Bioglass®/high density polyethylene composite for soft tissue applications: Preparation and evaluation

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Abstract: Particulate 45S5 Bioglass® with an average size of 46 μm was incorporated into a high density polyethylene (HDPE) for potential medical applications. Composites with Bioglass® volumes of 10, 20, and 40% were produced by a manufacturing process consisting of blending, compounding, powdering, and compression molding. The Bioglass® particles were well dispersed, and their homogeneous distribution in the polymer matrix, achieved after compounding, was retained during subsequent composite processing. The Young’s modulus and microhardness of the composites increased with an increase in Bioglass® volume while the tensile strength and fracture strain decreased. Fourier transform infrared spectra, obtained from Bioglass®/HDPE samples exposed for 20 h at 37°C to a simulated body fluid (SBF-9), demonstrated that composites of all the compositions examined developed the surface biological apatite layer equivalent to that for bulk Bioglass®. © 1998 John Wiley & Sons, Inc. J Biomed Mater Res, 42, 577–586, 1998.

Key words: Bioglass®; HDPE; composite; structure and property; bioactivity

INTRODUCTION

Many composite materials, including ceramic matrix composites and polymer matrix composites, have been developed for biomedical applications. Current polymer processing technology makes it possible to produce highly filled polymers of excellent quality, which enables us to manufacture bioactive, high performance ceramic/polymer composites as biomaterials.

Bioglass® is a family of bioactive glasses that elicit specific physiological responses, including the presence of surface-reactive silica, calcium and phosphate groups, and alkaline pH levels at interfaces with tissues. A particular advantage of Bioglass® of certain compositions is its ability to bond to both hard and soft tissues, an ability that has created a range of clinical applications. However, as for all monolithic bioactive glasses and ceramics, a disadvantage of Bioglass® is that it is a brittle solid and, as a consequence, its handling and mechanical properties may not be adequate for load-bearing applications. Nevertheless, Bioglass® has been used as a biomaterial in its own right, as a coating material, as a matrix, and as a toughening phase in a composite.

Ultrahigh molecular weight polyethylene (UHMWPE) has proven to be biocompatible and hence is widely used in the orthopedic field in areas such as total hip replacement. High density polyethylene (HDPE), on the other hand, can be used in tubing for drains and catheters due to its excellent toughness and its resistance to fats and oils. In order to produce bioactive composites that contain high volume percentages of bioactive phases (normally greater than 40 vol%), HDPE has been chosen as the matrix polymer because highly filled HDPE still can be melt processed using current extrusion and injection molding technology, which provides the option of mass production of implants at reasonable manufacturing costs.

Our extensive experience with combining hydroxyapatite (HA) particles with HDPE to form a bone analog has demonstrated an approach that allows appropriate mechanical properties, including ductility, to be developed while retaining a bioactive response in vivo. Considering that soft connective tissues, cartilage, and cancellous bone with low elastic moduli tend to be

A U.S. patent has been filed for the Bioglass®/HDPE composite.

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among the most resistant to adhesion with prostheses, Bioglass® is a natural choice as the bioactive phase in a composite intended for such applications. Therefore, the processing route developed for HA/HDPE has been used as a basis for producing a novel Bioglass® / HDPE composite that offers a distinctive combination of mechanical/biological performance and, hence, potential clinical applications. Such a composite material should exhibit high degrees of bioactivity and rapidly establish interfacial bonds with the surrounding tissue(s).

**MATERIALS AND METHODS**

A particulate Bioglass® (45S5 Bioglass®, US Biomaterials Co., USA) was incorporated into a high density polyethylene (Rigidex HM4560XP, BP Chemicals Ltd., UK) using the technology originally developed for producing HA/HDPE composites. The Bioglass® particles first were blended with HDPE granules. The blended material then was fed into a Betol BTS40L compounding extruder, and the extrudate was rapidly cooled through a bath of distilled water at room temperature. The maximum temperature of the composite during compounding was between 190° and 230°C, depending on the volume of Bioglass® in the composite. The extruded strands were subsequently dried and pelletized. The composite pellets were processed into composite powder in a Retsch (Type ZM1) centrifugal mill using liquid nitrogen as the coolant. Composite plates of 1.75 mm in thickness were produced by compression molding using a window-type mold. Composite with 10, 20, and 40% by volume of Bioglass® particles and unfilled HDPE were molded.

Prior to composite processing, the Bioglass® particles were characterized using a Malvern Mastersizer X for particle size analysis. The particle morphology was examined using a JEOL 6300F field emission scanning electron microscope (SEM).

The dispersion and distribution of Bioglass® particles in the HDPE matrix was investigated for composite of the three particle volumes after compounding and compression molding. The specimen preparation procedure included sectioning, mounting, grinding, polishing, and ultrasonic bath cleaning. The polished surfaces, after being lightly gold coated, were examined under a JEOL 6300 scanning electron microscope. According to the Archimedes principle, the density of Bioglass®/HDPE composite was measured using an Ohaus density determination kit. The theoretical density of the composite was calculated according to the “Rule of Mixtures.” Five square samples (1 cm × 1 cm) of each composition were used for the measurement.

The molecular mass of the polyethylene matrix at each processing stage was measured using high temperature gel permeation chromatography (GPC). The measurements were made using a Waters 150 CV instrument, operating at 140°C and with 1,2-dichlorobenzene as the solvent (allowance being made for the presence of filler).

The hardness of the composite was assessed by using a Schimadzu microhardness tester with a pyramid-shaped diamond indenter. For each composition of the composite, a square sample (1.5 cm × 1.5 cm) was cut from the compression-molded plate. The square samples then were embedded in an acrylic resin and ground on various grades of silicon carbide paper. Sufficient flow of tap water flushed away debris during the grinding process. The final preparation of each sample involved light polishing using a suspension of alumina of 7 μm in particle size. The sample then was dried by compressed air jets. An indentation load of 50 g was applied to the polished surface for 15 s and Vickers’ hardness number (VHN) subsequently obtained. Each sample was indented at least ten times, and each indent was at least two indent diameters away from the other. All the indents were made avoiding edges of the sample.

The bioactivity of composite having Bioglass® volumes of 10, 20, and 40% was evaluated by subjecting the samples at 37°C to a simulated body fluid (SBF-tris or SBF-9). The formation of a biological apatite layer on the composite surface, which was detected using Fourier transform infrared (FTIR) microscopy, is indicative of the bioactivity of the composite in vivo. Two simulated body fluids were used for the current investigation: SBF-tris which did not contain calcium or phosphate ions, and SBF-9, which did contain these ions.

**RESULTS**

The as-received particulate 45S5 Bioglass® exhibited a monomodal size distribution, with the average size being 45.7 μm but the distribution peak being located at approximately 69.7 μm (Fig. 1). The size of these Bioglass® particles did not observe a normal distribution but had a long tail region, indicating the presence of a relatively large amount (> 25 vol%) of small particles below 20 μm in diameter. SEM micrographs of typical Bioglass® particles are shown in Figure 2, which also provides evidence of the existence of a small percentage of large glass particles (> 100 μm).
The Bioglass® particles, small or large, are angular in shape, with sharp edges. The particle surfaces are smooth [Fig. 2(b)], which may affect considerably the mechanical properties of the composite.

Microscopic examination of polished surfaces revealed that Bioglass® particles were well dispersed in the composite and that a reasonably homogeneous distribution of Bioglass® particles in the polymer matrix had been achieved after the compounding process (Fig. 3). Subsequent composite processing by compression molding preserved these characteristics. Results obtained from image analysis showed that the area fraction of Bioglass® on the polished surfaces corresponded well with the nominal volume fraction of Bioglass® in the composite.¹³

The measured as well as calculated density of Bioglass®/HDPE composite is listed in Table I. The lowest ratio of measured-to-calculated density is 0.95 for the composite, with 40% Bioglass® particles. As for the molecular weight of polyethylene in the Bioglass®/HDPE composite, the results from high temperature GPC analysis are tabulated in Table II. For the composites of all compositions, the molecular weight distribution of HDPE matrix observes the normal distribution. The weight average molecular mass ($M_w$) was 250000 for the unfilled polyethylene, which had been compression molded directly from as-received polymer granules. (The experimentally determined $M_w$ value for the as-received polyethylene granules was 270000.) It is apparent that the addition of Bioglass® particles reduced the $M_w$ value while further thermal processing (e.g., from compounding to molding) caused an additional decrease in this value.

Results from microhardness tests are tabulated in

**Figure 1.** Size distribution of Bioglass® particles ($d_{0.1} = 7.62 \, \mu m$, $d_{0.5} = 45.73 \, \mu m$, $d_{0.9} = 90.64 \, \mu m$).

**Figure 2.** Morphology of Bioglass® particles: (a) SEM micrograph showing the presence of large Bioglass® particles; (b) the angular shape of individual Bioglass® particles.
An ascending trend of microhardness was observed for the Bioglass®/HDPE composite with the increase in Bioglass® volume. However, even for composites with 40% Bioglass®, the VHN values obtained were considerably lower than that of monolithic Bioglass® (VHN = 458 ± 9.4 for monolithic 45S5 Bioglass®14).

Bioglass®/HDPE composite specimens mostly fractured inside the gauge length during tensile tests. The values of Young’s modulus, tensile strength, and fracture strain of the Bioglass®/HDPE composite are shown in Table IV. The increase in Bioglass® volume gives an increase in Young’s modulus, with corresponding reductions in both tensile strength and fracture strain for the composite. Necking was noted in composite specimens with 10% Bioglass® during tensile testing but was not observed for composites with higher Bioglass® volumes. Figure 4 compares the initial stress–strain curves of the composite with different Bioglass® volumes (up to respective peak stress), showing different trends of Young’s modulus and tensile strength with the incorporation of Bioglass® particles in HDPE.

Results obtained from unfilled HDPE and composite with 20% Bioglass® at two testing speeds are tabulated in Table V. Figure 5 clearly shows that higher strain rate led to higher tensile modulus and tensile strength of a filled polymer while at the same time reducing the fracture strain.

SEM micrographs of tensile fracture surfaces of the composite are shown in Figure 6, effectively revealing the interfacial state of the Bioglass®/HDPE composite and the effect of Bioglass® particles on the local deformation of polyethylene that surrounds these particles. Fracture surfaces of composite with 40% Bioglass® that were macroscopically flat exhibited long polymer fibrils microscopically, indicating large polymer de-
formation (Fig. 7). Even at 40% Bioglass®, the particles were separated, and the surrounding polymer underwent large plastic deformation during tensile testing. The IR diffuse reflection spectrum obtained from composites with 40% Bioglass® after being treated with SBF-9 for 20 h showed that the composite developed a substantial crystalline apatite layer on the surface. However, because of the poor quality of diffuse reflection spectra from composites with lower Bioglass® volumes, infrared microscopy (IRM) was used instead to determine the bioactivity of the composite. For SBF-tris-treated composite samples, Figure 8(a) depicts three FTIR spectra obtained for (a) the Bioglass® particles in isolation, (b) the composite containing 40% Bioglass®, and (c) the composite containing 10% Bioglass® after a reaction time of 20 h. The spectrum for composites with 20% Bioglass® is not shown but is similar to spectrum (c). The 20-h time period is clinically significant and has been used for quality-assurance testing of bioactive glasses intended to bond with soft connective tissue. The shaded regions in Figure 8 correspond to the molecular vibrational modes characteristic of a microcrystalline biological apatite layer. These spectra indicate that only the composite with 40% Bioglass® and a pure Bioglass® particle developed the biological apatite layer in SBF-tris within 20 h. For SBF-9-treated composite samples, the resulting FTIR spectra are shown in Figure 8(b). The strong P-O stretching vibration at 1020 cm⁻¹ in all spectra demonstrates that all of the composites developed surface biological apatite layers equivalent to that for bulk Bioglass®. The crystalline peaks that should appear at 602 cm⁻¹ and 560 cm⁻¹ are not seen because the IR detector used cuts off at 700 cm⁻¹.

DISCUSSION

The Betol BTS40L machine is a closely intermeshing co-rotating twin-screw compounding extruder developed for generating high shear forces to disperse hard particles in polymeric matrices. Therefore, a good dispersion and a homogeneous distribution of Bioglass® particles in the polyethylene matrix were achieved after the compounding process for the Bioglass®/HDPE composites (Fig. 3). Such a distribution of Bioglass® particles is important because when a biological apatite layer develops between the Bioglass® and the surrounding tissue, these particles provide uniformly distributed anchors for the prosthesis. It is also encouraging to note that the normal methods of mechanical abrasion, such as grinding and polishing, can expose Bioglass® particles on the composite surface without experiencing the polymer smearing problem that is associated with some ceramic/polymer systems. Bearing in mind the envisaged biomedical applications, the homogeneous distribution of Bioglass® particles in the polymer matrix and the exposed Bioglass® particles on the composite surface together suggest considerable potential for the Bioglass®/HDPE composite as a soft tissue bonding biomaterial.

![Initial stress–strain curves of the Bioglass®/HDPE composites with different Bioglass® volumes.](581BIOGLASS®/HDPE COMPOSITE)
It also has been demonstrated that a near-theoretical density can be achieved for the Bioglass®/HDPE composite using current processing technology. The high temperature GPC analysis shows that polymer chain breakdown during the thermal processing is not severe and a molecular weight ($M_w$) of greater than 230000 always can be obtained for the Bioglass®/HDPE composite. The observed trend of decreasing molecular weight with increasing filler content is consistent with that for other bioactive composites.

It has been shown that the compression-molded Bioglass®/HDPE composite possesses considerable ductility when the Bioglass® volume is less than 30%. A higher filler loading reduces the ductility of the composites drastically. As indicated in Tables IV and VI, composites with Bioglass® volumes of 30% or below exhibit levels of elastic compliance, tensile strength, and fracture strain comparable to those of soft connective tissues. Composites with Bioglass® volumes in excess of 30% exhibit mechanical properties comparable to cancellous bone. It has been determined that the Young’s modulus of monolithic Bio-

glass® is 35 GPa. The incorporation of a particulate Bioglass® into the HDPE has resulted in a composite with a higher modulus as compared to HDPE ($E_{HDPE}$ = 0.68 GPa). However, modulus values predicted by the “Rule of Mixtures” are not achieved for the Bioglass®/HDPE system although the ascending trend is observed with the increasing amount of Bioglass® in the composite. A more sophisticated model needs to be developed for predicting the mechanical behavior and properties of this composite, as has been done for the HA/HDPE composite. By plotting Young’s modulus values of both the Bioglass®/HDPE and the HA/HDPE composites against the reinforcement volume (Fig. 9), it can be seen that at the same reinforcement volume, the modulus of the HA/HDPE composite is always higher than that of the Bioglass®/HDPE composite when the particle volume exceeds 10%. This difference is caused by the different sizes and morphologies of hydroxyapatite and Bioglass® particles as well as by different Young’s modulus values of reinforcements ($E_{HA}$ is approximately 80 GPa).

The testing condition obviously affects the mechanical properties obtained. Like ceramic particle or whisker-reinforced metals, filled polymers such as Bioglass®/HDPE composite also exhibit a sensitivity of strength and modulus to strain rate (Table V). Therefore, during long-term in vitro studies of Bioglass®/HDPE composites, the same testing conditions must be maintained in order to compare results.

There is no chemical bond between the glass particles and the polymer matrix for the Bioglass®/HDPE composites produced via the current manufacturing process. This effect may account for the decreasing composite strength with increasing Bioglass® volume.

### TABLE V

<table>
<thead>
<tr>
<th>Testing Speed (mm/min)</th>
<th>Young’s Modulus (GPa)</th>
<th>Tensile Strength (MPa)</th>
<th>Fracture Strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_{\text{Bioglass}^\circ} = 0%$</td>
<td>0.5</td>
<td>0.65</td>
<td>17.89</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>0.80</td>
<td>20.91</td>
</tr>
<tr>
<td>$V_{\text{Bioglass}^\circ} = 20%$</td>
<td>0.5</td>
<td>1.21</td>
<td>12.77</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>1.52</td>
<td>14.69</td>
</tr>
</tbody>
</table>

Figure 5. Effect of strain rate on the mechanical behavior of Bioglass®/HDPE composites ($V_{\text{Bioglass}^\circ} = 20\%$).
Particles of irregular shapes in the composite can act as nonbonded hard inclusions in the matrix, and the separation between the glass particle and the polymer matrix may begin at the sharp tips of the particle once mechanical load exceeds certain levels. With increasing amounts of Bioglass® particles in the composite there are more failure initiation sites, and the quick coalescence of small cracks in test pieces during tensile testing leads to decreased strength of the composites. Nevertheless, the Bioglass®/HDPE composite has sufficient modulus and strength to find applications in various areas.

The theory of hardness testing suggests that hardness is related to the yield strength of the material since the indent is formed as a result of plastic flow in that material. However, previous work on bone and HA/HDPE composite has shown that there exists relationships between microhardness of bone and its analogous material and Young’s modulus. But the hardness of bone is always higher than that of the HA/HDPE composite with the same amount of apatite. Such a difference is caused by the way in which the two phases (apatite and polymer) are arranged and bonded. The microhardness of Bioglass®/HDPE is even lower than that of HA/HDPE with an equivalent filler volume, but both composites follow the same trend of increasing hardness with the increase in filler volume (Table III). The major resistance to the penetration of the indenter in these two composites comes from a frictional force (as the reinforcing particles are forced to move in the matrix under the indenting load) and from resistance to deformation of the matrix. The obtained results indicate that filler size and morphology also play a significant part in determining the hardness of the composite. The results further suggest that microhardness could be used as an indicator of Young’s modulus of the composite (Fig. 10). This latter observation is particularly important for our investigation, as the mechanical evaluation of composite via microhardness testing requires only small but representative pieces of the material. During long-term in vitro study of Bioglass®/HDPE samples, if normal mechanical testing is not easily conducted, microhardness testing may prove to be a viable means of mechanical evaluation. Furthermore, indents can be made across the section of a sample so as to assess

**Figure 6.** Tensile fracture surface of the Bioglass®/HDPE composite: (a) $V_{\text{Bioglass}^\circ} = 10\%$; (b) $V_{\text{Bioglass}^\circ} = 20\%$ (c) $V_{\text{Bioglass}^\circ} = 40\%$.

Bioglass® particles of irregular shapes in the composite can act as nonbonded hard inclusions in the matrix, and the separation between the glass particle and the polymer matrix may begin at the sharp tips of the particle once mechanical load exceeds certain levels. With increasing amounts of Bioglass® particles in the composite there are more failure initiation sites, and

**Figure 7.** General view of a tensile fracture surface of a Bioglass®/HDPE composite ($V_{\text{Bioglass}^\circ} = 40\%$).
the degradation depth, if there is any, of the composite in vitro or in vivo. Therefore, values in Table III provide useful baseline data for such comparative studies.

Bioactive glasses, particularly those with compositions having SiO$_2$ levels ranging from 42 to 52% (e.g., 45S5 Bioglass: 45 wt% SiO$_2$, 6 wt% P$_2$O$_5$, 24.5 wt% CaO, and 24.5 wt% Na$_2$O), exhibit substantial bioactivity by rapidly bonding to bone and soft connective tissues. Such characteristics arise as a result of chemical reactions occurring at the surface of the Bioglass when exposed to ambient body fluids. Ion exchange results in irregular surface dissolution, increasing the presented area and forming a microcrystalline biological apatite layer on the roughened glass surface. This layer, which can form in as little as a few hours in vivo, bonds not only to bone but also to collagen fibrils. It is the latter type of bonding that is required for the prosthesis to achieve interfacial bonds with soft tissues.

The bioactivity testing conducted with SBF-tris indicated that

<table>
<thead>
<tr>
<th>Skeletal Tissue</th>
<th>Young’s Modulus (GPa)</th>
<th>Tensile Strength (MPa)</th>
<th>Strain to Failure (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cancellous bone</td>
<td>0.05–0.5</td>
<td>10–20</td>
<td>5–7</td>
</tr>
<tr>
<td>Articular cartilage</td>
<td>0.001–0.01</td>
<td>10–40</td>
<td>15–50</td>
</tr>
<tr>
<td>Tendon</td>
<td>1</td>
<td>80–120</td>
<td>10</td>
</tr>
</tbody>
</table>

Figure 8. FTIR spectra obtained from Bioglass*/HDPE composite and particulate Bioglass® after they were treated at 37°C for 20 h in (a) SBF-tris or (b) SBF-9 solution.

Figure 9. Comparison of Young’s modulus values between Bioglass*/HDPE and HA/HDPE composites.
cated that only composites with 40% Bioglass® were bioactive [Fig. 8(a)]. This probably is due to low concentrations of calcium and phosphate ions in the solution as a result of only a relatively small amount of Bioglass® particles being exposed to the solution for the composite with less than 40% Bioglass®. On the contrary, the SBF-9 solution already contains calcium and phosphate ions in the solution; thus there are sufficient concentrations of these ions for the formation of the biological apatite layer on the Bioglass® particles and, hence, on the composite surface. Composites with as little as 10% Bioglass® are bioactive in the SBF-9 solution.

The FTIR analysis has shown that the Bioglass®/HDPE composite, of all the compositions examined, developed a biological apatite layer after treatment with the SBF-9 solution, which confirms that the composite possesses bioactivity. The rate of apatite formation (i.e., the actual level of bioactivity), however, depends on the volume of the Bioglass® phase in the composite, which has been subjected to a systematic investigation.

By varying the amount of the bioactive phase (that is, Bioglass®) in the composite, a novel material can be tailor-made to meet the specific requirements for mechanical/biological performance, such as Young’s modulus and the degree of tissue bonding. Therefore, the Bioglass®/HDPE composite may be used to replace a range of hard and soft tissues, with the prosthesis having a variable in vivo attachment duration.

Now that the processing route has been established and the composite evaluated, further research on the Bioglass®/HDPE system will be directed towards the use of Bioglass® particles with smaller sizes and rounded shapes. The long-term in vitro and in vivo behavior of the Bioglass®/HDPE composite also needs to be investigated.

**CONCLUSIONS**

Bioglass®/HDPE composites containing up to 40% by volume of Bioglass® particles have been manufactured. Bioglass® particles are well dispersed and homogeneously distributed in the polyethylene matrix using established processing technology. It has been demonstrated that the Young’s modulus and micro-hardness of the composite increase with an increase in Bioglass® volume while the tensile strength and fracture strain decrease. A biological apatite layer develops on the composite surface when the composite is subjected to a simulated body fluid. By retaining the interfacial and chemical properties of bulk Bioglass®, the Bioglass®/HDPE composite offers unique advantages for applications as soft-tissue prostheses.

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