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The impact of medium chemistry to flowing liquid closed immersion ablation of bisphenol A polycarbonate.

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Abstract:

Equipment has been developed to enable KrF excimer laser ablation machining of a bisphenol A polycarbonate sample under closed thick film flowing liquid immersion. The liquid medium is easily changeable, offering the possibility of chemical modification of the material etching mechanism. Previous work using a medium of filtered tap water has proven the ability of this equipment to control debris; however, this medium had the simultaneous consequence of modifying the primary ablation characteristics from those achieved in ambient air. De-ionized (DI) water is a chemically similar medium that displays contrasting electrostatic properties and was used in this work with the intention of modifying the adhesion mechanisms active. Use of DI water resulted in close agreement of ablation characteristics observed using filtered tap water. Etch rate and threshold displayed a marginal loss in machining efficiency by magnitudes of 11.7% and 4.3% respectively when using DI water for immersion of laser ablation compared to filtered water. This loss is proposed to be caused by increased colloidal grouping of small debris particles to form medium sized items that more completely attenuate the laser beam. As with filtered water, the etch efficiency was also found to be flow velocity dependent due to changing fluid flow-plume interaction states. The mode of debris control afforded by the use of DI water as a laser ablation immersion medium was similar to that of filtered water. But, the volume of debris deposited was significantly greater and was deposited in closer proximity to the feature. Electrostatic insulation by DI water allows greater attraction of particles to the surface due to the suppression of Yukawa forces. Moreover, the action of colloidal aggregation of particles caused DI water to deposit a proportionally large volume of medium sized debris when compared to the proportional population of medium sized debris deposited by filtered water. This work demonstrates that choice of medium offers the immersed laser ablation user control of ablation characteristics without modification of laser parameters.
Introduction

Previously, the use of open flowing liquid immersion has been used in an attempt to control the production, ejection and deposition of laser ablation generated debris using a number of varied techniques and liquid media [1-3]. Such work is timely because laser ablation has enabled the revolution taking place in the field of micro and nano manufacturing [4-6], but further progress is jeopardized by laser ablation generated debris which causes attenuation of the beam, necessitates post-process cleaning, coats the laser optics, contaminates critical mechanical bearing surfaces, produces potentially dangerous build ups on electrical circuits and poses health and safety issues to workers [7-11]. Of arguably more concern is that now the capability of laser ablation machining has increased to a level where tooling performance is limited not by the repeatability and resolution of the machining method, but by the deleterious effects of the debris created during the process.

The complex combinations of interactions involved during ablation in gaseous and vacuum environments have been explored in detail, with a multitude of contributing effects identified [25, 26]. Others [27, 28] have investigated the impact of liquid immersion on excimer laser ablation. Katto et al. [29] and Sattari et al. [30] have independently characterised production rate, typical dimensions and chemistry of particles generated in very thick film flowing and stagnant ultra pure water immersed ablation respectively, yielding contrasting findings concerning fluence variation and wavelength. The effect of open immersion on the ablation rate of excimer laser ablation of bisphenol A polycarbonate demonstrated that splashing was a common occurrence during machining. Splashing was attributed to irregular but broadly increased plume pressure which significantly attenuated the laser beam en-route to the sample surface [31]. In a thick film regime, the volume of liquid above the ablation plume confines the plume expansion and prevents free expansion in the manner allowed by the less viscous medium of ambient air [32]; thus, the compressed high pressure ablation plumes
attack the surface of the sample to be machined causing a high etch rate [33, 34]. The resulting acoustic type mechanism more than compensates for the loss of laser etching due to the multiple contributing attenuation effects as the beam passes through the plume [35, 36].

Elaboudi et al. [35, 37] used 248 nm excimer radiation to ablate polymer targets including polycarbonate to go about explaining the specific ablation mechanism at work during a liquid (ultra-pure water) immersed ablation event. Their work supported the findings of previous authors [33, 32] insofar as the ablation threshold decreased when using liquid immersion compared to traditional ablation in ambient air. The evaporation driven by photomechanical interactions are primarily responsible for the ejection of debris material (which were the result of acoustic interactions) and the debris generated typically had a diameter of 50 nm and a chemistry close to that of the original material - supporting a “cold” or photomechanical removal mechanism. Elaboudi et al [38] also postulated that in addition to photochemical degradation, some debris was generated by a hydrolysis reaction as an explanation for the decreased ablation threshold of ultra-pure water immersed PET.

The mechanism of adhesion between particles and surfaces is complex [12]. In a dry system, three primary adhesion forces govern the interaction (Van der Waals [13, 14], Electrostatic [15, 16] and capillary [17, 18]), all of which are effected by particle size [19]. These forces are then augmented by secondary effects such as contact time [20, 21], adhesion force generated surface deformation [22] and surface topography [19]. Unlike macroscopic systems, where the role of gravity is predominant, at the microscopic scale Van der Waals forces dominate the interaction between particles [13, 14]. Once lodged to the surface Van der Waals, electrostatic double layer and capillary forces combine to adhere the particle to the surface [12]. In turn, this gives rise to the secondary surface deformation and time dependant effects that act to increase the adhesion force [20-22]. Immersion in water adds further complication: liquid immersion has been shown to halve the Van der Waals attraction [16]
and will significantly reduce or negate the action of capillary adhesion during emersion due to the increased correlation of liquid viscosities between the adhesion meniscus and the immersing fluid [12]. The action of electrostatic forces can be negated or even reversed by the use of a conducting liquid as a medium by the action of the Yukawa repulsion [23]. In this case the charge of the larger surface is conducted through the medium to the particle, giving both the same sign, causing electrostatic repulsion both in long range and contact electrostatic regimes. It is here that media chemistry can become important.

The choice of medium is critical in the adhesion system existent during laser ablation machining. The use of filtered water may have a distinct contrast in debris control performance to that of DI water. This is because DI water has much less capacity to conduct electricity than filtered water [24]; hence, the ability of these two similar fluids to negate or limit the effects of electrostatic adhesion forces may vary greatly. This could cause secondary effects that become evident in terms of surface topography, ablation rate or ablation threshold. The aim of this work is to investigate, identify and explain these possibilities.

Until now little work has been conducted to discretely describe the importance of the specific chemical attributes of the immersing liquid used. This work will explore the performance of de ionized (DI) water in the application excimer laser ablation of bisphenol A polycarbonate when immersed in a closed flowing thick film. Although this change in media is subtle it is important as DI water does not have the same capacity for electrical conduction as filtered water - a factor that may be critical in the control of small ablation debris [12].

**Experimental Procedure**

**Materials**

Bisphenol A polycarbonate (Holbourne Plastics, Ltd), was as received in 1200 mm x 1000 mm sheets of 0.5 mm thickness. Prior to excimer laser processing, the bisphenol A polycarbonate sheet was cut into rectangular sections of 8 x 12 mm² using scissors - a shear
cutting technique which avoids production of debris. Protective cover sheets were then peeled off each sample.

**Laser Details**

For both closed immersion and ambient air processing, an excimer laser (LPX200; Lambda Physique, GmbH) using KrF as the excitation medium was used to produce a beam with a wavelength of 248 nm. Thereafter, the beam was supplied to a laser micromachining centre (M8000; Exitech Ltd), where it was passed through a stainless steel mask to produce a 201 x 203 µm² rectangular image. The masked beam was then demagnified through a 4x optic (Francis Goodhall, Ltd) to produce an ablation spot with a depth of focus (DoF) of 6 µm. A profile of the masked beam was obtained using a beam profiler (SP620U; Spiricon, Ltd), which showed that the beam shape had an even distribution, with only a slight positive skew across the y-axis: demonstrating good positioning of the mask in the raw beam.

Focus was found by narrowing the focal range until satisfactory focus was achieved. Pulse energy was measured out of focus, using a power meter head (J50LP-2; Molectron Detector, Inc.) connected to a reader unit (Energy Max (EM)400; Molectron Detector, Inc.). Spot energies were measured six times for each sample — three times before the sample was machined and three readings were taken after the sample was machined. Each reading was taken after the system attenuator had been reset. In this way, any change in the beam between measurements and any inaccuracy in the positioning of the attenuator were accounted for.

**Ablation Threshold Features**

A sample included six machined sites, each produced using 50 pulses in the same machine run with uninterrupted DI water flow over the sample during machining. The system attenuator was used to change pulse energy by a repeatable amount between sites. Attenuator positions used were: 0.5, 0.6, 0.7, 0.8, 0.9 and 1.0; Figure 1 shows the corresponding fluence
values measured using this mask, for ablation in ambient air and under filtered water immersion respectively, given the 203 x 205 µm dimensions of the features machined.

Ablation Rate Features

6 sites were machined on each sample that was immersed by an uninterrupted filtered water flow, each produced using an increasing number of pulses (3, 6, 12, 60, 120 and 480 pulses) to produce an ablation rate matrix with a beam attenuated by a tool attenuator set at 126° from minimum transmission, resulting in a beam fluence of 580.7 and 578.1 mJ/cm² for ablation in ambient air and under filtered water immersion respectively, given the 203 x 205 µm dimensions of the features machined.

Fluence Measurement

This fluence data was calculated from pulse energy data taken using a pulse energy head (J50LP-2; Molecron Detector, Inc.) positioned above the focal point of the laser, and enumerated by a laser energy meter (EM400; Molecron Detector, Inc.). The fluence was calculated using the mean beam energy measured (averaging techniques were employed for experimental rigour: beam pulse energy was recorded 5 times before and after machining each sample, every value recorded was the mean value measured over 100 pulses - between readings the attenuator was reset to account for attenuator position errors); this way, any changes in laser output over time are accounted for.

Ablation Debris Control Features

The ablation debris samples were taken from the ablation rate samples produced for this work as described above. All features examined in this work have two neighbours: one lying 200 µm away from the sample on either side; critically, these features are aligned across the direction of liquid flow. One feature is produced before each of the samples inspected in this work using just 3 pulses, the feature inspected in this work is produced using 6 pulses, then
following this, another feature is machined to the right of the feature of interest using 12 pulses. The use of neighbouring samples is important in the context of this work: when machining features into a sample, it is common for multiple features to be machined at separate times or even during separate phases of manufacture [6]; thus, the importance of preventing cross contamination of debris produced from one feature impacting the quality of another is high. These samples have been produced with neighbours to represent this reality. 6 pulses were used for producing the samples that are the subject of this work to allow direct comparison to samples produced in earlier work [2].

**Ambient Air Laser Processing Procedure**

Samples machined in ambient air were produced using the same laser and micromachining equipment as the closed immersion ablation samples. The bisphenol A polycarbonate samples were mounted directly to the vacuum chuck inside the micromachining station (M8000; Exitech, Ltd). After lasing ended the sample was removed and placed into the cell of a sealed sample tray to protect them from atmospheric dust.

**Closed Immersion Laser Processing Set-up**

Figure 2(a) describes the critical experimental layout of the sample once clamped inside the immersion chamber, which was mounted to the side of the sample vacuum chuck of the laser micro-processing centre (M8000; Exitech, Ltd.). The sample was positioned in the centre of the flat aluminium table between the water supply and exit holes. The sample was retained by a recess in a spacer plate that lay in contact with the aluminium sample table. An O-ring cord, located by a rectangular groove in the sample table, provided a seal between the sample table and the spacer plate. On the top of the spacer plate a second oval groove was machined to locate another O-ring cord. This acted as a gasket between the spacer plate and the beam window – a 25 x 25 x 5 mm³ ultra-violet grade fused silica sheet (Comar Instruments, Ltd).
The beam window was retained by a diamond shaped recess in a third aluminium plate, 8 mm in thickness to provide stiffness to the whole sandwich assembly.

Figure 2(b) shows the water filtering and supply system. Filtered water originated from normal mains supply by wall tap. The water was poured into a domestic water filter (Britta, Inc.) situated at the top the water supply assembly to remove typical corrosive elements present in mains water. The water was then retained in a header tank located above the pump and, under the action of gravity, was forced into the 700 W pump (CPE100P; Clarke Power Products, Ltd.). When DI water was used it was purified (Elix 10 UV Water Purification System; Millipore, Corp.) and then poured directly in the header tank. The pump forced the water through a water flow velocity meter (FR4500; Key Instruments, Inc.) and then along a 3 m distance through a 6 mm outer diameter nylon tube to the inlet push-in elbow mounted to the bottom of the sample table. Last, the water was returned along a further 3 m through a 6 mm outer diameter nylon tube to a collection bucket. The pump was capable of producing 4.2 bar at the outlet, equating to a maximum flow velocity through the ablation chamber of 3.89 m/s, given losses along the supply and return tubing. Precise control of the flow velocity was provided by a variable valve of the flow-meter. Laminar flow velocities of 0.03 and 0.12, m/s were used for this work along with turbulent flow velocities of 1.85 and 3.70 m/s.

Sample Analysis Techniques for Ablation Threshold and Ablation Rate

The ablation depths were measured using a dragged needle profiler (CM300 Talysurf; Taylor-Hobson, Ltd). Five passes were made across the surface of the sample and into each feature at 50 µm intervals. To minimize the possibility of profile error, the mean average depth of each sample feature was then calculated from a selection of three profiles for each sample feature. To guard against outlier samples being produced and effecting the ablation threshold measurements taken, all data plotted for interpretation in these results are mean
average values taken from the data produced by three sample features machined using each flow velocity.

**Sample Analysis Techniques for Debris Control**

For numerical data to be produced from solid samples, a number of steps had to be taken to achieve the resolution of data across the broad area of samples machined for this work. Each sample was imaged digitally as an uncompressed bitmap in 9 sectors (bottom left, bottom, bottom right, left, centre, right, top left, top and top right) using reflective illumination and an optical microscope (Optiphot; Nikon Corp.), at 20x magnification onto a CCD photosensor (GXCAM-5; GT Vision, Ltd.). A blank micrograph was also taken to account for any dirt that may have been present in the microscope optics and to record the image brightness gradient produced by the illumination technique. The sector images were then digitally corrected in terms of brightness gradient and erroneous marks using software (Image Pro 6.2; Media Cybernetics, Inc.) and the blank micrograph as a datum image. The corrected sector images were then combined to a single, large, high resolution bitmap. This full colour bitmap was then converted to a binary data plot using software (Visilog Xpert 6.1; Noesis, Inc.) The numerical data of the three samples produced by each processing condition were then combined and averaged using code programmed in a matrix processing suite (MATLAB 2008b; The MathWorks, Inc.) to produce 6 final data sets for samples produced in ambient air and under closed thick film filtered water immersion at flow velocities of: 0.03, 0.11, 1.85, 2.78 and 3.70 m/s). This final averaged data was separated into ten groups classified by area size. This data could then be manipulated to produce general population density data, local population density data by sector or displacement data.

**Results and Discussion**

**Ablation Threshold**
The efficiency of the interaction between a laser beam and a material can be measured to ascertain the magnitude of the ablation threshold. High etch efficiency is indicated by a low threshold fluence, where minimal laser energy would be required to remove material from a substrate. In Figure 3 the ablation threshold of 248 nm KrF excimer laser radiation machining bisphenol A polycarbonate is plotted. This was sampled using multiple flow velocities (0.03, 0.1, 1.85 and 3.70 m/s) in two mediums. Trend lines have been fitted to all plots, black trend lines for DI water immersed samples and grey for filtered water. Only the lowest flow velocity used displays poor linear plot correlation for both liquids: an outlier exists at 522 mJ/cm² for filtered water and 561 mJ/cm² for DI water. Inspection and comparison of the remaining points for the two results machined at 0.03 m/s under differing mediums show great similarity. This is especially true for the features machined using high fluence, where the filtered water repeatedly provided lower etch efficiency than ablation under DI water. Lower fluence points are also similar. The fact that both trends appear similar, barring outliers, indicates that use of very low flow velocity closed thick film immersed laser ablation machining is highly fluence dependent.

This assertion is borne out somewhat by the plots shown in Figure 4(a) and Figure 4(b), where the etching threshold is plotted with respect to closed thick film immersed ablation flow velocity. Comparison between Figure 4(a) and Figure 4(b) highlights the large variance in performance between low and high fluence respectively. The agreement between DI and filtered water results is greater for high fluence regime results plotted in Figure 4(b) than those of low fluence results in Figure 4(a); however, both indicate use of DI and filtered water along with very low flow velocity (0.03 m/s) resulted in a loss of etch efficacy (signified by increased etch threshold fluence). This is a result that is in agreement with previous philosophy [36] that proposed pulsed beam obstruction by insufficient removal of debris produced by an earlier pulse in the low velocity flow. This reduced the contribution of
laser etching and therefore limited the volume of plume generated, reducing or removing the contribution of plume etching [33]. This phenomenon is explained as a result of low liquid volume refresh rate when compared to the laser pulse frequency. At 0.03 m/s flow velocity, this was just 0.7; compared to all other flow velocities, that had ratios larger than 11. At 0.03 m/s debris was not removed from the volume above the feature to be machined between laser pulses; thus, leaving debris ejected by an initial pulse suspended to obstruct the following pulse. Increased debris size magnified this problem as large debris absorbed larger volumes of laser energy in the following pulse before being ablated. Larger debris is encouraged by a non conducting medium such as DI water via the action of colloidal adhesion [16].

Further inspection of Figure 3, with attention paid to average etch depths plotted against the natural log of laser fluence used at the flow velocities of 0.12, 1.85 and 3.70 m/s in both filtered and DI water, shows that the etching threshold and therefore efficiency was similar in both media. Only the trend of DI water flowing at 1.85 m/s generates an abnormally high etching threshold at 144 mJ/cm². This was caused by an outlying depth value measured for the natural log of beam fluence measured at 375.67 mJ/cm², as indicated in Figure 3. Barring this, all points closely follow linear trends; therefore this point can be discarded, resulting in a more acceptable projected threshold fluence of 123.6 mJ/cm². The flow velocities all produced an etch threshold range of 9.99 mJ/cm² about a central value of 120.75 mJ/cm².

Further analysis is possible by inspecting the plot given in Figure 4(c) where the average etch rate interpolated by projecting the trend of all beam fluences tested is plotted with respect to the flow velocities used for machining. Measurement of ablation threshold by interpolation generally overestimates the true ablation threshold value of a material; however, for comparative means this technique remains valid. Figure 4(c) makes it clear that both immersion mediums produced similar etching efficacy, but the use of filtered water during closed thick film flowing immersed laser ablation generally produced higher efficacy than
both KrF excimer laser ablation of bisphenol A polycarbonate in ambient air and when using DI water as an immersion media by 4.3% and 8.6% respectively, which are both outside the margin of error of this work. Fluence dependency is also important at increased flow velocity, as shown by detailed inspection of the threshold fluence magnitude plotted in Figure 4(a) and Figure 4(b). Low fluence regime machining in both mediums required a typical threshold fluence value of 115 mJ/cm$^2$ - a value greater than that produced by low fluence machining in ambient air (88.7 mJ/cm$^2$). High fluence regime machining shows the opposite response, where efficiency was gained using both immersion mediums (producing a typical threshold of approximately 200 mJ/cm$^2$) over machining in ambient air, that required more than 250 mJ/cm$^2$.

Ablation rate

The etch rate achieved using 3, 6, 12, 60, 120 and 480 pulses when machining using differing closed thick film flowing immersion media during KrF excimer laser ablation showed repeatable trend. Figure 5 is a 3D chart describing the depth machined with respect to the number of pulses used and also the flow velocity used. Figure 5 shows that 0.03 m/s flow velocity resulted in equivalent machined depth or slightly lower machined depth when using filter water than that achieved when using DI water. Use of 0.11 m/s flow velocity follows this trend for 3, 6 and 12 pulses, but changes beyond this. Use of more than 60 pulses resulted in filtered water immersion having greater machined depth than DI water immersion. Use of turbulent flow velocities showed that filtered water produced increased etched depth for all pulse numbers. This suggests that filtered water provides increased etching efficiency once above the ablation threshold when using turbulent flow velocities.

Detailed analysis of the etch rates produced at the four flow velocities tested in this work using both mediums (0.03, 0.11, 1.85 and 3.70 m/s) is afforded from Figure 6, where the machined depth is plotted with respect to the number of pulses used to give linear
relationships. The fluences used to produce the samples machined with KrF excimer laser pulses immersed in filtered water were all within 3% of 578 mJ/cm². The measured fluences used to machined the samples using an immersing fluid of DI water were all within 2% of 561 mJ/cm². This 3% discrepancy in mean lasing fluence goes some way to explain some of the differences witnessed in the feature depths discussed previously. The etch rates given in the form of trend line gradients in Figure 6 show that the use of filtered water produced a mean increase in etch rate of 14.25 nm/pulse. This is a margin of 11.7% over the samples machined using DI water as a medium for closed thick film flowing liquid immersed ablation. Clearly, the entire 11.7% gain in etch rate cannot be attributed to the 3% advantage in fluence held by the filtered water samples. Furthermore, comparison of the calculated etch rates at each flow velocity showed that DI water produced a higher etch rate of 5.8 nm/pulse than filtered water only at the lowest flow velocity, 0.03 m/s. Filtered water produced an etch rate in excess of 15.7 nm/pulse greater than DI water at all other flow velocities.

Figure 7 plots the interpolated etch rates, shown graphically as linear trend line gradients in Figure 6, with respect to the flow velocities used to produce them for immersion ablation using DI and filtered water. Also included is a benchmark etch rate achieved using a similar laser fluence of 581 mJ/cm² in ambient air for comparison. There is good agreement between trends produced by both immersion mediums: etch rate generally increases with flow velocity. Excimer laser ablation of bisphenol A polycarbonate under closed thick film flowing DI water did not result in an etch rate greater than that achieved by excimer laser ablation in ambient air. Use of filtered water did result in an etch rate greater than that achieved in ambient air for both turbulent velocities tested for this work. The etch rate produced by laser ablation in DI water flowing at 3.70 m/s was 7.2 nm/pulse less effective than ablation in DI water flowing a 1.85 m/s. This supports the proposal [28] that an optimum flow velocity exists where the interaction of the flow with the ablation plume results in
distortion of the plume to reduce the beams traverse distance through the compressed plume. This action reduces the combined effects involved in laser beam attenuation whilst supporting the action of acoustic mechanism plume etching [33] by the intact but distorted ablation plume. At a sufficiently high velocity the plume was destroyed by the flow, resulting in the removal of the plume etching action but simultaneously providing increased access for the laser beam to the material surface. The minimal reduction in etch rate suggests the total etch rate is dominated by the action of laser etching.

**Flow – plume interaction states**

The close agreement of the samples machined under differing mediums is useful in support of the previously proposed [28, 36] set of flow-plume interaction states. The data described in Figure 4(a), Figure 4(b) and Figure 6 shows strong support for suspended debris that remains unmoved between pulses due to insufficient flow velocity, intercepting the following laser pulse. Increased laminar flow was sufficiently high to remove debris from above the feature between pulses, yet insufficient to distort the ablation plume during a pulse. The immersion of the ablation plume with liquid restricted the expansion of the plume, resulting in a plume of increased optical and physical density compared to that produced by ablation in ambient air. This compressed plume attenuated the laser beam producing the plume, reducing the beam energy that arrived at the material and as a result, reduced the laser etching efficiency. Simultaneously, the compressed plume reduced the loss in etch efficacy by the action of plume etching [33]. This scenario is indicated in actuality for the 0.11 m/s results in Figure 4(a), 4(b) and Figure 6, where the etch threshold drops sharply and the ablation rate increases markedly respectively. Increased flow velocity to 1.85 m/s resulted in the production of an optimum measured etch rate in Figure 6, where the plume was distorted by the flowing filtered water, reducing the path length that the beam had to endure through the plume to reach the material surface. As a result, the losses to the beam due to the combined optical
attenuation effects were lower. In concert, the distorted, but still intact ablation plume was providing a plume etching contribution. This occurrence can also be identified by the dip in threshold fluence in Figure 4(a). Further increase to the flow velocity began to destroy the ablation plume, allowing maximum access for the beam to the material surface, removing the plume etching contribution. This combination of events reduced the total etch rate as indicated by the DI water plots in Figure 6 and the increase in threshold fluence for DI water in Figure 4(a). The close agreement of DI water and filtered water in all of these analysis techniques shows that the scenario described above is plausible.

Impact of flow velocity on debris deposition when using de ionized water immersion with comparison to filter water immersion

The use of closed flowing thick film filtered water as an immersing medium has been shown to be effective in the control of laser ablation generated particulate debris [2, 3]. Filtered water is an electrically conducting liquid due to the impurities contained within it [24]. This is important in terms of its impact on the adhesion properties of the particles suspended within it. Electrostatic interactions are significant in the long range attraction and contact interaction of particles [14, 16, 23].

Figure 8 is given to allow simple comparison between samples machined under closed film flowing liquid immersion: 4 samples using filtered water and 4 others using DI water. The samples are paired by flow velocity. The results in Figure 8 show the number of particles of three specific size ranges (0 to 0.3375, 1.913 to 3.713 and 28.91 to 57.71 µm²) discretely by use of contour plots for four flow velocities: 0.03, 0.11, 1.85 and 3.70 m/s. Each group of result plots have been generated by taking the mean average of the deposition frequency of three separate machined samples to guard against experimental inaccuracy. The full results are split into 10 debris particle size classes. Here the smallest, middling and second largest particle size frequency plots are given as they are representative of findings of this work and
allow simple interpretation of the general trend of deposition across the entire surface. Frequency gradient legends are given for each set of results. These were calibrated to the maximum debris population registered for an average sample machined under each condition across all size classes. The legend is useful in assessing the magnitude of population of debris produced by each machining media.

Figures 8(a) and 8(b) demonstrate the similarity of the deposition trend of the debris at turbulent flow velocities in both mediums. In both filtered water and DI water samples the vast majority of debris was deposited down stream of the feature. Also, the characteristic localized high population density areas of the debris were visible in the turbulent flow DI water immersion results; thus, supporting the findings of previous work which explained that the high density deposition areas were the result of flow turbulence [3].

Laminar flow machined samples displayed for comparison in Figures 8(c) 8(d) also show clear similarity in deposition trend. Samples machined using laminar flows of DI water both demonstrated an even distribution of debris that was also evident on all of the filtered water machined samples. However, differences do exist: when machining using filtered water, only the lowest flow velocity, 0.03 m/s, showed evidence of significant deposition upstream of the feature; whereas the samples machined under DI water at both 0.03 and 0.12 m/s showed significant debris deposition upstream of the feature. This result supports the adhesion theory alluded to above and in the literature [12]. DI water does not conduct the larger electrostatic charge of the substrate to the machined particles as effectively as filtered water. This caused debris suspended by DI water to experience greater long range attraction forces towards the substrate surface, resulting in greater total debris population and frequency of upstream deposition. More debris is attracted to the sample surface when using the insulating DI water as opposed to the conducting filtered water.
Inspection of the frequency legends presented Figure 8 further supports the adhesion theory described above. DI water immersion machined samples show markedly larger magnitudes of deposition frequency than the samples machined under filtered water immersion. Conduction of the electrostatic charge of a large particle to a smaller neighbouring particle would set up a Yukawa repulsion between the two. Therefore the use of a non-conducting fluid should result in an increase in particle deposition when compared to the results demonstrated by filtered water, which has a typical conductivity of 0.005 to 0.05 S/m. DI water is a significantly better insulator, with a minimum conductivity of $1 \times 10^{-7}$ S/m because DI water has significantly fewer charge carriers available in the form of mineral ions from impurities [24].

The frequency gradient legends in Figure 8 reveal that the real volume of small debris produced was larger when machining under DI water than when machining under filtered water. The contour plots given for all flow velocities in Figure 8 show the proportion of medium size debris was much lower than the proportion of small size debris produced by KrF excimer laser ablation under closed thick film flowing DI water than features machined under closed thick film flowing filtered water. Large debris was less common when machining using DI water. A more detailed inspection of this can be given by using plot of debris frequency against debris size for multiple flow velocities, which is presented in Figure 9.

Figure 9 describes filtered water results as greyscale filled area plots behind line plots that show the frequencies of debris produced by ablation under DI water. This graph shows that the typical size of debris produced during immersed KrF excimer laser ablation is flow velocity and medium dependent. The images displayed in Figure 8 are distorted for reader interpretation (the greatly increased volume of small debris produced by DI water immersion meant that the range of shades available to indicate the volume of debris produced using filtered water was small and therefore difficult to interpret by eye). The large deposition of small debris in DI water can be directly credited to the dominating action of the electrostatic
insulation provided by the DI water compared to that of filtered water causing the smaller debris particles be attracted to the sample substrate. Moreover, the second lowest flow velocity returned the largest debris population of small debris in the same manner as filtered water. Dowding and Lawrence [3] state that this occurrence was caused by interaction between the slow moving suspended debris and the laser beam of the following pulse resulting in decreased laser fluence at the feature (and therefore a lower etch rate – which has been borne out, above) and a smaller volume of debris surviving at the lowest flow velocity than those above it. The volume of debris produced changes back to a more flow proportional relationship for all debris larger than 1.103 \( \mu \text{m}^2 \), the lowest flow velocity produced the largest volume of debris and the highest flow velocity the smallest volume of debris. This is a result in contradiction to that produced by filtered water; the increased electrostatic attraction between debris and a surface is size dependant: the force generated by electrostatic interaction dominated small debris but not larger species - where a flow drag dependency dominated. Capillary forces can be considered nil: the immersing liquid removes any meniscus between particles and the sample substrate. Van der Waals forces are halved by the presence of water. This implies the occurrence of electrostatic colloidal interactions, where multiple small debris particles combine to produce medium size particles. These are inversely proportional to drag [16] and therefore flow velocity. This is a situation that can be explained by stress induced on the particles by eddies in turbulent flow acting to break up medium and large colloids. Smaller colloids are less susceptible because of their smaller surface area for drag to be applied and the higher relative action of the adhesion forces on their constituent particles. Particles of medium size were proportionally markedly less common on DI water immersed samples than on samples machined in filtered water. Once again this can be explained by the action of the electrostatic insulation provided by the DI water, the particles are attracted to the sample surface more, which has a comparatively
large and typically opposite [16] electrostatic charge compared to the other surrounding suspended particles which typically have the same charge [23]. Thus, particles were motivated to repel each other. The total debris volume generated by flow velocities of 0.12, 1.85 and 3.70 m/s were separated in frequency by only 30% of the lowest population, compared to a 3300% range of flow velocity. This could be the result of a combination of electrostatic and Van der Waals forces on the remaining minority of particles, which formed large, strong colloids that were effected little by increasing turbulence.

Relationship between debris size and deposition displacement

Distribution skew can be used as a technique to measure the displacement of a typical particle of a specific debris size. A positive skew value is the result of a distribution where a greater proportion of the population lies between the mean and infinity, as shown in Figure 10(a); a negative skew value is the result of a distribution where a greater proportion of the population lies between the origin and the mean, as shown in Figure 10(b). A large skew value denotes a strong population ‘lean’, where the mean is further from the origin.

In Figure 10(b) a plot of the magnitude of skew for samples immersed by filtered water are plotted as the filled areas behind the line plots for DI water immersed samples to allow the simple comparison of the two. All of the skew values measured are positive, indicating that the majority of debris lies between the mean position and infinity. The magnitude of skew is lower when using DI water as an immersion medium for KrF excimer laser ablation, denoting lower displacement of the debris from the machined feature in flowing DI water than is achieved in filtered water. The plots indicate medium sized debris had the lowest typical displacement from the feature. Small debris had a larger typical displacement and the largest debris had the largest typical displacement. This result is inline with that of the filtered water, providing good support for previous findings in filtered water [3]. The fact that typical debris displacements are lower when using DI water gives more support for the proposal that the
electrostatic insulation increased the electrostatic attraction between debris and the sample surface resulting in earlier debris deposition from the fluid flow.

Inspection of Figure 10(c) allows quantifiable analysis of the same trends. Indeed, the smallest debris, of 0.66 $\mu$m$^2$, were consistently deposited approximately 230 $\mu$m downstream. Debris of cross sectional areas ranging from 1.10 to 3.75 $\mu$m$^2$, had lower displacement: less than 180 $\mu$m. This supports the adhesion theory cited above, where the attraction forces acting on the smallest debris were dominated more by flow drag. The displacement of debris over 3.75 $\mu$m$^2$ increases steadily for the debris generated in turbulent flow velocity DI water in the same way as was the case for 1.85 m/s filtered water immersion. The laminar flow DI water samples returned unstable results much like the laminar flow velocity filtered water samples. This result is inline with the idea that drag imparted on large debris particles increasingly dominates the adhesion forces that were proportional to size. The multiple vectors generated by eddies on the particles were small when compared to the general vector of the overall flow. The slow liquid volume refresh rate generated at laminar flow velocities meant the interruption and distortion of the flow by the laser generated plume was significant: the flow vectors generated became unstable, resulting in the high variance of debris deposition recorded.

Conclusions:
The use of differing mediums for closed thick film flowing liquid ablation by KrF excimer laser has impacted a number of laser machining factors markedly. Conduction of electrostatic charge through the medium has repeatedly been identified as the critical variation between filtered water and DI water, causing the variation between the results presented.

Measurement of the laser ablation threshold fluence is one method of defining the efficiency of a machining technique with respect to the laser energy supplied. The use of DI water immersed ablation was measured to have an ablation threshold that was 4.3% higher than that
of filtered water immersed ablation and 8.6% greater than that of laser machining in ambient air. In both mediums 0.03 m/s was found to produce the most unstable depth-fluence relationship. The plots generated describing etch depth achieved by a measured fluence were similar for both mediums tested, suggesting the trends described were reliable. Inspection of threshold dependency on pulse fluence magnitude showed a close agreement between the result produced by both mediums. This further demonstrates the accuracy of this work. The assertion that the efficiency of low fluence machining is deteriorated by the use of immersion ablation was maintained by the DI water results and further confirms the proposal that low flow velocity coupled with high laser pulse frequency results in high attenuation of the beam. This impacts low fluence machining more than high fluence machining.

Etch depths achieved in DI water and filtered water at flow velocities of 0.03, 0.11, 1.85 and 3.70 m/s were compared. In DI water flowing at 0.03 m/s etch depths achieved were greater than that recorded in filtered water flowing at the same velocity. However, as flow velocity increased this trend was reversed and filtered water produced markedly greater etch depths over 3, 6, 12, 60, 120 and 480 laser pulses than DI water. Analysis of this observation is possible by plotting the etch depth achieved by 0.03, 0.11, 1.85 and 3.70 m/s flow by using 3, 6, 12, 60 and 120 laser pulses in both DI and filtered water medium closed thick film flowing liquid immersed KrF excimer laser ablation. A 3% discrepancy was measured between the mean fluence used for machining the samples in each medium; however, this cannot explain the 11.7% etch rate variance between filtered water and DI water. The etch rate achieved by laser immersed machining in DI water did not exceed that produced by excimer laser machining in ambient air and was 11.2% lower than the mean ablation rate produced by immersion using filtered water across all flow velocities, which did produce greater etch rates than ablation in ambient air at 1.85 and 3.70 m/s. Furthermore, the trends of both mediums were similar in shape, supporting the theory of flow-plume interaction, where insufficient
liquid volume replacement above the feature coupled with high laser pulse frequency caused large losses in beam fluence. Laminar flow velocity that remained large enough to avoid fluid volume refresh problems confined the plume without distorting its shape, resulting in maximum traverse distance for the beam to endure through the optically dense compressed ablation plume. An optimum flow velocity existed above this, between 1.85 and 3.70 m/s, where the ablation plume was distorted, reducing the traverse distance of the beam through the plume whilst still providing a plume etching component. Above this velocity (3.70 m/s) flow velocity was so great it destroyed the plume before plume etching could occur, leaving virtually unobstructed access for the beam to the material.

Observation and discrete analysis of the debris deposition showed that the total volume of debris deposited by closed thick film flowing DI water immersed KrF excimer laser ablation was significantly greater than that by immersion using filtered water. This can be directly attributed to larger electrostatic attraction in DI water. Also, the proportion of medium sized debris generated using DI water was markedly larger for turbulent flow velocities. This can again be credited to the inability of DI water to support Yukawa repulsion - unlike filtered water which is a better conductor. This offers measurable proof for the explanations of beam obstruction by colloidal debris. The high density deposition areas downstream of the feature characteristic in turbulent velocity flows were evident with great similarity in geometry and size in both mediums used, supporting the proposal that these deposition areas were dictated by turbulence. Analysis of debris deposition displacement with respect to debris size using 0.03, 0.11 and 1.85 m/s flows showed that debris was retained in DI water flows over shorter displacements than in filtered water. Again, the action of electrostatic attraction can be cited for this. Medium sized debris was deposited with the least displacement downstream of the feature, offering further confirmation of the controlling balance of force on debris in the
flows between drag and adhesion. This tipped at 1.10 µm² from adhesion forces having the controlling stake to fluid drag dominating.
References:


Figure 1: A comparison of beam fluence generated at various attenuator positions recorded for both the filtered water samples and the ambient air samples.

Figure 2(a): the closed immersion ablation assembly: 1) sample; 2) base plate; 3) sample clamp and flow chamber spacer; 4) U.V. grade fused silica window for laser beam; 5) window clamp; 6) clamping bolts that squeeze components together. Figure 2(b): the fluid supply unit: 1) source water; 2) filtering; 3) filtered water storage; 4) centrifugal pump; 5) flow-rate control valve; 6) high pressure flow-rate controlled filtered water outlet to flow-rate ablation chamber.

Figure 3: Ablation depth against number of pulses to determine etching threshold fluence for closed thick film flowing filtered and DI water.

Figure 4: Fluence against flow velocity to give etching threshold fluence under closed thick film flowing filter and DI water for (a) low etch threshold fluence regime ablating, (b) average etch threshold fluence regime ablating and (c) high etch threshold fluence regime ablating.

Figure 5: Comparative 3D bar chart describing etch depth achieved in either medium by ‘n’ pulses using 0.03, 0.11, 1.85 and 3.70 m/s, with flow velocity increasing into the page.

Figure 6: Ablation depth against number of pulses to determine ablation rate for four flow velocities: 0.06, 0.11, 1.85 and 3.70 m/s, under closed thick film flowing filtered and DI water.
Figure 7: Measured ablation rate against the flow velocity for KrF excimer laser ablation in ambient air, under closed thick film flowing filtered water immersion and closed thick film flowing DI water immersion.

Figure 8: Discrete contour plots of particle density with respect to size class and flow velocity for closed thick film flowing filtered and DI water.

Figure 9: Frequency of debris particles against particle size to describe the total particle population of samples produced under closed thick film flowing filtered water immersion ablation at various flow velocities for filtered and DI water.

Figure 10(a): Schematic description of the typical distribution of (a(i)) positive skew, (a(ii)) negative skew, (b) the magnitude of skew with respect to debris size and (c) modal displacement from the machined feature with respect to size.
Figure 1
Figure 2

(a)

(b)
Figure 3

- $y = 6.2331x - 29.639$
- $y = 6.5345x - 31.474$
- $y = 6.0679x - 29.013$
- $y = 3.7001x - 17.882$
- $y = 6.3084x - 29.972$
- $y = 6.3028x - 30.1$
- $y = 5.7508x - 27.8$
- $y = 3.2602x - 15.049$

**Ln Fluence (mJ)**

**Feature Depth (μm)**

- DI 3.70 m/s
- DI 0.12 m/s
- Filter 3.70 m/s
- Filter 0.11 m/s
- DI 3.70 m/s
- DI 0.12 m/s
- Filter 3.70 m/s
- Filter 0.11 m/s

- DI water
- Filtered water
Figure 4

- Filtered water
- Ambient air
- DI water
Figure 5

Depth (µm)

Number of pulses and liquid type
Figure 6

<table>
<thead>
<tr>
<th>Feature Depth (μm)</th>
<th>Number of Pulses</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DI WATER</td>
</tr>
<tr>
<td>0.11 m/s</td>
<td>y = 0.118x + 0.3118</td>
</tr>
<tr>
<td>0.12 m/s</td>
<td>y = 0.1411x - 0.053</td>
</tr>
<tr>
<td>0.03 m/s</td>
<td>y = 0.095x + 0.4487</td>
</tr>
<tr>
<td>0.03 m/s</td>
<td>y = 0.0892x + 0.41</td>
</tr>
<tr>
<td>3.70 m/s</td>
<td>y = 0.1328x + 0.2531</td>
</tr>
<tr>
<td>1.85 m/s</td>
<td>y = 0.14x + 0.1488</td>
</tr>
<tr>
<td>0.12 m/s</td>
<td>y = 0.1411x - 0.053</td>
</tr>
<tr>
<td>0.03 m/s</td>
<td>y = 0.095x + 0.4487</td>
</tr>
<tr>
<td>0.03 m/s</td>
<td>y = 0.0892x + 0.41</td>
</tr>
</tbody>
</table>
Figure 7

Flow Velocity (m/s) vs. Ablation Rate (nm/pulse) for different conditions:
- Filtered water
- Ambient air
- DI water
Figure 8

\[
\begin{array}{c|c|c|c}
& 0 \leq A \leq 0.3375 & 1.913 \leq A \leq 3.713 & 28.91 < A < 57.71 \\
\hline
(a) & 0.0333 (l/s) & = & 3.70 (m/s) \\
\hline
(b) & 0.0167 (l/s) & = & 1.85 (m/s) \\
\hline
(c) & 0.0010 (l/s) & = & 0.11 (m/s) \\
\hline
(d) & 0.00025 (l/s) & = & 0.03 (m/s) \\
\end{array}
\]
Figure 10

(a)

(b)

(c)