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Wettability control on Microstructured Polypropylene Surfaces by means of O_2 Plasma

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ABSTRACT

Durable and wear resistant polypropylene surfaces with static contact angle (SCA) above 140° have been fabricated using standard photolithographic process and O_2 plasma etching followed by thermal annealing at 100°C. This microfabrication process leads to a hierarchical topography derived from the patterned microstructures and the sub-micron roughness caused by plasma. Hydrophobicity (SCA up to 145°) remained over 14 months after fabrication. This wetting behavior is attributed to the combination of the periodic array of micro-sized pillars with low aspect-ratio and the submicron roughness caused by O_2 plasma.

1 Introduction

Polypropylene (PP) is a synthetic, semicrystalline and hydrophobic thermoplastic polymer used in exceptionally wide range of injection-moulded products. This fact stems from the rigidity, toughness, and chemical and thermal resistance of PP. PP can be injected at relatively low temperature and pressure values. The demand for PP and polyolefins in general with unique wettability and functionalities has grown exponentially [1-4] due to the importance in many industrial and biological processes where self-cleaning, anti-bioadhesion, anti-

icing/fogging or water/oil separation are needed. Currently, many different “botton-up” and “top-down” techniques have been investigated to prepare superhydrophobic surfaces.[5, 6] Isotactic polypropylene (iPP) is the most used type of PP due to its high crystallinity, but it exhibits low wettability; quality that severely restricts the use of coatings for its chemical modification.[7]

In general, for a given surface free energy, the hydrophobic behavior can be enhanced by surface topography without altering their chemical composition. [8-10] By mimicking the nature, current research efforts are focused on suitable micro/micro and micro/nano roughness able to generate robust and durable superhydrophobic surfaces by cost-effective technologies for large scale manufacturing. Among those, porous iPP films prepared by direct casting of suitable iPP solutions on iPP sheets is very attractive of practical applications since it is a cheap and facile one-step process.[11] On the other hand, templating methods such as microinjection compression moulding appear to be promising for mass production of complex micro-nano scale features on polymer surfaces.[1-3] However, there are existing challenges related to the mechanical demoulding process [3, 4] due to moulded products often suffer from structural heterogeneity [12] which deteriorates the mechanical properties. The imprinting techniques usually involve a master piece, and its transferring to the polymer substrate in an opposite form. Hot embossing of thermoplastic foils in a nanoimprinting lithography machine has been revealed as a low cost technology for micro and nano-structuring of surfaces. The combination of macro Al moulds and microporous polycarbonate membranes, 20 μm thick, has been successfully applied as hierarchical template for superhydrophobic iPP films, 0.5 mm thick.[4]

We attempt to fabricate iPP surfaces with SCA above 140º by direct micro-structuring on iPP, i.e. in absence of a master. The polymer surface is processed by standard photolithography and treated further by O_2 plasma etching to achieve complex roughness. Depending on plasma composition and etching conditions, activation and/or cross-linking of PP polymers can occur

even at ambient pressure.[13, 14] In our case, the chemical etching of micro-patterned iPP sheets generates active sites with O_2 functionalities that improve the undesired wetting behavior but are subject to post-reactions. Hence, thermal annealing of O_2 plasma treated samples is performed to provoke a surface restructuring process that leads to a new energetically favourable hydrophobic state. This approach could be adapted for the fabrication of plastic labels or films with functional properties, easy to integrate in plastic items and microfluidic devices.

2 Experimental

2.1 Materials

Polypropylene sheets were made of polypropylene homopolymer, HB601WG, density 900 kg/m^3, from Borealis. The iPP sheets (homopolymer+2% masterbatch), 2 mm in thickness, were prepared by standard injection moulding machinery (Inymon) and cut into squared specimens (40 mm x 40 mm) for the purposes of this work. Photolithographic masks were designed by using CleWin5® software and printed in high resolution film by Microlithography Services Ltd. The selected photomasks (bright field) contain square-type features regularly distributed as follows: 17 µm size - 23 µm spacing; 17 µm size - 28 µm spacing; 19 µm size - 6 µm spacing, 16 µm size - 11 µm spacing.

2.2 Microfabrication Process

The iPP micro-structuring procedure followed in this work is briefly shown in Figure 1. First of all, aluminum thin film was deployed onto iPP surface in order to be used as an etching mask during O_2 plasma. Thus, electron beam physical vapor deposition (Edwards auto-500 clean room equipment) was used for the deposition of Al layer (200 nm) capable to smooth the roughness (below 100 nm) of pristine iPP surface. Secondly, the photoresist TI 35 ES (MicroChemicals GmbH) was spin-coated onto the surface (2 µm), followed by a soft baking step (100°C; 2 min); and photolithographic mask and iPP substrate were aligned by using a SÜSS MICROTEC Mask Aligner. Upon exposure to UV light (190 mJ/cm^2), the photoresist was developed (AZ® 400K developer MicroChemicals GmbH) and hardened following a

hard baking (140°C; 2 min). Afterwards, the exposed Al surface was subjected to chemical wet etching by H_3PO_4:HNO_3:CH_3COOH:H_2O solution (73 : 3.1 : 3.3 : 20.6 % vol) at 24°C for 4 min in order to etch the designs. Previous to plasma reactive ion etching (RIE) with O_2, the iPP specimens were thoroughly washed with acetone for TI 35 ES removal. The RIE conditions used in this work were 0.19 mbar, pressure chamber; 20 sccm O_2 flow and RF (13.56 MHz) power 300 W. Etching process was comprised of cycles 10 min in duration where the number of cycles depends on the target micro-structuring. Achieved etching rate using this procedure was 0.5 µm/min. Under these conditions, the iPP surface properties are modified via both energetic ion milling and surface oxidation by reactive oxygen species (ions and radicals). The volatiles and gaseous products (CO_2 and CO) are evacuated through the vacuum line; whereas the polar groups formed on the polymer surface during this oxidation can be lost again via post-reactions to lower the surface energy. Finally, the protective Al layer was removed with the H_3PO_4 etchant solution (4 min dipping time).

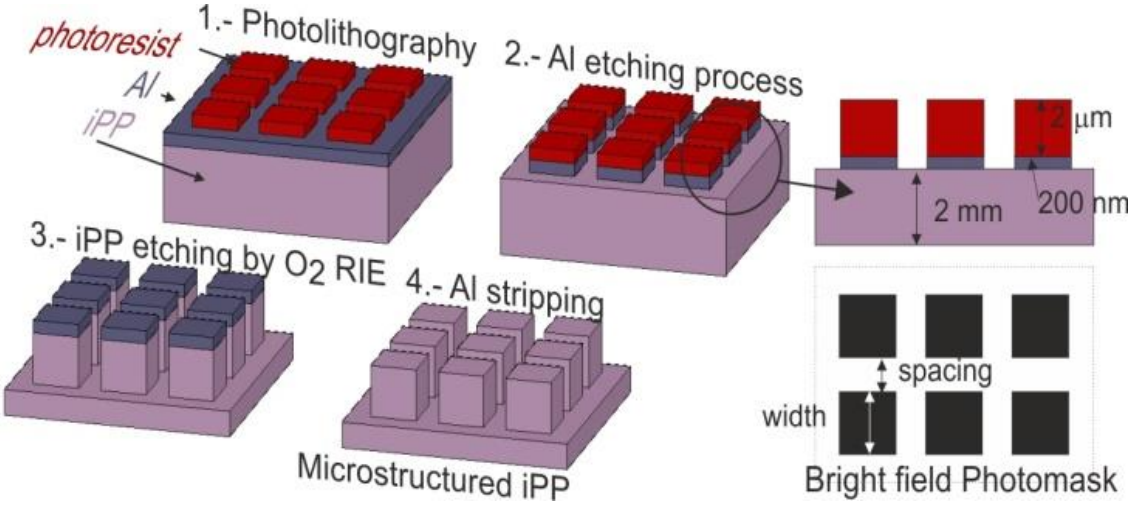

Figure 1. Direct Micro-structuring of iPP sheets by conventional Si based technologies.

2.3 Analysis and Characterization

All specimen images were taken by using an environmental scanning electron microscope SEM-Quanta FEG-250 (2.00 kV, 70 Pa). Two dimensional surface profile measurements

were carried out by stylus profilometry (contact measurement) DektakXT Bruker with a vertical resolution of 1Å. The wetting properties of the topographies fabricated were studied based on the static contact angle (CA) measurements. These were performed by using ATTENSION THETA200AUTO1 equipment with a high resolution CCD camera. The light source was mounted opposite to the camera. With a micro-syringe, water droplets of 6 µL (1.1 mm in diameter, i.e. sufficiently large compared with the typical roughness scale herein studied) were placed onto the microstructured iPP surface. Three independent measurements were performed on each sample to calculate the mean value and standard deviation (SD). The FTIR-ATR analysis of the polymer samples was carried out with VERTEX 70 equipment with microscope slide MKII Golden Gate ATR (Diamond crystal 45° with deep of penetration of 2 µm) from 4000 cm^{-1} to 600 cm^{-1}, 256 scans and resolution of 0.05 cm^{-1} to evaluate the chemical modification of the surface.

All samples were subjected to aging in order to assess on durability and wear-resistant properties. SCA was measured before and after aging period 420 days in duration. During aging process, typical bactericidal assays (not shown here) involving severe abrasion conditions, i.e. microorganisms detachment by vortex sonication in presence of 10 glass balls 3 mm in diameter for 30 min, were also performed.

3 Results and Discussion

Table 1 summarizes the main geometric parameters and wetting properties of the microstructured iPP samples. The topographic microstructure of the iPP samples herein prepared was chosen on the basis of related publications.[1, 2] SEM images of iPP patterns show the absence of larger area with missing or broken pillars. As an example, **Figure 2** illustrates our typical topography with sample iPP_5 prepared upon 10 min RIE exposure.

Table 2 shows wettability and surface roughness (evaluated by profilometry) of blank iPP samples, i.e. without any microstructure, before and after any etching and thermal process. These samples are the controls in order to demonstrate benefits of micropatterning for

improving surface hydrophobicity (see supporting information SI). As it was expected, the use of oxygen plasma etching increases the surface roughness of the polymeric substrate, from 100 nm up to 175 nm.

Table 1. Dimensions of the photomasks, dimensions, micro-roughness factor "r", area fraction "f_{solid}" of the microstructured iPP samples and wetting properties.

	Photomask		**Fabricated Microstructure**					**Experimental SCA ± SD**	
Sample	Width (μm)	Spacing (μm)	Depth (μm)	Width (μm)	Spacing (μm)	r*	f_{solid}**	0 days aging (º)	420 days aging (º)
iPP_1	17	23	18.6 ± 0.5	12.1 ± 0.8	27.0 ± 1.0	1.587	0.095	151 ± 6.4	145 ± 3.0
iPP_2	17	28	19.9 ± 0.7	14.0 ± 1.0	30.5 ± 0.9	1.561	0.099	152 ± 1.8	140 ± 1.7
iPP_3	19	6	6.8 ± 0.5	14.2 ± 1.2	10.9 ± 1.4	1.617	0.320	122 ± 6.3	110 ± 9.0
iPP_4	16	11	12.0 ± 0.3	15.3 ± 0.6	11.1 ± 0.8	2.054	0.336	144 ± 1.1	141 ± 1.7
iPP_5	16	11	5.1 ± 0.7	16.3 ± 1.0	10.5 ± 0.7	1.458	0.370	144 ± 3.5	140 ± 2.0
iPP_6	16	11	22.1 ± 1.4	11.2 ± 1.2	15.8 ± 1.5	2.356	0.172	144 ± 3.3	133 ± 7.2
iPP_7	16	11	26.9 ± 6.8	8.0 ± 1.3	18.8 ± 1.6	2.200	0.089	145 ± 5.0	122 ± 20.2
iPP_8	17	28	6.8 ± 0.9	14.3 ± 0.7	30.1 ± 0.7	1.197	0.104	142 ± 1.8	136 ± 6.8
iPP_9	19	6	17.7 ± 0.5	11.1 ± 1.7	14.0 ± 2.5	2.247	0.196	145 ± 3.3	130 ± 13.1
iPP_10	17	28	3.9 ± 0.4	13.7 ± 1.1	31.1 ± 1.1	1.105	0.094	144 ± 4.2	134 ± 5.0
iPP_11	15	10	11.5 ± 0.2	10.2 ± 0.9	15.5 ± 0.6	1.712	0.158	147 ± 2.8	138 ± 12.5
iPP_12	31	9	10.0 ± 0.6	27.7 ± 0.7	12.2 ± 1.2	1.694	0.482	147 ± 0.5	139 ± 3.6
iPP_13	31	9	4.4 ± 0.3	29.2 ± 1.2	10.6 ± 1.5	1.327	0.538	145 ± 1.7	135 ± 4.4
iPP_14	31	9	13.0 ± 0.8	28.0 ± 1.5	12.1 ± 0.8	1.904	0.488	145 ± 0.6	140 ± 0.6

*r is the micro-roughness factor calculated as the ratio among the actual surface and the geometric surface
**f_{solid} is the area fraction of solid surface in contact with a liquid

Table 2. Main surface characteristics of blank iPP samples before and after O_2 plasma etching and after thermal annealing

	Pristine iPP	**After O2 Plasma (RIE 30 min)**	**After Thermal Annealing (100°C, 72 h)**
Static Contact Angle ± SD (°)	98 ± 1	~ 5 ± 1	112 ± 3
Surface roughness (nm)	100 ± 16	175 ± 15	190 ± 14

The inherent surface roughness of pristine iPP sheets around 100±16 nm (see Figure S1 of the SI), attributed to the injection and de-moulding process, is clearly observed on the surface of

the ridge of the pillars (see Figure 2C) which is protected by the Al mask. Figure 3 underlines the topography changes for the surface of the valley due to O_2 plasma as a function of etching time. This morphology, characteristic of polyolefins, is commonly attributed to the difference in plasma susceptibility of spherulitic crystalline regions and the surrounding amorphous polymer matrix. The submicron roughness among pillars becomes more noticeable with etching time, i.e. with increasing the height of the pillars: from 175±14 nm up to 425±20 nm for 30 and 60 min RIE respectively. These values agree with those evaluated on blank iPP samples when exposed to similar conditions (see Table 2). In addition, there is no sharp change in roughness that occurs below 10 min etching time when compared to pristine iPP sheets. This submicron roughness enhancement is also noticeable in the sidewall of pillars (see Figure 2C) and in the under etching zones (see Figure ·3B and Figure 3C), where wettability could be greatly affected; but it cannot be determined by standard profilometry technique. According to SEM observations, the iPP samples are hierarchical structures where the nanoscaled roughness has been unintended incorporated to the microstructured surface.

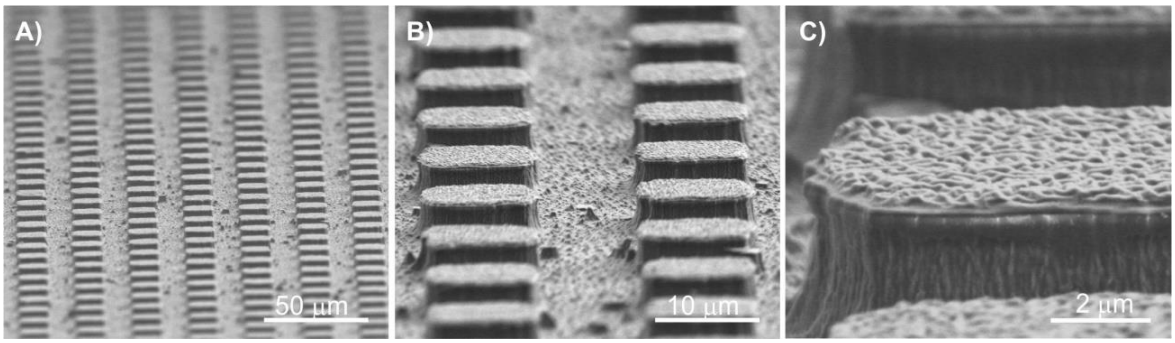

Figure 2. SEM images of iPP_5 sample.

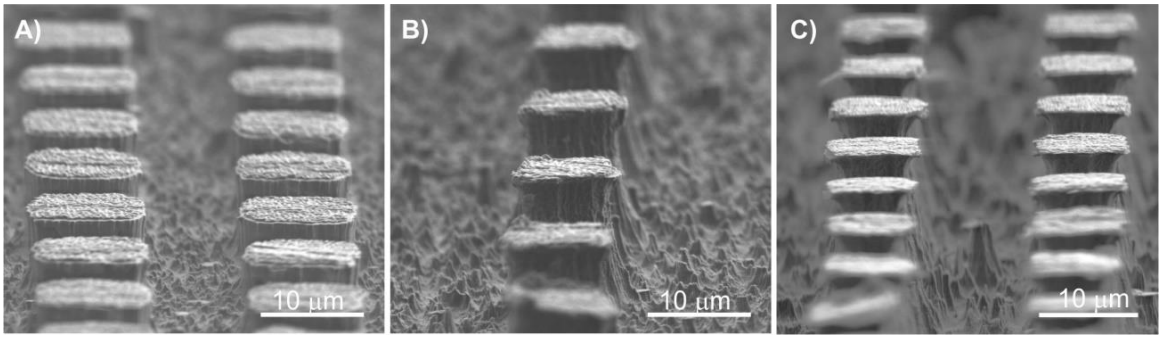

Figure 3. SEM analysis of the surface roughness among barrel-shaped pillars as a function of the etching time: A) iPP_4; B) iPP_2; and C) iPP_7

Table 1 also includes the static contact angle of iPP microstructured surfaces upon thermal annealing. On the first attempt, SCA measurements (not shown in Table 1) were performed after RIE. The so obtained values were clearly different from the published data on similar designs attained by hot embossing. In particular, 104±1°, 103±1°, 97±1° and 99±3° were recorded for iPP_1 to iPP_4 samples. For the iPP control, the wettability was notoriously modified, becoming more hydrophilic, i.e. from 98º down to 5º upon 30 min of O_2 plasma (see Table 2 and Figure S2 of SI).This experimental observation agrees with the chemical activity of plasma species, responsible for the formation of oxygen-containing functionalities on the iPP surface. In fact, air plasma based treatments are commonly used in the polymer industry to improve the wettability and adhesion properties.

Therefore, a final thermal annealing step at 100°C was included in the fabrication process for condensation of terminal functional groups. For the iPP control, the starting wetting behavior exhibited by pristine sample was restored, i.e. 112±3° (see Table 2). The annealing effect was also evidenced on microstructured iPP samples. It provoked a rise in the SCA value higher than 25º.

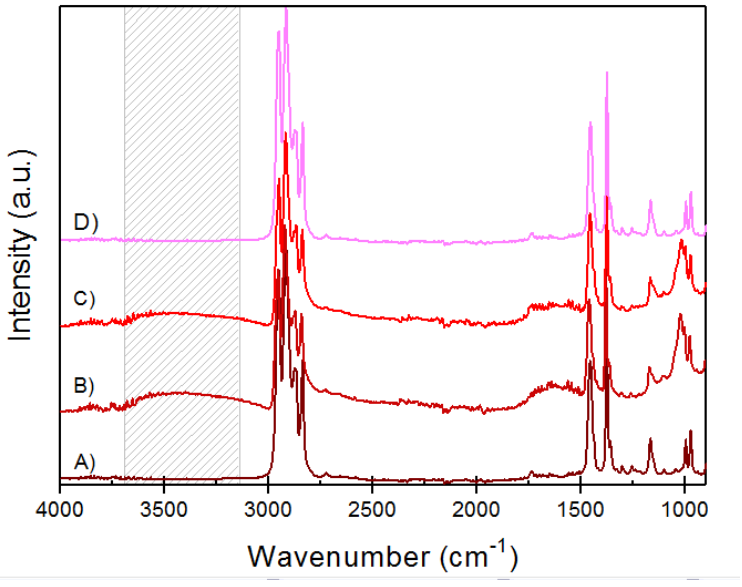

Figure 4. FTIR-ATR spectra for iPP samples: A) untreated iPP, B) microstructured iPP after O_2 plasma etching, C) microstructured iPP after O_2 plasma etching and followed by thermal annealing for 24h, and 72h (D).

For a better understanding, Figure 4 comparatively shows the FTIR-ATR spectra for pristine iPP (A); microstructured iPP after O_2 plasma etching (B); microstructured iPP after O_2 plasma etching and followed by thermal annealing for 24h (C) and 72h (D), respectively. Thus, chemical information of a more deeper region of the sample, i.e 2 microns, is provided for the rapid assessment on –OH removal as a function of the annealing conditions. The intensity of the characteristic absorption band of -CH_2- at 2922 cm^{-1} (asymmetric and symmetric stretching) was used as a reference. A clear qualitatively difference can be found between the FTIR-ATR spectra before and after plasma treatment. The increased absorption bands of OH-groups (2900–3700 cm-1), C=O ester, ketone and carboxyl groups (1680–1750 cm^{-1}) upon RIE is clearly noticeable; even on samples subjected to thermal annealing at 100°C for 24 h. Absorption intensities are also increased in between 900 cm^{-1} and 1200 cm^{-1} where the bands of O–H and C–O stretching vibrations are located. Conversely, upon annealing for 72h, the FTIR-ATR spectrum resembles the virgin iPP and the surfaces become hydrophobic. Control iPP samples (not shown here) also behaved similarly. Accordingly, all the microstructured samples were routinely subjected to this post-treatment before wettability measurements.

In Table 1, it can be seen that all the microstructured iPP sheets exhibited SCA > 120°. Static contact angle depends on the details of the drop placement so for a better understanding of superhidrophobicity behavior advancing and receding angle studies should be carried out. As it can be observed in Table 1, SCA values of the samples after exposure to severe abrasion tests and aging period for 420 days, remain almost unaffected; only in two samples iPP_3 and iPP_7, SCA decreases more than 10%. In the samples iPP_7. iPP_9 and iPP_11, that corresponds with the samples with sharper aspect ratio, a high standard deviation is also observed, this is because several columns have collapsed and uniformity of the surface is

lower (see Figure S3 of SI). However other shorter and thicker designs, like iPP_4 and iPP_5, have not been seriously affected by aging process (see Figure S4 of SI).

Based on surface profile measurements, the micro-roughness factor, denoted as "r" and the area fraction of the solid surface in contact with a liquid, denoted as "f_{solid}" have been calculated to evaluate the surface structure effect with both, the Wenzel and the Cassie-Baxter theory. The experimental SCA of pristine iPP flat sheet, 98±1°, was considered as Young´s CA.

The SCA values of patterned samples were compared with the apparent SCA values calculated from homogeneous, i.e. Wenzel equation, and heterogeneous, i.e. Cassie Baxter equation, equilibrium wetting conditions respectively,[15, 16] assuming one level of isotropic microscale roughness. In contrast, the profilometry and wettability of blank iPP sheets before and after etching process (see table 2 and SI) confirm resulting submicron scale roughness. The transition from Wenzel to Cassie Baxter wetting regimes on surfaces with hierarchical roughness, i.e. micro-micro or micro-nano structures, is still unclear for an optimal fabrication design.

The parity plot between experimental and calculated theoretical SCA values for all the samples prepared is depicted in Figure 5. Reported data for similar designs fabricated by hot embossing have been also inserted for a more quantitative understanding.[1] Our experimental results do not appropriately match with theoretical calculations. Values follow better the Cassie-Baxter equation characteristic of composite solid-air surfaces with heterogeneous wetting, i.e. the water drop lies on the top of the surface structure.[16] It is commonly accepted that the Cassie-Baxter model works with rougher surfaces and is more favourable if SCA < acos (-1/roughness factor), in agreement with the iPP samples herein prepared. By following Wenzel or Cassie-Baxter theoretical calculations, we have assumed isotropic microscale roughness. However, the submicron roughness (ridge top, sidewall, etched valley) and evolved surface chemistry during plasma and annealing make these polymer microstructures

very difficult to model by theoretical calculations. In fact, authors like Gao and McCarthy[17] put forward the importance of submicron roughness and chemistry of the solid in the contact line between liquid and air for a proper description of complex structures. Above all, it seems that a micro-structured pattern combined with submicron roughness positively contribute to the wetting properties of these polymeric micro and sub-micro hierarchical surfaces.

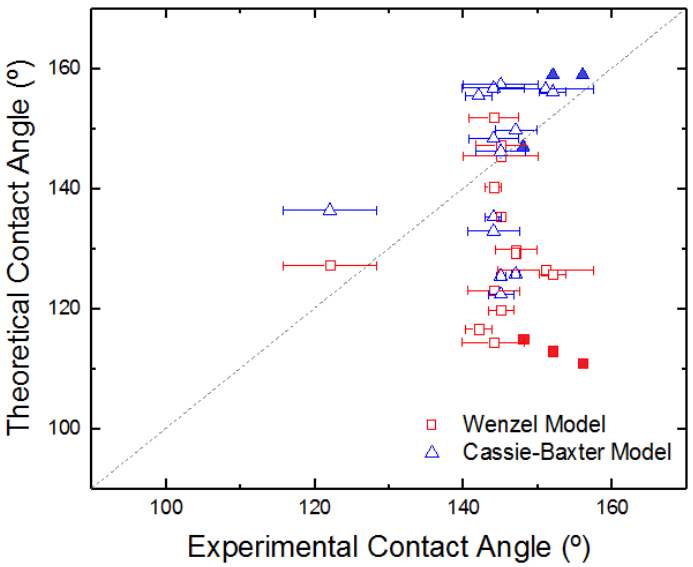

Figure 5. Comparison between experimental and theoretical C.A based on Cassie-Baxter and Wenzel theories. Empty symbols correspond to experimental values shown in this work; filled symbols correspond to data from Puukilainen et al.[1]

4 Conclusion

We have fabricated iPP surfaces with static contact angle above 140° by using a simple micro-structuration process based on standard photolithography, oxygen plasma and thermal annealing. This fabrication process leads to a hierarchical topography derived from the patterned microstructures and the sub-micron roughness caused by plasma. Achieved static contact angle rises up to 145° in some microstructured samples; and remains over 14 months after fabrication and exposure to severe abrasion tests. These wetting properties highlight the good resistance to mechanical degradation during aging period in agreement with the low aspect ratio of patterned microstructures of these samples. The described sequential procedure could be easily adapted for high volume manufacturing process of plastic elements[18] and microfluidic devices with tunable wetting properties.

Supporting Information

Additional supporting information is available in the online version of this article at the publisher's website or from the author.

Received: ((will be filled in by the editorial staff)); Revised: ((will be filled in by the editorial staff)); Published online: ((please add journal code and manuscript number, e.g., DOI: 10.1002/ppap.201100001))

Keywords: micropatterning; plasma etching; poly(propylene) (PP); Static contact angle; wear resistance

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Graphical Abstract

Durable and wear resistant polypropylene surfaces with static contact angle above 140° have been fabricated using standard photolithographic process and O_2 plasma etching followed by thermal annealing at 100°C. This durable wettability is attributed to the combination of the periodic array of micro-sized pillars with low aspect-ratio and the submicron roughness caused by O_2 plasma.

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