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Mechanical performance of novel bioactive glass containing dental restorative composites

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Short title: Mechanical performance bioactive glass composites

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Abstract

Objectives. Bioactive glass (BAG) is known to possess antimicrobial properties and release ions needed for remineralization of tooth tissue, and therefore may be a strategic additive for dental restorative materials. The objective of this study was to develop BAG containing dental restorative composites with adequate mechanical properties comparable to successful commercially available composites, and to confirm the stability of these materials when exposed to a biologically challenging environment.

Methods. Composites with 72 wt.% total filler content were prepared while substituting 0 – 15% of the filler with ground BAG. Flexural strength, fracture toughness, and fatigue crack growth tests were performed after several different soaking treatments: 24 hours in DI water (all experiments), two months in brain-heart infusion (BHI) media+*S. mutans* bacteria (all experiments) and two months in BHI media (only for flexural strength). Mechanical properties of new BAG composites were compared along with the commercial composite Heliomolar by two-way ANOVA and Tukey’s multiple comparison test (p ≤0.05).

Results. Flexural strength, fracture toughness, and fatigue crack growth resistance for the BAG containing composites were unaffected by increasing BAG content up to 15% and were superior to Heliomolar after all post cure treatments. The flexural strength of the BAG composites was unaffected by two months exposure to aqueous media and a bacterial challenge, while some decreases in fracture toughness and fatigue resistance were observed. The favorable mechanical properties compared to Heliomolar were attributed to
higher filler content and a microstructure morphology that better promoted the toughening mechanisms of crack deflection and bridging.

**Significance.** Overall, the BAG containing composites developed in this study demonstrated adequate and stable mechanical properties relative to successful commercial composites.

**Keywords:** Resin Composite; Bioactive Glass; Strength; Fracture Toughness; Fatigue; Bacteria; Hydration

1 **Introduction**

While the use of dental restorative composites has increased dramatically for posterior teeth, annual failure rates up to 15% have been reported depending on restoration class [1], and a review of the literature has suggested the average lifetime of posterior dental composites is only six years [2]. Secondary caries at margins has been considered for over twenty years the most common reason for restoration replacement [3-7]. The second most common reason is partial or complete fracture of the composite restoration, while other significant causes are erosion and discoloration [8,9]. It has been reported that the replacement of posterior composites is primarily due to fracture of the restoration within the first five years, but as a response to secondary caries thereafter [10], although this has not been observed in all clinical studies [11]. A review of the numerous causes identified for restoration replacements based on multiple surveys may be found in Deligeorgi et al, 2001 [12].
One of the most common reasons for secondary caries is biofilm (plaque) formation on the margin of the tooth and restoration. Bacteria in the plaque (e.g., *Streptococcus mutans*) metabolize sucrose to lactic acid which can demineralize tooth tissue [13,14]. Resin based composites may ideally provide good sealing of the cavity with no marginal gaps; however, polymerization shrinkage during placement, combined with cyclic mechanical loading during function, may lead to local interface failure and gap development. These marginal gaps can serve as suitable anchorage sites for bacterial colonies [15]. A minimum gap size exceeding 0.4 mm has been suggested for significant bacterial colonization of dental amalgam [16], but a similar relationship has not been discerned for composites. Moreover, increased roughness of the restoration increases the ability of bacteria to colonize a given area, by affecting pellicle formation and causing a favorable environment, often resulting in secondary caries formation [17,18]. Microfloral analysis of marginal biofilms revealed that anaerobic bacteria are dominant with *Streptococcus mutans*, *Actinomyces naeslundii* and *Lactobacillus casei* being the most abundant bacterial species [19]. Svanberg et al. found significantly larger *Streptococcus mutans* colony counts at the tooth interface with composite restorations compared to interfaces with amalgam [20].

One possible approach to increasing the resistance of restorations to secondary caries formation is to add agents that 1) negatively influence the micro-organisms and/or 2) promote remineralization of tooth structure after damage has occurred. In this regard, there is a substantial amount of published literature demonstrating the antibacterial qualities of various bioactive glass (BAG) compositions against many different bacterial species [21-33]. However, to date there have been no published studies of dental restorative composites
containing bioactive glasses. There are several concerns regarding the development of a successful bioactive glass dental restorative composite. First, there is a concern that BAG fillers not well adhered to the composite matrix will result in unsuitably low mechanical properties. Second, because the composite will leach ions there is a concern about the stability of the mechanical properties over time. Finally, it must be confirmed that sufficient antimicrobial and/or remineralization activity can be achieved in BAG containing composites to slow secondary caries at the marginal gaps of tooth restorations. The goal of this study is to address the former two issues, while the latter will be addressed in the future by ongoing studies. Accordingly, the objective of this paper was to test the hypotheses that new BAG-containing dental restorative composites can be developed with mechanical properties comparable to successful commercially available composites, and that the properties will remain adequately stable after aging in a bacterial environment.

2 Materials and methods

2.1 Materials

The bioactive glass (BAG) used in this study had the composition 65% SiO₂, 31% CaO and 4% P₂O₅ (mol%) and was produced by a sol-gel process, as previously described [34]. In brief, the BAG was produced from high-purity metal alkoxides including tetraethyl orthosilicate (TEOS, Si(OC₂H₅)₄), calcium methoxyethoxide (CMOE, C₆H₁₄O₄Ca), and triethyl phosphate (TEP, (C₂H₅)₃PO₄). All reagents were purchased (Sigma Aldrich), except the CMOE was synthesized from pure Ca metal and methoxyethanol, to produce a 20% solution in methoxyethanol, and this alcohol served as a mutual solvent for all of the alkoxides as well as being the water source used to initiate hydrolysis and glass formation.
The solutions were prepared in a dry nitrogen-environment glovebox, aged in distilled water, air-dried and stabilized in a dedicated furnace at 600°C to completely remove residual alcohols and alkoxide components, while retaining high surface area (between 200 to 300 m²/g). After rapidly cooling, the glass was ball milled in ethanol and sieved to a gross particle dimension of less than 38 µm. The particles were then further processed to a fine particle size (0.04-3.0 µm) using a Micronizer jet mill. (Sturtevant Inc., Hanover, MA).

Three BAG-containing composites were produced by mixing the glass into a 50:50 mixture of bisphenol A glycidyl methacrylate (BisGMA):triethylene glycol dimethacrylate (TEGDMA) monomers with 0.4 wt% of camphorquinone (CQ), 0.8 wt% of 4-dimethylaminobenzoic acid ethyl ether (EDMAB), and 0.05 wt% of 3, 5-di-tertbutyl-4-hydroxytoluene (BHT). Samples denoted as 5BAG, 10BAG, and 15BAG were produced by combining the resin with 3.0 µm average size silanated strontium glass (Bisco Inc.) and 5, 10, or 15 wt% unsilanated bioactive glass, respectively, to a total filler of 72 wt% and mixed in a DAC-150 speed mixer (FlackTek Inc., Landrum, SC) at 3000 rpm for 2 minutes. Control samples (denoted 0BAG) had the same formulation as 5BAG with 5 wt% silane treated aerosol-silica filler (OX-50, Degussa) substituted for the BAG.

Mechanical property values are compared to published literature values and also the full set of mechanical property experiments were conducted on the commercial composite Heliomolar (Ivoclar Vivadent AG, batch # 4432). Heliomolar has a composition of 19 wt% Bis-GMA + urethane dimethacrylate, 3 wt% decandiol dimethacrylate, 66.7 wt% total filler content (highly dispersed silicon dioxide + ytterbium trifluoride) along with prepolymer and <1wt% stabilizers, catalysts and pigments. Heliomolar is classified as an
inhomogeneous microfilled composite (< 1μm filler size) and was chosen for this study because it is a clinically successful example of a composite for anterior and posterior restorations [35-37].

2.2 Specimen preparation for mechanical testing

For flexural strength testing, three-point bend beams (N=10 for each composition) were prepared by dispensing the composite paste into 25 mm long quartz tubes (square 2 mm × 2 mm cross-section) followed by curing for 40 s on two opposite sides in a visible light curing unit (Triad II, Dentsply International, York Division, PA, USA). Compact-tension, C(T), specimens were made for fracture toughness (N=5 for each composition) and fatigue crack growth (N=3 for each composition) experiments. The composites were dispensed into a stainless-steel rectangular split mold, pressed flat, and cured for 40 s on each side as described above. The cured rectangular blanks were then machined into C(T) specimens as shown in Fig.1a. To enable observation and measurement of cracks, samples were ground and polished using progressively finer SiC grinding papers and alumina oxide polishing compounds down to 0.05 μm and finally finished with MasterPolish (Buehler, Lake Bluff, IL, USA). A sharp pre-crack (Fig.1b) was introduced by manually extending the starter notch using a razor blade until a pre-crack formed from the notch.

Fig. 1. location

2.3 Post-cure treatments
Specimens for all experiments were treated in two different ways: 24 hours aging in deionized (DI) water and 58 ± 3 days at 37°C in brain-heart infusion (BHI) media with *Streptococcus mutans* (strain ATCC25175) cultures growing in logarithmic phase with the media changed every other day. The longer of the two aging times was chosen since previous studies have estimated that is the amount of time needed for the specimens to become fully (>98%) saturated with water [38]. Lyophilized bacterial cultures were obtained from the American Type Culture Collection (ATTC, Manassas, VA, USA). All DI water aged samples were tested immediately after removal from the water. After the aging period in BHI media with *Streptococcus mutans*, composite samples were immersed in 50% bleach for 5 min and then rinsed with BHI three times. The specimens were then soaked in BHI without sucrose and stored in a refrigerator until mechanical testing. With the exception of the fatigue tests, all mechanical testing was performed within a day of removal from the test aging solution. Due to the time required for fatigue testing, some samples needed to be stored for days or weeks while waiting for testing, so these samples were continually stored in sterile BHI media at ~4°C. Finally, bending beams made from the experimental composites were also soaked in sterile BHI media without bacteria for ~60 days and used for strength testing.

2.4 Mechanical Testing

Flexure strength was tested in 3-point bending (20 mm span) on a universal testing machine at a cross-head speed of 0.254 mm/min, in general accord with ISO 4049 [39]. The
steel supports had rollers of 2 mm diameter and the loading piston was a steel ball of 2 mm diameter. The flexure strength was determined using the maximum load.

Fracture toughness tests were conducted on wet samples immediately after removal from the storage solution using a computer controlled hydraulic testing machine (Instron 8872, Canton, MA, USA). Tests were conducted in load control with a 1.1 N/s loading rate until fracture occurred. $K_{IC}$ was calculated from the peak load at fracture according to the standard stress intensity factor equation for the C(T) sample geometry [40].

Fatigue crack growth testing was done in general accordance with ASTM standard E647 [41], using computer controlled hydraulic testing machine (Instron 8872, Canton, MA, USA) and a sine waveform with frequency $\nu = 1.5$ Hz, which corresponds to a typical human chewing frequency [42]. A constant load ratio $R=P_{\text{min}}/P_{\text{max}}=0.1$ was used, where $P_{\text{max}}$ and $P_{\text{min}}$ are the maximum and minimum loads experienced during the loading cycle, respectively. Fatigue crack growth rates, $da/dN$, were characterized as a function of the stress intensity range, $\Delta K = K_{\text{max}} - K_{\text{min}}$, where $K_{\text{max}}$ and $K_{\text{min}}$ are the stress intensity values calculated from $P_{\text{max}}$ and $P_{\text{min}}$, respectively. After initial establishment of a high crack growth rate of $10^{-7}$-10$^{-6}$ m/cycle, the test was conducted in decreasing $\Delta K$ control using a normalized $K$-gradient $(1/\Delta K [d\Delta K/da])$ of -0.08 mm$^{-1}$. Crack length was determined by measuring the load point compliance using a capacitance displacement gage (HPT150, Capacitec, Inc., Ayer, MA) attached to the clevises of the testing machine. The sample compliance was converted to crack length using published calibrations [43]. Data points were collected roughly every 10$^{-5}$ m of crack extension. Samples were kept wet during the entire test using a sponge to surround the sample and a custom drip system to keep it wet.
After the test, the final crack length was measured optically. When the final compliance and optically measured crack lengths differed, the crack length data was corrected by assuming the error accumulated linearly with crack extension. From the crack length data, the crack growth rates \( \frac{da}{dN} \) were determined as a function of \( \Delta K \) by fitting over ranges of ~100 \( \mu m \) of crack length change.

For statistical comparisons of data, ANOVA followed by Tukey’s multiple comparison test was used with \( \alpha < 0.05 \) considered statistically significant.

After fatigue crack growth and fracture toughness experiments, both crack profiles and fracture surfaces, respectively, were examined using a scanning electron microscope (Quanta 600 FEG SEM, FEI Company, Hillsboro, OR) in order to discern crack-microstructure interactions and toughening mechanisms.

3 Results

3.1 Flexural strength results

Flexural strength and statistical test results are shown in Table 1. BAG composites did not show a significant difference in flexural strength as a function of the various soaking treatments. However, Heliomolar composites did show a significant reduction in flexural strength between 24h water and 2 months in bacteria. The experimental BAG composites all had superior flexural strength when compared to Heliomolar.

3.2 Fracture toughness results

Fracture toughness data and statistical test results for both Heliomolar and BAG composites is shown in Table 2.
Statistical analyses showed that the experimental BAG composites all have significantly higher fracture toughness compared to Heliomolar at 24 hours and after 2 months aging in bacteria (Table 2). Furthermore, the degradation in toughness of the experimental BAG composites after two months of aging was comparable to, or less severe (i.e., not significant) than Heliomolar (Table 2).

3.3 Fatigue crack growth results

Fatigue crack growth rate, \(da/dN\), results are shown in Fig. 2 plotted as a function of the stress intensity range, \(\Delta K\). Generally, the data for the 0 – 15BAG composites produced in this study overlapped considerably. Furthermore, the commercial composite Heliomolar showed inferior fatigue crack growth resistance for both aging conditions with the curves shifted to higher growth rates at a given stress intensity range. The difference between Heliomolar and the 0 – 15BAG composites was more pronounced for the 24 h water aging condition.

Fig. 2. location

Each curve in Fig. 2 was produced from a composite of \(N = 3\) samples measured over different, overlapping, ranges of growth rates; thus, fatigue crack growth data for each material was pooled and fit to the Paris law [44]:

\[
\frac{da}{dN} = C(\Delta K)^m
\]  

[1]

and mean values for the Paris exponent, \(m\), are given in Table 3. All of the composites showed decrease in \(m\) after two months aging in bacteria. The fatigue thresholds, \(\Delta K_{\text{TH}}\), below which cracks are presumed not to propagate was also assessed for each sample in
Table 3. Due to practical time limitations of testing, $\Delta K_{TH}$ was defined where growth slowed to a rate approaching $10^{-9}$ m/cycle. Since each curve in Fig. 2 was produced from multiple samples tested with different growth rates, the $\Delta K_{TH}$ given in Table 3 were taken from the sample tested at the slowest growth rates.

3.4 Crack Paths and Fractography

Due to similarities of the observed microstructures and crack-microstructure interactions for all of the BAG composites, only micrographs for the 0BAG and 15BAG composites will be shown as representative. Crack path observations were made on the fatigue crack growth specimens, while fracture surface observations were made on both the fracture toughness and fatigue samples.

Fig. 3. location

Figs. 3a & 3b show multiple crack deflections and crack bridging near the fatigue crack tip of a 15BAG composite. For the Heliomolar composite crack bridges were also observed at the crack tip (Fig. 3c). For all of the 0 – 15 BAG composites, but not Heliomolar, crack bridges were also found in the crack wake far behind the crack tip (Fig. 4a).

Fig. 4. location

Significant crack deflections were rarely observed in the Heliomolar composite and were located only at the widely spaced, large prepolymerized agglomerates of composite that were often ~20 µm or larger in size (Fig. 4b). Fig. 5 shows an equal magnification comparison of the crack paths for the 15BAG and Heliomolar composites over a larger amount of crack extension. On the microscale, the crack in the 15BAG composite appears
more tortuous due to the high frequency of deflection by particles (Fig. 5a), while for the Heliomolar composite there is some crack meandering over large extensions, but generally a less tortuous path on the microscale (Fig. 5b). Also, in Figs 3-5 there is evidence of BAG particle dissolution from the polished surfaces due to the 2 month aging treatment for the 15BAG composite (Fig. 3a, 3b, 4a, 5a) which was absent for the 0BAG samples (Fig. 5c).

**Fig. 5. location**

Overall, the 0 – 15BAG composites show a rougher fracture surface while the fracture surface of Heliomolar is smoother and entirely covered with resin (Fig. 6). It is seen in Figs. 6a & 6c that some of the particles of the 15BAG and 0BAG composites debonded cleanly from the matrix, giving a mixed matrix/interface crack path. In contrast, for Heliomolar (Fig. 6e) the crack always moved through the resin matrix leaving a polymer coating on the fracture surface. The resin coated fracture surface is seen more clearly in Fig. 6f at higher magnification where, in contrast, the smooth surface of debonded glass particles can be seen for the 0BAG and 15BAG composites at higher magnifications (Fig. 6b & 6d). Figs. 6a & 6c also show that the 0BAG composite has fewer debonded particles than the 15BAG composite. Approximately 94 debonded particles/mm$^2$ and 159 debonded particles/mm$^2$ were observed on the fracture surfaces for 0BAG and 15BAG respectively.

**Fig. 6. location**

4 Discussion

4.1 Mechanical behavior
Overall, BAG composites exhibited significantly better mechanical properties than Heliomolar both after aging in DI water for 24 h as well as after two months soaking in bacteria containing media. These differences in mechanical properties may be attributed primarily to differences in the material composition and microstructures, as will be discussed below. Also, Table 4 shows mechanical properties for two other commercial composites after 60 days soaking in H₂O. Generally, the strength, fracture toughness, and fatigue threshold properties of the BAG containing composites after soaking for two months in bacteria containing aqueous media are comparable to, or better than, these two popular commercial composites.

4.1.1 Flexural strength

The first notable difference between the microstructures is that the 0 – 15BAG composites have significantly higher filler particle concentration than Heliomolar (72 wt% versus 66.7 wt%, respectively). The higher measured strength values for the BAG composites is thus consistent with published observations for resin based dental composites that increased filler content leads to increased flexural strength [45,46] and that filler content is the dominant factor even with different filler morphologies [47].

It is interesting to note that the BAG composites showed no degradation in strength after soaking approximately two months in both sterile and bacteria containing media. Many commercial dental restorative composites demonstrate a loss in strength after similar long term aging in aqueous media [38,48-51]. This degradation in strength is attributed to water uptake causing plasticization of the resin matrix and/or a degradation of the matrix-
filler interface [38,48-51]. Since the BAG-containing composites are designed to have ions leaching out of the BAG filler, there is a legitimate concern that such ion leaching could lead to degradation of the filler, and thus decreased mechanical properties. While the SEM images show evidence for particle dissolution from the composite surface (Figs. 3-5), the mechanical testing results reflect that the flexural strengths of the present BAG composites are quite stable after aging two months in aqueous media.

4.1.2 Fracture toughness and fatigue crack growth resistance

While some correlations have been observed over a specific groups of composites [52], the fracture toughness and fatigue properties of resin based dental restorative composites often do not scale simply with factors like filler volume fraction or filler size and, rather, are highly dependent on the morphology of the composite microstructure [38,45,53-61]. Previous studies have suggested that microstructures that maintain good matrix/particle adhesion while promoting toughening mechanisms such as crack deflection and crack bridging are advantageous for achieving good fracture and fatigue properties [38,53-55,58,59,61].

Generally, it was observed that crack deflection and bridging was more pronounced in the BAG composites than in Heliomolar. Heliomolar is categorized as a microfill composite with filler size <1 µm; however, the microstructure is quite inhomogeneous and contains widely spaced large agglomerates composed of prepolymerized resin fillers added to increase overall filler volume and reduce curing shrinkage. Based on crack path (Fig. 5b) and fracture surface (Figs. 6e-6f) observations, cracks moved through the homogeneous
microfilled regions with few deflections, with significant high angle deflections only rarely observed at the occasional large agglomerate (Fig. 4b). Furthermore, the only detectable crack bridges were very small and only observed very near the crack tip (Fig. 3c). In contrast, the BAG composites contained significantly more medium to large sized particles capable of 1) deflecting the crack at the microscale and 2) creating large crack bridges that sustain load far behind the crack tip (Fig. 3-5).

Crack deflection and bridging are two toughening mechanisms that often act in concert; indeed, crack deflection commonly leads to crack bridging. Furthermore, natural tooth enamel and dentin are also toughened by those same mechanisms [62-65]. Both mechanisms increase the toughness by lowering the mode I stress intensity at the crack tip. Since both the fracture toughness and fatigue crack growth resistance are determined by the mode I stress intensity, both are generally improved by these mechanisms. With crack deflection, the microstructure forces the crack to deviate from the mode I path, causing a decrease in the mode I stress intensity at the crack tip. Crack bridging often results where the crack locally arrests or is deflected by microstructural inhomogeneities. As a result, load bearing bridges may be left in the crack wake due to either imperfect connection of the three-dimensional crack front, or new microcracks forming ahead of the crack tip. Overall, these mechanisms were observed to be more active in the BAG composites resulting in higher fracture toughness and fatigue crack growth resistance.

Some studies have shown particle/matrix debonding can be detrimental to the fracture and fatigue performance of resin based dental composites [38,54]. In the present BAG composites, some fraction of the particles were observed to cleanly debond from the matrix.
(Fig. 6); however, overall adequate properties were achieved nonetheless when compared to the commercially successful Heliomolar. Also, the fraction of debonded particles was higher for the 15BAG composition than the 0BAG composition, suggesting the lack of silane treatment of the BAG particles led to less particle-matrix adhesion. However, overall it may be concluded that since the majority of particles were well bonded even for the 15BAG case (Fig. 6a) adequate mechanical properties were achieved.

Although the fracture toughness and fatigue crack growth resistance for the BAG composites degraded somewhat after long term aging in aqueous media, the properties remained better than Heliomolar in all cases. A degradation in fracture toughness is not unusual for other commercial resin based dental composites after long term exposure to water [38]. Moreover, the fracture toughness and fatigue threshold properties of the BAG containing composites are comparable to, or better than, the popular commercial composites (Table 4) that were tested after two months soaking in water [38,54]. Overall, it is concluded that the presence of the BAG particles does not raise immediate concerns regarding long term stability of the mechanical reliability of these composites.

4.2 Limitations of this study

Although crack bridging was identified as a toughening mechanism for the BAG composites, in the present study the contribution of crack bridging was not quantified. Such quantification would require the measurement of the fracture resistance curves (\(R\)-curves) for the materials to separate out the contribution of bridging [38,53,61], and such studies are left for future work. Another limitation is the aging time was limited to roughly two
months. Although previous work suggests this is long enough to reach nearly full water saturation of the composite [38], it is unclear if degradation may occur at longer time scales and such studies are also left for future work.

5 Conclusions

Based on a study of the mechanical properties of a series of bioactive glass (BAG) containing composites, the following conclusions can be made:

1. All BAG containing composites exhibited superior mechanical properties over the commercial Heliomolar composite both after 24 hours in water and after 2 months in a bacteria containing aqueous media. Properties were also found to be comparable to, or better than, published values for two other commercial composites, Filtek Z250 and Filtek Supreme Plus.

2. The superior mechanical properties of the BAG composites compared to Heliomolar were attributed to: 1) a higher filler content; and 2) a microstructure morphology that better promoted the toughening mechanisms of crack deflection and bridging.

3. Overall, the BAG containing composites developed in this study demonstrated adequate mechanical properties relative to successful commercial composites.

Acknowledgements

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Table 1 – Mean flexural strengths with standard deviations in parentheses

<table>
<thead>
<tr>
<th>Material</th>
<th>24h DI Water</th>
<th>2 months bacteria</th>
<th>2 months media</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heliomolar</td>
<td>73.2 (4.4) *</td>
<td>61.7 (7.9) *</td>
<td>- *</td>
</tr>
<tr>
<td>0BAG</td>
<td>123.5 (16.2)</td>
<td>114.9 (12.3)</td>
<td>107.4 (12.8)</td>
</tr>
<tr>
<td>5BAG</td>
<td>112.8 (12.9)</td>
<td>108.4 (12.2)</td>
<td>107.4 (11.2)</td>
</tr>
<tr>
<td>10BAG</td>
<td>116.4 (14.2)</td>
<td>112.6 (13.0)</td>
<td>95.7 (16.2)</td>
</tr>
<tr>
<td>15BAG</td>
<td>116.9 (10.7)</td>
<td>105.6 (17.7)</td>
<td>101.2 (10.8)</td>
</tr>
</tbody>
</table>

\* denotes value has statistically significant difference from rest of column
Table 2- Mean fracture toughness results with standard deviations in parentheses

<table>
<thead>
<tr>
<th>Material</th>
<th>24h DI water $K_{IC}$ (MPa$\sqrt{m}$)</th>
<th>2 months bacteria $K_{IC}$ (MPa$\sqrt{m}$)</th>
<th>% decrease</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heliomolar</td>
<td>0.98 (0.17)$^a$</td>
<td>0.77 (0.02)$^a$</td>
<td>-21$^b$</td>
</tr>
<tr>
<td>0BAG</td>
<td>1.45 (0.13)</td>
<td>1.25 (0.15)</td>
<td>-13</td>
</tr>
<tr>
<td>5 BAG</td>
<td>1.52 (0.17)</td>
<td>1.12 (0.13)</td>
<td>-26$^b$</td>
</tr>
<tr>
<td>10BAG</td>
<td>1.54 (0.17)</td>
<td>1.40 (0.01)$^b$</td>
<td>-9</td>
</tr>
<tr>
<td>15BAG</td>
<td>1.31 (0.14)</td>
<td>1.10 (0.05)</td>
<td>-16$^b$</td>
</tr>
</tbody>
</table>

$^a$ denotes value has statistically significant difference from rest of column

$^b$ denotes statistically significant difference between the two aging conditions
Table 3 – Measured fatigue parameters: $\Delta K_{TH}$ values and Paris exponents

<table>
<thead>
<tr>
<th></th>
<th>24h in DI water</th>
<th>60 days in bacteria</th>
<th>% decrease in $m$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta K_{TH}$ (MPa$\sqrt{m}$)</td>
<td>$m$</td>
<td>$\Delta K_{TH}$ (MPa$\sqrt{m}$)</td>
</tr>
<tr>
<td>Heliom</td>
<td>0.40</td>
<td>23.0</td>
<td>0.53</td>
</tr>
<tr>
<td>0BAG</td>
<td>0.79</td>
<td>24.7</td>
<td>0.54</td>
</tr>
<tr>
<td>5BAG</td>
<td>0.70</td>
<td>14.3</td>
<td>0.54</td>
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<tr>
<td>10BAG</td>
<td>0.65</td>
<td>22.0</td>
<td>0.46</td>
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<td>15BAG</td>
<td>0.71</td>
<td>25.8</td>
<td>0.56</td>
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Table 4 – Published mechanical properties of some commercial composites with standard deviations in parentheses [38,54]

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<thead>
<tr>
<th></th>
<th>Flexural Strength (MPa)</th>
<th>Fracture Toughness* (MPa√m)</th>
<th>Fatigue Threshold (MPa√m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filtek Z250 (60 days H₂O)</td>
<td>91.4 (14.8)</td>
<td>1.26 (0.05)</td>
<td>0.54</td>
</tr>
<tr>
<td>Filtek Supreme Plus Plus (60 days H₂O)</td>
<td>52.7 (12.9)</td>
<td>0.81 (0.06)</td>
<td>0.41</td>
</tr>
</tbody>
</table>

*These toughness values are the maximum point of the fracture resistance curve, which gives an upper bound for the critical value of toughness, $K_{IC}$. 
Figure Captions

Fig. 1. (a) Schematic and dimensions of C(T) specimen and (b) optical micrograph of a typical pre-crack profile.

Fig. 2. Fatigue crack growth rate data for (a) 24h water aging and (b) 2 months bacteria aging treatments.

Fig. 3. Micrographs of crack tips (2 months bacteria treatment). a-b) Crack deflection and bridging at a fatigue crack tip in the 15BAG composite. c) Crack bridging at a fatigue crack tip in the Heliomolar composite. Direction of crack propagation was left to right.

Fig. 4. Micrographs of toughening mechanisms (2 months bacteria treatment). a) Crack bridge created by filler particle in the 15BAG composite. This bridge was located 0.052 mm behind the fatigue crack tip. b) A rare high angle crack deflection by a large prepolymerized agglomerate in the Heliomolar composite. Direction of crack propagation was left to right.

Fig. 5. Micrographs of fatigue crack paths (2 months bacteria treatment). Panel a) shows the 15BAG composite, b) the Heliomolar composite and c) the 0BAG composite. Direction of crack propagation was left to right.

Fig. 6. Fracture surfaces of fracture toughness samples for (a, b) 15BAG, (c, d) 0BAG and (e, f) Heliomolar composites after 2 months bacteria treatment.