Simulating the interface of carbon fibres with molten polymers and reactive monomers*

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Wilhelmy plate experiments were performed with carbon fibres submitted to different degrees of surface treatment and various viscous fluids. The relative solid–liquid velocity was varied between 20 and 260 μm s^{-1}. The recorded force shows contributions from hydrodynamics (connected to the fluid nature and viscosity and to the interfacial velocity) and surface-related effects (surface energetics of fibres and liquids). The use of viscous fluids in the simulation of the fibre–liquid interaction involving hot polymer melts and reactive monomers is discussed.

(Keywords: interfaces; carbon fibres; molten polymers)

INTRODUCTION

Many aspects of composites technology involve the flow of molten polymers or uncured monomers over fibre surfaces; prepregging, pultrusion and filament winding are typical examples. In all these technological steps, the nature of the fluid–fibre interface plays a fundamental role. Wetting problems can result in void formation, uneven matrix distribution and ultimately bad performance[1–3].

The behaviour of fibre and fluid in relative motion is affected both by hydrodynamic and surface tension effects[4–7]. Thus, the problem is one of a dynamic phenomenon rather than only a problem of thermodynamic equilibrium[5].

Experimentally, the fluid–fibre interface, with the phases in relative motion, can be probed by the Wilhelmy plate technique, where a fibre is immersed in a liquid at a controlled speed[8]. The force exerted by the fluid on the solid is recorded by means of a microbalance. The Wilhelmy plate technique is commonly used for contact angle measurements, which are generally performed at room temperature, using low viscosity liquids (e.g. water)[9]. Its application to determine the wettability of fibres by a viscous polymeric melt or an uncured fluid is, in principle, very interesting, since the recorded force contains contributions not only from interfacial forces but also from the shear stress exerted by the fluid on the solid surface[10]. Moreover, the control of the fibre–liquid interfacial velocity allows recording of transient and time dependent effects.

The practical exploitation of the Wilhelmy plate technique in the study of these systems, however, is hindered by experimental problems linked to the high temperature required to melt polymeric matrices; thermal convection currents from the oven affect the electrobalance reading, resulting in an insufficient signal-to-noise ratio. Although this problem has been solved by Sauer and Dipaolo[11], commercial Wilhelmy plate instruments do not allow high temperature measurements.

A different approach is to use model liquids, having a room temperature viscosity and surface energy that mimic the properties of fluids involved in composites technology. High temperature measurements are not required in these systems and all the intriguing features of the Wilhelmy plate experiment can be exploited. We have recently recorded and modelled the dynamic tensiograms of carbon fibres in such model liquids[10,12].

In this paper, we comment upon the use of the Wilhelmy plate technique in studying the wetting of carbon fibres by model viscous fluids.

EXPERIMENTAL

Carbon fibres

Wetting experiments were performed on untreated and plasma-treated intermediate modulus Magnamite IM7 carbon fibres (Hercules, tow size 12 K), provided without any surface treatment or sizing. As a comparison, sized Toho Rayon Tenax-J IM500 carbon fibres were analysed, chosen on the basis of a similar modulus and strength[13]. Oxygen plasma treatments of Magnamite IM7 fibres were performed using a parallel plate reactor, with the experimental conditions reported elsewhere[13].

Liquids

Two viscous fluids were used. The first was a 1.5% w/v polyethylene glycol (PEG)–water solution, using PEG ($M_w = 35\,000$ g mol^{-1}) from Fluka. The room temperature surface tension of this solution, measured as described below, was 63 mJ m^{-2}. The second fluid was fluorinated, with a surface tension of 19 mJ m^{-2}. This fluid was a Newtonian liquid and its viscosity at room

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temperature was about 0.641 Pa s. The PEG–water solution was non-Newtonian, therefore viscosity depended on shear rate; however, it was close to that of the fluorinated fluid.

Dynamic wettability measurements

Dynamic wettability was measured with a Cahn DCA-322 dynamic contact angle analyser. A single carbon fibre was fixed to a hook by means of an adhesive tape and the force on the fibre was measured as the liquid container was raised and withdrawn; a new fibre was used for every measurement. The stage velocity was varied from 20 to 260 μm s^{-1}. The fibre perimeter was measured for each fibre, immediately after the wettability measurement, by means of the wetting force at zero depth of immersion of a completely wetting liquid (n-heptane, Carlo Erba), using a stage speed of 50 μm s^{-1}.

The surface tension of the fluids was calculated by the wetting force at zero depth of immersion of a glow discharge cleaned glass slide of known perimeter.

RESULTS

Carbon fibres in fluorinated fluid

Typical high velocity (150 μm s^{-1}) wetting cycles of carbon fibres in the fluorinated fluid are shown in *Figure 1*. Several comments can be made. The shape of the force *versus* distance diagram is very different from the conventional Wilhelmy plate tensiogram[9]. In particular, the slopes of the advancing and receding tracks are not parallel and have an opposite sign, giving rise to divergent arms. As recently discussed and modelled[10,12], this behaviour is due to the effect of the shear stress exerted by the fluid on the fibre surface. The effect of the shear stress is negligible when conventional low viscosity liquids are used, but its role increases with increasing viscosity of the fluid and the interfacial velocity. In the case of Newtonian fluids, the slope can be calculated using the model of the falling cylinder viscometer[14].

Table 1 Advancing (Θ_a) and receding (Θ_r) contact angles of carbon fibres *versus* stage speed in fluorinated fluid and PEG–water solution

Sample	Stage speed (μm s^{-1})	Θ_a (deg)	Θ_r (deg)
Fluorinated fluid			
Untreated IM7	20	0	0
	70	13	0
	100	19	0
	150	42	0
	200	53	0
	260	57	0
Plasma-treated IM7	20	0	0
	70	13	0
	100	13	0
	150	38	0
	200	56	0
	260	54	0
Sized IM500	20	0	0
	70	13	0
	100	13	0
	150	40	0
	200	58	0
	260	60	0
PEH-water solution			
Untreated IM7	20	55	30
	70	60	21
	100	63	18
	150	65	0
	200	71	0
	260	85	0
Plasma-treated IM7	20	25	0
	70	31	0
	100	33	0
	150	35	0
	200	43	0
	260	53	0
Sized IM500	20	34	0
	70	38	0
	100	45	0
	150	50	0
	200	57	0
	260	62	0

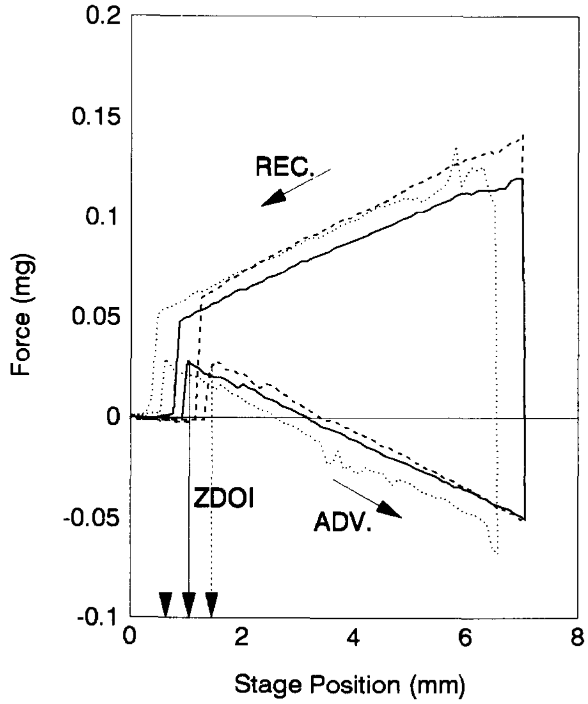

Figure 1 Wetting cycles of untreated IM7 (——), plasma-treated IM7 (·····) and sized IM500 (– – –) fibres in fluorinated fluids

Another point to note is that, despite the different nature of the fibre surfaces, all of them show nearly the same contact angle. The force at zero depth of immersion (ZDOI), that is where the first discontinuity is observed, is nearly the same. While we will return to this point in the Discussion, it is important to note that this behaviour, i.e. the same value of force at ZDOI hence the same value of contact angle irrespective of the fibre nature, is observed with all the stage velocities used (*Table 1*). At low stage speed, the fibres are completely wetted by the liquid, as expected from the low surface tension of the fluorinated fluid. As interfacial velocity increases, advancing angles increase, while no measurable receding angles are observed.

Carbon fibres in PEG–water solution

Typical high velocity (150 μm s^{-1}) wetting cycles of carbon fibres in PEG–water solution are shown in *Figure 2*. While the general shape of the tensiograms is similar to that shown in *Figure 1*, it is clear that, in this case, each fibre shows a different contact angle. The force at

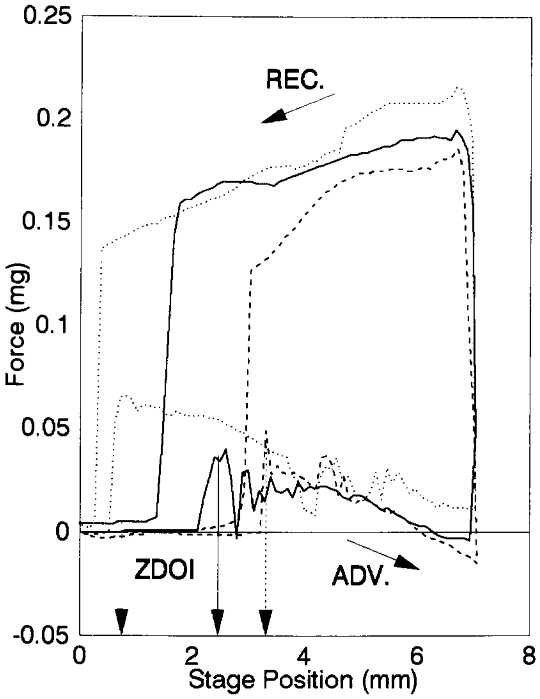

Figure 2 Wetting cycles of untreated IM7 (——), plasma-treated IM7 (·····) and sized IM500 (– – –) fibres in PEG–water solution

ZDOI is highest in the case of the plasma-treated fibre (that is, its contact angle is the lowest), and decreases for the sized and untreated fibres. These results are due to the fact that, unlike the fluorinated fluid, the PEG–water solution has a rather high surface tension and does not completely wet the fibres, even at low stage velocity, as shown in *Table 1*. As in the case of the fluorinated fluid, however, a noticeable effect of the interfacial velocity on contact angles is observed.

DISCUSSION

Before discussing the results in terms of interfacial energetics and hydrodynamic contribution to the fluid–fibre interface, it is important to emphasize that, since the Wilhelmy plate technique measures the force of a solid in relative motion within a liquid, its usefulness extends far beyond the simple contact angle calculation. The shape of the tensiograms shown in *Figures 1* and *2*, where the effect of the viscosity of the fluid on the force at the interface is clearly highlighted, confirm this point. The measurement is fine enough to distinguish between Newtonian and pseudoplastic fluids, as shown in *Figure 3*, where the measured slope of the tensiograms as a function of the stage speed are plotted (slope values are calculated from the mean of advancing and receding tracks[10,12]). No significant differences of the slopes for the different fibres were observed, as expected. As discussed elsewhere[10,12,15], the slopes are proportional to the product of the viscosity and the velocity. In the case of the Newtonian fluorinated fluid, a linear behaviour is observed, while in the case of the non-Newtonian PEG–water solution the dependence of the apparent viscosity on the interfacial velocity is readily observed.

Coming back to contact angles, the results show that, for both liquids used, contact angles are velocity dependent. This means that the forced motion of the fibre in the fluid falls within the Blake–Haines mode[4], where retarding effects induced by the interfacial viscosity make the hydrodynamics contribution important. According to the Blake–Haines theory, the slope is positive for the advancing angles and negative for the receding ones, which are only measurable in a few cases.

Comparing the two different fluids, at the lowest stage speed ($20\,\mu\mathrm{m\,s^{-1}}$), where dynamic effects should be minimized[12], no differences among the contact angles of the different fibres are observed with the fluorinated fluid, reflecting the fact that all fibres are fully wettable by the low surface tension fluid. It is important to note that the surface tension of the fluorinated fluid used is reasonably close to those observed for thermoplastic melts, given their temperature dependence[4]. In the same conditions, when using a higher surface tension fluid (the PEG–water solution) fibre surfaces are not fully wettable and advancing angles are related to the chemical composition of the surface. Accordingly, plasma-treated fibres are the most wettable, the untreated fibres are the least, while sized fibres are intermediate.

Taking into account the velocity effect on contact angles, *Figure 4* shows the difference in the measured contact angles of the different fibres in the PEG–water solution as a function of the stage speed. The resulting difference seems independent of the stage speed, despite the different values of the measured contact angles. Thus, it is possible to argue that there are two different contributions to the experimentally accessible contact angle and thus to the shape of the fluid front advancing on the fibre surface. The first contribution is due to surface chemistry and morphology, and can be observed at low interfacial velocities. The second, due to hydrodynamics effect, is independent of the surface composition and increases with the interfacial velocities. More information in this respect can be obtained assuming the angle obtained at the lowest stage speed is representative

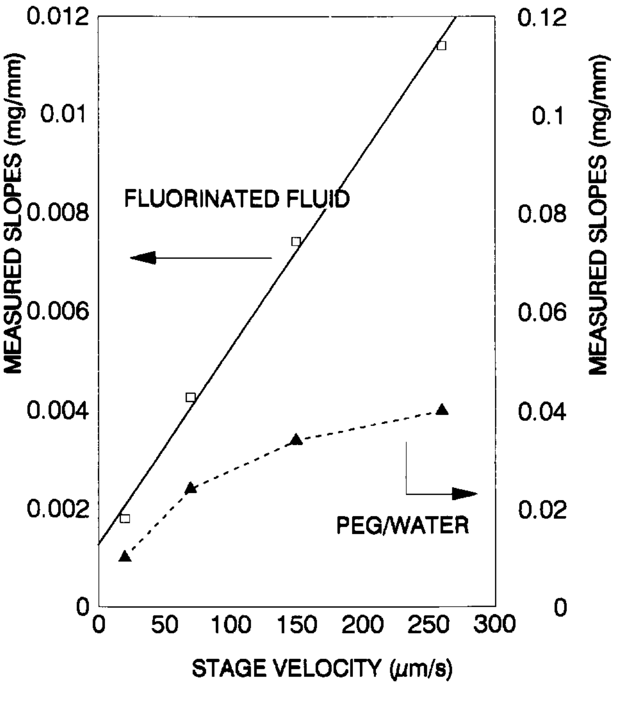

Figure 3 Effect of the stage velocity on the slope of the carbon fibre/fluorinated fluid and carbon fibre/PEG–water solution. Each point is the mean of the slopes of the three different fibres

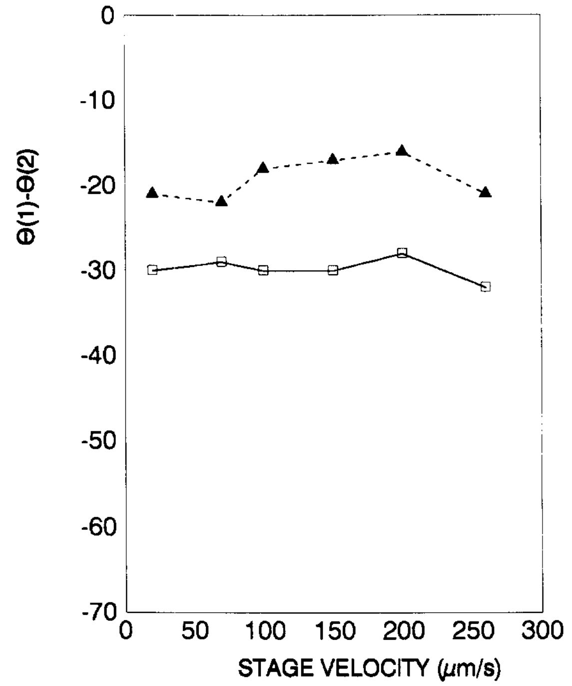

Figure 4 Effect of surface treatment on advancing angles in PEG–water solutions: --▲--, 1 = sized, 2 = untreated; —□—, 1 = treated, 2 = untreated

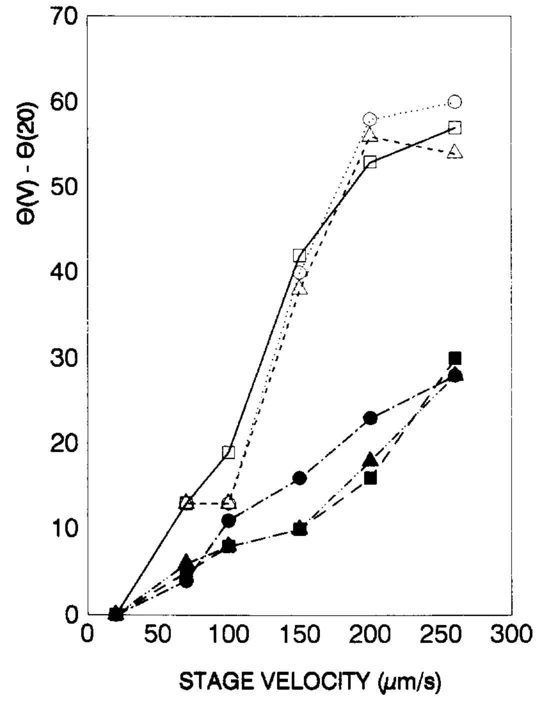

Figure 5 Hydrodynamic effects on advancing angles in PEG–water solution (solid symbols) and fluorinated fluid (open symbols) expressed as the contact angle value at a given velocity ($\Theta(V)$) minus the contact angle at $20\,\mu m\,s^{-1}$ ($\Theta(20)$). □, ■, Untreated; △, ▲, treated; ○, ●, sized

of the surface tension contribution, and subtracting it from those obtained at higher stage speeds. When plotting these values *versus* the stage speed (*Figure 5*), two groups of curves are obtained, showing that the hydrodynamic contribution depends on the fluid viscoelastic characteristics only. In particular, the lower effect observed in the case of PEG–water solution is due to the non-Newtonian nature of the latter, and the decrease of the (apparent) viscosity with velocity.

What information can be obtained from these data on the fibre–fluid interface in composites production? The fluorinated fluid used has a low surface tension which, due to the surface tension–temperature dependence of polymeric melts, falls within the region of molten thermoplastics[4]. Our results show that, in this case, the surface composition does not affect the macroscopic contact angle. The latter is controlled by the Blake–Haines mode of interaction and fibre wettability is basically a kinetic phenomenon.

On the other hand, the PEG–water solution has a higher surface tension, which make it more similar to uncured thermosets[4]. Kinetic effects are still very important (*Table 1*), but this time the nature of the surface affects the macroscopic contact angle. The increase of the relative solid–fluid velocity increases the contact angle but does not change the wettability rating of the different fibres since, as shown in *Figure 5*, the hydrodynamic contribution depends on the fluid viscoelastic characteristics only.

SUMMARY

In summary, Wilhelmy plate experiments are sensitive enough to detect interfacial effects due to the nature of the fluid (viscosity, Newtonian or non-Newtonian behaviour) and the relative solid–liquid velocity, as well as effects related to surface energetics.

Liquids whose room temperature behaviour mimics the properties of polymeric melts, can be used to simulate forces at interfaces during the fibre–melt interaction.

The solid–fluid interaction is greatly affected by the relative velocity. Moreover, a different contribution of the surface composition to the macroscopic contact angle in the case of low surface tension (similar to molten thermoplastics) and high surface tension (similar to uncured thermosets) fluids, is observed.

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