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# Biomimicking wetting properties of spider web from *Linothele megatheloides* with electrospun fibers

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ABSTRACT

In this study, we showed a simple approach to biomimic the wetting properties of spider webs, which can be mainly attributed to the geometry of fibers. We created biomimetic fibers using electrospun polyvinylidene fluoride (PVDF) with a wrinkled surface similar to the morphology of spider silk bundles produced by *Linothele megatheloides*. Without any chemical modification and copying the silk bundles geometry, we successfully translated the similar hydrophobic properties to an electrospun network of fibers. The novelty of this approach lays in obtaining similar macroscale roughness parameters, responsible here for wetting contact angles, due to the substitution of spider silk bundles with individual wrinkled electrospun fibers. The presented methods open new creative solutions for manufacturing anti-wetting surfaces.



## 1. Introduction

Water collection in nature is one of the major research concerning wetting of surfaces. Among many examples, spider webs are one of the most commonly observed and studied phenomena [1]. All spiders vary their silk compositions, surface roughness and size according to the function of webs: cocoons, nets, suspending threads and so on [2–3]. *Linothele megatheloides* is the spider that caught our interest as known for the intricate funnel webbing it constructs and also known as one of the biggest silk manufacturers in nature [4]. In this study, we investigate the web constructed by *Linothele megatheloides,* see Fig. 1, by verifying fibers morphology, diameter, web roughness and wetting properties. The focus of this study was to create biomimetic webs using electrospun polymers fibers to obtain hydrophobic properties using just a similar geometry to *Linothele* webs, without any chemical modifications. Previously electrospinning was identified as a suitable and versatile method to produce fibers networks for super-hydrophobic [5] and super-oleophobic properties [6].

We acknowledge a lot of studies taking the biomimetic approach by producing artificial silk, and modifying surface chemistry of fibers [7], however, our unique and simple approach had shown great possibilities of biomimetic wetting properties exposed in nature simply by controlling surface geometry at the macro scale. For this purpose, we chose one of the more commonly electrospun polymers, polyvinylidene fluoride (PVDF), which previously has shown the ability to create fibers with wrinkled morphology while electrospun from the mixture of two solvents, acetone and dimethylacetamide (DMAc) [8].

## 2. Materials and methods

### 2.1. Materials and electrospinning

*Linothele megatheloides* webs were obtained from the exhibition organized by *Araneus* at the Natural History Museum, Polish Academy of Sciences in Cracow, see Fig. 1.

PVDF ($M_w$ = 275000 g mol$^{-1}$, Sigma Aldrich, UK) was dissolved in solution DMAc and acetone (analytical standard, Avantor, Poland) in 1:1 ratio to produce a polymer solution with a concentration of 22 wt%. The solution was stirred for 4 h at a constant speed of 700 rpm at the heated plate to 50 °C (IKA RCT basic, Germany). Electrospinning of PVDF was carried with apparatus EC–DIG with the climate system (IME Technologies, The Netherlands) at T = 25 °C and H = 60%. The voltage of 15 kV was applied to the stainless needle with an inner diameter of 0.8 mm, keeping the

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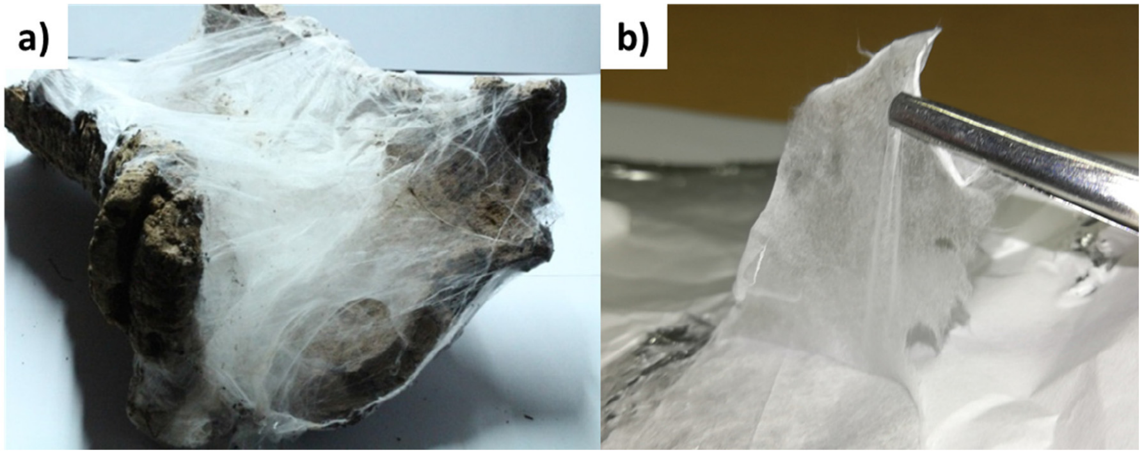


**Fig. 1.** Photographs representing a) *Linothele megatheloides* spider webs on the bark of the tree used for sampling, b) example of electrospun fiber mat.

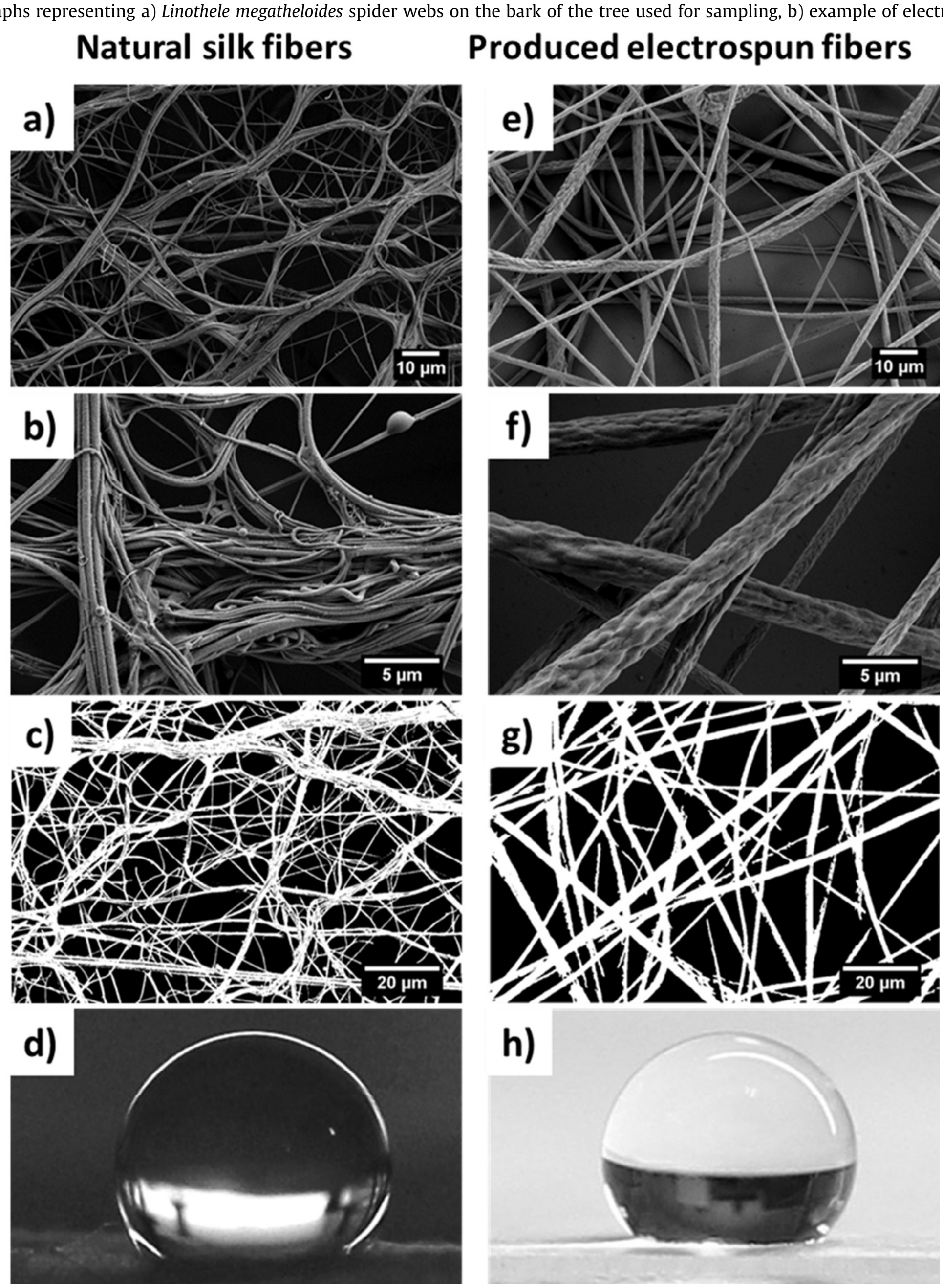


**Fig. 2.** Representative images of a), b) Silk fibers and bundles from *Linothele megatheloides* web and electrospun PVDF fibers and e) f) SEM micrographs, c), g) processed images for calculations of fraction of fibers and d), h) images of droplet of water used to measure the contact angles, respectively.

**Table 1**
The characteristic parameters measured for *Linothele megatheloides* web and electrospun PVDF fibers, including standard deviation (SD).

| Parameters | | Spider web | Electrospun fibers |
|---|---|---|---|
| Fiber/bundles diameter ± SD [μm] | | Fibers: 0.47 ± 0.15<br>Bundles: 2.10 ± 0.77 | 1.23 ± 0.50 |
| Fraction ± SD [%] | | 40.58 ± 6.37 | 38.99 ± 2.03 |
| Roughness | $R_a$ [μm] | 8.37 | 9.71 |
| | $R_q$ [μm] | 10.31 | 11.57 |
| | $R_z$ [μm] | 53.46 | 54.45 |
| | $R_t$ [μm] | 56.60 | 59.19 |
| Water contact angle ± SD [°] | | 130.61 ± 5.11 | 128.12 ± 2.12 |

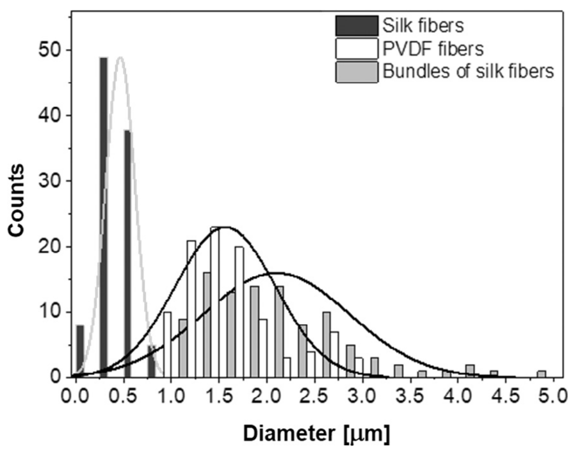


**Fig. 3.** Histograms representing fibers' and bundles' diameter distribution for spider silk and electrospun fibers.

18 cm distance to the grounded collector, and solution flow rate at 1.5 ml·h$^{-1}$.

*2.2. Characterization*

The samples were coated with 3 nm gold layer using rotary-pump sputter coater (Q150RS, Quorum Technologies, UK) and imaged using scanning electron microscopy (SEM, Merlin Gemini II, Zeiss, Germany), with U = 5 kV, I = 150 pA, keeping the working distance of 4 mm. Cross-sections from PVDF fibers and spider thread bundles were obtained using focused ion beam and SEM (FIB-SEM, Neon CrossBeam 40EsB, Zeiss, Germany) with $Ga^+$ ions U = 30 kV and I = 200 pA. SEM images obtained at 3 kV and 120 pA were analyzed with ImageJ (v1.51 g, NIOH, USA), to determine fiber diameters, fraction and cross-section contours.

The roughness analyses were performed using the Optical Profilometer (WYKO NT9300, Veeco, USA). All samples were placed on

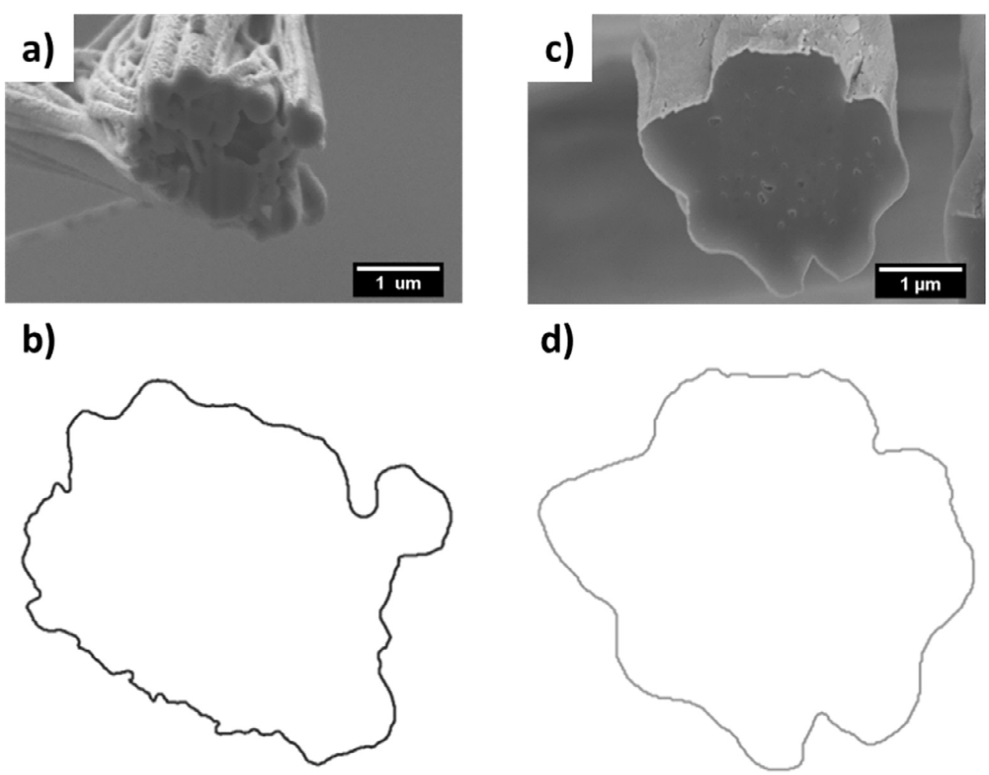


**Fig. 4.** Bundles of *Linothele* silk and electrospun fiber a), c) cross-sectional SEM micrographs with the same magnification, b), d) counter images obtained from SEM micrographs, respectively, and e) comparison of surface irregularity using the cross-sectional counter at the same magnification between these two samples.

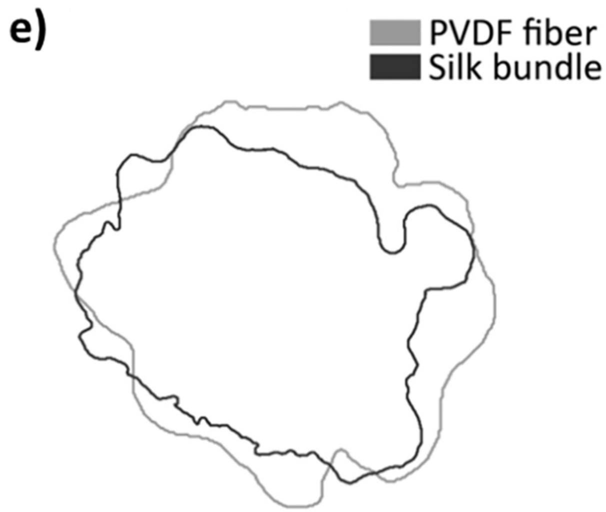


**Fig. 4** (*continued*)

glass slides and tested in the vertical scanning – interferometry (VSI) mode to examine roughness over the area of 437 × 583 μm. We chose the profilometry analysis over commonly used atomic force microscopy (AFM) due to a larger area that can be measured, which was more representative of webs constructed out of a few micron-sized fibers. The 3 μL droplets used for wetting experiments gave for spherical droplet radius of 890 μm. The four types of roughness parameters were measured: 1) $R_a$ – roughness average, 2) $R_q$ – root mean square roughness, 3) $R_z$ – average maximum height of the profile and 4) $R_t$ – maximum height of the profile. The details of all the roughness calculations and the graphical interpretations are in the Supporting Information, Fig. 1S.

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.matlet.2018.09.007.

Wetting properties were analyzed with a static contact angle using 3 μL volume droplets of deionized (DI) water (Spring 5UV purification system-Hydrolab, Poland) at T = 24 °C and H = 50%. Images of 10 droplets were taken within a few seconds from the deposition, using Canon EOS 700D camera with EF-S 60 mm f/2.8 Macro USM zoom lens and used to measure contact angle with ImageJ.

## 3. Results and discussion

Due to the geometrical arrangements of electrospun network and fibers morphology we successfully obtained very similar wetting angles for water in the range of 128° on electrospun PVDF fibers to the one observed on *Linothele megatheloides* spider's web, reaching 130°, see Fig. 2 and Table 1. Clearly, SEM images, (Fig. 2a and b), shown smooth surfaces of silk fibers with an average diameter of 0.47 μm that were stacked together in bundles of 2–10 fibers. The electrospun PVDF fibers were wrinkled (Fig. 2e–f), which was related to buckling instability during solvent evaporation and drying causing stress at the forming the shell structure of electrospun fibers, while the core contracted and pulled it.[9] The PVDF fibers did not form bundles but their average diameter was 1.23 μm, see histograms in Fig. 3, so comparable with the size of silk bundles, which was on average 2.10 μm. Note, the diameters were measured from top view from SEM images of silk bundles and wrinkled PVDF fibers, (see Fig. 2b and f).

Importantly, the cross-sectional images of spider silk bundles and individual PDVF fibers show very similar surface roughness at the same scale, as indicated with the FIB-SEM cross-sectional and counter images in Fig. 4. However, the silk fibers stick together to form bundles [7], which is not the case of electrospun fibers network [10], but the profilometry studies shown the similar roughness parameters, as listed in Table 1.

The main advantage of the hierarchical roughness that was created with the wrinkled fibers over the smooth fibers was the contact angle stability without any time-depended wetting transition to a hydrophilic surface. As the roughness of wrinkles was approximately ~230 nm, we created the multiscale phenomena of reduced pinning of liquid to the fibers' interfaces. Therefore, the adhesion between the liquid and solid surface was decreasing, leading to stable equilibrium situation preventing the liquid flow inside the network of fibers [11]. Similarities between electrospun fibers and spider webs were also funded in the fraction of fibers analysis, see Table 1. The fraction of fibers' surfaces was calculated to evaluate the pinning points for water with a solid surface, showing in white the possible area of contact in the analyzed surface from SEM images, (See Fig. 2c and g).

## 4. Conclusions

By using electrospun fibers we were able to create similar geometry to the spider webs and obtain almost identical wetting effects to those observed in nature. We showed one step manufacturing method of hydrophobic membranes without the need for any chemical modifications. Importantly, the similar structure of bundles made of silk fibers stick together, was substituted with individual wrinkled PVDF fibers. The key of produced surfaces is the hierarchical roughness with the application potential in anti-wetting surfaces or fog collectors. This study showed the straightforward way to create biomimetic hydrophobic surfaces made of polymer fibers.

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