Colloids and Surfaces A: Physicochem. Eng. Aspects 455 (2014) 164–173

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Equilibrium contact angle measurements of natural fibers by an acoustic vibration technique

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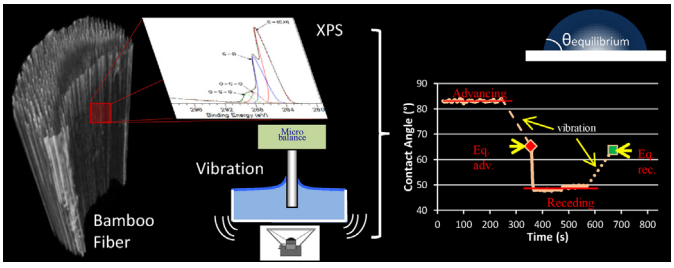
HIGHLIGHTS

- Equilibrium contact angles on natural fibers are measured.
- An acoustic vibration method was used to measure "equilibrium" contact angles on natural fibers.
- The equilibrium contact angle is measured directly before the fiber surface is affected by sorption or swelling.
- Equilibrium contact angles for test liquids on bamboo are stable and reproducible.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 7 February 2014
Received in revised form 21 April 2014
Accepted 23 April 2014
Available online 2 May 2014

Keywords:
Equilibrium contact angle
Wetting
Sound vibration
Photoelectron spectroscopy (XPS)
Natural fibers

ABSTRACT

Sorption of fluids during typical wetting experiments on natural fibers produces a zero receding contact angle situation, leading to an incomplete analysis of their wetting behavior. An acoustic vibration method was used to measure "equilibrium" contact angles on natural bamboo fibers. The correctness of the technique is verified by performing the experiment with polyethylene terephthalate (PET) fibers and films, and comparing these results with the average of the cosine functions of the advancing and receding angles for a given system. Surface energies and components of the surface energies of bamboo and PET fibers were estimated using the "equilibrium" contact angle data of various test liquids by using the acid–base approach. The results are in general agreement with X-ray photoelectron spectroscopy (XPS) analysis of the fiber's surface. The findings contribute to a better understanding of the complex phenomena occurring during wetting of natural fibers and suggest that the contact angle obtained by forcing relaxation through acoustic vibration is a reliable method for study the wetting behavior of natural fibers.

1. Introduction

Considerable attention has been given to the extraction, processing, and use of natural fibers as reinforcement of polymer composite materials. The major advantages of natural fibers over synthetic fibers are low cost, natural abundance, low carbon footprint, biodegradability, and good specific mechanical properties [1,2]. However, the generally hydrophilic nature of natural fibers produces low interfacial interactions with certain important hydrophobic thermoplastic matrices (such as polyethylene and polypropylene), leading to a poor interfacial strength, making necessary a proper study of the phenomena governing the interface of these composites.

Adhesion in a given fiber–matrix system can be estimated from the theoretical work of (physical) adhesion. In case chemical adhesion mechanisms are absent (as is the case for many composites

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http://dx.doi.org/10.1016/j.colsurfa.2014.04.054
0927-7757/

with a thermoplastic matrix), physical adhesion, in conjunction with mechanical interlocking will determine the adhesion. The quality of the impregnation and adhesion can be predicted and maximized by evaluating the compatibility of a given fiber–matrix system. This evaluation is made by estimating surface energies from contact angle measurements and calculating the wetting parameters (work of adhesion, interfacial energy, spreading coefficient, and wetting tension) [3,4]. Contact angles are a quantitative measure of solid–liquid molecular interactions and thus provide information on the surface energy of solids.

However, there are several phenomena affecting the wetting behavior of natural fibers that question whether usual experimental techniques (Wilhelmy method, drop geometry analysis), which are commonly thought to supply information on equilibrium properties of the fiber surface, are really doing so.

In the Wilhelmy technique, the wetting force is measured instantaneously, and always on a new contact line on a sufficiently smooth and chemically homogeneous surface during the continuous immersion of the solid in the fluid (dynamic advancing contact angle), or when the sample is being removed from the liquid (dynamic receding contact angle). Frequently, the experimental dynamic advancing contact angle (at very low velocities) is used to interpret surface energies of solids under the assumption of being a good approximation of Young's angle, although the advancing angle only represents a metastable state close to the static advancing angle (local minimum) [5,6]. In the same manner, a static receding contact angle also represents a local minimum; however, since its reproducibility is poor (due to sorption or swelling), this angle is less frequently reported. The phenomenon that produces this contact angle hysteresis may be related to the pinning of the contact line at heterogeneities [7–9]. These kinetic barriers produce a variation of the local contact angle around the contact line and explain why advancing angles are mostly representative of the portion of the surface which interacts unfavorably with the liquid, while receding contact angles represent portions of the surface with high interaction with the liquid.

However, the significance of the Young's contact angle as a quantitative measure of solid–liquid molecular interactions is based on equilibrium thermodynamic arguments; hence, a real equilibrium contact angle should be used to calculate surface energy components and wetting parameters. With the purpose of better describing both the low surface energy and the high surface energy components of the analyzed surfaces, a semi-empirical approximation suggested by Andrieu et al. [10] consisting in the average of the cosines of the advancing and receding angles, has been used by several researchers to estimate the cosine of the equilibrium angle (θ_{equ}) [11,12].

Although natural fibers have complex surface-related characteristics (liquid sorption, diffusion of extractives, different cross sections along the fiber length, surface roughness, or chemical heterogeneity), which make obtaining meaningful data from wetting measurements particularly challenging, the wetting behavior of natural fibers was modeled in previous work by using the Molecular-kinetic theory (MKT) [3,13]. The purpose of applying the MKT was to show that a similar theoretical contact angle versus wetting velocity dependency, as obtained for synthetic fibers, can be obtained for a natural fiber. Then, the compliance with MKT may ensure that a natural fiber surface represents a well-defined system for wetting analysis.

However, due to the adsorption of fluids on natural fibers during wetting experiments, usually a zero receding contact angle is obtained, leading to an incomplete analysis of their wetting behavior. In order to take into account the interaction of polar components and contact angle hysteresis properly, it would be very beneficial to measure the equilibrium contact angle directly before the fiber surface is affected by sorption or swelling.

As mentioned before, the common approach is to characterize a solid surface by measuring the receding and advancing contact angles. Another promising and relatively novel approach is to measure the contact angle that corresponds to the global energy minimum state, as obtained by the induction of vibration in the system [10,12,14–16]. The vibration allows the system to overcome the energy barriers between the metastable states and ideally to reach the equilibrium state. However, it is still uncertain how the most stable state can be identified. Some researchers suggest that a drop in the most stable state is axisymmetric, and then the shape of a drop can be monitored during and after a period of vibration until the most symmetric shape is reached [15]. Some others approaches refer to a relaxation period after a drop is formed [17] and the measurement of the same contact angle obtained by applying vibration from the advancing position and the receding position [14,16]. In the latter case, the contact angles measured in both situations should coincide to ensure that the system is not entrapped in a local minimum. This is the approach followed in this paper.

In this study, a procedure that is believed to measure "equilibrium" contact angles on bamboo technical fibers is discussed, using a modified Wilhelmy technique by applying acoustic vibration. The correctness of the technique is verified by performing experiments with PET fibers and films, and comparing these results with the average of the cosine functions of the advancing and receding angles for the given systems [10,12]. The drop on fiber method is also applied to assess the receding contact angle on bamboo fibers, which permits a more rapid measurement before sorption processes invalidate the measurement.

2. Materials and methods

2.1. Materials

Technical bamboo fibers of the species Guadua angustifolia were mechanically extracted from bamboo culms in the Department of Metallurgy and Materials Engineering at KULeuven. Polyethylene terephthalate (PET) films (thickness 0.2 mm) and fibers (diameter 0.4 mm) were obtained from the company Goodfellow (UK).

2.2. Materials preparation

For the contact angle measurements, the technical bamboo fibers underwent the following preparation procedure: after being selected (by means of an optical microscope), the fibers were cleaned, first with warm water for 1 h (90 °C), then wiped with ethanol with a piece of cotton tissue before being dried in a vacuum oven at 80 °C for 1 h. Bamboo fibers were further put in an autoclave to smoothen the lignin at the fiber surface under 3 bar of pressure at 150 °C for 1 h (see [3,13] for more details on this procedure). Only fibers that possess diameters between 80 and 150 μm were used.

The PET films and fibers were washed with a detergent (RBS-35 from Chemical Products) at a concentration of 4% (v/v) in water during 1 h under magnetic stirring, and next rinsed in ultrapure water (resistivity > 18 MΩ cm) at 90 °C for 1 h. The cleaned films were then dried under vacuum at 90 °C for 2 h and then conserved under silicagel.

2.3. Determination of the fiber perimeter

The method applied to determine the fiber perimeter was developed by Schultz et al. [18], and applied to natural fibers in our previous publications [3,13]. When hexane is used (0° contact angle), the Wilhelmy equation, $F = p\gamma_l \cos\theta$, becomes:

$$F = p\gamma_l \quad (1)$$