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Fibre reinforced thermoplastic composites for dentistry

Part I *Hydrolytic stability of the interface*

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Clinical implementation of fibre-reinforced composites (FRCs) for treatment of misaligned teeth requires a stability of the material under stress in a moist environment. The performance of the material is strongly dependent on its resistance to hydrolytic deterioration of the components. Of particular concern are the quality and durability of the interfaces between the fibres and the matrix. Scanning electron microscopy (SEM) was utilized to evaluate qualitatively the effect of water immersion on the interfaces between constituents in a variety of E-glass fibre-reinforced thermoplastics. A particular series of organosilane-coated fibres embedded in polycarbonate (PC) were chosen for further quantitative study of the residual shear strength of the interfaces using an embedded-single-fibre test. Annealed PC and maleated polypropylene (MPP) reinforced with bare E-glass fibres have an appropriate combination of mechanical properties and environmental stability for potential orthodontic applications. The usual sizing agents used for commercial E-glass fibres interfere with the bonding of the fibres to the matrix and the usual silane treatments used to promote bonding could lead to problems of hydrolytic stability under extreme conditions of stress and moisture.

1. Introduction

Over the last 30 years there has been a substantial amount of work published on the use of fibre reinforced composite (FRC) materials in dentistry [1–12]. Despite positive laboratory results, there has been only limited success in the use of these materials in clinical practice. However, the potential for FRCs in dental applications (such as splints, retainers, space maintainers and orthodontic wires) is very high.

The main advantages of FRC are aesthetics (translucency), direct bondability to the tooth structure and easy forming of the appliance in the dental office. In the orthodontic treatment of teeth misalignment, the possibility of varying the stiffness of a device relatively easily without changing its dimensions is an additional advantage [21].

While there is no concern about the time dependence of the mechanical properties of commonly used metal wires in the oral environment, both time and environment affect significantly the performance of FRC appliances [13–16]. These effects in long-fibre thermoplastic composites are assumed to be mostly due to the hydrolytic deterioration of the fibres, matrix and interface [17] as well as the viscoelastic character of the matrix [18].

The principal goal of this study is to investigate the resistance to hydrolysis of the interface in oriented glass-fibre-reinforced thermoplastic composites, which have the potential to replace metal wires in the treatment of teeth misalignment.

2. Experimental procedure

A variety of fibre-reinforced composites utilizing thermoplastic matrices and organosilane-coated E-glass fibres were exposed to 85 °C water for an extended period of time. Scanning electron microscopy (SEM) was used to evaluate qualitatively the effect of water immersion on the interface between constituents. A particular series of organosilane-coated fibres embedded in polycarbonate were chosen for further quantitative study of the residual strength of the interfaces using an embedded-single-fibre test [19].

Polycarbonate (PC) Lexan 181, polyethyleneterephthalate glycol (PETG), semicrystalline polypropylene (PP) and maleic anhydride modified polypropylene (MPP) were used as matrices. Properties, producers and processing conditions of the matrices are listed in Table I.

E-glass fibres were provided by Dow Corning in the form of continuous roving and 12 mm long chopped strands with an average diameter of 14 μm, an elongation at break of about 2% and a Young's modulus of 72 GPa.

The E-glass fibres were used either untreated or coated with silane coupling agents, provided by Union Carbide, Inc. (Tarrytown, NY, USA), to improve the adhesion between the matrix and the fibres. The untreated fibres were vacuum dried at 500 °C for 2 h before mixing to release weakly adsorbed water. The silane coupling agents used in this work are: aminopropyltriethoxylsilane (trade name A1100), glycidoxy-

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TABLE I Characteristics of the matrices

Matrix (producer)	Processing temperature (°C)	Young's modulus (GPa)	Yield strength (MPa)	Strain at break (%)
Polycarbonate (Lexan 181, GE Plastic, USA)	250	2.4	62	120
Polyethylene terephthalate glycol (co-polymer 6, Eastman Chemical USA)	230	2.3	34	110
Polypropylene (Mosten 58.412, Chemopetrol, Czechoslovakia)	200	1.8	38	1000
Maleated polypropylene (Research Institute Macromolecular Chemistry Czechoslovakia)	200	2.0	45	80

propyltriethoxysilane (trade name A187), methacryloxypropyltriethoxysilane (trade name A174), aminophenyltriethoxysilane (developmental sample Y9576).

The E-glass fibres were coated from a solution containing 5% silane, 5% water and 90% methanol using procedures described elsewhere [19]. Test specimens were prepared by compression moulding, as described below.

Specimens for fractographic analysis were prepared by mixing 10% by volume (20% by weight) short E-glass fibres with the thermoplastic for 10 min in a Brabender Plasti-Corder at 35 r.p.m. and at the temperatures shown in Table I for each thermoplastic. The matrices were dried under vacuum at 75 °C prior to mixing. Each mixture was compression moulded into sheets 100 × 100 × 4 mm using a hot press at a pressure of 12 tons. Notched bars 4 × 6 × 100 mm were cut from the compression moulded sheets. Fracture surfaces were obtained by fracturing the notched bars both in liquid nitrogen and at room temperature. Fractographic analysis was performed using a scanning electron microscope (Amray, USA). To evaluate qualitatively the effect of environmental attack on the interfacial adhesion and, consequently, on the mechanical properties of the composite, specimens were immersed for 100 h in water at 85 °C and then dried 100 h at 100 °C in a vacuum oven. They were then broken both at room temperature and in liquid nitrogen and examined by SEM.

Samples for the embedded-single-fibre test were prepared by laying a continuous glass fibre over the centre of a dog-bone-shaped specimen and fixing the fibre ends with tape. Two to three layers of a 10 wt % solution of PC in chloroform were then spread over the fibres. After evaporation of the solvent, a film of approximate thickness 0.1 mm covered the fibre and was diffusion bonded to the dog-bone underlayer. A number of specimens were also prepared by compression moulding instead of solution casting. The single-fibre dog bone was then loaded in uniaxial tension in the field of an optical microscope under polarized light. The fibre fractured into a distribution of fragment sizes, the critical fibre length was determined and the shear strength of the interface was calculated [20]. Tests were conducted using a MTS 880 servohydraulic loading machine, at a test rate of 0.5 mm min^{-1}. In order to quantify the effect of moisture on the shear strength of the interface, specimens for single-fibre tests were immersed in water under the same conditions used for the fractographic analysis.

For ductile thermoplastic matrices, the model proposed by Kelly and Tyson [36] can be used to estimate the shear stress transmission (i.e. the shear strength of the interface) from the fragment-length distribution [20]. It can be shown that:

$$T = \langle\sigma_f\rangle d_f/2l_c \qquad (1)$$

Where d_f is the fibre diameter, $\langle\sigma_f\rangle$ is the fibre strength at the critical fibre length, l_c, and T is the shear strength of the interface. The critical fibre length can be estimated as equal to 4/3 of the average fragment length (i.e. the length at the midpoint of the distribution). Measurement of the fibre diameter and strength at low gauge length allows T to be calculated from Equation 1.

3. Results and discussion

3.1. Fractographic analysis of short E-glass Fibre filled specimens

3.1.1. Polycarbonate

The fracture surfaces for PC/E-glass composites containing bare, water-washed fibres are shown in Fig. 1. Poor wetting of the fibres by the matrix accounts for the poor adhesion. Dental appliances used under these conditions would most certainly result in poor clinical performance of the composite. Since polycarbonate is relatively insensitive to water, no significant effect of the exposure to water is observed over the time period studied. Furthermore, there is no significant difference between the specimen broken at room temperature and in liquid nitrogen since the glass-transition temperature of PC (T_g = 150 °C) is well above room temperature.

Improved adhesion can be obtained by coating the fibres with silane coupling agents. Fracture surfaces for a PC/E-glass composite using A1100- and A187-silane-coated fibres are shown in Figs 2 and 3. However, unlike the situation with epoxy and polyester resins, there is no chemical reaction between PC and the silanes used [22]. Bonding is the result of better wetting alone, since there is little possibility of forming stable chemical bonds between the constituents. This can be shown by exposing the surface to chloroform, thereby dissolving the PC and leaving a bare glass surface behind. Significant deterioration of the interface is caused by the hydrolysis of the silane layer after exposure to 85 °C water. Even after long-term drying, the interface is not fully recovered and significant damage remains. The effect of different silanes on the degree of deterioration will be described fully below.

Rather than using hydrolyzable silanes to improve interfacial adhesion, the same effect can be accomplished by annealing the samples of PC/bare E-glass composite at 275 °C for 1 h (Fig. 4). Very little fibre pull-out and extensive plastic deformation near the fibre surface are observed. Both lower viscosity and a change of PC morphology at the annealing temperature results in a high-quality interface able to transmit substantial stresses from the PC to the reinforcing fibres. Generally, amorphous PC contains submicroscopic ordered domains similar to those in crystalline

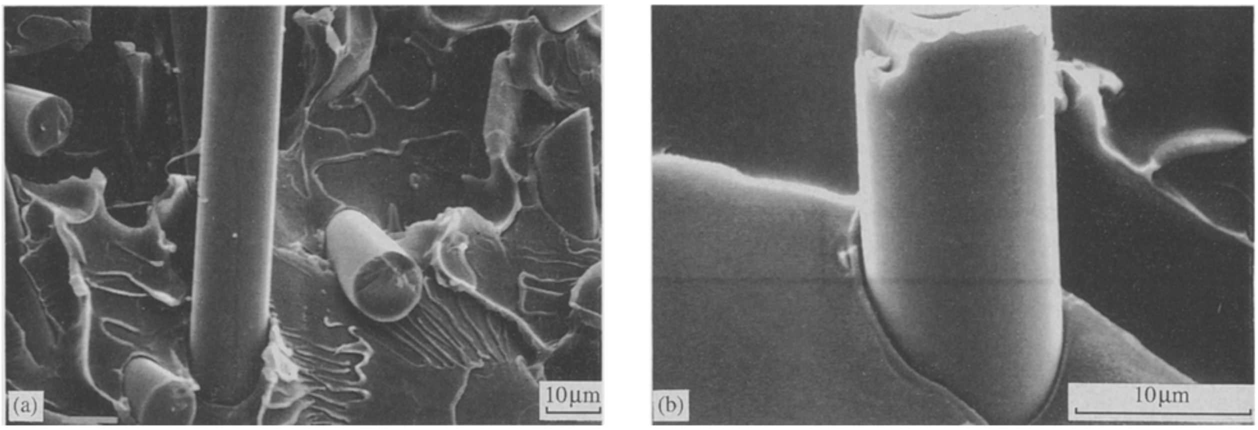

Figure 1 SEM micrographs of the fracture surfaces in PC/bare E-glass fibres showing poor wetting of the fibres: (a) as moulded, and (b) after immersion for 100 h in 85 °C water (broken in liquid nitrogen).

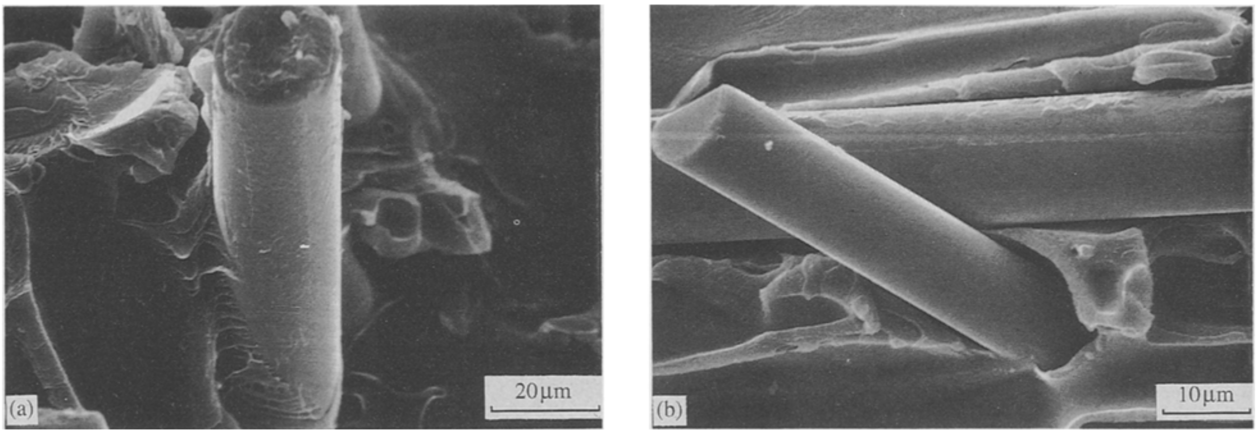

Figure 2 SEM micrographs of the fracture surfaces in PC/A1100-silane-treated fibres showing an improved wetting (broken in liquid nitrogen): (a) as moulded, and (b) after exposure to 85 °C water for 100 h.

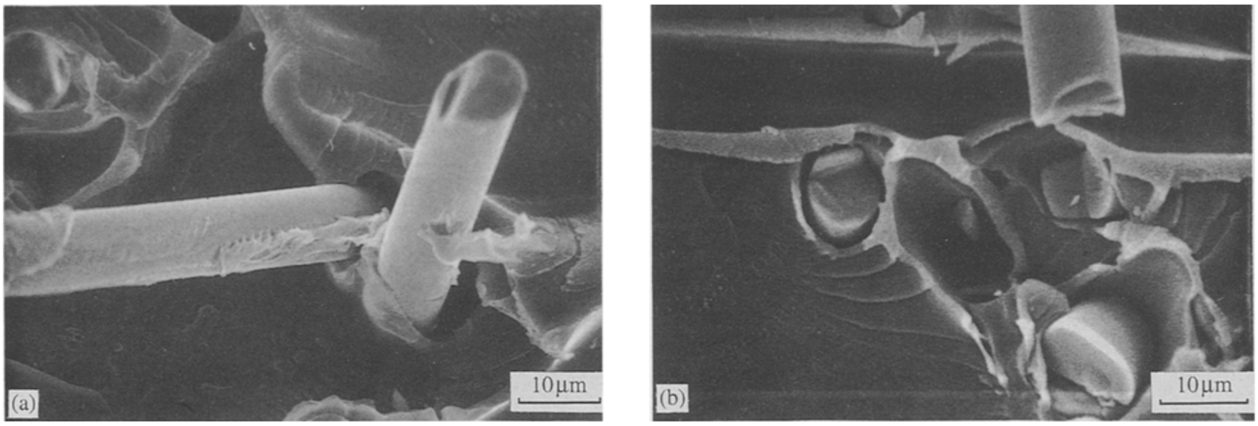

Figure 3 SEM micrographs of PC/A187-silane-treated E-glass fibres (broken in liquid nitrogen): (a) as-moulded, and (b) after exposure to 85 °C water for 100 h.

polymers [24–27]. At temperatures above 265 °C, the "melting point" of these domains, macroscopic long-range-order regions can be nucleated on the glass surfaces [24]. This highly ordered (or perhaps "transcrystalline") layer can apparently transfer stress from the matrix to the fibres more effectively, since it is in intimate contact with the surface and posseses an elastic modulus higher than the matrix in the bulk. Similar results were reported recently by Brady and Porter [28] for PC reinforced with both glass and carbon fibres. As the SEM observation reveals (Fig. 4b), there is relatively little deterioration of the interface after the exposure to water, presumably because of the relative impermeability of the "transcrystalline" region.

3.1.2. Polyethyleneterephthalate glycol

The SEM micrographs of PETG reinforced with bare and silane-treated glass fibres (Fig. 5) reveal significant differences from the PC-based composites. In both cases, the fibres are covered with a layer of matrix, suggesting cohesive fracture of the matrix rather than adhesive failure of the interface. Good wetting and the higher strength of the adsorbed interlayer, caused by mechanical constraints on the matrix in the immediate vicinity of the fibre surface, change the crack path, resulting in the tendency for cohesive matrix failure. The good wetting, even for the untreated fibres, is most probably due to the viscosity of PETG being lower than that of PC at the appropriate moulding temperatures. Since one cannot expect covalent bonding between the PETG and the silanes employed, there is no advantage in using silanes in this case.

Significant deterioration of the interfacial adhesion was observed after 100 h in 85 °C water (Fig. 6), even after long-term drying in the vacuum oven. "Blisters" were observed on the specimen surface indicating extensive hydrolysis of the matrix. The higher solubility and permeability of water in PETG make these composites less satisfactory in clinical use than the PC-based composites.

It is clear that a satisfactory level of adhesion can be obtained in E-glass-filled composites of both PETG and annealed PC. In addition to inducing transcrystallinity, high annealing temperatures stimulate transesterification reactions [29–32]. This process can reduce the matrix viscosity, thereby modifying the wetting characteristics and the deformation behaviour of the matrix itself [33].

3.1.3. Polypropylene

SEM analysis was performed on polypropylene composites reinforced with bare and silane-treated fibres (Fig. 7). It is evident that these systems exhibit very

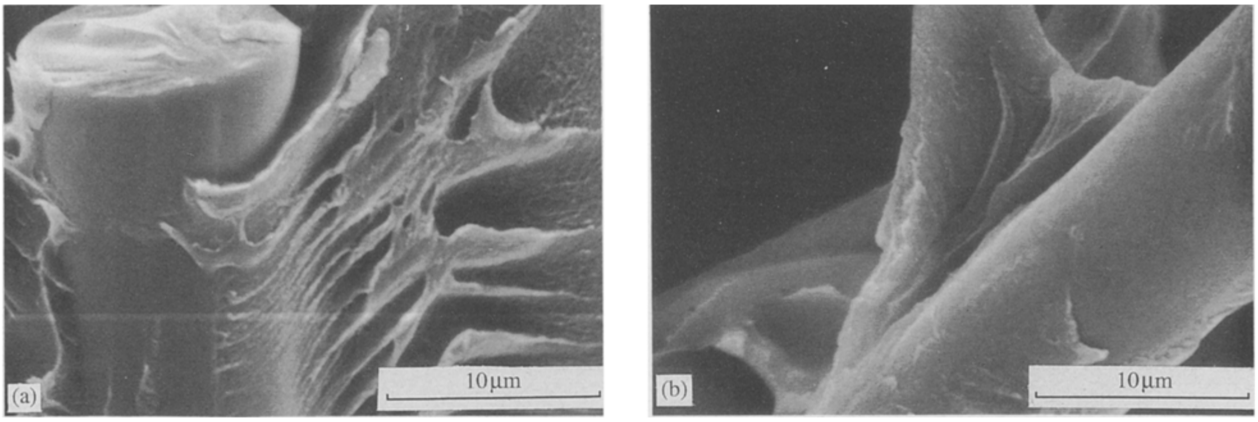

Figure 4 SEM micrographs of PC/bare E-glass composite annealed at 275 °C for 1 h: (a) as-annealed, (b) after immersion in 85 °C water for 100 h. (Broken at room temperature.)

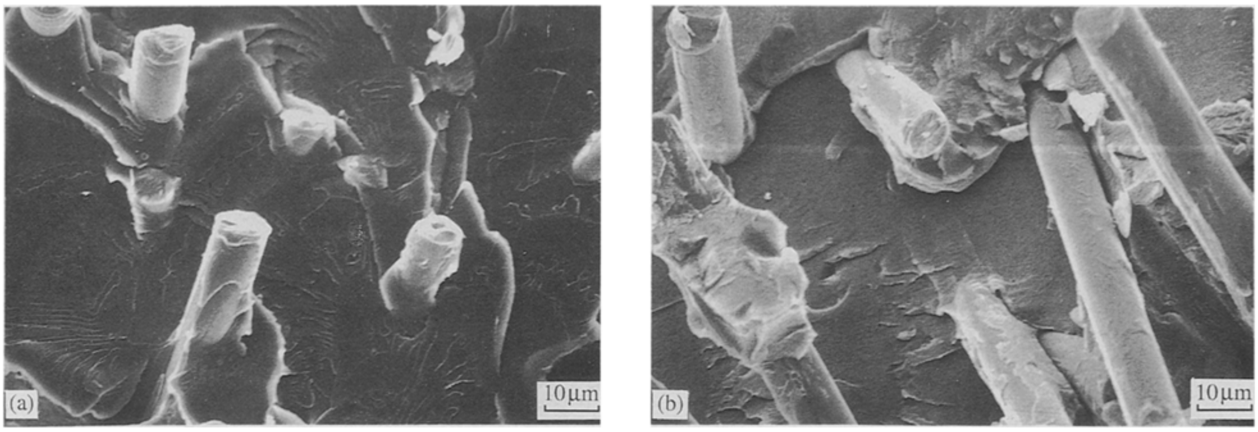

Figure 5 SEM micrographs of: (a) as-moulded PETG/bare E-glass, and (b) PETG/A1100-silane-treated E-glass. (Broken at room temperature.)

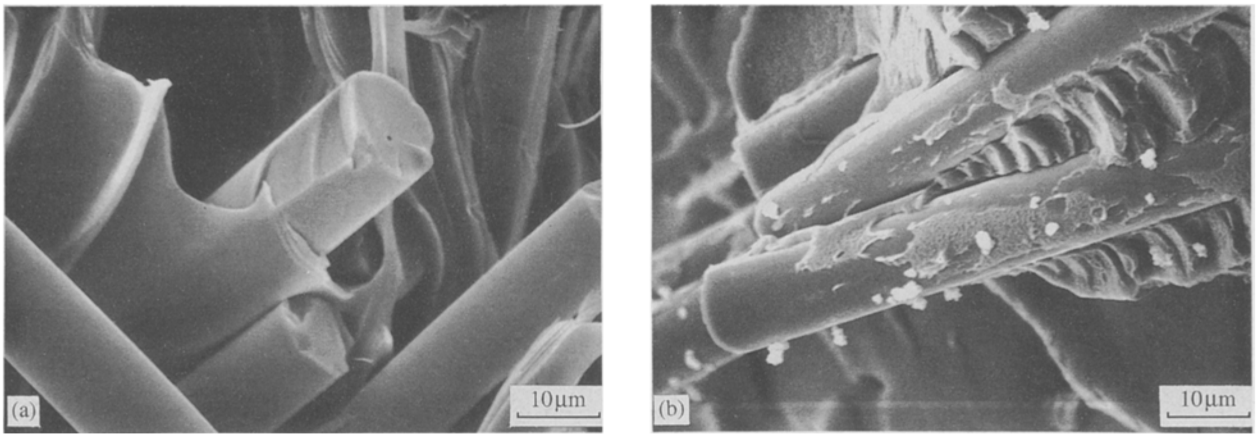

Figure 6 As Fig. 5 after immersion in 85 °C water for 100 h. (Broken at room temperature.)

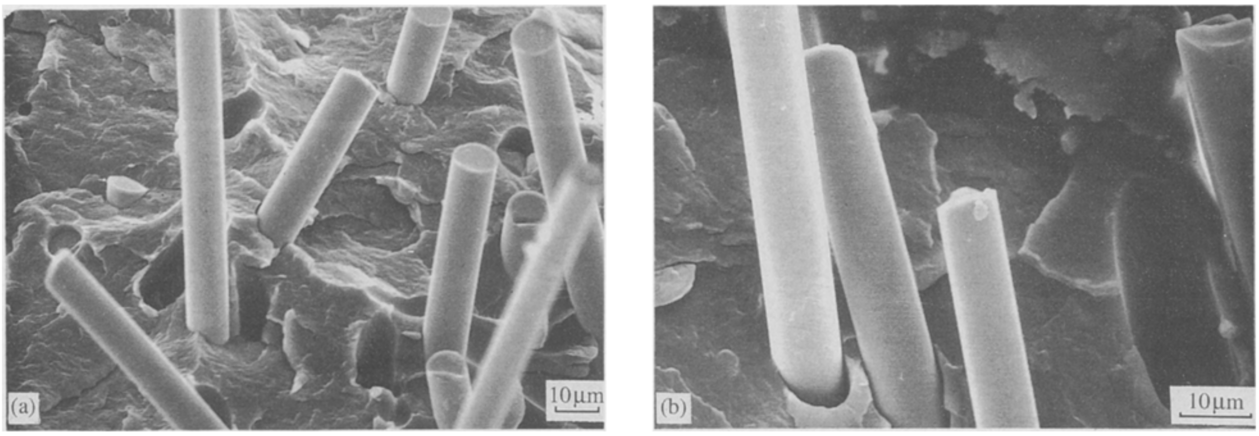

Figure 7 SEM micrographs of: (a) as-moulded PP/bare E-glass composites, and (b) PP/A-1100-silane-treated E-glass composites. (Broken in liquid nitrogen.)

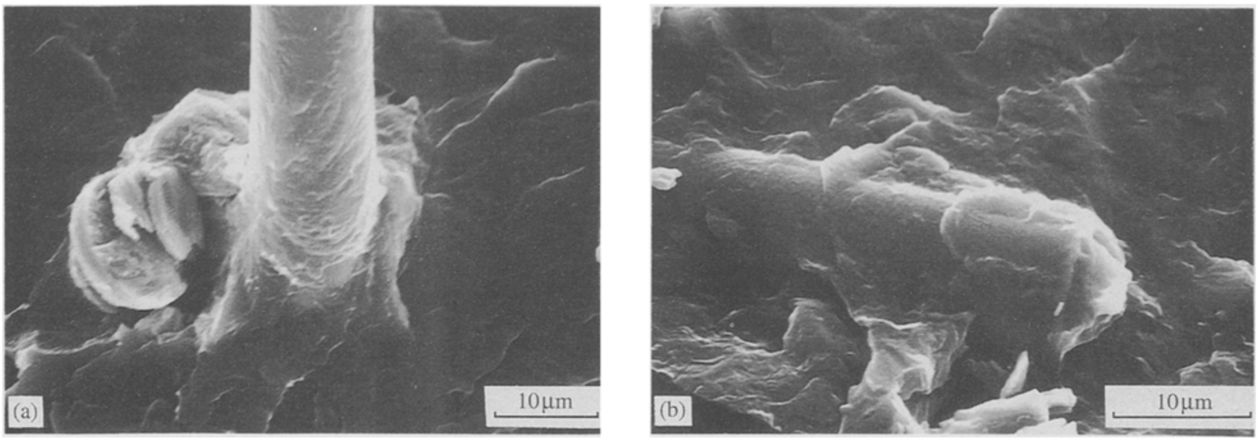

Figure 8 SEM micrographs of: (a) as-moulded MPP/bare E-glass composites, and (b) MPP/A1100-silane-coated E-glass fibre composites. (Broken in liquid nitrogen.)

poor interfacial adhesion. No significant effect of silane treatment is observed, eliminating these composites as competitors in dental applications. Copolymers of PP with maleic anhydride, however, can overcome the deficiencies of the PP/E-glass materials. Maleated polypropylene (MPP) exhibits good adhesion to both bare and silane-treated fibres (Fig. 8). In this case no debonding occurs at the fibre/matrix interface and the crack propagates through the relatively tough matrix phase. The reaction of the carboxylic groups of maleic anhydride with hydroxyls of the glass surface results in an acido-base chemical bond at the interface that appears to be highly resistant to hydrolytic degradation. The presence of an aminosilane layer on the fibre surface reduces the resistance of the interface to hydrolysis (Fig. 9) because of either a lower stability of the aminosilane/maleic anhydride bond or the poor hydrolytic stability of the siloxane layer. Composites of MPP reinforced with bare, water-washed E-glass fibres appear to be outstanding materials for dental application. They will be somewhat more difficult to process in a clinical

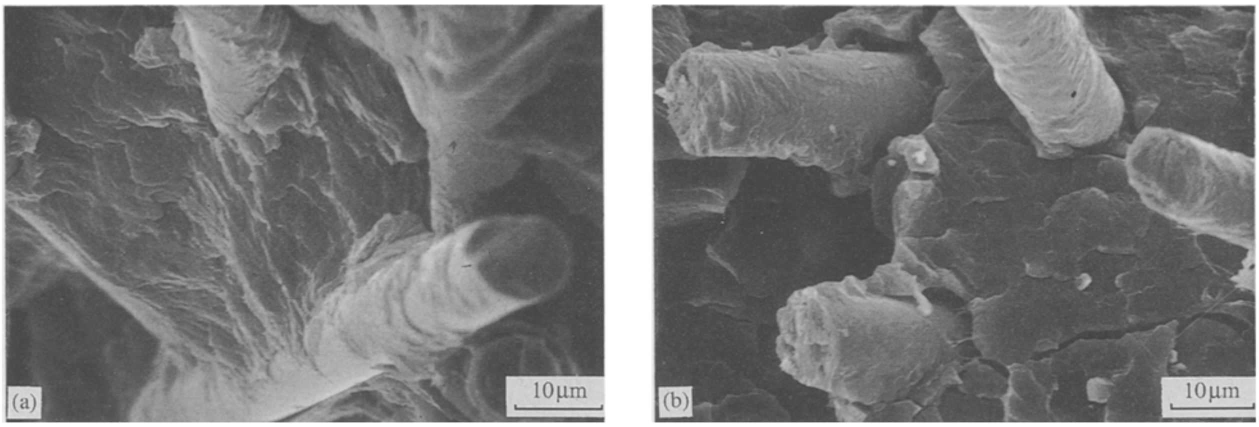

Figure 9 As Fig. 8 after immersion in 85 °C water for 100 h. (Broken in liquid nitrogen.)

setting than PC/E-glass fibre composites, but should be seriously considered for use as dental prosthetics.

3.2. Measurement of the shear strength of the interface

Based on the results of preliminary fractographic analysis of both clinical and laboratory specimens, the PC/E-glass composites were chosen for more detailed investigation of the hydrolytic stability of the interface. Bare, water-washed E-glass fibres and those treated with A1100 and Y-9576 silanes were used as the reinforcement. The embedded-single-fibre test was used to measure the stress transferability (shear strength) of the interface [19]. Since PC is a ductile material, Equation 1 is a reasonable estimate of the shear strength of the interface. The results are shown in Table II.

Unannealed PC/bare E-glass and PC/amino-silane-(A1100) coated E-glass exhibited an interface shear strength of the order of 12 to 16 MPa. The results for compression moulded and solution-cast specimens were virtually identical. In these cases, the stress transfer between fibre and matrix is due primarily to friction. As a rough estimate, the frictional force is calculated to be of the order of 10 MPa [34, 35]. Treatment of the E-glass with aminophenyl silane (Y-9576) provided a significantly higher stress transmisibility, with the measured interface shear strength reaching 32.2 MPa. (The yield strength of PC under the axisymmetric conditions of the test is estimated to be 41 MPa.)

After annealing the PC/bare E-glass specimens at 275 °C for 1 h the stress transferability increased substantially to a value of 35.9 MPa. This increase is clearly associated with the nucleation of "transcrystalline" PC on the glass surface as described above.

TABLE II Shear strength of the interface in PC/E-glass composites at room temperature

Silane	Compression moulded		Solution cast	
	l_c/d	T (MPa)	l_c/d	T (MPa)
None	117.3	12.6	117.2	12.8
None (annealed)[a]	55.7	35.9	–	–
A1100	117.2	12.8	116.4	16.3
Y9576	–	–	61.9	32.2

[a] Annealed at 275 °C for 1 h.

TABLE III Shear strength of the interface in PC/E-glass composites at room temperature measured after immersion in 85 °C water for 100 h/100 h drying at 100 °C under vacuum

Silane	Compression moulded		Solution cast	
	l_c/d	T (MPa)	l_c/d	T (MPa)
None	117.5	12.0	138.9	10.8
None (annealed)[a]	63.5	31.5	–	–
A1100	138.9	10.5	117.3	12.5
Y9576	–	–	115.1	16.5

[a] Annealed at 275 °C for 1 h.

The strength of the interface after immersion in 85 °C water for 100 h, followed by drying at 100 °C for 100 h, are shown in Table III. All except the annealed PC/bare E-glass composite have an interface strength of the order of 10 to 16 MPa, indicating stress transmission by friction alone. Even the Y-9576 treatment has lost its ability to transmit a high level of stress, probably due to a non-recoverable hydrolysis of the siloxane layer. The annealed material, on the other hand, retains its strength, indicating that the morphology of the PC at the interface renders it less susceptible to damage by exposure to water.

4. Conclusion

Although there has been considerable interest in the use of fibre reinforced thermoplastics in orthodontic applications, clinical implementation has resulted in limited success. When using such materials under stress in a moist environment, performance will be strongly dependent on the resistance of the material to hydrolytic deterioration of the components. Of particular concern are the quality and durability of the interfaces between the fibres and the matrix.

In this study we have screened a variety of E-glass-fibre-reinforced thermoplastic composites for the stability of the matrices and their interfaces with E-glass under extreme conditions of exposure to water. From the point of view of the integrity of the composite, the strength of the interfaces and the hydrolytic stability of the material, it appears there are number of fibre-reinforced thermoplastics that can be considered for dental application. Among those we have examined fractographically, and using single-fibre-composite tests to measure the interface strength, it appears that annealed polycarbonate and maleated polypropylene reinforced with bare E-glass fibres have an appropriate combination of mechanical properties and environmental stability for potential orthodontic applications. The best results have been obtained with unsized, untreated, water-washed fibres. The usual sizing agents applied to commercial E-glass fibres interfere with the bonding of the fibres to the matrix and the silane treatments usually used to promote bonding could lead to problems of hydrolytic stability under extreme conditions of stress and moisture. The use of bare E-glass fibres will create problems in the fabrication of devices, however, since they would be sensitive to mechanical and environmental damage during processing. We have shown that the moulding and annealing of a polycarbonate/bare E-glass composite can result in a strongly bonded, highly water-resistant interface through nucleation of highly ordered, or possibly transcrystalline, polycarbonate at the fibre/matrix interfaces. Structrual components from such a material should result in a stable, damage-resistant applicance for dental applications. Part II will describe the mechanical properties, particularly the fracture mechanisms, for oriented composite ribbon using some of the components described in this work.

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