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Wetting resistance of heterogeneous superhydrophobic coatings with orthogonally layered fibers

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ABSTRACT

Superhydrophobic coatings comprised of electrospun nanofibers are a low-cost alternative to micro-fabricated surfaces, and can be applied to substrates of any arbitrary geometry. Such coatings with orthogonally oriented layers have properties that allow their wetting resistance to be predictable for a range of solid volume fractions, fiber diameters, and contact angles. In this paper, we have presented a modeling strategy that solves for the air–water interface shape over several layers of such coatings to predict the resistance of superhydrophobic fiber coatings to hydrostatic pressures and to quantify the relationship between microstructure, meniscus penetration depth, and wetted surface area of the fibers. Slip length predictions are also provided to shed some light on the performance of such coatings in drag reduction applications. It was found that while failure pressure for a coating rises with reducing fiber spacing, there is a tradeoff with wetted fiber surface area relative to a bare substrate. This tradeoff can be offset, however, by using smaller fibers for an intended coating. This results in a higher failure pressure for the same wetted area fraction. The results generated in this work are discussed in relation to those reported in the literature whenever possible.

1. Introduction

A surface is regarded as superhydrophobic (SHP) when it exhibits an apparent contact angle with water greater than 150°. This is often achieved by applying a micro- or nano-scale roughness to a hydrophobic surface [1–4]. Such surfaces can be used for applications ranging from self-cleaning and drag-reduction to corrosion resistance and energy [4–6]. The essential attribute of SHP surfaces is their reduced water–solid contact area (wetted area) which helps decrease the friction between a moving body of water and the surface. This is due to the ability of SHP surfaces to trap air within their microstructure (see e.g., [7–10]). For an SHP surface in contact with water, the solid area in contact with water depends on both the surface morphology and the hydrostatic and/or hydrodynamic conditions of the system. A submerged SHP surface may be found to be in the Wenzel state (fully wetted), the Cassie state (fully dry), or in a series of transition states between the two extremes [9]. When an SHP surface comes into contact with water, the air–water interface (AWI) may penetrate into the pores of the surface depending on the wetting state of the surface. If the AWI penetrates too deeply into the pores, the SHP surface may no longer provide any drag reduction. In fact, it is quite possible that such a surface increases the drag force in certain hydrodynamic conditions [10].

A significant number of studies have been devoted to the manufacture and characterization of micro-fabricated roughness on a surface to impart superhydrophobicity (see e.g., [5]). However, fabricating micro- or nano-roughness remains a costly process, and applying them to geometries with arbitrary curvatures remains difficult. An alternative is to achieve the desired roughness by applying a hydrophobic material to the surface in the form of electrospun nanofibers [11–14] or apply a coating on the surface of a fibrous material [15–17]. The major problem with the conventional electrospinning process (or fibrous materials in general), however, is the lack of control over the orientation and spatial distribution of the fibers, making it difficult to predict the performance of the coating prior to its manufacturing. It has been shown that the conventional electrospinning process can be modified to produce coatings with some additional control over the orientation of the fibers and their spacing (e.g., [18–21]). Producing coatings with fiber layers arranged orthogonally with respect to one another similar to the one shown in Fig. 1 provides a means for engineering superhydrophobic coatings with more predictable performance. The example SEM image shown in this figure is from an electrospun superhydrophobic polystyrene mat with orthogonal fibers having an average fiber diameter of 2.4 μm and a mat solid volume fraction (SVF) of 7.5% [22,23]. Unlike coatings with random fiber orientations, orthogonally layered fiber mats have a degree of order to them that allows one to predict their overall performance based on an analysis conducted on a small portion of their structure, i.e., the spaces between

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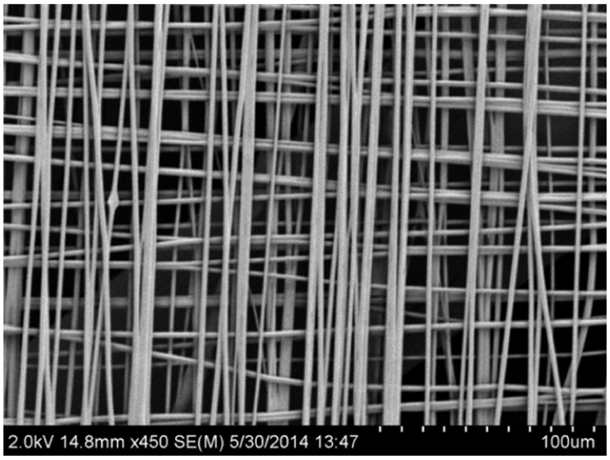

Fig. 1. SEM image of an electrospun superhydrophobic polystyrene mat with an average fiber diameter of 2.4 μm showing fiber-layers deposited orthogonally with respect to one another. The mat's average SVF and apparent water contact angle are about 7.5% and 140°, respectively.

the fibers conforming to a grid of rectangular cells. In this paper, we study the ability of orthogonally layered fibrous coatings to resist hydrostatic pressures. In particular, we obtain a critical pressure, the pressure at which a wetting transition can be expected, for coatings with different microstructures. This is accomplished by solving the surface energy equation across the AWI in the rectangular unit cells of the coatings to resolve the curvature of the interface to its minimum energy. These calculations are performed using the finite-element Surface Evolver (SE) code [24,25]. It is worth mentioning that the modeling methodology presented here can also be used in applications involving oil–water separation [26–30], water transport in fuel cells [31–34], waterproof barriers for underwater devices [35], and self-cleaning (e.g., [36,37]) among many others.

In the remainder of this paper, we will first establish the failure criteria with which we define critical pressure for a given coating (Section 2). We will then explain the details of constructing our model in Section 3, and also present a mesh-independence study to ensure that the numerical errors associated with our numerical calculations are negligible. In Section 4, we conduct a parameter study to determine the critical pressure of coatings with different fiber diameters and porosities, as well as contact angles. In addition, we will present an investigation on the effects of fiber size dissimilarity on the performance of SHP coatings. Finally, we state our conclusions in Section 5.

2. Critical capillary pressure

2.1. Coatings comprised of highly oriented fibers

In general, an SHP coating is regarded to have failed under hydrostatic pressures when the applied pressure is sufficiently high to overtake the capillary pressure of the coating. The only exception to this is the case of thin coatings with the air under the AWI completely trapped, like when a coating is fully submerged (in this case the entrapped air significantly contributes to the coating's resistance against the hydrostatic pressure [38,39]). For thick coatings (i.e., coatings for which the volume of the air displaced by a penetrating AWI is negligible compared to the volume of the air in the coating), even when submerged, the capillary pressure is the dominant force balancing the hydrostatic pressure exerted on the coating [40].

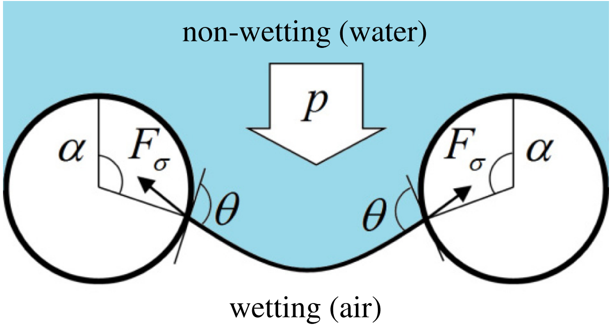

Fig. 2. Free body diagram of the balance of forces across the AWI between two parallel fibers.

For fibrous coatings with fibers highly oriented in a certain direction, the capillary pressure can be derived from the balance of forces acting on the AWI between the fibers (see Fig. 2) [40],

$$p_{FB} = -\frac{2\sigma \sin(\theta+\alpha)}{l-d\sin\alpha} \tag{1}$$

where the center-to-center distance l is related to the coating's SVF ε,

$$l = \frac{\pi d}{4\varepsilon}. \tag{2}$$

The critical capillary pressure p_{FB}^{cr} can then be obtained by differentiating Eq. (1) with respect to α, setting it equal to zero. Thus, critical capillary pressure across a bank of parallel fibers, expressed in terms of SVF and critical immersion angle α^{cr}, can be written as

$$p_{FB}^{cr} = -\frac{2\varepsilon\sigma}{d}\frac{\sin(\theta+\alpha^{cr})}{\pi-4\varepsilon\sin\alpha^{cr}}. \tag{3}$$

It is worth mentioning that Eq. (3) was successfully used in our previous study to produce a 2-D AWI tracking algorithm, and thereby predictive pressure–saturation correlations, for porous media comprised of unidirectional fibers [41].

As mentioned earlier, Eqs. (1) and (3) are obtained for when the AWI is only in contact with two parallel fibers (2-D geometries). For a 3-D fibrous coating composed of multiple layers of orthogonal fibers like the one shown in Fig. 1, the capillary resistance is stronger, and the solid–water contact area is different for each fiber-layer with which the AWI is in contact. This is compounded by another issue: for a single set of parallel fibers, complete wetting takes place when the AWI penetrates deep enough to reach a critical profile, at a critical immersion angle of α^{cr}, where the balance of mechanical forces over the AWI is no longer maintained [40,41]. As will be shown later in Section 3, our study indicates that an AWI that straddles across two or more layers of orthogonal fibers most often does not reach such a mechanical breaking point before it deflects laterally so as to meet itself under the fibers (across the symmetry boundaries). At this point, the AWI would probably coalesce with itself and break away from the first layer of fibers, nullifying the SHP characteristics of the coating by submerging the first layer. In such conditions, the capillary pressure right before the AWI coalesces with itself is taken in this work as the critical pressure (see the next section).

We previously used the Full Morphology (FM) algorithm to predict the resistance of submerged SHP fibrous coatings under elevated hydrostatic pressures [40]. The underlying principle of the FM method is to relate the size of the largest sphere that can fit into the void space between the fibers at any point in the 3-D domain to a fictitious pressure