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Re-crystallization of silica-based calcium phosphate glass prepared by sol–gel technique

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ABSTRACT

Bioactive glass (BG) is a potential material for treating dentin hypersensitivity owing to its high solubility. In this study, we synthesized 80S-BG bioactive glass samples using a sol–gel technique and mixed with various hardening agents. The obtained material could be used in human dentinal dentinal tubule occlusions. X-ray diffraction (XRD), scanning electronic microscopy (SEM), and Fourier transform infrared spectroscopy (FTIR) measurements were employed to investigate the physiochemical properties and dentinal dentinal tubule occlusion efficiency by mixing the 80S bioactive glass (80S-BG) with various hardening agents.

The major crystallite phase obtained on mixing 80S-BG with phosphoric acid (PA) was $Ca(H_2PO_4)_2{\cdot}H_2O$. The mixture of 80S-BG powders and 20, 30, or 40 wt% PA acted as a hardening agent and achieved a dentinal tubule penetration depth of 30.7–62.6 μm.

80S-BG on mixing with suitable PA agents exhibited a short reaction time and good operability, making it feasible for use in occluding dentinal tubules. 80S-BG mixed with hardening agents exhibited a greater potential for treating dentin hypersensitivity as compared to the 80S-BG not mixed with any hardening agents.

1. Introduction

Since the Food and Drug Administration (FDA) approved Bioglass 45S5 particulates to be used for dentinal hypersensitivity treatment (NovaMin) in 2004, several dental maintenance products have been developed [1–5].

The main composition of Bioglass 45S5 is 45% SiO_2–24.5% CaO–24.5% Na_2O–6% P_2O_5. It has been used in dentistry as an endosseous ridge maintenance implant to maintain the ridge shape and integrity after teeth extraction [6–10].

Bioglass 45S5 is processed at melting temperatures in the range of 1300–1450 °C followed by employing the casting of bulk implants or quenching to allow the formation of powders. Since the discovery of this melt-derived bioglass, a series of sol–gel composition glasses have been used to demonstrate the in vitro bioactivity in simulated body fluid (SBF) with up to approximately 90% SiO_2. These glasses exhibited the formation of a hydroxy carbonate apatite (HCA) layer [11].

The development of a sol–gel technique for producing bioactive sol–gel glasses in 1991 resulted in the production of glass samples with various compositional ranges. Sol–gel glasses are prepared at low temperatures. Owing to the high surface area and porosity of the obtained sol–gel glasses, a wide range of bioactive compositions can be obtained to achieve high bone bonding rates and excellent degradation/resorption properties [12–16].

A method of reducing dentin hypersensitivity usually involves protein precipitations. The chemicals are used to precipitate protein within the dentin tubules to reduce fluid disturbances. Although it has successfully reduced dentin hypersensitivity, it is gradually being eliminated due to it can induce a permanent color deposition on the teeth surfaces and create an irritated reaction around the gums and the dental pulp [17]. Currently, most of the procedures to treat dentin hypersensitivity involve dentinal tubule occlusion. Dentinal tubule occlusion is used the chemicals to seal the dentin tubules by forming crystals or minerals to reduce or seal the opening end of dentin tubules [18–22].

In this study, $80SiO_2$–$15CaO$–$5P_2O_5$ glass powders are prepared using a sol–gel technique. We hypothesize that on mixing $80SiO_2$–$15CaO$–$5P_2O_5$ glass powders with phosphoric acid (PA), a positive impact in the human dentinal dentinal tubule occlusion and reduction

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of the dentin penetration as compared to performing the same treatment without PA can be achieved. However, an empirical study for comparing the occlusion efficiency of $80SiO_2–15CaO–5P_2O_5$ glass powders mixed with various hardening agents in human dentinal tubules has not yet been performed.

This study explores the influences of dentin specimens smeared with $80SiO_2–15CaO–5P_2O_5$ glass (80S-BG) powders as a substrate, by using phosphate buffered saline (PBS) or PA as the hardening agent, on the re-crystallization behavior and human dentinal tubule penetration depth.

2. Materials and methods

2.1. Bioactive glass synthesis and dentin specimen preparation

The molar ratio of Si, Ca, and P of 80S-BG synthesized using the sol–gel technique was 80:15:5. 6.7 g tetraethyl orthosilicate (TEOS), 1.4 g $Ca(NO_3)_2·4H_2O$, 0.73 g triethyl phosphate (TEP), and 1 g 0.5 M HCl were dissolved in 60 g ethanol and stirred at room temperature for 1 day [23]. The mixture was then thermally treated at constant heating rates (10 °C/min) at calcination temperatures of ~ 600 °C for 2 h. After cooling, the 80S-BG powders formed were sieved through #325 meshes.

With a powder to liquid ratio of 1 g to 2 mL, 80S-BG powders were homogeneously mixed with various hardening agents, such as 20 wt%, 30 wt%, and 40 wt% PA, de-ionized water, or PBS. The mixtures subjected to various testing procedures in this study are listed in Table 1.

The dentine specimens were prepared using the caries-free human molars of healthy patients for surgical reasons. The teeth were obtained after approval of KMUHIRB-E(I)-20150073 from Institutional Review Board of Kaohsiung Medical University Hospital, Taiwan. Dentin specimen pretreatment and preparation procedures were employed as reported in our previous study [24]. The produced 80S-BG formulations were smeared on the dentin specimen surfaces and incubated at 37 °C with 100% relative humidity, for simulating the natural environment of the oral cavity. The occlusion time employed was 5–10 min. When the occlusion was complete, the dentin specimens were rinsed with a large quantity of de-ionized water for 20 s and submerged into anhydrous ethanol to stop any further reaction from occurring.

2.2. Textural characterization

X-ray diffraction (XRD, Rigaku D-max IIIV, Tokyo, Japan) at a scanning speed of 4°/min within 2θ in the range of 10–80° and Fourier transform infrared spectroscopy (FTIR) analyses (Thermo NICOLET 6700, MA, US) were employed.

To examine the re-mineralized morphologies and the elemental compositions of the cross-sections of the dentin specimens, the specimens were examined using a field emission scanning electron microscope (FESEM, Hitachi S-3000N, Hitachi, Tokyo, Japan). All the dentin specimens were purged for 12 h at 150 °C in the high vacuum degassing port of the adsorption analyzer. The specific surface areas of the dentin specimens were measured with the BET method (ASAP 2010, Micromeritics, USA) using nitrogen as an absorbent.

Table 1
Groups of 80S-BG mixed with various hardening agents tested in this study.

Testing sample	Abbreviation of group
80S-BG mixed with de-ionized water	80S-BG/W
80S-BG mixed with PBS	80S-BG/PBS
80S-BG mixed with 20 wt%, 30 wt%, or 40 wt% PA	80S-BG/20PA, 80S-BG/30PA, or 80S-BG/40PA

2.3. Re-crystallization ability evaluation using the human dentinal tubule penetration depth

After drying for 24 h, the dentin specimens were mechanically split open for performing the occlusion efficiency analysis. The specimens were split along a groove and coated with gold. The surface and cross-section microstructures of the specimens were analyzed to examine the occlusion efficiency on the dentin specimen surfaces and re-crystallization occurring in the dentinal tubules.

The occlusion efficiency and penetration depth in the dentinal tubules were calculated using the SEM images. 20 human dentinal tubules from 3 sets of SEM images were used for sampling. The occlusion efficiency was defined as the ratio of dentinal tubules exhibited re-crystallization to the total number of dentinal tubules. The penetration depth was defined as the average length of re-crystallization achieved for all the dentinal tubules (the unit: μm).

2.4. Statistical analysis

Statistical analysis was employed with JMP 9.0 software (SAS Institute Inc., Cary, NC, US). Differences with p values < 0.05 were considered statistically significant. A one-way ANOVA and a multiple comparison procedure (Tukey's Honestly Significant Difference Test) were employed to determine significant differences.

3. Results and discussion

3.1. Property analysis of the 80S-BG powder and formulations

80S-BG powder was mixed with de-ionized water, PBS, or 20 wt%, 30 wt%, and 40 wt% PA, and the obtained samples are referred to as 80S-BG/W, 80S-BG/PBS, 80S-BG/20PA, 80S-BG/30PA, and 80S-BG/40PA, depending on the contents in the mixture. The XRD patterns of the 80S-BG powder and the above-mentioned formulations are shown in Fig. 1. The diffraction peaks of the 80S-BG/W and 80S-BG/PBS formulations were similar to the diffraction peaks of the 80S-BG powders. The intensity of the peaks was almost the same for 80S-BG/20PA, 80S-BG/30PA, and 80S-BG/40PA. $Ca(H_2PO_4)_2·H_2O$ was formed on mixing 80S-BG powders with PA. The peaks corresponding to $Ca(H_2PO_4)_2·H_2O$ appeared at 22.9° and 24.1°. According to JCPD 70–1381 and literature, this phase corresponds to triclinic calcium dihydrogen phosphate [25]. These peaks were not observed in the XRD patterns of 80S-BG, 80S-BG/W, and 80S-BG/PBS.

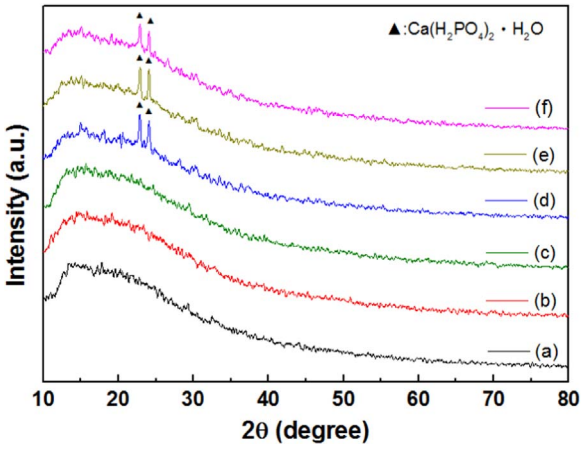

Fig. 1. XRD patterns of (a) 80S-BG, (b) 80S-BG/W, (c) 80S-BG/PBS, (d) 80S-BG/20PA, (e) 80S-BG/30PA, and (f) 80S-BG/40PA.