Thermoplastic fibre-reinforced composites for dentistry

Part II *Effect of moisture on flexural properties of unidirectional composites*

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The effect of a deterioration of matrix and matrix–fibre interface, caused by moisture, on the flexural properties (modulus, strength and ultimate strain) of unidirectional E-glass fibre-reinforced thermoplastics [polycarbonate, poly(ethyleneterephthalate glycol) and nylon 12] was investigated. Specimens of span/thickness ratio varying from 15 to 30, prepared from pultruded thermoplastic prepregs, were tested in directions parallel to and perpendicular to the fibre orientation as moulded and after immersion in water at 85 °C for 100 h. No significant reduction in longitudinal properties, controlled by fibre behaviour, resulted from exposure to water. A significant reduction in transverse properties, controlled by the matrix and interface behaviour, was observed. Polycarbonate/bare E-glass fibre composite annealed at 275 °C for 1 h before immersion in water exhibited a superior resistance to moisture attack. This phenomenon is attributed to the "transcrystalline" interphase near the fibre surface and good wetting of fibres by the matrix. Resistance against moisture favours this material for further clinical application as an orthodontic wire.

1. Introduction

The use of an orthodontic wire appliance for the alignment of teeth imposes a flexural loading on the wire. Successful application of fibre-reinforced composite (FRC) wires requires that they be capable of sustaining large deflections, possess a range of elastic moduli, have long-term stability in the oral environment, be easily formable and possess translucency [1]. Sufficient stiffness of the appliance is the most important clinical requirement on the material. A control of the stiffness of commonly used metal-based force systems has been achieved mainly through variation in the wire size and appliance design [2–6]. Contrary to metal single and braided wires, FRCs can provide a continuous range of stiffness without changing the cross-sectional dimensions, simply by varying the fibre volume fraction [7].

In the case of metal appliances there is little concern about the limits of applicable loads and the effects of the oral environment, since the material properties greatly exceed the clinical requirements. The elastic modulus of a standard metal orthodontic wire ranges from 190 to 10 GPa [8, 9]. Metals used in dentistry do not have constraints on the maximum deflection at a given span length (tooth misalignment at a given

interteeth distance), since they undergo plastic deformation after exceeding a critical stress. Common teeth misalignments are of the order of 4–5 mm on a span length of 8–10 mm and a common cross-section of metal wire is of the order of 0.5 mm × 0.5 mm.

However, the attainable mechanical properties of FRC materials are much closer to actual clinical needs. A typical polymeric FRC fails catastrophically when reaching a critical failure stress or strain. Since unidirectional composites under flexural loading fail in several different modes [10], the identification of the possible failure mechanisms and the effect of moisture on these properties are of critical importance. The effect of the oral environment on the stiffness and failure of FRC orthodontic wires is of great importance, since during the treatment FRC wire must sustain relatively large deflections for a long period, in a moist environment and under stress. The anisotropic character of FRC wire is another factor that must be taken into consideration. Since the transverse properties of unidirectional composites are generally poor, the triaxial stresses, inevitably created by placing of the wire appliance into the patient's mouth, lead to mechanical instability of the appliance and some limitation on the degree of allowable strain.

Since transverse properties are matrix-controlled, the susceptibility of the matrix and matrix–fibre interface to the hydrolytic deterioration will be crucial for the stability of the device in the oral environment.

Immersion in water can result in the degradation of both the strength and stiffness of glass-reinforced composites. An increase in temperature of the water generally accelerates degradation [11]. The type of glass and resin, the adhesion between phases, the water resistance of the interface and the presence of defects (voids and microcracks) will affect the durability of an FRC orthodontic wire in use. Although the properties of FRC often recover from the effect of water upon drying, chemical changes in the matrix or interface and/or degradation of the fibres under stress can lead to a non-recoverable deterioration of the material.

Penetration of water into a composite can occur by both diffusion and capillary flow. The permeation rate due to activated diffusion increases exponentially with temperature and is independent of the pressure. Capillary flow through defects (voids, crazes, etc.) and along non-bonded interfaces is dependent on the pressure [12]. The rate of water penetration through the interface is about 450 times more rapid than that through the resin [13].

Polymers containing ester groups [polycarbonate and poly(ethyleneterephthalate glycol)] have a propensity for undergoing chain scission by hydrolysis, resulting in degradation of resin properties [14]. Hydrolysis of those polymers is accompanied by a reduction in molecular weight and viscosity and an increase in concentration of –COOH groups [poly(ethyleneterephthalate glycol)]. The presence of glass results in a leaching of alkaline species during the immersion, which catalyses the hydrolysis [15]. Glass fibres may also degrade during water immersion, particularly if exposed to the medium while under stress [16]. Otto [17] found that E-glass fibres were not affected by water immersion for a period of 1 week, but thereafter showed a progressive non-recoverable degradation in strength because of a reduction in the effective cross-section.

The quality of the interface is of principal importance in determining the response of FRC materials to water exposure, since stress transfer must occur across this boundary. Degradation of interfaces in glass–fibre composites was variously ascribed to primary bond scission, weakening of secondary bonds or lubricity effects [18–20]. In Part I of this study [21] we showed the detrimental effect of moisture on the shear strength of the interface in a variety of E-glass fibre-reinforced thermoplastics.

Earlier it was also found that under simulated clinical conditions the span/thickness ratio and clamping of the specimen ends are of critical importance in determining the elastic properties and failure of FRC wires [22]. Since these effects will also exacerbate problems associated with the stability of an appliance, it will be necessary to separate the end-effects from the inherent behaviour of the material. In the present study we examined the effect of moisture on the flexural properties of FRC for dentistry, using standard large specimens in a three-point bending test,

rather than actual FRC wires under simulated clinical conditions, in order to provide a reference state for the behaviour of potentially useful matrix materials.

A three-point bending test on unidirectional FRCs is a useful way of obtaining design data, and in some cases it can provide the material properties of the composite studied. In an ideal case the loading in flexure causes normal stresses in the direction of fibres and shear stress in the plane perpendicular to the loading nose. Thus, the elastic modulus in flexure (E^{flex}), flexural strength (σ^{flex}) and ultimate strain (ε^{flex}) can be calculated from the measured force and deflection data. However, the behaviour of anisotropic unidirectional composites limits the use of simple beam theory, in that it underestimates the magnitude of stress beneath the load nose and does not take into account that the strength of glass fibres is a function of their length.

The aim of this study was to investigate the effect of moisture on the flexural modulus, strength and ultimate strain of thermoplastic composites reinforced with unidirectional E-glass fibres in directions parallel to and perpendicular to the fibre orientation, and to utilize well-known modifications of simple beam theory for the analysis of the experimental data.

2. Materials and methods

Pultruded unidirectional E-glass fibre-reinforced polycarbonate, poly(ethyleneterephthalate glycol) and nylon 12 were provided by Polymer Composites, Inc. (Winona, Minnesota, USA). The characteristics of the matrices and E-glass fibres are listed in Tables I and II. The fibre volume fraction was 0.30 ± 0.02 in all samples. Pultruded tapes were used as prepregs for the preparation of 12- and 24-ply unidirectional laminates via compression moulding in a closed mould. Specimens 10 mm wide were then cut from the compression-moulded sheets in directions parallel to and perpendicular to the fibres.

Specimens were tested in three-point bending with span lengths of 60 and 107 mm, using an Instron TTCM tensile tester (crosshead speed 5 mm min^{-1}) at room temperature. Two sets of samples were tested, one as-moulded and the other after exposure to water at 85 °C for 100 h followed by 100 h drying at 100 °C. Polycarbonate E-glass composites were annealed at

TABLE I Properties of constituents at room temperature

Component[a]	Tensile modulus (GPa)	Yield strength (MPa)	Yield strain (%)	Strain-at-break (%)
PC	2.4	62	7–10	80–150
PC[b]	2.7	78	7	50
Nylon 12	2.2	53	8	80
PETG	2.0	49	7–10	100–120
E-glass	72.0	1600–2100[c]	1.5–2.0[c]	1.5–2.0

[a] PC, Polycarbonate; PETG, poly(ethyleneterephthalate glycol).
[b] Annealed at 275 °C for 1 h.
[c] Brittle failure.

563

275 °C for 1 h in a hot press before immersion in the water in order to nucleate crystallization in the polycarbonate. The longitudinal and transverse values of the elastic modulus (E_L and E_T), ultimate strength (σ_L and σ_T) and strain (ε_L and ε_T) were calculated from load–deflection data.

Additionally, actual orthodontic wires of cross-section 0.5 mm × 0.5 mm, provided by Polymer Composites Inc. (Winona, Minnesota, USA), were tested after immersion in water at 37 °C under flexure of 20 and 40° over 60 days. Their stiffness was measured after different times of water immersion, using a device simulating clinical conditions [22] and the percentage reduction in stiffness was plotted against the time of immersion. Each experimental point represents an average from three to five specimens.

The fracture surfaces of the specimens broken in the flexure test were examined using an Amray IV scanning electron microscope (Amray, USA) to identify the failure modes.

3. Results and discussion
3.1. Elastic modulus in flexure
The longitudinal (E_L^{flex}) and transverse (E_T^{flex}) elastic moduli before and after exposure to water at 85 °C for 100 h were measured in flexure for span/thickness ratio (L/d) varying from 16 to 30. An analysis of the data is given in the Appendix and the results are shown in Fig. 1 and Table III.

There was no significant effect of the L/d ratio on the longitudinal modulus (E_L) over the range studied, suggesting that the effect of shear deformation on the total deflection is negligible under the experimental conditions used. Slight differences in E_L for com-

posites with different matrices can be attributed to an imperfect alignment of the fibres, caused by a small amount of flow in the mould, slight differences in the fibre content and the presence of minor defects introduced in the course of sample preparation. On the other hand, all values of longitudinal moduli are higher than the tensile modulus predicted using a simple rule-of-mixtures [10]

$$E_{cL} = v_f E_f + (1 - v_f)E_m \qquad (1)$$

where E_f and E_m are the tensile moduli of the fibre and matrix and v_f is the fibre volume fraction. The calculations of flexural modulus from tensile modulus are shown in the Appendix. The calculated values using Equation A4 are shown in Table III. The measured values of E_L^{flex} are somewhat greater than those predicted by Equation A4, whereas the measured transverse values are somewhat lower than the calculated values (Table III).

The exposure to water at 85 °C for 100 h caused only a minor reduction in the E_L^{flex} modulus (Fig. 1 and Table III), since after drying the interfacial friction assured transmission of sufficient load from the matrix to the long fibres at a very low strain level. It can be concluded that there is no significant effect of moisture on the longitudinal modulus under the conditions used, probably because the fibres, controlling the longitudinal behaviour of FRC wire, are not deteriorated by the moisture attack during a relatively short exposure.

TABLE II The yield strength of neat matrices under different loading conditions at room temperature

Matrix	Matrix yield strength (MPa)		
	In tension	In compression	In flexure
PC (Lexan 181)	62	85	97
PC (Lexan 181)[a]	78	106[b]	121
PETG (Kodak copolyester 6763)	49	62	70
Nylon 12 (Rilsan AMNO)	53	69	83

[a] Annealed at 275 °C for 1 h, dried at 100 °C for 100 h.
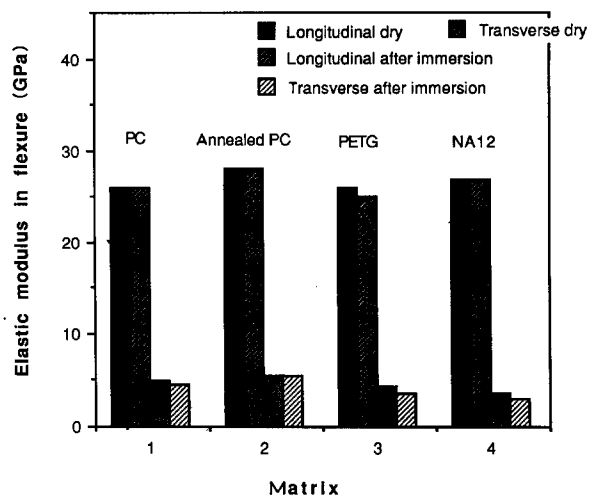[b] Estimated value.

Figure 1 Longitudinal and transverse elastic moduli in flexure for polycarbonate (PC), annealed PC, poly(ethyleneterephthalate glycol) (PETG) and nylon 12 (NA12) based composites with 30 vol % E-glass fibres, dry and after 85 °C water immersion for 100 h and 100 h drying at 100 °C.

TABLE III Elastic moduli of the materials studied, measured at room temperature

Material, $v_f = 0.30$	E_L^{flex} (GPa)	$(E_L^f)^{calc}$ (GPa)	E_L (GPa)	E_T^{flex} (GPa)	$(E_T^f)^{calc}$ (GPa)	E_T (GPa)
PC	26(26)	24.6	23.2	4.9(4.5)	5.1	4.9
PC[a]	28(28)	24.9	23.5	5.4(5.4)	6.0	5.7
PETG	26(25)	24.5	23.1	4.3(3.6)	4.9	4.7
Nylon 12	27(27)	24.4	22.9	3.7(3.1)	4.5	4.0

Values in parentheses are after exposure to water at 85 °C for 100 h and 100 h drying at 100 °C.
[a] Annealed at 275 °C for 1 h.

After the exposure to water a reduction in E_T^{flex} is observed of the order of 10–20% for all composites investigated, except for polycarbonate/E-glass annealed at 275 °C for 1 h before water exposure (Fig. 1). The E_T^{flex} modulus for annealed polycarbonate/E-glass remained unchanged after the immersion. Since the transverse properties are matrix-controlled, this can be attributed to the moisture-resistant properties of the matrix. The resistance of polycarbonate to moisture absorption is superior to that of poly-(ethyleneterephthalate glycol) and nylon 12, thus accounting for its better performance (Figs 2 and 3). Water immersion causes partial softening of polyamid matrix. The hydrolytic reduction in molecular weight of the poly(ethyleneterephthalate glycol) polyester probably accounts for its loss of stiffness.

The E_T^{flex} modulus for annealed polycarbonate/ E-glass remains unchanged after immersion. The development of an ordered interphase layer near the fibre surface increases both the elastic modulus of the matrix phase and its resistance to moisture, thus protecting the interface from dewetting and micro-cavitation phenomena under stress [23, 24]. This is confirmed by the results of fractographic analysis published earlier [21].

3.2. Longitudinal strength and strain-to-break in flexure

The mode of failure of unidirectional composites in flexure is very complex. Strength is commonly reported as the maximum on a stress–strain curve; however, in order to interpret its meaning it must be accompanied by a description of the failure mode. When loaded in flexure a unidirectional FRC can fail in tension either longitudinally or transversely, or in shear in the matrix, interphase or fibre [25]. The most common modes of failure are transverse splitting, brittle tensile failure with fibre pullout, interfacial shear failure, compressive failure due to micro-buckling or localized kinking of fibres and intra-laminar shear failure.

The beams with span/thickness ratio $(L/d) < 25$ exhibited failures by fibre buckling localized in very narrow bands (kink bands). This failure mode was first observed in carbon fibre-reinforced epoxy loaded either in flexure or in compression [25–27]. The microprocess is accompanied by some relief of local stresses as the crack propagates from the compressive side to the neutral plane. Further deflection of the beam causes a tensile failure of fibres on the tensile side of the beam, which leads to a catastrophic failure of the specimen. In some cases a small amount of intralaminar shear failure, initiated from the kink bands, was observed on the compressive side. However, none of the tested materials failed catastrophically due to an intralaminar shear failure or matrix transverse splitting. Constraints imposed on the beam by contact with the load pin probably inhibit the initiation of buckling. The ductility of the matrices was sufficient to inhibit transverse splitting at these fibre volume fractions.
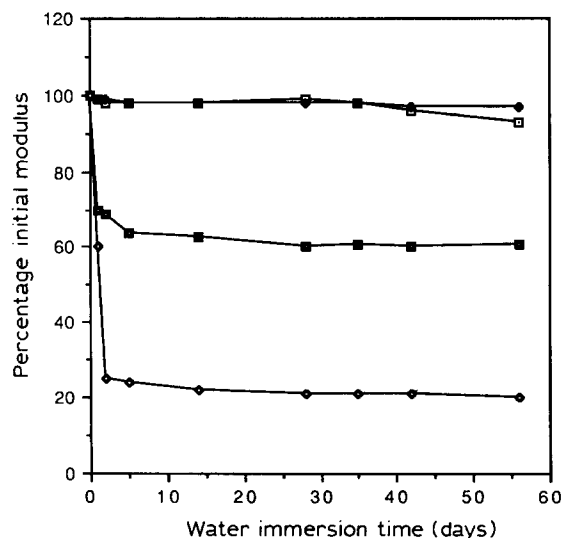

Figure 2 Dependence of the percentage initial elastic modulus in flexure for actual orthodontic wires on the period of water immersion [37 °C, 40° deflection, span length 1 in. (25.4 mm) measured for $L/d = 20$]. ($\blacklozenge$) Polycarbonate/40 vol % S2-glass fibres, ($\square$) polycarbonate/40 vol % E-glass fibres, ($\blacksquare$) neat polycarbonate and ($\diamond$) neat poly(ethyleneterephthalate glycol).
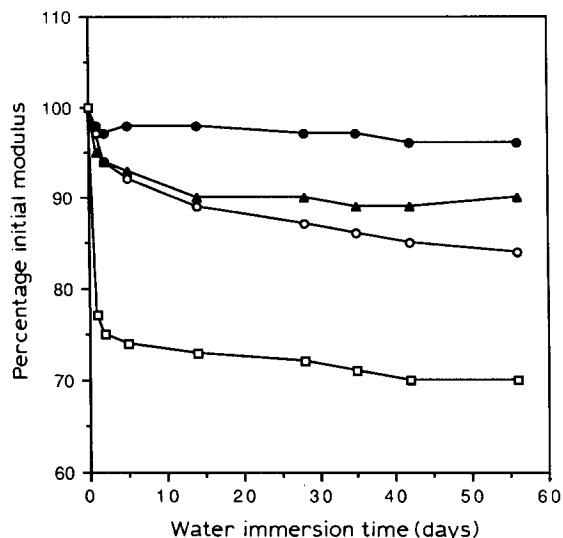

Figure 3 Effect of the matrix and fibre type on the retention of the percentage initial modulus for a series of actual orthodontic wires after immersion in water at 37 °C and deflection of 20° at a span length of 1 in. (25.4 mm). Modulus measured immediately after the removal from the water with $L/d = 20$. ($\bullet$) Polycarbonate/S2-glass, ($\blacktriangle$) nylon 12/S2-glass, ($\bigcirc$) poly(ethyleneterephthalateglycol)/ S2-glass and ($\square$) poly(ethyleneterephthalate glycol)/Kevlar 49.

The measured longitudinal flexural strength and strain-to-break for E-glass fibre-reinforced polycarbonate, annealed polycarbonate, nylon 12 and poly(ethyleneterephthalate glycol) are shown in Table IV and Figs 4 and 5. The longitudinal strengths were higher than the tensile strengths predicted by the rule-of-mixtures. This is not surprising, since the ratio between flexural and tensile strength varies commonly from 1.4 to 1.8 for a quasi-brittle matrix reinforced with E-glass fibres [28]. This phenomenon is often attributed to a shift of the neutral axis caused by a

TABLE IV Flexural strength and ultimate strain of the materials
studied

Material, $v_f = 0.30$	σ_L^{flex} (MPa)	ε_L^{flex} ($\times 10^2$)	σ_L^{flex} (MPa)	ε_L^{flex} ($\times 10^2$)
PC	965(992)	2.2(2.0)	83(63)	1.0(1.0)
PC[a]	1068(1024)	2.5(2.4)	137(124)	2.2(3.0)
PETG	750(720)	1.5(1.6)	75(51)	2.2(2.1)
Nylon 12	880(890)	1.9(2.2)	116(93)	2.2(2.2)

Values in parentheses are after exposure to water at 85°C for 100 h
and 100 h drying at 100°C.
[a] Annealed at 275°C for 1 h.

matrix cracking or yielding. However, a non-uniform
fibre distribution and the presence of interfacial de-
fects can result in an identical effect. The longitudinal
strains-to-break were of the order of the strain-
to-break of the fibre, as expected.

Both the longitudinal flexural strength and the
ultimate strain in flexure are unaffected by the ex-
posure to water at 85 °C for 100 h (Figs 4 and 5).
Since these properties are fibre-dependent, the relative
stability of the glass fibres and relatively low permeab-
ility of the matrices combine to maintain the longitud-
inal properties for short periods of immersion.

3.3. Transverse strength and strain-to-break
The transverse properties of unidirectional composites
are primarily matrix-controlled [29]. An enhanced
matrix–fibre adhesion can modify the character of the
local stress fields and a connectivity of the yielded
microzones adjacent to neighbouring fibres and, thus,
increase the transverse strength of the composite [30].
The transverse failure modes in flexure are tensile
(matrix tensile failure, debonding or fibres splitting) or
compressive (matrix shear failure or shear failure with
debonding and fibre crushing). In the composite
beams studied, the failure was always initiated on the
tensile side of the beam, accompanied by relatively
extensive non-linear stress–strain behaviour before a
catastrophic failure. It may be assumed, since there is
no observed fibre splitting, that matrix tensile failure
and debonding of constituents are the most likely
failure mechanisms. In all cases studied the transverse
strength was near the yield strength of the matrix.
Differences can be associated with modification of the
morphology of the matrix phàse due to the presence of
the fibres and to the quality of the adhesion between
components.

Ultimate failure is controlled by the strain magni-
fication caused by the presence of fibres. The lower
limit for ultimate strain is in the case of "perfect"
adhesion given by [31]

$$\varepsilon_{uc} = \varepsilon_{um}(1 - v_f^{1/3}) \tag{2}$$

where ε_{uc} and ε_{um} are the ultimate strains of the
composite and matrix, respectively. For $v_f = 0.3$ the
ultimate strain of the composite is about 0.3 times that
of the neat matrix. Using the yield strains reported in
Table I, composite ultimate strains in the range of
2–3% can be calculated, in good agreement with the
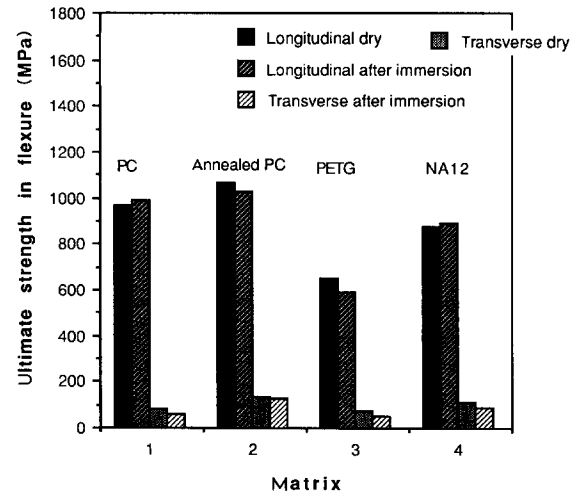experimental values.

Figure 4 Longitudinal and transverse strength in flexure for
polycarbonate (PC), annealed PC, poly(ethyleneterephthalate
glycol) (PETG) and nylon 12 (NA12) based composites with
30 vol % E-glass fibres, dry and after 85 °C water immersion for
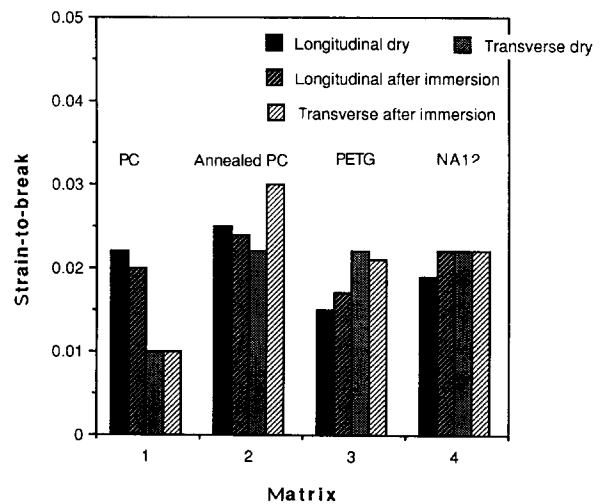100 h and 100 h drying at 100 °C.

Figure 5 Longitudinal and transverse strain-to-break in flexure for
polycarbonate (PC), annealed PC, poly(ethyleneterephthalate
glycol) (PETG) and nylon 12 (NA12) based composites with
30 vol % E-glass fibres, dry and after 85 °C water immersion for
100 h and 100 h drying at 100 °C.

In all cases immersion in water at 85 °C for 100 h
caused a significant deterioration of the transverse
strength, even after drying. In the matrices studied
plasticization due to water absorption, hydrolysis of
the matrix caused by transesterification [in poly-
(ethyleneterephthalate glycol)] and degradation of the
matrix–fibre interface by chemisorption of the water
at the interface all contributed to the irreversible
degradation of the transverse strength. Results of a
preliminary study on the effect of water immersion on
a series of òrthodontic wires using S2-glass, E-glass
and Kevlar-49 fibre-reinforced polycarbonate, poly-
(ethyleneterephthalate glycol) and nylon 12, measured
under simulated clinical conditions, parallel the
above-mentioned results (Figs 2 and 3).

4. Conclusions

The use of fibre-reinforced thermoplastic composites for orthodontic wire appliances are usually justified on the basis of aesthetics, ease of fabrication under clinical conditions, and the high stiffness and strength of these materials. In this and previous studies we have shown that the limiting factors in the practical utilization of these materials are the weakness and relative instability in a moist environment of the transverse strength and ultimate strain-to-break. A further difficulty is that when used in span–depth ratios below 15 damage at the clamping points, caused by high strain, results in a significant loss of longitudinal stiffness [22]. We estimate that in most cases the maximum allowable flexural strain is limited to 2%, thus limiting the utility of the FRC orthodontic wire to the latter stage of treatment.

The behaviour of these materials in clinical situations will be strongly dependent on the choice of matrix thermoplastic. Ideally, a water-impermeable plastic which bonds strongly to the fibre reinforcement should be sought. In our survey of a variety of E-glass fibre-reinforced thermoplastics we have found that a composite of bare E-glass fibres, devoid of the usual sizing and coupling agents, in a matrix of poly-carbonate and annealed for a period at 270–275 °C, exhibits the most satisfactory performance. Apparently, when the composite is annealed, the poly-carbonate forms a highly oriented (or perhaps trans-crystalline) layer on the bare E-glass surface, which is both well-bonded and water-impermeable. The transverse properties of the composite appear to have higher retention after long-term immersion in water, and thus favour this material for further clinical applications as an orthodontic wire.

Appendix

The three-point bending test is depicted schematically in Fig. 2. The maximum deflection in the centre of the homogeneous isotropic slender beam is, in the case of ideal bending, expressed as [32]

$$\delta = PL^3/(48E^{flex}I) \tag{A1}$$

where P is the applied force, I is the moment of inertia of the beam, L is the span length and E^{flex} is the elastic modulus of the beam in flexure. For a rectangular beam of width b and thickness d, Equation A1 can be used to determine the elastic modulus in flexure

$$E^{flex} = \frac{1}{4}[PL^3/(bd^3\delta)] \tag{A2}$$

For deep or short beams, a shear contribution to the total deflection must also be considered [29]. Assuming that the pure bend and shear deflections are independent, the total deflection in the centre of a centrally loaded simple supported beam can be written as [33]

$$\delta = PL^3/(48E^{flex}I) \{1 + \frac{3}{2}[1 + (E/2G)](d/L)^2\} \tag{A3}$$

where E is the tensile modulus in the direction of the beam length and G is the in-plane shear modulus. For

materials with E/G of the order of 16, which is typical for these composites, and span/depth ratio of 16–30, the shear contribution is of the order of 1–6% of the total deflection. This is comparable with the experimental error, and therefore the shear correction may be neglected.

Since the flexural loading is, in an ideal case, a combination of tension and compression, E_L^{flex} cannot be generally considered as a material property. The flexural modulus is equal to the tensile modulus only in the case when the tensile and compressive moduli are equal. However, commonly, the compressive and tensile moduli for glass fibre-reinforced composites differ by of the order of 20% [34]. The ratio between the flexural and tensile moduli of a homogeneous isotropic beam can be estimated as [32]

$$E^{flex}/E^{tens} = \{2(E^{tens}/E^{comp})^{1/2}/[1 + (E^{tens}/E^{comp})^{1/2}]\} \tag{A4}$$

A value of $E^{tens}/E^{comp} = 1.21$ was used to obtain the calculated values of E^{flex} in Table III. The effect described can be visualized as a shift of the neutral axis from the central plane of the beam.

A maximum stress of σ_{xx} in the direction of the beam main axis is, at the outer planes of the beam,

$$\sigma_{xx} = 3PdL/bd^3 \tag{A5}$$

The maximum strain ε_{xx} can be expressed as

$$\varepsilon_{xx} = 6\delta(d/L^2) \tag{A6}$$

All of the above expressions are derived for a homogeneous, isotropic material. It was, however, shown, using finite-element analysis, that the usual assumptions for an isotropic beam are also valid in the case of orthotropic materials subject to three-point bending, except for the calculation of the shear stress [35].

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