
Structure-dissolution relationships in bioactive phosphate glasses

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Abstract

Degradation of phosphate glasses in aqueous environments is interesting for biomedical applications. However, in order to be able to design materials with tailored solubility, it is imperative to obtain meaningful dissolution kinetics data to better predict in vivo performance. In the present work, structural characterization via P-31 MAS NMR and thermal analysis was correlated with both static and dynamic dissolution profiles of the system $45\text{P}_2\text{O}_5-x\text{CaO}-(55-x)\text{M}_2\text{O}$ (mol%; x: 25 to 40) with M = Li, Na or K, where the CaO:Na₂O ratio was varied while the phosphate content was maintained constant. Dissolution kinetics in Tris buffer (pH 7.4) were addressed through time-dependent P-31 solution NMR, pH and ICP-OES measurements. According to MAS NMR, all glasses were composed of pyrophosphate Q1 and metaphosphate Q2 species with chains from 8 to 9 phosphate groups in length. The glasses with the general composition $45\text{P}_2\text{O}_5-x\text{CaO}-(1-x)\text{Na}_2\text{O}$ showed an increase in the P-31 shielding with increasing CaO content. This substitution also produced a systematic increase in the T_g and T_c. Such relationships were expected owing to the higher field strength of calcium compared to sodium. Dissolution experiments showed congruent dissolution with the rate of degradation decreasing with increasing CaO content and field strength of the alkali cation (Li⁺ > Na⁺ > K⁺). The relative dissolution ratio among the series of glasses was maintained in both static and dynamic conditions. However, the latter provided a better picture of pH changes at early times, showing the average result of two competing reactions, thus ion exchange and hydrolysis of polyphosphates, being the CaO content proportional to relative more acidic pH values. This was consistent with P-31 solution NMR findings, which showed that the presence of CaO, trapped in complexes, led to hydrolytic degradation of long-chain phosphates into orthophosphate and trimetaphosphate.

Keywords: phosphate glasses, kinetics, dynamic dissolution, static dissolution, P31 MAS NMR, P31 NMR, pH, ICP OES, field strength, ion exchange, hydrolysis

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