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A combined criterion of surface free energy and roughness to predict the wettability of non-ideal low-energy surfaces

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ABSTRACT

The significance of wettability between solid and liquid substances in different fields encourages scientists to develop accurate models to estimate the resultant apparent contact angles. Surface free energy (SFE), which is principally defined for ideal (flat) surfaces, is not applicable to predict the wettability of real (rough) surfaces. This paper introduces a new parameter, namely normalized surface free energy (NSFE) as a combination of SFE and roughness, to predict the contact angle of liquids on non-ideal low-energy surfaces. The remarkable consistency of the predicted and measured contact angles of liquids on some rough surfaces also confirm the validity of the approach.

1. Introduction

Each material, including solid and liquid, comprises bulk and surface with their own specific properties. The majority of interactions between substances start from their surfaces. Thus, the characteristics of surface, rather than bulk, principally determine the behavior of the material. One of the most significant factors in this regard is “solid-gas surface free energy”. By tailoring the surface energy of a solid, it is possible to control reaction rate, wetting behavior, etc, which is critical for applications like catalysis, oil and gas industry, food production, physical and chemical vapor deposition, biology, wood and textile [1–9]. From this viewpoint, solid materials are classified in two groups: high- and low-surface energy materials, with surface tensions of hundreds to even thousands of mN/m and below 100 mN/m, respectively. Anyways, the determination of surface energy for solid materials mostly requires complicated calculations and/or experiments [10–14].

The most common method to determine the surface energy of solids is based on the measurement of contact angle due to its easy process. In this approach, the contact angle of two liquids on the surface of the studied substance is measured by the sessile drop method and then is used in different equations to determine surface energy. Fowkes [15–17], Owens-Wendt [18], Van Oss-Chaudhury-Good [19,20], Fox-Zisman [21], Neumann [22] are of methods to do so. All calculations and equations are derived based on the primary assumption that the surface is ideal, i.e. free of roughness. Nonetheless, to the best of our knowledge, there is no method reported to predict the contact angle of a liquid on random shaped non-ideal (rough) surfaces. In this regard, the current paper introduces a novel approach which uses a combined concept of surface energy and roughness, to predict the contact angles of liquids on a given rough surface. Note that the Wenzel and Cassie models merely establish a correlation among the ideal contact angle, the real contact angle and a roughness-dependent factor (the area fraction of the solid surface), which is different with the concern of the current paper. It is also noteworthy to mention that this model is only applicable to low surface energy materials, due to some primary assumptions used in the development of the model, as detailed below.

2. Model setup

Surface free energy (SFE) is a fundamental property of surface which is defined for ideal (flat) configuration; that is, SFE is independent upon roughness which is regarded as another characteristic of real surfaces. Indeed, most of real surfaces are heterogeneous and consist of two materials, a solid substance and air, where both of the constitutes are in contact with wetting liquids when the surface is hydrophobic. Hence, it is almost impossible to determine the SFE of a real surface. The situation is persistent even for surfaces which obey the Wenzel [23] and Cassie-Baxter [24] models used generally to characterize wettable and non-wettable surfaces, respectively. To overcome this challenge, a new surface parameter is here defined as called “Normalized Surface Free Energy (NSFE)” which combines the concept of SFE and roughness, thereby enabling us to predict the wettability of different liquids on such real surfaces.

In order to launch the arrangement of the proposed concept, the BS EN 828:2013 standard [25] is used, as below:

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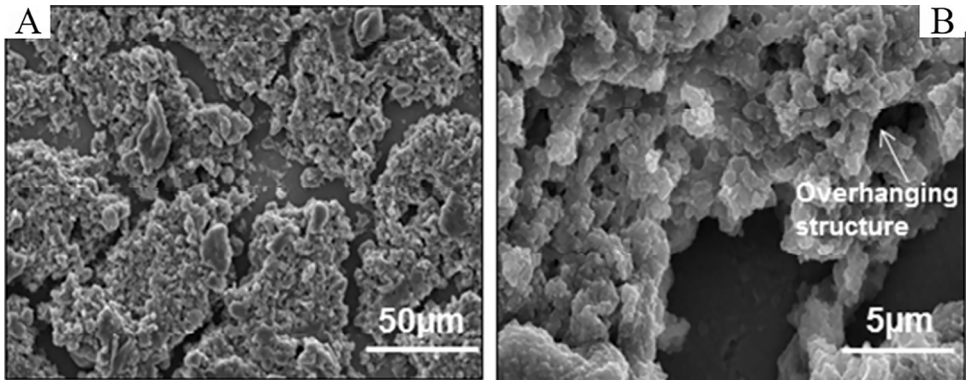

Fig. 1. Scanning electron microscopic (SEM) micrographs of the silica + PFOTS coating in two magnifications [26].

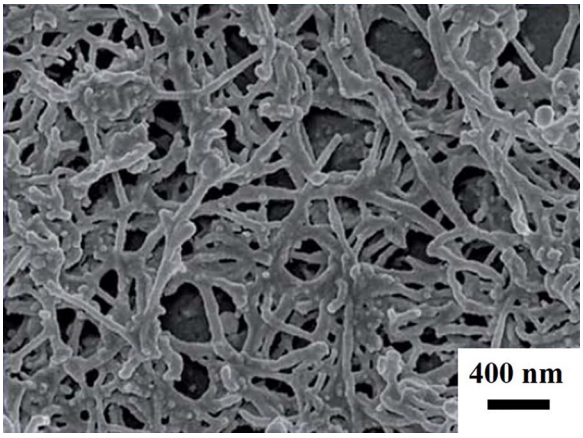

Fig. 2. SEM micrograph of the silica nanotubes coating modified with PFDTS [28].

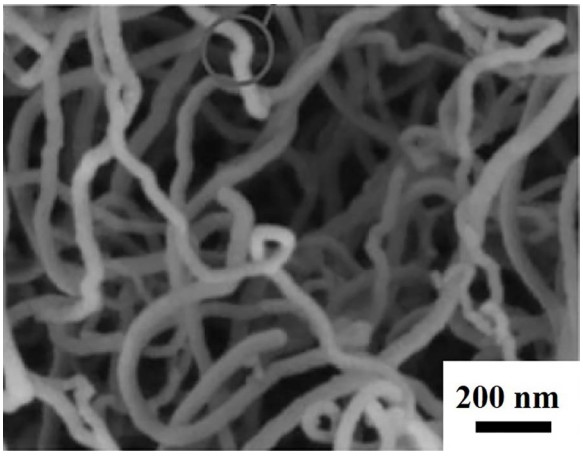

Fig. 3. SEM images of the silicone nano-filament deposit modified with PFDTS [29].

Table 1
Essential surface tension data of the selected liquids.

Liquid	γ_{lg} (mN/m)	γ_{lg}^{p} (mN/m)	γ_{lg}^{d} (mN/m)	Ref.
Water	72.8	46.4	26.4	[30]
Diiodomethane	50.8	0	50.8	[30]
Hexadecane	28.0	0	28.0	[31]
Ethylene Glycol	48.3	19.0	29.3	[32]
Toluene	29.1	27.8	1.3	[33]

$$0.5\gamma_{lg}(1+\cos\theta_Y) = \sqrt{\gamma_{sg}^{d}\gamma_{lg}^{d}} + \sqrt{\gamma_{sg}^{p}\gamma_{lg}^{p}} \quad (1)$$

where γ_{lg} is the surface tension of a liquid, θ_Y is the Young contact angle on a solid surface, γ_{sg}^{d} is the dispersive component of the solid SFE, γ_{lg}^{d} is the dispersive component of the liquid SFE, γ_{sg}^{p} is the polar component of the solid SFE and γ_{lg}^{p} is the polar component of liquid SFE. However, Eq. (1) is merely practical for ideal surfaces characterized to be entirely homogeneous and flat. Herein, to define NSFE as an extension of SFE, the master key is that the apparent contact angle (θ_a) on a real (rough) surface is substituted for Young contact angle (θ_Y) in Eq. (1), giving Eq. (2):.

$$0.5\gamma_{lg}(1+\cos\theta_\alpha) = \sqrt{\gamma_{sg}^{d*}\gamma_{lg}^{d}} + \sqrt{\gamma_{sg}^{p*}\gamma_{lg}^{p}} \quad (2)$$

Accordingly, γ_{sg}^{d*} and γ_{sg}^{p*} is converted into the dispersive and polar components of NSFE on the heterogeneous surface, respectively. For a given liquid with the known liquid-gas SFE components which are clearly independent of the solid surface under consideration, there are two unknown parameters consisting of γ_{sg}^{d*} and γ_{sg}^{p*} in Eq. (2). Therefore, the utilization of two different liquids with the known properties yields the mentioned unknown parameters. Eventually, γ_{sg}^{*} as the NSFE of the real solid is calculated as below:

$$\gamma_{sg}^{d*} + \gamma_{sg}^{p*} = \gamma_{sg}^{*} \quad (3)$$

After determining the components of NSFE, in order to predict the wettability of other liquids on the same real surface, Eq. (2) should be again used. But in this occasion, there is only one unknown which is the contact angle of the third liquid. It should be noted that the application of this method has two constraints which originate from the conditions of the BS EN 828:2013 standard:

1) The primary assumption for establishing Eq. (1) is that the equilibrium vapor pressure of the liquid on the solid surface is zero, which is satisfied only for low-SFE and hydrophobic surfaces Thus, Eq. (1) and thereby Eq. (2) can be merely used for low-SFE materials.
2) Concerning the first two liquids used to determine the NSFE of the surface, one should have a dominant dispersive component of surface tension like diiodomethane and the other should present the domination of the polar component like water.

3. Model verification

To ascertain the validity of the introduced approach, it is required to compare the amounts calculated and measured for several low-energy surfaces. To do so, the surface preparation and structure of four instances are first described below.

I) Nande et al. [26] deposited temperature-dependent switchable coatings of silica nanoparticles and 1H, 1H, 2H, 2H-perfluorooctyltrichlorosilane (PFOTS) on a steel substrate. In Fig. 1A, a