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Mechanical properties of the glass fibre–polyester interphase

Part I *Effects due to silanes*

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Single-fibre pull-out experiments have been carried out with glass fibres with and without silane coupling agents. Debonding was easiest when the fibre had a commercial coating on it which contained a silane and processing aids, and was relatively thick. Solvent extraction of the coating increased the bond strength, and total removal of it increased it still further. The strongest bonds were stronger than the polymer and probably failed by brittle fracture with a work of about 0.25 $\mathrm{kJ\,m^{-2}}$, much less than the estimated work of fracture of the polymer. After debonding, frictional sliding took place, with an interfacial pressure of 17 MPa, and with a coefficient of friction that was influenced by the interface in the same way as was the bond strength, i.e. greatest for the bare fibre, and least for the coated fibre. The silane coupling agent plasticized the polyester, and it seems highly probable that debonding took place in the interphase, when the fibre was coated, so that frictional sliding during post-debond pull-out was between the chemisorbed layer of silane and the polymer. The physisorbed layer of silane probably dissolved in the polymer, because the friction was not affected by solvent extraction.

1. Introduction

Fibre composites perform well only when stress can be transferred efficiently across the interface between fibres and matrix. To effect this the fibres are normally coated, and silanes are commonly used for glass fibres. These were pioneered by Erickson and Plueddemann [1]. Because the silane has a different chemical composition from the glass fibre substrate and the polymer matrix, an identifiable interphase between the fibre and matrix phases is formed. This is chemically bonded to the polymer, in the case of epoxies and polyesters, as a result of being involved in the curing reaction. It is commonly believed also to be bonded to the fibre [1], as shown in Fig. 1. This constitutes the chemisorbed layer. However, there is usually more than a monolayer of silane present, and so a physisorbed layer is also formed, and is also shown in Fig. 1 [2].

An interphase with good mechanical properties is expected to give a composite with good shear and compressive strengths, and the silanes used on glass make the reinforced polymers more durable in the presence of water. However, an interphase which is too strong can cause a composite to be rather brittle [3].

Four techniques are currently used to estimate the strength of the interphase. Early tests were the single-fibre pull-out test [4] and the fibre fragmentation test [5]. More recently the microtension [6] and microcompression tests have been introduced [7]. These tests and the results obtained with them have been critically reviewed [8]. Unfortunately, the results from the various tests do not usually correlate very well.

The pull-out test appears to be the easiest to interpret, although being a very difficult test to carry out. It has the advantage of being able to yield information on the polymer shrinkage pressure and the coefficient of friction of sliding after debonding, as well as giving the debonding force as a function of embedded length.

In earlier work the pressure in the interphase, arising from the cure shrinkage of the matrix resin, was measured by applying an external pressure. This gave somewhat scattered results [9]. It was later shown [10] that the scatter could be much reduced if a curve-fitting technique was used for results obtained using glass fibres with no external pressure applied. This method works with glass fibres because the stresses in the fibres are very high during the pull-out process (up to at least 4 GPa) and because of their relatively low Young's modulus, quite large Poisson's shrinkages (> 1%) occur in them, reducing the interfacial pressure significantly.

In this paper, the curve fitting technique is used to determine shrinkage pressure and friction coefficients during the pull out of single glass fibres, and the effect of various treatments on these interface properties are

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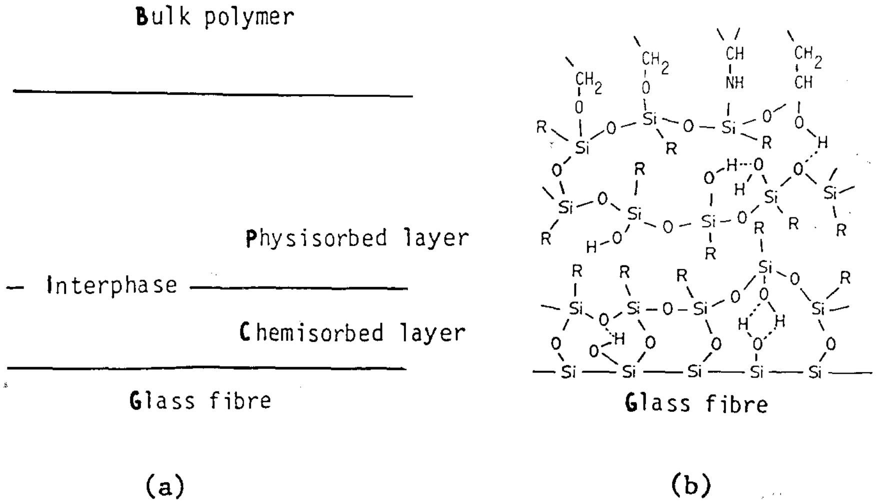

Figure 1 Schematic drawing of silane coating on a glass fibre.

examined. In addition, the debonding force is determined as a function of embedded length, and the work of fracture of the interphase is estimated.

2. Experimental procedure

The interphase properties were measured for fibres and polymers which had been modified in various ways. The fibres were E-glass, and had a polyester-compatible coating applied to them (475-FA-2200). Some of the fibres were used with the coating intact (i.e. as-received), some were used after treatment in various ways, i.e. (1) after extraction with tetrahydrofuran (THF): (2) after pyrolisation of the coating: (3) after pyrolisation and then coating with γ-methacryloxypropyltrimethyl siloxane (MPS); $CH_2C(CH_3)COO(CH_2)_3Si$: and finally (4) after coating with MPS and then extraction with THF.

The THF extraction was carried out by immersion at 20 °C for 1 h followed by drying at 70 °C for 1 h. The pyrolisation was carried out by heating to 400 °C for 10 min. The MPS coating was applied by dipping the fibres in a 0.1% aqueous solution of MPS for 5 s, then drying and curing at 130 °C for 12 h. The MPS-coated fibres were used immediately after curing; the other fibres were stored in a desiccator containing anhydrous silica gel prior to use. Fibre strengths were tested in the usual way by supporting them on a cardboard frame until safely mounted in an Instron machine. Stressing was carried out at a speed of 5 mm min^{-1}.

The polyester resin used was an isophthalic resin cured with 0.5% cobalt naphthenate and 2% methyl ethyl ketone peroxide. It was cured at 20 °C for 6 h followed by 80 °C for 12 h. Resin blocks were tested for Young's modulus, compressive strength and Izod impact strength according to the relevant ASTM procedures (D638, D695 and D256, respectively). The Poisson's ratio was also measured. For this an extensometer was used to determine the tensile strain and a strain gauge to measure the Poisson's contraction.

For some tests the polyester was modified by adding the MPS to it prior to the addition of the cobalt salt and peroxide.

The technique used for the embedment of fibres in the resin was basically the same as described previously [11]. The fibre was held in a slit rubber stopper, Fig. 2a, which had been coated with Dow Corning DC20 silicone release agent, and baked on at 80 °C for 6 h, prior to use. The stopper rested on a support while the fibre was held straight with a magnetic paper clamp which could be adjusted by sliding it on a vertical steel plate. The polyester resin was spread on the stopper using an eye dropper and the polyester was cured before the upper section of the fibre was cut off. The embedded length of the fibre was measured using a microscope, and then the assembly was embedded in more of the same polyester, Fig. 2b. The glass tube used from the block was removed when the resin was cured. The resin block produced was cylindrical, 22 mm diameter and 10 mm long. The fibre diameter was 22 μm. Specimens with no observable meniscus were used for pull-out tests.

For pull-out, the polyester was mounted in an Instron machine, and the fibre was attached to a 2 mm diameter copper wire connected to a 500 g load cell. The fibre was pulled out at a speed of 5 mm min^{-1}. The apparatus used is shown schematically in Fig. 3. Cyanoacrylate glue was used to bond the fibre to the wire, and care was taken to ensure that the wire was

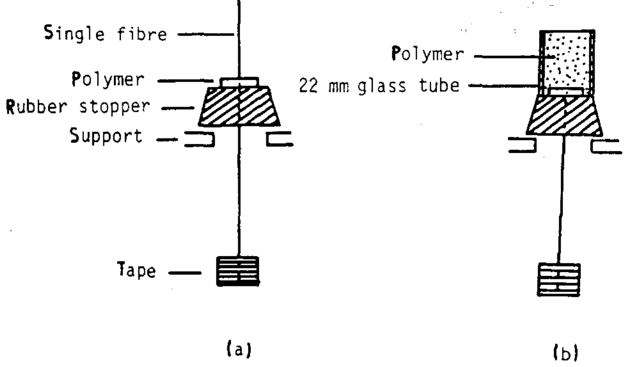

Figure 2 Method of embedment of a single fibre.

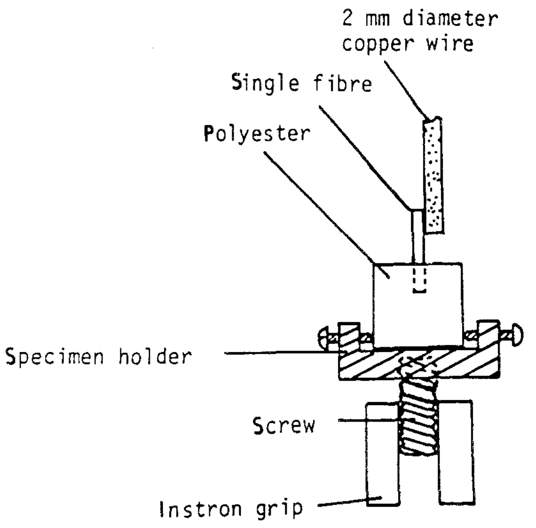

Figure 3 Apparatus used for the pull-out test.

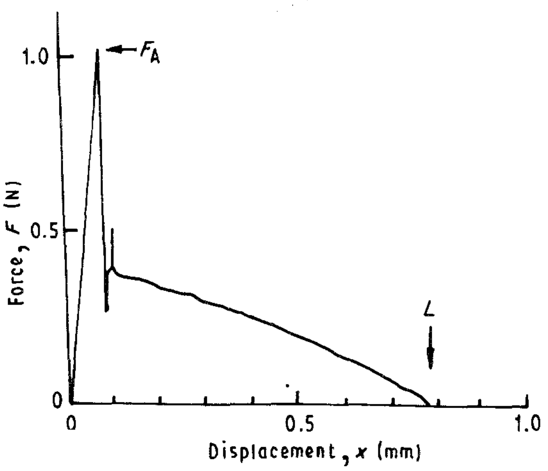

Figure 4 Typical pull-out curve. Fibre debonds when force = F_A.

within 1 mm of the polymer surface, and that the glued region extended to the lower end of the wire, so that the free length of fibre (i.e. the length embedded neither in polymer nor cyanoacrylate) was no greater than 1 mm.

3. Results

The properties of the resins are given in Table I. Fibre strengths were affected by the pyrolysis. The intact and THF-extracted fibres had strengths of 3.4 ± 0.4 GPa. The other fibres had strengths of 3.0 ± 0.3 GPa.

Fig. 4 shows a typical pull-out curve obtained with a short free length of fibre. It has two regions, (1) initial fibre stressing leading to interfacial failure, and (2) post-debonding friction. In the initial region the slope of the force–distance plot was governed mainly by the stretching of the free length of the fibre. Debonding occurred when the force, F, reached a critical value, F_A.

After debonding, the force decreased suddenly, and re-established itself as frictional sliding occurred. With relatively low Young's modulus fibres, such as glass, the frictional part of the plot was often curved. This arises because the frictional shear stress, τ_f, is given by

$$\tau_f = \mu P_f \qquad (1)$$

where μ is the coefficient of friction, and P_f is the pressure across the interface and increases as the fibre is pulled out. This pressure increases because the fibre stress induces a Poisson's shrinkage in the fibre, tending to pull the fibre surface away from the polymer. At the instant the fibre emerges from the polymer, the fibre stress and hence Poisson's shrinkage is zero, and the pressure, P_0, is that which arises solely from the

TABLE I Mechanical properties of polymers

MPS in polymer (%)	Young's modulus (GPa)	Compression strength (MPa)	Poisson's ratio	Work of fracture (kJ m^{-2})
0	2.9 ± 0.3	92 ± 5	0.34	2.4 ± 0.4
30	2.5 ± 0.4	80 ± 5	0.34	2.7 ± 0.5
60	2.0 ± 0.4	75 ± 6	0.34	3.0 ± 0.4

TABLE II Interface/interphase properties

Fibre coating	MPS in polymer (%)	μ^a	$P_0{}^a$ (MPa)	$\tau_{ed}{}^b$ (MPa)	τ_{fd} (MPa)	G_i (kJ m^{-2})	L_{max} (mm)
Intact	0	0.6	17	42	19	0.12	1.5
THF[c]	0	0.6	17	58	18	0.24	1.0
Pyrolysed	0	0.7	17	61	18	0.26	0.7
MPS	0	0.6	17	50	13.5	0.18	1.2
MPS-THF[c]	0	0.6	17	55	21	0.21	1.0
MPS-THF[c]	30	0.5	14	52	31	0.22	1.0
MPS-THF[c]	60	0.4	10	53	29	0.25	1.0

[a] Coefficient of variation is about 6%.
[b] Coefficient of variation is about 7%.
[c] Extracted with THF.

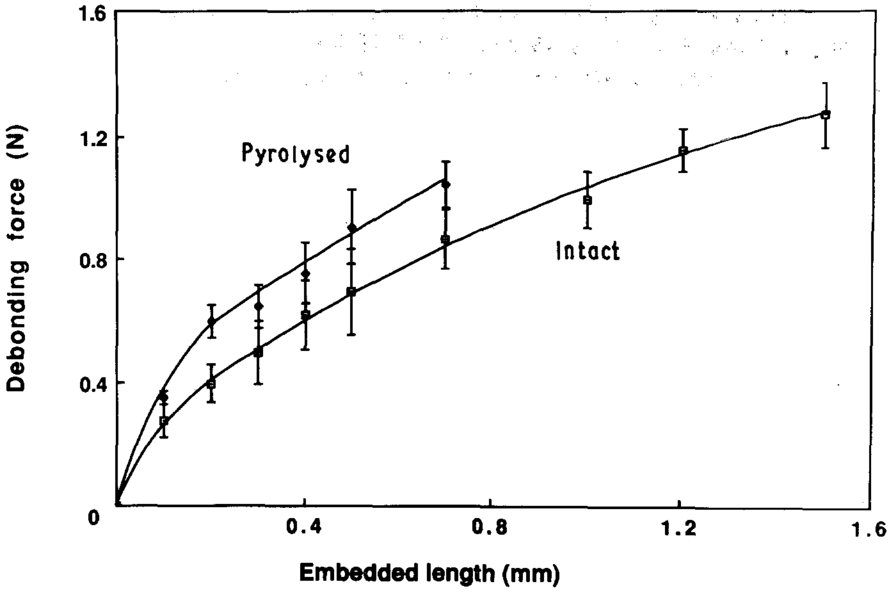

Figure 5 Debonding force versus embedded length for fibres with coating intact and with coating pyrolysed.

cure shrinkage of the polymer. P_0 can be estimated by curve-fitting the post-debonding part of the pull-out plot [12].

Table II gives results obtained by such curve fitting for μ and P_0 for fibres with different surface conditions for neat polyester, and polyester containing different amounts of MPS.

The debonding force was not a linear function of embedded length. Instead, in all cases, it had to be curve-fitted, to allow for friction occurring during the debonding process, as described by Piggott [13]. The curve fit produces values for the maximum elastic interfacial shear stress needed to cause debonding in the absence of friction, τ_{ed}, together with the frictional shear stress during debonding, τ_{fd}.

Fig. 5 shows two typical curve fits. Each point plotted is the result of five replicate tests, and the error bar represents ± 1 standard deviation. It will be noted that the debonding forces vary by more than ± 5%. Values of τ_{ed} and τ_{fd} obtained from these curves are given in Table II, along with the maximum length that could be pulled out L_{max}.

4. Discussion

The estimated pressures governing friction after debonding, (P_0), were not affected by the surface treatment: the pressures in each case came to 17 MPa (Table II). This suggests that the pressure estimation using this technique can be reproducible, because it is unlikely that the fibre surface treatment has more than a very local effect on the polymer and hence on the pressure. (Because the diameter of the polymer bar was 1000 times that of the fibre, even a thick layer of surface coating could not be expected to have much influence.) The presence of large quantities of MPS in the polymer, however, decreased the pressure quite significantly. It also seems to have plasticized the resin, reducing the Young's modulus and compressive strength, and increasing the Izod fracture energy (Table I). There was an approximately linear relation between P_0 and the amount of MPS used. This was also true of theYoung's modulus of the resin. Thus P_0 and E_m are also roughly linearly related, see Fig. 6. If the shrinkage pressure came about largely as a result of the thermal mismatch between the polymers and fibres during cooling from the curing temperature, P_0 should be proportional to E_m. However, the line in Fig. 6 does not go through the origin, but instead intersects the E_m axis at about 0.7 GPa. Thus it is possible that chemical shrinkage during cure is a significant component of the total shrinkage [10] and is less for the MPS than for the polyester.

The coefficient of friction was influenced to a small extent by surface treatment and by the nature of the polymer. The pyrolysed fibres gave marginally higher friction values than the coated fibres, and appeared quite clean after extraction, suggesting that $\mu = 0.7$ is characteristic of the glass–polyester interface. In the

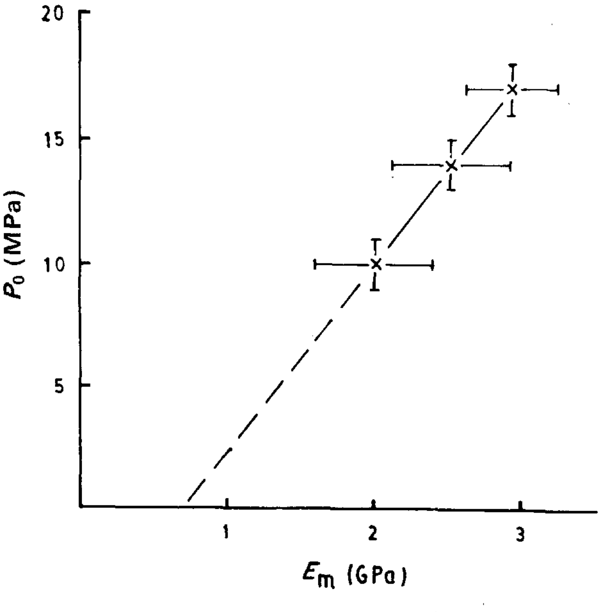

Figure 6 Shrinkage pressure versus Young's modulus for polyesters containing 0%, 30%, and 60% MPS.

case of the coated fibres, THF extraction made no difference, and MPS gave the same results as the commercial coating. If a physisorbed layer (see Fig. 1) exists after the fibre has been embedded, we could well expect failure and sliding to take place in this layer. Thus $\mu = 0.6$ should be characteristic of fibre still having some coating on it, sliding in a polymer.

Presumably the physisorbed layer dissolves in the polymer forming an interphasial region with different properties from the polymer matrix, as suggested by Graf *et al.* [2], because the coefficient of friction for the intact and THF extracted layers are indistinguishable both for the commercial coating and the MPS coating. When the polymer is softened by adding MPS to it in large quantities, the friction coefficient appears to decrease, possibly because the ploughing force [14] is likely to be less in this case.

τ_{fd} was always greater than μP_0, although theoretically it should have been equal to it [13]. This difference is particularly large in the case of the fibre pulled out from the polymer containing 60% MPS. A possible explanation is that the friction coefficient is much larger when sliding is fast, as it must be during the debonding process, which only takes milliseconds [15] as compared with 10 s or more for the post-debonding pull-out.

The maximum elastic shear stress at the instant of debonding, τ_{ed}, was estimated by curve fitting. The uncertainty in this estimate is governed largely by the standard deviation of the result at the lowest embedded length (0.1 mm) and is thus quite high, Fig. 5. Although some results at 0.1 mm appeared to be more variable than others, it was considered that overall the results were probably accurate to about ± 7%. Thus, we can see some significant differences in τ_{ed}, according to fibre surface treatment, see Table II.

THF extraction of the commercial silane coating significantly increases the apparent bond strength. So also does its more or less complete removal by pyrolysis. Putting an MPS coating on the pyrolysed fibre reduces the bond strength to a value slightly higher than the commercially coated fibre. This difference between the MPS-coated and commercially coated fibres, though barely significant, does suggest that there is a danger that the processing aids in commercial coatings reduce the interfacial shear strength. THF extraction of the MPS coating restores the interface strength to a value which is virtually indistinguishable from that of the THF-extracted commercial coating (55 MPa compared to 58 MPa, Table II). The THF is likely to remove almost all of the processing aids and the physisorbed silane; thus the commercial silane and the MPS, when chemisorbed, have almost identical effects on bond strength.

The strongest interface or interphase is not expected to fail at a shear stress greater than the shear strength of the adjacent polymer, because if the interphase is stronger than the polymer, the polymer adjacent to the interphase should be able to fail. However, this is not always the case, and one possible explanation is that the interface behaves like a Griffith crack. In this case there is an equivalent work of fracture, G_i, where [13]

$$G_i = [r(1 + \nu_m)\ln(R/r)/E_m]\,\tau_{ed}^2 \quad (2)$$

where $2r$ is the fibre diameter (22 μm) and $2R$ that of the polymer cylinder (22 mm). G_i values estimated using Equation 2 are given in Table II. It will be observed that these values are much smaller than the Izod values for the polymer, Table I, and that the interphase appears to be rather brittle, if indeed this explanation of the results is valid. (Note: fracture toughness testing of these polymers supports the high works of fracture obtained in Table I. Valid K_{Ic} values could not be obtained in notched three-point bending due to the high toughness of the polymer.)

Table I gives the compression strength of the polymer. The shear strength, τ_{mu}, is approximately equal to $3^{-1/2}$ of this, i.e. 53 MPa for the polymer without MPS dissolved or suspended in it. Thus in at least two cases (the pyrolysed fibre and the fibre in the 60% MPS polymer), τ_{ed} significantly exceeds τ_{mu}, and we conclude that the interphase is strong but brittle. The commercially coated fibre, on the other hand, has an interphase which is significantly weaker than the polymer.

5. Conclusions

The interface pressure between glass fibres and an 80 °C cured polyester was about 17 MPa, and was not affected by the fibre surface condition. When the polymer contained large amounts of a silane coupling agent (MPS) it was plasticized and the pressure was reduced.

The interface with the bare fibre gave the highest coefficient of friction, and it seems highly probable that the lower friction resulting from the use of silane coupling agents was due to the presence of a chemisorbed layer on the fibre, which remained bonded and constituted the sliding surface. The lowest friction was when it was sliding against what had presumably been the physisorbed layer of coupling agent.

The debonding of the fibre from the polymer was easiest when the fibre was coated with a reasonably thick layer of a silane coupling agent. Partial removal of this, using a solvent, increased the work of debonding, and virtual total removal by pyrolysis increased it still further. The interphase was sometimes stronger than the polymer. In this case it probably failed by brittle fracture, involving an interphase work of fracture of about 0.25 kJ m^{-2}.

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