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Towards ultrahydrophobic surfaces: a biomimetic approach

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Abstract

We report on efforts to mimic the wetting behaviour of surfaces or leaves of certain plants, which are rendered ultrahydrophobic through a dense layer of hairs grown on top of the leaf. We use a simple moulding approach to obtain elastic hydrophilic hydrogel networks with pillar structures that may serve as model systems for such hairy surfaces. In order to generate such structures, we first generate either a steel master or directly use a lady's mantle leaf. Second, the master is moulded against a silicone to yield an elastomer, which is a negative of the hairy surface. A subsequent radical polymerization in the negative leads to the formation of an elastic hydrogel even for the very high aspect ratios characteristic of the natural system. The results of some preliminary contact angle measurements on the obtained structures are discussed.

1. Introduction

During the last decade, the hydrophobicity of many biological surfaces has attracted considerable interest [1–5]. In particular, plant surfaces have been thoroughly examined and two types of leaf categories, which have strongly water repellent properties, have been found. The most prominent example of the first category is the lotus flower (*Nelumbo lucifera L.*), which exhibits a superhydrophobic surface. The lotus flower leaf surface is macroscopically smooth but shows a microscopic roughness on different length scales down to the submicrometre scale [6]. This structure, together with the presence of epicuticular wax crystalloids, leads to increased water repellency and reduced particle adhesion and is therefore the crucial factor for the self-cleaning mechanism observed on such surfaces.

As strongly water-repellent and self-cleaning surfaces are from a technological point of view very interesting, a large variety of approaches to ultrahydrophobic surfaces have been developed. They have primarily focused on mimicking the surface of the lotus plant,

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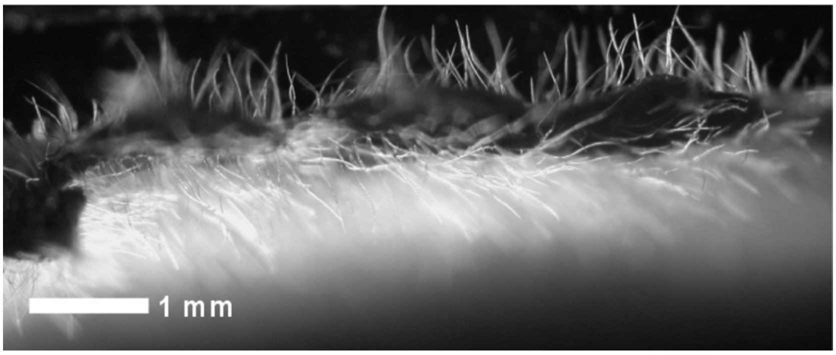

Figure 1. Optical micrograph of a lady's mantle leaf from the side. On both sides the leaf is densely covered with hair.

i.e. through the generation of a defined surface roughness via the use of plasma or etching processes or the combination of roughness and water repellent coatings [8–11]. Fewer investigations have led to elastic structures that mimic the hairs of a gecko's foot [12]. Even on the basis of only moderately hydrophobic materials, ultrahydrophobic surfaces with water contact angles considerably surpassing those of Teflon, which typically serves as an example for a very strongly water-repellent surface, have been generated following such an approach.

A second category of ultrahydrophobic plant leaves is represented by the lady's mantle (*Alchemilla vulgaris L.*) [7]. The leaves of this plant are covered with hairs, which apparently play an important part in the water-repellency of the leaf surfaces. The lady's mantle hair has a median diameter of 10 μm, a height of 1 mm and an average hair to hair distance of 500 μm, i.e. an aspect ratio of $\sim$100 (figure 1). Furthermore, contact angle measurements on a single hair revealed a hydrophilic character of the hair [13].

According to simple theories of wetting on a rough substrate, a rough hydrophilic surface should be even more hydrophilic than a smooth one [14]. Since the hairs certainly increase the roughness of the surface significantly, the water repellency of lady's mantle leaves is at first view somewhat surprising.

Herminghaus *et al* proposed a model for this type of hairy leaves where the elasticity of the plant hair as well as its area coverage accounts for the water repellence (figure 2) [13]. A bundle of elastic hair stuck into a liquid–air interface is considered, which leads to a deformation of the liquid surface, if the hairs' contact angle is different from 90°. This deformation, which costs energy, results in an attractive logarithmic potential between the hairs and leads to an energy gain. On the other hand, most of the hairs have to bend in order to form a bundle, which costs elastic energy. For a sample of infinite size, the combination of both contributions leads to a minimization of the total energy of the system if the hairs group into bundles of a particular size. This particular size depends on the height and separation of the hairs, their mechanical modulus and on the distance h between the leaf surface and the drop/air interface. As a result a water drop resting on such a bundle of hairs cannot come in contact with the substrate. A drop even when only slightly suspended in air, however, should have a shape only determined by its surface tension and thus have an almost perfect contact angle as far as non-wetting of the surface is concerned.

As part of our interest to investigate and understand dewetting processes at surfaces, we were intrigued at the possibility of preparing a model surface closely resembling the leaf surface of a lady's mantle. Together with the variation of parameters such as the elasticity, the aspect ratio and the average distance of the hairs it should be possible to determine the minimum

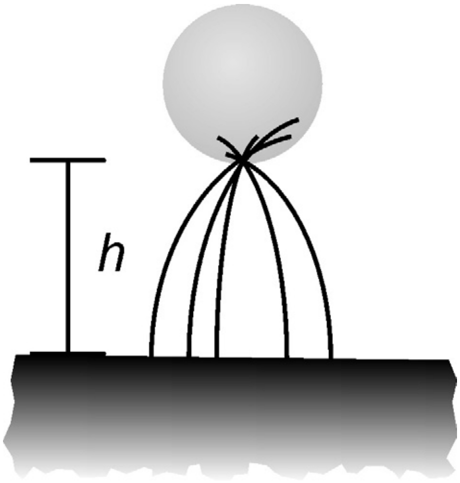

Figure 2. Schematic depiction of a water drop sitting on a bunch of elastic hair.

requirements for a hairy, water-repellent surface. The aspect ratio and average hair distance can be varied by changing the dimensions of the metal master, where minimum hair diameters of 30 μm, heights of up to 2 mm and minimum hair to hair distances of 50 μm can routinely be achieved. The elastic properties of the target structures can be adjusted via the crosslinker content. The lower the amount of crosslinker, the higher is the elasticity and water-swellability of the structure. Furthermore, by adding a comonomer during the polymerization, the elastic properties as well as the hydrophobicity of the system can be tuned.

Here, we report on preliminary results of experiments in the above-mentioned direction. We use a three-step approach to obtain elastic hydrogel pillars that may serve as model systems for such hairy plant surfaces. To obtain such structures we first generate master structures either in steel by wire-discharge machining or through the direct replication of the leaf surface in polymer. Second, the master is moulded against a silicone polymer, which is crosslinked to yield an elastomer, which is a negative of the hairy surface. A subsequent radical polymerization under crosslinking in the negative leads to the formation of an elastic hydrogel resembling the natural structure. The obtained hydrogels are hydrophilic, have aspect ratios from four up to 100 as in the natural system and show elastic properties, so that bundle formation of several pillars can be observed. We report on the generation of the structures and on the results of first wetting experiments.

2. Experimental section

2.1. Materials

2-hydroxyethylmethacrylate (HEMA) was purified using an Alox B column, distilled under vacuum from copper(I) chloride and stored under nitrogen at −30 °C. All other chemicals were used as received (PA grade).

2.2. Characterization

Optical micrographs were recorded using a TS 100 F inverted microscope coupled to an Olympus Camedia digital camera C-3030. Contact angles were measured using an OCA-20 set-up by Dataphysics equipped with a CCD frame grabber card and using an MCP 11 (Ga/In/Sn) alloy with a density of 6.5 g cm^{-3} and a surface tension of 665 mN m^{-1} (HEK GmbH, Lübeck). Extended focal imaging pictures were obtained using an Olympus BX 61 microscope with TH 4 light source and Soft Image Analysis software. A DSM 962 Zeiss scanning electron microscope served for the investigations of the stainless steel masters.

2.3. Wire electro-discharge machining (WEDM)

Stainless steel masters were made using a Charmilles Robofil 2020 SI microwire set-up. A tungsten wire of 30 μm diameter and a wire tension of 0.2 N mm^{-2} served as an electrode and was consumed with a speed of 3.2 m min^{-1}. As further process parameters a voltage of 80 V was applied, the pulse-on time was 1 μs and the pulse-off time was 22 μs. A current of 8 A was chosen.

2.4. Moulding of the masters

All steel masters were treated with 1,1,1,3,3,3-hexamethyldisilazane (HMDS) at 120 °C for 10 min prior to moulding. All leaf surfaces were immersed into a 0.5 mM solution of 3-(N, N-dimethylmyristylammonium)sulfonate and dried in air. Moulding of the steel structures was done with a mixture of curing agent and base (1/10 v/v) of Sylgard 184 (Dow Corning) [19] and subsequent curing at 70 °C for 3 h. For the moulding of the leaves a mixture of Wacker Elastosil 4370 A and 4370 B (1/9 v/v) (Wacker, Burghausen) was used, followed by curing overnight. Then the masters were peeled off the elastomer.

2.5. Remoulding of the leaf masters

The hydrophobic polyether GK-0274-170 (BASF AG) was molten at 50 °C and filled into the elastomer under vacuum. After the polyether had solidified it was separated from the elastomer.

2.6. Polymerizations

Polymerizations were performed in HEMA/ethanol mixtures (1/2 v/v) at 60 °C for approximately 4 h with 0.01 mol% azobis(2-isobutyronitrile) as a radical starter and 1.0 mol% ethylene glycol dimethacrylate as a crosslinker [15]. All solutions were degassed through at least three freeze–thaw cycles to remove all oxygen traces. The polymerization solution was given into an evacuated Schlenk flask (5×10^{-3} mbar) containing the elastomeric negative before it was vented with nitrogen. After polymerization the swollen network was released from the master by either peeling it off or dissolving the master for 5 h in a 1 M solution of tetrabutylammonium fluoride in THF. Then the networks were both extracted and swollen in ethanol.

3. Results

The generation of surfaces with hydrogel hairs is far from being trivial. On the one hand the structures are at 10 μm relatively small; on the other hand the aspect ratios are at 100:1 (height/width) quite challenging. 10 μm structures are very common in photolithographic processes; however, the aspect ratios of such processes are typically well below 10:1. On the other side high aspect ratios are quite common in mechanical processes, however, not for

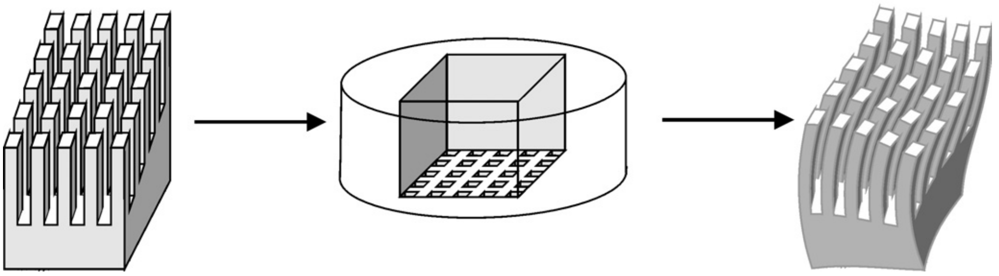

Figure 3. Schematic depiction of moulding approach for the generation of elastic networks with high aspect ratios.

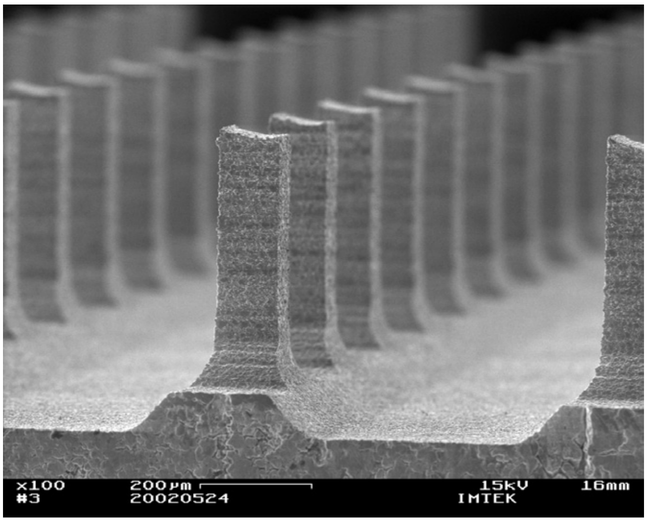

Figure 4. Scanning electron micrograph of mask 1.

the generation of structures in polymeric materials with the given structure sizes and feature densities.

Here we describe two approaches for the formation of elastic and hydrophilic microstructured polymer networks with very high aspect ratios of up to 100 as shown in figure 3.

In the first approach steel masks with high aspect ratios are generated using wire electro-discharge machining (WEDM) [16–18]. Moulding of the masters with an elastomer follows this step. Finally, a radical polymerization in the negative leads to the generation of hydrophilic and elastic networks, as described in detail in the experimental.

Via the WEDM method we obtained four stainless steel masks with aspect ratios of four to ten and dimensions as shown in table 1. As an example an SEM micrograph of mask 1 is shown in figure 4. HMDS was used as a mould release agent in a standard procedure to react with the hydroxyl groups of the metal oxide layer.

The pretreated masters were then immersed in the mixture of the two silicone components to yield an elastic negative after curing. An extended focal imaging (EFI) micrograph of a typical negative PDMS form is shown in figure 5. Besides the superstructure originating from the machining process one can see black squares that can be assigned to the pillar indentations.

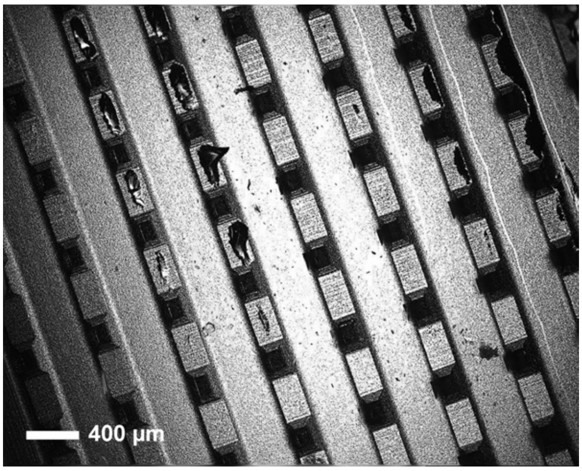

Figure 5. EFI micrograph of a PDMS negative mould.

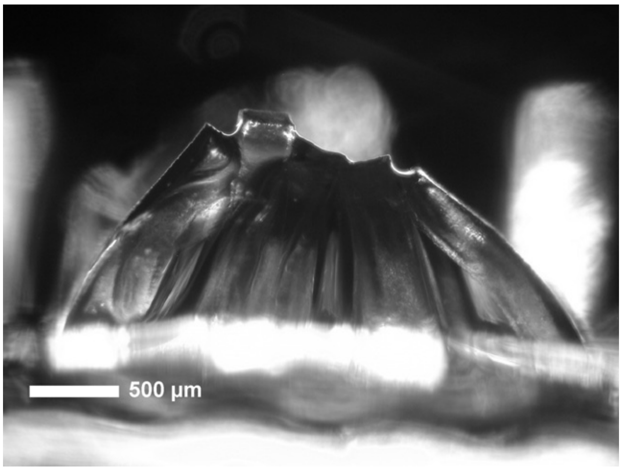

Figure 6. Optical micrograph of an ethanol swollen PHEMA network formed in the PDMS negative of mask 4. The pillars form a bunch.

Table 1. Specifications of stainless steel masks obtained by the WEDM process.

	Mask 1	Mask 2	Mask 3	Mask 4
Pillar base (μm)	80 × 100	48 × 22	43 × 50	165 × 170
Pillar height (μm)	525	150	250	1500
Pillar to pillar distance (μm)	400	450	450	700
Aspect ratio	~5	~4	~5	~9

After performing a radical polymerization in the negative, the formed network was removed from the elastomer and extracted in ethanol. During polymerization and extraction the network was strongly swollen. Upon removal from the ethanol extraction bath bunch formation of the pillars was observed (figure 6). After evaporation of some ethanol the pillars separated from each other and a regular network structure was observed (figure 7). It should be noted that figures 6 and 7 are optical micrographs of the same network.

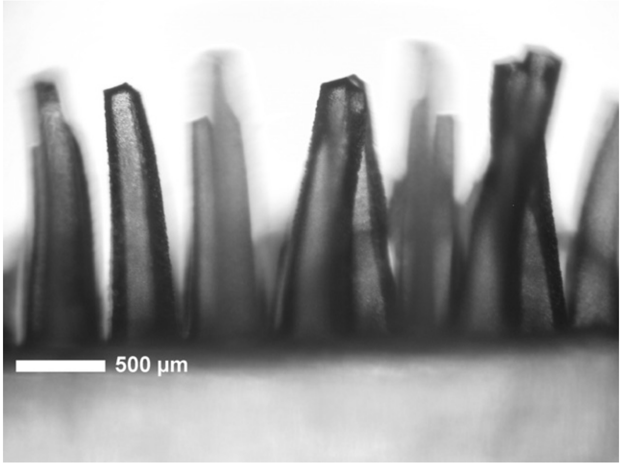

Figure 7. Optical micrograph of a regular pillar structure of the PHEMA network shown in figure 6 after evaporation of ethanol.

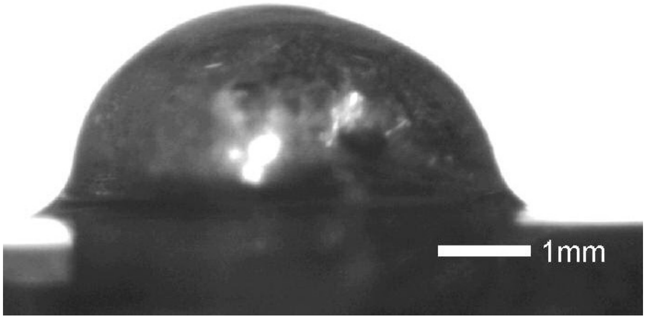

Figure 8. MCP 11 contact angles on a smooth PHEMA surface.

It was not possible to measure water contact angles on the structures because the network immediately incorporated the water and became strongly swollen. When oil instead of water was used the oil spread on the pillars. In order to determine the difference between the smooth and the pillar bearing PHEMA network a Ga/In/Sn alloy was used for contact angle measurements. The alloy is liquid at room temperature. Furthermore, it has a high surface tension (665 mN m^{-1}) and does not swell the microstructures. Although it is clearly not the material of choice to test the theoretical description of the wetting behaviour it allows us to obtain some interesting trends. Figures 8 and 9 show the results for the smooth and the microstructured PHEMA surface. It can be seen that the contact angle on the microstructured PHEMA surface is significantly higher than on the smooth one.

For creating a model surface with exactly the same dimensions as the plant, we followed a second approach in which a lady's mantle leaf was directly replicated with a silicone. To check the quality of the negative, a hydrophobic polyether was used for remoulding. An optical micrograph of the hydrophobic polyether structure is shown in figure 10.

A radical polymerization in the silicone master led to the formation of an elastic and hydrophilic network as is shown in figure 11. The silicone elastomer was dissolved in tetrabutylammonium fluoride [20]. Although bunches of hairs could be produced easily it

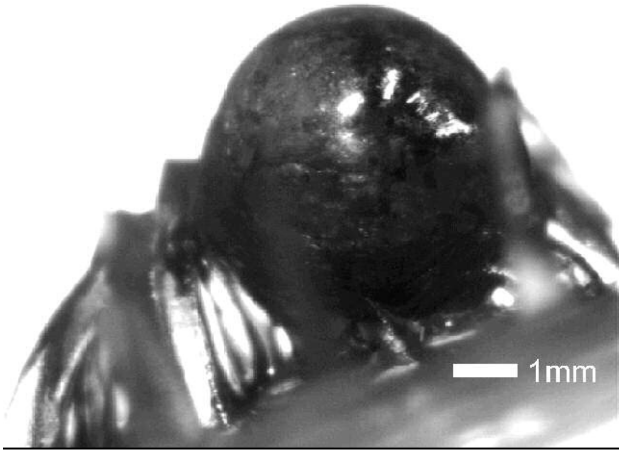

Figure 9. MCP 11 contact angles on a microstructured PHEMA surface.

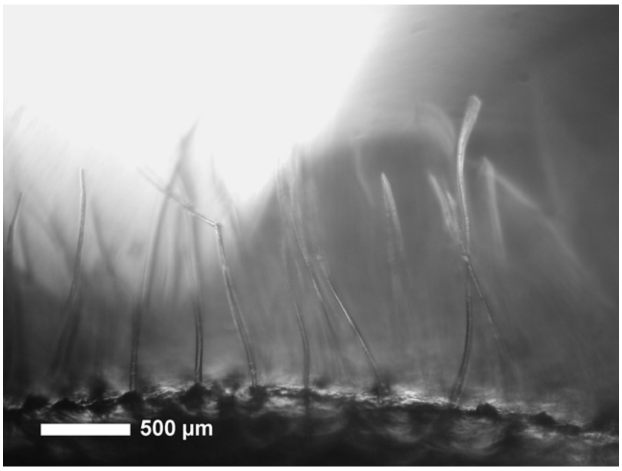

Figure 10. Optical micrograph of the hydrophobic polyether structure that was obtained by remoulding of the silicone elastomer, which was the direct mould of the lady's mantle leaf.

was not possible to measure contact angles on these structures because the obtained areas were too small to carry droplets.

4. Discussion

The WEDM process is the method of choice for small lot production. In comparison with conventional silicon technologies it is cheaper and faster. Approximately 4 h were needed for the production of one master structure. Moreover, the WEDM method can be used to create stainless steel masters with pillar microstructures where the pillar size can have a minimum diameter of 30 μm and a minimum separation of 50 μm. When going to smaller diameters the pillars easily break directly above their base due to thermal stress during the machining process [21]. Furthermore, as the diameter decreases one gets closer to the grain boundaries of the material and thus the possibility of breaking increases. This also holds true for the removal of the elastomeric negative from the metal master.

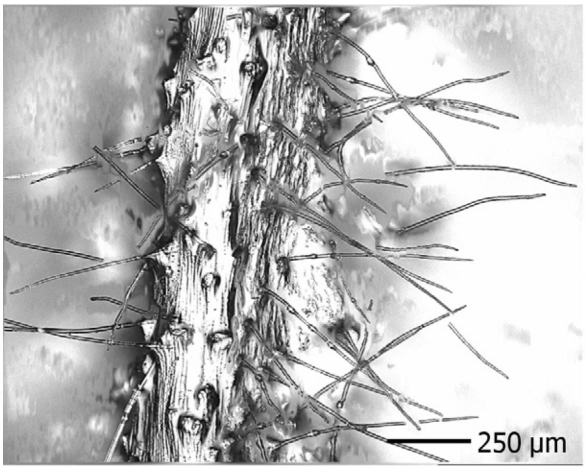

Figure 11. EFI micrograph of a PHEMA leaf vein.

The excellent quality of the PDMS mould is in line with the literature [22]. In figure 5 one can see that even the fine metal grooves of the master that were generated during the machining process have been reproduced in the PDMS.

The fact that one can already observe a bunch formation of the PHEMA pillar structures with an aspect ratio of just nine suggests that the ratio of height to diameter is large enough for this effect. This implies that even for a rather small aspect ratio of elastic surface structures a water repellent behaviour due to a bundle formation of the pillars might be found. This is corroborated by the contact angle measurements with the MCP 11 alloy on both the smooth and the pillar carrying PHEMA surface.

However, the water contact angle measurements on the created networks reveal an obvious difference between these and the natural structures. The water contact angle on a single lady's mantle hair was found to be below 60°. A water contact angle on the prepared PHEMA networks could not be measured because the network immediately incorporated any water deposited.

To obtain a stronger effect on the contact angle, networks have to be generated in further experiments which are somewhat hydrophilic but do not swell too strongly upon water addition. To help to make a proper choice of a polymer, in principle one could be guided by the surface chemistry of the plant itself. However, the reason why the hydrophilic plant hair does not take up any water is not completely clear. One of the possible explanations might be an additional mechanism to prevent the inflow of water into the structures. One suggestion in that direction is that even though the plant hair consists of a hydrophilic substance like cellulose, it might not be available in an amorphous but in a crystalline state, which could prevent water from intruding into the hairs. A second hypothesis lies in the assumption of a gradient along the plant's hair. In accordance with a lot of other hair species, it might be possible that the unicellular hair was covered with a cuticula before it died [23]. This cuticula is then subject to abrasion during the plant's life and the hair might show a smaller contact angle than initially.

A last reason for the different behaviour might be the difference in the chemistry of the pillar carrying structure. The hair on the lady's mantle sits on top of a leaf, which is covered with epicuticular waxes, whereas the model structure is completely hydrophilic. Possibly the biological barrier in the natural system is a further reason for the observed differences.

5. Conclusion

Preliminary results show that via a twofold moulding approach hydrophilic and elastic PHEMA networks could be prepared, which mimic roughly the structure of the leaf of a lady's mantle. In further experiments we will concentrate on the choice of appropriate polymers with suitable swelling behaviour and elastic properties. On the one hand the crosslink density of the polymer networks needs to be controlled, on the other hand an appropriate choice of the chemical composition of the network-building components will have a great influence on the wetting properties of the resulting hairy surface.

Acknowledgments

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