

Superhydrophobic Bio-Fibre Surfaces *via* Tailored Grafting Architecture

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Supplementary Information

Experimental

Instrumentation

Infrared spectra were recorded on a Perkin-Elmer Spectrum 2000 FTIR equipped with a MKII Golden GateTM, Single Reflection ATR System from Specac Ltd, London, UK. The ATR-crystal was a MKII heated Diamond 45° ATR Top Plate. Static contact angle measurements were conducted on a KSV instruments CAM 200 equipped with a Basler A602f camera, using 5 µL droplets of MilliQ water. The water contact angles were determined using the CAM software. Imaging of the surfaces was performed in tapping-mode on a NanoScope IIIa Multimode AFM, using silicon tips (supplied by Veeco) with resonance frequencies of 303-344 kHz (according to the manufacturer).

Materials

Copper(I) chloride (Cu(I)Cl, 99+%), copper(II) bromide (Cu(II)Br, 99%), *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA, 99%), 2-bromoisobutyrylbromide (98%), pentadecafluorooctanoyl chloride (97%) and Whatman 1 filter paper were used as received from Aldrich. 4-(dimethylamino)pyridine (DMAP, 99%), concentrated hydrochloric acid (HCl(aq)) and triethylamine (TEA, 99%) were used as received from Acros. Glycidyl methacrylate (GMA, 97 %, Acros) was passed through a column of neutral aluminium oxide prior to use.

Immobilization of 2-bromoisobutyryl bromide on filter paper

The procedure for immobilization of initiator on the surface was adopted from Carlmark and Malmström.¹ 2x3 cm pieces of the filter paper were used. Prior to use, the substrate was washed with acetone and tetrahydrofuran (THF) and ultrasonicated in both solvents. The hydroxyl groups on the surface were then reacted by immersing the substrate in a solution containing 2-bromoisobutyryl bromide (305 mg, 1.33 mmol, 66.3 mM), TEA (148 mg, 1.46 mmol, 73.0 mM) and a catalytic amount of DMAP in THF (20 mL). The reaction was allowed to proceed at room temperature on a shaking device over night. The filter paper was thereafter thoroughly washed with THF and ethanol and dried in a vacuum oven at 50 °C.

Grafting of GMA from initiator-modified filter paper

The grafting was accomplished by immersing the initiator-modified filter paper into the reaction mixture containing GMA (30 mmol, 4.3 g), Cu(I)Cl (0.14 mmol, 14 mg), Cu(II)Br₂ (17 μ mol, 4.0 mg), PMDETA (0.14 mmol, 25 mg) and toluene (4mL). The flask was sealed with a rubber septum and thereafter evacuated and back-filled with Ar-gas three times. The polymerisation was allowed to proceed for 1-6 h at 30 °C. After the polymerisation was completed, the filter paper was thoroughly washed in tetrahydrofuran (THF), dichloromethane (DCM), methanol, THF/water and finally dried under vacuum at 50 °C over night.

Opening of epoxide groups in PGMA-brushes

The epoxide groups in the PGMA-grafted filter paper were hydrolysed in a solution of THF (10 mL) and 12 drops of HCl(aq). The reaction was allowed to proceed for 45 minutes where after the filter paper was rinsed in THF, methanol and ethanol and dried under vacuum at 50 °C over night.

Attachment of pentadecafluorooctanoyl chloride to the hydroxyl functional PGMA-grafted filter paper.

The hydroxyl groups on the hydrolysed PGMA-grafted filter paper were reacted by immersing the substrate into a solution containing TEA (148 mg, 1.46 mmol, 73.0 mM) and a catalytic amount of DMAP in DCM (20 mL). Pentadecafluorooctanoyl chloride (574 mg, 1.33 mmol, 66.3 mM) was added and the acylation was let to proceed over night. The filter paper was thereafter washed in DCM, THF and ethanol and dried under vacuum at 50 °C over night.

Water contact angle measurements over time

In order to investigate the surface coverage of the modified filter paper water contact angle measurements were conducted over a time period of 50 minutes. Images of a deposited droplet were recorded every 5 minutes, and the CA was calculated.

CA over time for the fluorinated filter paper.

It could be seen that the CA was decreasing steadily over time for the fluorinated filter paper (Figure 1S). Just after deposition of the droplet, the CA was 150° suggesting a superhydrophobic nature of the surface. After 50 minutes the water droplet had been partially adsorbed and the CA had decreased to 84°, implying a hydrophilic character of the surface (Figure 2S). The adsorption indicates an insufficient surface coverage.

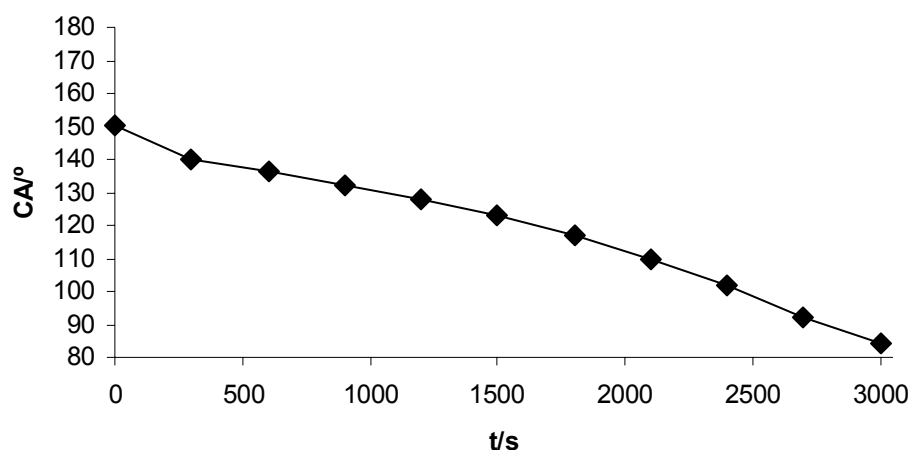


Figure 1S. Water contact angles over time for fluorinated filter paper.

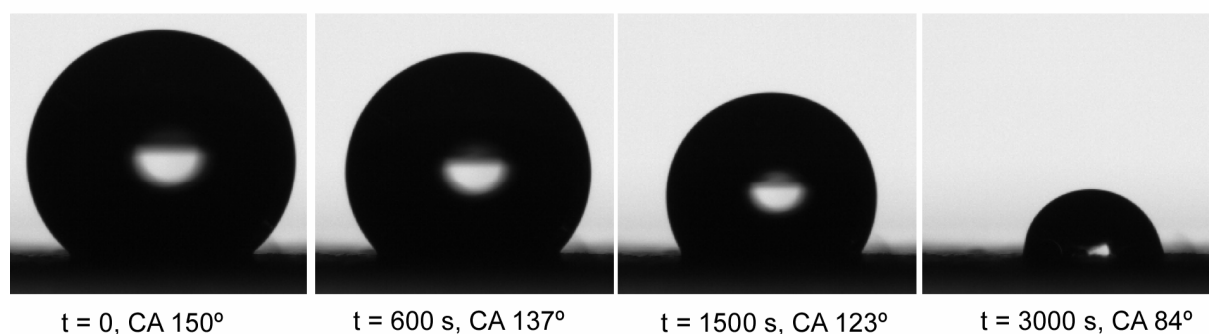


Figure 2S. Images of water droplet and water contact angles, on fluorinated filter paper after different time periods.

CA over time for the fluorinated “graft-on-graft”-modified filter paper.

No significant decrease of the CA could be seen for the fluorinated “graft-on-graft”-modified filter paper, as can be seen in Figure 3S. The initial CA was measured to 172°, and the final CA to 166° (Figure 4S). This slight decrease in the CA is probably due to the concurrent evaporation of water, resulting in a smaller droplet from which the CA is more difficult to calculate. The maintained superhydrophobicity implies a sufficient surface coverage with densely attached fluoroalkyl chains.

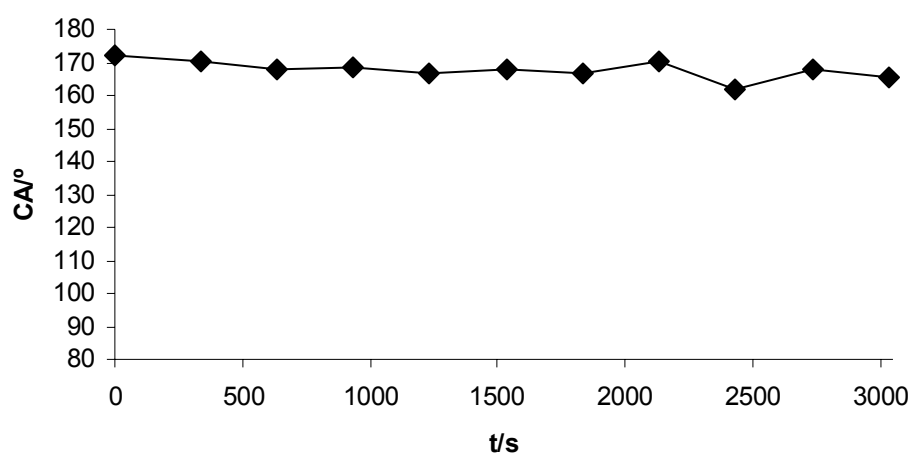


Figure 3S. Water contact angles over time for “graft-on-graft”-modified filter paper.

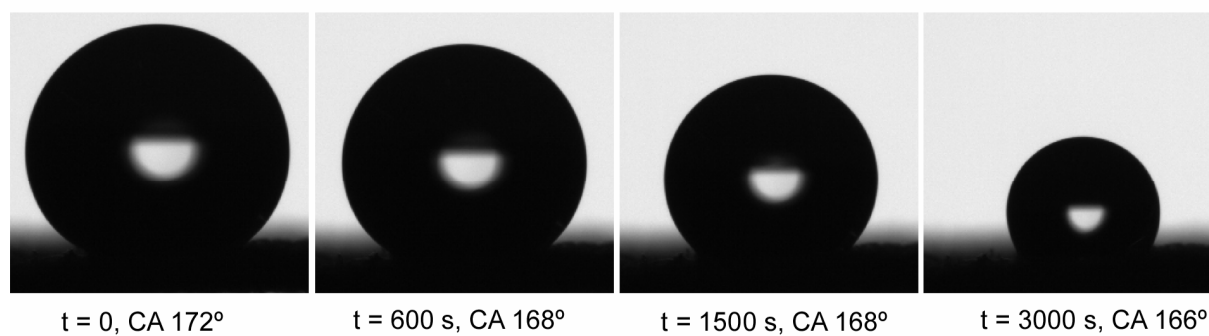


Figure 4S. Images of water droplet and water contact angles, on “graft-on-graft”-modified filter paper after different time periods.

1. A. Carlmark and E. Malmström, *J. Am. Chem. Soc.*, 2002, **124**, 900