

EFFECT OF PERFLUOROACRYLATE RATIO ON THE GENERATION OF STABLE SUPERHYDROPHOBIC SURFACES DISPLAYING LOW CONTACT ANGLE HYSTERESIS

Eren Simsek, Kazim Acatay and Yusuf Z. Menceloglu

Materials Science and Engineering Program
Sabanci University
Faculty of Engineering and Natural Sciences
Orhanlı 34956 Tuzla-Istanbul/Turkey

Introduction

Superhydrophobic surfaces possess a broad spectrum of potential uses especially as self-cleaning materials. The foundations of roughness-induced hydrophobicity were developed by Wenzel and Cassie-Baxter. Wenzel regime enhances water contact angle (WCA) by pinning of the liquid to the surface¹, whereas Cassie-Baxter regime enhances WCA by minimum contact with solid surface.² As a summary of their work, there exists a metastable Cassie-Baxter state in which air trapped between the water droplet and the cavities of the rough surface cannot exit and remains trapped beneath the droplet. Nonetheless, a small force application to the droplet causes the displacement of air by water and a higher contact of water with the surface results. In a hydrophobically stable state, the pressure application should not change the post-pressing WCA. If the regime evolved from a metastable to a high water-surface contact regime, the contact angle hysteresis and tilt angle of water droplet dramatically increases, because the surface is pinned by the water entering into the cavities. By this mechanism, the self-cleaning property becomes deteriorated. Thus, if the surface is not in a metastable state, it resists to higher pressures without losing its high WCA and maintains a stable hydrophobicity. Previously, we had shown that electrospinning, a novel method for polymer nanofiber production, can be utilized in order to generate superhydrophobic surfaces in an inexpensive and easy way.³ In this study, copolymers of styrene and acrylonitrile, which contain various ratios of perfluoroalkylethylacrylate, were synthesized and electrospun. We fixed the surface topography, but varied the fluoroacrylate ratio, in order to quantify the effect of monomer composition on the stability of the superhydrophobic surfaces. Drop pressing tests were applied in order to measure the WCA hysteresis, which is the main indicator of the superhydrophobic stability.

Experimental

Materials. Acrylonitrile (AN) and styrene (S) were purified by passing through an alumina column. Perfluoroalkylethylacrylate (PFA, Fluowet AC812) kindly supplied by Clariant, Azobisisobutyronitrile (AIBN, Fluka), tetrahydrofuran (THF, Aldrich), dimethylformamide (DMF, Aldrich) were used as received.

Instrumentation. Electrospinning of copolymers were performed by using CPS Model No 2594 high voltage DC supply and Univentor 801 syringe pump, at a vertically placed syringe coupled with 16-gauge stainless steel needle. The grounded aluminum foils were used to collect the film.

Viscosities of the polymer solutions were measured by DV-III Rheometer (Brookfield) coupled with a Wells-Brookfield Cone/Plate.

SEM imaging of the electrospun films was performed by using a LEO Supra VP35 FE-SEM, after sputter deposition of a thin conductive gold coating onto the films.

The contact angle measurements were done with a Krüss GmbH DSA 10 Mk 2 goniometer with DSA 1.8 software. At least 10 droplets of 5 mg freshly distilled ultra-pure water were averaged. For sliding angle measurements, at least 10 droplets of 10 mg water droplet was placed onto the films, and slowly inclined by a simple system. Drop pressing was performed by compressing a water droplet on the surface to be tested, with the most superhydrophobic surface, electrospun 10% poly(AN-co-PFA), from upside of the droplet.

Synthesis of Poly(Styrene-co-PFA) and Polystyrene (PS). Poly(S-co-PFA) copolymers were synthesized by reaction of styrene and 1, 3, 10 mol% PFA, and PS was synthesized by polymerization of styrene, at 65°C in THF. AIBN was used as the initiator in all of the reactions. The polymer was diluted with THF and precipitated in technical methanol.

Synthesis of Poly(Acrylonitrile-co-PFA) and Polyacrylonitrile (PAN). Poly(AN-co-PFA) copolymers were synthesized by copolymerization of AN and 1, 3, 10 mol% PFA, and PAN was synthesized by polymerization of AN at 65°C in THF. AIBN was used as the initiator. The polymer was dissolved in DMF and precipitated in distilled water.

Electrospinning of the Polymers. Poly(S-co-PFA) copolymers and PS were electrospun by dissolving in a 1:1 THF:DMF solution. Poly(AN-co-PFA) copolymers and PAN were electrospun by dissolving in DMF. Various viscosities of the solutions were tried in order to realize uniform topographies of the electrospun films.

Results

SEM Images of Electrospun Films

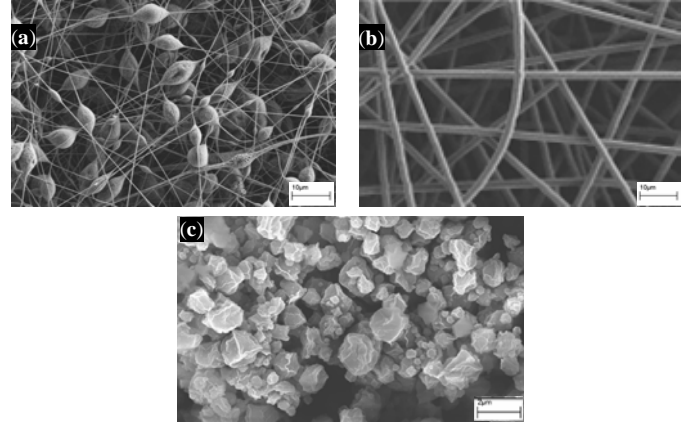


Figure 1. SEM images of the electrospun films of three possible structures: (a) bead on the fiber morphology of 1% -a- poly(S-co-PFA), (b) only fiber morphology of 3% poly(S-co-PFA) and only bead morphology of 10% poly(AN-co-PFA). The scale bars are 10 µm, 10 µm and 2 µm from (a) to (c), respectively.

Drop Pressing Tests

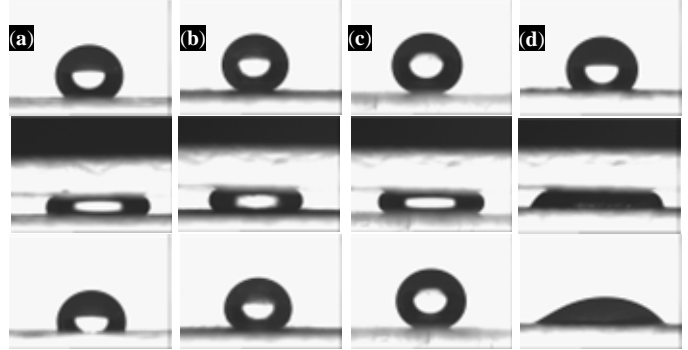


Figure 2. Images of the water droplets on electrospun films: Before (up), while (middle) and after pressing (down). (a) 1% -a- poly(S-co-PFA), (b) 3% poly(S-co-PFA), (c) 10% poly(AN-co-PFA) and (d) PAN.

Summary of the Test Results Applied

Table 1. Electrospun PS and poly(S-co-PFA) surfaces

PFA (% mol)	Visc. (cp)	Av. Dia. (µm)	WCA Cast film (°)	WCA E.Spun film (°)	After press. (°)	Hys.	Tilt angle (°)
0	64.0	2.9	92.0	143.2	92.5	50.7	-
1 -a-	42.7	Fiber: 0.27 Bead: 5.0	107.0	154.0	123.1	30.9	41.8
1 -b-	125.3	1.3	107.0	152.8	130.2	22.6	16.2
1 -c-	391.0	2.7	107.0	157.9	137.1	20.8	15.8
3	194.3	2.1	108.0	156.5	136.6	19.9	14.0
10	97.3	2.5	114.0	155.0	131.7	23.3	15.4

Visc. : Viscosity; Av. Dia. : Average diameter; Hys. : Hysteresis

All of the styrene containing polymers formed fiber only morphology except 1% -a- poly(S-co-PFA), which formed bead on the fiber morphology, at the corresponding viscosities. Water droplet do not slide at all on the electrospun PS (0% molar PFA loading) surface.

Table 2. Electrospun PAN and poly(S-co-PFA) surfaces

PFA (% mol)	Visc. (cp)	Av. Dia. (µm)	WCA Cast film (°)	WCA E.Spun film (°)	After press. (°)	Hys.	Tilt angle (°)
0	2.2	1.4	73.0	134.2	54.6	79.6	-
1	5.3	1.5	-	168.3	162.9	5.4	< 2
3	8.0	1.5	-	168.7	165.9	2.8	< 2
10	22.2	1.6	-	172.1	-	-	< 2

All of the AN containing polymers formed bead only morphology at the corresponding viscosities. WCA of PAN cast film (0 mol% PFA loading) was found 73° from the literature. It was not possible to form cast films, possibly due to the low molecular weight. Drop pressing test could not be applied to the electrospun 10% poly(AN-co-PFA), because the high superhydrophobicity precluded our efforts to restrain the water droplet on the test surface during compression. Also water droplet does not slide at all on the electrospun PAN surface.

Discussion

When we fixed the surface topography, the main parameter affecting the contact angle hysteresis was the chemical composition of the surface. Although the electrospun PS and PAN surfaces have rather high contact angle values when compared to their cast film forms, they also display very high hysteresis values to the effect that water droplet does not slide at all on these surfaces. This is presumably because they are in a metastable Cassie-Baxter state which starts after a critical WCA and related to the dominance of roughness. As water molecules enter inside the roughness and stick there, it would appear that the chemical composition itself cannot resist the compression. Moreover, the compressed air, if trapped beneath, is unable to restore the water droplet to its initial state. In other words, the regime is turned from metastable Cassie-Baxter to Wenzel, the CAH and sliding angle of water droplet dramatically increase, because the water entering into the cavities is pinned to the surface. This finding is related to strong hydrophilic interactions between water and sub-surface. In the case of electrospun poly(S-co-PFA) and poly(AN-co-PFA) surfaces, the fibers or the beads have themselves a higher hydrophobicity and the surface can resist pressing.

The higher hysteresis value of 1% -a- poly(S-co-PFA) may be due to the thin nature of the electrospun fibers which indicates that micron sized roughness is essential for creating superhydrophobicity such as in the case of lotus leaves⁴. A final but crucial point to note is the parallelism between the hysteresis and tilt angle values.

Conclusions

Neither the chemical composition of the polymer nor the surface roughness is alone adequate to form superhydrophobically stable surfaces. In order to accomplish low WCA hysteresis and tilt angle values, appropriate combination of the both is essential. It is possible to generate relatively hydrophobic surfaces even from hydrophilic polymers; however, high WCA values do not indicate the self-cleaning property solely. Low WCA hysteresis is required to provide the easy sliding of water droplet on the surface. Very low amount of PFA loading, such as 1% molar in the polymer, is sufficient to turn the metastable electrospun PAN surface into a superhydrophobically stable one, if appropriate topography is ensured. In addition, difference in the hysteresis values of fiber only poly(S-co-PFA) and bead only poly(AN-co-PFA) indicates that physical structure of the roughness is also a significant parameter affecting the self-cleaning property.

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