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The Interfacial Bond Strength in Glass Fibre-Polyester Resin Composite Systems Part 2. The Effect of Surface Treatment

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The Interfacial Bond Strength in Glass Fibre-Polyester Resin Composite Systems

Part 2. The Effect of Surface Treatment

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The effect of surface treatments on the bond strength in glass fibre-polyester resin composites has been investigated using single fibre interfacial shear strength specimens and the short beam shear test for interlaminar shear strength.

A range of bond strengths was obtained by using, either alone or in combination, the various components of the size formulation which is normally applied to the fibres, so that the interaction between the glass surface and the polyester ranged from Van de Waal forces through hydrogen bonding to covalent bonding, the bond strength increasing in that order.

The relative contribution to bond strength of mechanical bonding due to thermomechanical mismatch between the two components and of chemical bonding or physical interaction between the three phases, glass-surface treatment-resin, has been evaluated and found to be one third and two thirds respectively.

1. INTRODUCTION

Experimental and theoretical studies over the past decade have shown that the bond between the reinforcing fibre and the matrix has a significant effect on the mechanical performance of a composite material. For this reason the ability to control the interfacial bond strength is of major importance if the interface is to play its dual role of stress transmission between the two phases (which requires a strong bond) and of increasing the fracture toughness of the composite by deflecting crack growth and delocalizing stress at the crack tip (in which case a weaker bond is required).

The interfacial bond strength in glass reinforced polyester resin systems depends to a major extent upon the fibre surface treatment. The size applied to the fibre contains a coupling agent which promotes adhesion between the glass surface and the resin; a lubricant to reduce friction and abrasion during processing and a film forming polymer to promote adhesion between the filaments. The widely accepted guiding principle to the development of coupling agents is the Chemical Bonding Theory which implies that the coupling agent acts as a link between the resin and the glass, by the formation of covalent chemical bonds, to give molecular continuity across the interface. The stability of these covalent bonds helps to maintain the fibre resin adhesion under adverse environmental conditions. The linking is accomplished by using as the coupling agent a bifunctional molecule which is structurally tailored to give co-reactivity with both the glass and the resin. The common coupling agent for glass polyester systems is silane.¹⁻⁸ When the coupling agent is chemically bonded to the glass surface, the type of interactions are understandably complex with water bonded to silanol through hydrogen bonding, and silanol to silanol either through chemical condensation to form a siloxane (Si—O—Si) molecular bridge⁹ or through hydrogen bonding to give a three-dimensional molecular network.

The organofunctional silanes employed as coupling agents for thermosetting resins are highly specific indicating reaction between their functionalities with the appropriate functionalities in the resin precursor (i.e. the unsaturated polyester resin). Although sophisticated studies of the interactions of the fibre surface and selected treating compounds and resins is required to promote the chemical bonding theory from the present incomplete picture to its full status, there is no doubt about the improvement in the resistance to bond strength degradation by ageing or moisture¹⁰ which is obtained by means of a suitable coupling agent and which also leads to a lesser dependence on cure schedule for optimum strength.¹¹

Physical adhesion at the interface depends upon the ability of the two surfaces to come into close contact with each other when the molecular interaction then provides a substantial bond. The forces operative are highly localized (inversely proportional to the sixth power of distance) intermolecular dispersion forces.¹²

In order for the fibre and resin to come into close contact it is apparent that the resin must cover up every hill and valley of the microscopically rough fibre surface and displace all the air and that no weak boundary layer is formed. These conditions are satisfied if good wetting of the fibre by the resin is obtained and the finish applied to the fibre surface has to act as a wetting promoter. However, the effectiveness of the finish on the glass in improving bond strength and properties cannot be attributed to this factor alone.

The mechanical bonding at the interface is a result of friction between the

resin and the reinforcing fibres. Load transfer by means of friction requires a normal compressive stress at the interface and, for a composite stressed in tension parallel to the fibres, such stress can arise as a result of the different values of Poisson's ratio of the two components. A significant contribution to such a radial compressive stress comes from the shrinkage of the resin during the curing process and from the thermal contraction of the composite (since most polyester resin systems are hot-cured).

In this investigation the contribution to the overall bond strength of the various components of the size applied to the fibres has been evaluated and the relative importance of physical bonding, chemical bonding and mechanical bonding has been determined.

2. EXPERIMENTAL

2.1 Polyester resins

Two unsaturated polyester resins were used in the investigation; (a) Filabond 8000, a hot curing medium reactivity resin, crosslinked by styrene and supplied by Synthetic Resins Limited. (b) Crystic 195, a cold cure resin using methyl methacrylate as the coreactive solvent and supplied by Scott Bader Company Limited. With both resin systems an MEK peroxide catalyst and a cobalt naphthenate accelerator was used.

2.2 Glass fibres

The E-glass fibres used were supplied by Pilkington Research and Development Laboratories in the form of rovings with a nominal filament diameter of 30 μ m. Water spray had been applied to the fibres to protect them but otherwise they were regarded as untreated.

The chemical surface treatments applied to the fibres consisted of one or more of the following compounds;

1) γ -methacryloxypropyltrimethoxy silane, Union Carbide silane A174 (reactive towards both the glass and the polyester resin).

2) Phenyltrimethoxy silane, Union Carbide silane A153 (reactive toward the glass surface only).

3) Tetradecyl pyridinium bromide, Morpan TPB (a boundary lubricant).

4) Polyvinyl acetate, National 47–080 (a film forming polymer used to promote adhesion between filaments).

5) Silicone resin, Dow Corning Releasil 2540/2541 (unreactive towards both glass and resin).

The solutions used for surface treatment consisted of one or a combination of a number of these compounds in a dilute aqueous mixture applied in the following manner.

The glass rovings were heat cleaned in a furnace at 773°K for 2 hours to remove dust, grease and other low molecular weight organic substance but not chemi-sorbed water molecules. A solution of the "complete size" was then prepared. Deionized water was added to a 250 ml beaker and the pH adjusted to 3.5-4.0 by the addition of acetic acid with stirring. 0.3% Silane A174 was then added and the stirring maintained for half an hour. This was followed by the addition of 0.1% of Morpan TPB and 5% of polyvinyl acetate. The stirring was continued and the pH was maintained with in the same range by the addition of more acetic acid.

Fibre surface treatments			
Designation	Treatment		
A	Water only		
В	0.3% Silane A174 in water, pH adjusted to 3.5-4.0 with acetic acid		
С	0.3 % Silane A153 in water, pH 3.5-4.0		
D	0.3% Morpan TPB in water		
E	0.3 % Silane A174 and 0.1 % Morpan TPB in water, pH 3.5-4.0		
F	0.3% Silane A174. 0.1% Morpan TPB and 5% polyvinyl acetate		
G	silicone resin 2540/2541		
11	(applied as a non aqueous solution in a solvent) $5^{9/2}$ relaxing the solution		
н	5% polyvinyl acetale		

TABLE I

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A small bundle of fibres, containing some fifty filaments, was placed inside a thin glass tube. The solution for surface treatment was then allowed to drain through this tube while at the same time the fibre bundle was pulled slowly up and down to effect wetting; this was continued for 5 minutes. The fibre bundle was then allowed to dry at 286°K for up to 50 hours. This treatment is designated as treatment F. Other treatments and the corresponding designation are given in Table I.

2.3 Specimen preparation and testing

The interfacial bond strengths were measured using single filaments embedded in a block of resin tested in compression to give shear failure at the fibre-resin interface, and also by short beam shear tests on specimens containing 0.45 V_f of fibres.

These specimen configurations have been shown to be the most viable for the measurement of interfacial bond strength.¹³ The specimen geometries and methods of testing and monitoring interfacial failure have been described fully elsewhere.¹³

3. RESULTS

3.1 Interfacial bond strength measurements using rectangular specimens

Crystic 195 cold curing resin was used initially to avoid the complications which result from hot curing. The results are summarized in Table II which shows the apparent interfacial bond strength (i.e. the bond strength without taking stress concentration into consideration). The results of tests on selected treatments using a hot curing resin, Filabond 8000, are presented in Table III.

3.2 Interfacial bond strength measurements using short beam shear specimens

Short beam shear tests on systems using the same combination of fibre surface treatment, resin and curing conditions which were used with the rectangular specimens gave remarkably consistent results in most cases. The results are summarized in Table IV for Filabond 8000 resin and Table V for Crystic 195 resin. Only when a low strength resin combined with a strong interfacial bond did the short beam shear test show a drop in strength relative to the single fibre compression test.

Resin	Crystic 195			
Curing condition	Room temperat	ure, 7 days		
Fibre surface treatment	σ _s , MNm ⁻² (mean value)	No. of specimens tested	Coefficient of variation, %	Range
G	non-bonding	10		
С	22.2	8	9.2	5.2
D	25.2	8	8.9	7.0
н	37.1	10	13.0	17.7
Α	34.5	5	9.3	8.3
В	52.3	8	10.7	16.7
Ε	56.7	7	9.5	17.3
F	60.5	25	14.8	34.7

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Effect of fibre surface treatment on apparent interfacial shear strength

TABLE III

Resin	Filabond 8000			
Curing condition	Gelation at roo	m temperature, p	ost cured at 120°C fo	or 5 hours
		No. of		
Fibre surface treatment	σ _s , MNm ⁻² (mean value)	specimens tested	Coefficient of variation, %	Range
D	20.9	7	7.9	5.2
Α	36.8	7	6.5	8.6
В	54.7	7	11.9	15.8
E	51.9	6	7.2	7.3
F	57.4	7	13.2	19.7

Effect of fibre surface treatment on apparent interfacial shear strength

TABLE IV

Effect of fibre surface treatment on short beam shear strength

Resin Curing condit Depth to spar	Filabond 8 tions Gelation a n ratio 1:5.5	000 t room temperature,	post cured at 120°C for	5 hours
Surface treatment	Short beam shear strength MNm ⁻²	No. of specimens tested	Coefficient of variation, %	Range
C	23.6	5	4.4	2,6
D	25.5	5	2.4	1.6
Α	26.8	5	2.1	1.3
В	65.9	5	3.7	6.8
E	60.7	5	4.9	7.9
F	56.7	5	9.7	7.1

TABLE V

Effect of fibre surface treatment on short beam shear strength

Resin	Crystic 195
Curing condition	Room temperature for 7 days
Depth to span ratio	1:5.5

Surface treatment	Short beam shear strength MNm ⁻²	No. of specimens tested	Coefficient of variation, %	Range
С	24.4	5	3.0	2.0
D	28.6	5	4.1	3.0
Α	34.6	5	2.7	2.2
В	>41.7	5	2.2	2.2
E	>40.5	5	1.1	1.2
F	>39.7	5	1.7	1.7

The two resins showed considerable difference in the shape of the force deflection curves which were modified by the nature of the surface treatment. Treatments B, E, F used in connection with Filabond 8000 resin led to essentially linear force deflection curves reaching a peak of the order of 2500 N then dropping off suddenly. Failure was of the brittle type. Treatment A, C and D led to curves of multiple peaks suggesting a certain extent of premature debonding or fibre failure giving rise to stress relaxation. The peak value reached was only about 1000 N.



FIGURE 1 Load deflection curves for short beam shear test, Crystic 195 resin.

The behaviour of the crystic resin composite tested in short beam shear showed significant difference in the shape of the stress-strain curve and the appearance of the damaged (due to loading) specimen. The apparent strength for surface treatments B, E and F (Table V) showed a marked drop compared with the corresponding values listed in Table IV. The load deflection curves are shown in Figure 1. The weak bonding type C and D and moderate bonding type A showed relatively little change in shape or of the peak value of failure load while the strong bonding type B, E and F exhibited a yield region. A clean failure plane was not generally obtained. Specimen damage appeared to start in the region near the central loading nose where shear stress concentration was at its highest.¹³

The yielding of the specimen accounts for the "greater" sign for fibre surface treatment type B, E and F in Table V.

4. DISCUSSION

4.1 The interphase region and bonding between glass and resin

The interphase region is important because it is the region where stress transfer occurs. It consists of the glass-resin interface (and the coupling compound if the glass has been chemically treated to improve the overall bond strength) together with a thin layer of glass and resin on either side of the interface that is affected or restrained in mechanical response because of the mutual interaction of the two phases in close contact.

Three aspects of the interphase region warrant a deeper understanding, viz,

a) The nature of the bonding between the glass and resin, the extent of bonding in terms of percentage of active sites used and the distribution (random or concentrated in arrangement).

b) The possible structural modification of the adjacent molecules, of the resin in particular, which could result in a significant change in crack sensitivity of the material. The above consideration becomes important when the bond strength is approaching the shear strength of the matrix in the interphase region. Any significant shift from one mode of failure, interfacial or cohesive, to the other may affect the overall performance of the composite.

c) The stress-strain behaviour of the interphase material which is important when the interfacial bond is matrix-limited.

Tables II to V show that the apparent interfacial bond strength can be controlled simply by varying the surface treatment on fibres and that one can classify them arbitrarily in terms of relative effectiveness into three groups:

a) Weak bonding—silicone resin, unreactive silane, boundary lubricant, having a bond strength value of up to about 25 MNm⁻².

b) Intermediate bonding---moisture, polyvinyl acetate, with a bond strength of about 35 MNm⁻².

c) Strong bonding—any treatment containing reactive silane A174, for which the bond strength is greater than 50 MNm^{-2} .

There seems little doubt that thermomechanical mismatch alone cannot fully explain the order of magnitude of the measured bond strengths. In the case of a cold curing resin coupled to an unreactive silane (A153) the axial stress at debonding is still in excess of the radial compressive stress which is produced by shrinkage. The radial compressive stress at the glass resin boundary in the case of a hot curing system of similar thermal/mechanical constants which had undergone a temperature change of 100°C during curing was found to be 12.8 MNm⁻².¹⁴ Even allowing a frictional coefficient of unity, it is still a long way below the values inferred from the test results. The balance must come from other types of bonding, physical or chemical. It is necessary, therefore, to consider the interactions between the glass and resin in the presence or absence of the coupling agent. This can be done by considering each of the above three groups in turn.

The silicone resin coating (treatment G) acts as an effective barrier to any chemical bonding, be it hydrogen or covalent linkage, between the glass surface and the resin. This is to be expected as the silicone resin contains no functional group capable of any such reaction and very low wetting of the glass surface by the resin is obtained, the interface region of a specimen containing silicone treated fibre appearing optically very similar to one which had debonded over the whole length of fibre.

The very weak dipole-induced dipole intermolecular interaction between glass and silicone resin and between silicone resin and polyester resin falls off rapidly with distance of separation between atoms (inversely proportional to the sixth power of distance) and in these circumstances the only significant contribution to bonding comes from mechanical friction. However, the frictional coefficient is low and so is the overall bond strength. The silane reactive toward glass but not polyester (A153) (treatment C) shows a drop in bond strength relative to the moisture-coated fibre. This seems to suggest that some phenyltrimethoxysilane molecules do succeed in competing with the adsorbed water molecules for reactive sites but the other end of the molecule is incapable of forming hydrogen bonds or covalent bonds with the polyester. Some hydrogen bonding may take place between the glass surface and the resin as there is evidence that when a silane reacts with a glass surface some hydroxyl groups remain unreacted.¹

The surface treatment with a boundary lubricant, Morpan TPB (D) gave an overall bond strength comparable to treatment C. At the glass surface there exist metallic cations which diffuse into the aqueous phase because its high permittivity lowers the attractive forces between ionic species on the surface. This leaves an anionic surface which is capable of orienting cations. Thus, physical adsorption of an oriented monolayer of the long chain aliphatic cations of the lubricant occurs through ion exchange reactions with the glass surface and the lubricant is uniformly and strongly adsorbed, Figure 2.¹⁵ The long chain and small cations are not likely to give strong bonding with the resin. In this case, the adhesion of the resin to the glass is reduced by the presence of the lubricant and no chemical coupling can take place across the interface.

In view of the unexpectedly high bond strength of the water lubricated system (A), in the second group, the role of adsorbed water on the fibre surface must be evaluated. It is known that E-glass is easily hydrated by



FIGURE 2 Two possible bonding pictures. (a) Covalent bonding, (b) dynamic hydrogen bonding.

water and its surface saturated with hydroxyl groups whereupon complete wetting is obtained.^{16, 17} Also free water molecules exist on the glass surface. This can retard if not inhibit any chemisorption of silane on the glass surface by an insulating action.⁶ In the absence of a coupling agent the most likely interaction between glass and polyester resin is through hydrogen bonding as the carbonyl group in the polyester is polar in nature and can interact with the proton from water through electrostatic forces.

Surface treatment using polyvinyl acetate (treatment H) gave bond strengths very similar to the moisture-coated fibres. It is unlikely that polyvinyl acetate would compete favourably with adsorbed water for silicon sites and if the polyvinyl acetate interacts with the polyester it must be through the carbonyl group. This is dipole-dipole interaction and is of the same order of magnitude as hydrogen bonding in terms of breaking strength. However it is difficult to see how the polyvinyl acetate can be effectively bonded to the glass surface and in view of this it is more likely that the polyvinyl acetate dissolves in the resin during curing leaving the interface unaltered. Unless there is a high percentage of polyvinyl acetate in the cured resin network the matrix properties would not be expected to change significantly.

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Relative effectiveness of surface treatments B, E and F

Resin	Test method	Order
Filabond 8000	Single fibre shear	$\mathbf{F} > \mathbf{B} > \mathbf{E}$
Crystic 195	Single fibre shear	$\mathbf{F} > \mathbf{E} > \mathbf{F}$
Crystic 195	Short beam shear	$\mathbf{B} > \mathbf{E} > \mathbf{F}$

In the third, strong bonding group, in the presence of γ -methacryloxypropyltrimethoxysilane (A174) the apparent bond strengths fall into the 50-65 MNm⁻² region. In the range of surface treatments: B (silane A174 alone) E (A174 plus Morpan TPB) and F (A174, Morpan TPB and polyvinyl acetate), only silane A174 is potentially capable of raising the apparent bond strength to a level above that of the moisture lubricated fibre resin systems. Also, the relative order of magnitude reveals no trend in bond strength among the three different treatments, Table VI.

The variation is, in general, too small to reveal any significant change in the nature of bonding between glass and resin in the presence of these coupling agents. This would imply that neither the boundary lubricant nor the film forming polymer competes favourably with silane A174 for silicon sites. This silane, although of low polarity performs effectively by virtue of its higher chemical reactivity toward the resin in particular.

The silane provides functional groups which are reactive towards the glass surface as discussed earlier. The group X, Figure 2, is a reactive organic group, $CH_2 = C(CH_3)COO \sim$ designed to match the reactivity of the polyester system and which establishes strong covalent bonds with the resin, the vinyl group in the molecule acting in the same way as the styrene molecule, forming a bridge between the unsaturated polyester chains.

Thus, the bridging of the interface by the bifunctional coupling agent gives good adhesion through covalent bonds to both the resin and the glass. This chemical coupling may be considered to yield the ultimate in wetting in the form of molecular continuity from resin to glass.^{18, 19}

It must be borne in mind that the covalent Si—O bond is an order of magnitude higher than a hydrogen bond and a modest increase in apparent bond strength from about 35 to about 60 MNm⁻² would suggest an even smaller percentage of the silicon sites participating in covalent bond formation. Furthermore, if the silanol groups from the silane coupling agent are to undergo any intermolecular condensations, these groups must be near enough to each other and possess the favourable spatial conformation to permit such reaction to occur. The surface character of E–glass is such that is composed of a number of submicrosopic patches about 10 to 30 nm in diameter and about 10% of the area consists of patches or islands of silica surrounded by calcium magnesium boro alumino silicate.²⁰ If the bonding between glass and coupling agent, coupling agent and resin, coupling agent and coupling agent is covalent by silanol condensation and addition polymerization it would then be concentrated at a small fraction of the silica-rich micelles rather than distributed at random.

The above arrangement is unlikely from the statistical point of view, but a dynamic bonding picture is a reasonable alternative.²¹ In this case adhesion is described in terms of a dynamic equilibrium of making and breaking of hydrogen bonds between polymer segments (coupling agent bonded to the polyester resin) and the glass surface through the agency of a low molecular weight material, in this case water. The improvement of overall bond strength compared with surface treatment A, C, D and H is attributed largely to the improvement of coupling agent to polyester resin compatibility. The two possible bonding pictures are shown in Figure 2(a) and (b).

4.2 Structural perturbation of resin in the interphase region

The relatively high apparent strength of the interfacial bond resulting from the use of silane A174 poses an important question concerning the possible change in structure and properties of resin in the interphase region. From established analysis,²² one would expect increasingly more matrix cracking as the bond strength approaches the cohesive strength of the matrix. The crack sensitivity of the resin in the interphase is either mitigated or enhanced by the structural changes induced by the unusually high surface-to-volume ratio of the resin phase.²³ For a 45% V_f composite using 30 μ m unidirectional glass fibres, this ratio is approximately 110 mm⁻¹ and its magnitude will serve as an inverse measure of the liquid-like domain in which the long chain molecules possess the freedom to undergo cooperative structural adjustment.

The molecular picture of the probable structural variation is complicated because of the contiguous chain-like structure of the polymer molecule. Either the whole molecular chain has to be adjusted to the fibre surface or parts of it cooperate with connected segments of the same chain as the latter adjust to the surface. Cooperative response to neighbouring chains undergoing adjustment is also expected as large volumes may be swept out as chain segments undergo random gyration. It is probable that all these mechanisms are required to achieve intimate contact of polymer molecules with a solid surface.

It has also been suggested²⁴ that a concentration gradient of the constituents of the resin mixture (e.g. styrene, catalyst, accelerator, coupling agent and other additives) could be set up in the interphase region with the possible consequence of having different curing conditions which lead to the formation of resin of different properties. As a matter of convenience the interphase region can be treated as a layer of a certain thickness and with a set of distinct but constant properties. Even if the thickness is as small as 10 nm, there is still about 0.1% of surface-modified material in the matrix component of the composite. Its influence is stronger than this small percentage would suggest since it is in critical juxtaposition to the fibres and is the principal load transfer agent and supporting phase for the fibre.

4.3 Response of the interface to deformation and fracture

When a fibre composite is deformed to a certain extent fracture will initiate at structural discontinuities such as the fibre end region or voids present in the composite where stress concentration exists. If strong interfacial bonding is achieved in a void-free composite, discontinuities initially not present in the resin can be produced when a critical stress, viz. the yield stress of the resin is reached.²⁵ The existence of an effective energy absorption mechanism is important in governing how the composite will respond to an advancing crack tip. The efficiency of energy absorption is in turn affected by the distribution of bonds which connect the glass to the resin.

Consider a small crack in the matrix with its tip advancing toward and perpendicular to the interface. If there exists no energy-spreading mechanism and bonding is strong the concentrated force at the crack tip would penetrate the fibre, resulting in brittle failure because the restrained interphase material is not capable of undergoing any distortion or re-alignment. This has not been observed in high strength glass fibre polyester resin composites and therefore there must be an efficient energy-absorption mechanism operating at the interface. The distribution of bonds could have a significant effect on the efficiency of energy absorption. If they are arranged in some random but regular fashion, then, on spreading the crack-tip energy by peeling the resin off the glass surface, there is no ripping back of resin, such as one would expect when the bonds are concentrated in certain "button-like" areas in which case the peeling action would lift the loose resin surface and cause a "button" or two to break away from the glass.²⁶ Thus the movement of the non-connected areas of resin surface away from the glass absorbs the cracktip energy.

The surface characteristics of glass would favour the "button-like" arrangement of bonds and this supports the frequent observation of discontinuous debonding of the interface with high bond strength.¹³

5. CONCLUSIONS

In a glass fibre polyester resin composite the fibre to resin interfacial bonding results from :

a) Thermomechanical forces due to the mismatch of the two components.

b) Chemical bonding or physical interaction between the three materials, glass-surface treatment-resin.

If strong bonding is required the size formulation should include a silane which is capable of bonding with the glass and the resin. With this coupling agent the relative contribution of (a) and (b) to the overall bond strength is approximately one-third and two-thirds respectively.

It is possible to obtain a range of bond strengths through altering the contribution due to chemical bonding or physical interaction by surface treatment of the nominally uncoated fibres with different substances so that the interaction between the glass surface and polyester ranges from Van de Waals forces through hydrogen bonding to covalent bonding with bond strengths increasing in that order. Weak bonding can be obtained by surface treatment of the fibres with compounds which can interact with only one of the two components (i.e. resin and fibre). Untreated fibres give bond strengths somewhere in between these two extremes.

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