Water Sorption and Dimensional Stability of Three Glass Fiber–Reinforced Composites

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Purpose: Water sorption and dimensional stability of three fiber-reinforced composites were studied. Two composites (Vectris, FibreKor) were resin impregnated industrially, and one composite (Stick) was polymer preimpregnated but required further manual impregnation. ***Materials and Methods:*** Bar-shaped specimens of each material were prepared according to manufacturers' instructions. The water sorption and dimensional change of each specimen were calculated according to the change in its weight and dimension before and after immersion. Specimens were immersed in distilled water for 1, 7, 60, and 180 days. SEMs were taken to examine the quality of the fiber-matrix interface. The volume percentage of fiber content of each fiber-reinforced composite was experimentally estimated. ***Results:*** A general trend of increasing water sorption for each immersion period according to the material type was: Vectris < FibreKor < Stick. There were no significant differences in dimensional change among the materials and immersion periods. ***Conclusion:*** The preimpregnated fiber-reinforced composite (Stick) showed higher water sorption than the industrially impregnated fiber-reinforced composites (Vectris, FibreKor). Despite a variation in the water sorption of the fiber-reinforced composites studied, all were within a 32 μg/mm^3 criterion established by the ISO. The magnitude of dimensional change was small enough that it should not raise any significant clinical concern. *Int J Prosthodont 2004;17:195–199.*

Fiber-reinforced composite (FRC) materials used in dentistry frequently consist of glass fibers embedded in a methacrylate resin. Water is absorpted into the methacrylate resin by the process of diffusion. Water molecules ingress into the vacancies between the polymeric chains and push the chains further apart to cause an expansion.[1] The dimensional change of the resin because of water sorption is small and probably insignificant.[1,2] Drying of the resin reverses the dimensional change. However, the repeated wetting and drying of resin of the denture base will cause an irreversible warpage of the denture.[2] Absorbed water molecules also act as plasticizers to facilitate the movement of polymeric chains. One of the plasticizing effects is to facilitate the relaxation of internal stresses built up in the polymeric chains during polymerization. The stress relaxation could contribute to shape change.[2] In addition to altering the dimensions of the resin, water sorption causes a reduction in its strength. It is well-documented that water sorption into methacrylate denture base or denture reline materials decreases their strength.[3–6] It is also evident that water sorption decreases the strength of some FRCs.[7–9]

The amount of water sorption into the FRC matrix is affected by several factors. Water sorption generally increases with a decrease in the percentage fiber content of the FRC. This is due to an increase in the relative portion of water-absorbing polymer matrix in the FRC as the percentage fiber content decreases.[9,10] The inclusion of unidirectional or woven E-glass fibers in heat-cured polymethyl methacrylate (PMMA) denture resin was shown to decrease water sorption and improve dimensional stability.[11] However, the use of a type of experimental "prefabricated glass-fiber reinforcement" containing approximately 0.11 g PMMA

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Table 1 Fiber-Reinforced Composite (FRC) Materials Studied[10]

FRC core material	Lot No.	Composition	Fabrication procedure
Vectris Pontic, Ivoclar Vivadent	D94030	bis-GMA (24.5%), decandiol dimethacrylate (0.3%), triethyleneglycol dimethacrylate (6.2%), urethane dimethacrylate (0.1%), highly dispersed silica (3.5%), catalysts and stabilizers (< 0.3%), pigments (< 0.1%), resin-impregnated glass fibers (65.0%)	Initial polymerization for 1 min with light-curing unit (Targis Quick, Ivoclar Vivadent); final polymerization in light- and heat-curing unit (Targis Power, Ivoclar Vivadent) for 25 min
FibreKor, Jeneric/Pentron	57486	Resin-impregnated S-glass fibers (≈ 60%) in 100% bis-GMA matrix	Initial polymerization for 1 min with light-curing unit (Alfa Light II, Morita); final polymerization in light-curing unit (Alfa Light II) for 15 min
Stick, StickTech	1010321-R-0058	E-glass fibers preimpregnated with PMMA	Wetting of fibers with Stick Resin (StickTech); polymerization as for FibreKor

powder was shown to adversely affect dimensional accuracy of autopolymerizing and heat-cured PMMA denture resins. The diminished accuracy attributed to the fiber reinforcement was thought to be caused by the higher polymerization shrinkage, as the monomer liquid added during preparation reacted with the PMMA contained within the glass-fiber reinforcement.[12]

The hydrophilicity of the matrix polymer also affects water sorption. More hydrophilic resins, such as 2-hydroxyethyl methacrylate (HEMA) and bis-GMA, absorb more water than PMMA.[8,10] Furthermore, insufficient impregnation of fibers by the resin leaves air voids in the FRC that are susceptible to water sorption.[7–10] Traditionally, the preparation of an FRC for clinical use involves a tedious silanization process of the glass fibers. The impregnation of fibers following such a process and their adhesion to the matrix are variable.[7]

A few commercially available FRC systems, such as Vectris, FibreKor, and Stick (Table 1), are based on the use of resin-impregnated or polymer-preimpregnated glass fibers and standardized systems of fabrication to maximize fiber compaction and minimize air voids. Vectris and FibreKor were developed for primary use in fixed prosthodontics. Stick was originally developed for powder-liquid acrylates but found applications in fixed prosthodontics. Its use required further impregnation with resin. The purpose of the present study was to investigate the water sorption and dimensional stability of representative FRCs of these three systems. The hypothesis of the study was that there would be no significant difference in water sorption and dimensional stability of these FRCs.

Materials and Methods

Three FRCs, Vectris Pontic, FibreKor, and Stick, containing unidirectional glass fibers were selected for the study. The experimental protocol was adapted from ISO 10477:1992(E) for polymer-based crown-and-bridge materials.[13] Thirty-two bar-shaped specimens of each material were polymerized according to manufacturers' instructions in a Teflon (DuPont) mold with a cavity of 2 mm × 2 mm × 25 mm with the orientation of the unidirectional fibers placed along the length of each specimen. The materials were polymerized initially in the mold under a slide glass cover and then removed from the mold for final polymerization (Table 1). The length of each specimen was measured three times (± 0.01 mm) using a measuring microscope (PRM-2XYZ, Pika Seiko). The mean length of each specimen (D1) was calculated.

The polymerized specimens were transferred to a desiccator containing anhydrous silica gel maintained at 37 ± 1°C. After 24 hours, the specimens were transferred and stored in another desiccator maintained at 23 ± 1°C for 1 hour, and then weighed in an electronic scale (A 120 S, Sartorius) to an accuracy of ± 0.2 mg. Desiccation was repeated until a constant mass was obtained, ie, until the mass loss of each specimen was not more than 0.2 mg in any 24-hour period. The specimens were divided into four groups of eight for each material and were immersed in distilled water at 37 ± 1°C for 1, 7, 60, and 180 days. After immersion, each specimen was washed with water, blotted until its surface was free of visible moisture, waved in air for 15 seconds, and weighed 1 minute after removal from water (M1). The mean of three measurements of its length was expressed as D2. After this weighing, the specimens were reconditioned to constant mass (M2) in the desiccators as described earlier.

$$\text{Water sorption } (\mu g/mm^3) = (M1 - M2)/V$$
$$V = \text{volume of specimen} = 100\ mm^3\ (2\ mm \times 2\ mm \times 25\ mm)$$
$$\text{Change in dimensions } (\%) = (D2 - D1)/D1$$

The data were analyzed statistically using two-way analysis of variance (ANOVA). Factors were time and material. One-way ANOVA and Newman-Keuls post hoc comparison were applied when appropriate (95% confidence level). All tests were performed under

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Table 2 Water Sorption (μg/mm^3) and Dimensional Change (%) of Tested Fiber-Reinforced Composites

	1 d		7 d		60 d		180 d	
Material	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Water sorption*								
Vectris	5.4^{a}	0.9	7.3^{ab}	0.9	8.6^{ab}	0.9	9.4^{bc}	1.1
FibreKor	8.0^{ab}	1.6	11.6^{c}	1.7	14.4^{d}	1.8	16.3^{d}	2.4
Stick	15.9^{d}	2.7	23.6	2.2	39.1^{e}	5.2	40.9^{e}	5.2
Dimensional change								
Vectris	0.02	0.06	0.04	0.08	0.04	0.07	0.06	0.15
FibreKor	–0.01	0.15	0.00	0.04	0.02	0.64	0.11	0.08
Stick	0.01	0.05	0.03	0.06	0.05	0.10	0.03	0.09

*No statistically significant difference between groups with the same superscripted letter (one-way ANOVA, Neuman-Keuls; $P > .05$).
SD = standard deviation.

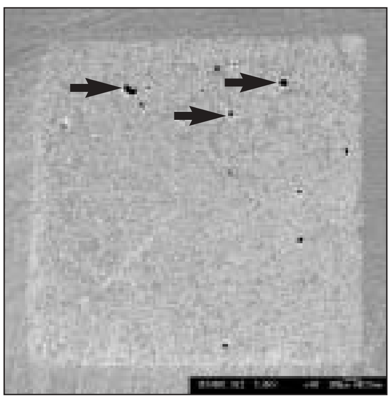

Fig 1 Cross-section of Vectris. *Arrows* = voids.

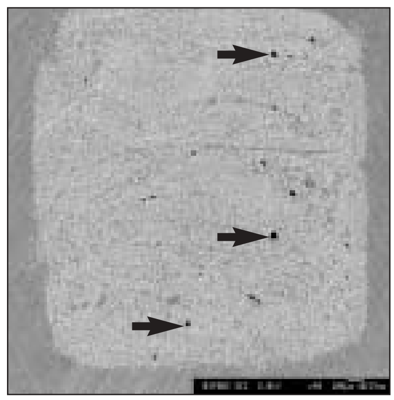

Fig 2 Cross-section of FibreKor. *Arrows* = voids.

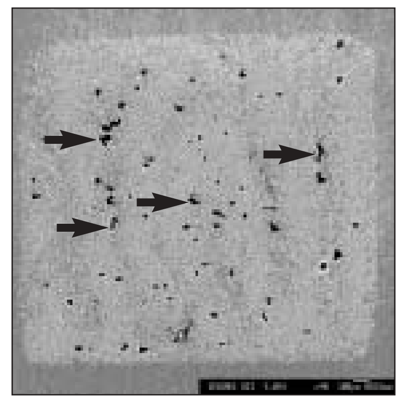

Fig 3 Cross-section of Stick. *Arrows* = voids.

uniform atmospheric conditions of 23.0 ± 1°C and 50% ± 1% relative humidity.

Representative specimens of the FRCs were embedded in resin and prepared for scanning electron micrographs (SEM). SEMs of the cross-sections of these specimens were taken at 40× and 500× to study the quality of the interface between fibers and their matrix and the presence, if any, of flaws, voids, or porosities.

The fiber content (vol%) of each FRC was determined by an ashing method.[14] Four specimens of each FRC were desiccated for 36 hours at 37°C and weighed to an accuracy of 1 mg. The specimens were then ashed for 45 minutes at 700°C. The weight of each specimen was measured before and after ashing with an electronic scale. The fiber content was calculated with the following formula:

$$V_g = W_g/\rho_g \div (W_g/\rho_g + W_r/\rho_r)$$

where V_g = vol% of fiber; W_g = wt% of fiber; ρ_g = density of fiber (Vectris: 2.53 g/cm^3, FibreKor: 2.43 g/cm^3, Stick: 2.54 g/cm^3); W_r = wt% of matrix; and ρ_r = density of matrix (Vectris: 1.18 g/cm^3, FibreKor: 1.18 g/cm^3, Stick: 1.19 g/cm^3).[8,15]

Results

Two-way ANOVA revealed significant differences ($P <$ .05) in water sorption attributed to material type, period of immersion, and interaction between these two variables. One-way ANOVA and Newman-Keuls post hoc comparison showed that water sorption increased with time for all materials ($P < .05$). A general trend of increasing water sorption for each immersion period according to the material type was: Vectris < FibreKor < Stick. Stick specimens of any immersion period showed significantly higher water sorption than any Vectris specimens. The amount of water sorption for each material became not significantly different between the 60- and 180-day specimens ($P > .05$; Table 2). Two-way ANOVA revealed no significant differences in dimensional change among the materials and immersion periods ($P > .05$; Table 2).

SEM of representative specimens of the three FRCs at 40× revealed the presence of voids within their matrices (Figs 1 to 3). The voids within Vectris and FibreKor appeared randomly located, scarcely dispersed, and did not exceed 100 μm in size. The voids within Stick assumed more complex shapes, were more frequently

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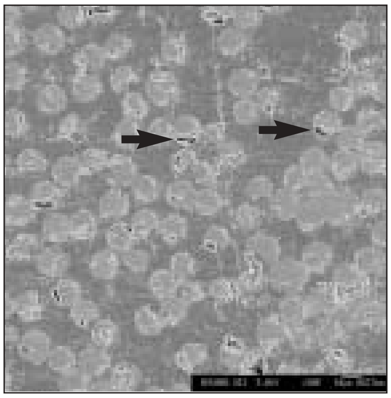

Fig 4 Vectris fibers in cross-section embedded in resin matrix *(darker background). Arrows* = voids.

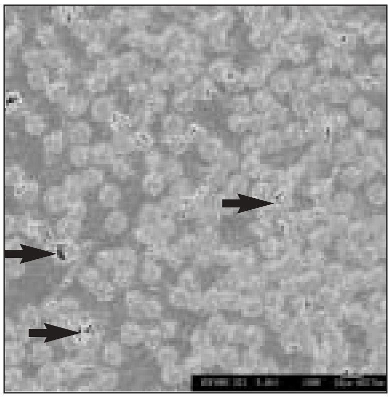

Fig 5 FibreKor fibers in cross-section embedded in resin matrix *(darker background). Arrows* = voids.

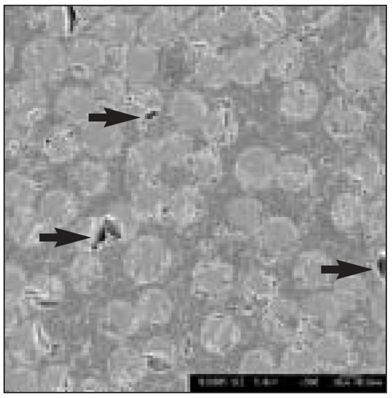

Fig 6 Stick fibers in cross-section embedded in resin matrix *(darker background). Arrows* = voids.

encountered, and exceeded 100 µm in size in some instances. At 500× magnification, the impregnation of the fibers for the three FRCs was generally good. Most prominent voids were located at or proximal to the fiber-matrix junction (Figs 4 to 6). The fiber contents of Vectris, FibreKor, and Stick were, respectively, 46.5% (standard deviation [SD] 0.6), 45.2% (SD 1.3), and 51.8% (SD 1.3) .

Discussion

Water absorbs into the FRC polymeric material by diffusion, a time-dependent process. As water molecules ingress into the FRC, unreacted monomer molecules and other small-size constituents egress from the FRC until an equilibrium is achieved wherein the weight of the FRC becomes essentially constant.[4,6,16] The water sorption measurement actually measured the net gain in weight of a specimen as a result of the ingress of water molecules and egress of monomers and other small molecules. The water sorption of all three FRCs gradually increased until 60 days; further immersion up to 180 days did not significantly change their water sorption. Thus, it appeared that the three FRCs achieved water sorption equilibrium sometime between 7 and 60 days.

The hypothesis that the three FRCs were not significantly different in water sorption was accepted. The present results suggested that water sorption among the FRCs in general, arranged in increasing order, was: Vectris < FibreKor < Stick. An FRC matrix of bis-GMA, such as that of Vectris or FibreKor, favors water absorption over a PMMA matrix, such as that of Stick, because of the higher hydrophilicity of bis-GMA. The matrix composition of the three FRCs does not explain the magnitude of water sorption among them, possibly because of the relatively low PMMA content in Stick (≈ 3% mass of the FRC) not imparting any significant effect. An FRC with a larger percentage matrix volume is likely to absorb more water. Stick possessed higher fiber content (51.8%) in comparison to Vectris (46.5%) or FibreKor (45.2%), which were similar. The lowest percentage matrix volume of Stick among the FRCs does not explain why its water sorption was the highest.

Defects such as voids, cracks, and unbonded interfaces within the FRC increase water sorption and may increase the susceptibility of the FRCs to mechanical failure. From the SEMs obtained, it appeared that the fibers of all three FRCs were reasonably well impregnated by the matrix resin. However, more voids were present within the matrix of Stick than either Vectris or FibreKor, particularly at or near the fiber-matrix junction. It is known that manufacturing or preparation processes that encourage the inclusion of such defects in the FRC increase the probability of water sorption.[8,10,17] The different preparation processes of the three FRCs may explain the difference in water sorption. The heat and light preparation process of Vectris is said to increase compaction between laminates of the material and decrease defects. The longer polymerization time of Vectris likely resulted in a higher degree of conversion and cross-link density. FibreKor and Stick use manual adaptation of their fibers, so compaction may be lower than that of Vectris. Furthermore, Stick fibers as manufactured are glass fibers impregnated with a highly porous PMMA polymer matrix that requires the additional process of wetting with a solvent-free resin or a liquid-powder resin mixture. Conversely, impregnated fibers of Vectris and FibreKor do not require wetting prior to use. The fiber polymer preimpregnation process used for Stick, which is partly user controlled, might have resulted in more defects and correspondingly accounted for higher

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water sorption. It should be noted that the manufacturer of Stick has recently developed a polymer-monomer gel-impregnated glass fiber specifically for fixed prosthodontics application. The material is purported to be more homogenous in structure.

Save for the dimensions of the specimens, the method of determining water sorption in the present experiment was identical to that of ISO 10477:1992(E) for polymer-based crown-and-bridge materials.[13] The ISO specification mandates that the water sorption of materials not exceed 32 µg/mm^3 after 7-day immersion. All three FRCs met the criterion for the 7-day specimens. The hypothesis that the three FRCs were not significantly different in water sorption was accepted. There were no significant differences in dimensional change among the FRCs studied. The dimensional changes were of an order between 0.01% and 0.10%. Such magnitude of change is unlikely to be of any significant clinical concern.

Conclusions

Under the conditions of the present experiment, the following conclusions can be drawn:

1. The amount of water absorbed into each FRC studied generally increased with time.
2. The water sorption by the FRCs, in increasing order, was: Vectris < FibreKor < Stick. Water sorption at 7 days by all FRCs was within 32 µg/mm^3, a criterion adopted from ISO 10477:1992(E) for polymer-based crown-and-bridge materials.
3. All FRCs were considered dimensionally stable.

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