

Determining the contact angle between liquids and cylindrical surfaces

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Abstract

One of the simplest methods of measuring the quantities for estimating the adhesion properties of materials (i.e., the adhesion work, the surface energy, and the interfacial tension between certain liquids and a surface) requires the determination of the contact angle between the liquid and the surface. In the case of plane surfaces the determination of the drop dimensions makes it possible to calculate the contact angle by the sessile drop method, but in the case of cylindrical surfaces (such as the monofilaments), several methods were developed to improve the accuracy of the contact angle measurements. This paper presents a comprehensive method for precise evaluation of the contact angle between liquid drops and monofilaments by establishing a differential equation describing the drop contour. This equation makes it possible to accurately compute the contact angle using the dimensions of the drop. A comparison of the values of the contact angle calculated by our method and those obtained by other approaches is made. We applied our method in the case of polyamide-6 monofilaments treated using dielectric barrier discharge, knowing their medical applications in surgical sutures.

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1. Introduction

The adhesion properties of surfaces, especially polymers, are important in obtaining the better biocompatibility demanded for medical applications. The surface energetic characteristics are essential because many interactive processes take place at the contact between human tissue and the implant surface [1]. Polymer materials having a minimum interfacial tension with water should have maximum biocompatibility, in particular good compatibility with the blood, and low thrombogenic effects [2]. Plasma treatment is a convenient technique for enhancing the material biocompatibility and controlling the interfacial tension of the implanted solid surface with tissues and biological fluids [3].

Using the contact interface parameters such as adhesion work (W_A), interfacial tension (γ_{SL}), dispersive and polar energy components (γ_{SV}^d and γ_{SV}^p), and surface polarity ($P = \gamma_{SV}^p/\gamma_{SV}$), one can perform an investigation of the adhesion properties and the biocompatibility of materials aimed to work

in contact with the human body. For example, the values of W_A and γ_{SL} indicate the blood compatibility of the implant surface, the adherence of biological cells on polymer surfaces, or the preferential absorption of plasma protein on the implant surface [2–4]. W_A , γ_{SL} , γ_{SV}^d , γ_{SV}^p , and P can be calculated using theoretical models that need precise measurement of the contact angle between the solid surface and two or more liquids.

For plane surfaces the contact angles can be directly evaluated by the sessile drop method, using the geometrical contour of a liquid drop on the solid surface. If θ_{profile} is the drop contact angle on the solid surface at the three-phase contact point, and $\theta_{\text{calculated}}$ is the angle defined by the drop height K and liquid–solid interface length L , a frequently used approach is to consider $\theta_{\text{profile}} \approx 2\theta_{\text{calculated}}$, with $\tan \theta_{\text{calculated}} = 2K/L$. Obviously, better approximation of the contact angle can be obtained by numerically solving the drop contour equation and the accuracy of the result will depend on the numerical method and on the operator's skill in reading the drop dimensions (K and L). Usually, an error of 2° is accepted.

This approximation cannot be used for cylindrical surfaces. In this case, one has to combine the theoretical modeling on the basis of Laplace balance equation with a rigorous method

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for measuring the drop dimensions. The Laplace equation allows finding, for selected boundary conditions, the differential equation of the drop contour, which can be solved only numerically. Various numerical computation methods and particular selections of drop dimensions (e.g., length, height, surface area, volume) have been proposed to estimate the contact angle θ , the results being presented as graphs and/or tables [5–8]. As a consequence, reading errors occur and propagate in evaluating the values of W_A , γ_{SL} , γ_{SV}^d , γ_{SV}^p , and P . Moreover, to discuss the efficiency of plasma treatments in enhancing the biocompatibility of materials it is necessary to analyze and compare the values of γ_{SL} using a unique method for contact angle evaluation [2].

The aim of our study is to find a differential equation of the drop contour that would make it possible to determine the contact angle of liquids on monofilaments accurately in order to avoid the use of graphs and tables.

2. Theoretical considerations

When a liquid drop is placed on a horizontal rigid plane surface that is smooth, it spreads over the surface until the mechanical and thermodynamic equilibrium is attained. The equilibrium is described by the Young–Dupree equation,

$$\gamma_{SL} - \gamma_{SV} + \gamma_{LV} \cos \theta_0 = 0, \quad (1)$$

where θ_0 is the equilibrium contact angle resulting from the action of the three interfacial tensions: solid–vapor (γ_{SV}), solid–liquid (γ_{SL}), and liquid–vapor (γ_{LV}). θ_0 is measured inside the liquid phase and is defined by the tangents to the liquid–vapor and solid–liquid interfaces.

The strength of the interface adhesion forces and, as a result, the adhesion surface properties are directly proportional to the thermodynamic adhesion work or adhesion energy (W_A), expressed as

$$W_A = \gamma_{SV} + \gamma_{LV} - \gamma_{SL} + \pi_e, \quad (2)$$

where π_e is the equilibrium spreading pressure of the liquid's vapor on the solid surface and W_A is defined per unit area. Using Eqs. (1) and (2) and taking into account that, for many solids having low surface energy, as the polymer surfaces, π_e is practically zero, the formula of the adhesion work is

$$W_A \cong \gamma_{LV}(1 + \cos \theta_0). \quad (3)$$

After finding the value of W_A one can calculate, by various methods, the two components of the surface energy, i.e., the dispersive (γ_{SV}^d) and polar (γ_{SV}^p) components. For example, Owens and Wendt [9] and Fowkes et al. [10] set a geometric mean formalism, with the relation

$$W_A = 2\sqrt{\gamma_{SV}^d \gamma_{LV}^d} + 2\sqrt{\gamma_{SV}^p \gamma_{LV}^p}, \quad (4)$$

where γ_{LV}^d and γ_{LV}^p are the dispersive and polar components of the liquid energy. Thus, using Eq. (3) and Eq. (4) for two different liquids, one can calculate γ_{SV}^d and γ_{SV}^p , after measuring the contact angle. The same equations could be used for evaluating the adhesion properties on cylindrical surfaces, therefore contact angle measurement is needed, too.

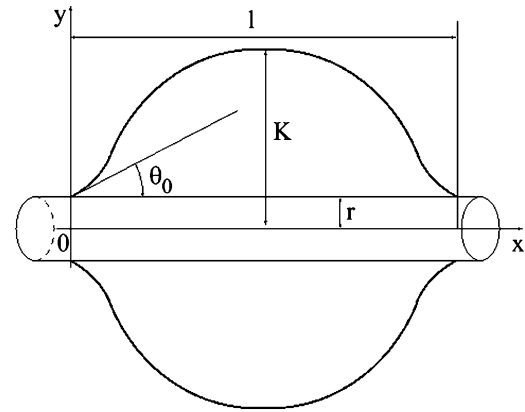


Fig. 1. Liquid drop on a monofilament: length (l), height (K), monofilament radius (r), and contact angle (θ_0).

In the following we present the main equations describing the drop contour on cylindrical surfaces, established after making several assumptions. The surface is considered to be a perfect cylinder (e.g., a monofilament), rigid, smooth, homogeneous, and isotropic (an ideal solid). The liquid drop is supposed to have a symmetric shape with respect to the x -axis, being coaxial with the filament due to the interaction by capillary forces at interface, the gravity effect being negligible.

When the mechanic and thermodynamic equilibrium of the drop is attained, the pressure difference ΔP is described by the Young–Laplace equation:

$$\Delta P = \gamma_{LV}(1/R_1 + 1/R_2). \quad (5)$$

Here, ΔP is the pressure difference between the liquid and vapor phases, γ_{LV} is the free energy of the liquid–vapor interface, and $(1/R_1 + 1/R_2)$ is the total curvature of this interface. The curvatures $1/R_1$ and $1/R_2$ are perpendicular to each other. Commonly, the ratio of the excess pressure to the liquid free surface energy, $\Delta P/\gamma_{LV}$, is considered constant. If parameters such as the filament radius (r), the maximum radius of the drop in the plan normal to the filament axis (K), and the length of the drop along the filament (l) are accurately measured (Fig. 1), it is possible to determine the contact angle by various methods [5–8].

One of these methods [6] requires the $\Delta P/\gamma_{LV}$ ratio to allow calculation of contact angle. The other [5,7,8] use graphs containing plots of the contact angle as a function of the drop length and height and/or tables containing values of Legendre's standard incomplete elliptic integrals of the first and second kind. Our aim is to find an equation describing the drop contour using only directly measurable dimensions of the drop, such as its length and height, and the fiber radius.

Yamaki and Katayama [6] have proposed a second-order differential equation of the interface contour in the (x, y) coordinate system,

$$\frac{d^2 y}{dx^2} = -\frac{\Delta P}{\gamma_{LV}} \left[1 + \left(\frac{dy}{dx} \right)^2 \right]^{3/2} + \frac{1 + (dy/dx)^2}{y}, \quad (6)$$

which requires the following boundary conditions:

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