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Wettability of carbon nanotube fibers

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ABSTRACT

Carbon nanotube (CNT) fibers are interesting alternatives to carbon fibers as fibrous reinforcement. However, good interfacial adhesion between the fibers and the matrix is difficult to control. Wetting of the fiber reinforcement with the matrix strongly determines the interfacial strength. Therefore, accurate characterization of the wettability of CNT fibers is one of the most important cornerstones to improve the interfacial adhesion. In this work, dynamic contact angle measurements were conducted on individual CNT fibers by using a modified tensiometric method based on the Wilhelmy method combined with a synchronized optical observation. The CNT fiber-liquid interactions were monitored in-situ, and accurate measurements of the contact angles were achieved. Contact angles on CNTs were estimated through a modified Cassie-Baxter model on the basis of the experimental contact angle values of CNT fibers. Subsequently, the non-polar and polar surface energy components of the CNTs were obtained. Then, the wetting parameters (work of adhesion, spreading coefficient and wetting tension) were predicted by using the surface energy values of both the CNTs and a series of polymers (PP, MAPP, PET, PVDF, and PVA). The results indicate that PVA is in terms of wetting the most suitable matrix for the preparation of CNT fiber polymer composites.

1. Introduction

Carbon nanotubes (CNTs) have received considerable attention owing to their unique 1D structure, and their exceptional mechanical and electrical properties combined with light weight [1,2]. Assembling them into a fiber (which is in fact a yarn although commonly referred to as fiber) is a way to circumvent the difficulties of manipulation and dispersion of individual CNTs and to make them more accessible for applications, e.g. as reinforcement in polymer composites [3–5] and as electrode casted with polymer electrolyte in energy devices [6,7]. For these applications, the interfacial adhesion between the CNT fibers and the matrix plays a critical role, in particular for the mechanical performance of the composite materials [8]. There are, in general, three mechanisms contributing to the interfacial adhesion: physical interactions, mechanical interlocking and chemical bonding [9]. In the case of non-functionalized CNT fibers, the contribution of the chemical bonding can be neglected. When physical interactions dominate, the interfacial strength can be correlated to the wettability and surface energies of the CNT fibers and the matrix [10].

According to van Oss et al. [11], the surface energy of a solid can be split into Lifshitz-van der Waals, acid and basic components. These components reflect the wetting properties of a solid-liquid system, and are used to calculate the amplitude of the physical adhesion between the solid and the matrix. To derive the surface energy components of CNT fibers, accurate contact angle measurements are required. Two main methods are currently used to estimate the wettability of fibers: the direct optical method and the Wilhelmy method. The latter one can also provide information on surface transitions (e.g., surface roughness and heterogeneity) on a short time scale [12].

The Wilhelmy method consists of measuring the capillary force exerted by a liquid on a solid substrate [13]. As the diameter of a single CNT fiber is about 20 μm, testing its wettability using the Wilhelmy method is very challenging because slight variations in the fiber diameter can significantly affect the contact angles [14]. Apart from the influence of the diameter, there are still underlying problems. Some studies [15] reported that thin fibers can bend

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when contacting the liquid surface or inexact capillary force caused by liquid uptake could also lead to incorrect measurements of contact angles.

Despite the above-mentioned issues, the Wilhelmy method has been intensively applied to study the wettability of single carbon fibers [16], surfaced modified carbon fibers [17,18], CNT grafted carbon fibers [19] and natural fibers [20–22], with fiber diameter ranging from several to hundreds micrometers. Only a few studies have directly addressed the wettability of individual CNTs [10,23,24]. Barber et al. [23] used atomic force microscopy and the Wilhelmy method to measure contact angles between a single CNT and various liquids, and found that wettability was less favorable when the liquid became more polar. The relevancy of the Wilhelmy method at the nanoscale to derive equilibrium contact angles, particularly in wetting experiments with CNTs, was demonstrated by Seveno et al. [24]. So far, to the authors' knowledge, studies dedicated to the dynamic wetting of CNT fibers are not available.

Several reports studied the interface between CNT fibers and epoxy: for instance, Deng et al. [8] suggested insufficient interactions between CNT fibers and epoxy matrices according to a low interfacial shear strength, whereas Vilatela et al. [25] showed that the infiltration of epoxy into CNT fibers could provide good interfacial adhesion. Nevertheless, a more comprehensive understanding of the wetting properties of CNT fibers is still lacking and is now a requirement for the development of CNT fibers based polymer composites. Moreover, wetting on individual CNTs at the nanoscale is of essential importance because that, in the CNT fiber/polymer composites, the contact is between the surface of CNTs and a liquid [26]. A modified Cassie-Baxter model enables to evaluate the contact angle formed by menisci with nano-fibers from the apparent contact angle formed by external meniscus with a micro-yarn [27].

In the present study, the wettability of CNT fibers has been investigated. The Wilhelmy method combined with an optical technique was employed for measuring dynamic contact angles on CNT fibers with different test liquids. This methodology permits us to monitor the structure of the fibers (diameter, surface defects and swelling/shrinking) during the tests and to correlate the contact angle variations with the motion of the contact line. Moreover, the optical technique allows the estimation of contact angles by fitting the shape of the meniscus formed around CNT fibers, providing consistent results with the Wilhelmy method. A modified Cassie–Baxter model was used to characterize the wettability of CNTs on the basis of wetting of CNT fibers. Polar and non-polar components of the solid-surface energy of CNTs were then calculated by using the acid-base approach [28]. Finally, physical adhesion between CNTs and different polymers could be predicted, providing the possibility to select the most appropriate one in terms of wetting, for the preparation of CNT fiber polymer composites.

2. Materials and methods

2.1. Materials

CNT fibers spun from multi-walled CNT arrays were used as solid substrates in this study. The CNT arrays were synthesized by the chemical vapor deposition (CVD) method reported previously [29]. Briefly, the CNT arrays were grown on $Fe/Al_2O_3/SiO_2/Si$ wafers by using the oxidative dehydrogenation reaction of C_2H_2 and CO_2 at 750 °C. The as-grown CNTs were multi walled with a mean diameter of 15 nm and an average wall number of 10. The thickness of the vertically aligned CNT array was about 300 μm. The CNTs have a low defect density and a good crystalline order, as revealed by TEM images and Raman spectra [29].

CNT fibers were then fabricated by dry spinning method [30], for which a CNT web was drawn out from CNT arrays and the web was simultaneously being densified and twisted (as schematically shown in Fig. 1). The densification was realized by wetting the fibers with acetone during the spinning process and the twist was induced by a motorized rotating table. Densification based on the acetone evaporation resulted in a shrinkage of the fiber diameter from ~65 μm to ~20 μm (Fig. 2a and Fig. 2c). As can be seen in the enlarged images (Fig. 2b and d), the space between the individual nanotubes and CNT bundles significantly reduced after densification. The compactness of the CNT structure is an important criterion as it limits liquid penetration and can therefore prevent errors [21,31] during contact angle measurements. By controlling the width of the CNT web and the speed of the table rotation, fibers with a twisting density of 8 mm^{-1} (number of twist per unit length) and a twisting angle of 10° were produced (Fig. 2c). It has to be noticed that, due to the looseness of the CNT structure in non-densified fiber, no obvious torsion is observed in Fig. 2a.

For the contact angle measurements, deionize water (DW), ethylene glycol (EG), diiodomethane (DIO) and n-Hexane were selected as test liquids based on their surface tension and acid-base components. The main properties of these liquids are summarized in Table 1 [32].

2.2. Contact angle measurements

2.2.1. Tensiometric method

Dynamic contact angle measurements at low speed were performed at 25 °C and 65% relative humidity, with a Krüss K100SF tensiometer (accuracy: 0.1 μg). This technique consists of dipping a single fiber into the test liquid and withdrawing it. During this process, the forces exerted by the liquid on a fiber are measured and used to calculate a series of dynamic contact angles. In practice, a CNT fiber is attached to the fixed fiber holder, and the vessel stage moves up (advancing) or down (receding) at a constant fixed low velocity (Fig. 3).

The dynamic contact angle θ can be calculated from:

$$F_{measured} = F_{capillary} + G - F_{buoyancy} = p\gamma_l \cos\theta + mg - \rho g V_{immersed} \quad (1)$$

where $F_{measured}$ is the force detected by the microbalance, p the fiber perimeter, m the fiber mass, g the gravitational acceleration, and $V_{immersed}$ the immersed volume of the fiber. The weight of the fiber (G) was measured and zeroed before starting each experiment. The calculated maximum buoyancy force is in the order of 10^{-6} mN (when assuming no liquid uptake inside the fiber), and can be neglected when compared with the capillary force. Consequently, Eq. (1) can be simplified to

$$F_{measured} = p\gamma_l \cos\theta \quad (2)$$

The Wilhelmy method has the advantage of high accuracy when testing contact angles of fine fibers with known diameters [13]. However, analyzing the wetting behavior of single fibers with micrometer-scale diameters is very challenging because small variations in the fiber perimeter and $F_{measured}$ can largely affect the calculated contact angles. Moreover, the results can be incorrect if the fiber is dipped non-perpendicularly to the liquid surface or if it even bends during the measurement [15,33], which is most likely to occur but not detected by a tensiometer. In our previous publication [16], the improvement of the accuracy of the contact angle measurement of a single carbon fiber by using a modified tensiometric method was reported, which takes into consideration both the intrinsic variability of the fiber diameter and the extremely small amplitude of $F_{measured}$. This modified tensiometric method