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Production of monetite-based Inorganic Phosphate Cement (M-IPC) using hydrothermal post curing (HTPC)

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ABSTRACT

A new hydrothermal post curing (HTPC) technique is developed in this study to overcome the long term evolutions such as shrinkage and cracking of Inorganic Phosphate Cement (IPC). HTPC is based on thermally induced transformation of the unstable calcium phosphates phases, e.g. brushite and amorphous calcium phosphate (ACP), into more stable phases, e.g. monetite, with prevention or minimization of the bulk shrinkage during the treatment. To achieve this effect, sufficient pore moisture is kept in IPC during the transformation stage. This way, the increase of skeletal density thus does not necessarily lead to significant global bulk shrinkage, since the contraction of the skeleton is replaced internally by an increase of the pore size. This effect can be obtained by post curing in the autoclave, when a sufficiently high temperature is used to provoke the necessary structural transformation, combined with a pressure high enough to force the pore moisture and the released bound water to stay inside the pores. After evaluation of this technique, it was noticed that the monetite percentage in the hydrothermally post cured IPC products increases from 26% to 39%, compared to the heated reference IPC. It is also verified that additional pore volume replaced the bulk shrinkage that would occur when IPC is heated without autoclave pressure. This new modified IPC end product is called monetite-based IPC (M-IPC).

1. Introduction

Calcium based phosphate cements exist for a long time but have never been used on a large scale for construction and high temperature applications. Three decades ago calcium phosphate cements were first used for the remodelling of bone defects and as coating for dental and orthopaedic implants. During this period, the first generation of bone substitute materials was proposed [1]. Rapid setting calcium phosphate cements are considered as the second generation of bone substitute materials. These cements are generally based on a combination of two or more calcium phosphate powders, reacting together in an aqueous medium to form a putty-like paste consistency [1,2]. These cements can precipitate into different end products (e.g. hydroxyapatite, calcium deficient apatite, brushite, etc.) after full conversion [3]. Chemically, the setting reaction of these cements induces high variations of pH, and their chemical reaction is highly exothermic [4–6]. A new room temperature hardening phosphate cement whose setting time can be controlled, has been developed at the Vrije Universiteit Brussel (VUB). This material is called Inorganic Phosphate Cement (IPC) and is available under the commercial brand name Vubonite [7]. Due to its non-alkaline environment during and after setting and hardening, IPC can be combined with glass fibre reinforcement, contrarily to traditional cements. Such a textile reinforced cementitious composite is an interesting material in those applications where high load-bearing capacity, good fire resistance and lightweight constructions are demanded [8]. Also, complex shapes can be produced easily without need of labour intensive shaping of the reinforcement. IPC is a two-component system, consisting of a calcium silicate powder and a phosphoric acid-based solution of metal oxides. After hardening, the material's mechanical properties are similar to those of Portland cement based materials. All components being inorganic, IPC can be used in elevated temperature applications such as moulds for shaping of composites with thermoplastic matrix or post-curing of thermosets. However, it was found [9,10] that several challenges arise when using IPC for construction and other industrial applications, in particular for high temperature applications. These challenges include shrinkage and early cracking due to ageing effects or heating. It was observed [11] that (glass fibre reinforced) IPC tends to show cracking during ageing, indicating that even at ambient conditions restrained shrinkage of the IPC matrix can lead to the introduction of internal

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tensile stresses in the IPC, high enough to introduce cracking. This shrinkage results from the dehydration at ambient conditions. The meta-stable calcium phosphate phases show considerable dehydration during several months [10]. These ongoing chemical transformations over a long time contributed significantly to the phase instability of the material. In this investigation we will present a new post curing technique to overcome these shortcomings and to obtain an end product with an improved dimensional and thermal stability. An overview of the most important calcium phosphate phases and basic chemistry of IPC can be found in [12–16].

2. Hydrothermal post curing (HTPC)

2.1. Basic theory

Calcium phosphate transformations in IPC are one of the main causes of thermally induced shrinkage by heating up to ~220 °C [9]. Contraction of solid phase due to chemical transformations, e.g. brushite to monetite, causes high reduction in the bulk volume of the material at 220 °C [10]. Also, one of the main factors behind ageing phenomena in IPC is the presence of brushite and amorphous calcium phosphate (ACP), which partially lose their bound water over time to transform to other stable phases [9,10]. A hydrothermal post curing (HTPC) process is developed in the present study [9] to overcome the most serious challenges due to long term evaluations or at increased temperature: cracking and shrinkage. HTPC is based on thermally induced transformation of the unstable calcium phosphates phases into more stable phases with prevention or minimization of the bulk shrinkage during the treatment. To achieve this effect, sufficient pore moisture is kept in IPC during the transformation stage. This way, the increase of skeletal density [10] thus not necessarily leads to global bulk shrinkage, since the contraction of the skeleton is counteracted internally by an increase of the pore size. This effect can be obtained by post curing in the autoclave, when a sufficiently high temperature is used to provoke the necessary structural transformation, combined with a pressure high enough to force the water – which comes from initially free water and water released according to (Eq. (1))during the heat treatment – to stay inside the pores.

$$CaHPO_4 \cdot 2H_2O = CaHPO_4 + 2H_2O \tag{1}$$

Brushite = Monetite + water

2.2. Practical considerations

Hydrothermal post curing is a function of the temperature, pore moisture, and time. These parameters are discussed in the preceding paragraphs.

2.2.1. Temperature

Theoretically, a temperature range at which brushite dehydrates by loosing its water molecules [see Eq. (2)] is proposed for hydrothermal post curing. This temperature range varies between 80 °C and 220 °C. At temperatures lower than the transformation temperature range, the dehydration of brushite to form monetite will be very slow [17]. The dehydration of brushite to monetite up to 220 °C can be represented by the following reaction:

2.2.2. Pore moisture during the HTPC process

It is crucial to keep a sufficient amount of moisture within the pores during the thermally induced chemical transformation. This pore moisture has an effect on the restructuring of the pore system and the chemical phases on microstructural levels. This moisture could play a major role in the formation of additional porosity to replace the contraction of the solid skeleton. Therefore a sufficient pressure should be applied to keep the pore moisture under its boiling point.

2.2.3. Duration of HTPC

The duration of HTPC should be sufficient for the chemical transformations to occur, particularly the dehydration of brushite to monetite. These transformations can be accelerated by increasing the HTPC temperature.

2.3. General procedure

The liquid and powder components (see Section 4.1) of IPC were mixed and poured in a polycarbonate mold. The mold was left at room temperature (RT) for one day for setting. Weights and lengths of specimens were measured after setting and recorded to be used as reference measurements. Afterward, the specimens were wrapped in aluminum foil and put in the autoclave for hydrothermal post curing, Fig. 1. The following outlines the general HTPC procedure:

1 In order to obtain a high percentage of pore moisture during the heating, the external pressure (P_m) was increased at ambient temperature. When the peak pressure was reached, the autoclave temperature was increased up to the peak temperature (T_c). (Pressure should be high enough to prevent excessive evaporation of pore moisture at the peak temperature).
2 The peak temperature and pressure were maintained for sufficient time (t_f).
3 At the end of the post curing, the autoclave temperature was decreased until ambient conditions, while the pressure was maintained at its peak value.
4 After a short period of time, the pressure was decreased slowly, to avoid the sudden evaporation of pore moisture, until ambient conditions were reached again.

3. Experimental procedure

3.1. Reference Inorganic Phosphate Cement (IPC) synthesis

IPC is a two-component system, consisting of a calcium silicate powder and a phosphate acid-based solution of metal oxides [7]. The powder component, Wollastonite ($CaSiO_3$) NYAD®200 of NYCO was used. The liquid mixture was a phosphoric acid solution, containing metal cations and a retarding agent following [7]. The weight ratio of powder to liquid used for all IPC mixtures in this research was 1/1.25, corresponding to a Ca/P ratio of 1.23. The two components of the IPC, the liquid and the powder, were mixed for 5 min at a speed of 1500 rpm with a blade mixer, in order to obtain a homogeneous mixture. The mixture was poured slowly, while being vibrated, into polycarbonate moulds. After the mould was filled, it was sealed by tape and left for 24 h at ambient conditions, during which period the material sets. The plates of IPC were removed from the mould, wrapped in a plastic foil and put in an oven at 60 °C for another 24 h.

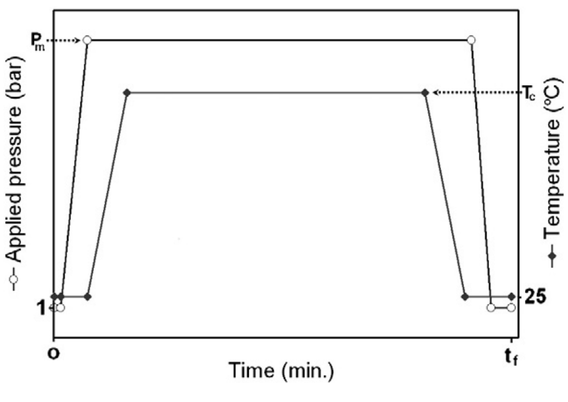

Fig. 1. Programming of the autoclave on pressure and temperature for hydrothermal post curing.

These new specimens were referred to as “reference specimens” or “reference IPC” in this research. This definition indicates that these specimens were not yet exposed to ageing, heating or any other treatment. Reference IPC is used in all the experiments to evaluate the hydrothermally post cured IPC.

3.2. Case study: monetite-based Inorganic Phosphate Cement (IPC) synthesis with HTPC at 150 °C

The hydrothermally post cured specimens were prepared as explained in Section 3.3. In this preliminary study, post curing temperature is set to 150 °C. This temperature was selected to assure the dehydration of the brushite [17] within short time. To keep the moisture within the pores during post curing, an external pressure of 10 bar was applied on the specimens at 150 °C by using the autoclave as shown in Fig. 1. The period of the hydrothermal post curing was ~700 min.

3.3. Heat exposure procedure (bulk specimens)

The effect of heating on the properties of IPC was determined after exposing bulk specimens to various temperatures. All subsequent tests were performed at room temperature. The following heat exposure procedure was used in this research:

1. The zero measurements (reference) were recorded immediately after curing at room temperature for 24 h.
2. The test specimens were placed in the oven.
3. The oven was brought to the required temperature.
4. The required temperature was maintained during the specified period of time (usually 24 h).
5. After the exposure period, the specimens were removed from the oven, and then brought back to ambient temperature before further testing.
6. The properties of interest were measured (e.g. length, stiffness ….)
7. After placing the same specimens in the oven, the temperature was increased to the next required temperature and steps 4 to 7 were repeated with the same specimens until the highest required temperature (usually 300 °C or 1000 °C) was reached.

At least three specimens were used for each test. The specimens were examined visually before and after each exposure step. Any differences in appearance of the test specimens before and after exposure were observed, compared and recorded.

3.4. Ageing

The reference and the monetite-based specimens were aged for 12 months at ambient conditions without any sealing.

3.5. Analytical techniques

3.5.1. X-ray diffraction (XRD)

X-ray diffraction (XRD) was carried out on powdered and non-powdered samples using a Siemens D5000 diffractometer, using a Cu Kα radiation with an applied voltage of 40 kV and a current of 40 mA. XRD scans were measured from 15° to 70° 2-theta at a scan rate of 2°/min.

3.5.2. Thermogravimetric analysis, and dynamic mechanical analysis

For the thermogravimetric analysis (TGA) a TGA7 from PerkinElmer was used, purged with Helium. Powdered samples (~40 mg) were tested. The heating rate was 5 °C/min.

In the thermomechanical analysis (TMA) a DMA7 instrument from PerkinElmer was used purged with Helium, with a quartz parallel plate probe (diameter 1 mm). A cube of $5\times5\times5\text{mm}^3$ was tested. The heating rate was 5 °C/min.

3.5.3. Optical microscope

In this research, we restricted our study to the cracking patterns on the surface of the specimens. To detect the cracking, an ink solution was used to colour the specimen surface. An optical microscope was then used to scan the specimens, while a digital camera fixed to this microscope captured the images.

3.5.4. Mercury intrusion porosimetry

An AutoPore IV Series 9500 from Micromeritics was used. The samples were placed in a closed cell called Penetrometer and evacuated. After reaching a low vacuum level (~3 kPa), the cell was filled with mercury and pressure was increased continuously to 400 MPa. The maximum pore diameter was 300 µm, the surface tension 0.485 N/m and the contact angle 130°.

3.5.5. Impulse excitation technique (IET)

The stiffness of the specimens was measured by using the Impulse Excitation Technique (IET). In this investigation, specimens with dimensions $15\times30\times320\text{ mm}^3$ were prepared to meet the requirements of this technique [18]. The specimens were supported at the nodes of resonance and struck by a small metallic stick at their centre. The fundamental resonant frequency was measured via a piezoelectric transducer in contact with the specimen. Further details on the test methodology and calculations are given in reference [19].

3.5.6. Compressive and three-point bending strength

The specimens were tested in three-point bending and in compression. Testing was performed at room temperature with an Instron universal testing machine model 1195. The specimen's dimensions were: height = 15 mm, width = 30 mm and length 160 mm, the distance between the supports was 120 mm and the speed of the machine head during testing was 0.1 mm/min. Compression tests were performed on the broken specimens from the three-point test, with loading area $= 40\times15\text{ mm}^2$ and height = 30 mm, while the speed of the machine head during testing was 2 mm/min.

4. Results and discussion

4.1. Formation of monetite-based IPC as a result of hydrothermal post curing

Fig. 2 illustrates the XRD patterns of the IPC without post curing, reference IPC and the hydrothermally post cured IPC (M-IPC). The IPC without post curing (cured IPC at room temperature for 24 h) shows the presence of brushite and wollastonite (W) as presented in the

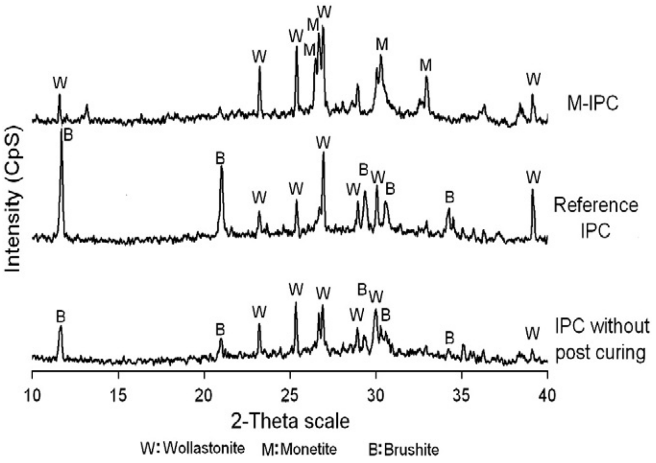

Fig. 2. XRD patterns (qualitatively) of powdered IPC specimens without post curing, reference (post cured at 60 °C) and hydrothermal post curing (HTPC).

lower XRD pattern. It is observed that the intensity of XRD diffraction lines corresponding to brushite (B) increases with reference curing (post cure at 60 °C). However, after hydrothermal post cure, it is observed that brushite disappears, at the expense of monetite (M). Wollastonite peaks are observed in the three specimens.

More detailed information regarding the phase composition and bound water is provided by TGA as shown in Fig. 3. This figure illustrates a TGA test of two specimens with reference and hydrothermal post curing. The total mass loss as a result of evaporation and dehydration of water is 25.7% as shown in Fig. 3A. The mass loss above 105 °C of IPC and M-IPC is 12.1% and 18.1% respectively. These results show that an observable percentage of bound water is released with HTPC to form M-IPC.

Brushite is transformed into pyrophosphate according to following reactions:

$$CaHPO_4 \cdot 2H_2O(s) \rightarrow CaHPO_4(s) + 2H_2O\,(g) \tag{2}$$

$$2CaHPO_4(\mathrm{s}) \rightarrow Ca_2P_2O_7(\mathrm{s}) + H_2O\,(\mathrm{g}). \tag{3}$$

Current studies showed that the bound water corresponding to meta-stable phases, i.e. amorphous calcium phosphate and brushite, redistributes over time and thus plays a major role in phase instability of the end products. [10] It is observed in Fig. 3 that the two dehydration steps and the large steady weight loss below 220 °C corresponding to brushite and ACP respectively disappeared with HTPC. It is important to choose the temperature and time of HTPC such that these transformations to monetite occurred completely [10]. Remark that the M-IPC specimen take up some water after the HTPC during storage. As a result, some mass loss is observed below 150 °C.

Decomposition of monetite exhibits a step of mass loss at the temperature range 390 °C–515 °C. It is observed that the percentage of monetite is significantly increased with hydrothermal post curing. To estimate the percentage of monetite in IPC, the mass loss in the temperature range 390 °C–515°C stemming from the decomposition of monetite is used. This dehydration and transformation of monetite ($CaHPO_4$) to calcium pyrophosphate ($Ca_2P_2O_7$) causes a reduction in molecular weight by 6.6%, Eq. (3). It is observed that the IPC loses 1.7% by using reference post curing, and loses 2.6% by using hydrothermal post curing. Thus the maximum percentage of monetite increases from 26% (reference specimens) to 39% with hydrothermal post curing.

Fig. 4 shows the TMA test of reference IPC and M-IPC. M-IPC exhibits less cumulative shrinkage with heating until 850 °C as shown in Fig. 4A. While reference IPC exhibits strong shrinkage steps (peaks in the derivative), it is observed that in M-IPC below 390 °C the shrinkage is much smaller and smoother, Fig. 4B. The large shrinkage of reference IPC is a result of the dehydration and the transformation of brushite and ACP phases. For example, the transformation of brushite (with skeletal density 2.32 g/cm^3) to monetite (with skeletal density 2.89 g/cm^3) is the main factor behind the shrinkage in IPC at a temperature range of 105 °C to 220 °C. This process was not observed in M-IPC because this transformation already occurred during the HTPC.

An important observation is that the shrinkage due to the HTPC is only 0.06%, comparable to the shrinkage of the reference post cure. The large shrinkage of about 1.5% which is seen in Fig. 5 for the reference IPC upon heating to 150 °C (the HTPC temperature) is thus not observed during the HTPC. This proves that the HTPC chemically stabilizes the material without introduction of large thermomechanical stresses.

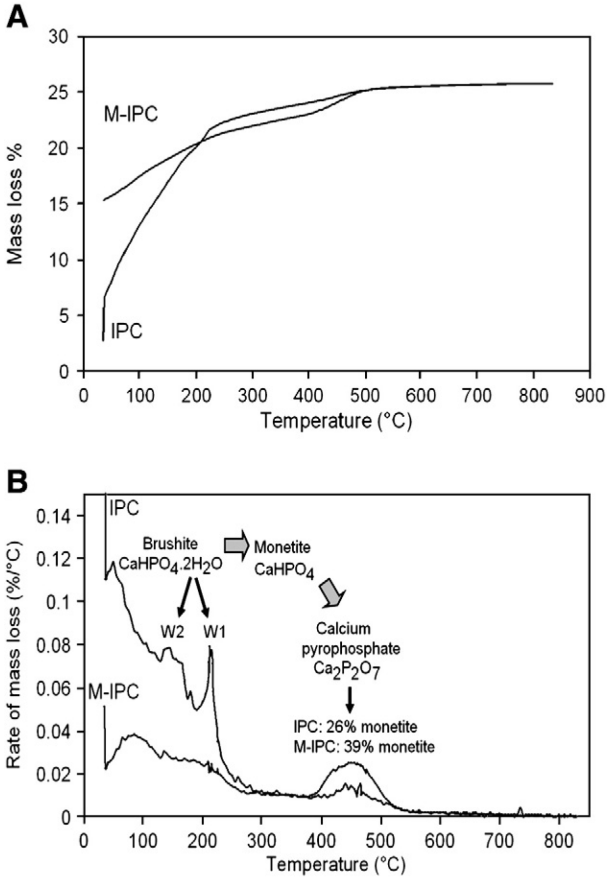

Fig. 3. TGA test of IPC and M-IPC, A. Cumulative mass loss as function of temperature, B. Derivative of A.

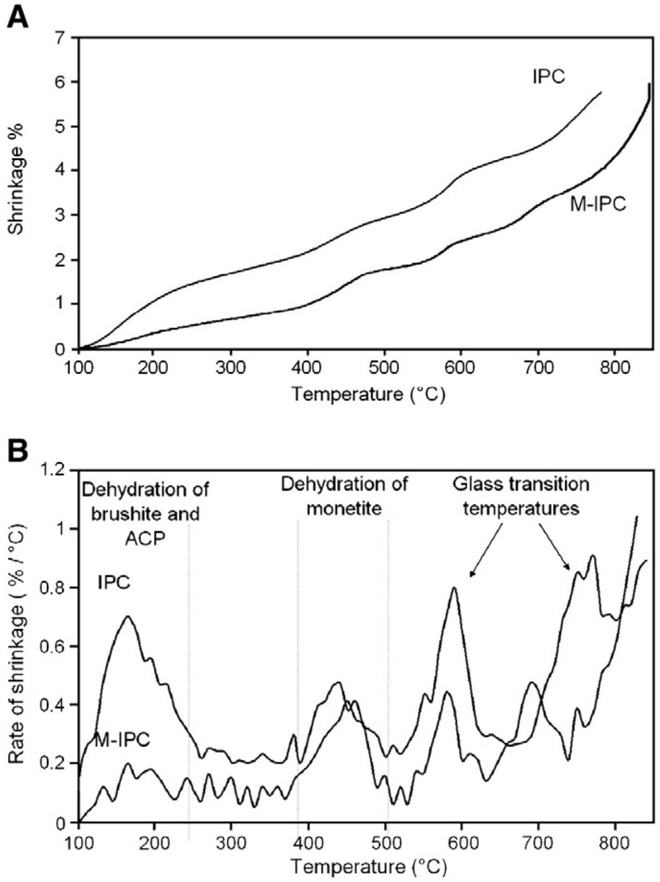

Fig. 4. TMA test of IPC and M-IPC, A. Cumulative shrinkage as function of temperature, B. Derivative of A.

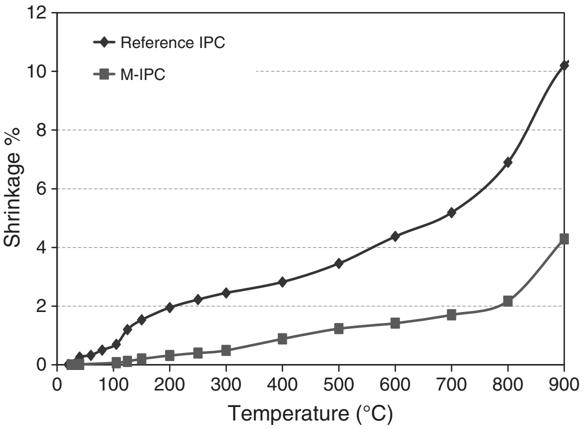

Fig. 5. Effect of HTPC on shrinkage of IPC as a function of temperature, the zero measurement is recorded before post curing (The heat exposure procedure).

Although M-IPC contains a high percentage of macrospores and porosity (to be discussed in Section 5.2), it is observed that M-IPC exhibits less shrinkage by heating at glass transition temperatures (Tg), i.e. above 515 °C, Fig. 4B. This is an indication of a reduction in the percentage of these amorphous phases.

The thermomechanical behaviour of IPC has already been determined by using TMA (Fig. 4). However, the data obtained by TMA exclude the measurements under 105 °C (including zero measurements at room temperature). In order to obtain complete data, two series of specimens were tested on shrinkage according to the heat exposure procedure, Section (4.3). The first series was post cured at 60 °C for 24 h (reference IPC), and the second series was post cured hydrothermally at 150 °C (M-IPC). The lengths of these specimens are monitored during this experiment involving heating to 900 °C. Fig. 5 illustrates the shrinkage of specimens with reference and hydrothermal post curing as a function of temperature. At 105 °C, the M-IPC specimens show a shrinkage that is 10 times lower than that of the reference specimens. This ratio decreases with increasing the exposure temperature until it becomes around 1/3 rd of the shrinkage of the reference specimens at 800 °C. However, the shrinkage of the reference specimens increases more with temperature than the M-IPC specimens.

According to the previous discussion, the increment in monetite percentage with HTPC could be a result of one or more of the following: 1) brushite is transformed into monetite, 2) more CaP (monetite) is formed through reactions of wollastonite, and 3) crystallization of a fraction of ACP. Monetite is one of the most stable phases of CaP at elevated temperatures. Therefore, increasing the percentage of this phase in the end products improves the phase stability in a wide range of temperatures and reduces the aging effects.

4.2. Effect of HTPC on the IPC pore system

This section is directed toward studying the effect of locking the moisture within the IPC pore spaces during HTPC on the pore system of the end products. The pore structure of two groups of specimens, IPC and M-IPC, is evaluated by using mercury intrusion porosimetry (MIP), each of these groups containing two specimens. Fig. 6 shows the incremental and cumulative pore size distribution of reference IPC and M-IPC. The two specimens of a group that are used in these tests show the same pore size distribution and the same porosity. This is an indication that these measurements are fairly reproducible.

As a result of HTPC, the percentage of the macropores increases as shown in Fig. 6A from 1% up to 16%, and the porosity increases from 30% up to 37%. A peak of pores is observed around 27 nm in reference IPC, Fig. 6B. Two peaks of pores are observed around 35 nm and 110 nm in M-IPC. This way, the increase of skeletal density as a result of thermally induced chemical transformations thus not necessarily leads to global bulk shrinkage, since the contraction of the skeleton is replaced internally by an increase of the pore size and porosity with HTPC.

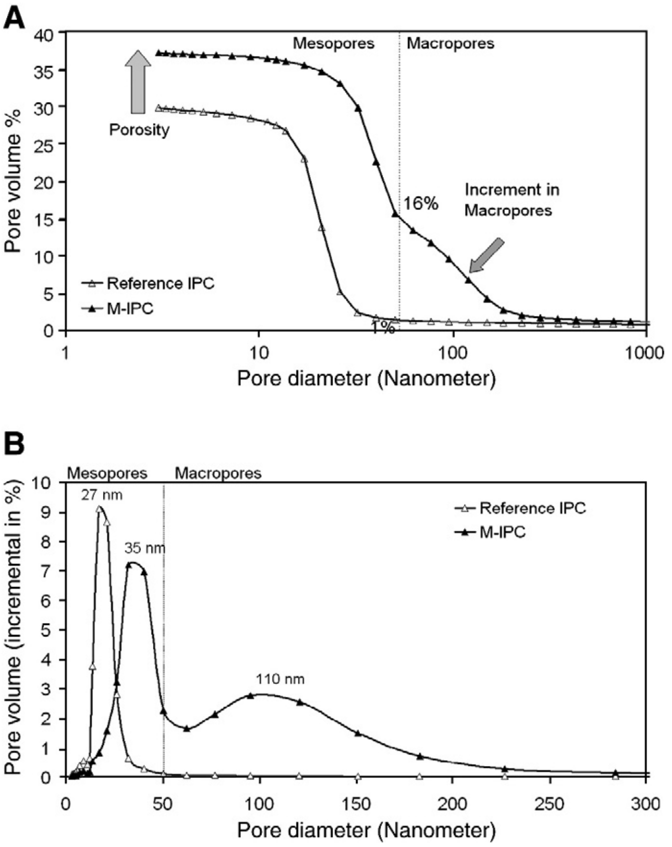

Fig. 6. Pore distributions of Reference IPC, after heating at 150 °C, and M-IPC (Mercury intrusion porosimetry), A. Cumulative, B. Incremental.

4.3. Thermomechanical stability and effects on engineering properties

The microstructural and chemical changes that occur in hydrothermally post cured IPC (M-IPC) have a high effect on cracking, stiffness and strength. These properties are systematically investigated as a function of the temperature by optical microscope, the Impulse Excitation Technique (IET), and mechanical testing. Reference IPC specimens are used in all tests to evaluate the effect of HTPC.

4.3.1. Cracking

Cracks in IPC could be the result of capillary stresses, thermally induced chemical transformation or thermal gradients. Fig. 7 shows the comparison between M-IPC and reference IPC. While the second specimens exhibit severe micro-cracking and macro-cracking, already in the temperature range of 40 °C–105 °C, M-IPC specimens show no visible cracks until 700 °C.

4.3.2. Stiffness

The stiffness of reference IPC drops at 105 °C as shown in Fig. 8. This sharp reduction in stiffness is mainly induced by the formation of a network of microcracks as shown in Fig. 7. On the other hand, the initial stiffness of specimens decreases by ~15% after hydrothermal post curing, but they retain a high percentage (80%) of their initial stiffness at temperatures up to 800 °C. Above this temperature, the glass transition temperature of one or more of the IPC components is reached [8], thus an increase of stiffness is observed after cooling to ambient conditions. These results show that the stiffness of M-IPC specimens is relatively stable up to 800 °C.

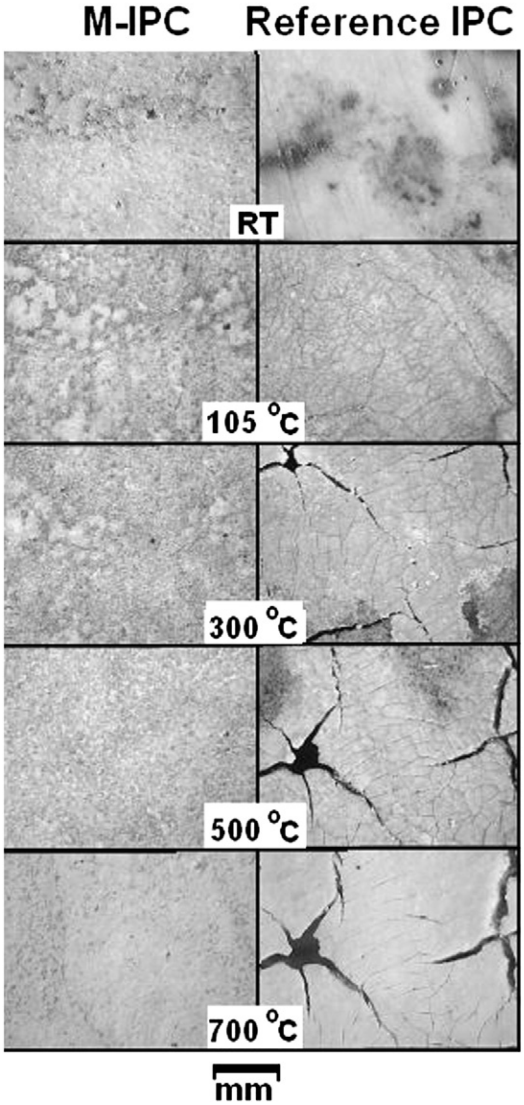

Fig. 7. Reference IPC is compared with M-IPC on cracking as a function of temperature (Optical microscope).

4.3.3. Strength

Although the chemical, thermal and dimensional stability of IPC is highly improved by hydrothermal post curing (HTPC), this is not the case for the compression strength. Fig. 9 illustrates the compressive strength of IPC after reference and hydrothermal post curing. The specimens lose 60% of their compression strength after HTPC. HTPC is known to change the pore structure as shown in Fig. 5. Consequently, M-IPC has lower compressive strength. Exposing the specimens up to 300 °C slightly reduces the compressive strength of reference IPC and has no observable effect on the compressive strength of M-IPC.

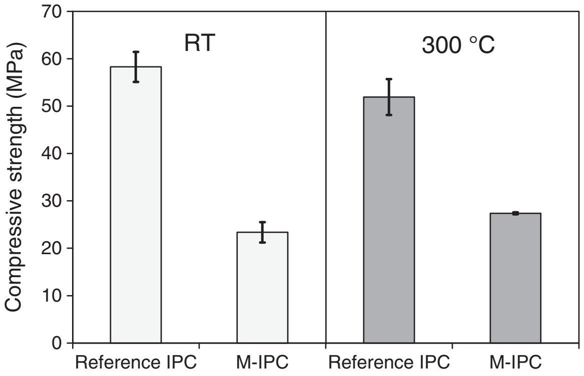

Fig. 9. Compressive strength of reference IPC and M-IPC at room temperature (RT), and after exposure to 300 °C.

The bending strength of IPC decreases by 19% with HTPC as shown in Fig. 10. Exposure of specimen to 300 °C causes a sharp decrement in strength of reference IPC by around 50% and an increment by 30% of M-IPC. This drop in the bending strength of reference IPC results mainly from the formation of a network of microcracks along with macrocracks, Fig. 7. After exposure at 300 °C, the bending strength of M-IPC is twice as high as reference IPC. These results reveal that M-IPC is stable at various temperatures.

The disadvantage of M-IPC is the reduction of its compression strength even at 20 °C, which is a result of the increment in pore spaces and formation of larger percentage of macropores. However it seems that M-IPC fully retains or even increases its strength, both bending and compression, after exposure to elevated temperatures with low shrinkage. This high mechanical performance of M-IPC at elevated temperatures results from high-cracking resistance with heating as shown in Fig. 7. Monetite is one of the most stable calcium phosphate phases at elevated temperatures [10]. Therefore, only limited shrinkage is exhibited by M-IPC with heating.

4.5. Ageing effects on IPC with HTPC

Evaluations for ageing effects and chemical stability of IPC with HTPC are performed throughout the storage for 12 months at ambient conditions. The aged specimens are compared with non-aged specimens by using TGA. These tests are intended to determine the changes

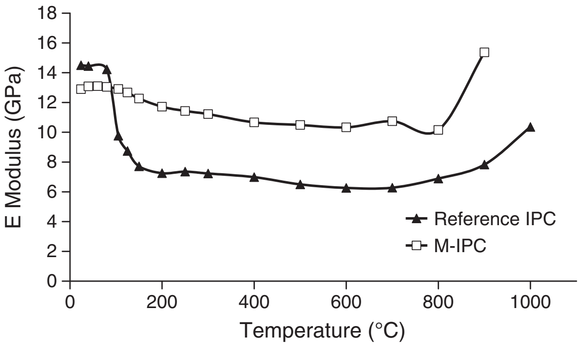

Fig. 8. Stiffness profile of reference IPC and M-IPC as a function of temperature.

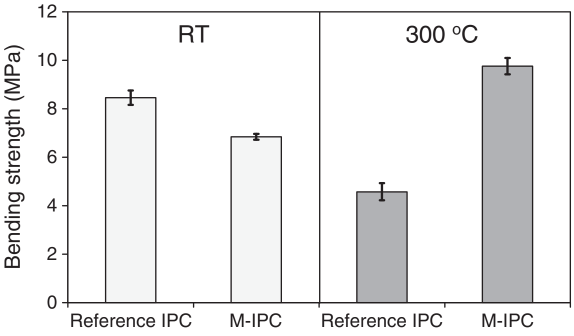

Fig. 10. Bending strength of reference IPC and M-IPC at room temperature (RT), and after exposure to 300 °C.

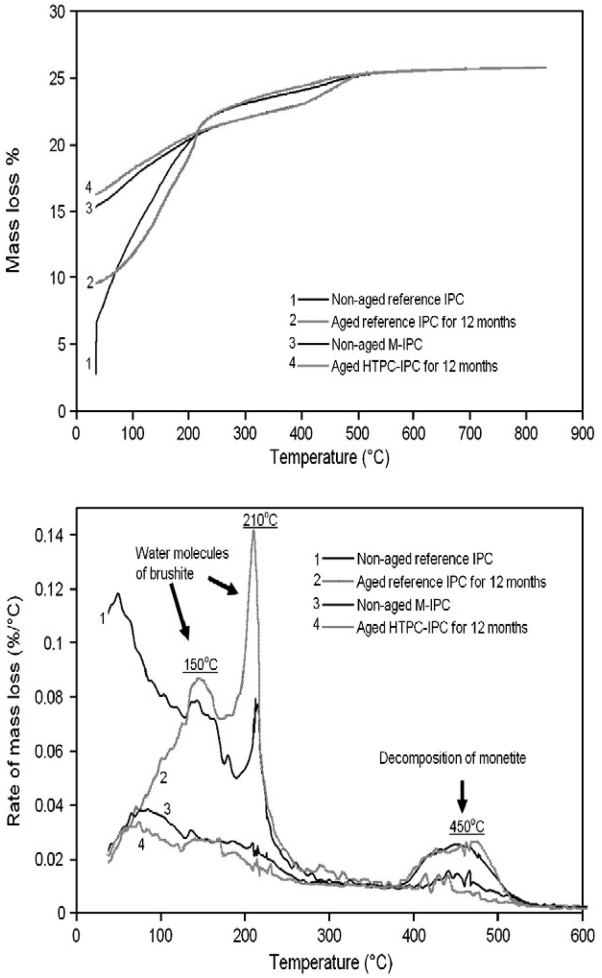

Fig. 11. TGA test of specimens with reference post curing (at 60 °C) and hydrothermal post curing: non-aged and aged for 12 months.

in chemical phases and composition at various temperatures after ageing. The thermogram is shown in Fig. 11. From this figure, one can notice that brushite is transformed into monetite at 220 °C. Thereafter, at 390 °C–515 °C, it turns into calcium pyrophosphate ($Ca_2P_2O_7$). Two main zones of release of bound water are observed in Fig. 11:

1) Room temperature — 220 °C: Unlike reference IPC, no changes are detected in M-IPC after ageing for 12 months. This is an indication that the CaP phases in IPC are chemically stable over time.
2) Dehydration peak at a temperature range of 390 °C–515 °C: This peak represents the dehydrated water molecules as a result of the transformation of monetite to calcium pyrophosphate. It is also observed that the percentage of monetite in these specimens has not changed after ageing for 12 months.

Contrary to reference IPC, M-IPC exhibits the same distribution of bound water after ageing for 12 months. This confirms that with HTPC, IPC exhibits much better long term phase stability than reference IPC.

The ageing effects are also studied by measuring linear shrinkage and bending strength. While reference IPC exhibits shrinkage of 0.17% during the 12 months of ageing period, M-IPC shows no significant changes in its dimensions. These specimens are also subjected to a three-point bending test after 12 months of ageing at ambient conditions as shown in Fig. 12. It is observed that the average bending strength of reference IPC and M-IPC increases 1.4 times by ageing at ambient conditions for 12 months.

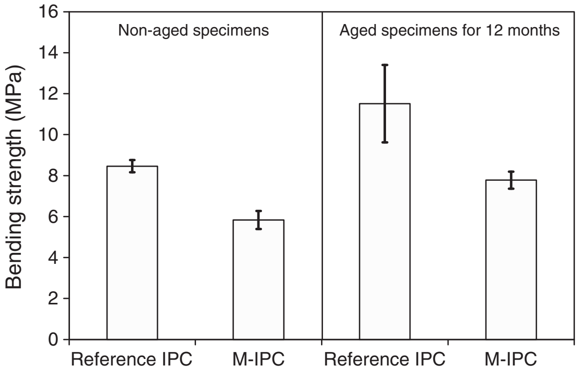

Fig. 12. Changes in the bending strength and shrinkage of reference IPC and M-IPC after ageing for 12 months at ambient conditions.

5. Conclusions

A hydrothermal post curing is proposed to resolve some problems caused during ageing of an Inorganic Phosphate Cement, IPC. As a result of this hydrothermal post curing (HTPC), a monetite-based IPC (M-IPC) is formed. It is found that brushite but probably also amorphous calcium phosphates present in IPC transform into monetite. It was determined that the monetite percentage in the end IPC products increased from 26% to 39% as a result of HTPC. Compared to reference IPC, monetite-based IPC exhibits a good stability over time and as a function of temperature. One of the main factors leading to ageing is the presence of physicochemically bound water, which is mainly associated with CaP phases. HTPC liberates most of this water and thereby reduces ageing effects. Unlike the non-treated (reference) IPC, no significant changes are observed in bound water and dimensions of M-IPC over time. HTCP also enhances high temperature microstructural stability and thermo-mechanical stability. When heating up to 390 °C, HTPC-IPC preserves its initial chemical phases, i.e. monetite. In addition, HTPC-IPC retains its mechanical properties after exposure to high temperature. HTPC also contributed to an increased bending strength and enhanced dimensional stability under high temperature conditions. The results presented here strongly indicate that HTPC restructures the IPC pore system. This change in the pore system is a result of one or two of the following mechanisms: 1) formation of new pores and, 2) coarsening of the original pores. The additional porosity reduces the bulk shrinkage of the specimens by replacing the thermally induced contraction (local shrinkage) of the solid skeleton. During the hydrothermal post curing, very low bulk shrinkage is recorded. For example, after heating at 105 °C, specimens with hydrothermal post curing show a shrinkage that is 10 times lower than that of the reference specimens. This difference in shrinkage reduces by increasing the exposure temperature till it becomes around 1/3rd of the shrinkage of the standard specimens at 800 °C. One disadvantage of HTPC is the high decrement by around 60% in compression strength compared with reference IPC. Also, HTPC increases the complexity of material processing and is costly, thus it is recommended only for high temperature applications and for industrial applications. HTPC can be obtained by different procedures as a function of temperature, pressure and time. This will be investigated in more detail in a following paper.

References

[1] A. Tofighi, K. Schaffer, R. Palazzolo, “Calcium phosphate cement (CPC): a critical development path”, Key Engineering Materials 361–363 (2008) 303–306.

[2] L. Sun, H.H.K. Xu, S. Takagi, C. Chow, “Fast setting calcium phosphate cement-chitosan composite: mechanical properties and dissolution rates”, Journal of Biomaterials Applications 21 (3) (2007) 299–315.

[3] S.C. Liou, S.Y. Chen, H.Y. Lee, J.S. Bow, "Structural characterization of nano-sized calcium deficient apatite powders", Biomaterials 25 (2004) 189–196.

[4] M. Bohner, P. Landuyt, H.P. Merkle, J. Lemaitre, "Composition effects on the pH of a hydraulic calcium phosphate cement", Journal of Materials Science: Materials in Medicine 8 (11) (November, 1997).

[5] M.P. Hofmann, A.M. Young, U. Gbureck, S. Nazhat, J.E. Barralet, "FTIR-monitoring of a fast setting brushite bone cement: effect of intermediate phases", Journal of Materials Chemistry 16 (2006) 3199–3206.

[6] B. Flautre, M. Deschamps, C. Delecourt, M.C. Blary, P. Hardouin, "Porous HA ceramic for bone replacement: role of the pores and interconnections—experimental study in the rabbit", Journal of Materials Science: Materials in Medicine 12 (8) (2001) 679–682.

[7] Inorganic Resin Compositions, their preparation and use thereof, EP 0861 216, Vrije Universiteit Brussel

[8] H. Cuypers, "Analysis and design of sandwich panels with brittle matrix composite faces for building applications", doctoral thesis, Vrije Universiteit Brussel (VUB), 2002.

[9] M. Alshaaer, "Optimization of properties of Inorganic Phosphate Cement (IPC) for construction and high-temperature applications", doctoral thesis, Vrije Universiteit Brussel (VUB), 2006.

[10] M. Alshaaer, H. Cuypers, G. Mosselmans, H. Rahier, J. Wastiels, "Evaluation of a low temperature hardening inorganic phosphate cement for industrial applications", under review at Cement and Concrete Research.

[11] P. Van Itterbeeck, "Duurzaamheidsonderzoek van Inorganic Phosphate Cement (IPC)", Master thesis "in Dutch". Department of Architecturel Engineering, Vrije Universiteit Brussel, 2004

[12] G. Mosselmans, M. Biesemans, R. Willem, J. Wastiels, M. Leermakers, H. Rahier, S. Brughmans, B. Van Mele, "Thermal hardening and structure of a phosphorus containing cementitious model material phosphoric acid-wollastonite", Journal of Thermal Analysis and Calorimetry 88 (3) (2007) 723–729.

[13] A.L. Oliveira, R.L. Reis, "Pre-mineralisation of starch/polycrapolactone bone tissue engineering scaffolds by calcium-silicate-based process", Journal of Materials Science : Materials in Medicine 15 (2004) 533–540.

[14] P. Kumta, C. Sfeir, D. Lee, D. Olton, D. Choi, "Nanostructured calcium phosphates for biomedical applications: novel synthesis and characterization", Acta Biomaterialia 1 (2005) 65–83.

[15] E. van der Wal, "Bioactivity and surface reactivity of RF-sputtered calcium phosphate thin films", PhD thesis, Universiteit Utrecht, Katholieke Universiteit Nijmegen, Holland, 2003.

[16] S.V. Dorozhkin, M. Epple, Biological and medical significance of calcium phosphates, Angewandte Chemie International Edition 41 (2002) 3130–3146.

[17] M. Sedlak, A. Beebe, "Temperature programmed dehydration of amorphous calcium phosphate", Journal of Colloid and Interface Science 47 (2) (May 1974) 483–489.

[18] T. Lauwagie, H. Sol, G. Roebben, W. Heylen, Y. Shi,"Validation of the Resonalyser method: an inverse method for material identification". Publications at ISMA (International Conference on Noise and Vibration Engineering), September 2002, pp. 687–694.

[19] A. Wolfenden, M.R. Harmouche, G.V. Blessing, Y.T. Cjen, P. Terranova, V. Dayal, V.K. Kinra, J.W. Lemmens, R.R. Phillips, J.S. Smith, P. Mahmoodi, R.J. Wann, "Dynamic Young's Modulus Measurements in Metallic Materials: Results of an Interlaboratory Testing Program", Journal of Testing and Evaluation, JTEVA 17 (1) (1989) 2–13.