

Vibrational Study on the Bioactivity of Portland Cement-Based Materials for Endodontic Use

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In the last decade, white Portland cement was developed as endodontic sealer and root-end filling material. This new material was investigated because it sets in the presence of water, an important property for dental materials. One of the main disadvantages when using white Portland cement is its extended setting time and difficult handling.

This study was aimed at investigating modified Portland cement-based materials with regard to their bioactivity (i.e. the capability of forming a calcium phosphate layer in physiological fluids) after treatment for different times (from 1 to 90 days), at 37°C, in Dulbecco's Phosphate buffered saline (DPBS) and Hank's balanced salt solution (HBSS).

To evaluate the influence of a calcium phosphate on bioactivity, two cements were investigated: wTC 1% (derived from white Portland cement) and wTC-TCP (wTC 1% added with tricalcium phosphate). ATR/FT-IR and micro-Raman spectroscopy were used to investigate the presence of deposits on the surface of the cements and the composition changes of the cement as a function of storage time.

Micro-Raman and ATR-FTIR analyses of the wTC-TCP cement treated with DPBS revealed the presence of a calcium phosphate deposit already after one day of storage, as suggested by the presence of the IR bands at about 1025 cm⁻¹ (asymmetrical stretching of phosphate group), 600 and 560 cm⁻¹ (bending of phosphate group) and of the Raman band at 963 cm⁻¹ (symmetrical stretching of phosphate group). At the same storage time, wTC1% showed a thinner deposit. The thickness of the deposit was evaluated by the analysis of the micro-Raman spectra recorded in the section of the samples and by the $I_{960(\text{phosphate})}/I_{990(\text{cement})}$ (Raman) and $I_{1030(\text{phosphate})}/I_{950(\text{cement})}$ (IR) ratios obtained on the surfaces of the samples.

At increasing storage times in DPBS, the thickness of the deposit increased as well as its crystallinity and the bands of carbonated apatites appeared at 1460-1415, 1025, 960, 600-560 cm⁻¹ (IR, carbonate ion in a B-type carbonated apatite, asymmetrical stretching, symmetrical stretching and bending of phosphate, respectively) and 1074, 1050, 965, 606-595-436 cm⁻¹ (Raman, carbonate stretching, asymmetrical stretching, symmetrical stretching and bending of phosphate, respectively). After 60 and 90 days of treatment with DPBS, the bands of the cement were no longer observable for wTC-TCP, while they were detectable for wTC 1%. This result indicated a better bioactivity for the former than for the latter.

The composition changes of the cement (ettringite/silicate ratio) were evaluated on the surface and in the interior of the samples by the I_{990}/I_{860} (Raman) and I_{1110}/I_{950} (IR) ratios.

Bands at 3640 cm⁻¹ (IR) and 360 cm⁻¹ (Raman), attributable to Ca(OH)₂, were observable in the interior of all the samples, but not on their surface. This result indicated a Ca(OH)₂ release in the storage medium, which appeared slightly more pronounced for wTC-TCP. This behaviour, confirmed by pH measurements of the storage fluids, is known to render the material biocompatible. The samples treated with HBSS showed analogous trends; however, bioactivity was noticeably less pronounced than in DPBS, according to the lower phosphate concentration in the former than in the latter. Ca(OH)₂ release was less significant as well.