests was a methanol solution of Fast Green for Food Coloring (FCF; $\geq 90\%$,

SigmaAldrich) and Rhodamine 6G (Rho6G; $\sim 95\%$, SigmaAldrich) at a concentration of 1 mg/L each. A ternary mobile phase comprised of ethyl acetate (EtAc; ChromaSolv[®] $\geq 99.7\%$, Sigma), methanol (MeOH; ChromaSolv[®] $\geq 99.9\%$, Sigma) and deionized (DI) Water (Milli-Q water purification system, Merck Millipore, USA) at 8:1:1 v/v was used for the separations.

Platform fabrication

Our group has previously reported on the use of Nd:YAG lasers for the fabrication of microchannels on COP which forms the basis for this work.^[16,17] A BrightSolutions WEDGE HF 1064 Nd:YAG laser used in this study to fabricate the UTLC plates. The system had a wavelength of 1064, a maximum average output power of 1.6 W and a tunable pulse width and repetition rate which was fixed at 600 ps and 10 kHz respectively for this study. The beam was rastered in the xy-plane using a Raylaser S-12 2D scanning galvanometer and the position of the substrate in the beam waist was controlled using a PI M-404-4PD 1D nanoposition stage. For this work, the laser beam diameter was kept constant at 100 μm .

The plates consisted of three 65 mm \times 25 mm areas comprising of V-shaped microchannels with a 100 μm inter-channel distance, on an 80 mm \times 30 mm COP substrate, with three plates per substrate, allowing for an $n=3$ for each substrate.

Platform testing and analysis

As the morphology of the microchannels has a significant effect on the flow behavior of the mobile phase: parallel microchannels, and two crosshatched morphologies with a 45° and 23° angle with respect to the direction of flow. To allow visualization of this flow behavior, the plates were immersed in a 1 mg/mL aqueous methylene blue solution in methanol. A sealed container was filled with a small volume of dye solution, which sat at room temperature to allow for the atmosphere inside to condition for 10 min. The plate end was then immersed in the dye solution for a fixed time after which it was removed, and the dye front position recorded optically using a Camag TLC Visualizer 2.

To further demonstrate the flexibility of the UTLC plates in low-cost analytical applications, post-separation imaging was performed using an iPhone SE (First Generation, Apple, USA) in High Dynamic Range (HDR) mode. ImageJ was used to analyze the recorded plate images with grayscale values extracted for each chromatogram, with a background subtraction applied if necessary, to reduce noise resulting from the ambient lighting conditions.

Results and discussion

Plate morphology and solvent flow

The three plate morphologies trialed were examined via SEM, which is shown in Figure 2. The results are similar to

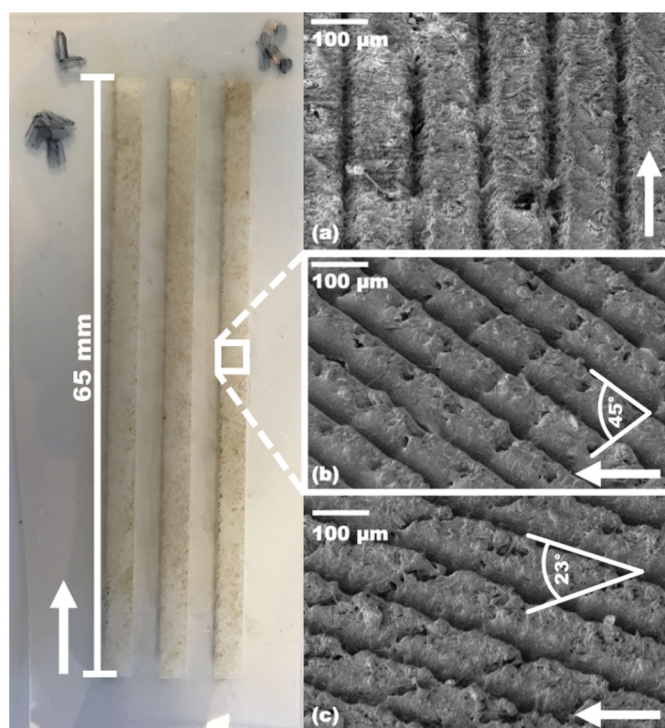


Figure 2. SEM micrograph of the ablated substrate showing microchannels (a) parallel channels, (b) 45° crosshatched channels and (c) 23° crosshatched channels, with the direction of mobile phase flow is indicated.

Table 1. Dimensions for the three microchannel morphologies measured via 3D profilometry.

Morphology	Hatching angle	Depth (μm)	Width (μm)
Parallel	N/a	13.5 ± 4.2	58.6 ± 2.8
45° Hatch	+	23.7 ± 10.8	67.7 ± 3.9
	-	10.9 ± 4.3	55.8 ± 10.1
23° Hatch	+	25.1 ± 5.6	78.6 ± 3.2
	-	5.4 ± 1.0	56.9 ± 13.6

our previous reported work, but with crosshatched channels exhibiting a smoother profile than the parallel channels, potentially a result of the longer processing time for the crosshatched plates. Dimensional analysis of the microchannels was performed via 3D optical profilometry (Table 1). The two crosshatched patterns exhibited two microchannel depths and width, resulting from the hatching patterns being processed as two separate passes. Microchannels with a positive hatching angle were ablated first and showed a larger depth and width than those processed at a negative hatching angle.

To examine the effect of microchannel morphology on the flow of solvent, the plate ends were immersed in a dye solution and the position after a fixed time recorded. Figure 3 shows the dye position up to 270 s. The parallel microchannels exhibited the fastest flow, reaching a position of 35.3 ± 7.29 mm after 30 s, with the dye solution eluting off the end at 65 mm after 270 s. The 23° and 45° hatched microchannels remained on the plate up to 270 s, however the 23° exhibited a lower reproducibility than either the parallel or 45° hatched microchannels.

This lower repeatability for 23° hatched channels is due to the larger variance in the depth between channels with a

positive and negative hatching angles. Determining optimal laser parameters to ensure uniform channel depths would allow for more repeatable flow behaviors in these channels, however, difficulty in producing highly repeatable surface structuring of COP and cyclic olefin copolymers using laser processing has previously been noted, due in part to the photothermal ablation mechanism. The use of femtosecond lasers for material processing, which have a much smaller heat affect zone on the substrate, may be a potential route toward increasing microchannel uniformity.^[18]

Both the 23° and 45° crosshatched channels demonstrated slower flow behavior, which may be a result of mixing and recirculatory flow at each vertex within the hatching pattern.^[19] The slowest flow behavior was seen for the larger 45° angled channels, potentially resulting from increased mixing between channels at the vertices. Previous work on additively manufactured planar chromatographic plates showed significant streaking with parallel microchannels, with separated analyte spot diameters ranging from 5 to 20 mm.^[20] The crosshatching of channels may help to mitigate this streaking by allowing increased interaction between the analytes and the stationary phase through a slower development time. As the UTLC plates do not have a porous sorbent layer, this increased interaction time was deemed favorable, and given these results, it was decided to proceed with the 45° crosshatched plates to the organic separation tests in this study.

Separation of organic dyes

To examine their feasibility as a planar chromatographic platform, a proof-of-concept separation of a binary organic dye mixture was performed using FCF and Rho6G as analytes, which have previously been used for TLC validation.^[21,22] This separation on the UTLC plate was then compared to commercial RP-TLC plates to allow benchmarking of the platform capabilities. As there was no visible wetting of the plate to allow for solvent front visualization, the development time was fixed at 270 s, and a value for the maximum solvent position of $Z_x = 30.2 \pm 0.5$ mm was used (as determined from the plate wetting studies) to calculate the retardation factors, R_f , for the UTLC plates. For the tests performed on the RP plates, the development time was also fixed at 270 s, and as the solvent front position was visible, it was experimentally recorded for each test.

The comparison between the UTLC plate and the commercial RP-TLC plate and the resultant chromatograms is shown in Figure 4. Similar retardation behaviors were seen for both plates, as shown in Table 2, however significant tailing behavior was seen for the Rho6G on both plates. Though tailing was less evident for FCF, the distance traveled was comparatively less than the Rho6G. Unlike the RP-TLC plates, the distance between the separated analytes on plate, i.e., the separation resolution, was low. Due to the lack of a porous sorbent layer and the limited interaction of the mobile phase with the FCF, some analyte was retained at a Z_x less than zero. Due to this behavior, determining an accurate retardation factor was not possible. With further

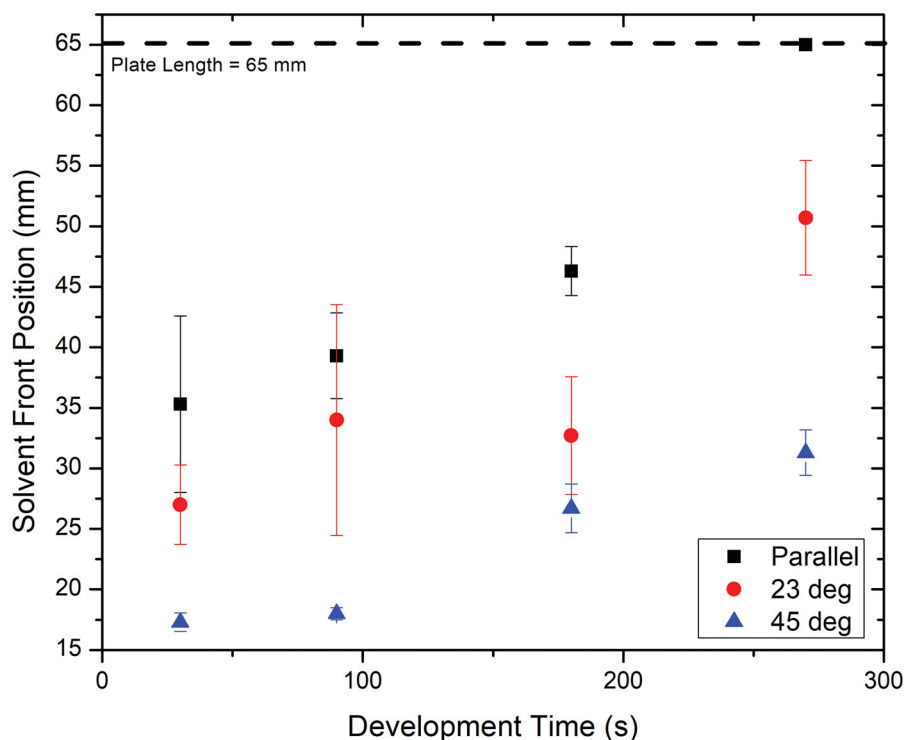


Figure 3. Solvent front position for set development times as determined by the plate dye wetting studies for the three plate morphologies ($n = 3$).

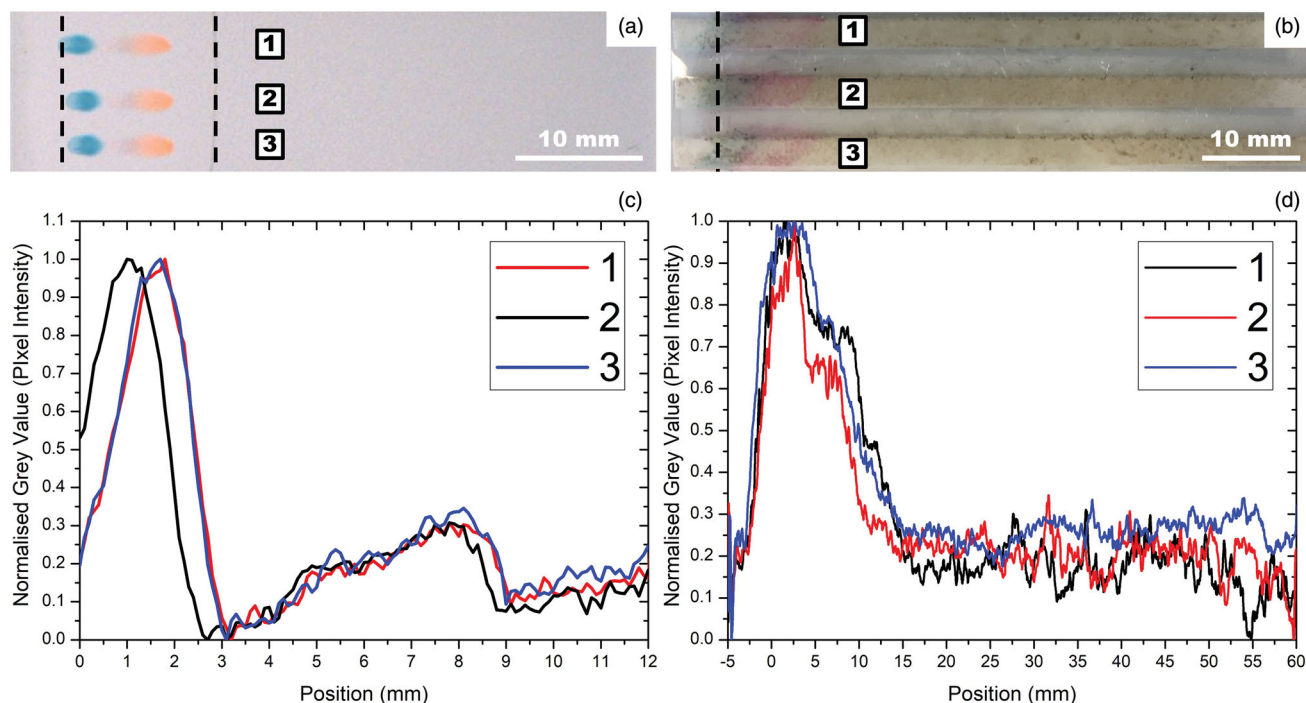


Figure 4. Plate images and chromatograms of the RP-TLC plate (a,c) and the UTLC platform (b,d). The Fast Green appears as blue, and the Rhodamine 6G as orange/pink.

method development, and increased mobile phase interaction with the FCF, determination of an accurate R_f would be possible.

Also evident was significant streaking of both analytes, which is similar to the streaking characteristics seen in other novel polymer-based open capillary planar chromatography platforms.^[20] Aspect ratio has been noted to play a large

part in the generation of vortices in microfluidic channels,^[19] as such the produced channel geometries may require optimization to reduce mixing and mitigate the streaking behavior. This streaking also presented a significant challenge in accurately determining the retardation factors from the acquired chromatograms. Though the analytes were visible from imaging, the extracted grayscale intensities

Table 2. Retardation factors for the UTLC and RP-TLC plates.

Analyte	Retardation factor (R_f)	
	UTLC	RP-TLC
Fast Green FCF	>0.09	0.10 ± 0.07
Rhodamine 6G	0.18 ± 0.11	0.57 ± 0.08

revealed only a small change in intensity between the FCF and Rho6G.

Separation was achieved over approximately 11 mm of UTLC plate, compared to 9 mm on the RP-TLC plate, although the analytes on the UTLC plate were not discreetly resolved. Previously reported separation distances range from 5 mm on metal-oxide nanowire UTLC plates^[23] to 30 mm on carbon nanotube-based plates.^[24] The streaking on the laser-textured plate may potentially be mitigated through ensuring that the channels are fully cross-connected. As seen in Table 1 there is a significant difference in the depth of the channels depending on hatch angle with channels of a positive hatching angle being deeper than those with a negative angle. The smaller channel depth of one hatching pattern being lower may impede the flow of the mobile phase, thus increasing the uniformity in channel depth by optimization of the laser processing conditions may reduce streaking of analytes resulting in higher separation resolutions.

Conclusions

We have presented an initial investigation into utilizing laser ablation to fabricate microchannels on a polymer substrate, which was applied toward planar chromatography. The laser fabricated UTLC plate performed in a similar manner when compared to an RP-TLC plate under the same chromatographic conditions. While the behaviors seen between the two plates were similar, benchmarking of the UTLC platform against other TLC plates, including those with novel functionalisation is still ongoing to further elucidate the capabilities of the laser fabricated UTLC plates.

Though further work is required to increase the performance of the UTLC plate in comparison to commercially available plates, it nonetheless validates laser ablation as a potential route for fabrication polymer microchannel separation platforms. Furthermore, ability to tailor the surface chemistry through known surface functionalisation routes for COPs would allow unique capabilities and applications for the UTLC plate, something which is not possible with traditional sorbent layer plates. The non-porous nature of the UTLC plate surface could also allow for simplified elution of the analytes for quantitative analysis using techniques such as mass spectrometry, which has been hyphenated with other planar separation technique successfully.^[25] Ultimately, there is strong potential for laser ablation as a route toward the low-cost development of planar separation platforms.

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