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Behaviour of photopolymerized silicate-glass-fibre-reinforced dimethacrylate composites subjected to hydrothermal ageing

Part I *Steady-state sorption characteristics*

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Steady-state water sorption due to hydrothermal ageing (37 °C) was determined via gravimetric methods for both an unreinforced dimethacrylate copolymer network and for composites of the copolymer reinforced with two different silicate yarn products – S2-glass® and quartz. The copolymer sorbed 4.9 ± 0.3 wt% and the composites sorbed 0.5–2.5 wt%. For the two types of composites, two different positive linear correlations were established between the sorption gain and the copolymer content in the composites. In the case of the S2-glass® composites, the sorption gain was fully explained in terms of sorption in the copolymer; and normalization of these data by the mass fraction of copolymer yielded a constant sorption value matching that of the unreinforced copolymer. After normalizing the data for the quartz composites, an additional positive correlation was established between the water gain (per unit weight of copolymer) and the linear density of interfacial surface area. For both types of composites the sorption response was stable over a three-month ageing period. © *1998 Chapman & Hall*

1. Introduction

While composite materials have enjoyed wide acceptance in the defense, aerospace, transportation, and construction industries, their use as medical implants is limited by stringent biocompatibility constraints and the harsh environment of the body. One exception is the use of particulate-reinforced dimethacrylates as dental restoratives, which followed Bowen's introduction of silica-reinforced *bis*-GMA in the late 1950s [1–3]. If these dimethacrylate composites were further developed, via the replacement or augmentation of particulate reinforcement with long-fibre reinforcement, the excellent *in vivo* performance might be exploited in a broader range of applications – including non-compressive load bearing. This prospect has prompted the authors' development of a new composite-forming process called photo-pultrusion [4, 5] and their investigation of its utility in forming unidirectional-fibre-reinforcement-plastic (UFRP) composites from photo-activated dimethacrylate copolymers and continuous silicate-glass fibres. Because the continuous reinforcement is not amenable to special treatment of the fibre surfaces, particular emphasis is placed on identifying "off-the-shelf" reinforcement products that will bond readily with the dimethacrylate copolymer in the photo-pultrusion process.

Although the basic mechanical properties of several pristine UFRP materials was highlighted in previous work [6], the behaviour of these materials in a warm aqueous environment was unknown. Part I of this study focuses on the steady-state sorption behaviour of hydrothermally aged photo-pultruded UFRP composites made with two different commercially prepared silicate-glass yarn products; Part II [7] focuses on the concomitant degradation in the mechanical properties.

Kalachandra and Turner [8] studied water sorption in photopolymerized copolymer networks of *bis*-GMA with triethylene glycol dimethacrylate (TEGDMA) and found that the water gain varied from 3–6 wt% as the proportion of TEGDMA varied from 0–100 wt%. Kalachandra and Kusy [9] later reported water gains of 1.4 and 6.2 wt% for homopolymers of *bis*-GMA and TEGDMA, respectively, that were prepared by gamma irradiation. In a study on the effect of fillers on water sorption in composites [10], Kalachandra reported a water gain of 7.15 wt% for a pure TEGDMA polymer that was prepared by heating with a peroxide initiator.

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However, when two types of inorganic filler particles were added to form composites, they sorbed either at or above the level expected based upon the proportion of polymer in the composites. Similarly, Kalachandra and Wilson [11] reported a gain of 3.85 wt% in a *bis*-GMA/TEGDMA copolymer mixed in a mass ratio of 3/1, but the addition of silanated silicate fillers increased the gain in the composites above what was attributable to the copolymer alone. In both of these latter two studies, the filler–matrix interface was suspected of accommodating excess water.

In the current study the water sorptions of *bis*-GMA/TEGDMA fibre-reinforced composites and unreinforced copolymer are examined using gravimetric methods. The influences of filler amount, filler type, and interfacial surface area are determined via regression analysis and statistical inference. The filler amount is highlighted as the most influential parameter, and the interfacial surface area plays an additional minor role for one of the filler types.

2. Materials and methods

2.1. Preparation of materials

2.1.1. Composite specimens

Composites were formed from a photopolymerized copolymer network reinforced with continuous 9 μm diameter filaments of either S2-glass® (Owens Corning Co., Toledo, OH, USA) or quartz (Quartz Products Co., Louisville, KY, USA) (fused silica). The comonomer was prepared from *bis*-GMA (Polysciences Inc., Warrington, PA, USA) and TEGDMA (Polysciences Inc., Warrington, PA, USA) mixed in a 61/39 mass ratio with 0.4 wt% benzoin ethyl ether (Aldrich Chemical Co. Inc., Milwaukee, WI, USA) added as a UV-initiator. Except for rewinding, the S2-glass® and quartz filaments were used as received, i.e. in the form of yarns having 204 and 120 filaments, respectively, which were prepared with proprietary organosilane sizing agents.

Round-sectioned composite "wire" measuring 0.5 mm in diameter was formed continuously at a linear rate of 1.27 mm s^{-1} via photo-pultrusion, using a Super-Spot MKII UV-lamp (Lesco Inc., Torrance CA, USA) (nominal power ≈ 5 W cm^{-2}). The reinforcement level was varied from 33–66 vol% by changing the number of yarns contained in the composites (Table I).

TABLE I Reinforcement composition of composites studied

Reinforcement filament type	Number of yarns	Reinforcement level (vol %)
S2-glass®	5	33.0
	7	46.3
	8	52.9
	10	66.1
Quartz (fused silica)	9	35.0
	10	38.9
	11	42.8
	12	46.7
	13	50.5
	14	54.4
	15	58.3
	16	62.2

2.1.2. Copolymer specimens

Eight unreinforced copolymer discs measuring 5 mm in diameter by 1.65 mm thick were formed from the comonomer mixture described above. The comonomer was injected into a mould that was formed by a cylindrical hole in a Teflon® sheet sandwiched between two 1 mm thick glass coverslips. The UV-lamp was used to irradiate the specimens via a 1 m liquid light-guide with a 5 mm bore. A timed shutter on the lamp controlled the exposures, as the specimens were irradiated on both sides from a fixed distance of about 4 mm from the end of the light-guide. In order to determine an exposure time that would ensure complete polymerization without excessive degradation, a microhardness test was performed on specimens that were formed using a range of exposure times. The test was performed 23 h post-exposure, using a Kentron® microhardness tester with a Knoop hardness indentor under a 300 g load. A 60 s/side exposure time was selected based upon the results of the test (Fig. 1).

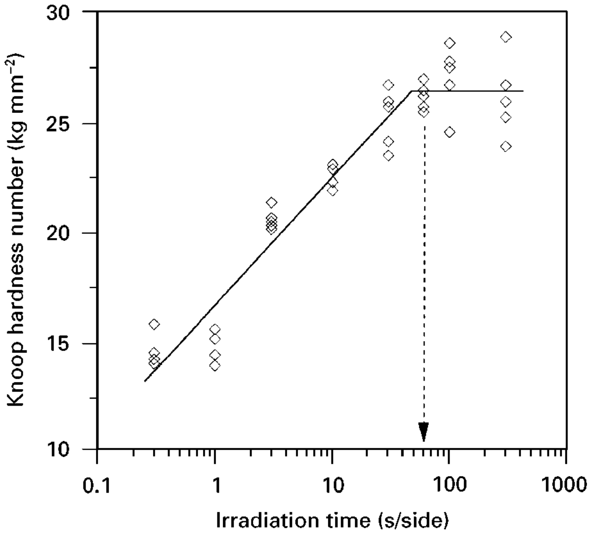

Figure 1 Knoop hardness of photo-polymerized discs, as a function of the irradiation exposure time (s/side), measured 23 h post-exposure. The dashed line highlights the 60 s/side exposure time used to form unreinforced copolymer sorption specimens.

2.2. Experimental procedure

2.2.1. Composites

Short specimens were cut from the continuous material in 60 mm lengths. In order to minimize any contribution to sorption from the crushed regions at the specimen ends (caused by cutting), 3–4 mm of the ends were covered with a quick-setting epoxy (Hardman Inc., Belleville, NJ, USA). After storage in air at 25 °C for 1 d, the specimens were immersed in a 37 °C bath of deionized water. Over the next 3 mon, at times ranging from 1–98 d, a specimen from each material type at each level of reinforcement was withdrawn from the bath. Excess water was immediately removed from the surface of each specimen by gently blotting with Kimwipe® tissue. Blotting was followed by removal of the epoxy-coated ends. Each specimen was weighed (± 0.01 mg) to obtain a "wet" weight (WW). After drying for 2 h under house vacuum (≈0.17 MPa) at 100 °C and cooling to 25 °C in a vacuum desiccator over Drierite® ($CaSO_4$), each specimen was weighed a second time to obtain a "dry" weight (DW). The water gain (WG) was calculated according to

$$\mathrm{WG} = \left(\frac{\mathrm{WW} - \mathrm{DW}}{\mathrm{DW}}\right)100\%. \tag{1}$$

2.2.2. Copolymer

Initial weights were determined for the as-prepared copolymer discs. Ageing was conducted in a 37 °C water bath for 1 mon – a liberal estimate of the time necessary for the system to reach steady-state. This estimate was calculated via the following three steps: (1) obtain a conservative value of the diffusion coefficient for the copolymer ($0.75 \times 10^{-8}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$) [8] ; (2) use this value in Steffan's approximation (for a conventional solution to Fick's laws of diffusion in plane sheet geometry) [12] to calculate the time necessary for the system to reach 90% WG; and (3) multiply the result by an assurance factor of four. After removal from the bath, the specimens were blotted dry and the WW recorded. Drying was accomplished at 100 °C under house vacuum for 17 h, followed by cooling to 25 °C in a vacuum desiccator over Drierite®. The DW was recorded, and the WG was computed according to Equation 1. The content of labile material, i.e. any volatile or water-soluble fraction in the unaged specimens, was calculated via substitution of the initial weight for the WW in Equation 1.

3. Results

3.1. Sorption in composites

Over the span of reinforcement levels and ageing times, the WG values ranged roughly between 0.5 and 2.5 wt% for the S2-glass® composites (Table II) and between 1.5 and 2.5 wt% for the quartz composites (Table III). Relatively little change occurred after the first day. For both types of composites, the most highly reinforced materials sorbed the least, while the copolymer-rich composites sorbed the most. This reverse hierarchical behaviour is illustrated for the S2-glass® composites (Fig. 2).

TABLE II Water gain in S2-glass® composites (wt %)

Reinforcement level (vol %)	Ageing time (d)						
	1	3	7	14	30	62	92
33.0	2.6	2.1	2.5	2.5	2.6	2.3	2.1
46.3	1.5	1.7	1.4	1.2	2.1	1.7	2.0
52.9	1.1	1.3	1.7	1.5	1.7	1.6	1.7
66.1	0.4	1.0	1.0	1.2	1.2	1.5	1.3

TABLE III Water gain in quartz composites (wt %)

Reinforcement level (vol %)	Ageing time (d)						
	1	2	7	14	28	63	98
35.0	2.6	2.1	2.5	2.4	2.4	–	–
38.9	2.2	2.2	2.2	2.2	1.9	2.6	2.6
42.8	1.8	2.1	1.9	2.0	2.1	2.3	2.4
46.7	1.8	2.1	2.4	2.3	2.1	–	–
50.5	1.5	2.1	2.5	2.0	1.6	1.5	2.3
54.4	1.5	1.7	1.8	1.5	1.8	1.8	2.0
58.3	1.5	1.6	1.7	1.8	2.1	1.9	1.7
62.2	1.3	1.6	1.5	1.5	1.7	1.7	1.9

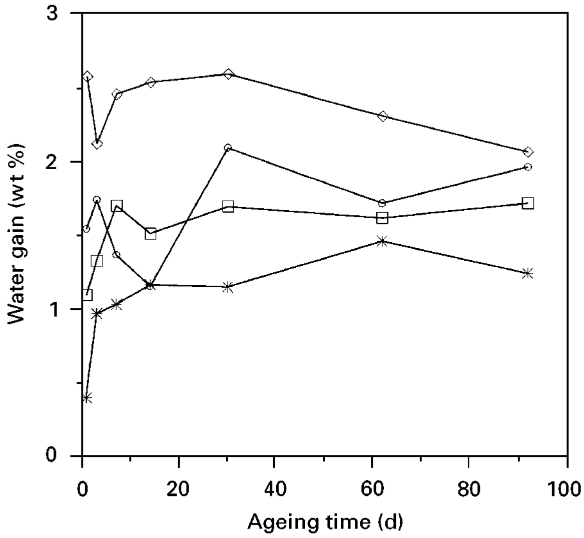

Figure 2 Water gain in S2-glass® composites (expressed as a percentage of the dry composite weight) as a function of ageing time. The four curves are for different levels of reinforcement (vol %); (◇) 33.0; (○) 46.3; (□) 52.9; and (∗) 66.1. Note the reverse hierarchical order. The data are connected with straight lines for clarity in grouping, not as a proposed mechanism of behaviour.

3.2. Sorption in unreinforced copolymer

Water gain in the unreinforced copolymer discs was 4.9 ± 0.3 wt%. The content of labile material present prior to ageing was 0.6 ± 0.1 wt%.

4. Discussion

4.1. Time response

Based upon a conservative estimate of 1.5×10^{-8} $\mathrm{cm}^2\,\mathrm{s}^{-1}$ for the diffusion coefficient in the composites [10, 11] and a simple Fickian diffusion model, the sorption response of these composites should reach over 80% of the steady-state value within 24 h. Thus, the temporal variance in the data (Fig. 2) is puzzling and suggests the inadequacy of the model and/or the presence of measurement noise. Many possibilities exist to explain deviation from the simple diffusion model, two of which are discussed below.

Because of their multiphase structure, composites are particularly susceptible to facile diffusion at the interphase boundaries [10, 11]. Facile diffusion occurs via inordinately conductive pathways formed by interruptions in the regular molecular structure of a material, *e.g.* flaws or grain boundaries. While such a mechanism would seemingly only hasten the gain of water, and thus, the onset of a steady-state response, the accommodation of a diffusion hyperflux at the fibre–matrix interface raises the distinct possibility of degradative ageing of the composite. In a UFRP, swelling can be constrained parallel to the fibre axes by differences in expansion between the fibre and matrix phases, resulting in axial shear stresses at the interfaces. If the interfaces are weak or susceptible to hydrolysis, the periodic release of stress at critical points of attachment would introduce sudden shifts in the balance between the osmotic pressure and the internal tension in the intermolecular network. The outcome would destabilize and prolong the transient sorption response.

A second mechanism is also likely. Researchers have identified the presence of residual monomer in even the most highly polymerized dimethacrylate systems [13–18], and the leaching of these monomers in aqueous environments is also documented [14, 17]. Inoue and Hayashi [14] measured levels of residual *bis*-GMA that was leached into 37 °C water from dimethacrylate composite dental restoratives. If these levels are adjusted from a composite basis to a polymer basis, and if allowance is made for the likelihood of other monomer(s) being present at comparable level, the results agree with the level of labile material in the present copolymer discs prior to ageing (0.6 ± 0.1 wt%). Because the dynamics of the exchange and interaction between water and monomer are not understood, the influence on the sorption dynamics remains unclear.

Despite the unexplained variance in the data, the overriding impression of the sorption response is that WG occurs quickly and then stabilizes. The absence of either a large increase or decrease in the WG over the 3 mon period suggests that any degradative mechanisms are relatively finite, which implies long-term stability.

4.2. Effect of reinforcement level and filament type

Examination of Fig. 2 suggests that the content of copolymer in these composites is a primary influence upon the steady-state WG. To elucidate this point further, sorption data for composites at different reinforcement levels were normalized according to the copolymer content to yield an *adjusted* WG (AWG)

$$\mathrm{AWG} = \frac{\mathrm{WG}}{\mathrm{MF_{CP}}} \tag{2}$$

where $\mathrm{MF_{CP}}$ is the mass fraction of the copolymer in each composite. The $\mathrm{MF_{CP}}$ is calculated from the volume fraction of reinforcement (V_F), and the respective relative densities of the fibre and copolymer, (ρ_F and ρ_CP), as follows

$$\mathrm{MF_{CP}} = \left[1 + \frac{V_\mathrm{F}\rho_\mathrm{F}}{(1 - V_\mathrm{F})\rho_\mathrm{CP}}\right]^{-1} \tag{3}$$

The ρ_F values ($\mathrm{gmcm^{-3}}$) used in Equation 3 are 2.5 and 2.2 for the S2-glass® [19] and quartz [20] filaments, respectively, and the ρ_CP value is 1.2 [8]. When the AWG versus ageing time is plotted for the S2-glass® composites (Fig. 3), the WG curves of Fig. 2 collapse on to one another, and the former hierarchy is lost. The AWG of the entire group averages about 5 wt% (of the copolymer), which compares favourably with the 4.9 ± 0.3 wt% WG measured in the unreinforced copolymer discs.

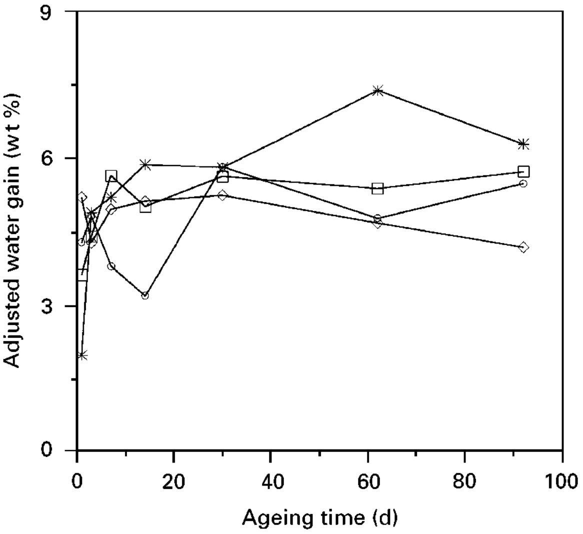

Figure 3 Adjusted water gain in S2-glass® composites (water gain expressed as a percentage of the weight of *copolymer* in each dry composite) as a function of ageing time. For the same levels of reinforcement (vol %) as shown in Fig. 2, note the absence of a hierarchical order.

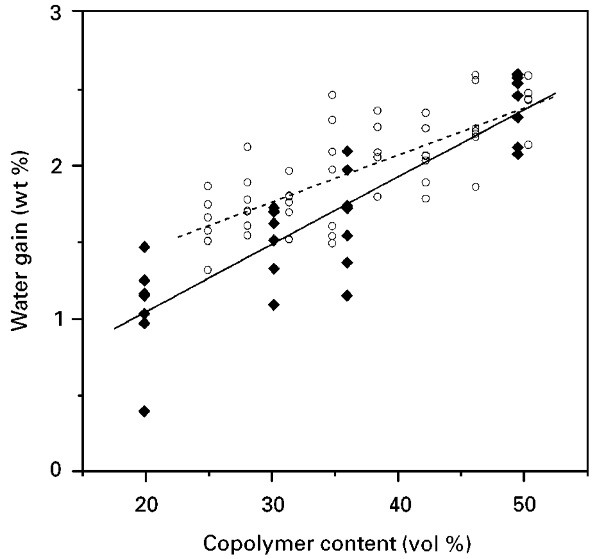

Figure 4 Water gain in (--O--) quartz and (—◆—) S2-glass® composites as a function of the copolymer content (vol %). Data collected at different ageing times are undifferentiated. Note the divergence of the curves at low copolymer levels, i.e. high reinforcement levels.

By ignoring the temporal variation in the data, i.e. grouping data collected at different times for each reinforcement level, the steady-state WG is plotted for the two types of composites as a function of the copolymer content (Fig. 4). Regression analysis of the data revealed a distinct linear correlation model for each type of composite. The slopes are significantly different from zero as well as being different from one another ($p \leqslant 0.03$). The y-intercepts are also different from one another ($p \leqslant 0.003$); however, the y-intercept for the S2-glass® composite is not significantly different from zero.

The strong positive correlation of WG with the copolymer content supports the obvious argument that the copolymer is responsible for sorption in these composites. This explanation is further supported for the S2-glass® composites by the fact that the prediction of WG for a theoretical composite of zero copolymer content, based on extrapolation of the regression model, cannot be differentiated from zero with any statistical certainty. Finally, the prediction of the model for a theoretical S2-glass® composite of pure copolymer is within one standard deviation of the mean WG value measured for the unreinforced copolymer discs (4.9 ± 0.3).

By contrast, the sorption in the quartz material cannot be fully explained on the basis of copolymer content alone. The more-gradual slope and non-zero y-intercept of the quartz regression model highlight the divergence in the behaviour of the two materials at low copolymer levels, i.e. high reinforcement levels. These outcomes suggest that a second sorption mechanism is active in the quartz composites – one which correlates positively with the reinforcement level. Because the sorption of water by the quartz fibres is negligible at 37 °C [11, 21–24], the most logical explanation is that additional water is being incorporated at the fibre–matrix interface.

To prove this point, the AWG is plotted (Fig. 5) against the linear density of interfacial surface area (L-DISA) in the composites, which is a direct function of the fibre content. The AWG for the S2-glass® composites is relatively constant, as would be expected if the copolymer is the only mechanism for sorption. In fact, regression analysis reveals that the S2-glass® composites are statistically independent of the L-DISA. Moreover, a t-test between the mean AWG for S2-glass® and the mean WG in unreinforced copolymer reveals no significant difference. In contrast, the AWG for the quartz materials increases slightly as the L-DISA increases; the slope is significantly non-zero ($p \leqslant 0.001$), indicating a positive correlation between AWG and the L-DISA. Finally, the y-intercepts for the two models are statistically the same, indicating like behaviour towards the pure-copolymer end of the reinforcement spectrum, where the influence of the L-DISA is diminished. However, this statistical sameness may be partly due to the amplification of the uncertainty of the models that accompanies their extrapolation beyond the range of the data.

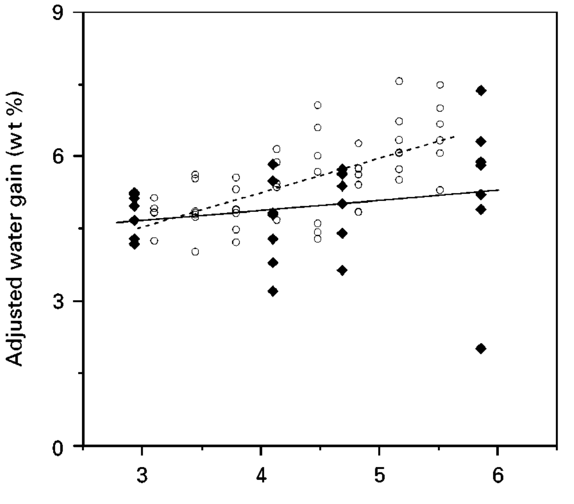

Figure 5 Adjusted water gain in (--○--) quartz and (—◆—) S2-glass® composites as a function of the linear density of interfacial surface area. Data collected at different ageing times are undifferentiated. Note the relative flatness of the S2-glass® curve.

5. Conclusions

Photo-pultruded composites of *bis*-GMA/TEGDMA copolymer that are reinforced with two different commercially prepared silicate-glass yarns exhibit different behaviours with respect to steady-state water sorption. Composites made with the S2-glass® yarn will sorb in direct proportion to the content of copolymer, which can be expected to gain about 4.9 ± 0.3 wt%. Composites made with the quartz yarn will sorb primarily in proportion to the copolymer, but will accommodate additional water at the fibre–matrix interface. In both cases, the water gain is relatively constant between 1d and 3 mon, which is indicative of some stability.

While both of these materials may be useful as biomaterials, the presence of water at the fibre–matrix interface of the quartz composite is indicative of a poor interfacial bond. Precluding special treatments, the as-prepared S2-glass® yarn forms a superior bond with the photopolymerized *bis*-GMA/TEGDMA copolymer network. The resulting S2-glass® composites should perform better than the quartz composites in structural applications.

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