

Characterisation of Fibre Surfaces by Wetting Techniques

The development of a stable bond between the resin matrix and the fibre reinforcement in a composite material depends on the efficiency of adhesion at the interface. The fibre surface energy is one influence on the formation of a stable bond.

The surface energy of fibre has been shown to influence both the processing and final properties of composite materials. Flow of resin through a fibre preform can be affected by the wetting properties of the fibre. The properties of the fibre-matrix interface influence the mechanical properties of a composite material.

This Measurement Note summarises the theory underlying wetting measurements for fibres and presents a standardised procedure for determining the surface energy of a fibre using a wetting balance. This standardised procedure has been demonstrated by measurement of the wetting characteristics of carbon and glass fibres with various surface treatments.

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Introduction

The processing and final properties of a composite material can be affected by the properties of the fibre surface. Both physical and chemical characteristics of the fibre are important. The physical properties of the fibre surface can be quantified in terms of the surface roughness which is the subject of another measurement note [\[1\]](#).

The properties of the fibre surface can be engineered by modification of the fibre surface chemistry. Typically, a glass or carbon fibre is heat treated and/or coated with size following manufacture. The size can have a number of functions: to protect the fibre surface, to make the fibre easier to handle and to improve the adhesion between the fibre and the matrix. It is possible to tailor the fibre size to maximise adhesion with a particular resin. The surface energy of a fibre can be measured using wetting techniques

Wetting Techniques

The wetting of a fibre surface is a function of both the physical and chemical properties of the interface. The surface energy of a solid can be determined from the contact angle between the solid surface and a liquid of known surface tension.

[Figure 1](#) illustrates the appearance of a liquid surface in contact with a suspended fibre. The liquid forms a meniscus around the fibre. The angle θ between the surface of the fibre and the surface of the liquid is known as the contact angle.

The so-called Young equation may be obtained by equating the components of the surface energy as shown in [Figure 2](#):

$$\gamma_s = \gamma_{sL} + \gamma_L \cos \theta$$

where γ_S is the surface energy of the solid-vapour interface, γ_{SL} is the surface energy of solid-liquid interface and γ_L is the surface tension of the liquid. This equation is not valid when θ equals 0° i.e. the liquid is fully wetting. This equation forms the basis for methods to determine the surface energy of a solid surface.

A standardised procedure for the determination of the surface energy of a single fibre is presented in the [box](#) below.

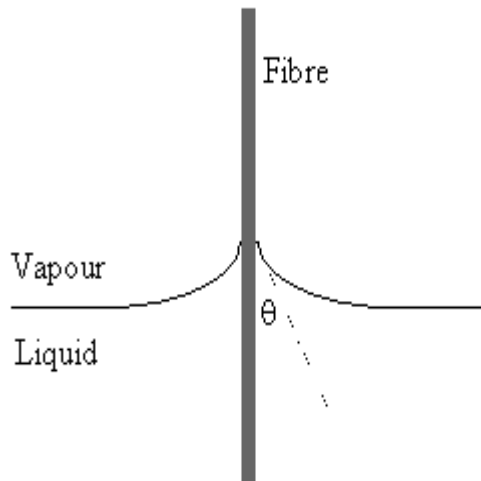


Figure 1. Schematic illustrating a suspended fibre in contact with a liquid.

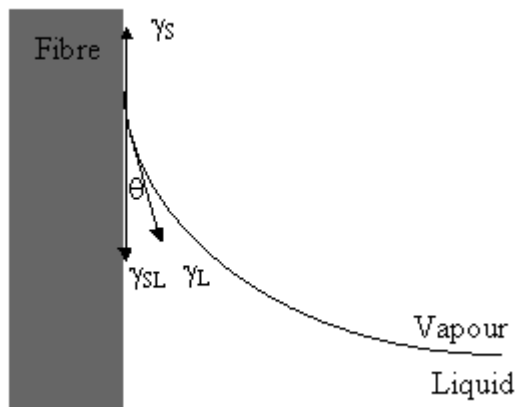


Figure 2. Schematic illustrating the surface energy components at a fibre surface.

Notes On Procedure

The standardised procedure was developed in collaboration with users of this technique in industry and academia.

The analysis used in the standardised procedure is the geometric mean analysis. This analysis is relatively unsophisticated but has been shown to produce results that are in good agreement with other, more sophisticated, techniques.

The buoyancy effect has been neglected in this procedure. For fibres this effect is generally negligible because of the small volume of the fibre.

Fibre Measurements

Fibre measurements were performed in accordance with the standardised procedure. Three probe liquids were used for the single fibre measurements: deionised water, ethylene glycol and bromonaphthalene. Standard values for γ_L^d , γ_L^p (defined in the standardised procedure) were used after confirming that the surface tension of the liquid was in good agreement with the standard value. These standard values are shown in [Table 1](#).

Results

Wetting Curves

A typical wetting curve is shown in [Figure 3](#). The surface of the liquid is at the 2 mm position. A large increase in force, to values around 0.07 mg, can be seen as the fibre is immersed in the liquid. After the fibre has been immersed 4 mm the fibre is withdrawn, the force is around 0.11 mg, and finally the force drops again as the fibre loses contact with the liquid. The hysteresis, the difference between the advancing and receding curves, of this wetting trace can be seen clearly. The surface energy results shown are for the advancing curve because this represents the wetting of the fibre.

Table 1

Probe Liquid	γ_L in mN m ⁻¹	γ_L^d in mN m ⁻¹	γ_L^p in mN m ⁻¹
Deionised water	72.80	22.50	50.30
Ethylene glycol	48.30	29.30	19.00
Bromonaphthalene	44.60	44.60	0.00

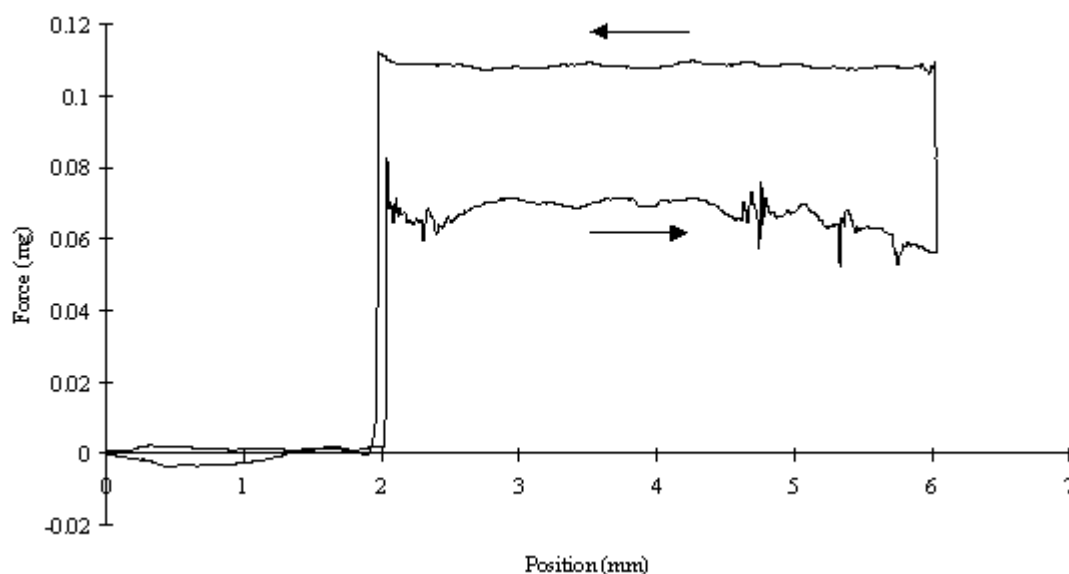


Figure 3. Wetting trace for a carbon fibre immersed in ethylene glycol.

1 Scope

This procedure describes the use of a dynamic contact angle analyser (DCA) to measure the surface energy of a fibre. Polar and dispersive components of surface energy are determined. The DCA is used to determine the contact angle between the fibre and several liquids of known surface energy.

2 Apparatus

2.1 Dynamic contact angle analyser consisting of a moveable platform and a microbalance. The platform should be capable of moving at a speed of 20 $\mu\text{m}/\text{second}$. The balance should have a resolution of 0.1 μg .

2.2 Nichrome wire, 0.10 to 0.15 mm in diameter

2.3 A range of analysis grade standard probe liquids. The liquids should be chosen so that the surface tension of the liquid is higher than that of the fibre and that data are obtained at a range of values of γ_L^p/γ_L^d (see Section 6).

2.4 A glass container for the probe liquids. The inside diameter of the container should be sufficiently large that the sides of the container do not influence the behaviour of the fibre.

2.5 An optical microscope

3 Calibration

3.1 The DCA motor and balance should be calibrated according to the manufacturer's instructions.

4 Sample

4.1 A hook is formed in one end of a length of nichrome wire. A single fibre approximately 10 mm in length is glued to the straight end of the wire. (A cyanoacrylate adhesive has been found to be suitable for this purpose.) It is important to ensure that the part of the fibre to be tested is not touched and is free of adhesive.

4.2 An optical microscope should be used to confirm that only one fibre is attached to the wire.

5 Procedure

5.1 The nichrome wire should be attached to the balance so the fibre is suspended vertically and above the surface of the liquid.

5.2 The platform should be raised at a speed of 20 $\mu\text{m}/\text{second}$ until the fibre is immersed in the liquid to a depth of 4 mm.

The point of contact between the fibre and the liquid may be defined as an increase in the recorded mass of 0.01 mg.

5.3 The platform should be lowered at a speed of 20 $\mu\text{m}/\text{second}$ until the platform has returned to the starting position

5.4 The measurement should be repeated five times for each liquid using a fresh fibre sample each time.

It may be possible to automate steps 5.2 and 5.3.

6 Calculation of fibre surface energy

6.1 The contact angle θ for a circular fibre may be calculated from the expression:

$$\cos \theta = \frac{F}{\pi d \gamma_L} \quad (1)$$

where F is the wetting force recorded by the balance, d is the diameter of the fibre and γ_L is the surface tension of the probe liquid used. The preferred method for diameter measurement is given in the Appendix.

6.2 The work of adhesion of the fibre W_A is calculated from the expression:

$$W_A = \gamma_L(1 + \cos \theta) \quad (2)$$

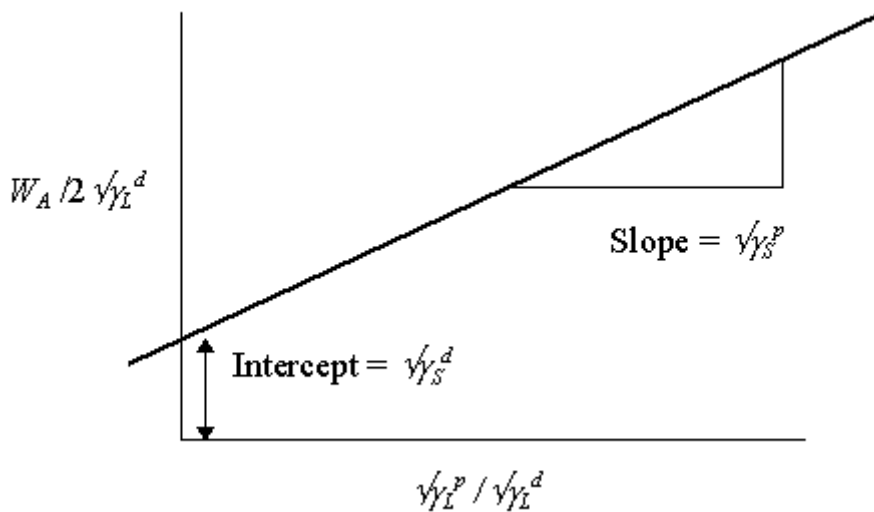
6.3 The surface energy of both the fibre (subscript s) and the liquid (subscript l) consist of polar and dispersive contributions i.e.

$$\gamma_s = \gamma_s^d + \gamma_s^p \quad (3)$$

$$\gamma_L = \gamma_L^d + \gamma_L^p \quad (4)$$

where γ_s is the surface energy of the fibre, γ_s^d is the dispersive component of the surface energy of the fibre, γ_s^p is the polar component of the surface energy of the fibre, γ_L^d is the dispersive component of the surface tension of the liquid, γ_L^p is the polar component of the surface tension of the liquid.

6.4 The values of γ_s^d and γ_s^p are obtained by plotting the $W_A/2\gamma_L^d$ against γ_L^p/γ_L^d for each fibre tested. A straight line is fitted to the data by linear regression with a slope of γ_s^p and an intercept of γ_s^d as shown below.



Appendix. Procedure for measurement of fibre diameter

The fibre diameter may be determined experimentally using the same apparatus used to determine the contact angle. The procedure described above should be followed using a liquid with a low surface tension, such as hexadecane. The liquid will fully wet the fibre resulting in a contact angle of 0° . A knowledge of the force on the fibre and the surface tension of the liquid enables the fibre diameter to be calculated from

[Equation 1.](#)

Carbon Fibres

A range of carbon fibres were tested to investigate the effect of surface treatments on the surface energy of carbon fibres.

The adhesion of carbon fibres is usually improved by thermally oxidising the fibre after manufacture. A size may also be applied to the fibre, usually an epoxy resin, to protect the fibre and to retain the fibre in a tow which makes the fibre easier to handle.

Surface energy results for four types of carbon fibre with various surface coatings/treatments are shown in Tables 2 and 3.

Carbon fibres that had been oxidised were compared with identical fibres that had not been oxidised. The surface energy for these samples are shown in Table 2. It can be seen that the treatment results in an increase in the overall surface energy of the fibre. This increase is the result of a large increase in the (long range) polar surface energy. There is also a decrease in the (short range) dispersive energy.

Similarly carbon fibres with and without an epoxy sizing were tested. The results for these fibres are shown in Table 3. It can be seen that the size has very little effect on the surface energy; there is a slight increase in γ_S^d and a slight decrease in γ_S^p . However, the appearance of the tows is very different. The sized fibre is retained in a discrete tow and fibres must be separated deliberately, while for the unsized fibre the tow breaks up readily. Clearly, for these fibres the purpose of the size is to improve the handling of the fibre rather than to improve the adhesion of the fibre. The adhesion of the fibre is improved by oxidative treatment.

Glass Fibres

A range of glass fibres with different surface treatments were investigated. In this case the surface treatments were tailored to be suitable for particular resins. For glass fibres the size is more important than for carbon fibres because the adhesion of uncoated glass fibres is very poor. Hence, the adhesion of glass fibres depends entirely on the size which is applied to the glass fibre.

Results for the range of glass fibres studied are shown in Table 4. It can be seen that the total surface energy does not show great variation between the different sizings. In fact, the total surface energy is highest for the water sized fibre. The water sizing is the most basic size and would not be expected to show the greatest adhesion in practice.

These results illustrate that the surface energy is only one factor in determining the efficiency of the adhesion in a composite material. As well as the surface roughness the details of the surface chemistry are important. Measurement of the surface energy does not discriminate between specific groups at the surface. For instance, the surface energy of the fibres with epoxy or polyester compatible sizing are lower than the water sizing. However, these fibres would be expected to bond more efficiently to the corresponding matrix because the size contains chemical groups specifically to bond to the matrix material.

Table 2. Effect of treatment on the surface energy of carbon fibres.

Test fibre (diameter in μm)	γ_S (mJ m ⁻²)	γ_S^d (mJ m ⁻²)	γ_S^p (mJ m ⁻²)
Untreated carbon fibre (7)	44.8	44.0	0.8
Treated carbon fibre (7)	70.0	26.0	44.0

Table 3. Effect of size on the surface energy of carbon fibres

Test fibre (diameter in μm)	γ_S (mJ m ⁻²)	γ_S^d (mJ m ⁻²)	γ_S^p (mJ m ⁻²)
Unsized carbon fibre (7)	46.4	40.2	6.2
Sized carbon fibre (7)	46.5	41.0	5.5

Table 4. Effect of size on the surface energy of glass fibres.

Test fibre (diameter in μm)			
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	γ_S (mJ m ⁻²)	γ_S^d (mJ m ⁻²)	γ_S^p (mJ m ⁻²)
Glass fibre with water size (17)	50.6	37.5	13.1
Glass fibre with epoxy compatible sized (18)	42.9	40.2	2.7
Glass fibre with polyester compatible sized (16)	41.6	36.2	5.4
Glass fibre with complete size - polyester and epoxy compatible (18)	46.0	36.1	9.9

Concluding Remarks

It has been shown in this measurement note that wetting techniques offer a relatively straightforward method for determining the surface energy of fibres. However, the relevance of these quantities to the processing and final properties of a composite material has yet to be established.

Liquid moulding processes might be expected to be affected by the surface energy of the fibre. Work by Steenkamer *et al.* [2] found that the permeability of a fabric was influenced by the liquid used. However, more recent work by Hammond and Loos [3] showed that the permeability was independent of the liquid used.

There is a similar situation concerning the final properties of composite materials. Jacobash *et al.* [4] stated that there was generally no correlation between the surface energy of the fibre and mechanical properties. While work by Larson and Drzal [5] found that an increase in the surface energy of the fibre resulted in materials with improved flexural and shear strengths.

Clearly, there is no consensus at present concerning the relevance of fibre surface energy to the processing, final properties or durability of a composite material. Accurate data are necessary to establish these relationships. Until such a framework is developed the utility of wetting techniques will be limited to providing information that complements data from other surface specific techniques.

A further limitation is that the surface energy does not account for all the influences on adhesion. Surface roughness and surface chemistry may not have the same effect on the adhesion in a composite material as they have on the surface energy. Hence, these measurements provide a general indication of the surface energy which does not necessarily correspond to the adhesion to a specific resin.

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