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Microstructural characterization of dental zinc phosphate cements using combined small angle neutron scattering and microfocus X-ray computed tomography

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ARTICLE INFO

Article history:
Received 7 October 2016
Received in revised form
14 January 2017
Accepted 17 January 2017

Keywords:
Zinc phosphate cements
Small angle neutron scattering
X-ray micro-computed tomography
X-ray powder diffraction
Zinc oxide
Acid-base cements

ABSTRACT

Objective. To characterize the microstructure of two zinc phosphate cement formulations in order to investigate the role of liquid/solid ratio and composition of powder component, on the developed porosity and, consequently, on compressive strength.

Methods. X-ray powder diffraction with the Rietveld method was used to study the phase composition of zinc oxide powder and cements. Powder component and cement microstructure were investigated with scanning electron microscopy. Small angle neutron scattering (SANS) and microfocus X-ray computed tomography (XmCT) were together employed to characterize porosity and microstructure of dental cements. Compressive strength tests were performed to evaluate their mechanical performance.

Results. The beneficial effects obtained by the addition of Al, Mg and B to modulate powder reactivity were mitigated by the crystallization of a Zn aluminate phase not involved in the cement setting reaction. Both cements showed spherical pores with a bimodal distribution at the micro/nano-scale. Pores, containing a low density gel-like phase, developed through segregation of liquid during setting. Increasing liquid/solid ratio from 0.378 to 0.571, increased both SANS and XmCT-derived specific surface area (by 56% and 22%, respectively), porosity (XmCT-derived porosity increased from 3.8% to 5.2%), the relative fraction of large pores $\geq$50 μm, decreased compressive strength from 50 ± 3 MPa to 39 ± 3 MPa, and favored microstructural and compositional inhomogeneities.

Significance. Explain aspects of powder design affecting the setting reaction and, in turn, cement performance, to help in optimizing cement formulation. The mechanism behind

Abbreviations: ZPC, zinc phosphate cement; l/s, liquid to solid weight ratio; MIP, mercury intrusion porosimetry; SANS, Small angle neutron scattering; XRPD, X-ray powder diffraction; QPA, quantitative phase analysis; SEM, scanning electron microscopy; XmCT, microfocus X-ray computed tomography; S_V, surface area of pores per unit volume of sample investigated; *D*, pore diameter.

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http://dx.doi.org/10.1016/j.dental.2017.01.008

development of porosity and specific surface area explains mechanical performance, and processes such as erosion and fluoride release/uptake.

1. Introduction

Zinc phosphate cements are a class of acid-base cements which find application in dentistry largely as luting or lining agents [1]. ZPC is one of the oldest dental cements, being introduced in the 1880s. Because of the inferior mechanical and biological properties, compared to some of the more recent bioactive restorative materials [2,3], the use of ZPC has significantly declined, although it possesses a successful track record, supported by clinical evidences [4,5]. However, a huge resident population of cemented restorations still exists, making the understanding of structure-limited properties important for the interpretation of their clinical longevity. ZPC is supplied as a liquid component, consisting in a solution of phosphoric acid (45–65%) containing up to about 3% of aluminum and possibly zinc (up to 10%), and a zinc oxide powder. Additions to the solution are aimed at gaining control over the reaction rate and the heat of reaction. Reactivity of the powder is reduced by annealing ZnO at temperatures between 1000 °C and 1400 °C, after mixing it with about 10 wt% of MgO. Sometimes, fluxing agents, like borax, are added to improve the degree of sintering [6]. In analogy with MgO employed in magnesium phosphate cements [7], the thermal treatment results in ZnO of higher mean crystallite size and particles with smooth surface [8,9]. With these compositions, the first product of the setting reaction is completely amorphous, and the presence of aluminum has been recognized to play a crucial role in modifying the chemistry of the reaction and stabilize the amorphous fraction [10–12].

The study of the setting reaction showed that this first product is an amorphous zinc phosphate hydrate which forms at the surface of the ZnO particles [11]. Crystallization of zinc phosphate is thought to be hindered by the disorder introduced by the polymeric complexes formed when Al is introduced in the phosphoric acid solution [12] or by the entanglement of chains of aluminum phosphate hydrogel embedding the particles [11]. In the latter case, the experimental evidences pointed to an amorphous zinc phosphate with composition $Zn_2P_4O_{12}{\cdot}8H_2O$, a cyclophosphate in which some of the water molecules are loosely bound. This was found consistent with the crystallization of hopeite ($Zn_3(PO_4)_2{\cdot}2H_2O$) from the amorphous, an occurrence observed in aged commercial cements [13,14]. The compressive strength of the cement was shown to increase with the increase in the powder fraction [15–17] up to values above which probably the wetting of ZnO particles is compromised, in analogy with other dental cements [18]. In the clinical practice, the liquid to solid weight ratio (l/s) is optimized for the specific applications, therefore, variable amounts of unreacted ZnO can be found in the final cement [10,16]. It follows that the ZPC can be considered as a composite material and the interaction between ZnO grains and the amorphous matrix has important implications for the longevity of the restoration. In this respect, crack deflection around composite particles, a well-documented toughening mechanism [19,20], has been observed in ZPCs [16].

On the other hand, pores are fracture initiation sites under load [21,22], although, in glass materials they are considered more stress concentrators rather than flaws, as for polycrystalline or glass-ceramics [23]. In general, since ZPCs are highly defect-limited, the measure of the porosity is a significant parameter for their characterization. The final porosity of the cement can be strongly affected by the mixing technique adopted and the viscosity of the paste (dependent on l/s) during preparation [18,24,25]. The imperfect homogenization of the powder was found to yield clusters of ZnO particles which develop large irregular pores with diameter $D > 5\,\mu m$ [16] of deleterious nature [23]. In this respect, a distinction should be made between the large pores (>1 μm in size) and the smaller meso-micro-pores (as defined in Ref. [26]). In fact, the amount of the former has been directly related to the cases of failure of the restorations and, in general, was found to correlate negatively with the mechanical properties [21,24]. Much less information is available about the latter. Few examples of characterization of porosity in ZPCs are reported [16,27,28], in some of them optical techniques were used [16,27], which show obvious limits of representativeness and accessible range in pore size. A technique usually employed to retrieve the pore-size distribution in solids is mercury intrusion porosimetry (MIP). However, MIP possess several drawbacks that can sometimes lead to misleading results [29]; it is destructive, it relies on the assumption of cylindrical pore shape and it is limited to the detection of open porosity [30]. Reliability of MIP results might be also impaired by microstructural changes occurring in the sample under the vacuum conditions required for the analysis. Substantial loss of chemically bound water in the porosimeter has been observed in magnesium phosphate cements [31]. Furthermore, availability of MIP for the next future is threatened by the progressive mercury phase out ratified by many countries in 2013 [32].

In any porous material, a further critical descriptive parameter of its microstructure is the S_V specific surface area. Being related to the degree of subdivision, it is most sensitive to changes in the smallest microstructural details and controls to a large extent the rate of the chemical and/or physicochemical reactions, therefore the behavior of the material in applications. Dissolution/erosion, take up or release of elements from solution (such as fluoride) are of interest for restorative materials, and they have been shown to be more surface-dependent rather than volume-dependent [33].

SANS has been recognized to be a valuable tool for the evaluation and quantification of a statistically representative microstructure (and nano-structure) of heterogeneous mate-