# Hierarchical, Plasma Nanotextured, Superamphiphobic Polymeric Surfaces

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**Abstract**

A facile, mass production amenable, rapid method for making superamphiphobic / amphiphobic surfaces by random plasma nanotexturing of polymers in plasmas is presented. Plasma etched and simultaneously randomly roughened (nanotextured) polymethylmethacrylate (PMMA) Polyether-ether-ketone (PEEK), Cyclic-olefin-copolymer (COC) and Polydimethylsiloxane (PDMS) substrates show hierarchical roughness and complex high-aspect-ratio morphology. Here, they are investigated as superamphiphilic surfaces after plasma etching or superamphiphobic surfaces, after plasma deposition of a thin fluorocarbon film following plasma etching. We show that polymer surfaces etched in oxygen (PMMA, PEEK, COC) or $SF_6$ (PDMS) plasma for few minutes (with texture height< 600nm) exhibit excellent superamphiphobic behaviour, while surfaces treated for longer time show porous-like filamental morphology (filaments several microns height), which is coalesced and stabilized upon wetting, allowing their potential long-term use. Superamphiphobic / amphiphobic behaviour is observed in all cases

## 1.Introduction

Wetability (amphiphilicity or amphiphobicity) is a fundamental property of a surface, being affected by both the chemical composition and the surface morphology [1,2]. Superamphiphobic surfaces (on which water or other liquid drops roll and have a large contact angle (typically>$150^o$) with a very small contact angle hysteresis (typically<$10^o$)) are being extensively studied, due to their potential practical application as self-cleaning, anti-icing, anti-fogging, anti-fouling, low adhesion, and drag reduction surfaces [3].

Several techniques to produce superamphiphobic surfaces have been exploited [4,5], including stochastic or biomimetic bottom-up approaches [6,7]. Using these approaches hydrophobicity can be easily achieved, while amphiphobicity needs a more careful design. Plasma processing induces roughening of polymers at the nanoscale, and thus plasma-induced polymer nano-roughness control may lead to new nano-manufacturing processes and products. If a morphology containing ordered micron or submicron posts is desired, colloidal lithography may be used in combination with plasma processing to create ordered micro-scale structures, while simultaneously nanotexturing these structures during plasma etching. The combination of colloidal lithography and plasma etching results in a hierarchical (triple-scale) topography (ordered micro posts with random dual scale texture of a few hundred nano and a few tens nano) with controllable undercut profiles which enhance oleophobicity [10].

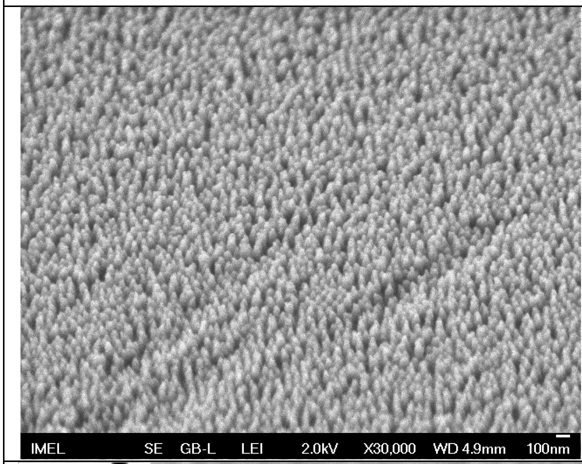
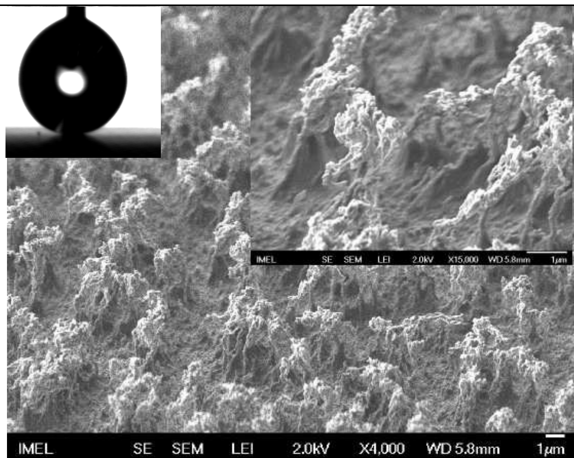
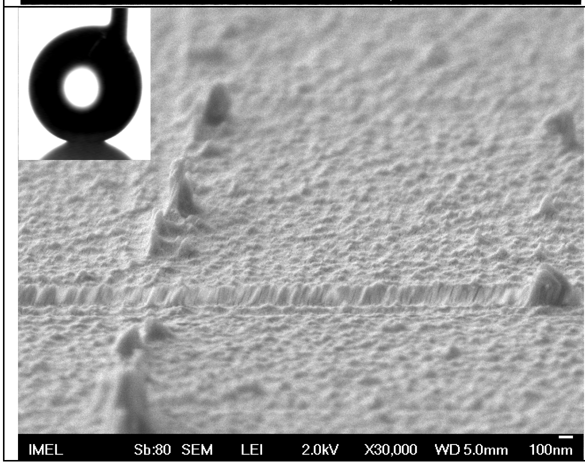
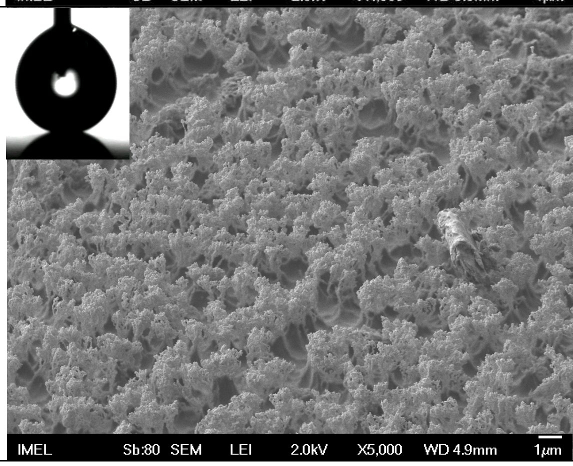
In this work, we present our technology for manufacturing stochastic or quasi-ordered, hierarchical superamphiphobic, amphiphobic and superamphiphilic polymer surfaces using plasma etching.

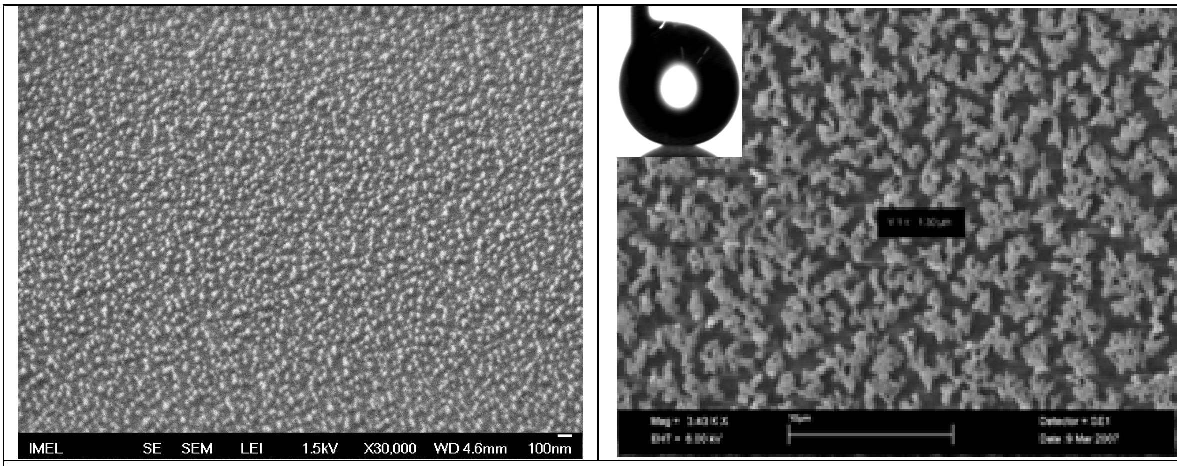
## 2.Results and discussion

### 2.1 Stochastic random topography

All plasma processes were performed in our Micromachining Etching Tool (MET) by Alcatel, equipped with a helicon source (at 13.56 mHz) providing RF power up to 2,000 W. Typical values are 1,900 W, 0.75 Pa, 100 sccm, –100 V, 15°C. Surfaces after plasma etching become amphiphilic. The same reactor was also used for conformal deposition of a thin fluorocarbon film after plasma etching using $C_4F_8$ gas at conditions (900 W,0 V, 5.33 Pa $C_4F_8$, deposition rate 30 nm $min^{-1}$) that conformally deposits a thin fluorocarbon (FC) film after plasma etching to render the surface amphiphobic.

We begin with a brief description of what plasma nanotexturing actually is. When a polymer surface is etched and a few micrometres of material have been removed, nanotexture (nanoroughness) may develop on its surface, and roughness may increase linearly with time. Starting from a flat surface, within minutes, one can get a rough quasi-ordered surface. For longer plasma etching time order is reduced and the surface becomes filamental (right column fig1). X-ray photoelectron spectroscopy (XPS) analysis reveals relatively large surface concentration of aluminium present in oxide form, coming from sputtering of the alumina dielectric dome, and the anodized aluminium clamping ring of our etch tool . This 'hard' etch inhibitor creates micromasking and leads to the development of nanotexture. In nanoscience terminology the plasma directs the assembly of a rough nanotexture on the top surface of the polymer. The XPS results suggest that nanotexture is a result of plasma–wall interactions [8]. Oxygen is used to nanotexture PMMA, COC, PEEK, and $SF_6$ is used to nanotexture PDMS. We note that the nanotexture is dual scale comprising approximately 600nm heigh, 200nm wide and 50nm wide columnar structures for 1min plasma treatment.

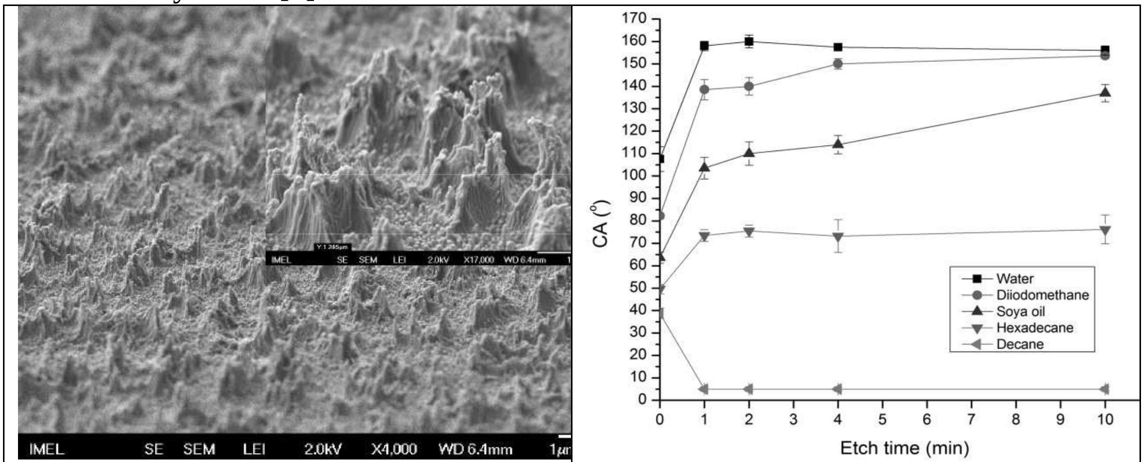
| **1min plasma etching** | **10min plasma etching** | |
|---|---|---|
|  |  | **PMMA** |
|  |  | **COC** |




**P D M S**

**Figure 1.** SEM, AFM images of polymer surfaces showing the quasi ordered to random nanotextured topography created after plasma treatment in various polymers after 1min (left column) and after 10 min (right column). Notice how the small order present in the 1min etched surfaces is decreased as etching time increases. 5μl water droplets on such surfaces after plasma fluorocarbon deposition is also shown. Water contact angle measurements for all surfaces are between$155^0$-$165^0$.

All surfaces are hydrophobic after 1 min of plasma treatment, while longer treated surfaces for more than 4 min exhibit amphiphobic properties: water contact angle is larger than $160^0$, while for other liquids contact angles are larger than $130^0$. For long plasma treatments the resulting filamanetal nanostructures are not mechanically stable. To stabilise the surface before hydrophobization we immerse the surface into water; upon drying the nanofilaments coalescence in shorter more compact hierarchical microhills, due to capillary forces. The wetted-dried surface is mechanically stable [9].




(a) (b)

**Figure 2.** (a) PMMA 10 min treated surface after wetting and drying, where the coalescence of filamental structures occurs leaving behind hierarchical microhills, (b) Static contact angle for various liquids versus etching time of PMMA. Data are taken after wetting-drying of fibrous structures to cause coalescence, and coating with fluorocarbon plasma-deposited film. Water and diiodomethane roll on the surface, while oils stick.[9]

## 2.2 Deterministic quasi-ordered topography

Uniform, self-assembled, closely packed arrays of PS spheres (1&3 μm) are fabricated after spinning the colloidal particles (fig 3a), followed by plasma etching with a moderate bias voltage and duration (fig3 b, c) resulting in undercut hierarchical pillars (fig3c) that exhibit superamphiphobic behavior for various test liquids (fig3d).

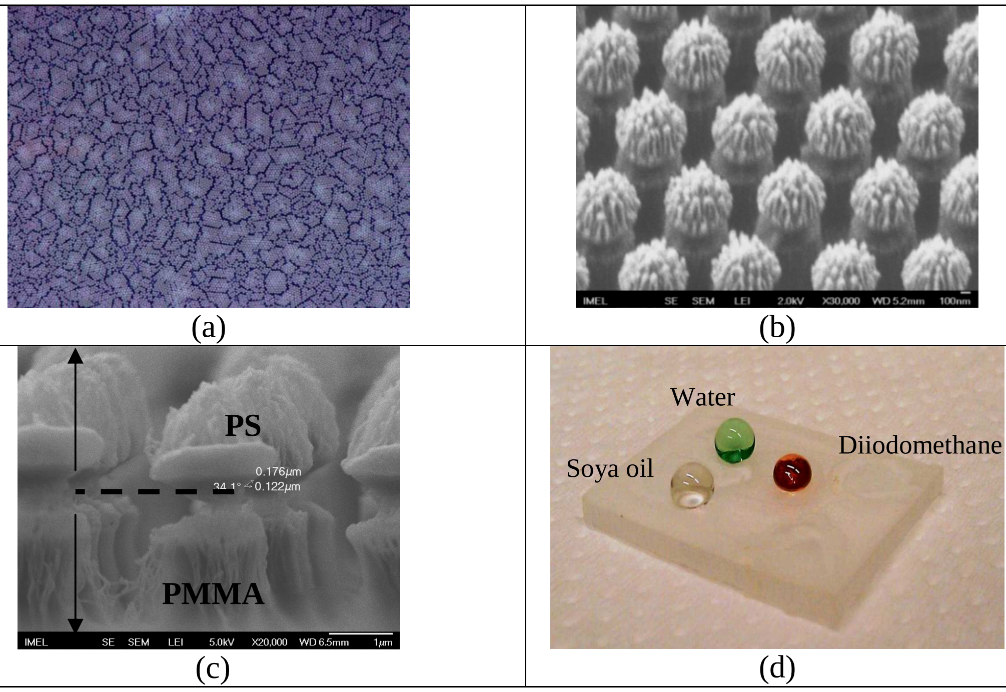



**Figure 3. (a)** 1μm PS particles on PMMA substrate (optical microscope magnification × 100), **(b)** Hierarchical (triple-scale) roughness micro-pillars produced by the combination of colloidal lithography of 1μm particles followed by plasma etching and dual-scale nano-roughness on the top of the pillars formed during plasma etching (tilt $40^0$). **(c)** Undercut, reentrant topography of a PMMA surface after 3μm PS colloidal microparticle lithography followed by a two-step etching process in Oxygen plasma. The first anisotropic etching step (3.5min) produces the column, while the second isotropic etching (2.5 min) step enhances the re-entrant shape of the pillar, by etching isotropically both the PMMA and the bottom PS hemisphere. Notice the top nanotexture on the top half PS hemisphere, **(d)** Fluorocarbon coated, Oxygen plasma treated superamphiphobic PMMA surface at optimal conditions [10]

These surfaces are truly multiscale with roughness in the micron, hundred-nanometer, and ten nanometer range. In addition these surfaces have micron scale order (coming from the colloidal lithography) and nanoscale randomness coming from plasma nanotexturing, resulting in ordered superamphiphobic surfaces, exhibiting excellent wetting repellent properties [10].

## 3 .Conclusions

In conclusion, plasma etching and nanotexturing technology is an attractive path to micro- or nano-structured polymeric surfaces of polymers with varying degrees of order. 'Smart' amphiphobic surfaces may be fabricated either as open surfaces or as embedded in polymeric microsystems to produce new 'smart' devices. Applications in fluid control (e.g. producing slip-less flow) on surfaces, anti-icing, protein and/or cell adsorption / antifouling are some of the applications of such surfaces.

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