The interfacial properties of fibrous composites

Part III   Effect of the thickness of the silane coupling agent

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The dependence of the magnitude of the interfacial parameters for a glass-fibre-reinforced polypropylene on the thickness of the applied silane layer on the glass-fibre surface was investigated. The interfacial parameters studied included the interfacial-shear strength, the interfacial coefficient of friction, the interfacial-frictional stress and the shrinkage pressure. These parameters were evaluated from pull-out data using a recent model. The results indicate that the maximum interfacial-shear strength is obtained at a critical thickness of the silane layer on the treated fibre. Both the interfacial-frictional stress and the interfacial coefficient of friction decreased with increased thickness of the silane coat.

1. Introduction

It is known that good fibre–matrix adhesion is necessary to obtain high strengths in composites. For this reason, silane coupling agents are commonly utilized to improve and promote adhesion between the reinforcing fibres and the polymer matrix in composites. Silane treatment of the reinforcing fibres offers a further advantage in that it allows retention of fibre–matrix adhesion (and hence the mechanical properties of the composite) in the event of any ingress of water to the fibre–matrix interface. Fibre-surface treatment is especially important where the natural adhesion between fibre and matrix is poor, as is the case in glass-fibre-reinforced polypropylene. Although the importance of fibre-surface treatment is known, there is no understanding of the effect of the thickness of the coupling agent on both the interfacial and mechanical properties of the composite. Therefore, this is the focus of the present work. This is the third in a series of papers on the interfacial properties of fibrous composites.

The mechanical properties of a composite can be considered [1] in terms of its interfacial parameters. Interfacial parameters such as the interfacial-shear strength, τ_i, the interfacial-frictional stress, τ_f, the interfacial coefficient of friction, μ, and the shrinkage stress of the matrix on the fibre, P_0, are important as they effect [1] the strength and toughness of the composite. The tensile strength of a composite increases with τ_i. However, the toughness of a composite increases with μ and P_0.

The interfacial parameters τ_i, τ_f, μ and P_0 can be determined using the method outlined previously in [2, 3]. The value of μ can also be determined separately from sliding-friction experiments using similar fibre and matrix materials.

2. Experimental procedure

The silane coupling agent (Dow Corning Z-6032) used contains a vinylbenzyl and amine organic and a tri-methoxysilyl inorganic group. The polypropylene (PP) used was a homopolymer from Shell Chemicals (KM6100). Tapered fibres, as well as constant-diameter glass fibres, were prepared from E-glass rods in the laboratory. The average fibre diameter was 200 μm.

Silane-treatment solutions with 1, 5, 20 and 30 wt % silane were prepared. Silane treatment of the fibres were carried out by dipping the fibres into the silane solutions for 10 s. It has been established [4] that the thickness of the silane coat on the treated fibre is dependent on the concentration of the silane solution and not on the dipping time of the fibre in the treatment solution. The thickness of the silane layer in the pull-out specimens was determined by examining the polished cross-section of the treated fibre by scanning electron microscopy (SEM). The surfaces of some treated fibres were also examined by SEM. It can be seen from Fig. 1 that, within the range tested, the thickness of the silane coat on the fibre was proportional to the concentration of the treatment solution.

The pull-out specimens were compression moulded at 250 °C for 8 min and then quenched in water. Specimens with different embedded-fibre lengths were prepared. The pull-out tests were conducted on an Instron testing machine at a crosshead speed of 5 mm min^{-1}. After the tests, the extracted fibres were coated with gold–palladium for examination by SEM. The matrix blocks from the tests were sectioned to expose the "holes" created from fibre pull-out. The surfaces of these holes in the matrices were also prepared for examination by SEM. The tensile modulus, E_m and compressive moduli, E_{mc} of the polypropylene

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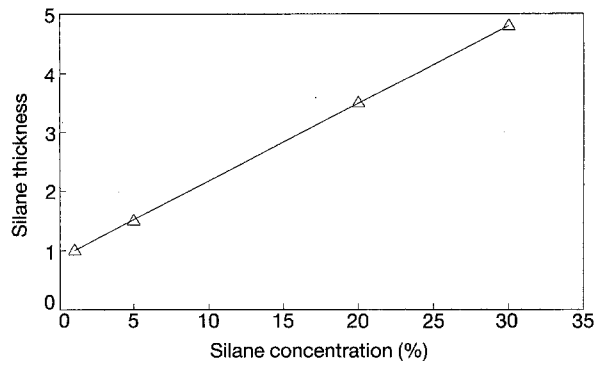*Author to whom correspondence should be addressed.

Figure 1 A plot of thickness (μm) of the silane coat on the treated fibre against the concentration of the silane-treatment solution.

are [3] 1.40 and 0.86 GPa respectively. The experimental details are outlined elsewhere [5].

3. Results and discussion
3.1. Character of the silane coat and failure surfaces
Under SEM, the surfaces of the above treated fibres appeared to be plain, smooth, uniform and featureless with virtually no silane agglomerates. This is in contrast with a previous study [5] where numerous silane agglomerates of varying sizes existed on the surface of the silane coat. This observed difference is probably not important since the silane agglomerates do not promote transcrystalline growth on the treated fibre surface [5], and this difference is therefore unlikely to affect the fibre–matrix adhesion at the interface.

The typical appearance of the surface of the extracted fibres is shown in Fig. 2. Apart from occasional random clusters of matrix, the surface of the 1%-silane-concentration treated fibre appeared to be uniform and smooth (see Fig. 2a). In contrast, the treated-fibre failure surface of the 20%-silane-concentration specimen was rough and undulating (see Fig. 2b). It was observed that the roughness of the failure surfaces increased with the silane concentration.

Micrographs of the treated 20% silane extracted fibre surface at higher magnifications are shown in Fig. 2c and d. There was no apparent or distinct boundary between the silane and polypropylene layer on the fibre surface. This observation suggests that the lumps of material on the fibre surface are probably made up of a thick base layer of silane coated with a mixture of silane and polypropylene. This deduction appears to be substantiated by the existence of an inverse-V-shaped fold in the silane layer at the centre of the micrograph in Fig. 2d. It is apparent that this artefact is surrounded by regions covered with a layer of polypropylene with occasional larger particles. This outer layer of a silane–polypropylene mix and polypropylene, as well as the larger particles of polypropylene, was subjected to deformation during pull-out. The larger polypropylene particles are probably formed at locations where the interfacial crack propagates into the polypropylene matrix.

A typical appearance of the matrix hole is shown in the lower portion of the micrographs in Fig. 3. The
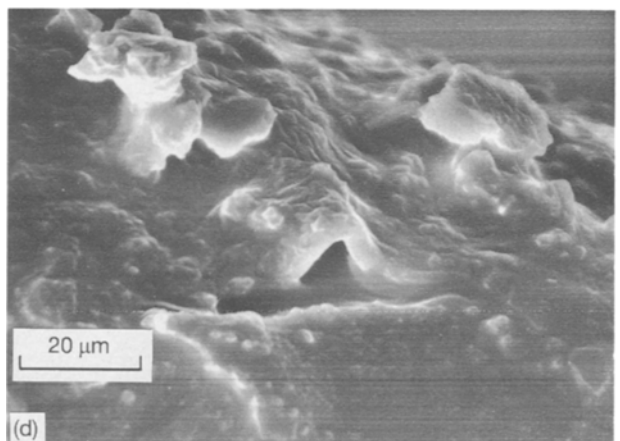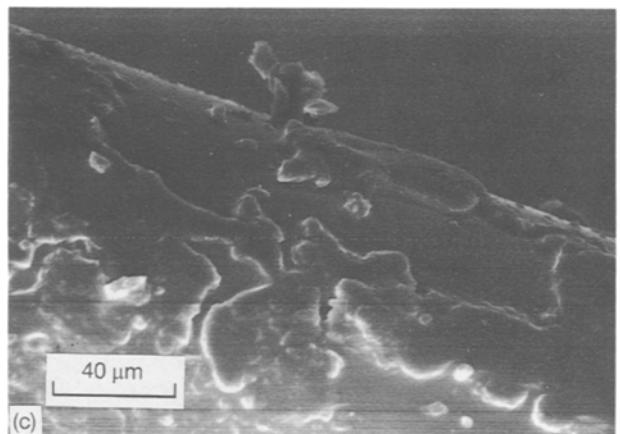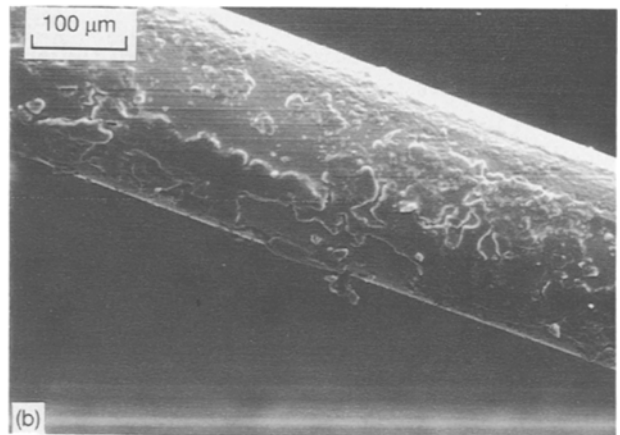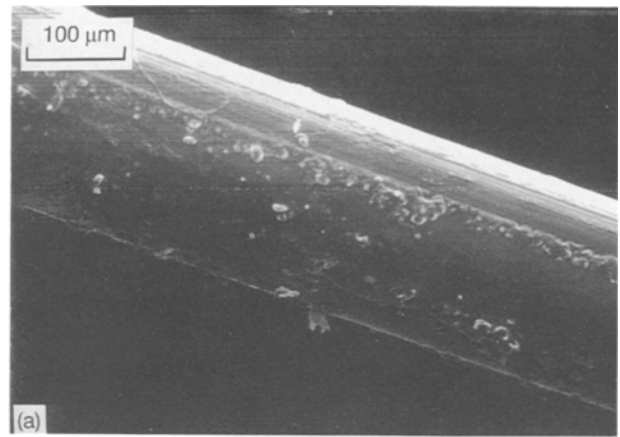

Figure 2 Typical appearance of the extracted fibre surface: (a) 1% silane, (b) 20% silane, (c) 20% silane, and (d) 20% silane.
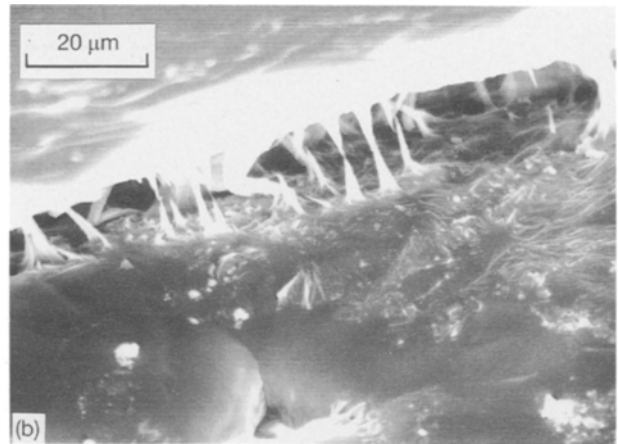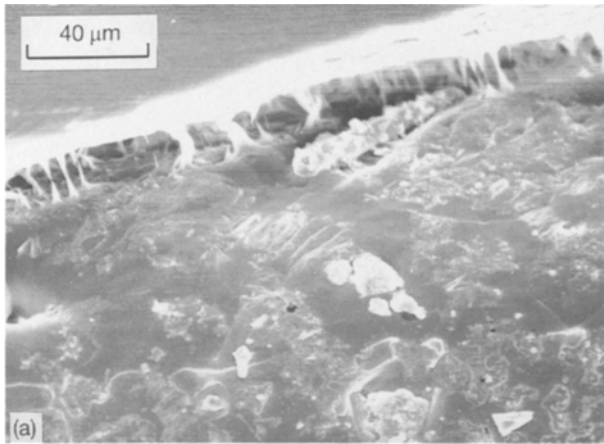
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Figure 3 Typical appearances of the matrix hole in a treated 20% silane specimen.

plain top section in the micrographs corresponds to the bulk matrix which is separated from the matrix hole by the intense white boundary. The matrix failure surface was featureless apart for some debris and white regions representing local regions which had been deformed. There was no significant difference in the appearance of the matrix holes in all the specimens.

Some polymer fibrils exist at the edges of the matrix hole (see Fig. 3b). These fibrils probably developed due to deformation of the polymer at the edge of the matrix hole during microtoming. Tearing the polypropylene matrix at the fibre–matrix interface during pull-out can similarly form fibrils on the extracted fibre surface (see the top centre of Fig. 2c). A few large fibrils were indeed observed by SEM on the extracted fibre surfaces. These fibrils were not abundant; this is probably due to the fact that most smaller fibrils would be torn from the surfaces and left as debris during fibre pull-out.

3.2. Interfacial parameters

A plot of debonding force F_d against fibre embedded length, L, for the 1% silane specimens is shown in Fig. 4. The experimental data, the linear regression line utilized to determine I_0 (the intercept of the regression line on the x axis), and the theoretical plot which best fits the data are shown in Fig. 4. The curves of best fit for the results from the 5%, 20% and 30%
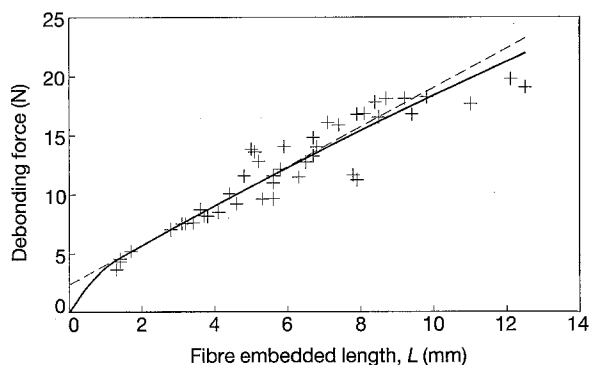

Figure 4 A plot of the debonding force against the embedded length for the 1% silane specimen: (+) pull-out data, (– – –) linear regression line, and (——) debonding theory.
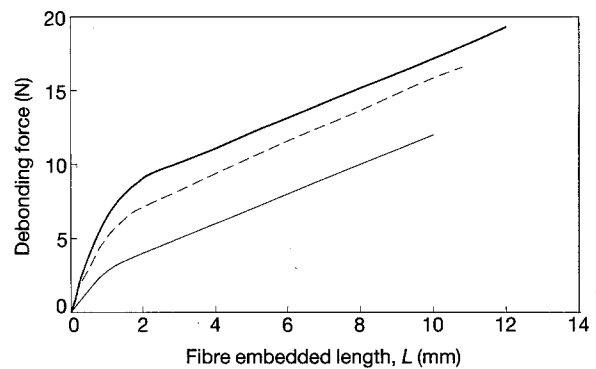

Figure 5 A plot of debonding force against embedded length for: (– – –) the 5%, (——) the 20% and (——) the 30% silane specimen.

silane specimens are as shown in Fig. 5. A summary of the calculated interfacial parameters is given in Table I. The interfacial coefficient of friction, μ, was calculated using pull-out data from the tapered fibre specimens. Plots of the variation of the interfacial parameters with the concentration of the silane solution are given in Figs 6 and 7.

It is interesting to note that although their L_c-values differ, the curves for 5%, 20% and 30% silane at $L > L_c$ appear to be parallel (see Fig. 5). The values of τ_f for these specimens are similar (see Table I). It has

TABLE I A summary of the interfacial parameters calculated for the specimens

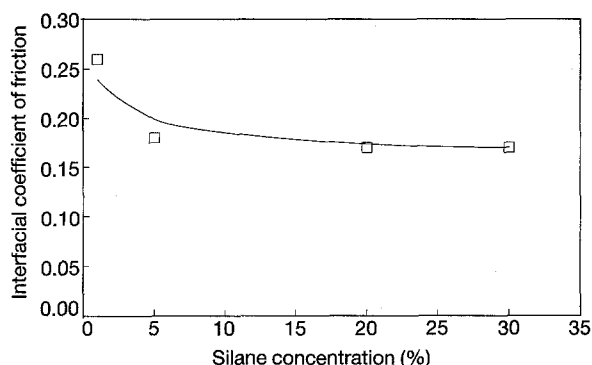| Number	Sample			
	A	B	C	D
Number of pull-out data	45	51	45	17
Silane concentration (%)	1	5	20	30
Thickness of silane coat on fibre (μm)	1.0	1.5	3.5	4.8
L_c (mm)	1.25	1.75	1.9	1.1
Interfacial-shear strength, τ_i (MPa)	7.5	10.0	13.0	4.2
Shrinkage pressure of fibre, P_0 (MPa)	11.2	11.2	11.2	11.2
Interfacial coefficient of friction, μ	0.26	0.18	0.17	0.17
Interfacial frictional stress, τ_f (MPa)	2.9	2.0	1.9	1.9

Figure 6 Variation of the interfacial coefficient of friction with the silane concentration.
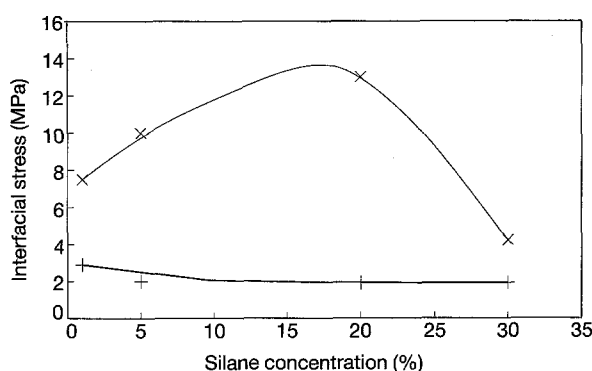

Figure 7 Plots of ($\times$) τ_i and ($+$) τ_f against the concentration of the silane-treatment solution.

been established [3] that the interfacial-frictional-shear stress, τ_f, during fibre pull-out is proportional to the gradient of the plot of F_d against L in the region $L > L_c$. Hence, the above observation suggests that the sliding characteristics of the treated fibre on the matrix during the pull-out process in the 5%, 20% and 30% silane specimens were similar.

In contrast, the gradient for $L > L_c$ in the 1% silane specimen was greater (cf. Figs 4 and 5) than that for the 5%, 20% and 30% silane specimens. Hence, as expected, the calculated value of τ_f was larger (see Table I) for the 1% silane specimen. This suggests that the sliding characteristics of the 1% silane treated fibre on the matrix is different from that in the other specimens. This difference can probably be attributed to the differences in the thicknesses of the silane coatings. In the 1% silane specimen, where the silane coat is thin, the few random lumps of matrix on the treated fibre surface contribute to increased friction and roughening during the pull-out process. On the other hand, in situations where the silane coat is thick (as in the 5%, 20% and 30% silane specimens), the thicker silane coat acts as a cushion for the matrix lumps on the fibre thereby reducing the frictional stresses during the pull-out process. This is despite the fact that the amount of matrix lumps on the fibre increased with silane concentration. Therefore, the thickness of the silane coat has a significant effect on τ_f.

It can be seen from the plot of the interfacial coefficient of friction against silane concentration that

this "cushioning effect" becomes significant in specimens treated with silane solutions with greater than 5% silane concentration. This corresponds to a silane coat greater than 1.5 μm (see Fig. 1). A decrease of 35% was obtained in the magnitude of the interfacial coefficient of friction, μ, with increasing thickness of the silane coat (see Fig. 6). This indicates that the work expended during pull-out, and hence the toughness of the composite, would decrease with increasing thickness of the silane coat.

The variation of the interfacial shear strength, τ_i, with the concentration of the silane solution is shown in Fig. 7. The magnitude of τ_i increases to a maximum and then decreases with further increases in the thickness of the silane coat. Such a trend is similar to that obtained for the dependence of the actual strength of an adhesive joint on the thickness of the adhesive. It can be seen from Fig. 7 that the maximum interfacial-shear strength is attained at a silane concentration of 18% (or at a silane thickness of about 3.2 μm, from Fig. 1). However, such use of the appropriate silane thickness to obtain the optimum yield strength would also lead to a decrease in the toughness of the composite.

4. Conclusion

It was found that the amount of matrix lumps on the failure surfaces of the extracted fibre increased with the concentration of the silane-treatment solution. The silane and polypropylene appear to mix well since no distinct boundary was observed between these phases. The thickness of the silane coat affected the sliding characteristics of the extracted fibre on the matrix during the pull-out process. This led to a decrease in the interfacial coefficient of friction, μ, and would result in a composite of lower toughness. An optimum silane thickness exists whereby τ_i, and therefore the composite strength, is a maximum. However, optimization of a glass–polypropylene composite to obtain high strength through proper control of the thickness of silane coat invariably leads to a reduction in toughness.

References
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