

Femtosecond laser induced porous surface on polymethyl methacrylate for filmwise condensation to improve solar still productivity

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HIGHLIGHTS

- Filmwise condensation forms on the laser textured lines due to the porous surface.
- Cassie-Wenzel droplet state transition is seen on the porous hydrophobic surface.
- Laser texturing improves heat dissipation of the PMMA cover.
- Freshwater output decrease with an increase in laser textured surface area ratio.
- Modified PMMA morphology and chemistry remain stable after repeated experiments.

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ABSTRACT

The decline in freshwater availability has spurred research into employing solar desalination technology. Recent research has concentrated on investigating the use of surface modification to improve the productivity of solar still for desalination. This paper presents the use of femtosecond laser texturing to induce a porous surface on the polymethyl methacrylate (PMMA) cover of a solar still for producing filmwise condensation. Vertical lines 2.5 mm wide were fabricated on the PMMA surface using ultrafast laser texturing, and experiments were conducted using the modified cover on a solar still at a constant basin water temperature. Results show that the static water contact angle measured on the cleaned laser textured surface is hydrophobic. However, the formation of the porous structure leads to a change in wetting state from Cassie-Baxter to Wenzel upon exposure to water vapour. This change in wetting state enables the formation of filmwise condensation under the continuous presence of water vapours. The solar still productivity improves by 15.4 % and 23.1 % using both cleaned and uncleaned laser textured surfaces respectively. The modified surface is stable upon repeated exposure to water vapour, thus proving to be an excellent surface modification method for enhancing PMMA covered solar still performance.

1. Introduction

The decline in availability of freshwater is a growing concern as the trend forecasts a rapid increase in water stress regions worldwide [1]. Therefore, a substantial amount of research has been dedicated towards enhancing the current water purification methods including

desalination methods. Desalination has proven to be the main method for freshwater production, particularly in arid regions whereby the main source of water is seawater [2]. Solar desalination is classified into two main categories which includes indirect desalination method such as reverse osmosis and multi effect distillation, as well as direct desalination method such as using solar still. Solar still is advantageous over

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other more energy intensive desalination methods since water production requires little to no external energy and mostly relies on the heat energy provided from the solar radiation [3]. However, solar still is limited by its higher cost of freshwater produced due to its low productivity [4].

Numerous enhancement methods to improve the solar still productivity have been investigated. Enhancement methods include the addition of thermal energy storage, micro/nano-particles, and heating or cooling of the solar still basin and cover [5–8]. More recent studies have focused on the role of surface modification on the solar still basin and cover to improve the evaporation and condensation process [9]. Enhancement of the evaporation was made by coating the basin with materials with high absorptance to increase the thermal performance of the solar still. Common materials for basin absorber surface coating include black paint, bitumen, and black paint mixed with nanoparticles such as copper oxide (CuO), carbon and titanium dioxide (TiO₂) [10–12]. Surface modification was used to enhance the rate of condensation by improving the heat dissipation on the cover by inducing dropwise condensation mode or accelerating condensate formation via filmwise condensation. Cover surfaces are commonly altered using nanoparticles based coating such as silicon (Si) and TiO₂ [13]. Solar still productivity shown enhancement of up to 53 % with nanoparticle coated basin absorber and 44 % using cover surface coating [14,15].

Despite the enhancement showed using the surface modification method, altering the cover surface for improving the solar still performance is challenging. Results from previous studies shown a different outcome in the solar still performance depending on the solar still condensation modes [13]. Both filmwise and dropwise condensation mode on the solar still cover are crucial to enhancing the productivity of the solar still due to their different role in improving the formation and removal of the freshwater condensate [16]. However, having a single condensation mode is disadvantageous due to the possibility of increased condensate dripping from the cover or decreased condensate collection due to water pooling at the edge of the cover [15].

Surface alteration on polymer-based cover materials such as polycarbonate (PC), and polymethyl methacrylate (PMMA) proved to be arduous due to increased condensate dripping from dropwise condensation at low tilt angle [17]. Polymer-based materials have some advantages over glass as a solar still cover due to their high transparency, lightweight and low cost. Hence, the use of polymer-based materials is often adapted for the design of a low cost solar still [18–20]. However, polymer-based materials do not perform as well as a glass due to the low wettability of the surface and slow heat dissipation, particularly for PMMA covers [21]. The current method for solar still surface modification using coating have also shown to have an effect on increasing the thermal resistance of the surface [16]. Moreover, surface coating are a non-permanent surface modification whereby degradation of the coating will occur over time affecting the solar still performance [22].

Laser texturing has been shown to be a promising surface modification method [23]. Laser texturing allows better control on the surface wettability depending on laser parameter selection [24]. Parameters such as laser fluence, focusing distance, line spacing, laser wavelength and type of laser used control the laser textured surface topography which in turn influences the surface wettability [25–27]. Cleaning the laser textured surface also affects the surface wettability by producing a low wetting surface due to the removal of debris [28]. Besides, laser machining accuracy and precision to produce versatile pattern and precise line designs on the surface promotes synergetic effect to enhance water production through faster droplet growth and removal [29,30]. Studies on laser-induced patterns for water harvesting application show promising results in improving the efficiency of the surface to collect water droplets [31,32]. Laser texturing also creates a permanent surface modification compared to coating techniques that degrade over certain time, particularly when exposed to high humidity [33,34]. Studies on laser machined surfaces found an improvement in the rate of heat

transfer of the modified surface [35,36]. However, the use of laser texturing for surface modification in the solar still desalination application has been limited to only absorber and evaporator surfaces [37,38].

Based on previous studies, limitations of a single condensation mode in solar stills cover leads to issues such as condensate dripping and a decrease in distillate collection, particularly for polymers-based covers. Current surface modification methods for solar still covers using coatings have also been observed to raise thermal resistance and degrade over time, affecting the performance of the solar still. The utilization of laser texturing as a surface modification method in solar still desalination applications has been primarily limited to absorber and evaporator surfaces. This limitation creates an opportunity to explore its potential as a modification technique for cover surfaces. Therefore, this paper aims to investigate the use of femtosecond laser texturing for surface modification to improve the condensation and thus the productivity of solar stills using a polymer-based cover. Polymethyl methacrylate (PMMA) was selected as the cover as it is the most common material used after glass for a solar still cover. The modified PMMA cover was characterized using the sessile drop method, scanning electron microscope (SEM), atomic force microscopy (AFM) and fourier-transform infrared spectroscopy (FTIR) in order to understand the change in surface structure and chemistry after laser texturing. The effect of surface modification on the solar still productivity was studied for different surface area ratio (SAR) of the laser textured lines. Furthermore, the effect of cleaning after laser texturing on the solar still performance was also investigated. The change in the surface wettability and solar still productivity was carried out to observe the stability of the surface structure with repeated exposure to heat and water vapour.

2. Methodology

2.1. Laser texturing and experimental setup

A 3 mm thick PMMA sheet was used as the solar still cover. The surface was textured using a femtosecond laser (Yb:KGW) with a pulse duration of 300 fs at a wavelength of 1030 nm. Laser machining was performed by raster scanning the PMMA surface at a scanning speed of 50 mm/s, with a line spacing shift of 2 μm and a laser power of 50 mW. Vertical lines with a width of 2.5 mm were engraved on the surface. Two different post processing methods were carried out to observe the difference in wettability and its effect on the solar still output, namely i) without cleaning and ii) after cleaning. For the cleaned surface, the machined PMMA was placed in distilled water and cleaned for a duration of 15 min in an ultrasonic bath.

A simple laboratory experimental setup was designed to study the effect of the laser textured PMMA cover on the solar still freshwater output. A mini solar still with a basin surface area of $2.5 \times 10^{-3} \text{ m}^2$ was fabricated using PMMA of the same thickness as the cover (3 mm). The dimensions of the mini solar still are shown in Fig. 1a. A PMMA tube was used as the condensate collecting trough with one end fully covered and other end was attached to a flexible tube connected to the graduated cylinder. A cover tilt angle of 25° was chosen for this experiment based on previous studies on surface modifications for solar still [17]. Artificial seawater used for the basin water was prepared using table salt and deionized water to produce a saline water with a similar salinity of 3.5 % to seawater. The height of the basin water used was 0.5 cm. A data logger (NI-9212) and thermocouples type-T were attached to the solar still to measure the temperature of basin water, vapour, inner cover, and outer cover of the solar still. The schematic and picture of the setup are as depicted in Fig. 1.

A hot plate was used as heating source to ensure that the saline water remains within the range of $55 \pm 1.5^\circ\text{C}$ throughout the experiment. Before commencing the experiment, the saline water was first heated to 50°C before placing it in the solar still basin. Once the saline water was placed in the basin, the PMMA cover was sealed using tape to avoid

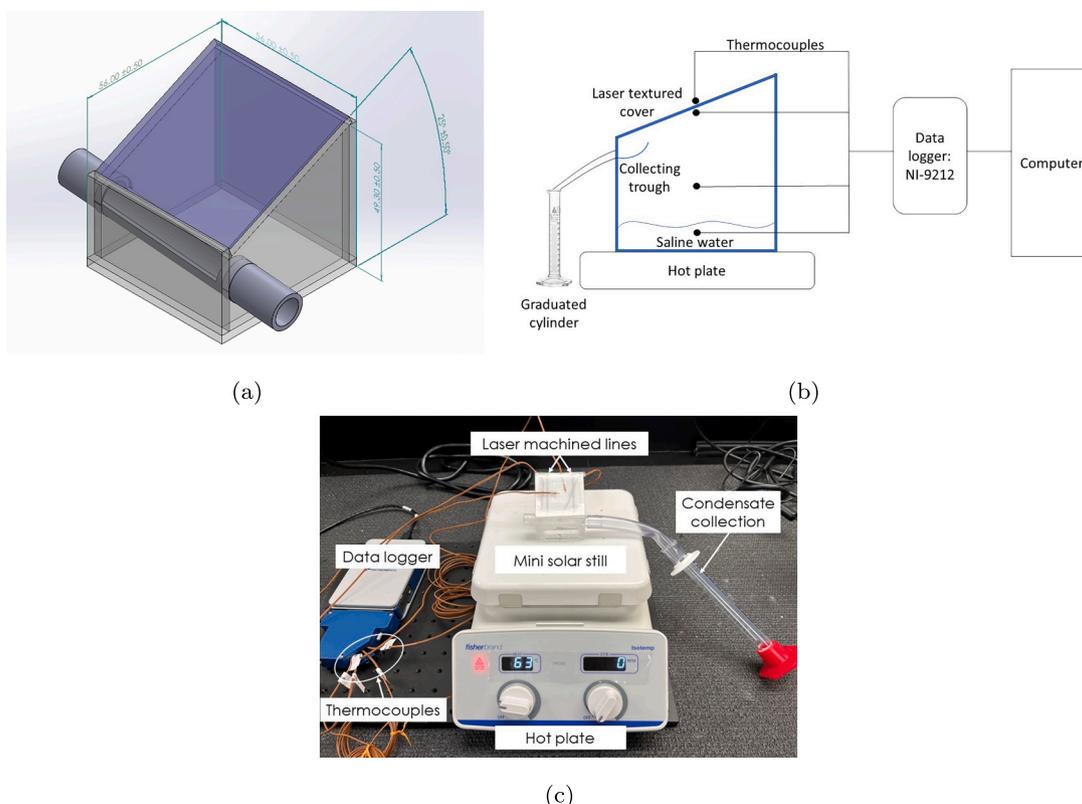


Fig. 1. (a) Drawing of the mini solar still (dimensions in mm) (b) Schematic of experimental setup (c) Picture of the actual setup.

vapour leakage. The laboratory surrounding temperature and relative humidity during the experiment was kept around $23 \pm 1^\circ\text{C}$, and $33 \pm 1\%$, respectively. The inner cover, outer cover, vapour, and saline water temperature in the still were measured at 10 min intervals and the total condensate collection was recorded after 150 min.

2.2. Uncertainty analysis

Table 1 shows the standard uncertainty and accuracy of the measuring instruments used in this study. The uncertainty of measured data is calculated using the following Eq. [39]:

$$u = a / \sqrt{3}$$

Where u represents the standard uncertainty and a is the accuracy of measuring instrument.

2.3. Surface characterization

Sessile drop method was used to measure the water contact angle of the laser machined surface. A distilled water droplet of $1 \mu\text{L}$ was deposited onto the machined surface and images of the droplet was captured within 3 s after the droplet was placed on the surface. Multiple measurements were taken along the machined lines to assess the consistency in water contact angle measurements. Surface roughness and morphologies were characterized using atomic force microscopy, AFM (Park Systems NX10) and a scanning electron microscopy, SEM (Carl

Table 1 Measuring instruments accuracy, range and uncertainty.

Instruments/Sensors	Range	Accuracy	Uncertainty
Type-T thermocouple ($^\circ\text{C}$)	-250 - 350	± 1	0.7
Temperature data logger ($^\circ\text{C}$)	0-100	± 0.33	0.2
Graduated cylinder (mL)	0-10	± 0.1	0.07

Zeiss Microscopy GmbH, GeminiSEM 500). Fourier-transform infrared spectroscopy, FTIR (Thermo Nicolet NEXUS870-FTIR-ESP) in the reflectance mode was also used to characterize the surface chemistry for the uncleaned and cleaned laser-textured surfaces, before and after the solar still experiment.

3. Results and discussion

3.1. Wettability of surface and condensation mode

Table 2 shows the water contact angle measured on PMMA before and after laser texturing. The surface has a low contact angle right after machining and the contact angle increases after the cleaning process. This observation is aligned with previous studies on laser texturing of PMMA whereby the presence of debris after texturing leads to hydrophilicity of the surface [28]. Since the debris formed from laser texturing are very fine, they are difficult to observe in the rough and porous laser textured region. However, the presence of debris is visible on the smooth and uncleaned PMMA surface close to the laser machined region as depicted in Fig. 2a. The effect of cleaning shows an obvious removal of the debris on the PMMA surface as shown in Fig. 2b.

Despite the high water contact angle for the cleaned laser textured surface, it was found that the surface exhibits a filmwise condensation during the experiment whereby this condensation mode is commonly observed on hydrophilic surfaces [40]. In order to understand the formation of filmwise condensation on the laser textured surface, the surface chemistry and morphology were further examined using FTIR, SEM and AFM. The FTIR results show that there is no significant difference in

Table 2 Water contact angle measurements.

PMMA	Before cleaning	After cleaning	After experiment
75 $^\circ$	21.0 $^\circ \pm 2$	90.8 $^\circ \pm 2$	81.5 $^\circ \pm 3$

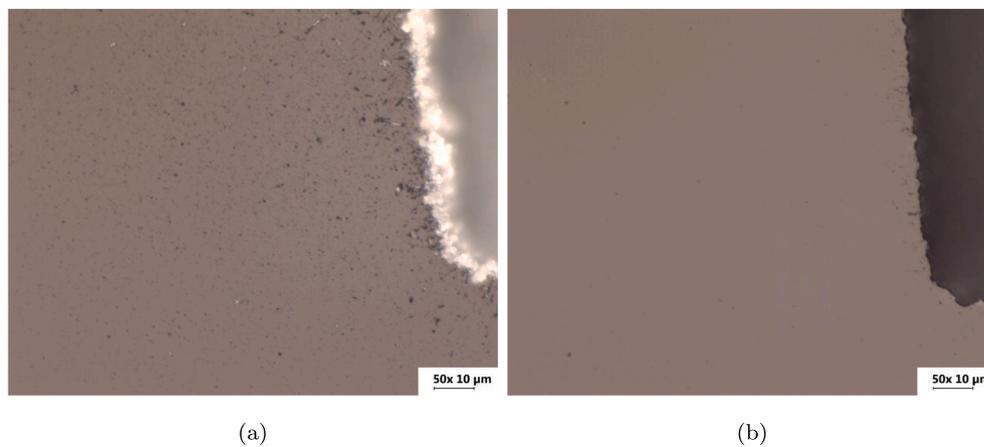


Fig. 2. Debris on the PMMA surface (a) before cleaning and (b) after cleaning (50× magnification).

surface chemistry between the cleaned and uncleaned surface as illustrated in Fig. 3. This observation is similar to a previous study whereby there was no change in the PMMA surface chemistry after femtosecond laser machining [28]. Nonetheless, the SEM results illustrated in Fig. 4b and c reveal a porous surface for the PMMA after laser texturing, in contrast to the smooth surface observed prior to laser texturing, as depicted in Fig. 4a. The percentage of porosity obtained through analysis of the SEM images using the ImageJ software is approximately $21.8 \pm 2\%$ (19.9 % for Fig. 4b and 23.8 % for Fig. 4c) [41]. The formation of laser induced porous structures commonly occurs on polymer materials even with a low laser pulse energy of $5 \mu\text{J}$ [42,43]. The formation of a porous structure results in a drastic increase of the PMMA surface roughness from 1.24 nm to 458 nm after laser texturing as illustrated in Fig. 5. The change in porosity after laser texturing allows the surface to trap the water vapours. The cohesive nature of water pulls the subsequent water droplet onto the surface which increases the tendency of the surface to form a film hence promoting filmwise condensation rather than dropwise condensation. Although initially the water droplet was in a Cassie-Baxter state during contact angle measurement in air, the water contact angle reduces once the droplet transitions to the Wenzel state after absorption occurred on the porous hydrophobic surface [44,45]. As shown in Fig. 6, the contact angle measurement changes depending the amount of water left on the surface. After having been submerged in

water, the laser textured surface water contact angle is initially close to zero (it cannot be measured) and increases as the water dries from the porous surface. Therefore, water contact angle measurements cannot be used to determine the condensation mode observed on porous surfaces, which depends on external stimuli such as prior exposure to water vapour and the Cassie-Wenzel transition [46–48].

3.2. Transparency of the surface

Besides texturing the surface, laser surface modification has been shown to have an effect on the surface transparency and colour [49]. In the actual solar still application, reduction in the surface transparency negatively affects the solar still productivity due to lower basin water temperature from the decreased amount of solar radiation entering the basin. Hence, it is imperative to consider the adverse effect of laser machining on the transparency of the PMMA cover. Fig. 7 shows the transmittance of the laser textured surface under various conditions at visible light wavelengths (400 nm to 780 nm) measured using a Thorlabs compact spectrometer (CCS200). When the textured surface is dry, the transmittance level for both the cleaned and uncleaned surface is less than 10 %. The cleaned surface has a slightly higher average transmittance of 5.2 % compared to the uncleaned surface transmittance of 2.1 %. The surfaces were then wetted by fully submerging the laser textured PMMA in distilled water. Transmittance was measured immediately after the surfaces were removed from the water and an opposite trend is observed whereby the uncleaned surface boast a higher average transmittance of 47.6 % compared to the cleaned surface at 37.2 %. For both dry and wet condition, the effect of leftover debris is obvious for the uncleaned surface. The transmittance of the textured surface is reduced when dry due to the debris diffusing the incoming light. However on the wetted surface, the debris attract water droplet onto the surface to form a film, as proven by the low water contact angle measured, thus increasing the ability of the surface to transmit light.

3.3. Effect of porous surface on improving solar still productivity and heat transfer

The effect of using laser texturing for improving the solar still condensate output was conducted by varying the SAR of the textured PMMA surface from 10 % to 30 % by increasing the number of laser textured lines (2, 4 and 6 lines) on the solar still productivity. Since there is a drastic change in water contact angle measurement between the cleaned and uncleaned surfaces, both surfaces were examined to understand the consequence of cleaning the textured surface on the solar still productivity. Fig. 8 shows the freshwater output and the temperature difference between the inner and outer cover, $T_{\text{cin-out}}$ and between basin water and inner cover, $T_{\text{w-cin}}$ for different SAR.

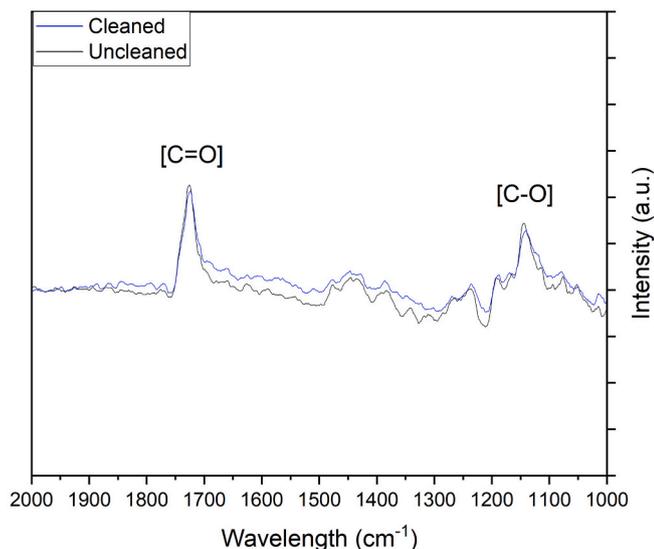


Fig. 3. FTIR results showing similar peaks of C–O (1148cm^{-1}) and C=O (1730cm^{-1}) groups for both cleaned and uncleaned PMMA textured surfaces.

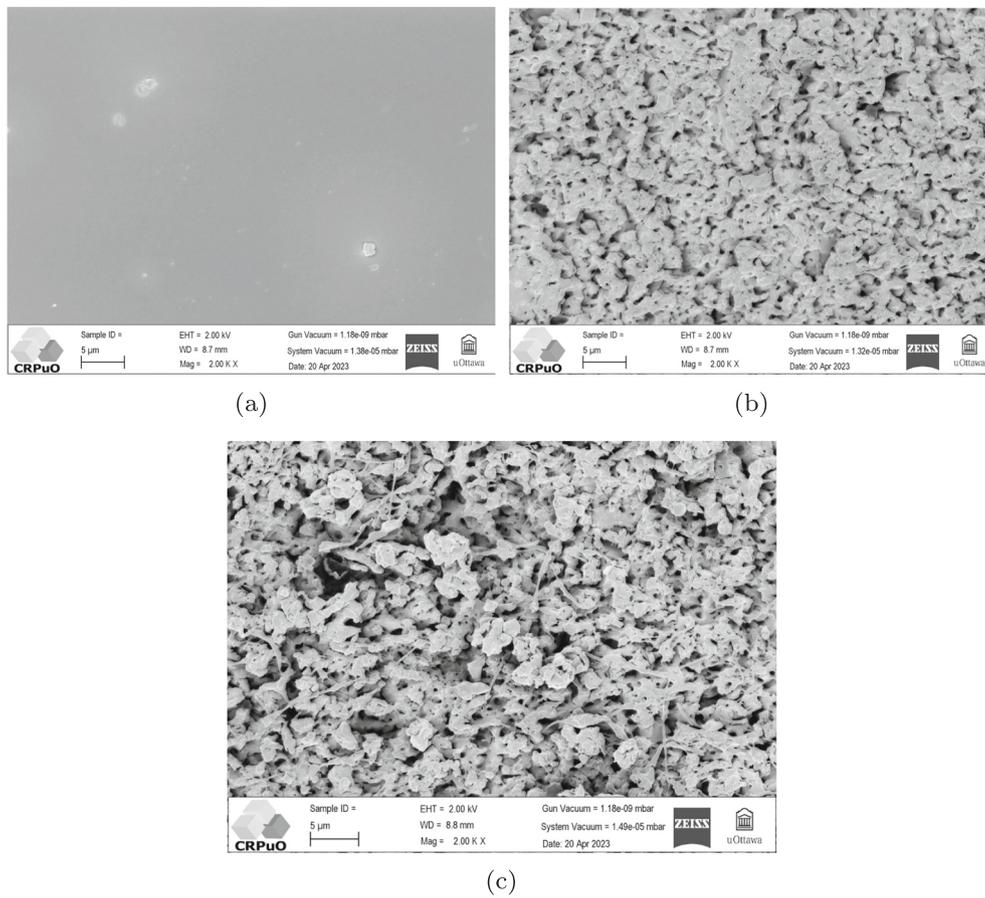


Fig. 4. SEM images of the PMMA (a) before laser texturing, (b) after laser texturing (uncleaned surface) and (c) after cleaning of the laser textured surface.

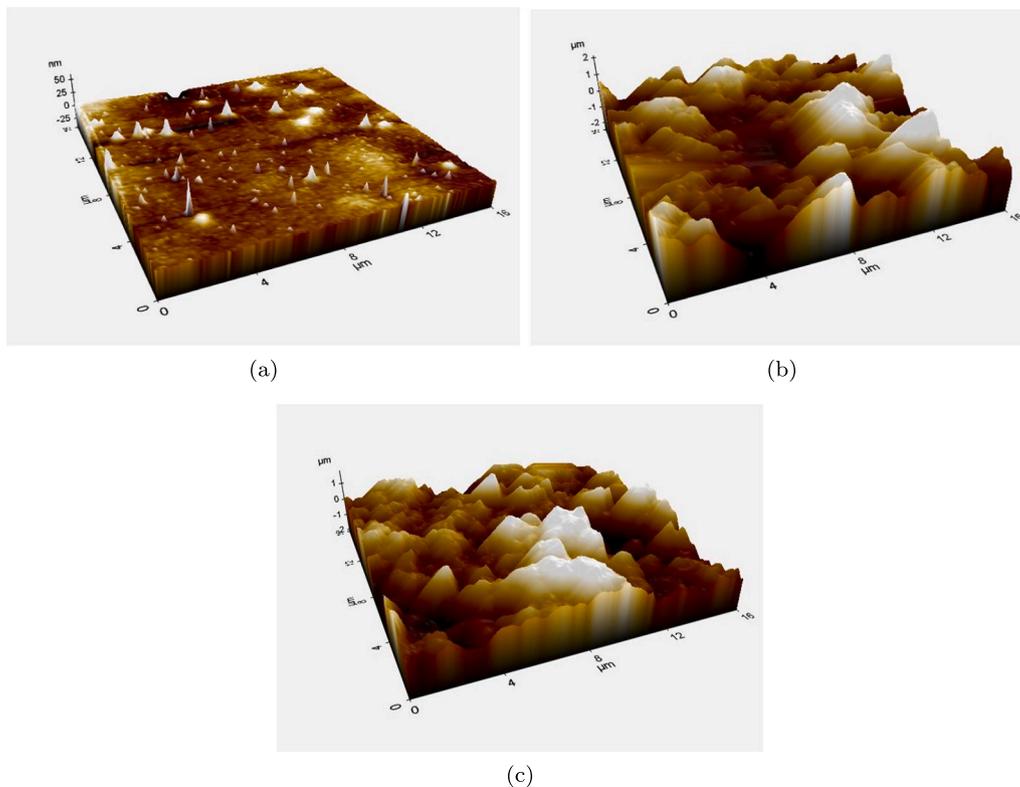


Fig. 5. AFM images for (a) unmodified PMMA (b) after laser texturing (uncleaned surface) and (c) after cleaning of the laser textured surface.

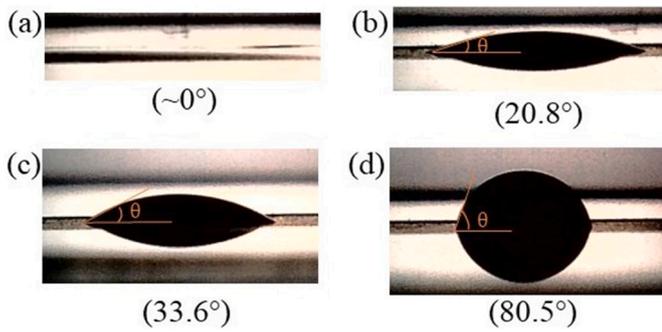


Fig. 6. Water contact angle measured for the conditions: (a) Immediately after surface was fully submerged in water (b) Surface is wet (c) Surface is partially wet (without excess water) (d) Surface is dry (without visible water stain).

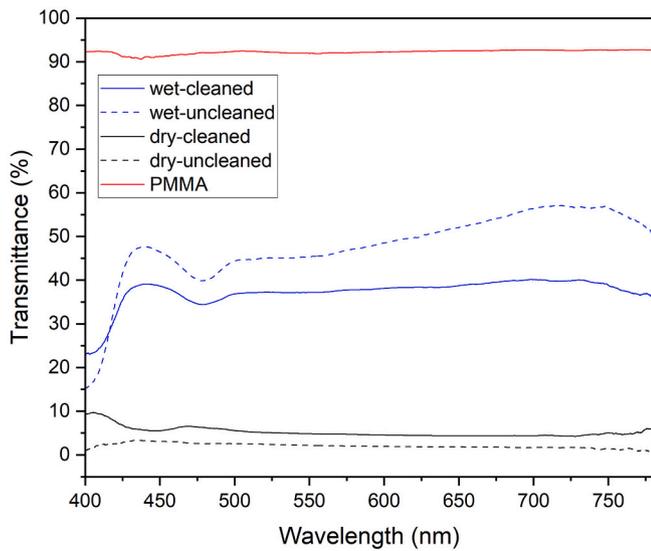
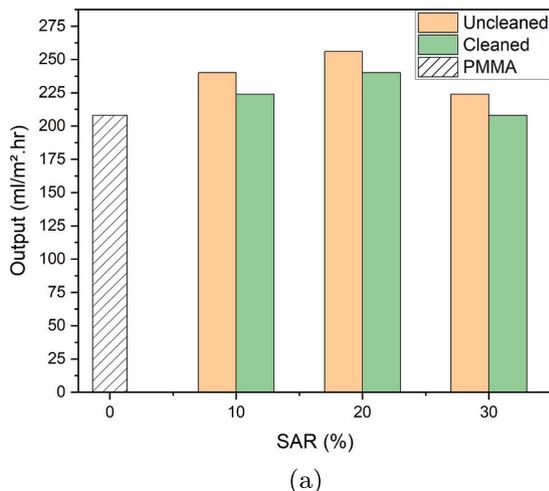


Fig. 7. Transmittance of the laser textured PMMA surface in wet and dry conditions for both cleaned and uncleaned surfaces.

Solar still productivity is mostly correlated to the change in T_{w-cin} . Although there is a drop in T_{w-cin} after laser texturing with 10 % SAR for both cleaned and uncleaned surfaces, the freshwater output is higher compared to the untextured PMMA due to the presence of a filmwise



condensation mode on the laser textured lines. Filmwise condensation on the textured lines promotes water flow and collection (as opposed to the dropwise condensation mode that occurs on the PMMA surface) as shown by the increase in freshwater output from 10 % to 20 % SAR. For both cleaned and uncleaned surfaces, there is a jump in T_{w-cin} when increasing the SAR from 10 % to 20 %. Further increasing the SAR from 20 % to 30 % however did not result in a change of T_{w-cin} . Despite that, $T_{cin-cout}$ dropped with an increased in SAR which indicates that laser texturing results in an improved heat dissipation of the PMMA cover. Although filmwise condensation is often associated with reduced heat transfer efficiency, the improvement in the heat transfer of the PMMA cover is observed due to the increase in surface area from the porous structure and the removal of PMMA material which counteracts the thermal resistance of the water film [50].

Nonetheless, the positive effect of laser texturing on the heat transfer performance of the solar still with increased SAR is not reflected on the freshwater output of the solar still. The highest output found for both the cleaned and uncleaned cover was at 20 % SAR followed by 10 % and 30 %. This drop in freshwater output with addition of laser textured lines (i. e. SAR) is a result of the adverse effect of filmwise condensation on condensate collection due to the increase in retention of water droplets on the textured surface thus reducing the amount of freshwater output collected by the solar still. Therefore, the optimal freshwater output relies on the balance between the amount produced on the untextured PMMA surface (fast droplet detachment but low volume) and the laser textured lines (high droplet volume but slow detachment) [16]. Besides, the uncleaned laser textured surfaces consistently showed a slightly higher output than the cleaned laser textured surfaces as seen in Fig. 8a. The highest freshwater output obtained for the uncleaned and cleaned laser textured surface is 23.1 % and 15.4 %, respectively. The higher amount of condensate collection is expected due to the hydrophilic effect from the presence of debris on the laser textured surface. Nonetheless, a drop in freshwater output reaching similar levels with cleaned laser textured surface (30 % SAR) occurs after repeated experiment on the uncleaned surface due to the removal of debris by the water droplets as shown in Fig. 9. Previous studies done on wetting effect of laser machined lines often disregard post machining cleaning which leads to a pseudo-hydrophilic surface, hence providing a biased and non-reproducible water contact angle results on laser machined lines over time.

3.4. Stability of the laser textured surface after experiments

Fig. 9 depicts the increase in water contact angle measurement as the debris are removed from the uncleaned laser textured surface. The water

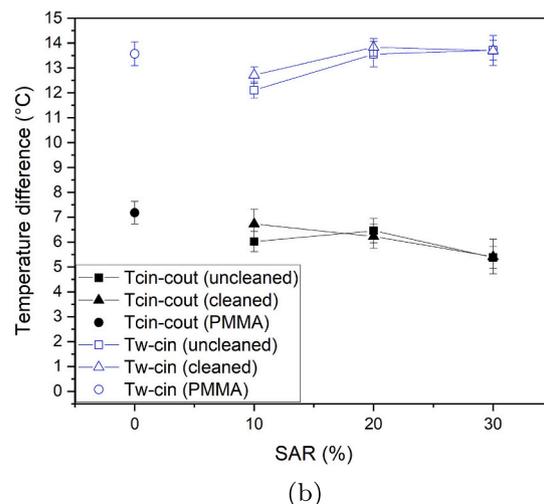


Fig. 8. (a) Freshwater output of the solar still (b) The average $T_{cin-cout}$ and T_{w-cin} for different PMMA cover surface modification.

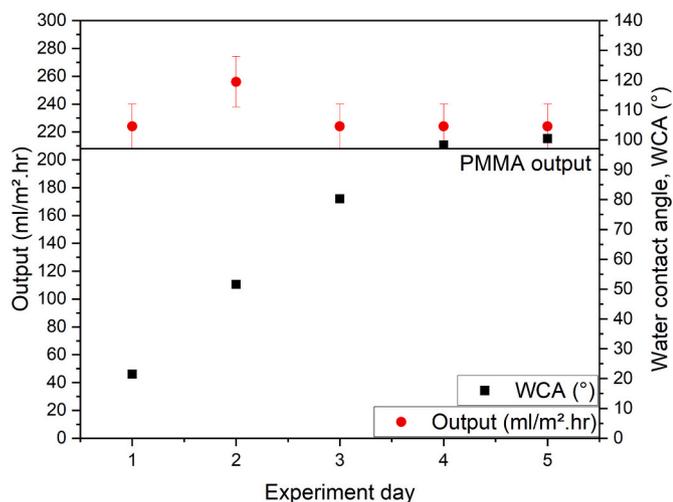


Fig. 9. Change in water contact angle measurement and freshwater output after repeated experiment using the 10 % SAR uncleaned laser textured surface (straight line refer to PMMA freshwater output).

contact angle reaches a similar value compared to the cleaned surface (90°) on the third day of the experiment. The surface contact angle measured shows a smaller change, and the solar still productivity remains constant for the last 3 days of the experiment indicating that a persistent exposure to water vapour does not alter the textured surface morphology or chemistry. Indeed, Fig. 10 shows that the surface morphology and chemistry are almost unchanged after the experiment compared to before the experiment (see Fig. 4). The lack of change indicates that exposure to condensate does not affect the surface morphology or chemistry of the laser textured surface. Table 3 shows the percentage of change in the freshwater output obtained using the coating techniques [13,17] and the current laser texturing method for surface modification on polymer cover. A positive change of up to 23.1 % was achieved using the current laser texturing method for PMMA at a cover tilt angle of 25°. Hence, the use of laser texturing as a permanent surface modification on PMMA cover for solar still application is a promising technique that can provide a high freshwater output without degradation over time.

Table 3

Comparison between the different surface modification on the solar still productivity using polymer cover [13,17].

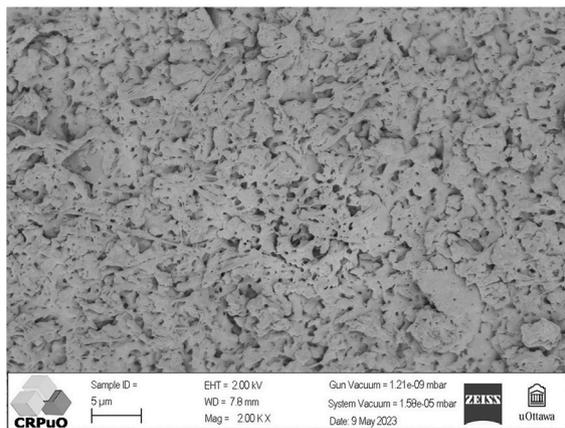
Cover material	Freshwater output (mL/m ² .hr)	Comparison to unmodified PMMA (%)
Coating using Si		
PET	241.43	-9.0
PMMA	223.36	-10.0
PC	206.79	-11.0
PVC	200.71	-11.5
Coating using TiO ₂		
PET	292.00	+9.8
PC	265.36	+14.1
PVC	260.93	+15.0
Laser texturing (current study)		
PMMA	256.00	+23.1

4. Conclusion

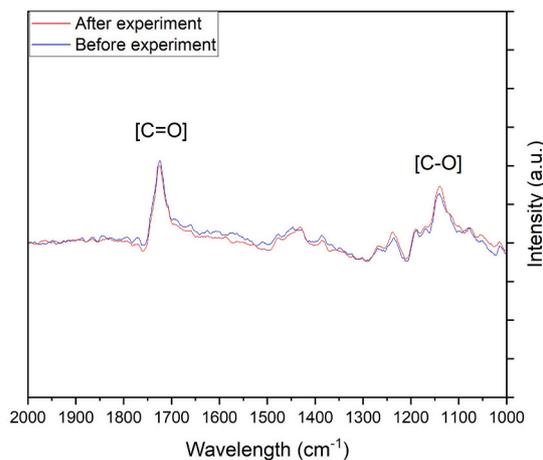
In summary, investigation on the use of femtosecond laser texturing for surface modification of PMMA cover for improving solar still productivity was performed. The laser textured surface shows a decrease in water contact angle compared to the PMMA surface before cleaning due to the presence of debris. The water contact angle increases to a hydrophobic state after cleaning the surface. Despite the increase in water contact angle, the surface porosity and high roughness produce a filmwise condensation mode which is usually observed on low water contact angle or hydrophilic surfaces. The formation of a filmwise condensation mode results in an improved solar still productivity by up to 23.1 % for the uncleaned surface and 15.4 % for the cleaned surface. The solar still productivity also increases with an increase in SAR from 10 % to 20 %, however the output reduces when the SAR is further increased to 30 % due to the retention of water droplet on the laser textured surface. The laser texturing method also shows improvement towards the heat transfer capability of the PMMA cover. The surface morphology and chemistry remain unchanged after the experiment and is consistent with a constant fresh water output observed over repeated experiments. This study demonstrates the potential of ultrafast laser texturing as a surface modification method to improve the productivity of PMMA covered solar stills.

CRedit authorship contribution statement

Nursyahirah Mohd Shatar: Conceptualization, Methodology, Investigation, Formal analysis, Writing – original draft. **Mohd Faizul**



(a)



(b)

Fig. 10. (a) SEM image of the surface after experiment (b) FTIR results of the laser textured surface before and after experiment.

Mohd Sabri: Supervision, Validation, Funding acquisition, Writing – review & editing. **Mohd Faiz Mohd Salleh:** Supervision, Visualization, Funding acquisition, Writing – review & editing. **Mohd Hanafi Ani:** Supervision, Methodology, Funding acquisition, Writing – review & editing. **Xitong Xie:** Investigation, Formal analysis. **Arnaud Weck:** Supervision, Resources, Methodology, Funding acquisition, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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