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Early-age deformation, drying shrinkage and thermal dilation in a new type of dental restorative material based on calcium aluminate cement

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Abstract

Dimensional changes during the first hour of hydration for small specimens of a dental material based on calcium aluminate cement (CAC) was examined. The study was conducted on specimens prepared in two different ways. First, intact tablets (three pieces per test) dipped in water were measured. Second, compacted specimens from four tablets were measured after 10 min of hydration. The dimensional changes were studied in both wet and dry conditions at 37 °C and in a dry condition at 25 °C. In the wet environment at 37 °C no dimensional change of the samples was observed. At normal room humidity (RH 55%) at both temperatures, shrinkage of 0.35–0.40% was observed. For comparison to the early-age drying shrinkage, a study of the drying shrinkage in mature material, hydrated for 50 and 100 days, respectively, was conducted. Furthermore the thermal expansion coefficient was determined and found to be close to that of tooth substance.
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1. Introduction

The dimensional stability of cement-based materials is of fundamental importance for its maintenance in different applications. Recently, in civil engineering, there has been a growing interest in understanding the hydration properties related to dimensional changes. This is the result of the modern development of high-performance, high-strength and self-leveling concretes, which attracted renewed attention to problems such as early-age cracking [1] associated with dimensional changes (shrinkage) of these materials. This shrinkage can either be a result of autogenous shrinkage, drying shrinkage or both. Drying shrinkage is a process where water is removed from concrete by evaporation, whereas autogenous shrinkage is a consequence of hydration reactions including chemical shrinkage [2]. Furthermore, tests have shown an influence of thermal dilation on the autogenous deformation at hydration [3].

In particular for dental filling materials, shrinkage might cause gap formation at the interface towards the tooth substance. If a gap forms, bacteria will inevitably ingress into the cavity and caries will develop. Therefore, a complete sealing of the dental cavity is important. Also, if the dental material expands too much there will be a risk of cracking in either the filling, the tooth substance or both.

In October 2000 a calcium aluminate cement (CAC)-based dental filling material was launched in the Swedish market under the name Doxadent. Previous data of this material revealed a slight expansion of the material of about 0.2% after 1 year [4]. The main part of the expansion is developed during the first month. However, in the method used in those experiments (acrylic split-pin expanders) the dimensional change during the first hour is not measured since the initial values are not taken until after about 30 min after mixing [5]. Doxadent starts to harden already after 5–10 min. Therefore, it is essential to investigate how the first hour of hydration influences the dimensional changes.

Measurements with acrylic split pins for the first five days of this material are presented in Fig. 1. (The variations of data with time in the figure basically show the error of ± 0.05% in the method and not dimensional changes in the material [5].)

The objective of this work is to disclose the importance of water vapor or water supply for this type of material after

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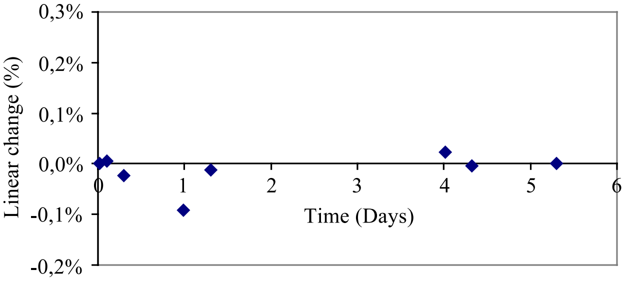

Fig. 1. Early-age data for the CAC-based dental restorative material measured with the acrylic split pins [2].

the insertion of a filling in a tooth cavity. By comparing early-age hydration in a dry and wet environment, respectively, the early-age hardening properties of this material will be better understood. For comparison of the drying shrinkage in fresh and mature material, respectively, the sensitivity for drying of the material with time will be shown. Also the thermal expansion coefficient was calculated to assess what possible influence it has on the dimensional characteristics of the material.

2. Materials

The material is based on Secar 71®, a CAC produced by Lafarge Aluminates. Zirconium dioxide is added to achieve radio opacity of the material, making X-ray analysis of the tooth in the dental practice possible. The typical chemical composition expressed as oxides in the cured material is presented in Table 1.

This dental material is made from very fine grained cement, and is compacted to a far higher degree than the usual cement paste.

The material is delivered to dentists in bulk form in the shape of small cylindrical tablets (Fig. 2), which are manufactured in a mechanical press under uniaxial high pressure [6]. The tablet absorbs a solvent with lithium chloride as accelerator before insertion and compaction by a dentist in a tooth cavity. Due to the compaction degree selected a sufficient amount of liquid is immersed to assure a low w/c ratio and the mechanical properties of the material. (The consistency of the material is more like the consistency of amalgam, like a formable damp and adhesive powder, and not like a gooey fluid like dental composites [7].)

Table 1
Chemical composition of hydrated calcium aluminate based restorative material in weight percent

Oxide	Fraction (%)
Al_2O_3	43
CaO	19
H_2O	15
ZrO_2	19
Others: (Si, Fe Mg, Ti and alkali oxides)	< 4
Total	100

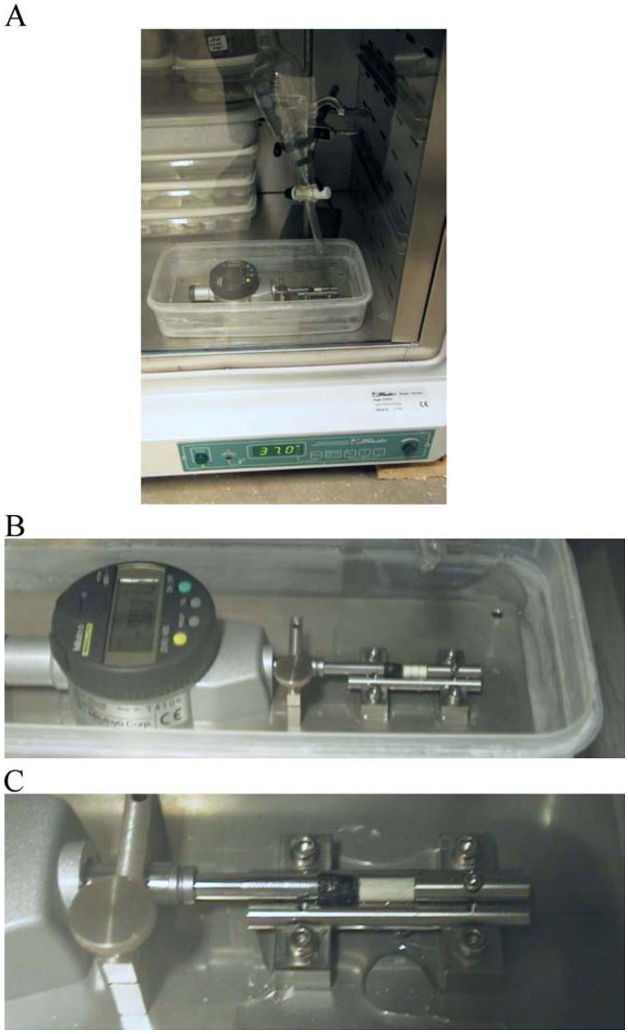

Fig. 2. (A) Experimental setup. (B) Three tablets (Ø4 × 9 mm) under length change measurement. (C) A prepared specimen (Ø4 × 10 mm) under measurement. (A–C) Water continually drops on the specimen to ensure a wet hydration environment in the specimens.

For the expansion/shrinkage tests different specimen geometries were used for practical purposes. The longer the specimen, the better the resolution. However, for the early-age measurements long and thin pins are too fragile to handle since the hardening commences after 5–10 min.

3. Experimental

3.1. Early-age measurements

A Mitutoyo digimatic indicator 543-450B with a sensitivity of 1 μm and an accuracy of ± 1.5 μm in the temperature interval 0–40 °C was used for the measurements. The restrain from the measurement gauge was 1.2 N

Fig. 3. Packing of pin specimens with dentist tools.

according to the manufacturer. No adjustments to the data obtained were made for this restraining force.

This study was conducted on two different kinds of specimens, tablets and prepared specimens, to assess any difference in their early-age hydration deformation properties. First, intact tablets were made to fully absorb water and thereafter placed in a row in position for length change measurement (three tablets with the dimension Ø4 × 3 mm, with a total length of 9 mm). Second, specimens were compacted with dentist tools in a hole (with the dimension Ø4 × 10 mm) in a plastic mould. After 10 min of hydration these specimens were demoulded and placed in position for measurement.

The dimensional changes were measured continually every minute during an hour. The environment during the test was either wet (deionised water) or dry (room humidity = 55% RH) and the temperatures selected were 37 °C and room temperature (24 °C).

3.1.1. Wet measurements

Wet measurements were conducted only at 37 °C. To keep the samples wet during the experiments a drop bottle was placed above the specimen. Well in position, a drop of water fell every 5 s. The experimental setup is presented in Fig. 2A–C.

Fig. 4. Edge-shaped hardened specimen on top of the mould.

Fig. 5. The setup of the digimatic indicator.

3.1.2. Dry measurements

Dry measurements were conducted at both 37 °C and at room temperature (24 °C). This was done to examine the influence of the different phases developed at 24 and 37 °C, respectively, on the magnitude of the drying shrinkage.

3.2. Drying shrinkage and thermal dilation measurements

Both the drying shrinkage and the thermal dilation measurements were conducted on mature material with the Mitutoyo digimatic indicator. Pins were made by compaction of CAC-based dental filling material into a mould of the dimensions 25 × 2 × 2 mm (Figs. 3 and 4). (The preparation of such pins is difficult to conduct with this type of material in comparison to an analogous preparation made with polymer-based dental composites. However, by use of wet-pressed granulated powder instead of tablets the packing process is somewhat simplified [8].)

The specimens were demoulded after 5 min of hydration at 37 °C and afterward put back for further hardening. All specimens were cured in water for at least 50 days. Before measurements the ends of the specimens were formed into tips to make the assessments more exact.

3.2.1. Drying shrinkage

Drying shrinkage measurements were also conducted with the Mitutoyo digimatic micrometer (Fig. 5) on four different specimens. The wet specimens were manually placed in the correct position into the measurement device, where they air-dried. (The relative humidity in the room at measurement was about 55%.) Initial and end length values

Fig. 6. The specimen lineup at measurement.

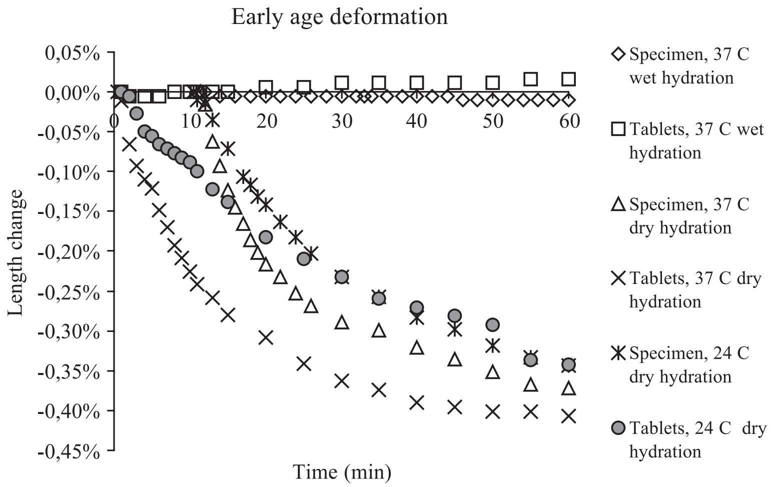

Fig. 7. Results of early-age hydration deformation at different temperatures and humidity.

were observed. (However, the drying shrinkage measurements were only of a comparative nature for showing the importance of wet hydration for this type of material.)

3.2.2. Thermal dilation

Measurements of the thermal length change were conducted in the same way. Before assessment the specimens were dried in an oven at 70 °C. Then each specimen was picked by hand from the oven (at 70 °C) and placed in the correct position into the measurement device at room temperature, 24 °C (Fig. 6). The time for placement into the correct position took only few seconds. Measurements were repeated three times on each of four specimens, all together 12 measurements. The oven temperature and the room temperature were controlled continuously.

3.3. The microstructure

The microstructure of the material was studied in a LEO 440 scanning electron microscope (SEM) in both backscattering (BE) and secondary electron (SE) mode.

4. Results

4.1. Wet hydration stability and drying shrinkage during the first hour

The early-age dimensional change is presented in Fig. 7, where every data point represents the mean value of two specimens. For intact tablets a small expansion of approximately 0.02% was detected after 1 h. A small shrinkage of 0.01% was detected in compacted specimens. The estimated spread in data points is approximately ± 0.015% according to the measurement gauge manufacturer. In the wet environment at 37 °C almost no deformation of the samples was observed, while the samples hydrated at room humidity (dry hydration) had shrinkage of about 0.35–0.40%. The curve

Table 2
Net deformation in dry hydrated samples after 1 h

Hydration condition	Tablets (%)	Compacted specimens (%)	Average deformation (%)
Wet 37 °C	− 0.010	0.017	0.004
Dry 37 °C	− 0.407	− 0.372	− 0.388
Dry 24 °C	− 0.342	− 0.343	− 0.342

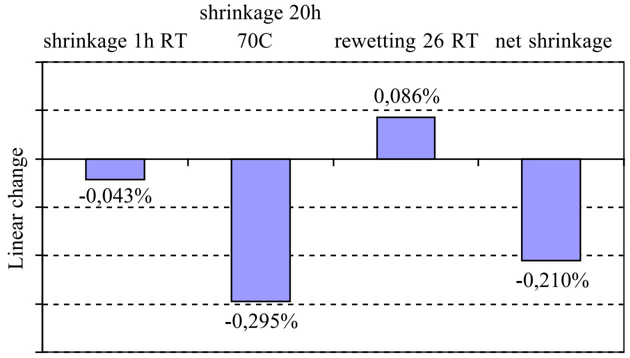

Fig. 8. Dimensional changes in the CAC-based dental filling material of 50 days age due to temperature and humidity differences. The values represent the mean values from four pins.

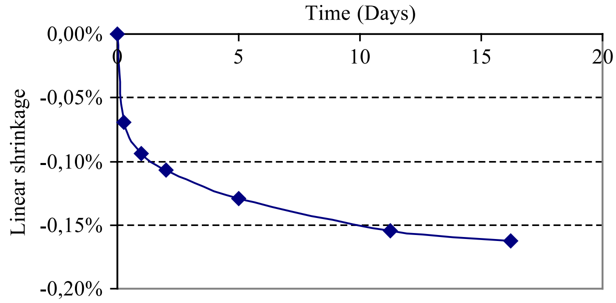

Fig. 9. Drying shrinkage during 15 days at room temperature (24 °C) and RH 60% in mature (100 days) CAC-based dental material. (The first hour the pins were dried at 37 °C storage in an oven at the same humidity.)

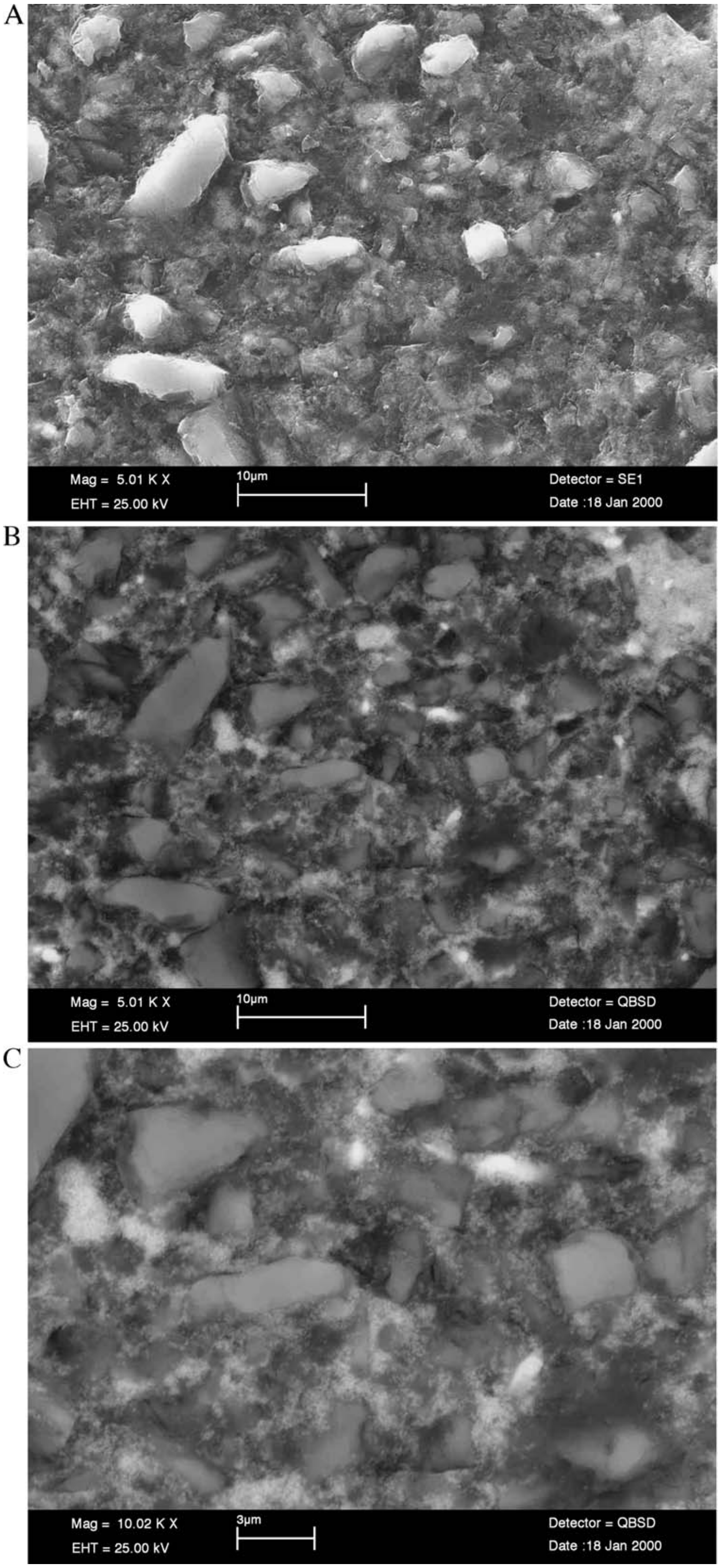

Fig. 10. The microstructure of Doxadent specimens, secondary (A) and backscattering (B, C) electrons images. The specimens were carefully polished in a diamond slurry.

for the compacted specimen, hydrated dry at 37 °C, starts to converge already after 1 h. At 37 °C the shrinkage is higher than at 24 °C, where the net shrinkage is almost the same for both types of specimen, but at 37 °C the shrinkage is lower in the compacted specimens (see Table 2.)

4.2. Drying shrinkage in mature specimens

The drying shrinkage of the mature samples is only 0.04% after 1 h in room temperature, and after 1 day of drying at 70 °C the shrinkage is still less than the shrinkage of 0.35% in the fresh samples at RT. After a drying and rewetting cycle, a shrinkage of 0.2% remains due to a net water loss in the material. Thus, most of the water movement is irreversible when drying at a high temperature (Fig. 8).

For the mature material hydrated for 100 days the drying is less than 0.07% on the first day, and after continued drying for 2 weeks the shrinkage increased to 0.15% (Fig. 9).

4.3. The thermal expansion coefficient

Specimens cured in water for 50 days were dried in an oven at 70 °C and thereafter placed into position for measurement at room temperature (24 °C). Three measurements were conducted on each of four 25-mm bars. From the data and a P value of .05 the overall average thermal expansion coefficient was calculated, $\alpha = 8.8 \pm 1.2 \times 10^{-6}$ K^{-1} ($\sigma_\alpha = 0.6 \times 10^{-6}$ K^{-1}).

4.4. The microstructure

In Fig. 10A–C the SEM images show the typical microstructure developed. Fig. 10A shows the reflection of the surface of the secondary electrons—the topographic contrast. Fig. 10B and C shows the BE electron image—the atomic number contrast. The large white grains in Fig. 10A are anhydrous cement grains of calcium aluminates. The white areas in images B and C are small zirconia particles or agglomerates of zirconia. The light gray areas are the anhydrous grains, and the gray areas are hydrates where the darker gray areas are most likely gibbsite. Some submicron porosity is also found as the small black areas in Fig. 10C.

The SEM images thus reveal a very dense material with all grains being smaller than 10 μm.

5. Discussion

To better understand the behaviour of this type of material in comparison to other cement-based materials, some of its specific properties are emphasized again. This cement-based material is very fine grained, it never “sets” in a conventional sense but is highly compacted at preparation and has a w/b ratio below 0.25. It is much denser than conventional concrete and its porosity is low [4]. The material is never used nor tested in volumes greater than 0.5 cm^3, but often in even smaller bodies. Therefore, the influence of any thermal dilation due to the heat of hydration during the setting is negligible. (The thermal expansion coefficient might, however, change slightly as a function of the maturity in the material [9].)

Water in cement paste can generally be classified into three groups: capillary water (free water), gel water (physically bound water) and chemically bound water (nonevaporable water) [10]. The free water occupies the capillary pores and the physically adsorbed water occupies the gel pores. Any change in the amount of free or adsorbed pore water (physically bound to the solid surface) generates deformations of the cement matrix [11]. Also the hydration reactions will, in a dry condition, result in self-desiccation, which also increases the shrinkage [12]. Furthermore, capillary water cannot exist in a cement paste at relative vapor pressures less than about 0.40. Therefore, most of the drying shrinkage of 0.35% observed in Fig. 7, at RH 55%, is explained by evaporation of free pore water [13]. In the wet hydration condition at 37 °C, resembling the situation in the mouth, Doxadent exhibits no shrinkage during the first hour. During hydration, contracting forces (capillary forces) influence the orientation of precipitating hydrates. In the dry hydration condition the bulk material contracts because no new water can enter the material as in the wet hydration process where the capillary forces, generated from chemical shrinkage, only cause new water to enter the material. No difference between the behaviour of tablets and compacted specimens was observed.

However, other deformation mechanisms, such as self-desiccation and autogenous shrinkage, also influence these results. These results only disclose the material’s performance under certain conditions. In order to thoroughly describe the mechanisms controlling this behaviour there is a need for more testing. The interaction between these different deformation mechanisms are described, for example, in Refs. [2,13,14].

Another study in saturated air at 37 °C found the shrinkage to be in the range of 0–0.1% during the first 24 h of hydration [15]. This finding correlates well to the 1-h findings reported in wet and dry hydration, respectively.

Likewise the shrinkage of only 0.4% in the mature material at room temperature (Fig. 8) is from free water evaporating. (Compare with the drying shrinkage of the fresh material.) But at the higher temperature of 70 °C the drying shrinkage is almost 0.30%. At this high temperature, both free water and physically bound water evaporate in the drying process. The rather large net shrinkage after a drying and rewetting cycle is explained by the loss of physically bound water not being reversible. Also, part of the smallest pores collapse due to the action of capillary forces when evaporation takes place. Therefore, the amount of free water is lower at rewetting.

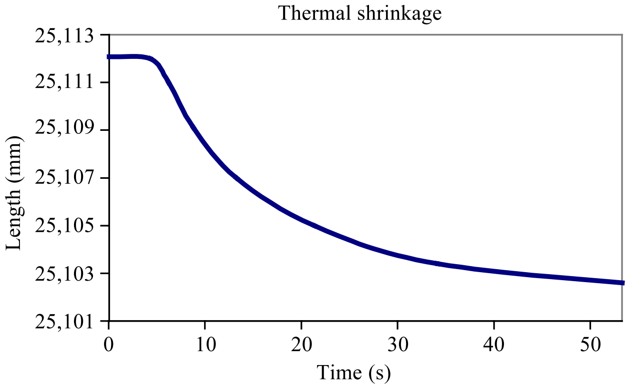

Fig. 11. Schematic curve of the lengths decrease during cooling based on observations.

From data in Figs. 8 and 9 it is seen that the drying shrinkage in the material decreases as the maturity of the material increases. A mature cement-based material has a higher fraction of hydrates and less free water that can evaporate. The hydrates build up a more rigid skeleton to withstand the contraction stress at evaporation. The influence of temperature on evaporation is also evident when comparing the 1-h drying shrinkage at RT in Fig. 8 with the 1-h drying shrinkage in Fig. 9 at 37 °C.

The thermal expansion coefficient measurements showed no shrinkage during the first few seconds after positioning of the specimen pin. Thereafter the shrinkage started to be observed. If a continuous data plot had been conducted, it would have looked somewhat like the curve in Fig. 11, with a short plateau before the length starts to decrease.

Therefore, the cooling of the specimen during the time between taking it from the oven into measurement position was not assumed to affect the result. The thermal expansion coefficient of 9×10^{-6} K^{-1} is somewhat lower than what could be expected, since the main calcium aluminate hydrate developed, Katoite, has a thermal expansion coefficient of 18×10^{-6} °C^{-1} [16]. However, ordinary Portland cement (OPC) paste has a coefficient ranging from 11×10^{-6} °C^{-1} to more than 16×10^{-6} °C^{-1} [17], and the thermal expansion of CAC paste is lower than that of OPC paste [18]. Other reasons for this rather low thermal expansion coefficient are as follows:

The material is denser than most other cement paste materials tested (Fig. 10).

The low w/c ratio of approximately 0.15–0.20, gives a higher fraction of anhydrous grains and a lower ratio of hydrates. Anhydrous cement grains, like most aggregates in concretes, have a lower expansion coefficient than the hydrates, for example, for Grossite (CA_2), $\alpha_{CA2} \approx 2 \times 10^{-6}$ °C^{-1} [19]. (The anhydrous grains, the light gray subjects in Fig. 10B and C, consist of CA or CA_2 [20,21].) These grains restrict any type of geometrical change. (Compare filler materials in concrete.)

The additive of zirconium oxide also influences the total thermal expansion to some extent. The thermal expansion coefficient for zirconia is $\sim 10 \times 10^{-6}$ °C^{-1}.

The observed thermal expansion coefficient of 9×10^{-6} K^{-1} is on the same level as that of tooth structures with a coefficient of $(8–11) \times 10^{-6}$ K^{-1} [7]. (This is for a mature and dry material with no evaporable gel or capillary water left in the material matrix.)

6. Conclusions

This new type of dental filling material based on Ca aluminates exhibits no early-age shrinkage or expansion if it is properly handled for operation in wet environments. In a wet hydration condition at 37 °C, Doxadent exhibits high dimensional stability during the first hour, but in a dry hydration condition the shrinkage is approximately 0.35%. Thus, the material is sensitive to drying, especially during the initial hydration time.

The thermal expansion coefficient is estimated to be similar to that of tooth substance.

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