Supplementary information of

"Fabrication of COC micromodels with wettability heterogeneities: method and influence on fluid transport"

Camille Brigodiot *[a], Elliot Speirs [a], Cédric Guyon [b], Michaël Tatoulian [b] and Nicolas Pannacci [a]

[a] IFP Energies nouvelles, 1 et 4 avenue de Bois-Préau, 92852 Rueil-Malmaison, France

[b] Chimie ParisTech, PSL University, Institut de Recherche de Chimie Paris, UMR 8247, 11 rue Pierre et Marie Curie, 75005 Paris, France

* Corresponding author: camille.brigodiot@ifpen.fr

Surface treatment methodology

Description of the atmospheric plasma

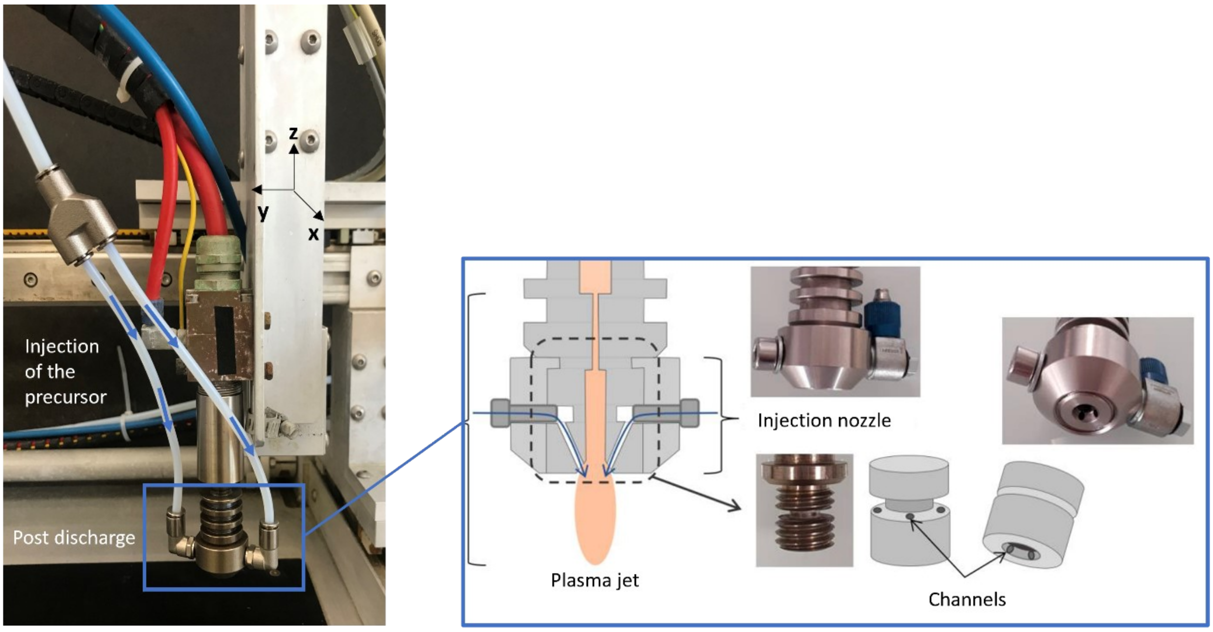

Figure SI.1: Picture of the plasma nozzle. Insert: scheme of the injection nozzle. The blue arrows indicate the injection path for the precursors.

The atmospheric plasma system is from AcXys Technologies and is composed of three command modules and a moving nozzle (see Figure SI.1 for the moving nozzle). The frequency is configured using the ULS command module, which also displays the power and gas flow parameters. The atmospheric pressure plasma jet nozzle is installed on a motorized xyz table, controlled by the Quickset module, allowing it to scan the sample surface at a constant speed of 150 mm/s, ensuring uniform treatment. The plasma jet is produced by introducing air at a flow rate of 32 L/min into the plasma torch. The ULC module controls the injection of the liquid organosilicon precursor (TEOS) from a pressurized tank into the treatment nozzle, with a flow rate adjustable between 10 and 500 µl/min. A carrier gas, flowing at a rate of 5 to 25 L/min, vaporizes the liquid precursor, which is then introduced into the post-discharge region through pipes positioned on either side of the nozzle. The liquid precursor injection is controlled by a flowmeter before being nebulized and transported by the carrier gas to the deposition nozzle. [1,2]

Characterisation of the silica-like deposition

Infrared spectra were acquired using a Fourier-transform infrared spectrometer (Cary 660 Spectrometer; Agilent, Les Ulis, France) spectra were collected from 4000 to 500 cm^{-1}, at a resolution of 4 cm^{-1}. One hundred scans were made for each measurement. The background (air) was taken before each measurement.

As demonstrated before by Bourg et al. [1], the characteristic bands of SiO_2-type thin film deposition are between 1225 and 1078 cm^{-1}. Figure SI.1 shows the spectra obtained for different conditions of TEOS deposition. As expected, the spectrum of the untreated COC sample does not present the bands around 1225 cm^{-1} while it is present for the two samples with TEOS deposition. It is interesting to note that the intensity of this characteristic peak is higher when the PECVD treatment is followed by a rinsing step with water.

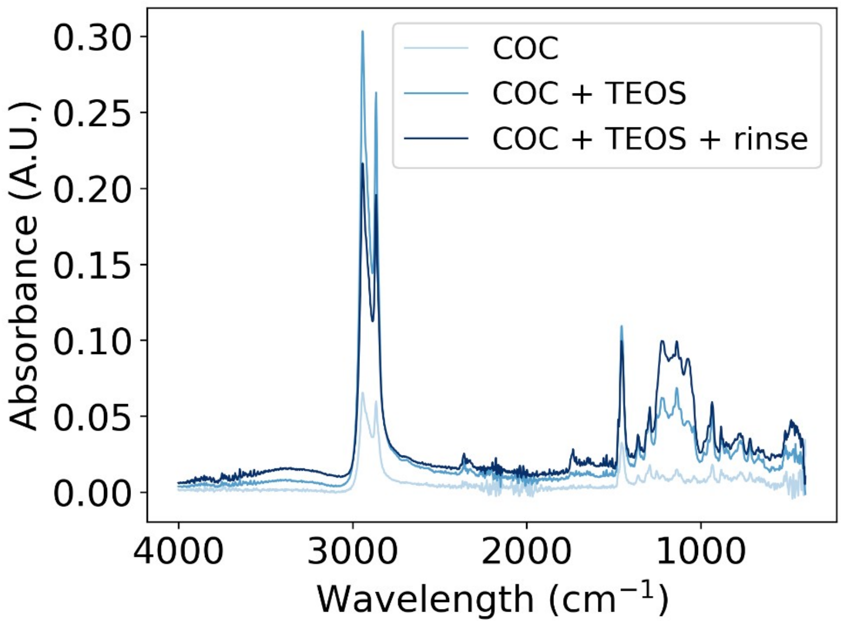

Figure SI.2: IR spectroscopy for different surface treatment on COC. For the two treated samples, four passes of TEOS deposition were made.

Tortuosity of the micromodel

The tortuosity of the micromodel has been determined by the plug im! [3] software developed by IFP Energies nouvelles and its map, from Speirs' work [4], is displayed in Figure SI.3, corresponding to the different radial directions of the micromodel. The inset provides a scheme of the pillars' layout.

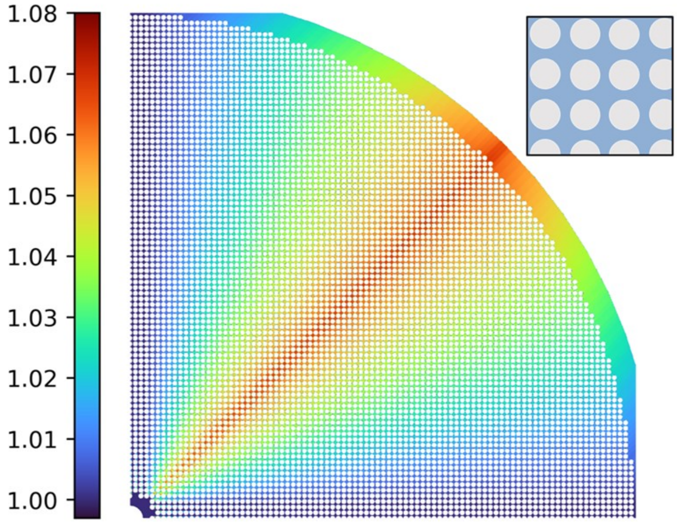

Figure SI.3: Tortuosity map of a quadrant of a square porous media. The radial geometries have a radius of 6.5 mm and the posts have a diameter of 50 µm.

Characterisation of the water-in-oil emulsion

As mentioned in the section 2.5 Fluid injection, we have studied the injection of a water-in-oil emulsion in micromodels with wettability heterogeneities. The emulsion and especially its stability has also been investigated, by measuring the droplet stability through time. To do so, the coefficient of variation (CV) has been measured for the emulsion in the bulk, as shown in Figure SI.4.

The coefficient of variation is defined as the sample standard deviation of the droplet volumes divided by the mean droplet volume $\bar{V}_{drop}$:

$$CV = \frac{\sqrt{\frac{\sum_{i=1}^{n}(V_i - \bar{V}_{drop})^2}{n}}}{\bar{V}_{drop}}$$

With n the number of droplets considered in the image analysis and V_i the volume of the droplet n°i.

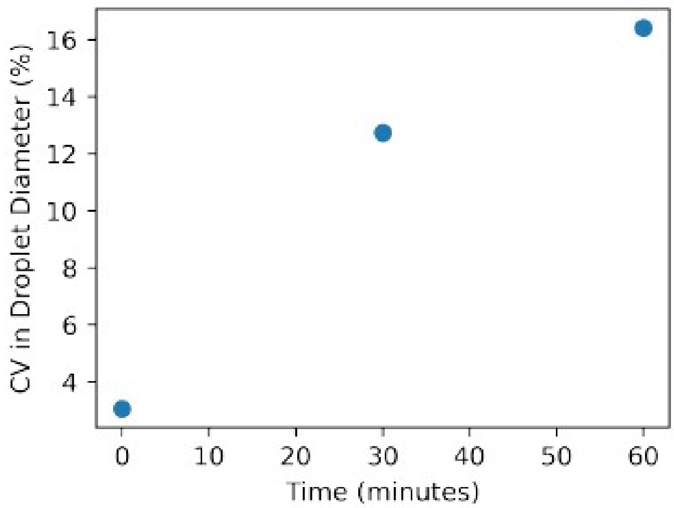

Figure SI.4: Coefficient of variation in droplet diameters at 30-minute intervals. The emulsion was collected in a plastic beaker and the droplet diameters observed under a microscope after stirring the collected emulsion and placing a few drops of it on a glass slide.

According to Figure SI.4, despite the repeated agitation of the droplets and even after one hour, which is much longer than the experimental time we have performed in our work, the coefficient of variation in droplet diameter did not surpass 16 %. Therefore, we have considered the emulsion to be stable in bulk during at least the first hour.

References

[1] Bourg S., Griveau S., d'Orlyé F., Tatoulian M., Bedioui F., Guyon C., Varenne A. Surface functionalization of cyclic olefin copolymer by plasma-enhanced chemical vapor deposition using atmospheric pressure plasma jet for microfluidic applications, *Plasma Processes and Polymers*, 2019, **16,** 6, 1800195. DOI: 10.1002/ppap.201800195.

[2] Segondy S., Rio C., Landais S., Guyon C., Rousseau F. Development of a Low Power Plasma Reactor for the Local Deposition of YSZ Thermal Barrier Coatings at Atmospheric Pressure, *ITSC2022*, 2022, 447-452. DOI: 10.31399/asm.cp.itsc2022p0447.

[3] plugim!: Open source, customisable software for signal, and image processing, https://www.plugim.fr/.

[4] Elliot Speirs. *Emulsion transport in two-dimensional porous media : influence of geometric and surface heterogeneities*. Université de Rennes, 2024.