Fabrication of Super-hydrophobic Surfaces and Studies of Water Flow in Super-hydrophobic Micro-tubes

Zhijia Yu, Xinghua Liu, Subin Huo, Shanpeng Song, Baohe Wang, Guozhu Kuang

School of Chemical Engineering, Dalian University of Technology, room 317, Chem. Eng. Lab., West Campus, 2 Linggong Rd., Ganjingzi District, Dalian 116024, China
Email: yuzhijia@dlut.edu.cn

Abstract. Hierarchical alveolate structures of micro-nano scale were prepared on stainless steel substrates with chemical etching. Fine papillae stand on protuberances are found. After fluorination treatments, the surfaces exhibit super-hydrophobic properties, with water contact angles of 163°. Stainless-steel micro-tubes with super-hydrophilic and super-hydrophobic surface were fabricated with chemical etching and chemical etching-fluorination treatment respectively. The effect of surface wettability on the fluid flow in micro-tubes was investigated with water as the working fluid. The experimental setup was designed in such a way that the investigation of the pressure drop and friction factor was possible. It is found that friction factor in super-hydrophilic micro-tube is in good agreement with Hagen-Poiseuille theory at low Reynolds number (Re<600), while higher than classical values at higher Reynolds number. The pressure drop of water flowing in super-hydrophobic micro-tube decreases compared with that in super-hydrophilic micro-tube, with the maximal decrease of 39%, which indicates the prospective utilization in process industry.

1. Introduction
Recently, super-hydrophobic surfaces have aroused much interest because of their great advantages in applications [1]. For example, it can prevent snow from sticking on the antenna outside, keeping excellent signal emitting and receiving. It can also resist metallic erosion and contamination. In fluid flow, it can reduce friction drag. As a common knowledge, liquid flow in narrow tubes generally encounters great pressure drops, which hinders the development of micro processing. Therefore, the fabrication of super-hydrophobic surfaces and some hydrophobic machine parts or elements is of great significance for technical innovation. Up to now, many works were focused on super-hydrophobic surfaces fabrication methods and researches, such as chemical vapor deposition [2], sol-gel processing [3], etching technique [4, 5], electro deposition [6], and others. The effective means for fabricating super-hydrophobic surfaces are (1) configuring a proper hierarchical roughness on a low free energy substrate and (2) lowering the free energy of a micro/nanostructured surface. In this paper, Hierarchical alveolate structures of micro-nano scale were prepared on stainless steel substrates with chemical etching. After fluorination treatments, the surfaces exhibit super-hydrophobic properties, with water contact angle of 163°. Stainless-steel micro-tubes with super-hydrophilic and super-hydrophobic surface were fabricated with chemical etching and chemical etching-fluorination treatment respectively. Water flow experiments were performed, which could show some features of the water flow in super-hydrophobic micro channels.
2. Fabrication of Super-hydrophilic on Stainless Steel Substrate

An etchant consists of ferric trichloride, hydrochloric acid, and phosphoric acid designed for chemical etching procedure. 8 grams of ferric trichloride was dissolved in 30ml of water. And then 2ml of 37% (wt) hydrochloric acid, 2ml of 85% (wt) phosphoric acid, and 2ml of 30% (wt) hydrogen peroxide solution were added. The tested stainless steel 304 (SS304) plate with a dimension of 30mm×20mm×0.2mm was brushed with emery paper (500#), washed ultrasonically with deionized water, and then etched in the prepared etchant for 20 min at room temperature. After etching, the specimens were immediately rinsed ultrasonically with water and dried at 50 °C in air. Tridecafluoroctyltriethoxysilane was dissolved in ethanol to form an about 1% (wt) ethanol solution. The etched metallic specimens were immersed in the fluoro-alkyl-silane (FAS) solution for 30 min to 1 h at room temperature, and then heat treated at 100 °C for 30 min to 1 h. The function of surface fluorination is to form a low energy thin film of a monomolecular layer on the substrate surface via the following chemical reaction:

\[ \text{Absorption} \rightarrow \text{Hydroxylation} \]

The microstructure of the metallic surface was observed using a scanning electron microscope (SEM, JEOLJSM-6460LV, Japan). Water contact angles were measured using a contact angle meter (Contact Angle System OCA20, Dataphysics Co., Germany). The values reported are averages of five measurements made on different areas of the surfaces. Equilibrium contact angles of 5-μL water drops were measured by sessile drop method.

The morphology of SS304 substrate after etching is shown in figure 1. A kind of hierarchical roughness forms with fine nano-sized papillae standing on micro-protuberances. After fluorination treatments, the surfaces exhibit super-hydrophobic properties, with water contact angle up to 163° as shown in figure 2.

Figure 1. SEM images from low to high magnifications (a:×1000, b:×8000) of the super-hydrophobic stainless steel surface. The etching time is 20 min.
3. Fabrication of Super-hydrophilic and Super-hydrophobic Micro-tubes

The material of micro-tube is stainless-steel 304. Firstly, ethanol and distilled water were used to wash the inner wall of the micro-tube. Then, the micro-tube was etched by flowing FeCl3 solution through the micro-tube. The concentration of FeCl3 solution and the etching time were controlled. The etched micro-tube was rinsed again with distilled water in ultrasonic washer. So the super-hydrophilic micro-tube was prepared. After the water flow measurements were taken in the hydrophilic case, coating treatment was applied by flowing FAS solution for about 30 minutes. At last, the micro-tube was baked in an oven at 100°C for 30 minutes.

The water repellency of the super-hydrophobic micro-tube was examined by cutting down the tube at the radius. It can be seen from the photograph shown in Fig. 3 that the inner wall of the tube exhibits excellent water repellency, where the droplets are nearly spherical. Water drops on the super-hydrophilic micro-tube, however, spread quickly, forming a thin liquid film on the inner wall of the tube.

4. The Pressure Drop Study on Water Flow in Super Hydrophobic Micro Tube

A schematic diagram of the pressure drop measurement is shown in Fig.4. Deionized water was pumped from the water tank into the buffer tank, and then flew through a micro-tube, the test section. The volumetric flow rate was measured by flow-meter which was calibrated by the standard weighing method. A pressure transducer (model DPST-DP) was connected to the two ends of the micro-tube. The inner-diameter of micro-tube used in experiment is 1.08mm, and the length is 162 mm. Two copper-constantan thermocouples were placed at the ends of the micro-tube to measure the inlet and outlet temperatures of water. The measurement devices for temperature and pressure drop were
connected to the computer data acquisition system.

The effects of surface wettability on pressure drop in the micro-tubes are shown in Fig. 5. It can be seen that the relationship between pressure drop and volume flow rate in super-hydrophilic micro-tube is in good agreement with Hagen-Poiseuille theory at low volumetric flow rate while the pressure drop becomes larger than classical values at high volumetric flow rate. This discrepancy may attribute to the effects of surface roughness of the micro-tube wall.

It is also found that the pressure drop of water flowing in super-hydrophobic micro-tube is less than that in super-hydrophilic micro-tube, with a maximal decrease of 39% (Fig. 7). As seen in Fig. 6, the difference becomes greater along with the flow velocity increasing. From Fig. 7, it can be seen that the dimensionless pressure drop reduction (calculated by equation (2)) decreases along with the flow velocity.

\[
\Pi = \frac{\Delta P_s - \Delta P_q}{\Delta P_s}
\]

(2)

where the subscript q denotes super hydrophilic, and s super hydrophobic.

The effects of surface wettability on the friction factor f in the micro-tubes are shown in Fig. 8. It is found that the friction factor of water flowing in super-hydrophilic micro-tube agrees well with classical values at low Reynolds number (Re<600) while becomes larger with the increase of Reynolds number. What’s more, it also can be seen that the friction factor in super-hydrophobic micro-tube is smaller than that in super-hydrophilic micro-tube.

These experimental results indicate that the decrease of surface hydrophilic capability can facilitate the momentum transport in micro-tubes. That the shear-free air-water interface reduces the flow friction coefficient may be the reason for the pressure drop reduction in super-hydrophobic micro-tube. It can be found that the chemical etched surface is configured into a hierarchical roughness with a micro-nanostructure. The rough surface can trap air in its caves, forming an “air cushion” between water and the solid. When water flows on such a surface, the air cushion functions as a shear-free layer, decreasing the pressure drop evidently.

![Figure 5. Effects of surface wettability on pressure drop](image-url)
Figure 6. Difference of pressure drop between super-hydrophilic and super-hydrophobic micro-tube vs. flow velocity

Figure 7. The dimensionless pressure drop reduction vs. flow velocity

Figure 8. Effects of surface wettability on friction factor

5. Conclusion
Hierarchical alveolate structures of micro-nano scale were prepared on stainless steel substrates with chemical etching. Fine papillae stand on protuberances are formed. After fluorination treatments, the surfaces exhibit super-hydrophobic properties, with water contact angles of 163°. Stainless-steel micro-tubes with super-hydrophilic and super-hydrophobic surface were fabricated with chemical
etching and chemical etching-fluorination treatment respectively. The effect of surface wettability on water flow in micro-tubes was investigated. The pressure drop and the friction factor of water flowing in super-hydrophilic micro-tube are in good agreement with Hagen-Poiseuille theory at low flow rate and Re respectively, but they are higher than the ordinary values at higher flow rate and Re. The pressure drop and the friction factor of water flowing in super-hydrophobic micro-tubes are smaller than those in super-hydrophilic ones, and the differences increase with the flow velocity. The wettability treatment of solid surface may benefit the miniaturization of macro processing.

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7. References
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