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Wetting behaviour and surface properties of technical bamboo fibres

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ABSTRACT

Bamboo fibres recently attracted interest as a sustainable reinforcement fibre in (polymer) composite materials, due to specific mechanical properties which are comparable to glass fibres. To achieve good wetting and adhesion of the bamboo fibre with different polymers, the fibre surface needs to be characterized. The wetting behaviour of technical bamboo fibres is studied experimentally by using the Wilhelmy technique, and the results are modelled using the molecular-kinetic theory. A novel procedure, based on an autoclave treatment, allows stable and reproducible advancing contact angles to be measured. In this way, meaningful information on interfacial interactions can be obtained, allowing improvement of the bamboo-polymer interface. Additionally, for comparison, the wetting behaviour of synthetic poly(ethylene terephthalate) (PET) fibre is studied. This article aims at contributing to a better understanding of the complex phenomena occurring during wetting of natural fibres. The results indicate that the high concentration of lignin on the surface of bamboo fibres is responsible for their wetting properties, whereas typical phenomena affecting wetting experiments on plant fibres can be minimized.

1. Introduction

Among the many different kinds of natural fibres used in composite materials, bamboo is deemed to have one of the most favourable combinations of low density and good mechanical properties: the specific strength and stiffness of bamboo fibres are comparable to those of glass fibres [1]. However, many natural fibres have several disadvantages such as poor wettability, incompatibility with some polymeric matrices and high moisture absorption by the fibres [2].

A major difficulty is related to the fibre–matrix adhesion. Bonding between the reinforcing fibre and the matrix has a significant effect on the properties of the composite since stress transfer and load distribution efficiency at the interface is determined by the degree of adhesion between the components. Using the experimental data obtained from wetting measurements, fibres and matrices can be examined and matched in terms of their surface components in order to improve the interfacial properties; predicting and verifying their compatibility allows more suitable combinations and therefore better composites to be made.

There are a variety of techniques for measuring wetting of single fibres. The most common methods include both the Wilhelmy technique and fluid geometry analysis. The former consists in a measurement of the liquid weight lifted in the meniscus by the spreading of the liquid upwards on a fibre, while the latter is concerned with the profile determination of a barrel-shaped volume where the fibre is wetted by a finite volume of liquid (a droplet) [3–5] or of a meniscus in the case of fibre wetting by an infinite reservoir [6,7]. In the case of natural fibres, both methods are hardly applicable due to surface irregularities and perimeter variation. To avoid these complications, the characterization of the wetting behaviour of natural fibres has been reported through the use of the modified Washburn or capillary-rise method [8]. However, this method does not allow the influence of wetting velocity on the determined contact angle to be studied. If surface irregularities are minimized, the Wilhelmy technique represents a good option to study the wetting of solids at different immersion velocities.

The interpretation of experimental wetting data depends on wetting theories. These have been derived to describe wetting on an ideal surface wherein complexities in relation to their wetting behaviour such as the viscoelastic response of a polymer surface to a wetting liquid [9], contact angle hysteresis due to surface irregularities or chemical heterogeneity [10,11] are assumed to be absent. Therefore, wetting phenomena can be modelled with some success

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for synthetic materials, in which the phenomena mentioned above are not expected to play a major role [12].

In order to predict the wetting properties of solids, several theoretical models were developed. Among them, two approaches focus on the location of energy dissipation during the wetting of a solid by a liquid: viscous dissipation in the bulk of the liquid (hydrodynamic model), and dissipation in the close vicinity of the solid near the wetting line (molecular-kinetic theory) [13,14]. These models obtained for synthetic materials revealed the dependency of dynamic contact angle on wetting velocity (depending on both speed and direction of displacement). As wetting velocity approaches zero, the wetting quasi-equilibrium parameters are obtained and may refer to either an advancing (wetting) or a receding (dewetting) contact angle. The difference between advancing and receding contact angles is called hysteresis.

However, similar approaches to model wetting behaviour cannot normally be applied to natural fibres due to complex phenomena at their surface. Barsberg and Thygeseny [12] argued that plant fibres may give rise to various complex phenomena during wetting experiments which are typically not found for synthetic fibres: liquid sorption/diffusion into the surface layers, diffusion of low-molecular-weight compounds (extractives) from the surface layers into the liquid, different "glassy" behaviour of the chemical constituents of the surface layers or viscoelastic response of the surface layers to the liquid. As a consequence, the influence of such phenomena on the wetting behaviour of natural fibres may be a possible source of invalidation of typical experimental techniques for measuring wetting.

Moreover, the difficulties in the characterization of the wetting properties of natural fibres are increased as a result of the complexity of their overall microstructure which by far exceeds that of synthetic materials. This complexity is due to the natural fibre hierarchical organisation at different length scales and the presence of different materials in variable proportions such as cellulose, hemicellulose, lignin and pectin [15,16]. It is claimed that some liquids can penetrate the natural fibre structure [12,17], allowing wetting properties of natural fibres to be affected by sorption and diffusion. For instance, technical bamboo fibre consists of bundles of more than one hundred elementary fibres. An elementary fibre consists of several layers where crystallized cellulose nano-fibrils are aligned with different angles with respect to the longitudinal fibre axis and are bound together with hemi-cellulose and lignin [18–20]. A schematic illustration of the complexity of bamboo fibre micro- and nano-structure is shown in Fig. 1.

The wetting properties of natural fibres (and solids in general) are determined by molecular interactions between their surface and liquids. If these molecular interactions can be evaluated by means of well described advancing and receding contact angles (quasi-equilibrium parameters), it is then possible to evaluate surface energy components by means of theories such as Owens–Wendt and acid–base approaches, which are based on the theoretical Young contact angle, assuming that an equilibrium state can be reached.

The surface condition and surface constitution of technical bamboo fibres play an imperative role in the interfacial strength of their composites. While information about bamboo fibre microstructure already exists, as mentioned above, the nature of the surface of technical bamboo fibres (used as reinforcement fibre in composites) is still unknown due to the fact that topography, chemical constituents and constituents distribution (mainly lignin and cellulose) are affected by the method of extraction such as steam explosion, retting, chemical extraction, or mechanical processes [21–25].

The aim of the present work is to examine whether technical bamboo fibres can be considered a well defined system for which reproducible and stable advancing contact angles can be measured. Treatment of the fibres was proposed in such a way that typical phenomena known to affect wetting experiments in plant fibres may play a limited role. In this manner, meaningful information on interfacial interactions can be obtained, allowing improvement of the bamboo composite interface.

2. Theoretical basis

2.1. Molecular-kinetic theory

The molecular-kinetic theory was developed by Blake [14] to explain the wetting properties of solids. It employs Frenkel and Eyring's explanation of the process that takes place during the momentum transport of liquids, viewed as the movement of a molecule from one local energy minimum to another [26].

This theory in its basic form discards the explicit energy dissipation due to viscous flow and focuses instead on energy dissipation occurring in the immediate vicinity of the moving contact line due to the process of attachment or detachment of fluid molecules from the solid surface [13]. The macroscopic behaviour of the wetting line is explained by the individual molecular displacements occurring within the three-phases contact line [27]. These displacements occur randomly but progressively in the direction of the moving contact line [28].

According to Blake [14], during spontaneous spreading, a liquid drop exhibits a dynamic contact angle θ that depends on the instantaneous contact line velocity ν and decreases progressively toward a static contact angle θ_0 at $\nu = 0$. In forced wetting, the substrate is moved at constant speed to drive the contact line at a given velocity, forming a stable dynamic contact angle θ (v). The displacement of the contact line depends on the frequency of forward and backward molecular displacements within the three phases zone, K_+ and K_-, respectively. At equilibrium, $\nu = 0$ and the net rate of displacement is zero, so that $K_+ = K_- = K_0$, where K_0 is the equilibrium displacement frequency. According to this theory, energy is dissipated by dynamic friction associated with the moving contact line.

If the driving force for wetting is taken to be the out-of-balance surface tension force γ $(\cos\theta_0 - \cos\theta)$, then the relationship between ν and θ is given by:

$$\nu = 2K_0\lambda \sinh\left[\frac{\gamma\lambda^2}{2kT}(\cos\theta_0 - \cos\theta)\right] \quad (1)$$

where λ is the average length of each molecular displacement, k is the Boltzmann constant, T the absolute temperature, and γ the surface tension of the liquid. The complete derivation of this model is presented by Blake [14].

3. Materials and methods

3.1. Materials

Technical fibres (bundles of elementary fibres, see Fig. 1) were mechanically extracted from *Guadua angustifolia* bamboo culms in the Department of Metallurgy and Materials Engineering (MTM) at KULeuven. Polyethylene terephthalate (PET) monofilaments (diameter 800 μm) from Goodfellow were used to compare the wetting behaviour of synthetic and bamboo fibres. Ultrapure water (18.2 Ω cm resistivity, Millipore Direct Q-3 UV) was used to study the fibres' wetting behaviour. Lignin powder Protobind 1000 was supplied by Granit from Switzerland.

3.2. Fibre preparation

The technical bamboo fibres that were examined underwent the following preparation procedure. After being selected (by means