COPPER- AND ZINC-BEARING COMPOSITE MEMBRANES FOR PERIODONTAL REPAIR

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Introduction
Periodontitis (inflammation and destruction of the tooth attachment apparatus) is one of the most widespread diseases in the world [1]. Polymer-bioactive glass composite membranes can be used for the guided tissue regeneration (GTR) of diseased periodontal structures [2]. GTR involves the placement of the membrane to exclude soft epithelial and gingival tissues from the exposed tooth in order to facilitate the regeneration of the more slow-growing periodontal ligament and hard tissues [1]. Bioactive glasses incorporating antimicrobial ions such as silver, zinc and copper have been shown to resist biomaterial-centred infection; although, the presence of these metal ions is reported to reduce bioactivity in some instances [3]. Chitosan, a biodegradable carbohydrate polymer, is a popular choice for GTR membranes as its structure resembles that of bone extracellular matrix [2]. In the present study, copper- and/or zinc-bearing bioactive glasses were prepared by the sol-gel process and incorporated into chitosan membranes by solvent-casting. The in vitro bioactivity and degradation rates of the chitosan-bioactive glass membranes were evaluated with respect to their potential use as GTR membranes.

Materials and Methods
Bioactive glass (BG), in the system SiO₂-P₂O₅-CaO, was prepared by the sol-gel method [3] and ion-exchanged with copper or zinc by immersion in 50 mM metal nitrate solution for 24 h (to produce samples BG-Cu and BG-Zn, respectively). BG samples incorporating a combination of both copper and zinc ions were similarly prepared by exposure to mixed metal nitrate solutions at concentrations of 25 mM (BG-25mix) or 50 mM (BG-50mix) with respect to both metals. The resulting gel-glasses were calcined in air at 680 °C for 2 h to decompose the nitrate ions and stabilise the glasses. The samples were characterised by X-ray diffraction analysis (XRD), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDX). Chitosan and bioactive glass were blended in 1% aqueous acetic acid solution at a chitosan:glass mass ratio of 5:1. The solutions were cast on to polycarbonate surfaces and dried in air at 60 °C. The in vitro bioactivity of the composite membranes was evaluated by monitoring hydroxypatite (HA) formation on their surfaces in simulated body fluid (SBF) at 1, 3, 7 and 14 days [4]. HA was confirmed by FTIR, SEM and EDX. The extent of degradation of the membranes during residence in SBF was evaluated on a mass basis. Each analysis was carried out in triplicate.

Results and Discussion
XRD and FTIR analyses indicated that all glass samples were essentially amorphous with traces of calcite (CaCO₃) prior to calcination. Calcined BG, BG-Cu and BG-Zn samples were similarly shown to be amorphous with trace quantities of calcite. In addition to the glassy matrix, samples BG-25mix and BG-50mix were found to comprise HA at approximately 2 and 12%, respectively. Hence, the incorporation of a combination of copper and zinc into the glass induced the progressive crystallisation of HA during calcination which resulted in glass-ceramic products.

The characteristic sharp doublet of crystalline hydroxyapatite at 570 – 605 cm⁻¹ appeared in the FTIR spectra of all composite membranes following a residence time of 1 day in SBF, which intensified as a function of time. The presence of HA was additionally confirmed by SEM and EDX. In contrast, pure chitosan membranes did not elicit the precipitation of HA within the 14-day timeframe. Similar rates of degradation were observed for all specimens irrespective of their composition.

Conclusions
In combination, the presence of copper and zinc promotes the crystallisation of HA during the calcination of the sol-gel-derived glasses to form glass-ceramic products. All chitosan-bioactive glass composites were found to exhibit bioactivity in vitro. Further work is now in progress to investigate the biocompatibility, mechanical properties and antimicrobial activity of these potential GTR membranes.

References

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