Wettability and surface analysis of glass fibres

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Received 23 April 1999; revised received and accepted 9 August 1999

The wettability of glass fibres used as reinforcement for thermoplastics and thermosets has been studied. Contact angles have been determined by the Wilhelmy technique and the wetting parameters such as work of adhesion, fibre surface energy and interfacial energy have been calculated. The fibre surfaces have been analysed by scanning electron microscopy. It is observed that the wettability of the glass fibres is related with the fibre finish and is independent of the fibre diameter for the fibres with the same cross-sectional shape.

Keywords: Contact angle, Glass fibre, Surface analysis, Wettability

1 Introduction

Surface wettability of textile and technical fibres is a key factor in many process techniques and end-use characteristics. In dyeing, finishing and coating processes, the adhesion and wicking properties affect the process parameters and the final characteristics of the material: Fibre surface modification through physical or chemical treatments may be necessary to improve the wettability and dye and coating adhesion.

Absorbency, stain repellency, compatibility (e.g. with biological materials), hydrophobicity and hydrophilicity of textiles and textile-related materials are influenced by the surface characteristics of these materials.

In composites, the adhesion between the reinforcing fibre and the matrix influences the mechanical properties of the material. Measurements of surface energies can predict the compatibility of these materials. Often, the interface can be engineered by modifying the fibre surface chemistry to optimize the adhesion between fibre and matrix. This can be controlled by the surface energy analysis.

As the nature of physical interaction between liquids and solids is important for practical interest, the measurement of contact angles and the calculation of surface energies can lead to a better understanding and even an improvement of these interactions by modification.

While the contact angle measurement is feasible with flat solid surfaces, it becomes much more difficult when the wettability of a textile filament is determined.

The present paper reports the wettability and surface analysis results of the glass fibres which are used as reinforcement for thermoplastics and thermosets. The contact angles and the wetting parameters, such as work of adhesion, fibre surface energy and interfacial energy, of different varieties of glass fibres have been compared.

2 Theory

2.1 Contact Angle

The quantitative measure of liquid-solid interaction is the contact angle (θ), made by a liquid placed against a solid. The angle θ is defined as the angle made between the normals to the solid and liquid surfaces (measured in the gas) at the point of interest along the three-phase interline (Fig. 1). This is the same as the angle made between the solid surface and the tangent to the liquid-gas surface (drawn in the liquid) in the plane perpendicular to the interline at the point of interest. The contact angle may be related to the surface energies (γ's) of the three interfaces by Young’s equation:

\[ \cos \theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} \]

... (1)

![Fig. 1—Contact angle as a measure of wettability](image)
where \( \gamma_{sv} \) is the effective boundary tension of the solid-vapour interface (or solid/vapour interfacial energy); \( \gamma_{ls} \), the effective boundary tension of the solid-liquid interface (or solid/liquid interfacial energy); and \( \gamma_{l} \), the liquid surface tension.

When \( \Theta = 0 \), the solid is said to be ‘wet out’ by the liquid. The liquid then, if there is sufficient room, spreads out to form a monomolecular film. In view of Young’s equation, this situation is favoured by high \( \gamma_{sv} \) and, low \( \gamma_{ld} \) and \( \gamma_{l} \).

When \( 0^\circ < \Theta < 90^\circ \), the liquid is said to wet the solid, but not completely. The solid prefers, to some extent, to be covered by the liquid as opposed to the gas.

When \( 90^\circ < \Theta < 180^\circ \), the liquid is said ‘not to wet’ the solid. This situation is favoured by high surface tension liquids on low surface energy solids.

A limiting case is \( \Theta \to 180^\circ \).

### 2.2 Contact Angle Hysteresis

Contact angle hysteresis is defined as the difference between advancing \( (\Theta_{adv}) \) and receding \( (\Theta_{rec}) \) contact angles. This hysteresis occurs due to the wide range of metastable states which can be observed as the liquid meniscus scans the surface of a solid at the solid/liquid/vapour interface. As there are free energy barriers between these metastable states, a true equilibrium contact angle is impossible to measure in real time. For an ideal surface wet by a pure liquid, the contact angle theory predicts only one thermodynamically stable contact angle. However, the ideal surface is rarely found. To fully characterize any surface it is important to measure both advancing and receding contact angles and report the difference as the contact angle hysteresis.

The hysteresis effect can be classified in thermodynamic and kinetic hysteresis. The sources of thermodynamic hysteresis are surface roughness and surface heterogeneity. The kinetic hysteresis is distinguished by time or cycle dependant changes in the contact angle. It can be due to the surface deformation, liquid penetration, surface mobility and surface reorientation.

Measurements of contact angles between fibres and liquids can be made with a dynamic contact angle microbalance based system. The contact angle \( \Theta \), when a liquid of surface energy \( \gamma_{l} \) wets a fibre of diameter \( d \), may be determined by measuring the wetting force \( F \), using the following Wilhelmy equation \( F = \pi d \gamma_{lv} \cos \Theta \) ...

The buoyancy term is neglected for thin fibres \((r < 50 \mu m)\).

### 2.3 Work of Adhesion

The work of adhesion \( (W_a) \) is the work required to reversibly separate one bulk phase (liquid) from another bulk phase (solid). It is easily calculated from a contact angle measurement using the following equation:

\[
W_a = \gamma_{lv} (1 + \cos \Theta) = \gamma_{lv} + \gamma_{sv} \gamma_{ld} \]

### 2.4 Fibre Surface Energy

Surface energetic analysis of fibres is done by measuring the contact angle of a variety of liquids having known polar and dispersive components of their total surface free energy. This method assumes that the total surface free energy across an interface \( (\gamma) \) can be split into components corresponding to the non-polar or dispersive interactions \( (\gamma^d) \) and the the polar interactions \( (\gamma^p) \):

\[
\gamma = \gamma^d + \gamma^p \]

The assumption generally holds for low surface energy solids such as polymers.

The work of adhesion is calculated by using the Eq. (3). Using the substitutions

\[
\gamma_{lv} = \gamma_{lv}^{d} + \gamma_{lv}^{p} = \alpha_{lv}^{2} + \beta_{lv}^{2} \text{ and } \gamma_{sv} = \gamma_{sv}^{d} + \gamma_{sv}^{p} = \alpha_{sv}^{2} + \beta_{sv}^{2} \]

the following equation can be obtained:

\[
W_a (\gamma_{lv}^{d}) \alpha_{lv}^{2} + \gamma_{sv}^{p} (\beta_{sv}/\alpha_{sv}) \]

Hence, if \( \gamma_{lv}, \gamma_{sv}^{d} \) and \( \gamma_{sv}^{p} \) are known and the contact angle \( \Theta \) is measured for a range of liquids, then a plot of \( W_a / (2 \alpha_{lv}) \) vs \( \beta_{sv}/\alpha_{sv} \) will yield a straight line with the slope and intercept providing a solution to \( \gamma_{sv}^{d} (\gamma_{lv}^{d}) \) and \( \gamma_{sv}^{p} (\gamma_{lv}^{p}) \)

### 2.5 Interfacial Energy

The interfacial energy can be calculated as follows:

\[
\gamma_{lv} = \gamma_{sv} + \gamma_{lv} - W_a \]

### 3 Materials and Methods

The E-glass fibres used as reinforcement for thermoplastics (polyolefines) and thermosets (epoxy, polyester) were taken out of a glass roving and were treated with different kinds of silanes. Four types of glass fibres, viz. GF1 (from a 68 tex roving with sizing), GF2 (from a 272 tex roving) for thermoplastics, GF3 (from a roving) for thermoplastics, and GF4 (from a 2400 tex roving) used as
reinforcement for thermosets, were selected for the study.

Measurements were made with a Cahn DCA 322 microbalance based system (Fig. 2). The wetting liquids used were hexadecane ($\gamma_{hv} = 27.6$ dynes/cm), water (milli-Q; $\gamma_{hw} = 72.6$ dynes/cm) and ethylene glycol ($\gamma_{hc} = 48.3$ dynes/cm). The cosines of the contact angles between fibres and liquids were calculated from the measured forces and the surface tensions of the wetting liquids. The work of adhesion, the fibre surface energy and the interfacial energy were also calculated.

The contact angle was determined by measuring the force on a fibre which is dipped in a liquid according to the Wilhelmy balance principle.

The fibre was suspended from the microbalance via a little clamp, and its weight in air was zeroed out before contact. The wetting liquid reservoir was mounted on an elevator which could be raised or lowered at a slow steady rate. The experiments were carried out at a rate of 40 $\mu$m/s. The liquid was raised until a force change was registered as a result of first contact with the suspended sample. The liquid then was raised further to produce a specific depth of immersion of the sample. The apparent weight at this depth was recorded on a chart recorder and was fed to a computer for storage and analysis. The final depth used for the experiments was 5 or 10 mm. Thereafter, the liquid in the dish was lowered at a carefully controlled rate while the force was measured by the electrobalance. The force was then converted to the contact angle using Eq. (2).

In most cases, 5 or 6 specimens of each kind of sample were run and a plot of force as a function of depth of immersion was constructed. A typical curve is shown on Fig. 3.

As the liquid is first brought into contact with the fibre, the force jumps to the advancing interline condition. The slope of the line results from the buoyancy correction. When the liquid level movement is stopped and reversed, and the meniscus is reoriented, the force trace yields the receding contact angle.

The perimeters of the fibres were calculated from the measurements in the liquid hexadecane for which a total wetting out of the fibre by the liquid took place ($\theta = 0$). The fibres surfaces were analysed by scanning electron microscopy.

4 Results and Discussion

The perimeters of the fibres calculated from the DCA measurements in hexadecane, advancing contact angles ($\theta_{adv}$), receding contact angles ($\theta_{rec}$), and the contact hysteresis (the difference between advancing and receding angles) are given in Table 1. Table 2 shows the work of adhesion, the fibre surface energy and the interfacial energy. A typical curve from DCA measurements is shown in Fig. 4. Scanning electron micrographs of the different glass fibres are shown in Fig. 5.
Table 1—Advancing and receding contact angles of glass fibres

<table>
<thead>
<tr>
<th>Fibre</th>
<th>Perimeter (Hexadecane)</th>
<th>Water</th>
<th>Ethylene glycol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\cos \theta_{adv}$</td>
<td>$\theta_{adv}$</td>
<td>$\theta_{adv}$</td>
</tr>
<tr>
<td>GF1</td>
<td>0.0366</td>
<td>0.23</td>
<td>76.46</td>
</tr>
<tr>
<td>GF2</td>
<td>0.0422</td>
<td>0.33</td>
<td>70.84</td>
</tr>
<tr>
<td>GF3</td>
<td>0.0719</td>
<td>0.26</td>
<td>74.98</td>
</tr>
<tr>
<td>GF4</td>
<td>0.0564</td>
<td>0.51</td>
<td>59.06</td>
</tr>
</tbody>
</table>

$\theta_{adv}$—Advancing contact angle; and $\theta_{rec}$—Receding contact angle

Table 2—Wetting parameters of glass fibres

<table>
<thead>
<tr>
<th>Fibre</th>
<th>Perimeter, mm (Hexadecane)</th>
<th>Water</th>
<th>Ethylene glycol</th>
<th>$\gamma_{sv}$, dynes/cm</th>
<th>$\gamma_{ls}$, dynes/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>GF1</td>
<td>0.0366</td>
<td>89.60</td>
<td>67.14</td>
<td>28.03</td>
<td>11.03</td>
</tr>
<tr>
<td>GF2</td>
<td>0.0422</td>
<td>96.43</td>
<td>70.82</td>
<td>33.05</td>
<td>9.22</td>
</tr>
<tr>
<td>GF3</td>
<td>0.0719</td>
<td>91.41</td>
<td>72.18</td>
<td>28.84</td>
<td>10.02</td>
</tr>
<tr>
<td>GF4</td>
<td>0.0564</td>
<td>109.92</td>
<td>86.26</td>
<td>41.64</td>
<td>4.31</td>
</tr>
</tbody>
</table>

$\gamma_{sv}$—Solid-vapour interfacial energy, $\gamma_{ls}$—Solid-liquid interfacial energy, and $W_a$—Work of adhesion

Fig. 4—Force vs. immersion depth for GF4

The advancing contact angles of the glass fibres GF1, GF2 and GF3 measured in the polar liquids (water and ethylene glycol) are high but still lower than 90°. As the fibres are treated with a special finish for non-polar thermoplastics, their wettability with polar liquids has to be low.

A remarkable difference is observed in the contact angle hysteresis between the glass fibres GF1 and GF2 which were supplied by the same company and have the same applicability. The thermodynamic contact angle hysteresis is mainly due to the differences in receding contact angles. Miller et al. observed that the filament diameter has no effect on the wettability as assumed by the Wilhelmy method. If the difference in fibre diameter can be excluded, the lower receding contact angle of GF2 can be explained by the presence of more higher surface energy components on GF2. These components tend to resist the dewetting of the receding fluid front, thus lowering the receding angle.

The scanning electron micrographs of glass fibres (Fig. 5) show that all the fibres have a smooth surface. Fibre finishes are seen on GF1, GF2 and GF3. On comparing the scanning electron micrographs of GF1 and GF2, no remarkable difference on the surface is seen. The thermodynamic hysteresis does not seem to be due to the differences in surface roughness.

The advancing contact angle of the glass fibre GF4, which is treated with a finish for thermoset polymers as polyester and epoxy, is lower than that of the fibres used as reinforcement for thermoplastics. The surface polarity of GF4 is higher.

The wettability of the glass fibres, used for reinforcement of thermoplastics with different diameters and same cross-sectional shape is independent of the diameter. The same observations regarding the wettability of nylon monofilaments are made by Miller et al. The wettability of GF4, a glass fibre with a finish for thermosets, is higher than that of the glass fibres finished for thermoplastics. This means that the work required to separate the glass fibre GF4 from water and ethylene glycol is higher. These results can be explained by the stronger polar interactions between the fibre and the liquids.

Measurements of the surface energies can lead to a prediction of the compatibility of the reinforcement fibres with the polymer matrix. A total surface energy...
for a polymer film is 24.04 dynes/cm (ref. 10), and that for a polypropylene melt at 200°C is 16.9 dynes/cm (ref. 11). No data for thermoset polyester and epoxy are available. On comparing the surface energies, it is observed that GF1 and GF3 will have better wettability and adhesion with polypropylene.

5 Conclusion
The wettability of the glass fibres with a finish for thermosets is higher in polar solvents than that for the glass fibres used as reinforcement for thermoplastics. Wettability is independent of the fibre diameter for the fibres with the same cross-sectional shape. The
difference in contact angle hysteresis between the fibres can be explained by the difference in presence of higher surface energy components. On comparing the wettability of the fibres and the polymers, it is observed that some fibres could be expected to have a better adhesion with some polymers.

References
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