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Polymer Surface Modification: Topography Effects Leading to Extreme Wettability Behavior

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ABSTRACT: The surface oxidation of polyethylene (PE) and the surface reduction of Teflon (FEP) were studied with regard to the surface topography of the film samples that were used and the resulting water wettability. Anodized aluminum membranes were used as nanomolds to impart fibrillar topographies to the polymer surfaces. Water contact angles of smooth PE ($\theta_A/\theta_R = 93°/75°$) decreased to $\theta_A/\theta_R = 68°/46°$ upon oxidation with potassium chlorate/sulfuric acid solution. Smooth FEP film samples changed from $\theta_A/\theta_R = 111°/100°$ to $\theta_A/\theta_R = 64°/45°$ upon reduction with sodium naphthalide solution. Contact angles of PE and FEP increased to 172°/160° and 174°/172°, respectively, upon introduction of the fibrillar topography and both decreased to ∼0°/0° after oxidation and reduction, respectively. That topography can be used as a tool in polymer surface modification is emphasized.

Introduction

In the current decade, there has been an explosion[1−16] of publications describing how topography can be used to control wettability, and there are many examples of “superhydrophobic” surfaces based on simultaneous control of chemistry and topography. It is now abundantly clear that topography is an important and useful variable in controlling surface properties. A wide variety of methods have been employed that involve sequential or concurrent modification of topography and surface chemistry. Most of these can be divided into three approaches: coating rough surfaces with layers of a hydrophobic material,[12,16−22] roughening hydrophobic materials,[23−26] and simultaneous coating/roughening methods.[10,27−29]

The field of research that can be termed “polymer surface modification” was very active a decade to three decades ago, and numerous conferences and symposia were dedicated to this topic. We refer to three books[30−32] published in three different decades that are compilations of chapters written by contributors at international meetings during this period and one textbook[33] that gives a view of the thoughts, objectives, and activities of this field at this time. This field of research is now quite advanced and serves as a tool in countless other fields, for instance, biocompatibility,[34] sensors,[35] “smart” surfaces,[36] microfluidics,[37,38] and self-cleaning surfaces.[39] Chemical methods for modifying a wide variety of commercially available polymers are now available. Polyethylene and polypropylene surfaces can be modified by oxidation.[40−44] Fluoropolymers are modified by reduction[45−49] and subsequent chemistry[50−52] of the reduced surface layer. Nylon[53−55] and polyester[56−59] surfaces can be modified by amide- and ester-directed reactions. Poly(*p*-xylylene)[60] and poly(ether ether ketone)[61−63] surfaces react by aromatic substitution and carbonyl addition chemistry, respectively.

In retrospect, it is surprising that topography was not used as a variable to control wettability and other surface properties of modified polymers. The effect of topography on wettability was certainly known,[64−69] but it was not used in this research field as a tool for property control. Our group regarded anomalously high or low contact angles as aberrations due to roughness and as annoyances; interpreting data from smooth surfaces was more straightforward, and we normally abandoned approaches that led to surfaces with roughness. We reported contact angles of one surface as $\theta_A/\theta_R = >150°/0°$,[47] but regarded it as a failure. It is now clear that it was a mistake to not have done the chemistry we reported on surfaces of variable topography. If we had used model topographies with different length scales, earlier insight into what has been discovered in the present decade[1−16] would have been uncovered. It is not practical, nor is it necessary, to “go back” and remedy this mistake; the results can now be foreseen. Here we show that these types of results can be predicted, at least qualitatively, and describe the effects of topography on two of the most standard polymer surface modifications: oxidation of polyethylene and reduction of Teflon. Only one topography was studied and compared with smooth surfaces, but the results show that topography can induce enormous changes in wettability. This demonstrates that control of topography can change surfaces from having unexceptional water contact angle behavior to being “superhydrophobic” or “superhydrophilic”.

Experimental Section

Materials and Methods. Anodized aluminum membranes (Anodisc 0.2 μm) containing ∼200 nm diameter pores were purchased from Whatman. These membranes are 13 mm in diameter and are 60 μm thick. They are commonly held in cartridges and used for filtration. The two faces of the membrane are different, with one face exhibiting smoother polygonal shaped impinging cells of ∼200 nm diameter. This face was placed in contact with polymer film samples in experiments described below. The channels between the two faces are cylindrical and parallel. Poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP) was obtained from DuPont as smooth ∼125 μm thick film. Ultrahigh molecular weight polyethylene film (PE) (∼125 μm thickness) was purchased from McMaster−Carr. Film samples were rinsed with ethanol before use. Water purified by reverse osmosis was further purified using a Millipore Milli-Q system that involves reverse osmosis, ion exchange, and filtration steps (10^{18} Ω/cm). Other reagents and solvents were obtained from Aldrich and used without further purification.

Contact angle measurements were made with a Ramè−Hart telescopic goniometer equipped with a Gilmont syringe and a 24 gauge flat-tipped needle. The probe fluid was water, purified as

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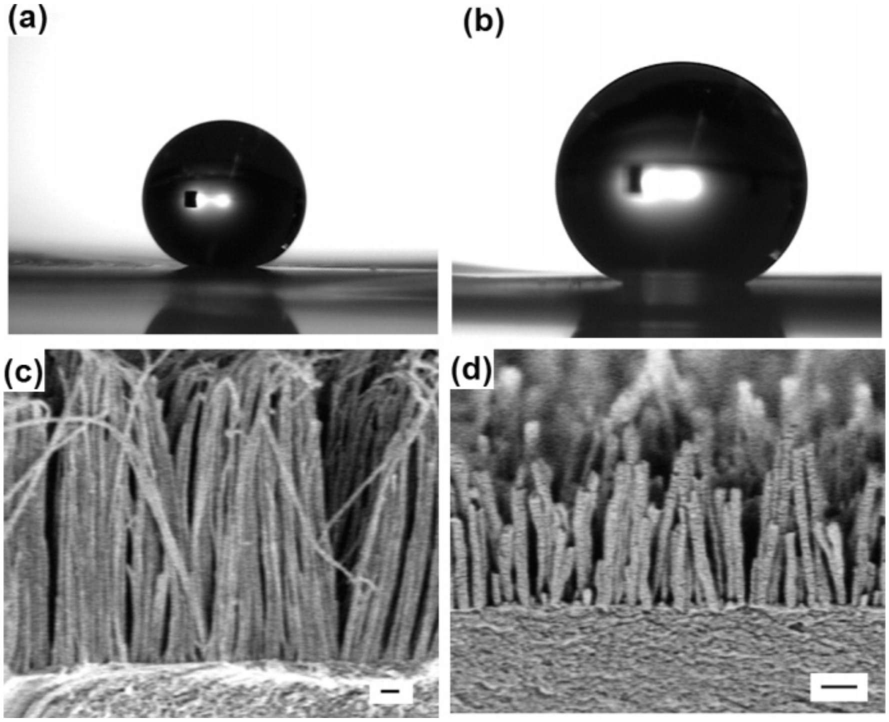

Figure 1. (a) Water droplet pinned at a defect on a sample of ^{III}FEP. (b) Water droplet at rest on a ^{III}PE surface. (c,d) SEM images of ^{III}FEP and ^{III}PE, respectively (scale bars = 1 μm).

described above. Dynamic advancing (θ_A) and receding angles (θ_R) were recorded while the probe fluid was added to and withdrawn from the drop, respectively. X-ray photoelectron spectra (XPS) were recorded on a Physical Electronics Quantum 2000 spectrometer with Al Kα excitation at a spot size of 100 μm at 25 W. Spectra were obtained at 75° takeoff angles with respect to the plane of the sample surface. A JEOL 6320A field emission scanning electron microscope was used to obtain SEM images. Specimens were prepared by freeze fracture in liquid nitrogen.

Introduction of Topography to FEP and PE Film Samples. An alumina membrane was placed on top of a slightly larger FEP film sample, and this assembly was placed on a hot plate at 240 °C under vacuum. After 30 min, the temperature was increased to 290 °C and held for an additional 30 min. The hot plate was turned off, and the assembly was allowed to slowly cool to room temperature. An identical procedure was used for the PE film samples except that they were heated first at 60 °C for 30 min and then at 170 °C for 20 min.

The assemblies, subsequent to these thermal treatments, were submerged in 1 wt % NaOH solution in water/isopropanol (8:2 v/v) for >2 h. After the alumina membrane dissolved, the "nanoimprinted" polymer film samples were rinsed with copious amounts of water/isopropanol (8:2 v/v) to remove residual NaOH and aluminate salts.

Reduction of FEP Surfaces. Sodium naphthalide solution was prepared by dissolving 0.5 g (4 mmol) of naphthalene in 25 mL of THF and then cutting very small pieces of sodium (0.17 g, 7.4 mmol) into the solution under nitrogen. After 2 h of stirring, the dark-green solution was transferred via cannula to a Schlenk tube which contained FEP film samples. Reduction was allowed to proceed at room temperature for 24 h. The reaction solution was removed, and samples were rinsed with copious amounts of THF and water. Samples were then dried under vacuum.

Oxidation of PE. PE film samples were submerged in a sulfuric acid solution of potassium chlorate (10 mg/mL) for 3 h at room temperature in an open flask. Oxidized samples were washed with copious amounts of water and then THF and dried under vacuum at 60 °C.

Results and Discussion

To show in a simple and straightforward manner that topography control can have an obvious and significant impact on polymer surface modification, we chose very standard polymers, polyethylene and Teflon, and very standard chemical surface modification reactions, oxidation[40−44] of polyethylene, and reduction[45−49] of Teflon. Our choice of technique to introduce topography is less obvious (three separate reasons), and the background of this choice is from ongoing work in our laboratories. (1) We showed that heating polymer film samples in contact with anodized aluminum membranes causes the polymer to be drawn into the pores of the membrane by capillary forces. We reported[70] micrographs of arrays of polymer "posts" that were formed after membrane dissolution. (2) We discussed[71] and showed[12,13,72] in other work why an array of posts is an ideal geometry to disrupt contact lines and affect wettability. (3) The technique is simple, involves an inexpensive commercially available anodized aluminum membrane, and we could conveniently do this in our laboratories.

Introduction of Topography. An FEP or PE film sample (~1.5 cm × ~1.5 cm) was placed on a clean hot plate, and a 13 mm diameter anodized aluminum membrane (AAM) was centered on it. After one or the other heating protocols described in the experimental section, the hotplate was turned off and allowed to cool. The FEP/AAM or PE/AAM assembly was submerged in basic solution to dissolve the membrane. We abbreviate these topographically modified samples ^{III}FEP and ^{III}PE; the superscript is meant to convey their fibrillar structure (see below).

Water droplets do not come to rest on the ^{III}FEP surface and move spontaneously to the regions of FEP that were not treated with the AAM. Figure 1a shows a droplet at rest pinned at a defect on this surface. Water contact angles were measured as $\theta_A/\theta_R = 174°/172°$. A smooth sample of FEP exhibits $\theta_A/\theta_R = 111°/100°$. Water droplets do come to rest on horizontal surfaces of ^{III}PE (Figure 1b), but roll off when the sample is slightly tilted. Water contact angles measured for ^{III}PE were

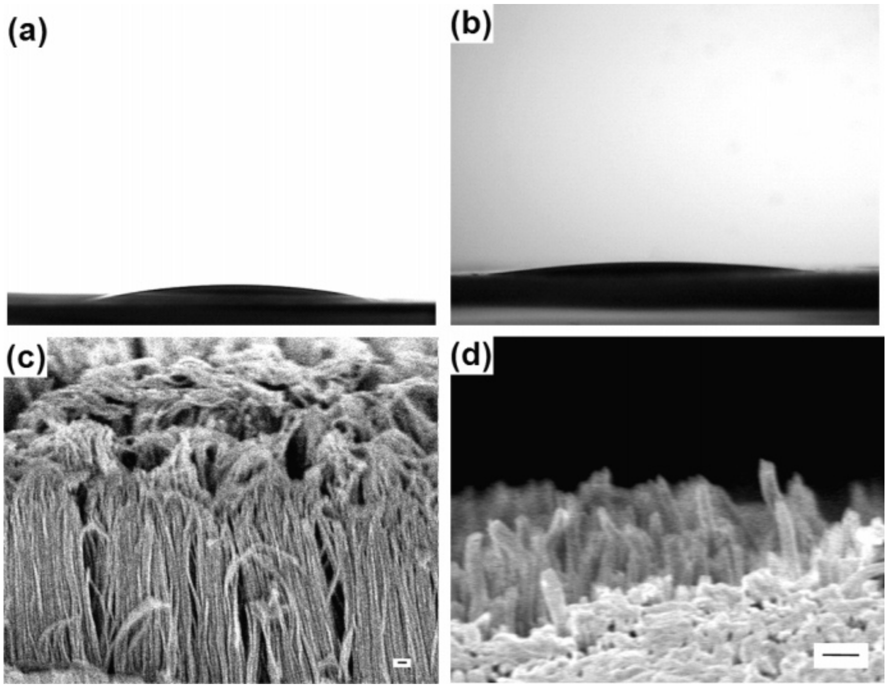

Figure 2. (a,b) Water droplets that have spread on $^{III}FEP^{RED}$ and $^{III}PE^{OX}$ surfaces, respectively. (c),(d) SEM images of $^{III}FEP^{RED}$ and $^{III}PE^{OX}$, respectively (scale bars = 1 μm).

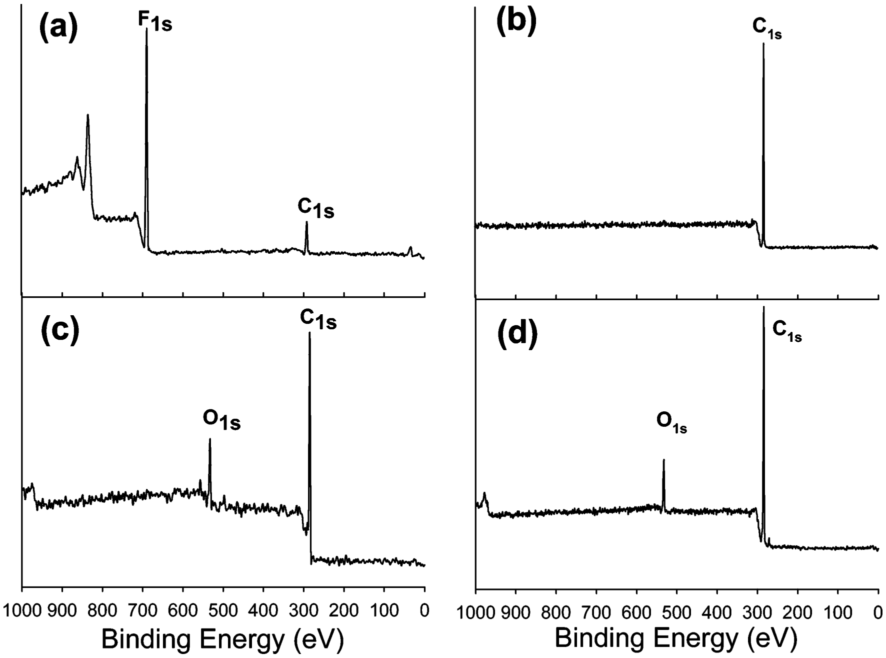

Figure 3. XPS spectra of (a) ^{III}FEP, (b) ^{III}PE, (c) $^{III}FEP^{RED}$, and (d) $^{III}PE^{OX}$.

$\theta_A/\theta_R = 172°/160°$; smooth samples of PE exhibit $\theta_A/\theta_R = 93°/75°$. Parts c and d of Figure 1 show SEM images of freeze-fractured cross sections of ^{III}FEP and ^{III}PE, respectively.

Both ^{III}FEP and ^{III}PE samples contain arrays of ~200 nm diameter fibrils that are roughly perpendicular to the planes of the film samples. These are not "pretty pictures" and cannot be described as "arrays of pillars," but more accurately as "carpets" or "lawns." We have adjusted the height (and aspect ratio) of polystyrene fibrils of this type[70] by tuning the conditions (heating times and temperatures and rates of heating and cooling) of the processing or using polymer samples with different melt viscosities. We did not undertake these studies with ^{III}FEP and ^{III}PE because the dramatic contact angle changes in these samples met our objectives.

The geometry of these "lawns" gives rise to the high contact angles and the low hysteresis observed. More precisely, these surfaces form tortuous and discontinuous three-phase contact lines with water droplets. We have discussed this issue at length in recent publications.[13,29] Here we wish to emphasize that the change in topography gives rise to a dramatic change in contact angles, from $\theta_A/\theta_R = 111°/100°$ to $\theta_A/\theta_R = 174°/172°$ for FEP $\rightarrow$ ^{III}FEP and from $\theta_A/\theta_R = 93°/75°$ to $\theta_A/\theta_R = 172°/160°$ for PE $\rightarrow$ ^{III}PE.

Chemical Modification. Standard chemical modifications that we have carried out many times in our laboratories were used to modify FEP and PE. Both are brutal nonselective reactions that degrade the samples. Potassium chlorate/sulfuric acid completely converts hydrocarbon materials to carbon dioxide leaving residual carboxylic acids[73] and sodium naphthalide reduces FEP to carbon that is subsequently oxidized in air.[48] After oxidation of PE (smooth, as-received film), the water contact angles decreased from $\theta_A/\theta_R = 93°/75°$ to $\theta_A/\theta_R = 68°/46°$. Reducing a smooth FEP film sample caused contact angles to change from $\theta_A/\theta_R = 111°/100°$ to $\theta_A/\theta_R = 64°/45°$. The hydrophobic surfaces became more hydrophilic.

The "superhydrophobic" surfaces, $^{\mathrm{III}}$FEP and $^{\mathrm{III}}$PE, respectively, were exposed to the same conditions of reduction and oxidation just described. Both of these surfaces ($^{\mathrm{III}}$FEP$^{\mathrm{RED}}$ and $^{\mathrm{III}}$PE$^{\mathrm{OX}}$) were completely wet by water droplets; the droplets spread rapidly due to capillary forces and wet the entire sections of the samples that had been exposed to the AAM, indicating that $\theta_A/\theta_R = \sim 0°/0°$ for both surfaces. Parts a and b of Figure 2 show photographs of water droplets spread on $^{\mathrm{III}}$FEP$^{\mathrm{RED}}$ and $^{\mathrm{III}}$PE$^{\mathrm{OX}}$ surfaces, respectively. The "puddles" with apparently very low, but finite contact angles are resting on completely wet surfaces; the areas covered by these puddles are much smaller than the areas topographically modified by the AAMs. We interpret these puddles as due to portions of the posts or lawn that are exposed on the surface of the completely wet surface, forming a composite surface, and are sensed by the additional water volume.

Parts c and d of Figure 2 show SEM images of freeze-fractured cross sections of $^{\mathrm{III}}$FEP$^{\mathrm{RED}}$ and $^{\mathrm{III}}$PE$^{\mathrm{OX}}$, respectively. The $^{\mathrm{III}}$FEP$^{\mathrm{RED}}$ structure looks similar to and unchanged from the structure of $^{\mathrm{III}}$FEP (Figure 1c). This was (and is) surprising to us. The FEP copolymer is completely reduced from a composition of $CF_2 \rightarrow C$ (see below: all of the fluorine is removed). This stoichiometric change corresponds to a mass loss of 76 wt %. This requires that the density of the fibrils must decrease by a factor of ~4 upon reduction and that the fibrils must consist of porous (at some length scale) carbon. Oxygen is introduced by autoxidation when $^{\mathrm{III}}$FEP$^{\mathrm{RED}}$ is exposed to air (see below), increasing the fibril density. The $^{\mathrm{III}}$PE$^{\mathrm{OX}}$ surface (Figure 1d) is highly degraded, and many of the $^{\mathrm{III}}$PE fibrils have been shortened, flattened, broken, or bent. If less severe oxidation conditions or shorter reaction times were used, we expect that more of the structure of $^{\mathrm{III}}$PE would have been retained and that similar wettability results would have been observed. The structure/wettability of $^{\mathrm{III}}$FEP$^{\mathrm{RED}}$ suggests this.

The chemistry that occurs upon reduction of $^{\mathrm{III}}$FEP and oxidation of $^{\mathrm{III}}$PE is nicely reflected in the XPS spectra of the reactant and product surfaces. These are shown in Figure 3. The fluorine that is present in $^{\mathrm{III}}$FEP is completely removed and replaced by oxygen in $^{\mathrm{III}}$FEP$^{\mathrm{RED}}$. $^{\mathrm{III}}$PE exhibits only a carbon photoelectron line, and the spectrum of $^{\mathrm{III}}$PE$^{\mathrm{OX}}$ indicates that significant oxidation has occurred.

Summary

Standard chemical modifications of standard polymer surfaces, oxidation of polyethylene and reduction of Teflon, were carried out. Unexceptional wettability increases (decreases in water contact angles) of smooth film samples, which are consistent with literature values, were observed. Fibrillar topographies were introduced to these polymers by heating them in contact with anodized aluminum membranes. These surfaces exhibit extreme hydrophobicity. Treatment of these surfaces with the same reagents that induce modest decreases in contact angle for smooth surfaces cause them to exhibit extreme hydrophilicity. The dramatic results of these simple experiments indicate that topography is a useful variable to modulate when using surface modification to control wettability.

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