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2019

Wang, Z. K., Zheng, H. Y., Thwe, A. M., Chen, G., & Lam, Y. C. (2019). Femtosecond laser pulse inducing hydrophilicity and hydrophobicity on polycarbonate surfaces. *Journal of Laser Applications*, 31(2), 022504-. doi:10.2351/1.5096074

<https://hdl.handle.net/10356/90325>

<https://doi.org/10.2351/1.5096074>

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Cite as: J. Laser Appl. 31, 022504 (2019); doi: 10.2351/1.5096074

Submitted: 14 March 2019 · Accepted: 14 March 2019 ·

Published Online: 5 April 2019

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Note: This paper is part of the Special Collection: Proceedings of the International Congress of Applications of Lasers & Electro-Optics (ICALEO® 2018).

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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 the water contact angle 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. X-ray photoelectron spectroscopy-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 results would be useful in microfluidics chip design and fabrication with controlled surface wetting properties.

Key words: femtosecond laser irradiation, polymer surface wettability, laser surface modification, polycarbonate, surface treatment

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I. INTRODUCTION

Wettability is one of the most important aspects of microfluidics applications, and it significantly influences the reagent flow behavior in microfluidics 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 the 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 nanometer 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 metals, glass, polymers, and ceramics.^{1–9} Polycarbonate (PC) is a widely used substrate, similar in chemical properties to but stronger in strength than polymethyl methacrylate (PMMA), for the manufacturing of various microfluidics 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 microfluidics applications. Modification of surface wettability for polymer PC is an important research topic remained. 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 the water contact angle (WCA) from high hydrophilicity to high hydrophobicity.¹⁰

Laser irradiation is an effective method to modify the surface wettability in selected areas with a significant process flexibility. It has been reported that a nanosecond Nd:YAG laser (1.06 μm) can reduce the WCA from 70° to 40°. ¹¹ The nanosecond UV excimer laser (193 nm) can modify the WCA in a range of about

67°–150°. ¹² The different wetting behavior was caused by the different laser–material interactions. Under a linear absorption mechanism, PC absorbs UV laser beams such as excimer, but transmits near-infrared laser beams such as Nd:YAG. The long wavelengths such as Nd:YAG lasers lead to mainly a photothermal process. In contrast, the shorter wavelengths such as UV excimer laser have high photon energy. Besides the photothermal effect, it results in photochemical decomposition. Ultrashort laser pulse has an ultrahigh peak power which leads to a nonlinear absorption mechanism in which there is little photothermal effect, different surface modification phenomena can be expected to be achieved. ¹³

In this study, wettability of the PC surface was modified by femtosecond laser irradiation under varied laser parameters and post-ultrasonic treatment.

II. EXPERIMENT

The PC substrate irradiated by a laser was commercially available, which has a thickness of 1.8 mm. The laser used was a femtosecond laser (CPA2001 Clark-MXR), which has a wavelength of 775 nm and a pulse duration of 150 fs. The femtosecond laser was operated at 1 kHz in pulse frequency and 300 mW in laser power. The focal lens used has a focal length of 106.5 mm, which produced a spot radius of about 15 μm under a laser fluence of 42.46 J/cm². A 5 mm by 5 mm surface area was horizontally raster-scanned at a shifting pitch of 25 μm through a galvanometer scanner. The scanning speed was studied from 0.5 to 2060 mm/s. The sample surface was modified under varied laser fluence, which was adjusted through changing the focus distance. The distance between the PC surface and the laser focal plane was changed to be positive or negative. It indicates that the laser focal spot was above or below the sample surface, respectively.

The loose debris on the laser-modified sample was removed by either dry air or nitrogen blowing. It was confirmed that such postprocessing by either gases has no effect on the measurement of WCA. For characterization of surface wettability, the WCA (variation range below $\pm 1^\circ$) was measured at room temperature using a VCA Optima XE. The ambient air relative humidity was 60%. The water droplet was 0.5 μl dropped onto the PC surface. Surface morphology of laser irradiated substrates was characterized by using an optical microscope. The arithmetic average of absolute values (R_a) for 2D measurement and arithmetic mean deviation of the surface (S_a) for 3D measurement were examined using a Stylus Profilometer (brand of Taylor-Hobson Form Talysurf Series 2).

Post-treatments, ultrasonication in de-ionized (DI) water and/or ethanol, on the laser irradiated samples were carried out for 3 min to analyze the stability of modified surfaces. The post-treated samples were flushed with nitrogen gas prior to conducting WCA measurement. PC samples modified to exhibit highly hydrophobic, hydrophobic, hydrophilic, and highly hydrophilic conditions were selected for post-treatment study.

III. RESULTS AND DISCUSSION

A. 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

FIG. 1. Effect of scanning speed on water contact angle under a laser pulse energy fluence of 42.46 J/cm².

the pristine PC surface was 82°. At lower scanning speeds investigated (0.5 and 1 mm/s), the measurements of WCA show that the surfaces were nearly nonwetting. 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.

During the 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 three times for each sample. Figure 2 shows the detailed stage movement of the 1 complete cycle of up and down procedure during measurement of WCA for highly hydrophobic surface.

However, when the equipment measuring conditions were changed, or other measuring methods such as hand pipette were

FIG. 2. Measurement of WCA on highly hydrophobic surfaces (0.5 and 1 mm/s).

employed, the water droplet could be dropped on the sample surface. Therefore, a similar volume of DI water ($0.5\ \mu\text{l}$) was pipetted onto the same low scanning speed irradiated sample using a precision ($0.1\text{--}1\ \mu\text{l}$) hand pipette (Transferpette S D-1, Brand, Germany), and the measurement of WCA of 144° , shown in Fig. 3, was possible.

In order to compare all the samples under the same equipment measuring conditions with consistency, the WCA of 144° measured by dispensing the water drop via a hand pipette was considered only as an indicative result. The samples of low scanning speeds 0.5 and $1\ \text{mm/s}$, which were not possible to measure using the VCA Optima XE machine, were considered to be greater than the measured value of 150° as in Fig. 1. The reasons of the estimation of WCA to be greater than 150° will be explained in effect of focal distance on WCA.

When scanning speed was greater than $1\ \text{mm/s}$, 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 $2\ \text{mm/s}$ in scanning speed and kept reducing with increasing scanning speed. At $25\ \text{mm/s}$, WCA was less than 5° , which indicated the highly hydrophilic surface. The WCA maintained to be less than 5° until $55\ \text{mm/s}$, which was shown in Fig. 1. Beyond $55\ \text{mm/s}$, the hydrophilicity slowly decreased with respect to increased scanning speed.

Since the WCA of raw PC was around 82° , the wettability of almost nonmodified surface, which can be achieved when the scanning speed was extremely high, was expected to be around 82° .

FIG. 3. Water contact angle of the surface modified by scanning speed $0.5\ \text{mm/s}$ (dispensed water using a hand pipette).

FIG. 4. Measurement of WCA on highly hydrophilic surfaces ($25\text{--}55\ \text{mm/s}$).

Therefore, in order to obtain the expected profile of wettability, the WCA of surface, which was modified with a scanning speed up to $2060\ \text{mm/s}$, was examined. The maximum water contact angle achieved was 65° , which was still less than WCA of nontreated surface within the investigation range, up to a scanning speed of $2060\ \text{mm/s}$.

For measurement of highly hydrophilic samples, at the instance when the water droplet contacted the surface modified PC, it spreaded immediately. Most of the WCAs of samples less than 10° were very difficult to measure as the water spreaded 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 is shown in Fig. 4.

The measurement of some water contact angles on the PC surfaces, which were modified by scanning speeds from 57 to $2060\ \text{mm/s}$, is shown in Fig. 5. From scanning speed $200\ \text{mm/s}$ onward, the changes of WCA were very slight although the scanning speed was varied significantly.

B. Changes of WCA with focal distance

The focus was varied from $+8.5\ \text{mm}$ to $-8.5\ \text{mm}$. Two scanning speeds, 2 and $5\ \text{mm/s}$, which produced hydrophilic surfaces at a focal length with a constant laser power of $300\ \text{mW}$ and a shift pitch of $25\ \mu\text{m}$, were used for this work.

Super-hydrophobic surfaces, WCA of $>150^\circ$, were achieved by defocusing focal distances with scanning speeds 2 and $5\ \text{mm/s}$. The measured WCA values were plotted in Fig. 6, and it shows the symmetry of WCA of increasing and decreasing focal distance sides, and similar WCA values were obtained with respect to the

FIG. 5. WCA modified by varied scanning speeds (a) $57\ \text{mm/s}$, (b) $200\ \text{mm/s}$, (c) $800\ \text{mm/s}$, (d) $1100\ \text{mm/s}$, and (e) $2060\ \text{mm/s}$.

FIG. 6. WCA changing with defocusing focal distance. Plot as 180° for undropped water droplets during WCA measurements.

defocusing distance. Moreover, the profiles of wettability for both scanning speeds were similar too.

For scanning speed 2 mm/s, until the defocusing distance +1 mm, the water spread within 3 s after it was dropped onto the modified sample surface. At the defocusing distance of +1.5 mm, the hydrophilicity decreased to 54.2° . From defocusing distance +2 to +3.5 mm, the wettability of the surface was suddenly changed to highly hydrophobic, WCA of $>150^\circ$ since the water could not be dispensed on the surface. Although the stage was moved up and down for three times for each sample of highly hydrophobic surfaces, it was found that the modified surface could not attract the water drop, and the water droplet could not stick to the sample surface. But at the defocusing distance of +4.5 mm, the water can be dropped easily onto the surface and the WCA was measured as 150° . Therefore, it is considered that the WCA of the surface which repelled the water droplet would likely be greater than 150° . The hydrophobicity kept decreasing until 85.9° at +8.5 mm.

Since the profile was symmetrical for both increasing and decreasing focal distances, the wettability obtained by decreasing focal distances was similar to increasing focal distances. The water spread at a defocusing distance of -0.5 mm and suddenly transformed from highly hydrophilic surface to highly hydrophobic surface at a defocused distance of -1 mm. From -1 to -2.5 mm, the WCA of the sample surface was also greater than 150° , which was highly hydrophobic, since water drop could not stick to the modified surface. At the defocusing distance of -3.5 mm, the WCA was dropped from highly hydrophobic to 142.3° and became 76.8° at a defocused distance of -8.5 mm.

For the scanning speed of 5 mm/s, the modified surfaces were highly hydrophilic at defocusing focal distance until +1 mm. At the +1.5 mm defocused distance, the WCA increased to 32.2° . From that, it suddenly changed from hydrophilic to hydrophobic surface, 141° at a defocused distance of +2 mm. It decreased by increasing the focal distance, and it became 88.9° at +8.5 mm. Since the profile was nearly symmetrical, the decreasing focal distance produced similar WCA results. At a defocusing focal distance of -1 mm, the WCA was considered greater than 150° as the water could not stick the modified surface; and at -2.5 mm, the WCA was 145° . As similar to the increased focal distance

profile, the WCA was decreasing until 89.6° at a defocusing focal distance of -8.5 mm.

It is noted that the WCA profile is not identically symmetrical under the two scanning speeds. There was a slight difference between positive defocus and negative defocus for WCA at a scanning speed of 5 mm/s. While highly hydrophobic surface, WCA of $>150^\circ$, could be attained at negative defocus, in contrast, WCA of 141° was obtained at positive defocus. It could be due to the minor difference in laser modification to the surface and energy for higher scanning speed. It was considered that laser energy was stronger when the surface to be modified was nearer to the focal lens. It was not obvious at a scanning speed of 2 mm/s, this could be because the surface would receive enough energy for modification per unit time at slow speed.

Figure 7 shows the various WCA by defocusing focal distances and proved that the WCA was close to the same defocusing focal distance in positive and negative directions.

It was because the laser spot sizes for the same decreasing and increasing focal distance were the same, which was shown in Fig. 8. Therefore, the amount of material removals per unit area, the overlapped distances, and the distance between each laser spot size were the same for both defocusing sides. Since the overlapped distance also played a part in control over the WCA, it was found that the wetting behavior was the same for the same overlapped distance laser irradiated surface.

C. Surface morphology of laser irradiated surfaces

The patterns, obtained from optical microscope, of scanning speed from 0.5 mm/s to about 60 mm/s were similar, and it can be clearly seen in Fig. 8 that the entire surface of the selected area to be machined was fully modified. Figure 9 shows the fully laser irradiated surfaces obtained at different scanning speeds and different results of WCA. The first picture is the morphology of the surface modified by scanning speed 0.5 mm/s, and its WCA was greater than 150° . The second one was the surface which was irradiated by scanning speed 2 mm/s, and the WCA was 44.8° . Similarly, the

FIG. 7. Similar WCA for the same defocusing focal distance. (a) Increasing focal distance, (b) decreasing focal distance.

FIG. 8. Focal spot changing with defocusing focal distance.

third one gave the highly hydrophilic surface, which was less than 5° WCA, and the scanning speed of the laser was 51 mm/s.

From scanning speed 60 mm/s onward, the laser could not irradiate the entire selected surface area. The overlap areas were lesser and lesser, and the distance between spot sizes was further with respect to the laser scanning speed. The reason for achieving various patterns was due to different overlap distances and the varied distance between each laser spot size, which were resulted by varied higher scanning speeds. When the femtosecond laser was scanned under a much higher scanning speed, pulses were not connected to each other, and thus the sample surface was modified by individual shot separately. Therefore, in order to machine a channel path, it was necessary that the laser interacts with the surface with multiple shots under relative slow speed.

Figure 10 shows the 10 selected pictures from increasing focal distance and decreasing focal distance, from +8.5 to -8.5 mm, which were modified by using scanning speed 2 mm/s. It has been found that the spot sizes irradiated on the sample surface were increasing by changing the focal distance. The changes in spot sizes deposited on the sample surface were more visible at a defocused distance of 4.5 mm. The spot size modified at the surface was getting larger from a defocusing distance of 6.5 mm. At the defocused distance of 8.5 mm, the spot size deposited on the sample

FIG. 10. Surface morphology at different defocusing distances (the same scale).

surface was the biggest among them (Fig. 8). Therefore, their overlapped areas were significantly enlarged accordingly.

The surface morphologies of the laser modified surface were varied with beam scanning overlapped areas. At the defocusing distance of 0.5 mm, the modified surface was superhydrophilic with WCA less than 5° . But, highly hydrophobic surfaces were attained at the defocusing distance of 2.5 mm. The hydrophobicity decreased by increasing overlapped areas. The WCA at the defocusing distance of 8.5 mm was the lowest within the investigated range. The WCA, at the defocused distance of 8.5 mm, was around 80° , close to the pristine PC surface. This was achieved when the defocused distance exceeded a threshold value, i.e., laser fluence exceeded a threshold value.

D. Effect of roughness on WCA

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

It has been found that surface roughness was different due to the difference in scanning speed. From wide WCA range, the highly hydrophobic surface with WCA of greater than 150° , highly hydrophilic surface, WCA of less than 5° , and hydrophilic surfaces, WCA of 34.6° , 47° , and 66° were analyzed. The selected six samples covered the wide range of scanning speeds: 0.5, 2, 29, 131, 500, and 2060 mm/s. The relationship of surface roughness and water contact angles of varied laser scanning speeds was shown in Fig. 11. The values of Sa, Ra, and WCA for a specific scanning speed were grouped together with an ellipse for easy identification.

According to Fig. 11, the Sa for speed of 0.5 mm/s was $6.47 \mu\text{m}$ and Ra was $5.46 \mu\text{m}$. At the speed of 2 mm/s, the surface Sa and Ra reduced to 3.08 and $3.00 \mu\text{m}$, respectively, which was

FIG. 9. Morphology of the surfaces under varied speeds (the same scale).

FIG. 11. Changes of WCA and surface roughness with scanning speed. Morphology by a stylus profilometer (left) and by an optical microscope (right).

about 50% from the roughness measurements of scanning speed 0.5 mm/s.

From the scanning speed of 29 mm/s onward, the roughness indicators, both Sa and Ra decreased to less than 1 μm . Figure 11 shows the hydrophilic surfaces with low surface roughness modified by higher scanning speed. The roughness was decreased by increasing scanning speed, and at the scanning speed of 2060 mm/s, the Sa was as low as 0.19 μm and Ra was 0.07 μm .

The slow scanning speed produced high surface roughness, which was due to the larger modified area on the scanned sample surface, as shown in Fig. 10. It was because the laser with slower scanning speed ablated more material at each modified unit area per unit time. As for high scanning speed, the material ablated per unit area was lesser and the overlap area of laser shots was smaller; thus, the surface roughness was low. Figure 12 illustrates the concept of the differences of surface morphology, specifically the overlapped area, of the sample surfaces, which were modified under high, medium, and low laser scanning speeds.

On the relationship between wettability and surface roughness, it has been observed that highly hydrophobic surface WCA of $>150^\circ$, had very high surface roughness, which was Sa 6.47 μm or Ra 5.46 μm . Hydrophilic surfaces had low surface roughness, compared to the highly hydrophobic surface in this experiment. But among hydrophilic surfaces, there were slight differences in roughness values due to the scanning speeds even for same surface WCA. For instance, both scanning speeds 2 and 500 mm/s produced the hydrophilic surfaces, WCA 44.8° and 47° , respectively. Although both samples had approximately the same WCA, the Sa of modified surface with scanning speed 2 mm/s was 3.08 μm , which was more than 10 times higher than 0.238 μm , modified by scanning speed 500 mm/s. The Ra of modified surface with scanning speed 2 mm/s was 3.0083 μm , which was about 20 times higher than 0.1543 μm , modified by scanning speed 500 mm/s. The comparison of both surfaces modified with speed 2 and 500 mm/s is shown in Fig. 11.

It was because under the case of surface modification by separated spots (obtained by 500 m/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, Fig. 11 shows that high surface roughness

FIG. 12. Effects of overlapped area with scanning speed. (a) High speed, (b) medium speed, and (c) low speed.

contributes 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 surprised 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 an increase of laser modification.

In order to further investigate the effects of surface roughness on the wetting behavior of laser modified PC surface, among 22 samples of defocused focal distance study with a scanning speed of 5 mm/s, four samples of different WCAs were analyzed selectively. The selected samples covered the half spectrum of WCA, from highly hydrophobic to hydrophobic. 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 Fig. 13. According to the measured results, samples B and C have a more obvious ripple feature than samples A and D, whose ripple features were minimal. The sample A had the highest WCA and the 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 samples 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, by comparing samples 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 13 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 Figure 13. As the laser focal distance used to irradiate the sample surfaces is increased in the order from A, B, C, to D, this indicates that the laser fluence could play the key role in determining the change in WCA.

Figure 14 shows a comparison of the two surfaces: highly hydrophilic surface, sample E (at focus $+0.5$ mm, high fluence) and

FIG. 13. Surface roughness of hydrophobic surfaces at focus of (A) -1 mm, (B) $+2.5$ mm, (C) -3.5 mm, and (D) $+5.5$ mm at a scanning speed of 5 mm/s.

FIG. 14. Surface roughness of highly hydrophilic and highly hydrophobic surfaces at focus of (E) $+0.5$ mm, (F) $+3.5$ mm at scanning speed of 2 mm/s.

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 $3 \mu\text{m}$) although the WCA and the laser fluence were quite different. Furthermore, it is noted that the surface roughness of the sample in Fig. 14 was above $5 \mu\text{m}$, while the surface roughness of samples A and F was less than $3 \mu\text{m}$. The similar surface wetting behavior 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 key role compared to surface roughness. The surface wettability modification on PMMA using femtosecond laser irradiation is controlled by laser induced chemical bond change and not due to the modification of surface roughness.¹³ The changes in WCA under varied laser fluence might be due to the chemical modification of the laser irradiation to the surface.

E. Discussion on mechanism of WCA modification

The reported studies have found that the groups containing chemical bonds such as C—O, C=O, and O—C=O at polymer surfaces influenced the modification of surface hydrophilicity.^{14–16} The literature shows that for the improvement 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 reason for hydrophilicity of polymer surfaces because the bond polarity of C=O is more intense compared to chemical bond of C—O.¹⁴ As discussed in Secs. III A–III D, 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 get deep understanding on the modification of surface wettability obtained through laser irradiation, XPS analysis was used to determine the chemical bonds with a VG ESCALAB 220i-XL. XPS spectra O 1s from a raw PC surface and surfaces were irradiated by laser at different conditions. To get an insight of the photochemical process induced by the photodegradation,^{11,13,17} the C 1s XPS

TABLE I. Relative concentration of O/C functional groups (at. %).

	Chemical bond	Raw PC	Laser ablated PC samples			
			Laser fluence 1.91 J/cm ² Focus −3.5 mm Speed 5 mm/s WCA 132°	Laser fluence 3.59 J/cm ² Focus +2.5 mm Speed 5 mm/s WCA 149.1°	Laser fluence 8.67 J/cm ² Focus −1.5 mm Speed 2 mm/s WCA, cannot drop	Laser fluence 42.46 J/cm ² Focus 0 mm Speed 35 mm/s WCA <5°
Nonpolar groups	C 1s C—H/C—C	63.8	65.1	68.1	71.2	59.4
	C 1s 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	C 1s C—O	11.7	13.4	12.4	13.7	18.8
	C 1s O—(C=O)—O	...	...	...	...	3.6
	C 1s O—C=O	0.7	...	...	...	...
	C 1s C=O	5.7	4.5	3.4	1.8	...
	O 1s O=C	16.6	14.6	14.4	12.5	9.0
	O 1s O—C	...	...	...	...	7.5
	Sum	34.7	32.5	30.2	27.9	38.9

spectra of the irradiated surfaces were measured. From the deconvolution of XPS spectra C 1s and O 1s, the variations of chemical bonds have been identified for functional groups both polar and nonpolar. The chemical bond amount measured was summarized in Table I. The level of laser energy deposition controls the level of photodegradation, which shows the level of wettability.¹⁸ Table I shows that high fluence induced the highest concentration of polar groups and the lowest concentration of nonpolar groups such as C 1s C—C, showing high hydrophilicity. In contrast, the low fluence produced the highest concentration of nonpolar group C 1s C—C, and low total concentration of polar groups when comparing to raw PC surface, which shows an 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 the laser fluence but also the scanning speed and laser spot size, as indicated in Fig. 5. Thus, by controlling of the laser energy deposition, the WCA modification can be achieved to be rich in polar groups or nonpolar groups through laser induced chemical changes in PC surface.

IV. CONCLUSION

The full spectrum of surface wettability, ranging from highly hydrophilic to highly hydrophobic over a wide range of WCA from below 5° to above 150°, has been achieved using femtosecond laser irradiation of PC substrate through controlling of scanning speeds and laser fluence. The highly hydrophobic surface was achieved by modifying the surface under both high laser fluence and low laser fluence. For highly hydrophilic surface (WCA ~5°), it can only be achieved by employing a laser scanning speed from 25 to 50 mm/s coupled with high laser fluence.

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. 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.

In summary, the surface wettability modification of PC by femtosecond laser irradiation to achieve either more hydrophilic or hydrophobic has been done successfully. The flexibility of femtosecond laser is accentuated here as it is capable of modifying PC surface to achieve the full range of wettability from WCA less than 5° to WCA >150°. With such flexibility, localized surface modification is possible and no additional equipment or chemical treatment is required. Femtosecond laser surface modification offers many useful applications, for instance, capillary electrophoresis, where hydrophobic and/or hydrophilic surfaces can be created at specific locations of a channel.

ACKNOWLEDGMENTS

This study was supported by A*STAR Singapore Institute of Manufacturing Technology SIMTech, Project No. C09-M-052 and Guangdong Science and Technology Department, China, Project No. 2016B01011304. The authors are grateful to June ONG Lay Ting of A*STAR Institute of Materials Research and Engineering for XPS measurements and analyses.

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