Mechanical properties of a permanent dental restorative material based on calcium aluminate

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This paper deals with some important mechanical properties (hardness, dimensional stability, compressive and flexural strength) of an experimental version of a translucent calcium aluminate dental restorative material. All samples investigated have been made from pre-pressed tablets, with a compaction degree of $\sim$ 60%, hydrated using a 0.15 wt % Li salt solution as an accelerator. The samples were stored in water at 37 °C between the measurements. As reference materials one composite, Tetric Ceram, and one glass ionomer, Fuji II, were used with specimens prepared according to the manufacturer's recommendations. For the reference materials some of the properties were published data. The results show that the calcium aluminate material has sufficient mechanical properties to be used as a permanent dental restorative taking as a reference the ISO 9917 and the ISO 4049 as well as the reference materials. In addition the results indicate that the mechanical properties are controlled by the microstructure, which is mainly determined by the grain size of the filler.

Introduction

On today's dental market there exist three major groups of filling materials. These materials are metals (amalgam), polymers (composites) and glass-ionomers. With the pros and cons of these materials in mind a profile for the ideal filling material can be defined. The ideal material should be: biocompatible, environmentally friendly, durable, cost and time effective, aesthetic and have thermal and electrical conductivity similar to tooth structure. A group of materials that has the potential to fulfil the ideal properties is ceramics and in particular the chemically bonded ceramics (CBC). A CBC is a ceramic that is formed through chemical reactions instead of being formed by a sintering process, which is the traditional way to produce a ceramic material. In dental history there have been attempts to develop chemically bonded restorative materials, e.g. zinc-phosphate and silicate cements, but due to low strength and low chemical stability these systems did not function as permanent filling materials. Focus has now turned to a new group of CBC materials, i.e. the calcium aluminate system. The system has several benefits making it suitable for use as a dental restorative:

- The material is biocompatible (also during hardening) and is environmentally friendly [1, 2].
- The material forms hydroxylapatite *in situ* and creates a chemical and biological integration with teeth and bone [3].
- General characteristics of calcium aluminates are rapid hardening and high initial strength [4].
- The material is acid resistant [4].
- Possibility of making *in situ* room-temperature preparations with adjustable rheology and hardening time.
- During hardening the water uptake is substantial and enough for the hydrates to fill up the initial porosity yielding a high strength end product [4].
- Thermal properties are comparable with tooth tissue.

The present paper investigates some of the most important mechanical properties (hardness, dimensional stability, compressive and flexural strength) of an experimental version of a translucent [5] calcium aluminate dental restorative material and discusses the material with regard to the necessary mechanical

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properties of a restorative according to ISO standard 4049 and 9917. Since the material is an experimental version no clinical studies have yet been done.

Materials and methods

Materials

The material is based on mono calcium aluminate ($CaAl_2O_4$) with a maximum particle size of 10 μm. To obtain radio opacity combined with translucency, dental glass is used as filler material. In this investigation two mean grain sizes (1.5 and 3.5 μm) of the dental glass are investigated with regard to hardness and expansion. In flexural strength and compression only the finer filler grain size was tested. For comparison, a composite (Tetric Ceram) and a glass-ionomer (Fuji II) were also tested regarding hardness and flexural strength. Two inorganic expansion-controlling additives are also added in small amounts to the material.

Micro hardness

The Vickers hardness was measured with a Matzusawa MXT 50 micro hardness tester using a load of l00 g. The samples were made from 3 mm tablets hydrated in 0.15 wt % Li salt solution and then condensed into 4 mm holes in acrylic blocks, using dental instruments. The samples were stored for at least 14 days in water at 37 °C before being measured. Prior to testing the samples were polished in steps down to a fineness of 4000 grit silicon carbide grinding paper. For each composition at least 10 indentations on two different samples were made. Two different filler grain sizes were studied (1.5 and 3.5 μm). The hardness of the composite Tetric Ceram and the glass-ionomer Fuji II was measured with the same technique.

Dimensional stability

The dimensional stability was evaluated as the linear dimensional change over time. Tablets were hydrated in a 0.15 wt % Li solution and condensed into expanders using dental instruments. The expansion is measured as a function of the distance between the two moving ends of the split-pin acrylic expander, Fig. 1 [6]. The gap is measured in a stereomicroscope using a scale on a piece of glass placed over the end of the expander. A zero value, used as reference, was taken after immersion in 37 °C water for 30 min. This value can be used as the reference value for zero expansion since the expansion is very close to zero during the first hour [7]. The expanders were then stored in 37 °C water and measurements were performed at different periods of time up to 122 days. Two different filler grain sizes were studied (1.5 and 3.5 μm).

Flexural strength

The flexural strength was measured according to ASTM F394 standard for ceramic materials. A circular plate of the material is supported on three balls placed on a circle of specified diameter, in this case 4 mm support diameter for samples of 5 mm diameter. The test plate is loaded in the center by a fourth ball with a diameter of 1.6 mm, Fig. 2. The plate is loaded until failure and the maximum force required is measured. In this test the force was measured using a loading cell on which the test fixture was placed. The maximum load is registered and recalculated to MPa using the ASTM F394 equations. Before measuring an adhesive tape is placed on one side of the test piece and a thin non-adhesive plastic film on the other side to even out the stresses over the specimen surface. The adhesive tape does not give an error in flexural strength if the tape is placed on the compressive side of the sample [8].

The flexural strength were measured for the bio-ceramic calcium aluminate material and compared with Tetric Ceram and Fuji II. The calcium aluminate samples were made from 3 mm tablets hydrated in 0.15 wt % Li solution and condensed by hand using dental instruments into a 5 mm tablet mold. For each sample three tablets were used. After condensing a uniaxial pressure was

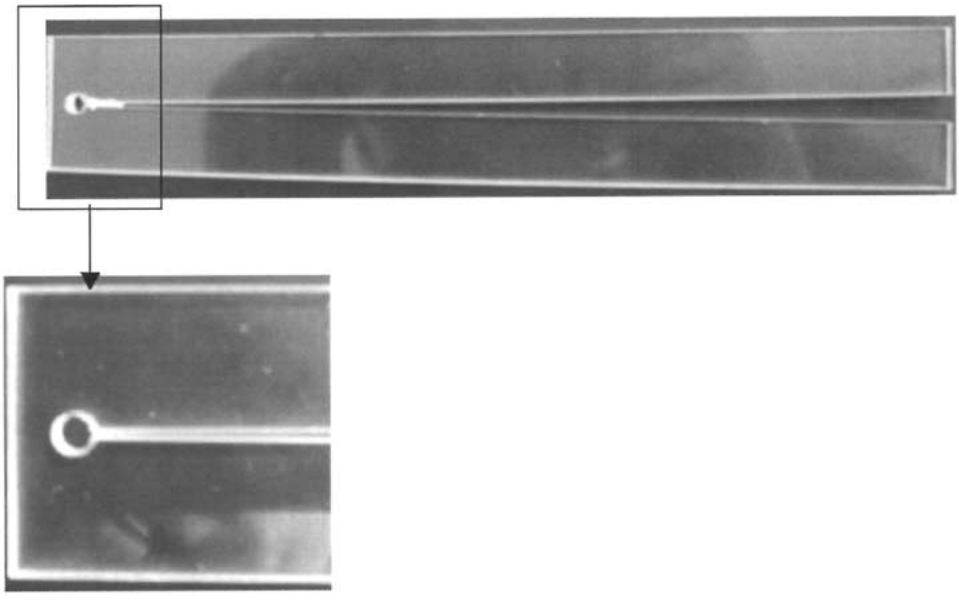

Figure 1 Overview picture of a split-pin acrylic expander.

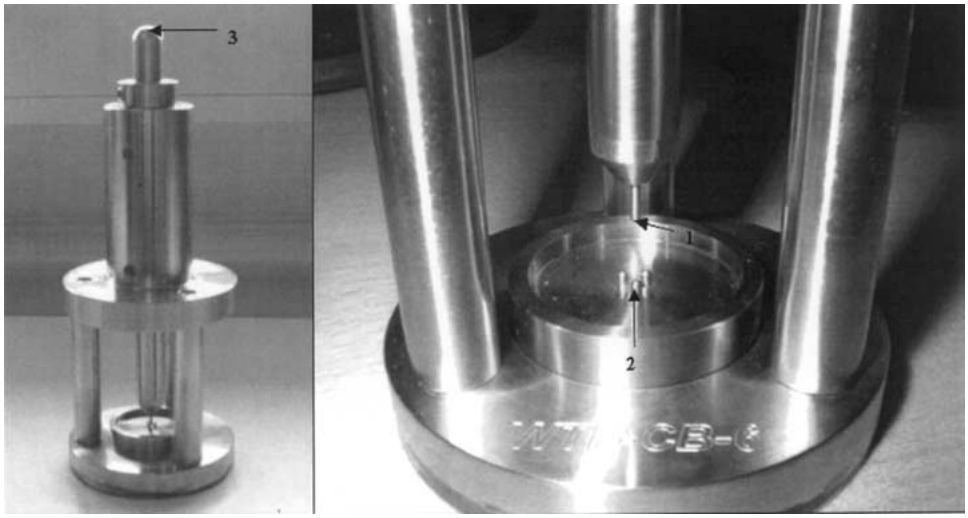

Figure 2 Overview picture of the flexural strength test jig and a close up on the sample support balls and the loading ball. 1, loading ball; 2, three supporting balls; 3, self centered loading piston with the loading ball in the end.

applied with a small hydraulic press using a piston fitting in the mold. The pressure applied when pressing is chosen so that the sample does not get a compaction degree of more than maximum 2% higher than the original tablets. The samples were stored in 37 °C water for 14 days. All samples were polished with increasing fineness down to 4000 grit silicon carbide grinding paper to give a diameter to thickness ratio of 6–8, before measuring. Only samples without any visible defects were measured.

Compressive strength

The compressive strength was measured using circular rods with a diameter of ~ 4 mm and a height of ~ 7.5 mm. Samples were made from 3 mm pre-pressed tablets hydrated in a 0.15 wt % Li salt solution and manually packed into sample forms with dental instruments. After demoulding, the end surfaces were polished with 4000 grit silicon carbide grinding paper in order to achieve as plane parallel surfaces as possible. Before testing the samples were stored 2 weeks in water at 37 °C. The tests were done using an Instron Universal instrument with Si_3N_4 plates in contact with the material and a flattened steel ball on top of the sample to compensate for possible unevenness of the surfaces.

Results

Micro hardness

Finer filler grains gave a higher hardness than coarser, Fig. 3. The hardness of the composite Tetric Ceram was 71 HV(100 g) and for the glass-ionomer Fuji II it was 59 HV(100 g). Thus the hardness of the bioceram is significantly higher than the composite and the glass-ionomer.

Dimensional stability

The results from the expansion measurements can be seen in Figs. 4 and 5. Each point in the diagram is a mean value of the expanders set for a given composition. A finer filler grain size yielded a lower expansion than that

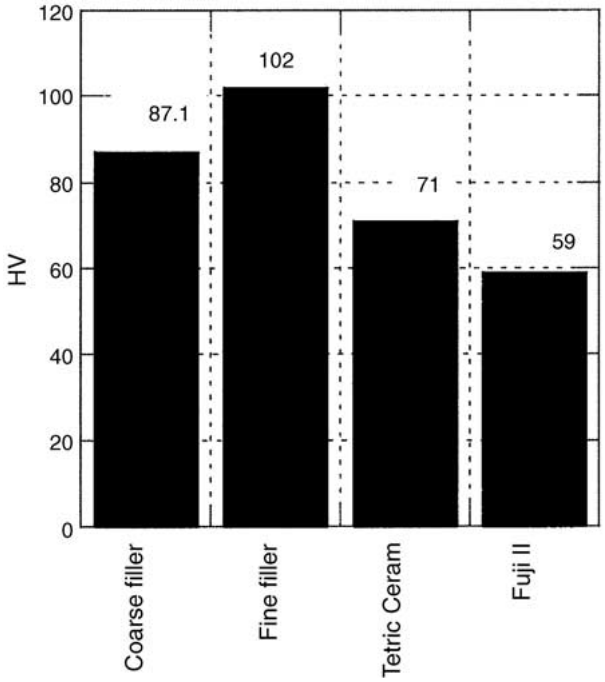

Figure 3 Vickers micro hardness of mixtures with coarse and fine filler grain sizes and also hardness of the reference materials.

of the coarser grain size, in the interval 0–0.1% compared with 0.1–0.2%. The differences between the mixtures with the same filler grain size are depending on the small amounts of inorganic additives added that was mentioned earlier. It should be noted that the measurements at longer testing time (80 days and above) is a mean value of measures taken 3 days in a row, this to minimize the error originating from the expanders.

Flexural strength

The results of the flexural strength test, presented in Fig. 6, are a summary of the values for the samples that were without visible edge or other defects. The mean value is 106 MPa and the standard deviation is 28.8 MPa. The flexural strength of Tetric Ceram and Fuji II has been found to be 142 and 41 MPa, respectively.

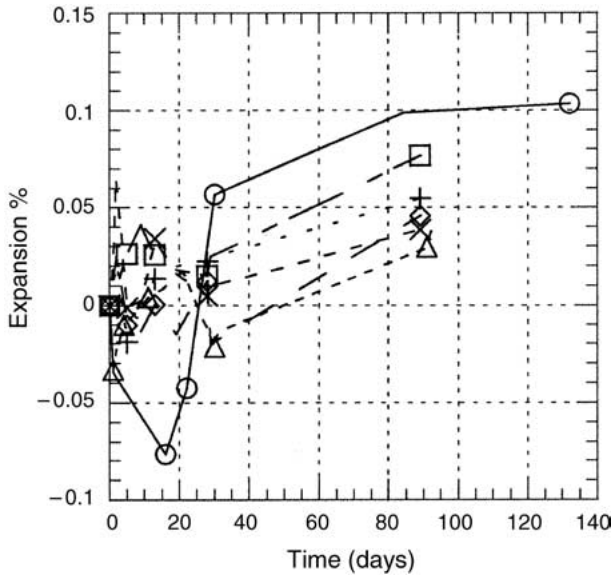

Figure 4 Expansion results for mixtures with 1.5 μm filler grain size.

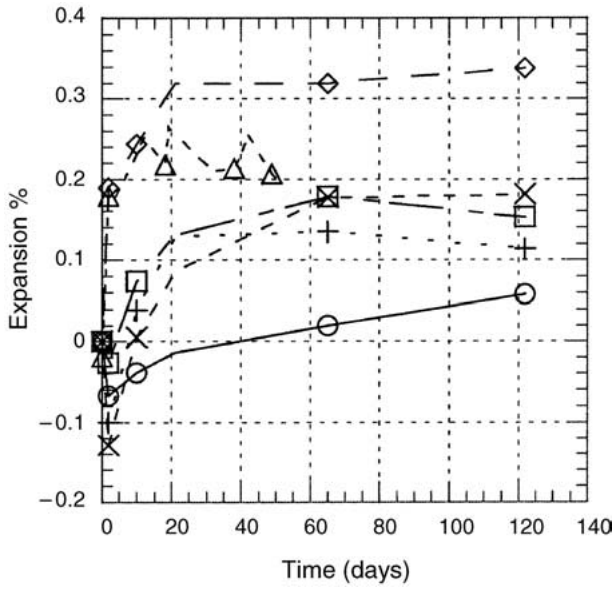

Figure 5 Expansion results for different mixtures with 3.5 μm filler grain size.

Compression strength

The compression strength can be seen in Fig. 7. Five samples were measured and the mean value was 182 MPa with a standard deviation of 12.5 MPa. The compressive strength for Tetric Ceram is reported to be 300 MPa (Technical documentation on Tetric Ceram) and for Fuji II 160 MPa (Technical documentation for Fuji II).

Discussion

The grain size of the filler has been shown to be an important factor for the properties of the material. A smaller filler grain size gives higher hardness and improved dimensional stability (lower expansion). The size of and the distance between the filler particles together with the original grain size of the calcium aluminate control the microstructure of the material. To achieve an adaptive microstructure with small hydrate grains that easily fill up pores, giving a dense body, and that adjusts to the shape of the available space, the

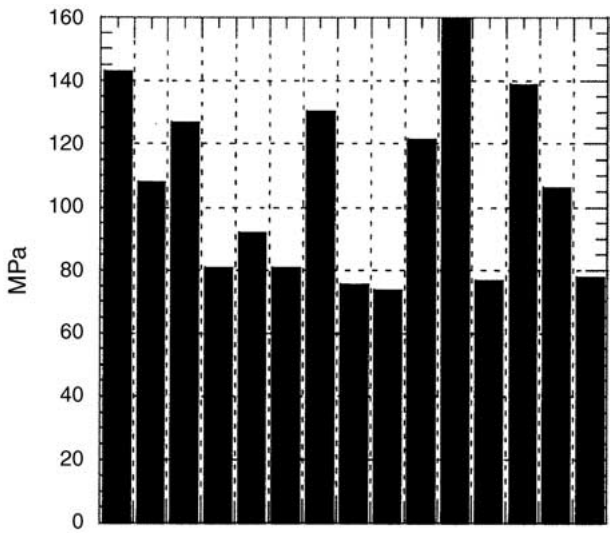

Figure 6 Flexural strength values for 1.5 μm filler grain size.

distance between filler particles should be small. This distance can be called the mean free path of the material, e.g. the distance through which a cement hydrate can grow before its growth is stopped by a filler particle. The dense and adaptive microstructure obtained by minimizing the mean free path is probably what gives high hardness and an improved dimensional stability. A short mean free path can be achieved by decreasing the filler particle size and compressing the unhydrated calcium aluminate as much as possible. The ideal microstructure from a mechanical point of view should be achieved when the hydrates exists as a thin film around evenly distributed and finely dispersed filler particles.

When testing mechanical properties of a ceramic material in general and a calcium aluminate based ceramic in particular with regard to the inherent material strength the importance of producing a sample without flaws and micro cracks is crucial. If a flaw of above the critical size is introduced, for instance during sample preparation, this flaw will decide the outcome of the test and not the material. The flaw becomes the strength-controlling factor see Equation 1. The sensitivity towards flaws and cracks has its origin in the general fracture

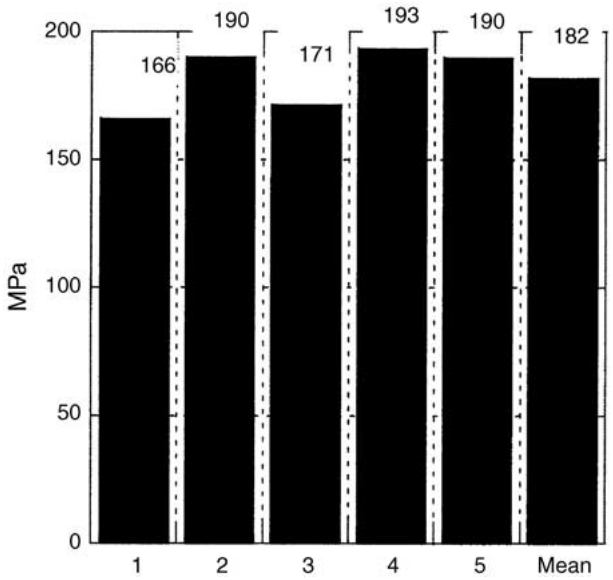

Figure 7 Compressive strength data for fine grain filler.

behavior of ceramics and their linear elastic behavior with rather high Youngs modulus [9, 10]. This also makes the geometry of the test piece a critical issue, since crack initiation and stress concentrations leading to failure often occur at sharp edges or flaws. When testing a material with the intention of finding the inherent strength, a sample geometry that is as round and edge free as possible should be chosen. This is why the ASTM 394F was selected for the flexural strength testing. The rather high standard deviation obtained in the flexural and compression strength measurements can be explained by interpretation of the basic equation for fracture mechanics in ceramics (Equation 1):

$$K_{1C} = Y\sigma_f\sqrt{c_{\text{crit}}} \quad (1)$$

where K_{1C} = critical stress intensity factor, i.e. fracture toughness; Y = geometrical constant (1.12–1.98, depending on crack position and shape, often ~ 1.7); σ_f = fracture stress; c_{crit} = size of largest defect.

K_{1C} can be considered to be a material parameter. For calcium-aluminate it is about 0.7–1 $\text{MPam}^{1/2}$. Equation 1 thus implies that the fracture strength is dependent on the defect size, which is statistically distributed and differs from sample to sample. Equation 1 also underlines the fact that flexural strength testing reflects the size of the largest defect present in the sample, rather then the actual strength of the material. The maximum potential flexural strength is ultimately controlled by the grain size of the material. If the sample body is 100% homogenous and pore free then the largest grain become the largest defect and thus strength controlling. If applying Equation 1 to the highest measured flexural strength in this paper, using a K_{1C} of 0.7 it gives a largest defect size of $\sim 15\,\mu\text{m}$. This is in the range of the microstructure for the material, which has a largest grain size of $10\,\mu\text{m}$ in unhydrated state, thus indicating that this value is somewhat lower than the true inherent strength of the material.

The mechanical properties measured of the new translucent material are sufficient for a permanent restorative filling material as compared with the standards available, ISO 4049 for composites and ISO 9917 for dental cements. Compared with the composite Tetric Ceram, the calcium aluminate material is superior in hardness, somewhat lower in mean flexural strength but with peak values comparable to the composite and lower in compression. When compared to Fuji II the material is superior both in hardness and flexural strength and somewhat higher in compression strength. When viewing the strength results (flexural and compression) the difficulties of sample preparation become clear. The compression strength of a ceramic material is normally two or three times higher than the flexural strength of the same material [11]. In this case the compression and flexural strength are on the same level. This leads to the conclusion that the samples tested for compression strength was not optimal. Flaws were probably introduced during condensing and/or the surfaces were not parallel. The small expansion of the material in combination with the hydration mechanism (dissolution and precipitation) yield a tight seal towards the cavity wall and radically reduces the probability of leakage and as a consequence a reduced risk of secondary caries to develop.

Conclusions

The mechanical properties of this experimental version of a translucent calcium aluminate-based dental restorative material have been shown to be in accordance with the ISO standards for dental restorative materials. The material has a small and optimized expansion over time, which is below 0.1% after 4 months. The mechanical properties seem to be controlled by the microstructure, where the grain size is the most important parameter. Experimental data underlines the influence of sample preparation induced flaws and cracks on the strength detected.

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