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MICROSTRUCTURE-PROPERTY RELATIONS IN THE MECHANICS OF DENTAL CEMENT PASTE OF TYPE "BIODENTINE"

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Abstract: The biomaterial "Biodentine" exhibits very interesting mechanical porperties, with a strength exceeding those of the biological tissue "dentine". In the case of decay, replacement of the latter by the former is a clinically very interesting option. The question remains why Biodentine, being chemically very similar to ordinary Portland cement, outperforms the latter up to such a significant degree. The experiments (nanoindentation, ultrasonics, light microscopy, mechanical testing) and micromechanical models reviewed in this paper give indications towards answers to the aforementioned question. They concern the very high fineness of the cement power, with micrometer-to-submicrometer particle size, the formation of calcite-reinforced hydration products, and a pronouncedly uniform loading state throughout the microstructural hydrate networks, as fingerprint of an optimized load carrying mechanism.

1 INTRODUCTION

The dental cement paste of type "BioDentine" is characterized by extraordinary strength properties, exceeding those of the biological tissue called "dentine" [1]. This tissue makes up the central base of a human tooth, being surrounded by a shell consisting of enamel, the hardest and stiffest material found in the human body [2]. Accordingly, injection of Biodentine cement powder together with a dedicated liquid, is a preferable solution for replacing heavily decayed dentine-made portions of the neck and the crown of human teeth. At the same time, the question remains how the Biodentine biomaterial can reach strength values beyond 300 MPa [3], while being, in terms of chemistry, very close to Portland cement used in the construction industry, with associated strength values of building materials amounting typically to some 100 MPa [4]. This question motivated a comprehensive investigation [5,6,7] on Biodentine hardened cement paste, combining experimental, theoretical, and computational approaches: nanoindentation [8,9], ultrasound [10,11], mechanical testing [12,13], and continuum micromechanics-based computations [14,15]. Key insights gained from this campaign are summarized and reviewed throughout the remainder of the present paper.

2 NANOINDENTATION

Nanoindentation refers to pressing a hard tip into a material surface, in order to determine the material's elastic modulus. The latter results from the Poisson's ratios of the probed material and of the tip material, from the contact area between tip and surface, as well as from the initial slope of the unloading branch of the relation between the indentation force and the indentation depth.

Experimental realization of a flat surface indented by a hard tip requires the roughness of that surface to be smaller than half of the contact indentation depth, as hardness values start to vary considerably once this requirement is not fulfilled any more [16,17].

The size of the tested halfspace which is essentials "felt" by the indenter when probing elastic properties, i.e. the size of the "NI-probed domain", exceeds the contact indentation depth by a factor ranging between ten and more than one hundred. This has been shown by tests on the surfaces of stiffer "inclusions" embedded into softer "matrices" [9,18]. Hence, elastic values determined, according to Oliver-Pharr's halfspace theory, for indented inclusion surfaces not fulfilling the aforementioned size requirement are too small, and accordingly, they are physically meaningless.

The size of the tested material volumes associated with the NI-probed elasticity values follows from a standard separation-of-scales requirement [14,15]: the structural length scale needs to be separated, at least by a factor of about ten, from the size of the representative volume element (RVE) on which the material is defined [10]. Identifying the structural length scale as the square root of the contact area, and relating the latter – according to the Oliver-Pharr method [8] – with 24.5 times the contact indentation depth, yields RVE-size to be at most half of the contact indentation depth [9,19].

Hence, indenting hardened Biodentine cement paste up to a maximum indentation depths of 140 nm, which is associated with the force-over-displacement slope relevant for elasticity determination, entails characterization of material volumes with a characteristic size of 50 nm. For the corresponding results to be physically meaningful and stable, the roughness - according to the argumentation given above - needs to be smaller than 70 nm: A dedicated polishing protocol lasting for 20 hours, involving the use of carbide grinding paper with a grain size of 5 microns yields a satisfactory roughness of only 18 nm [3]. Moreover, in case harder portions of the surface are probed, the 50 nm-sized material volumes are tested throughout a domain measuring some 15 microns.

5748 such indentations were performed on a regular grid with a spacing of 70 microns, so that the individual load-displacement tests are largely independent from each other. The corresponding results exhibited a very large spread, with values ranging from less than 1 GPa up to 200 GPa. With the particle size of the cement powder[1] lying in the micron-to-submicron range, we expect these values to be dominated by unhydrated clinker grains on the one hand, and by different types of hydrate products on the other hand [21,22]. Accordingly, the normalized histogram representing all test-specific indentation modulus values at a bin width resolution of around one gigapascal is considered as being the superposition of different probability distribution functions which are associated with different micro-constituents of hardened cement paste. In more detail, the normalized histogram of indentation moduli can be optimally represented through three lognormal distributions, with low, medium, and high median and mode values, respectively. The lower and medium median values, amounting to 45 and 62 GPa, are considerably larger than those known for low- and high-density hydrates in ordinary Portland cements [21,22]: This can be explained by submicron-sized unhydrated calcite particles which effectively reinforce the hydrate foam consisting of solid calcium silicate hydrates (sCSH) and gel pores in between. On the other hand, the high median value, amounting to 92 GPa, is lower than that known for unhydrated clinker, namely 124 GPa [18], which indicates that the indented clinker inclusions are smaller than the NI-tested domains. Still, the volume fraction of unhydrated clinker as derived from the integral over the lognormal distribution with the high median value, agrees well with that determined from light-microscopic images [5].

[1] In contrast to ordinary Portland cement (OPC), the cement powder does not only comprise calcium silicates, but also a substantial portion of calcium carbonate [20].

3 ULTRASOUND

Ultrasonic pulses with frequencies ranging from 50 kHz to 20 MHz were sent through samples of hardened cement paste, being of cylindrical shape with 1 cm height and 0.5 cm diameter [5]. Corresponding longitudinal and transverse pulse (or wave) velocities were virtually independent of the applied frequency, and amounted to 5 km/s and 2.5 km/s, respectively [5,6]. Given a sample mass density of 2.4 g/cm^3, this yields normal stiffness values around 57 GPa. According to the separation-of-scales requirement [14], this stiffness is associated with RVEs being much smaller than the wavelengths ranging from 0.25 mm to 100 mm, i.e. with RVEs of sizes ranging from 250 microns to 10 mm. Hence, the overall stiffness of an RVE of Biodentine cement paste lies between the NI-probed stiffnesses of the two distinct calcite-reinforced hydrates, being both associated with much smaller RVEs of 50 nm size, and hence qualifying as micromechanical phases in an RVE of hardened cement paste; for additional considerations concerning stiffnesses at different length scales, we refer to Section 5.

4 MECHANICAL TESTING

Uniaxial compressive tests were performed on prismatic samples with height/diameter amounting to 9 mm /5 mm and 6 mm / 4 mm, respectively [7]. They allow for the realization of quasi-homogeneous stress states in the center region of the samples where the failure process is initiated. The uniaxial stress-strain behavior turns out to be of rather elasto-brittle nature, with axial splitting or spread disintegration as failure modes, being associated with strength values exceeding 250 MPa at ages of 28 days [7].

5 MICROMECHANICS-ENABLED DATA INTEGRATION AND INTERPRETATION

Continuum micromechanics provides a rigorous theoretical framework to link the mechanical properties of a material defined on an RVE to the mechanical properties, the volume fractions, the shapes, and the interactions of the constituents (or material phases) making up the aforementioned overall material [14]. When leaving shapes and interactions aside, the classical Voigt [24]|and Reuss [25] bounds [14] give access to the lowest and highest overall (“homogenized”) stiffness which can arise from phases with given stiffnesses and volume fractions. Considerung the NI-probed stiffness values as phase properties associated to very many phases with volume fractions arising from the normalized histogram results in normal stiffness tensor components between 74 GPa (lower “Reuss” bound) and 78 GPa (upper “Voigt” bound): They are significantly larger than the ultrasonically determined normal stiffness of 57 GPa. This discrepancy underlines the existence of an additional phase with a very small volume fraction and vanishing stiffness, which nevertheless needs to have a major effect on the overall behavior of Biodentine hardened cement paste. Such a phase is typically characterized by an extreme shape, with one length dimension being negligible with the two other dimensions: It consists of cracks [26]. In order to conceptualize and integrate the information given in Sections 2 to 4 with this micromechanics-enabled “detection” of cracks and to deepen to general understanding of the mechanical functioning of the Biodentine biomaterial, an RVE of hardened cement paste was investigated by yet another micromechanical model [6], with very many spherical hydrate phases representing the lognormally distributed stiffnesses of high- and low-density calcite-reinforced hydrates, one spherical phase each representing unhydrated clinker and zirconium inclusions, respectively, as well as many penny-shaped crack phases [27,28], being uniformly oriented in space directions. This model underlines that the median, rather than the mode values of the hydrate stiffness probability distributions are the appropriate input for single-phase modeling in hydrates. More importantly, use of the concentration tensor concept [29,30,31] allows for linking the macroscopic paste-related strains to the microstrains at the phase level. When, in addition, adopting a lognormally

distributed hydrate strength, the concentration tensor distributions imply a fairly uniform utilization level throughout the many calcite-reinforced hydrate phases, indicating a high level of optimization of the material, and providing the cause for the spread disintegration observed as failure pattern at mature material age.

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