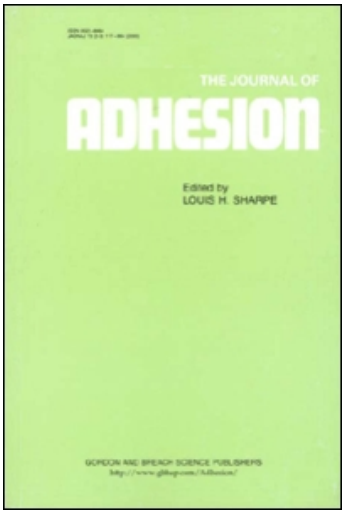

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Liquid/Fiber and Solidified-Liquid/Fiber Contact Angles Compared

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Data are presented showing that the contact angle formed by a liquid resin droplet placed on a single fiber is comparable with a receding contact angle. This was ascertained by comparing Wilhelmy wetting force measurements with liquid droplet profile analysis. Subsequently, the latter analysis was carried out on cured (solidified) epoxy droplets placed on Kevlar® fibers. Dimensional changes observed after curing showed that the contact angles of the solid droplets were smaller than that for liquid resin; however, the presence of residual stresses because of adhesion to the fiber may make droplet profile analysis inaccurate for obtaining an equilibrium receding contact angle for the solid droplets.

Keywords: Wettability; contact angle; interface; fiber; resin

INTRODUCTION

Since it is extremely difficult to make an accurate direct measurement of a static contact angle of a liquid on a fiber surface, two somewhat indirect methods have been employed by most investigators. One is the Wilhelmy wetting force measurement from which it is possible to calculate a value for the contact angle without actually measuring it. The other is the droplet profile analysis method developed by Carroll [1–3], which analyzes the overall shape of a single droplet that has been applied to a fiber. This analysis is extrapolated to obtain a value for the equilibrium contact angle at the three-phase intersection.

In the past, we have used droplet profile analysis to determine the contact angle at the fiber/solid resin droplet interface [4]. Because we are concerned that such solid/fiber contact angles may not be the same as their liquid/fiber counterparts, measurements have been carried out on fiber/resin systems, using both techniques, before and after resin curing.

The Wilhelmy wetting force measurement technique is illustrated in Figure 1. A single filament is suspended from one arm of a recording electronic microbalance and is partially immersed in a reservoir of the liquid of interest. The liquid advances and recedes along the filament as the liquid reservoir is raised and lowered. The wetting force is recorded and the contact angle value computed from Eq. (1):

$$F_w = \gamma_L \cdot P \cdot \cos\theta \tag{1}$$

where F_w is the recorded wetting force, γ_L is the surface tension of liquid, P is the perimeter of the fiber and θ is the contact angle at the interface.

In some cases, the Wilhelmy method presents practical difficulties. For example, it is difficult to conduct the experiment when the liquid is a thermoplastic resin that has a high melting temperature. The liquid reservoir must be heated, and resultant air turbulence must be

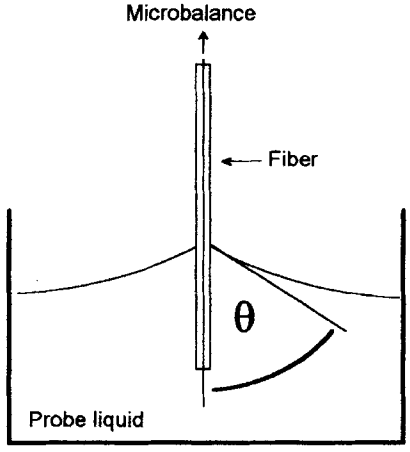

FIGURE 1 Wilhelmy wetting experiment.

minimized to obtain accurate weight measurements from the microbalance. Obviously, it would be difficult to conduct the test with a thermosetting resin that cures during the wettability scan. If the resin is sufficiently viscous, the fiber may be too flexible to penetrate the liquid surface; if the resin is dense, the buoyancy correction will be significant.

The droplet profile analysis method developed by Carroll [1–3] is useful in such cases. A symmetrical droplet of liquid is applied directly to the fiber. An analytical expression relating droplet length and maximum radius and fiber radius to the contact angle has been derived, leading to Eq. (2) and (3) [1]. All the variables and parameters are defined in Figure 2.

$$-\frac{dz}{dx} = \frac{x^2 + ax_1x_2}{[(x_2^2 - x^2)(x^2 - a^2x_1^2)]^{1/2}} \tag{2}$$

$$a = -\frac{x_1 - x_2\cos\theta}{x_2 - x_1\cos\theta} \tag{3}$$

The contact angle between the fiber surface and the resin can be determined using measurements of the droplet and fiber dimensions,

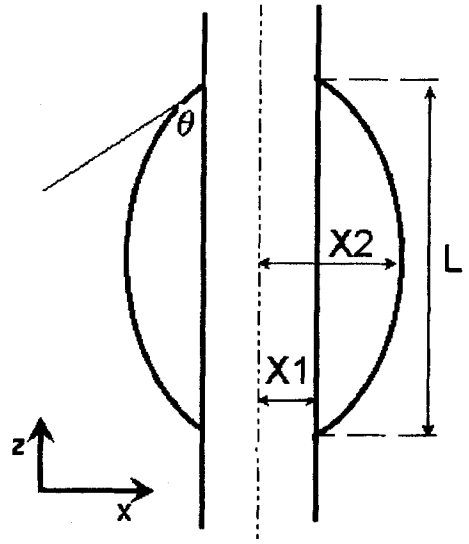

FIGURE 2 Definition of symbols for droplet-on-fiber system.

by finding a θ value which satisfies the following boundary conditions:

$$\text{at } z = 0, \quad x = x_1$$

$$\text{at } z = L/2, \quad x = x_2$$

The drawback of this method is that the computation for contact angle value is very sensitive to small changes in the fiber and droplet dimensions. Typical fibers range from 7 to 12 μm in diameter and, to avoid gravitational effects on droplet shape, the droplet size is limited to almost the same magnitude as the fiber. For systems using extra-fine fiber, it becomes difficult to obtain accurate dimensional measurements. We, therefore, need to obtain reliable and repeatable measurements of the fiber and resin droplet. At TRI, using a video micrometer attached to a microscope, we can measure dimensions of fiber and droplet to 0.1 μm accuracy, sufficient for confident contact angle value computation.

Presumably, the contact angle value obtained using the Wilhelmy method and the droplet method should be identical. However, there is no report in the literature comparing contact angle measurements of a given fiber/resin system using the two methods. In this report, we present comparative experimental results for an epoxy resin on carbon, glass and polyethylene fibers.

Some researchers have used this droplet profile analysis to estimate contact angles at solid droplet/fiber interfaces. However, due to the shrinkage of the resin during curing and/or cooling, solid/fiber contact angles may not be the same as their liquid/fiber counterparts. This question has also been studied.

EXPERIMENTAL

Materials

Contact angles of neat epoxy resin (Epon828®, Shell) on E-glass, unsized poly(acrylonitrile) (PAN) carbon (AS4, Hercules) and polyethylene (650 denier Spectra® 1000, Allied) fibers were determined using the Wilhelmy method and the droplet method at room temperature.

The E-glass fiber was cleaned in ethanolic KOH to remove surface contamination. The AS4 and Spectra 1000 fibers were used as received. Another version of carbon fiber with lower surface energetics, designated as AS4-300, was obtained by heating the AS4 at 300 °C in nitrogen.

Wilhelmy Method

As shown in Figure 1, a single filament suspended from one arm of the microbalance was first advanced into neat epoxy resin and then pulled out. The scanning velocity was 3 μm/sec, slow enough to avoid significant viscous drag from the epoxy resin. The wetting forces were recorded and the contact angles calculated using Eq. (1).

Droplet Method

Fiber samples were mounted horizontally between two supporting rods. Neat epoxy resin was applied to the fiber from the tip of a needle to form spherical droplets. A typical resin droplet is shown in Figure 2. The length of the droplet, L, the maximum radius of the droplet, x_2, and the radius of the fiber, x_1, were measured under the video micrometer (Model 305, Colorado Video, Inc., Boulder, CO) at room temperature. The CVI Model 305 accepts composite video signals from a camera (NEC T123, approximate magnification 2.5x) attached to a microscope (Zeiss Axioskop 20, magnification 500x). It superimposes two movable vertical cursors on the image in a monitor screen, as shown in Figure 3. The displacement of the two cursors generates a linear DC voltage, which is displayed on a digital voltmeter. This displacement is calibrated and used to measure the dimensions of the droplet/fiber system. To minimize the uncertainty inherent in subjective location of image boundaries, the device superimposes a video waveform on the monitor screen that displays the gray level of the image at the cursor. This allows more objective and repeatable determination of dimensions based upon a predefined gray level for the image boundary. Reproducibility to 0.1 μm was achieved routinely with this instrument.

For each fiber/resin combination, 25 specimens were prepared and tested. A computer program evaluated Eq. (2) and (3) using Runge-Kutta numerical integration. The program computed contact angle values from fiber and droplet dimensions for each specimen. Numerical

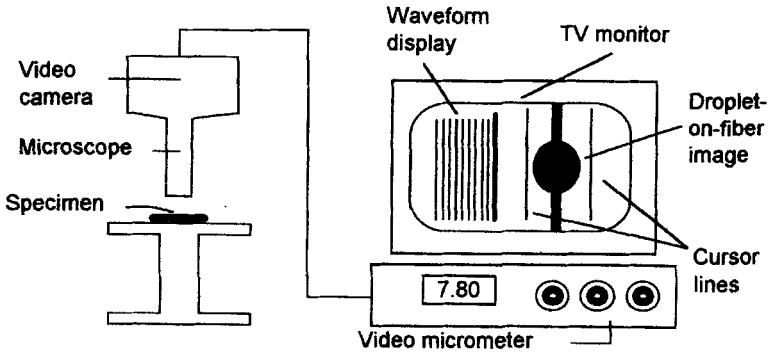

FIGURE 3 Instrumentation for measuring dimensions of droplet-on-fiber system.

solutions in table form can also be obtained from the author of Reference [1].

Epoxy resin with curing agent (methylene dianiline, Stephenson), weight ratio: resin/curing agent = 4/1, was also used to study the effect of curing on the size of droplets. Resin droplets were cured on Kevlar 49® fiber and untreated pitch-based graphite fiber at 80°C for 2 hours followed by 150°C for 3 hours. The dimensions of fibers and resin droplets were measured before and after curing using the video micrometer.

RESULTS AND DISCUSSION

A typical Wilhelmy wetting force (advancing and receding) scan of neat epoxy resin on a fiber is shown in Figure 4. Table I lists the contact angle cosine data obtained from the Wilhelmy and droplet methods. The results show reasonable consistency between the contact angle cosine obtained using the droplet method and the receding mode contact angle cosine from the Wilhelmy method. However, some discrepancy occurs as the contact angle cosine value becomes smaller. As shown in Figure 5, the liquid resin was applied to the filament by touching it with an applicator with resin on its tip, transferring some resin to the fiber. Once the applicator was removed, while the volume of the liquid remains the same, the surface area of the resin started to shrink due to its surface tension, forming a more spherical droplet. This process created contact angles equivalent to

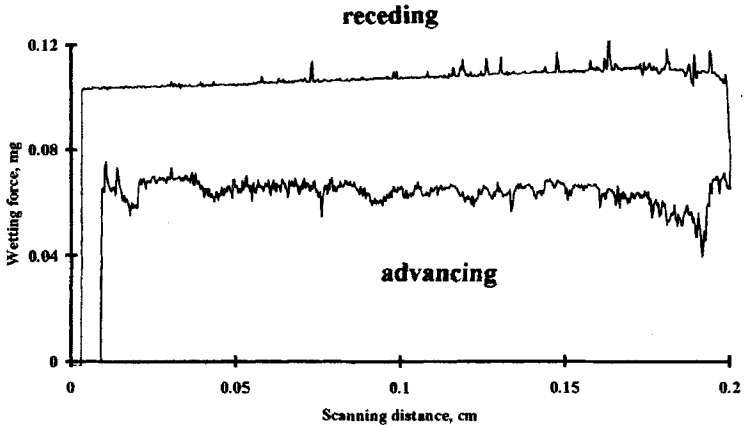

FIGURE 4 Wetting force trace of epoxy resin on AS4 fiber.

TABLE I Contact angle cosine obtained using Wilhelmy and droplet methods

	(Average ± 95% conf.)		
	Wilhelmy method*		Droplet method
System	$\cos\theta$, adv	$\cos\theta$, rec	$\cos\theta$
Glass/epoxy	0.328 ± 0.026	0.664 ± 0.030	0.750 ± 0.056
Spectra/epoxy	0.344 ± 0.085	0.747 ± 0.147	0.878 ± 0.048
AS4-300/Epoxy	0.425 ± 0.033	0.868 ± 0.047	0.890 ± 0.026
AS4/Epoxy	0.529 ± 0.007	0.913 ± 0.033	0.870 ± 0.034

*adv: advancing mode; rec: receding mode.

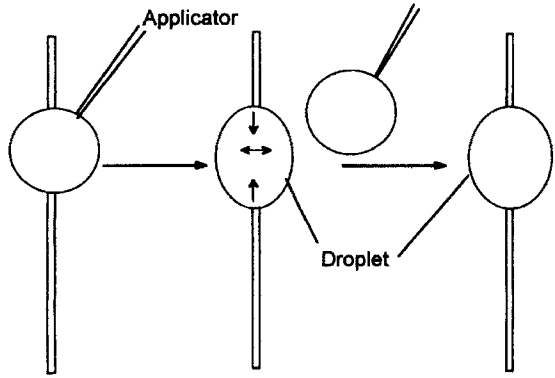

FIGURE 5 Resin droplet shrinks in the axial direction (volume does not change) after being applied to the fiber, resulting a receding mode contact angle at the fiber/resin interface.

receding mode measurements from the Wilhelmy method. However, it is possible to obtain advancing mode contact angle data by very carefully step-wise adding liquid to a small droplet.

It is worth noting that, based on the advancing mode contact angle data from Wilhelmy measurements, the AS4 fiber treated at 300°C (AS4-300) is less wettable by the epoxy resin than the untreated AS4 fiber. However, the receding mode data do not show much difference. Since the droplet method only evaluates the receding mode contact angle, this method does not show different wettabilities between AS4-300 and AS4 fibers. It is apparent that, although the droplet method can be a good alternative method for estimating the contact angle at the interface, it may not be suitable under all circumstances.

For epoxy resin cured with curing agent at an elevated temperature, volume reduction is expected from both crosslinking and cooling. Therefore, the dimensions of the resin droplet will be different after curing. Tables II and III list the dimensions and computed contact angles before and after curing of Kevlar 49/epoxy and pitch/epoxy

TABLE II Droplet dimensions of Kevlar 49®/epoxy before and after curing

Kevlar 49/Epoxy	*Before curing*	*After curing*
θ, degree	12.8	8.65
$\cos\theta$	0.975	0.989
Ratio of X_2 (before/after)	1.04 ± 0.02	
Ratio of L (before/after)	0.98 ± 0.03	

TABLE III Droplet dimensions of untreated pitch-based graphite fiber/epoxy before and after curing, μm

Fiber/Epoxy	*Before curing*	*After curing*
θ, degree	35.7	28.3
$\cos\theta$	0.815	0.880
Ratio of X_2 (before/after)	1.07 ± 0.05	
Ratio of L (before/after)	0.99 ± 0.03	

specimens, respectively. For both systems, the cured epoxy droplets shrink in the transverse direction, as shown by the reduction of maximum diameters of the droplets. However, there is no dimensional change in the longitudinal direction. The data clearly show that the adhesion between the fiber and resin prevents the droplet from shrinking in the axial direction. Consequently, the droplets become thinner, resulting in a smaller "geometric" contact angle at the interface, as shown in Figure 6. However, since the droplet profile analysis is based on an equilibrium state of the system, the equilibrium contact angle values can only be evaluated correctly when the resin is free from stress, *i.e.*, either in a liquid form or in a solid form but allowed to be relaxed from any stress. The fact that droplets only shrink in their transverse direction but can not shrink in the longitudinal direction because of interfacial adhesion indicates that there is a residual stress built up at the interface. Therefore, without knowing the relaxation time of the solid resin and/or at what stage of resin curing is the interfacial adhesion strong enough to prevent the resin from shrinking, we can not

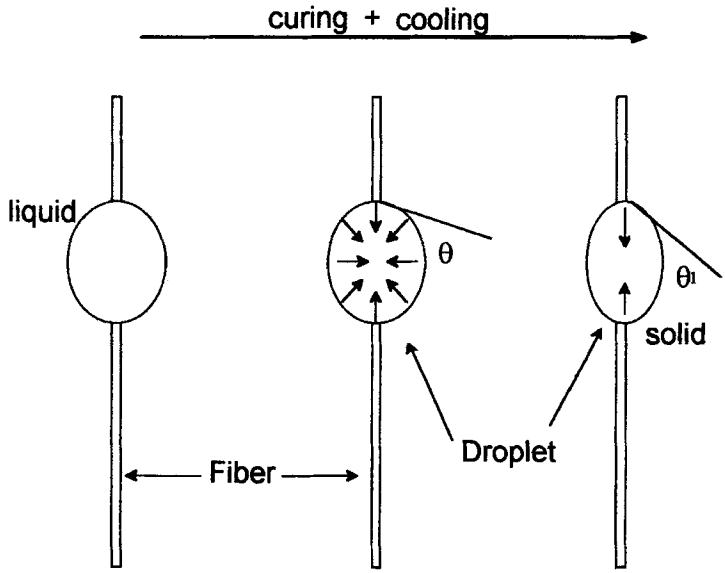

FIGURE 6 Resin droplet shrinks after curing and cooling. The fiber/resin interfacial adhesion prevends the droplet from shrinking in the axial direction. Note that $\theta_1 < \theta$.

apply Eq. (2) to obtain the contact angle value at the solid droplet/fiber interface. In other words, although we did observe a smaller geometric contact angle at the interface, we cannot say that it is the equilibrium contact angle between the solid droplet and the fiber.

CONCLUSION

Measurement of the contact angle between fiber and resin was conducted on four systems using liquid droplet profile anlaysis. The results were compared with contact angle values obtained by Wilhelmy wetting force measurements. The data show reasonable consistency between the two methods over the range studied and indicate that, because of the way that the droplets were applied, the droplet method measures the receding mode contact angle. Comparison of the dimensions of the epoxy resin droplets before and after curing shows that droplet profile analysis may not be applicable to solid droplets and that the solid/fiber contact angles may be different from their liquid/fiber counterparts.

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