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Investigation on polycarbonate surface wetting property with femtosecond laser irradiation and ultrasonic treatment

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Abstract

This study investigated the use of ultrashort femtosecond laser pulses to induce either hydrophilic or hydrophobic surfaces on polycarbonate (PC). It has been observed that controlled modification of wettability could be achieved over a wide range of water contact angle (WCA) from below 5° to above 150°. It has been shown that the pulse energy fluence and total energy deposition onto PC are the important factors in determining the laser-PC interaction, and therefore the different level of wettability on PC surface. XPS-spectra measurement indicates that the modification was caused dominantly by laser induced chemical bond changes. The changes in surface morphology may not noticeably contribute to the surface wettability. The stability investigation on the wetting property of laser modified surfaces has shown that ultrasonication in DI water or in ethanol led to decrease in hydrophobicity, and the decrease was more pronounced for super-hydrophobic surfaces. The level of hydrophilicity decreased as well for the laser induced hydrophilic surfaces. However, the change in hydrophobicity by post-treatment was not significant. The results would be useful in microfluidic chip design and fabrication with controlled surface wetting properties.

Introduction

Wettability is one of the most important aspects of microfluidic applications as it significantly influences the reagent flow behaviour in microfluidic channels, ease of adhesion of cells, optical signal detection and protein unselective adsorption. In order to control the wettability of the polymer surface, surface treatment methods are employed. The methods can be categorized into two main groups: modification of the morphology, roughness and the chemical composition of the surface; and generation of an additional thin layer on the polymer surface. Since the polymer properties typically depend on the surface morphology and chemical composition, it is

important to make sure that the properties of the modified surface do not change during treatment. The thickness of the additional layer is preferred to be in nm scale, because a thick layer can affect the good properties of the bulk material. However, it is challenging to produce the expected ideal thickness practically.

Many researchers have been studying different modification methods to control the surface wettability of various materials, such as preparation of super-hydrophobic surface on stainless steel [1], wettability modification of Rare Earth Mg Alloy for bioapplication [2,3], hydrophobic surface on PDMS for increasing or reducing adhesive force [4], hydrophilicity modification of polycarbonate [5], wettability modification of polystyrene surface [6], Surface Wettability Modification of Cyclic Olefin [7]. Polycarbonate (PC), which has similar chemical properties to but higher in strength than polymethyl methacrylate (PMMA), is a widely used substrate, for the manufacturing of various microfluidic devices. Not only PC is biocompatible, it also has excellent optical transparency; therefore, it has been one of the most commonly used materials for various microfluidic applications. Modification of PC surface wettability remains an important research topic. Most of the techniques introduced are only able to control the wettability of PC in only half of the wettability spectrum – either more hydrophilic or hydrophobic, but not both ways. These methods lack flexibility to modify pristine PC in a wide range of WCA from high hydrophilicity to high hydrophobicity [8].

Laser irradiation is one promising method to modify surface wettability in selected areas with significant process flexibility. It has been reported that high power CO₂ laser (10.6 μm) ablation can increase the WCA from 68.4° of pristine surface to 125° after laser ablation [9]. The surface obtained is hydrophobic. Nanosecond (ns) Nd:YAG laser (1.064 μm) ablation can reduce the WCA from 70° of pristine surface to

1 40° after laser irradiation [10]. The surface obtained
2 is hydrophilic. Nanosecond UV excimer laser (193
3 nm) can modify the WCA in a range of about 67-150°
4 after laser irradiation [11]. The surface wetting
5 property achieved is hydrophobic, although the
6 hydrophobicity is in wide level compared to CO₂
7 laser ablation. Lasagni et al reported that WCA can
8 be modified from 87.8° to 120° through 263nm laser
9 surface interference patterning [12]. The surface
10 wetting property achieved is still hydrophobic.
11 Riveiro et al. has well summarized the status on PC
12 surface wetting property modification with laser
13 surface irradiation recently [13]. So far, the surface
14 wettability achieved under various laser conditions is
15 in a higher WCA range, the surface is hydrophobic.
16 However, in practical application such as
17 manufacturing of microfluidics, hydrophilic surface
18 and super-hydrophilic surface are often required for
19 liquid joining or separation in microfluidic channels.
20 Furthermore, the stability of the wettability of the
21 modified surfaces during liquid flowing is also very
22 important in order to get constant and accurate flow
23 rate in microfluidic channels. Unfortunately, so far
24 the study on these areas haven't been found in the
25 current literatures.

26 It is understandable that the different wetting
27 behaviour is caused by the different laser-material
28 interactions. Under a linear absorption mechanism,
29 PC absorbs UV excimer laser beams, but transmits
30 Nd:YAG laser beams. The long wavelengths CO₂
31 and Nd:YAG lasers result in mainly a photothermal
32 process. In contrast, the shorter wavelength UV
33 excimer laser has high photon energy. In addition to
34 photothermal effect, it causes photochemical
35 decomposition. In our previous studies on
36 femtosecond laser ablation of PMMA, it has been
37 found that as ultrashort laser pulses have ultrahigh
38 peak power resulting in a nonlinear absorption
39 mechanism namely multiple photon absorption with
40 little photothermal effect, various surface
41 modification phenomena can be expected such as
42 chemical degradation, chemical bond modification,
43 surface morphology and roughness modification
44 under laser ablation [14, 15]. A wide range of WCA
45 on PMMA surfaces has been achieved through
46 femtosecond laser ablation of PMMA for liquid
47 sample separation in different microfluidic channels
48 [16].

49 Considering the practical application in microfluidics
50 manufacturing, a wide range of WCA, from highly
51 hydrophilic to highly hydrophobic, is normally
52 required. Furthermore, stability of the wetting
53 behaviour of the channel surface is critical during the
54 flowing of the liquid samples. Therefore, in this

55 study, wettability of the polycarbonate (PC) surface
56 was investigated through surface modification by
57 femtosecond laser irradiation under varied laser
58 conditions and post ultrasonic treatment on the laser
59 modified surfaces.

60 Experimental

61 Commercially available 1.8 mm thick PC substrate
62 was irradiated by a fs laser (CPA2001 Clark-MXR,
63 wavelength 775 nm, pulse width 150 fs and M² 1.5).
64 At 1 kHz repetition rate and 300 mW attenuated
65 power, the laser beam was focused by a 106.5 mm
66 focal lens which produced a focal spot radius about
67 15 µm with laser fluence of 42.46 J/cm². Through a
68 galvanometer scanner, 5 mm by 5 mm surface area
69 was horizontally raster-scanned at a line shifting
70 pitch of 25 µm which produced a line overlapping of
71 16.67% at laser spot size of 30 µm. The scanning
72 speed was varied from 0.5 mm/s to 2060 mm/s which
73 produced a varied pulse overlapping for different
74 levels of surface irradiation. Furthermore, the sample
75 surface was modified by varying laser fluence
76 through adjusting the defocusing distance Z, i.e. the
77 distance between the PC surface and the laser focal
78 plane, with positive or negative Z indicating that the
79 focal plane is above or below respectively to the
80 sample surface.

81 The loose debris on the laser-modified sample was
82 removed by either dry air or nitrogen blowing. It was
83 confirmed that such post-processing by either gases
84 has no effect on the measurement of WCA. To
85 characterize surface wettability, WCA (variation
86 within ±1°) was measured in room temperature and
87 ambient air conditions (relative humidity 60%) using
88 VCA Optima XE, by releasing a 0.5 µl droplet onto
89 the surface. Three measurements per sample were
90 performed to determine the WCA after laser
91 irradiation in the same day. Optical images of the
92 modified surfaces were taken under bright field with
93 a MX51 Optical Microscope (Olympus, Japan).
94 Surface morphology of laser irradiated substrates was
95 characterized by using optical microscope.
96 Arithmetic average of absolute values (Ra) for 2D
97 measurement and arithmetic mean deviation of the
98 surface (Sa) for 3D measurement were examined
99 using a Stylus Profilometer (Taylor-Hobson Form
100 Talysurf Series 2).

101 Post treatments, ultrasonication in DI water and/or
102 ethanol, on the laser irradiated samples were carried
103 out for 3 minutes to analyze the stability of modified
104 surfaces. The purity of the ethanol was 99.5% (Green
105 Tropic product Pte Ltd, Singapore). Ultrasonication
106 was carried out under frequency of 50 Hz and power

of 100 watts were used for all post-treated samples. The post treated samples were flushed with nitrogen gas prior to conducting WCA measurement in the same day. PC samples modified to exhibit super-hydrophobic, hydrophobic, hydrophilic, and super-hydrophilic conditions were selected for post treatment study.

Results and Discussion

Effect of Scanning Speed on WCA

Figure 1 shows the changes of WCA with varied scanning speeds. According to the results shown in the graph, the WCA of the pristine PC surface, was 82°. At lower scanning speeds investigated (0.5 mm/s and 1 mm/s), the measurements of WCA show that the surfaces were nearly non-wetting. The water drop dispensed from the VCA Optima XE machine could not stick easily onto the low scanning speed irradiated surface. The difficulty of contacting the water droplet made it difficult to measure the WCA accurately. However, at higher scanning speeds, all hydrophobic or hydrophilic surfaces under the same equipment measuring conditions could be easily measured as the water droplet could stick on the laser modified surfaces.

Figure 1. Effect of scanning speed on water contact angle under laser pulse energy fluence of 42.46 J/cm², power of 300 mW and focus placed on the sample top surface."

During measurement of WCA, the sample was brought upward to contact the water droplet at the tip of the syringe needle, and brought downward by controlling the up and down movement of the stage. The syringe needle was stationary and only the stage was moving up or down. For highly hydrophobic samples, it was found that the water droplet repelled

the sample surface and could not stick to the sample surface. The stage up and down procedure was carried out 3 times of each sample. Figure 2 shows the detailed stage movement of one complete cycle of up and down procedure during measurement of WCA for highly hydrophobic surface. According to the most common definitions, a surface can be described as super-hydrophobic, when its water contact angle (WCA) is higher than 150° [17]. The primary prerequisite for a material or surface to be called super-hydrophilic (super-wetting) is that water (liquid) spreads on it completely (to a nearly zero apparent contact angle; not measurable accurately by optical systems, <5-10°) at material/product functioning conditions [17]. Thus the surfaces irradiated at slow speeds of 0.5 and 1 mm/s were considered to be super-hydrophobic surfaces as shown in Figure 2 that the water droplet cannot be dropped down on these surfaces.

Figure 2. Unable to drop down the water droplet to PC surfaces during measuring of WCA on highly hydrophobic surfaces irradiated at 0.5 mm/s and 1 mm/s with focused beam under power of 300 mW.

In order to determine the value of WCA, a hand pipette was employed, the water droplet could be dropped on the sample surface manually. A similar volume of DI water (0.5µl) was pipetted onto the same slow scanning speed irradiated sample using a precision (0.1 to 1µl) hand pipette (Transferpette S D-1, Brand, Germany), and WCA of 144.4° was obtained. It may not be reasonable to roll out the external force from hand dropping and the self-weight of water droplet. Furthermore, in order to compare all the samples under the same equipment measuring conditions with consistency, the WCA of 144.4° measured by dispensing the water drop via hand pipette was considered only as an indicative result. The samples of low scanning speeds 0.5 mm/s and 1 mm/s, which was not possible to measure using the VCA Optima XE machine were considered to be greater than the measured value of 150° as in Figure 1. The reasons of the estimation of WCA to be greater than 150° will be explained in effect of focal distance on WCA. There, WCA of 149.7° was measured when changing the laser irradiation focus.

When scanning speed was greater than 1 mm/s, the water drop could easily stick to the sample surface, therefore, the actual WCA of the modified surface could be measured easily. It was found that the highly hydrophobic surface conditions decreased sharply and the surface was transformed to hydrophilic with increasing scanning speed. The WCA was measured to be 44.8° at the scanning speed of 2 mm/s and kept reducing with increasing scanning speed. At the scanning speed of 25 mm/s, WCA was less than 5°, which indicated the highly hydrophilic surface. The WCA maintained to be less than 5° until the scanning speed of 55 mm/s which was shown in Figure 1. Beyond 55 mm/s, the hydrophilicity slowly decreased with respect to increased scanning speed.

Since the WCA of raw PC was around 82°, the wettability of almost non-modified surface, which can be achieved when the scanning speed was extremely high, was expected to be around 82°. Therefore, in order to obtain the expected profile of wettability, the WCA of surface, which was modified with scanning speed up to 2060 mm/s, was examined. The maximum water contact angle achieved was 65°, which was still less than WCA of non-treated surface within the investigation range, up to scanning speed of 2060 mm/s. From scanning speed 200 mm/s onwards, the changes of WCA were very slight although the scanning speed was varied significantly. For measurement of highly/super hydrophilic samples, at the instance when the water droplet contacted the surface modified PC, it spread immediately. Most of the WCA of samples less than 10°, were very difficult to measure as the water spread to the entire surface, and sometimes even across the boundary of the microscopic viewed area. It could be barely seen the angle of water droplet to measure, which were shown in Figure 3.

Figure 3. Measurement of WCA on highly hydrophilic surfaces (25 mm/s to 55 mm/s)

Figure 4 shows the morphologies of the surfaces irradiated under various speeds. The surface morphology observed under optical microscope for

scanning speed from 0.5 mm/s to about 60 mm/s were similar and the entire surface irradiated was fully modified. When the scanning speed was exceeding 60 mm/s, the sample surface was selectively modified instead of the entire surface modification. The pulse overlapping was getting less, i.e. the distance between laser spots was getting larger with increasing the laser scanning speed during every single line scan. The shifting pitch between lines was kept to be constant at 25 μm. The reason for achieving various patterns was due to the different pulse overlap level and the increased distance between laser spots with increasing of the scanning speed during every single line scan.

Figure 4 Morphologies of the surfaces under varied speed showing the localized, selectively modification with isolated laser spots at higher speed instead of the overlapped spots at slow speed.

At slow speed, the laser pulse was overlapped. Following the equation shown below, the pulse overlapping number can be calculated.

$$\text{Pulse number} = \left(\frac{\text{Spot diameter (30}\mu\text{m)}}{\text{Scanning speed (mm/s)}} \right) \times \text{Frequency (1KHz)}$$

At high speed, the laser pulse was isolated. The isolated pitch between two pulses can be calculated with the equations shown below:

$$\text{Spot to spot distance (mm)} = \frac{\text{Speed (mm/s)}}{\text{Frequency (1/s)}}$$

and

$$\text{Spot overlapping} = \frac{(\text{Spot } \emptyset - \text{Spot to spot distance})}{\text{Spot } \emptyset}$$

The calculated pulse number and pulse overlapping results were summarized in Table 1. Clearly, the

Table 1 shows that at slow speed, when speed was less than 30 mm/s, the laser pulse was overlapped. The range of pulse overlapping was calculated to be from 60 to 1 for speed from 0.5 mm/s to 30 mm/s. The entire sample surface was modified by the overlapped pulses. Laser energy was increasingly deposited to the PC surfaces with the increase in pulse number. The level of the modification of PC surface was high, which produced high values of WCA. At high speed, when speed was exceeding 30 mm/s, the laser pulse was isolated. The sample surface was selectively, localized, modified by the separated individual spots. The isolated pitch between two pulses was from 31 μm to 2.06 μm for speed from 31 mm/s to 2060 mm/s. Laser energy was decreasingly deposited to the PC surfaces with the decrease in pulse number at increased scanning speed. The level of the modification of PC surface was reduced significantly, which produced low values of WCA. Therefore, the value of WCA can be flexibly controlled through controlling of the pulse energy deposition and thus the PC surface modification level. This would provide a very flexible method to modify the surface wettability of the channels either highly hydrophilic or hydrophobic in manufacturing of the microfluidics.

Table 1 Pulse number and its overlapping at different scanning speed.

Speed, mm/s	Pulse number	Spot/pulse overlapping	Total energy, J/cm ²	WCA
0.5	60	Several tens pulses	2547.6	>150° /Can't drop
1	30		1273.8	>150° /Can't drop
2	15	10 to 20	636.9	44.8°
3→10	10→3	A few pulses	424.6→127.38	17° - 26.2°
11→30	2.73→1		115.8→42.46	<5°
31→60	Isolated, (31→60 μm)		41.09→21.23	
61→300	Isolated (61→300 μm)		20.88→4.25	16.6° - 50°
305→2060	Highly isolated (0.305→2.06mm)		4.18→0.618	50° - 65.9°

29

30 Changes of WCA with Defocusing Distance

31 The defocusing distance was varied from +8.5 mm to
32 -8.5 mm, i.e. the laser focus was adjusted to be above
33 up to +8.5 mm or below the sample surface up to -8.5

34 mm. Two scanning speeds, 2mm/s and 5mm/s, which
35 produced hydrophilic surfaces when laser focus was
36 placed on the sample top surface at the constant laser
37 power of 300 mW and shift pitch of 25 μm as shown
38 in Figure 1 and Table 1, were used for investigation
39 of the effect of defocusing distance on the change of
40 WCA.

41 Super-hydrophobic surfaces, WCA >150°, was
42 achieved at scanning speed of 2 mm/s and 5 mm/s
43 when the defocusing distance was adjusted. Figure 5
44 is a plot of WCA of the irradiated surface and the
45 laser fluence against the defocusing distance. When
46 the laser focal plane was positioned on the sample top
47 surface, valid WCA could not be measured as the
48 water droplet spread rapidly across the surface with
49 boundary beyond the field of view of the microscope.
50 However, one could deduce that WCA approached 0°
51 indicating super-hydrophilicity. With an increased in
52 defocusing distance, WCA increased, indicating a
53 decrease of surface hydrophilicity.

54

55

56 Figure 5. WCA of the irradiated surface and the
57 laser fluence against the defocusing distance. Plot as
58 180° for un-dropped water droplets during WCA
59 measurements.

60 For scanning speed of 2 mm/s, until the defocusing
61 distance +1 mm, the water spread within 3 seconds
62 after it was dropped onto the modified sample
63 surface. At the defocusing distance +1.5 mm, the
64 hydrophilicity decreased to 54.2°. From defocusing
65 distance +2 mm to +3.5 mm, the wettability of the
66 surface was steeply changed to highly hydrophobic,
67 WCA >150° since the water could not be dispensed
68 on the surface. Although the stage was moved up and
69 down for 3 times for each sample of highly
70 hydrophobic surfaces, it was found that the modified
71 surface could not attract the water drop, and the water
72 droplet could not stick to the sample surface. But at
73 the defocusing distance +4.5 mm, the water could be
74 dropped easily onto the surface and the WCA was
75 measured as 150°. Therefore, it is considered that the

1 WCA of the surface which repelled the water droplet
2 would likely be greater than 150° . The hydrophobicity
3 kept decreasing until 85.9° at $+8.5$ mm.

4 When the laser focal plane was placed below the
5 sample top surface, the water droplet spreaded
6 quickly at defocusing distance -0.5 mm. Then, the
7 irradiated surface was suddenly transformed from
8 highly hydrophilic surface to highly hydrophobic
9 surface at defocusing distance -1 mm. From -1 mm
10 to -2.5 mm, the WCA of the sample surface was
11 greater than 150° , which was super-hydrophobic,
12 since water drop could not stick to the modified
13 surface. At the defocusing distance -3.5 mm, the
14 WCA was dropped from super-hydrophobic to
15 142.3° , and dropped to 76.8° at defocusing -8.5 mm.

16 For the scanning speed of 5 mm/s, the modified
17 surfaces were highly hydrophilic at defocusing
18 distance until $+1$ mm. At defocusing distance $+1.5$
19 mm, the WCA was increased to 32.2° . From that, the
20 modified surfaces steeply changed from hydrophilic
21 to hydrophobic s, the WCA was 141° at defocusing
22 distance $+2$ mm. the WCA was decreased with
23 increasing of the defocusing distance and it reached
24 88.9° at $+8.5$ mm. When the laser focal plane was
25 placed below the sample top surface, similar
26 changing trend in WCA was observed. The WCA
27 was increased with increasing the defocus negatively.
28 At defocusing focal distance -1 mm, the WCA was
29 considered greater than 150° as the water could not
30 stick the modified surface; and at -2.5 mm, the WCA
31 was 145° . Similar to the positive defocusing distance
32 profile, the WCA was dropped to 89.6° at defocusing
33 distance -8.5 mm.

34 It is noted that the WCA profile is not identically
35 symmetrical with respect to the defocusing distance.
36 There was a slight difference between positive
37 defocus and negative defocus for the WCA. Actually,
38 the WCA and defocusing distance were well
39 corresponded to each other with respect to the
40 symmetrical axis. The issue was that the symmetrical
41 axis was shifted to a positive defocusing distance.
42 Possibly, the reason could be attributed to that the
43 optics was misaligned in our laser beam focusing
44 system which distorted the laser focus. It may be also
45 possible that the sample was misplaced not to make
46 the laser focal plane precisely at the sample top
47 surface. Thus, the misalignment or misplacement
48 produced a different focal spot size on the sample
49 surface at an identical defocusing distance for the
50 positive defocus and negative defocus. Furthermore,
51 the possibility of a shielding effect of the plasma
52 plume observed over the area during laser irradiation

53 cannot be ruled out from the contribution to the
54 asymmetry of the defocusing distance.

55 When based on that the values of WCA obtained
56 were symmetric with respect to the defocusing
57 distance, i.e. similar values were obtained for the
58 same distance magnitude. For constant applied laser
59 power, the same defocusing distance (whether
60 positive or negative) will have the same laser fluence.
61 As the spot size was increased with increasing the
62 defocusing distance, the laser fluence was
63 accordingly decreased at a constant laser power, as
64 plotted in Figure 5. The laser flunces decreased
65 (either with positive or negative defocusing distance)
66 WCA increased. At high laser fluence range from
67 42.46 J/cm² to 25.32 J/cm² with defocusing distance
68 within ± 0.5 mm, hydrophilic surfaces were produced.
69 At low laser fluence range below 11.45 J/cm² with
70 defocusing distance out of the range of ± 1 mm
71 hydrophobic surfaces were produced. Only when the
72 fluence was below 0.37 J/cm² (i.e the magnitude of
73 the defocusing distance was 8 mm or more), WCA
74 decreased to a value similar to that of the pristine PC
75 surface without surface irradiation. This indicates
76 that the level of fluence is below the threshold to
77 cause any noticeable changes to the PC surface. Thus,
78 Fig. 5 indicates that the laser fluence is the key factor
79 in determining the value of WCA. The change in
80 WCA, and thus surface wetting characteristics, over
81 the range of fluence investigated was significant.

82 Figure 6 shows the 10 selected samples from
83 increasing the defocusing distance and decreasing the
84 defocusing distance, from $+8.5$ mm to -8.5 mm,
85 under scanning speed of 2 mm/s. The spot size
86 irradiated on the sample surface increased at
87 increasing the defocusing distance, accordingly,
88 which caused different laser fluence and pulse
89 overlapping at PC surfaces. The increase in spot sizes
90 deposited on the sample surface was more obvious at
91 defocusing distance above 4.5 mm. The spot size
92 modified at the surface was getting larger from
93 defocusing distance 6.5 mm. At the defocusing
94 distance 8.5 mm, the spot size deposited on the
95 sample surface was the biggest among them.
96 Therefore, their overlapped areas were significantly
97 enlarged accordingly.

98 The surface morphologies of the laser modified
99 surface were varied with beam scanning overlapped
100 areas. At the defocusing distance of 0.5 mm, the
101 modified surface was superhydrophilic with WCA
102 less than 5° . But, highly hydrophobic surfaces were
103 attained at the defocusing distance of 2.5 mm. The
104 hydrophobicity decreased by increasing overlapped
105 areas. The WCA at the defocusing distance of 8.5

1 mm was the lowest within the investigated range. The WCA, at the defocusing distance of 8.5 mm, was around 80°, close to pristine PC surface. This was achieved when the defocusing distance exceeded a threshold value, i.e., laser fluence exceeded a threshold value. Therefore, the different surface morphology was obtained at different laser defocusing distance. However, the surface morphology was similar at the same magnitude of the defocusing distance either positive or negative.

11

12

13 Figure 6 Different defocus producing different spot
14 size and laser fluence, thus different surface
15 morphology.

16

17 Effect of Roughness on WCA

18 Effect of surface roughness on wettability was one of
19 the important factors. The Sa values from three
20 dimensional measurement and Ra values from two
21 dimensional measurement were measured by Taylor
22 Hobson stylus profilometer. In order to cover the
23 whole range of experiments, six samples with
24 different wettability and scanning speeds were
25 selected for study out of 285 samples of varied laser
26 scanning speeds.

27 It has been found that surface roughness was different
28 due to the difference in scanning speed. From wide
29 WCA range, the super-hydrophobic surface with
30 WCA of greater than 150°, super-hydrophilic surface,
31 WCA of less than 5°, and hydrophilic surfaces, WCA
32 of 34.6°, 47°, and 66° were analyzed. The selected six
33 samples covered the wide range of scanning speeds:
34 0.5mm/s, 2 mm/s, 29 mm/s, 131 mm/s, 500 mm/s,
35 and 2060 mm/s. The relationship of surface
36 roughness and water contact angles of varied laser
37 scanning speeds was shown in Figure 7. The values
38 of Sa, Ra and WCA for a specific scanning speed

39 were grouped together with an ellipse for easy
40 identification.

41 According to Figure 7, the Sa for scanning speed of
42 0.5 mm/s was 6.47 μm and Ra was 5.46 μm. At the
43 speed of 2 mm/s, the surface Sa and Ra reduced to
44 3.08 μm and 3.00 μm respectively, which was about
45 50 percent from the roughness measurements of
46 scanning speed 0.5 mm/s.

47 From the scanning speed of 29 mm/s onwards, the
48 roughness indicators, both Sa and Ra decreased to
49 less than 1 μm. Figure 7 shows the hydrophilic
50 surfaces with low surface roughness modified by
51 higher scanning speed. The roughness was decreased
52 by increasing scanning speed and at the scanning
53 speed of 2060 mm/s, the Sa was as low as 0.19 μm
54 and Ra was 0.07 μm.

55 The slow scanning speed produced the high surface
56 roughness, which was due to the larger modified area
57 on the scanned sample surface, as shown in Figure 7.
58 It was because the laser with slower scanning speed
59 ablated more material at each modified unit area per
60 unit time. As for high scanning speed, the material
61 ablated per unit area was lesser and the overlap area
62 of laser shots was smaller, thus the surface roughness
63 was low.

64 The relationship between wettability and surface
65 roughness, it was observed that super-hydrophobic
66 surface, WCA of >150°, had very high surface
67 roughness, which was Sa 6.47 μm or Ra 5.46 μm.
68 Hydrophilic surfaces had low surface roughness,
69 compared to super-hydrophobic surface in this
70 experiment. Among hydrophilic surfaces, there were
71 slight differences in roughness values due to the
72 scanning speeds even for same surface WCA. For
73 instance, both scanning speeds 2 mm/s and 500 mm/s
74 produced the hydrophilic surfaces, WCA 44.8° and
75 47° respectively. Although both samples had
76 approximately same WCA, the Sa of the modified
77 surface with scanning speed 2 mm/s was 3.08 μm,
78 which was more than 10 times higher than 0.238 μm,
79 modified by scanning speed 500 mm/s. The Ra of
80 modified surface with scanning speed 2 mm/s was
81 3.0083 μm, which was about 20 times higher than
82 0.1543 μm, modified by scanning speed 500 mm/s.
83 The comparison of both surfaces modified with speed
84 2 mm/s and 500 mm/s are shown in Figure 7. The
85 results further again indicate that the WCA is
86 determined by the laser modification level. Different
87 surface morphology produced at different speed may
88 have similar WCA. At slow speed like 2 mm/s, the
89 whole PC surface area was modified by the
90 overlapped laser spots, which produced a rough

surface. At high speed like 500 mm/s, PC surface was selectively modified by the isolated laser spots, which produced a relatively smoother surface. Size of the modified surface area plays an important role to determine the WCA. Here, it may need to point out that the surface looks like polished for those surfaces which were modified at high speed by isolated spots in Figure 7. The morphology appeared as polished structure at high speed like 500 mm/s may come from the metallic tip of the stylus surface profiler meter during the 3D measurement, as the surface was modified by isolated spots and no polished structure was observed under optical microscope, as shown in Figure 7. So such polished structure was not produced by laser irradiation, which should have no contribution to the change of WCA.

It was because under the case of surface modification by separated spots (obtained by 500m/s in this comparison), the size of the total modified area on the surface determines the changes in WCA, i.e., the surface wettability. Although the laser scanning speed influenced the surface roughness, it is not reasonable to simply compare the influence of surface roughness on the changes of WCA because roughness did not fully contribute to the wetting characteristics. Nonetheless, Figure 7 shows that high surface roughness contributed to a high level of hydrophobicity when the whole virgin surface has been modified by laser ablation at a range of low scanning speeds. Naturally it is not surprising that at a high speed range when the entire virgin surface is not fully modified due to the less spot overlapping, the surface is smoother and the surface hydrophilicity increases with increasing of laser modification.

In order to further investigate the effects of surface roughness on the wetting behavior of laser modified surfaces, among the 22 defocusing samples, 4 of them which covers the half spectrum of WCA from highly hydrophobic to low hydrophobic were selected to be analysed. The profiles of analyzed surface roughness of hydrophobic surfaces at different defocus lengths (A: -1 mm, B: +2.5 mm, C: -3.5 mm, D: +5.5 mm) are shown in Table 2. According to the measured results, sample B and C had a more obvious ripple feature than sample A and D, whose ripple features were minimal. Sample A had the highest WCA and sample D had the lowest WCA among them. It indicates that the WCA of the surface was not only influenced by the surface roughness feature (or ripple) of the sample.

To compare sample A and C, sample C was irradiated at low fluence (larger defocus) and it had a surface with higher roughness than sample A which was

irradiated at high fluence. On the other hand, comparison of sample C and D, sample C was irradiated at high fluence and it had a surface with higher roughness than sample D which was irradiated at low fluence. The results show that surfaces with high roughness can be obtained under high laser fluence (smaller defocus) and also can be obtained under low laser fluence.

Figure 7 Changes of WCA and surface roughness with scanning speed indicating that different surface morphologies may have a similar WCA, and the size

of selectively modified area contributes to WCA under a defocusing distance 0 mm (focused beam) with a constant power of 300mW. Morphologies measured by stylus profilometer (left) and by optical microscope (right).

Table 2 also shows that the high WCA can be obtained under the condition of high surface roughness, as well as from low surface roughness. Therefore, the correlations between surface roughness and WCA were unclear according to the results in Table 2. As the laser focal distance used to irradiate the sample surfaces are increased in the order from A, B, C, to D, this indicates that the laser fluence could play the key role to determine the change in WCA.

Table 2 Surface roughness for samples modified at different laser defocuses.

Sample	Defocus, mm	Speed, mm/s	WCA	Sa, μm	Ra, μm
A	-1	5	$>150^\circ$	2.39	0.65
B	+2.5	5	149.7°	1.22	1.12
C	-3.5	5	132°	2.9	3.12
D	+5.5	5	110°	1.65	1.28
E	+0.5	2	5°	2.99	2.33
F	+3.5	2	$>150^\circ$	1.97	2.08

Table 2 also shows a comparison of the two surfaces among the 22 defocusing samples: highly hydrophilic surface, sample E (at focus +0.5 mm, high fluence) and highly hydrophobic surface, sample F (at focus +3.5 mm, meaning at low fluence). The difference of roughness (both Sa and Ra) and ripple features of the two surfaces was not significant (less than 3 μm) although the WCA and the laser fluence were quite different. Furthermore, it is noted that the surface roughness of the sample in Figure 7 was above 5 μm , while the surface roughness of the sample A and F was less than 3 μm . The similar surface wetting behaviour was obtained under the different surface roughness. This indicates that the surface, either hydrophilic or hydrophobic surface, is not determined solely by the surface roughness. Namely, the laser-induced surface chemical modification should play a more important role rather than the surface roughness. The surface wettability modification on PMMA using femtosecond laser irradiation is dominantly caused by laser induced chemical bond modification and not by a change in surface roughness [14]. The changes in WCA under

varied laser fluence might be due to the chemical modification of the laser irradiation to the surface.

Discussion on Mechanism of WCA Modification

In the reported studies, it has realized that oxygen-containing groups on polymer surfaces such as C–O, C=O and O–C=O, influenced the change of surface hydrophilicity [14-16, 18]. Literature shows that for the enhancement of the wettability of polymer surfaces due to the chemical bond modifications, for instance, plasma ion implantation, the concentration of polar groups or bonds determined the WCA of the surface.

C=O double bond is the main factor for hydrophilicity of polymer surfaces because the polarity of C=O bond is more intense than that of C–O bond [14]. As discussed in earlier sections, it has been determined that the surface morphology and the surface roughness did not fully contribute to the changes of WCA of laser irradiated surfaces. In order to analyze the detailed relationship between surface modification induced by the laser irradiation and the transformation of the surface wettability, it is necessary to determine the changes in chemical composition on the surface of both pristine and modified PC. This can be determined via X-ray photoelectron spectroscopy (XPS).

To gain an insight on the changes in surface wettability induced by laser irradiation, XPS analysis using a VG ESCALAB 220i-XL was employed to identify the chemical bonds. The O 1s XPS spectra from a raw PC sample and samples irradiated by laser at different conditions. To understand the photochemical process caused by the photodegradation [11, 19, 20], the C 1s XPS spectra of these three samples were measured. The deconvolution of the C 1s and O 1s XPS spectra allows identification of the variations of chemical bonds for polar and non-polar functional groups. The relative amount of the chemical bonds was summarized in Table 3. The level of laser energy deposition determines the degree and nature of photodegradation, which dictates the level of wettability [14]. Table 3 shows that high fluence produced the highest concentration of polar groups and the lowest concentration of non-polar group C1s C–C, indicating high hydrophilicity. In contrast, the sample surface subjected to low fluence has the highest concentration of non-polar group C1s C–C, and low total concentration of polar groups as compared to raw PC surface, indicating increased hydrophobicity. There could be a threshold in laser energy deposition to determine the surface water

contact angle whether hydrophilic or hydrophobic. WCA would be determined by not only laser fluence but also the scanning speed and laser spot size, as indicated in Figure 4. Thus, by controlling the laser energy deposition, controlled modification of WCA can be achieved by surface chemical changes to be either rich in polar groups or non-polar groups.

Table 3. Relative amount of oxygen / carbon functional groups, (At.%).

Sample			C	B	G	H
			Laser fluence 1.91 J/cm ²	Laser fluence 3.59 J/cm ²	Laser fluence 8.67 J/cm ²	Laser fluence 42.46 J/cm ²
	Chemical bond	Raw PC	Focus -3.5 mm	Focus +2.5 mm	Focus -1.5 mm	Focus 0 mm
			Speed 5 mm/s	Speed 5 mm/s	Speed 2 mm/s	Speed 35 mm/s
			WCA 132°	WCA 149.7°	WCA, Can't drop	WCA <5°
Non polar groups	C1s C-H / C-C	63.8	65.1	68.1	71.2	59.4
	C1s Pi-Pi*	1.5	2.4	1.7	0.8	1.7
	Sum	65.3	67.5	69.8	72.0	61.1
Polar groups	C1s C-O	11.7	13.4	12.4	13.7	18.8
	C1s O-(C=O)-O	-	-	-	-	3.6
	C1s O-C=O	0.7	-	-	-	-
	C1s C=O	5.7	4.5	3.4	1.8	-
	C1s C-O	11.7	13.4	12.4	13.7	18.8
	O1s O=C	16.6	14.6	14.4	12.5	9.0
	O1s O-C	-	-	-	-	7.5
	Sum	34.7	32.5	30.2	27.9	38.9

Stability Studies of the Modified Surface

After achieving the wide range of WCA on modified PC surface, it is important to determine the robustness or stability of the modification. A few methods can be used to perform the post treatment such as: time aging in different gases, thermal annealing, chemical wash and ultrasonication etc. In this study, ultrasonication with chemical washing was used to accomplish the stability study. The highly hydrophilic surfaces attained by controlling scanning speeds of the laser, and the highly hydrophobic surfaces and hydrophobic surfaces achieved by defocusing the focal distances, were selected to study the stability of wetting behavior.

The samples were immersed in the solution which was ethanol or DI water. The beaker or container which contained the solution with samples was placed in an ultrasonic bath and subjected to ultrasonic vibration for 3 minutes. The samples were dried by nitrogen after ultrasonication, before measurement of WCA, in order to remove the residuals of water, which may affect the results of WCA. The measurement of WCA was carried out before and after ultrasonication and the results were shown in Table 4. The samples were chosen based on the WCA of the laser modified surfaces in order to cover the wide range of hydrophobic surfaces. The samples B, and G to L, highly hydrophobic sample and low hydrophobic samples, were modified under low fluence by defocusing the focal distance from -1.5 mm to +5.5 mm. Sample H was modified by scanning speed 35 mm/s with focused beam. It shows that the super-hydrophobic surfaces and hydrophobic surfaces suffered a decrease in WCA after subjected to ultrasonication with DI water and ethanol, but still remained as hydrophobic surfaces. As for the super-hydrophilic surface, the WCA increased after post treatment. In other word, the post treatment modified the wettability of the laser modified area, and reduced the wetting properties: super-hydrophilic to hydrophilic and super-hydrophobic to hydrophobic.

On another hand, the large drop in WCA on sample G, B and H after ultrasonication in DI water might be due to the modification of the chemical bonds on the surfaces. The bonds were easily broken during ultrasonic treatment as they were weaker and unstable after modification by laser irradiation.

Table 4 Changes of surface wettability after post treatment.

Sample	As Laser Irradiated	DI Water Treated	Ethanol Treated
G	>150°	106.5°	121°
B	149.7°	97.2°	91.3°
I	135.4°	128.5°	124°
J	130.3°	117.6°	114.4°
K	124.2°	114.5°	121.9°
L	123.1°	110.5°	120.1°
H	5°	49.7°	14°

60

Like DI water treated samples, the WCA of both highly hydrophobic and low hydrophobic samples was reduced by a range from 59° to 2.3°. There was larger decrease of WCA in sample G and B, which

decreased from $>150^\circ$ to 121° and from 149.7° to 91.3° respectively. For sample K and L, only a slight decrease in hydrophobicity was observed. For samples G, K, and L, the WCA of the sample surfaces, ultrasonication in ethanol, was lower than that ultrasonic treated in DI water. It was because ultrasonic energy of solvent (ethanol) as compared to water is actually lower due to lower cavitation energy. There are however competing factors due to chemical strength and cavitation energy.

In ethanol, unlike post treatment in DI water, the wettability of highly hydrophilic surface, sample H, increased by 9° in WCA, after post treatment in ethanol. Although the WCA decreased after ultrasonication in ethanol, the highly hydrophobic surface and hydrophobic surfaces maintained their hydrophobicity, and the highly hydrophilic surface maintained its hydrophilicity.

In order to investigate the reasons of the changes in wettability of the ultrasonic treated PC surfaces, the morphology of the laser irradiated surface without post treatment, DI water treated surface and ethanol treated surface were analyzed. It was possible that the debris from the laser modification was removed with post ultrasonic treatment. However, Figure 8 shows that although the wetting behaviour was changed after post treatment, there was no significant change in the surface morphology under optical microscope observation.

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Figure 8 Surface morphology for samples a) laser irradiation only, b) DI water post-treated and c) ethanol post-treated after laser irradiation (same scale).

To further investigate the effect of post-treatment on the WCA, the surface roughness of the three selected samples in Figure 8 have been three dimensionally characterized with Stylus Profilometer. The measured results were summarized in Table 5. It shows that for highly hydrophobic surface, the roughness, both S_a and R_a increased after ultrasonication in DI water, and increase more after ultrasonication in ethanol. However, the increase in surface roughness did not cause further increase in WCA. For the hydrophobic surface with WCA of 130.3° , the surface roughness did not contribute much in changes of WCA too. For the highly hydrophilic surface with WCA of $<5^\circ$, the surface roughness after post treatment slightly decreased, however, the change in surface roughness is not remarkable. It is hard to conclude that the slightly smooth surface after post treatment has attributed to the increase the WCA. Nonetheless, debris produced by laser surface ablation may contribute to the surface roughness. After ultrasonication, debris was cleaned away and porous rough surface induced from laser ablation may be well exposed and thus causing a slight change in surface roughness. In summary, the post treatment can cause both surface hydrophobicity and hydrophilicity to decrease. However, the minor change in surface morphology may not contribute to the wetting behaviour changes. As ultrasonication is a stringent cleaning imposed on laser modified surfaces, the chemisorbed species which were as debris produced during laser ablation may contribute to the WCA change have been washed away from the PC surfaces. Thus, the WCA was reduced due to cleaning of the chemisorbed species during post-treatment. Other possibilities to be responsible for the WCA change, ultrasonication may result in additional changes to the chemical bonds on the laser modified surfaces including the surface cavitation energy generation during ultrasonication. In the near future study, the detailed XPS analysis may need necessarily to be carried out to determine the surface chemical structure changes under ultrasonic treatment.

Table 5 Surface roughness measured three dimensionally with stylus surface profilometer.

Sample	As Laser Irradiated			DI Water Treated			Ethanol Treated		
	WCA	Sa, μm	Ra, μm	WC A	Sa, μm	Ra, μm	WCA	Sa, μm	Ra, μm
G	$>150^\circ$	1.97	2.08	106.5°	2.44	2.46	121°	2.66	2.42
J	130.3°	2.9	2.52	117.6°	3.12	2.15	114.4°	2.84	2.84
H	5°	0.49	0.43	49.7°	0.43	0.39	14°	0.37	0.31

Conclusion

In summary, the surface wettability modification of PC by femtosecond laser irradiation to achieve either more hydrophilic or hydrophobic has been done successfully. A wide range of water contact angles from $<5^\circ$ to $>150^\circ$ can be successfully achieved by controlling of laser energy deposition level (laser fluence and pulse number). High laser fluence (e.g. 42.46 J/cm²) with several tens pulses overlapped resulted in super-hydrophobic surfaces. A few pulses overlapped led to highly hydrophilic surfaces. Isolated pulses with no spot overlapping led to hydrophilic surfaces. At Laser fluence in range of <42.46 J/cm² to 25.32 J/cm², a few of pulses to 30 pulses overlapped resulted in hydrophilic surfaces. At low laser fluence below 11.45 J/cm², above 40 pulses to hundreds pulses overlapped led to hydrophobic surfaces.

The changes in chemical bonds on the surface as a result of different laser irradiation conditions, were postulated as the main contributing factors in determining the wettability of the modified PC surface. Polar groups induced in laser irradiation resulted in a hydrophilic surface. Non polar group induced in laser irradiation resulted in a hydrophobic surface. The physical changes, which were the morphology and the roughness of the surface, influenced the surface wettability of the laser modified PC surfaces as a minor factor. At slow speed, whole surface was modified by overlapped spots. At high speed, surface was selectively, localized, modified by isolated spots. Different defocus produces different laser fluence and spot size, thus different surface morphology. Surface roughness may contribute to WCA. Size of selectively modified area contributed to WCA. Different surface morphology could have a similar WCA.

The stability of the wetting behavior of the laser modified PC surfaces under post treatments using ultrasonication in DI water and ethanol showed that the super-hydrophobic surfaces and hydrophobic surfaces reduced their hydrophobicity, but maintained as hydrophobic surfaces. Similarly, the highly hydrophilic surfaces reduced their hydrophilicity, but also maintained as hydrophilic surface. It was found that DI water modified the wettability of the surface stronger than ethanol although ethanol was a stronger solvent, likely due to the stronger cavitation energy generated in DI water as compared to ethanol.

With the flexibility of femtosecond laser irradiation, localized surface modification is possible and no additional equipment or chemical treatment is required. Femtosecond laser surface modification may offer many useful applications, for instance, capillary electrophoresis, where hydrophobic and / or hydrophilic surfaces can be created at specific locations of a channel.

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