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Technical note

Bioactive glass surface for fiber reinforced composite implants via surface etching by Excimer laser

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ABSTRACT

Biostable fiber-reinforced composites (FRC) prepared from bisphenol-A-glycidyldimethacrylate (BisGMA)-based thermosets reinforced with E-glass fibers are promising alternatives to metallic implants due to the excellent fatigue resistance and the mechanical properties matching those of bone. Bioactive glass (BG) granules can be incorporated within the polymer matrix to improve the osteointegration of the FRC implants. However, the creation of a viable surface layer using BG granules is technically challenging. In this study, we investigated the potential of Excimer laser ablation to achieve the selective removal of the matrix to expose the surface of BG granules. A UV–vis spectroscopic study was carried out to investigate the differences in the penetration of light in the thermoset matrix and BG. Thereafter, optimal Excimer laser ablation parameters were established. The formation of a calcium phosphate (CaP) layer on the surface of the laser-ablated specimens was verified in simulated body fluid (SBF). In addition, the proliferation of MG63 cells on the surfaces of the laser-ablated specimens was investigated. For the laser-ablated specimens, the pattern of proliferation of MG63 cells was comparable to that in the positive control group (Ti6Al4V). We concluded that Excimer laser ablation has potential for the creation of a bioactive surface on FRC-implants.

1. Introduction

Biostable fiber-reinforced composites (FRC) are promising alternatives to metallic implants due to the excellent fatigue resistance and the mechanical properties matching those of bone [1]. FRCs prepared from bisphenol-A-glycidyldimethacrylate (BisGMA)-based thermosets reinforced with E-glass fibers have been successfully used in dental reconstructions [2,3]. Clinical use of non-load-bearing FRC implants has already commenced in cranial reconstructions [4]. In addition, preclinical studies demonstrated the potential of BisGMA-based FRC implants in load-bearing orthopaedic applications [5,6]. Bioactive glass (BG) granules can be incorporated into the surface of the FRC implants to improve their osteointegration. The bioactivity of BG is manifested in the formation of direct chemical bond between BG and bone through the cascade of chemical reactions and cellular activity [7–9]. Formation of a calcium phosphate (CaP) surface reaction layer is a crucial aspect of bone bonding. BG granules are certified for clinical use i.e. as bone graft substitutes [10–13]. However, our previous studies revealed technical challenges in the creation of a feasible surface layer using BG granules [5,6]. A large number of unreacted BG granules were trapped inside the polymer matrix, while the surface area of the granules exposed by grinding was insufficient to achieve notable improvement in the osteointegration of the implants [5]. In addition, the mechanical treatment, i.e. grinding, of the implant surface led to the disengagement of the granules either before or after the implantation [5]. Therefore, there is a need for the development of new techniques for the incorporation of BG granules in the surfaces for the FRC implants.

Surface ablation of polymers by Excimer lasers was demonstrated in the early 1980s [14,15]. Studies with laser ablation of the composites revealed selective removal of the polymer matrix and

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Table 1
Summary of materials used for the preparation of the specimens.

Material	Type of material	Manufacturer
Bisphenol-A-glycidyldimethacrylate (BisGMA)	Co-monomer	Röhm Chemische Fabrik GmbH, Darmstadt, Germany
Triethylene glycol dimethacrylate (TEGDMA)	Co-monomer	Aldrich Chemie GmbH, Steinheim, Germany
2-(Dimethylamino)ethyl methacrylate (DMAEMA)	Activator	Fluka Chemie GmbH, Buchs, Switzerland
Camphorquinone	Photoinitiator	Sigma-Aldrich GmbH, Buchs, Switzerland
Bioactive glass (BG) S53P4, granules: 315–500 μm fraction, oxide composition (wt%): SiO_2 53%, Na_2O 23%, CaO 20%, P_2O_5 4%	Osteoconductive surface component	Vivoxid Ltd., Turku, Finland

exposure of the reinforcing glass fibers [16,17]. We hypothesized that with this setup, Excimer laser ablation would allow selective removal of the thermoset matrix and the exposure of the BG granules, which in turn, would enhance the osteoconductivity of the FRC implants without the disengagement of BG granules.

2. Materials and methods

2.1. Methodology of the study

The targeted implants are intramedullary nails reported previously [5,22]. The core of the implants is reinforced with long glass fibers while the relatively thick surface layer (~1 mm) contains unreinforced resin embedded with bioactive glass granules. Therefore, for the sake of simplicity, we excluded the reinforcing phase from consideration and used unreinforced thermosets in all experiments.

This study included four experiments. The first experiment, a UV–vis spectroscopic study, was carried out to investigate the differences in the penetration of light in the thermoset matrix and BG. The second experiment was carried out to establish the optimal laser ablation parameters. The third experiment was performed to study CaP formation on the surfaces of the specimens immersed in simulated body fluid (SBF) [18]. The fourth experiment was performed to study MG63 cell proliferation on the surfaces of the specimens to verify the absence of negative effects of laser radiation. The laser ablation parameters used in the third and fourth experiment, were based on the results obtained in the second experiment.

2.2. First experiment: UV–vis spectroscopic study

Two groups of specimens, BG and thermosets, were used in the UV–vis spectroscopic study. Materials used for the preparation of the specimens are listed in Table 1.

Rectangular-shaped BG specimens (10 × 10 mm) were cut from a 1 mm-thick BG S53P4 plate. This determined the shape of the specimens used in this experiment. The BG specimens were prepared in three different thicknesses: 1.3 mm, 0.5 mm, and 0.2 mm by grinding with silicon carbide paper of 1000, 2400, and 4000 grit, with further polishing with 0.1 μm alumina paste. Ethanol was used in grinding and polishing to avoid the formation of reaction layers. Subsequently, the specimens were cleaned ultrasonically in ethanol.

Impression molds made from dental putty were used to prepare the thermoset specimens. The photopolymerisable resin was prepared by mixing BisGMA (70 wt%) and triethylene glycol dimethacrylate (TEGDMA) (30 wt%) with camphorquinone (CQ) (0.7 wt%) and 2-(dimethylamino)ethyl methacrylate (DMAEMA) (0.7 wt%) [19]. Thereafter, the resin was poured into the molds and briefly pre-cured (40 s) by a hand curing device (Optilux 501, Kerr, Danbury, USA). Next, the thermoset specimens were taken out of the molds and cured in vacuum light oven (Visio Beta vario, 3 M/ESPE, Seefeld, Germany) for 15 min at ambient temperature. Subsequently, in order to reduce the amount of residual monomers, the specimens were placed in a light oven (Liculite, Dentsply De Trey GmbH, Dreieich, Germany) for 25 min. During the time, the temperature of the curing chamber increased to 90 °C. The thermoset specimens were ground with silicon carbide paper of 1000, 2400, and 4000 grit, and further polished with 0.1 μm alumina paste. Water was used in grinding. The thermoset specimens were prepared in four different thicknesses: 1.3 mm, 0.5 mm, 0.2 mm and ~0.05 mm. After the preparation, the specimens were cleaned ultrasonically in water.

Light transmittance in the range of 270–340 nm was studied using UV–vis spectrophotometer (Shimadzu UV-1601, Shimadzu Corp. Tokyo, Japan).

2.3. Preparation of the thermoset and thermoset-BG specimens

Disc-shaped specimens (Ø8.6 mm, thickness 3 mm) were used in the second, third and fourth experiments. Two experimental groups of specimens were prepared. The specimens in first group, termed “thermoset”, were made of photopolymerisable resin. The specimens in the second group, termed “thermoset-BG”, were made of photopolymerisable resin with a surface layer of BG S53P4 granules entrapped in the resin.

In the thermoset group, the preparation method was similar to that used in the first experiment. The specimens were grit-polished (granulometry: 1200).

In the thermoset-BG group, the preparation method was modified to incorporate BG granules. After pre-curing (40 s) with a hand curing device, a thin layer of resin was applied to the oxygen inhibited resin surface of the specimens. The specimens were then pressed against BG granules spread over a flat surface. Another thin layer of resin was added and the specimens were once again pressed against BG granules. The excess BG granules were removed by tapping on the back of the specimens. Thereafter, the final resin layer was applied on top of the granules. Subsequently, the thermoset-BG specimens were light-cured using procedures identical to the ones used to cure the specimens in the thermoset group. The thermoset-BG specimens were not grit-polished. Materials used for the preparation of the specimens are listed in Table 1.

2.4. Second experiment: optimization of processing parameters in laser ablation

Only thermoset-BG specimens were used in this experiment. Excimer (XeCl) laser (ASX-750, MPB Technologies Inc, Tallinn, Estonia) with a wavelength of 308 nm and a pulse width of 28 ns (FWHM) was used for the ablation of the thermoset resin covering the BG granules. To proceed with the surface ablation, the specimens were mounted on a custom-made computer-controlled stage, which allowed precise spatial positioning. Laser beam was partially focused by a lens. The laser beam remained static during the experiment. In turn, the specimen was moved by the stage. To process a larger area, the specimen was repositioned, without overlapping of the areas affected by the laser beam. A schematic illustration of the impact of the laser beam on the specimen surface is shown in Fig. 1. A series of experiments was carried out to