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Mechanical properties of self-setting composites: influence of the carboxymethylcellulose content and hydration state

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Abstract The impact of the carboxymethylcellulose (CMC) content on the mechanical properties of calcium phosphate–calcium carbonate–CMC composite cements for bone substitution was investigated. The relevance of the compressive test conditions (wet or dried composite cements) is discussed and models are proposed to better understand the mechanisms involved in the mechanical properties of the composite materials. Based on a modelisation using the Voigt model for dried composite cements, we show that a minimum of CMC content of around 10–20 % is needed to enhance the mechanical properties of the dried composite materials (up to 86 MPa for the composite including 50 wt% CMC) through the formation of a mineral–organic entangled network. The compressive strength of the wet samples is low (<3 MPa)

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but the gain observed in the dried composites is encouraging and might be extrapolated to wet conditions if we were to use a less hydrophilic polysaccharide.

Introduction

Calcium phosphate-based cements (CPCs) are the subject of great interest as bone-filling materials and have been studied for about 30 years [1]. This cementitious form has many advantages: the material can be initially injected as a paste, paste, which fits the shape of the defect to be filled and greatly facilitates surgery. Then, in vivo, at the temperature of the body, it hardens and forms—in most cases—more or less crystallised apatite. It is considered that the similarity of the set cements to the structure and composition of bone mineral as well as their osteoconductivity gives them excellent biological properties, including the ability to be partly or totally resorbed by bone cells and to lead to bone neoformation. However, without any additives, the injectability of these cements is often limited by a filter-pressing phenomenon during paste extrusion (i.e. the separation of particles/powder from liquid within the syringe, resulting in plugging and partial paste extrusion). Moreover, the composition and the porous microstructure, which are very interesting in terms of bioresorbability, generally lead to brittle behaviour and low fracture toughness, which are often associated with relatively low compressive strength [2]. As a consequence these materials are mainly indicated for non-weight-bearing bone repair, but the enhancement of the paste handling and mechanical properties is one of the major challenges to be overcome for these bone substitute materials.

The introduction of a polymer in either the liquid [3, 4] or the solid phase [5, 6] has thus been studied in different

CPC formulations. The idea of inorganic–organic composite materials is consistent with a biomimetic approach, with the bone organ exhibiting exceptional physico-chemical and mechanical properties as a composite material that combines a fibrillar collagen matrix with mineral apatite nanocrystals [7]. Thus, the addition of a polymer into phosphocalcic cements could give some cohesiveness to the material and prevent its disintegration into particles—which are potentially phlogogenic—at the site of the implantation [8]. On the other hand, a combination of the mineral cement with polymers could improve the mechanical properties of the materials because of their intrinsic physico-chemical properties and their impact on the microstructure of composite cements [9]. Among biocompatible polymers, polysaccharides have been widely used in biomaterials thanks to their excellent properties such as non-toxicity, hydrophilicity, certain stability with respect to the pH variations and the variety of their structures [10]. The most common polysaccharides found in tissue-engineering biomaterials are alginates [11], chitosan [12], celluloses [13], even hyaluronic acid [14] and their derivatives.

In this study, we worked on a calcium carbonate–calcium phosphate ($CaCO_3$–CaP) mineral cementitious matrix that has already shown interesting physico-chemical and biological properties [15–17]. In order to improve the cohesion of the paste, we chose to introduce carboxymethylcellulose (CMC), an anionic hydrophilic polysaccharide. Diverse studies carried out on CMC as an additive in Portland cement have led to a slight increase in the compressive strength and toughness of the material [18, 19].

A few studies report the use of CMC as an additive in bone cements. It has been introduced in both the liquid phase [20] and the solid phase [5] of α-tricalcium phosphate (α-TCP) cements. Besides providing a better cohesion and malleability of the paste, CMC significantly enhanced its injectability through a lubrication effect when introduced, at rather low concentrations, into the solid phase [5]. Kobayashi et al. also conducted an in vivo study on BoneSource $^®$ cement (based on tetracalcium phosphate (TTCP) and dicalcium phosphate anhydrous (DCPA)) associated with CMC to facilitate injection. Good results were observed in terms of osteoconductivity, biocompatibility, and resistance to compression, but the specific role of CMC in those properties was not explicitly stated [21]. Finally, Park et al. have used a combination of a CMC gel and an apatitic cement based on amorphous calcium phosphate in order to introduce mesenchymal stem cells into the material and to protect them from the cytotoxicity of the paste before setting [22]. Thus CMC seems to be a good candidate to improve the physico-chemical properties of $CaCO_3$–CaP cements while preserving their biological activity.

Most studies report the mechanical behaviour of set cements in dry state, although they are used in wet environments after in vivo implantation. The objective of this study is to thoroughly investigate the mechanical properties of $CaCO_3$–CaP–cellulose composite cements in the dry and wet states and to understand the role of CMC in the control of these properties.

Materials and methods

Composite cement preparation

The mineral powders brushite $CaHPO_4 \cdot 2H_2O$ and vaterite $CaCO_3$ were synthesised as previously described [17]. The reference cement (C-REF), without polysaccharide, was prepared by mixing deionised water as the liquid phase with a solid phase composed of an equal mass of vaterite and brushite. Composite cements were obtained by adding a polysaccharide, carboxymethylcellulose (CMC, Ashland, Aqualon$^{(R)}$ 7H4XF-PH, pharmaceutical grade) as a powder into the solid phase before mixing it with water. For all samples, the water/solid weight ratio (W/S) was 0.70. After mixing, the wet paste was placed into silicon moulds and left in a water-saturated atmosphere at 37 °C for setting and hardening during 48 h. After 2 days, the hardened reference and composite cements were withdrawn from the mould. The "wet cements", analysed just after setting and hardening, were named C−xCMC−w, with x being the weight percentage of CMC (from 2 to 50 wt% in the solid phase). The "dried cements", C−xCMC−d, were dried during an additional 5 days in air in a drying oven at 37 °C after setting and hardening.

Mechanical characterisation

Mechanical tests were carried out with uniaxial compression loading at a rate of 0.8 mm min^{-1} using a Hounsfield S-Series testing machine on cylindrical samples (height = 19.5 mm; diameter = 10.5 mm) of both wet and dried cements.

Few studies have attempted to quantify the toughness of cements containing polymer. Yet, given the brittleness of the calcium phosphate-based materials, improved toughness has been reported in the literature as one of the main challenges ahead [23]. Thus, in order to discuss this property, we evaluated the energy at maximum stress (E_c), which corresponds to the sum of the elastic energy stored reversibly and the energy dissipated irreversibly in the material and allows an estimation of the magnitude of the toughness. This parameter must be considered carefully, as it is dependent on the experimental conditions, but nevertheless it appears to be a valuable mechanical characteristic

that allows a comparison of different samples analysed in the same conditions. From the stress–strain diagrams, we also determined the compressive strength (R_c), the strain for R_c (ε_c) and the elastic modulus (E) (Fig. 1).
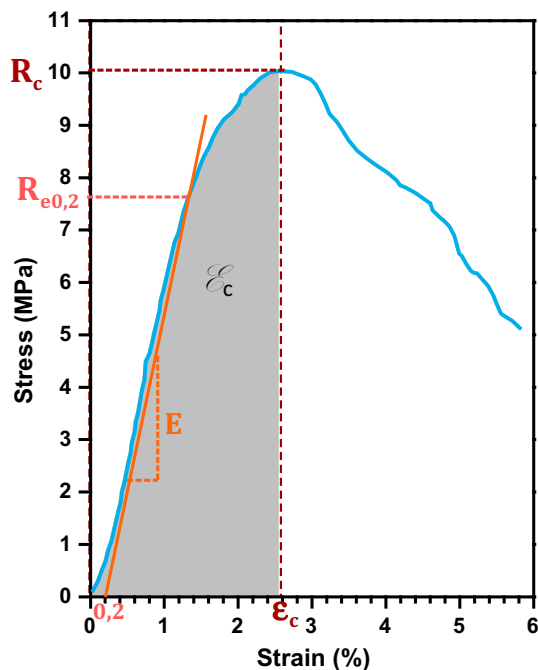
Physico-chemical characterisation

Powder X-ray diffraction (XRD) measurements were performed using a CPS-120 INEL diffractometer with a Co anticathode ($\lambda_{Co} = 1.7903$ Å). Scanning electron microscopy (SEM) micrographs were obtained using a Leo 435 VP microscope (samples were coated with silver before observation). A mercury intrusion porosimeter (Autopore IV 9400 Micromeritics$^{\circledR}$ Instruments) was used to determine the total porosity of the composite cements.

Results

Composite material feasibility

Figure 2 shows the XRD patterns of set and dried composite cements containing different amounts of CMC after 48 h of maturation at 37 °C and 5 days of drying. These X-ray patterns are similar for all the materials: all the diffraction peaks can be readily indexed as vaterite and nanocrystalline apatite phases. The brushite, which was totally consumed during the setting, does not appear on the XRD patterns. Thus, when up to 50 wt% CMC powder is introduced into the solid phase, the organic phase (CMC) does not prevent the occurrence of the setting reaction and does not seem to change the overall process of dissolution–reprecipitation involved in this reaction [17].

Mechanical properties

A stress–strain diagram of each composition is shown in Fig. 3. Like most of the mineral cements, C-REF exhibits a brittle behaviour with only an elastic deformation. In contrast, the composite cements show smooth curves and a plastic deformation: the addition of CMC conferred some ductility on the material. The mechanical characteristics determined from the curves obtained for dried (Fig. 3a) and wet (Fig. 3b) composite samples are very different in terms of order of magnitude and in terms of the influence of the CMC content introduced in the cements. The compressive strength R_c of the dried samples of the reference cement was four times higher (12.7 ± 2.7 MPa) than that of the wet ones (3.2 ± 1.1 MPa) (Table 1). Interestingly, although the mechanical properties were weakened by the low CMC content (C−2CMC−d and C−2CMC−w), the strength of the dried materials increased considerably at higher CMC contents, being up to 86.2 MPa for the composite that included 50 wt% CMC (Fig. 4a, Table 1). Nevertheless, this effect was not observed in the wet samples, whose compressive strength remained at a low value of around 1 MPa for any CMC content in the composite. The elastic modulus E showed exactly the same behaviour as the compressive strength in both dried and wet composite samples (Fig. 4b): a loss when the CMC content increased from 0 and to 2 wt% CMC and then a gain from 0.6 to 2.3 MPa when the CMC content increased from 2 to 50 wt% for dried-composite-cement composition, although wet composite 207cements kept a lower elastic modulus (<0.1 MPa). However, interestingly, the addition of CMC improved the ductility of the material, particularly for the wet cements. Both the strain ε_c and the energy $\mathscr{E}_c$ at maximum stress R_c increased significantly with CMC content beyond ca. 10 wt% (Fig. 4c, d). Thus, as is apparent from the mechanical compressive test on the cement blocks (Fig. 5), even if the compressive strength seems particularly low for a bone-filling material, it is interesting to notice that the cohesion and integrity of the material were particularly improved by the addition of the polysaccharide.

Microstructure and porosity

Figure 6 shows the micrographs of the two cements C−2CMC−d and C−30CMC−d as examples of composite samples with low and high polysaccharide contents, respectively. In the first one, polysaccharide was hardly observed (Fig. 6a). The microstructure is typical of that

Fig. 1 Stress–strain curve: example of data treatment and determination of the four parameters: compressive strength (R_c), strain for R_c (ε_c), elastic modulus (E) and energy at maximum stress ($\mathscr{E}_c$)

Fig. 2 X-ray patterns of the set and dried composite cements containing 2–50 wt% CMC compared to the cement C-REF, without polysaccharide (*V* vaterite, *Ap* apatite)
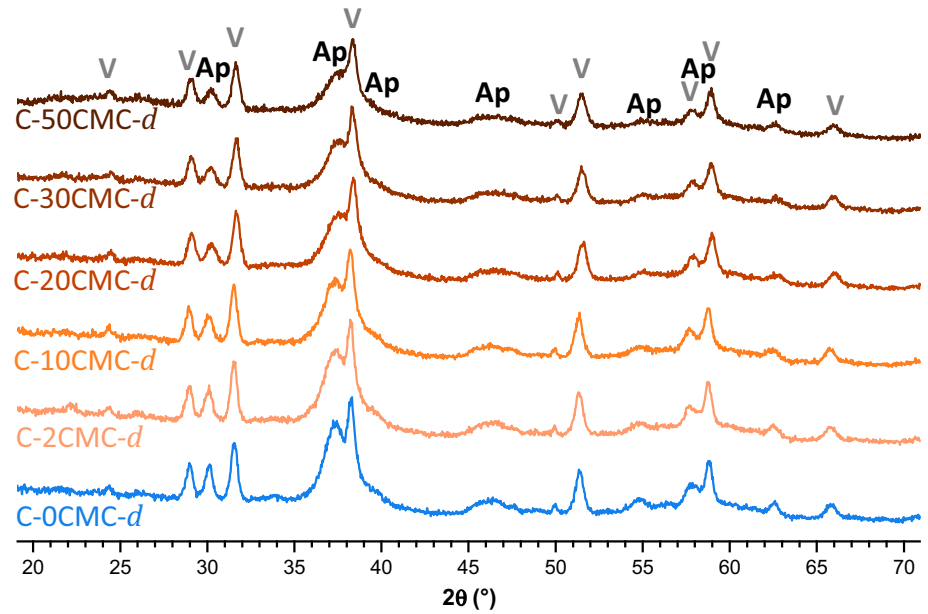
Fig. 3 Representative stress–strain curves obtained for the mineral cement C−0CMC and composite cements containing 2–50 wt% CMC **a** after drying and **b** without drying (wet cements)
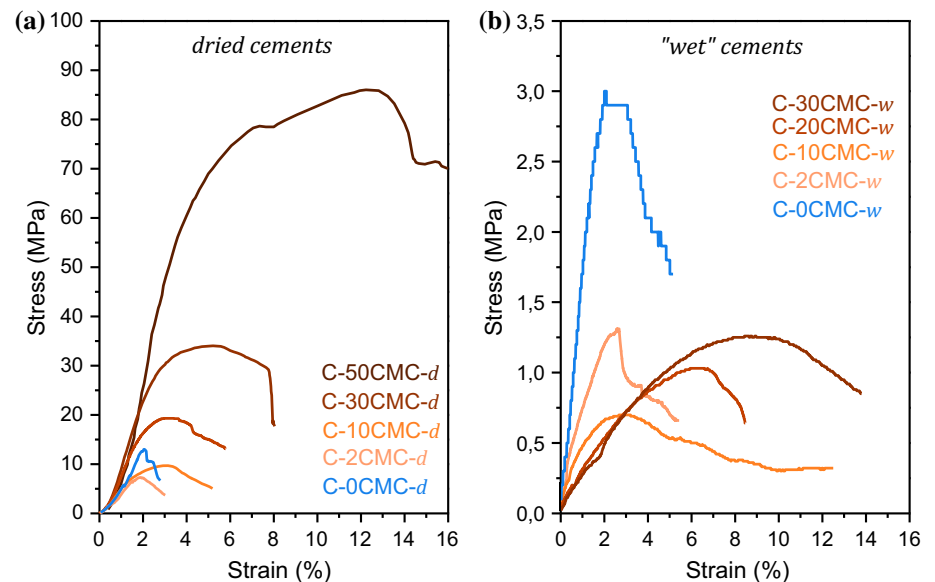
observed for vaterite–brushite reference cements, with a rough aspect that could be associated with micro- and nano-porous material and with some almost spherical macropores that were attributed to the formation of CO_2 bubbles during the setting reaction related to the vaterite reaction [17]. On contrast, CMC was clearly identified in different zones of C−30CMC−d composite cement (Fig. 6b). It appeared like a smooth or wrinkled veil that was particularly visible in the macropores. Moreover, the latter lost their spherical shape, most probably due to an increase in the viscosity of the liquid phase including the hydrophilic CMC and higher constraints on the materials at the gas/paste interface.

The characterisation was supplemented by a porosity analysis of the dried samples, which highlighted an important loss of porosity in the composite cements, from 88 % for C−0CMC−d and C−2CMC−d to 24 % for C−50CMC−d (Table 2).

Discussion

Mechanical properties of wet versus dried composite cements

The mechanical characterisation of both wet and dried samples confirmed the importance of the material

Table 1 Young's modulus (E), compressive strength (Rc), strain for R_c (ε_c) and energy ($\mathcal{E}_c$) for dried (d) and wet (w) samples

	E (GPa)	R_c (MPa)	ε_c (%)	$\mathcal{E}_c$ (kJ m^{-3})
C−0CMC−d	0.89 ± 0.40	12.7 ± 2.7	2.1 ± 0.4	119 ± 11
C−2CMC−d	0.61 ± 0.18	6.1 ± 1.7	1.5 ± 0.4	49 ± 24
C−10CMC−d	0.62 ± 0.04	9.5 ± 0.5	2.8 ± 0.3	163 ± 26
C−20CMC−d	1.20 ± 0.16	18.5 ± 2.3	2.5 ± 0.4	270 ± 65
C−30CMC−d	1.40	34.0	5.3	1200
C−50CMC−d	2.27	86.2	12.3	7590
C−0CMC−w	0.22 ± 0.03	3.2 ± 1.1	1.6 ± 0.6	28 ± 10
C−2CMC−w	0.08 ± 0.02	1.1 ± 0.1	1.4 ± 0.9	11 ± 6
C−10CMC−w	0.03 ± 0.01	0.7 ± 0.1	2.9 ± 0.6	16 ± 4
C−20CMC−w	0.02 ± 0.001	1.0 ± 0.1	6.2 ± 0.4	44 ± 3
C−30CMC−w	0.02 ± 0.001	1.2 ± 0.1	8.8 ± 0.4	72 ± 5

Mechanical parameters of the reference and various composite cements determined from the stress–strain curves (Fig. 3)

preparation for the nature of the results, which is not always mentioned or precisely described in the current scientific literature. Regarding the two series of composite materials studied (wet and dry composites), it is clear that the hydrophilic nature of CMC is a determining factor for the mechanical properties of these composite materials. After water absorption and swelling, the mechanical strength of the polysaccharide is degraded, together with its structure, which could be considered as a highly viscous liquid phase or a soft matter phase rather than a real solid phase within the composite material. This explains the low impact of this polysaccharide on mechanical properties such as the compressive strength or the elastic modulus and even a decrease of these values: they are determined mainly by the mineral phase, whose proportion decreases as the CMC content increases. On the other hand, this "soft matter phase" enhances cohesion in the material, improving the ductility and toughness and thus increasing the strain percentage at the rupture point.

These wet conditions are most likely a better approximation of the in-use conditions of these self-setting composite materials in vivo as bone substitute materials than the dried samples and must give more predictive results. Nevertheless a better understanding of a water-containing mineral–polysaccharide composite system is complex. The study of the dried samples, by removing water, simplifies the system and is of interest for further investigation of the interaction between the organic and inorganic phases in the composite materials.

Elastic modulus and porosity of the dried composite cements

The introduction of CMC into the CaCO$_3$–CaP cements has an impact on two parameters of great importance with regard to the mechanical properties: the relative content of mineral and organic phases and the porosity of the cements. Both of them change the microstructure of the material, which is directly correlated to its mechanical behaviour. In particular, if we only consider the composite cements, the elastic modulus increases considerably with the CMC content (Fig. 4b). Thus, one important question is whether this phenomenon is linked to the composite character of the material or to the decrease of its porosity.

The elastic modulus of a composite material is a function of the modulus and the volume fraction of each of the constitutive phases. Two main models have been proposed in the literature to describe this relationship: the Reuss model, for short-range interactions in the second phase introduced into the matrix (as particles, platelets or short fibres, for example), and the Voigt model for long-range interactions, as in an entangled network of the second phase. Given our observations on the SEM micrographs (Fig. 6), the latter model seems the most relevant to describe our system: the polysaccharide appears as a "binder" between the materials, covering the particles and connecting them together. Following this hypothesis, the elastic modulus could be expressed as in Eq. 1:

$$E = \alpha_{Ap} \cdot E_{Ap} + \alpha_V \cdot E_V + \alpha_{CMC} \cdot E_{CMC} \qquad (1)$$

with E_{Ap}, E_V and E_{CMC} the elastic moduli of apatite, vaterite, and CMC, respectively, and α_{Ap}, α_V and α_{CMC} their volume fractions. Taking into account the porosity (P), the relationship between these volume fractions can be expressed as follows (Eq. 2):

$$\alpha_{Ap} + \alpha_V + \alpha_{CMC} + P = 1 \qquad (2)$$

considering the air in the pores as an additional phase whose elastic modulus is zero in the Voigt model.

The volume fractions of each phase are difficult to determine: our data are mainly expressed as weight fractions and a precise determination of the apatite and CMC
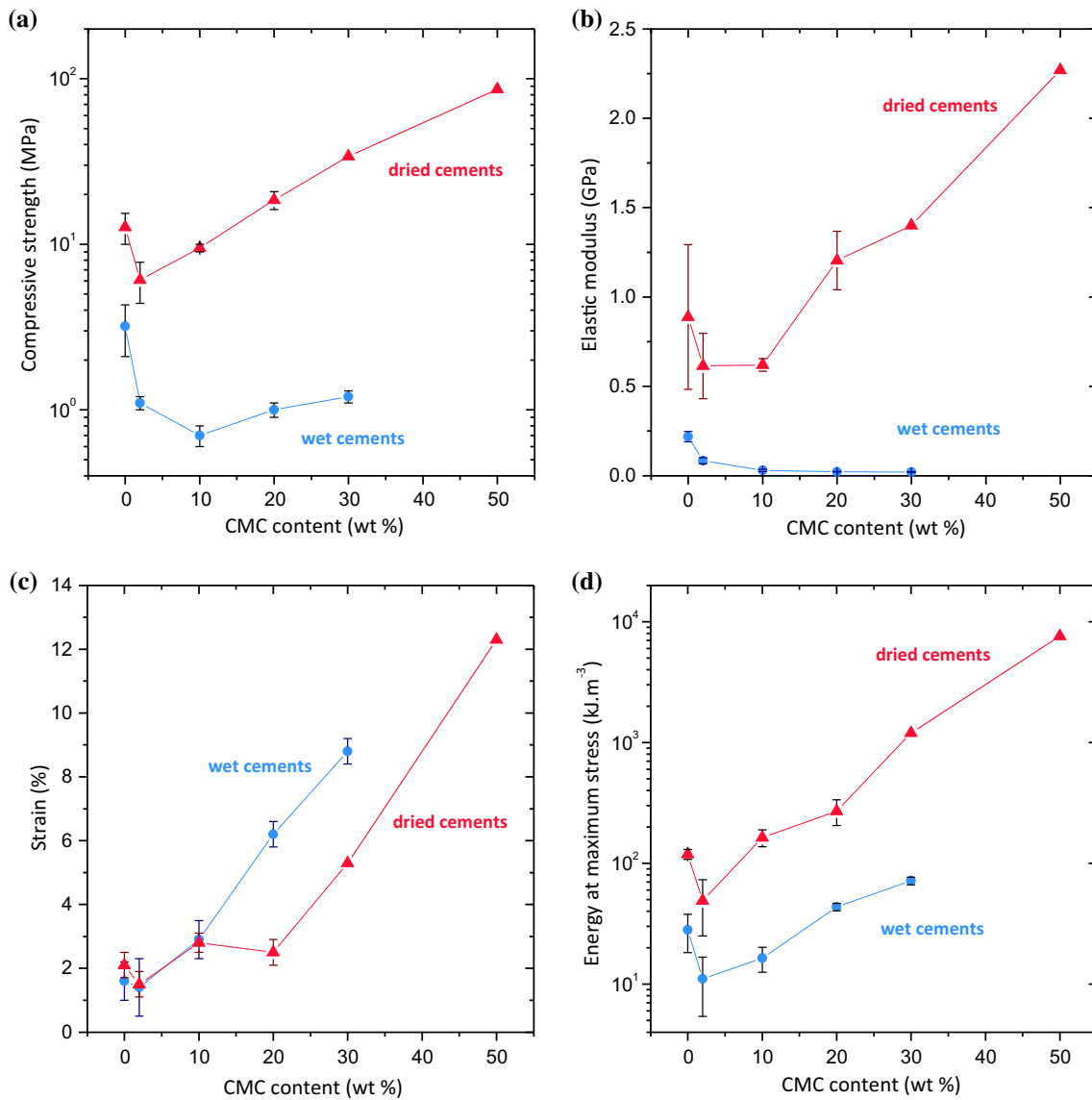
Fig. 4 **a** Compressive strength, **b** elasticity modulus, **c** strain at maximum stress and **d** energy at maximum stress as a function of CMC content in composite cements

Fig. 5 Photographs of the wet composite cement blocks, including various amounts of CMC, after the compressive test
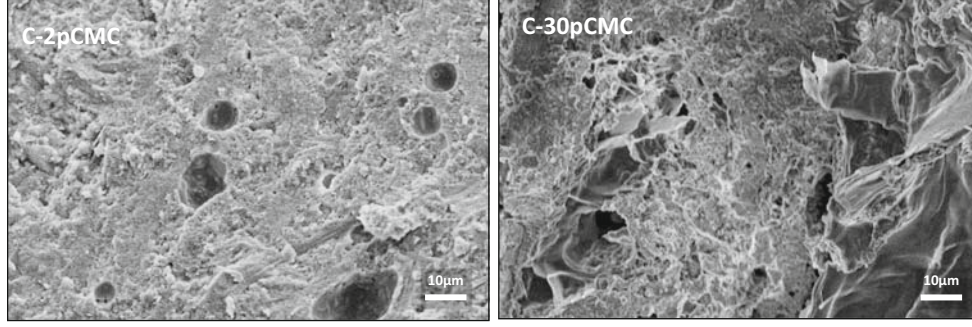
Fig. 6 SEM micrographs of dried composite cements including low (C−2pCMC) and high (C−30pCMC) amounts of CMC

Table 2 Total porosity of composite cements

	P (%)
C−0CMC−d	88
C−2CMC−d	88
C−10CMC−d	66
C−20CMC−d	55
C−30CMC−d	59
C−50CMC−d	24

densities in the cements after setting and drying would be particularly complex. We therefore made several assumptions and approximations:

(i) The density of the CMC is about 1.6 [24, 25]. It might be lower in the cement after swelling in the presence of water and setting of the mineral matrix. Nevertheless we chose the value of $d_{CMC} = 1.6$ after checking that a lower density did not significantly change the model used or the results are presented below.

(ii) The density of the apatite depends on its stoichiometry, which ranges from 3.2 for a stoichiometric apatite, $Ca_{10}(PO_4)_6(OH)_2$, to 2.6 for a poorly crystallised apatite with a maximum carbonation rate, $Ca_8(PO_4)_4(CO_3)_2\square_2$. The actual stoichiometry of the apatite formed in the cement is between these two extreme values and is closer to that of a deficient carbonated and HPO_4-containing apatite (according to a complementary analysis that is not presented in this paper), so we chose the latter as a model ($d_{Ap} = 2.6$).

(iii) The density of the vaterite is 2.6. This value allows us to simplify the model by considering the apatite–vaterite (Ap−V) mineral system as a single phase of density $d_{Ap−V} = 2.6$.

Finally, the mass loss due to the release of CO_2 involved in the setting reaction was also measured (not presented in this paper) and taken into account. With these assumptions and approximations, we estimated the mass and volume compositions presented in Table 3.

According to assumption (iii), the elastic modulus can thus be rewritten as in Eq. 3:

$$E = \alpha_{Ap−V} \cdot E_{Ap−V} + \alpha_{CMC} \cdot E_{CMC} \tag{3}$$

which can be expressed as a function of α_{CMC} and P (Eq. 4), taking into account Eq. 2:

$$E = f(\alpha_{CMC}, P) = (1 − \alpha_{CMC} − P) \cdot E_{Ap−V} + \alpha_{CMC} \cdot E_{CMC} \tag{4}$$

In order to express the elastic modulus as a function of α_{CMC} only, the porosity was modelled as a function of this volume fraction of CMC in the materials (Fig. 7). The most suitable mathematical model has proven to be a parabolic function extrapolated for $\alpha_{CMC} \in \,]0;1]$. A constraint that the graph of the function must pass through the point (1, 0) was added to determine the second-order polynomial (Eq. 5) in order to propose a relevant physical model; indeed, a material having a volume fraction of $\alpha_{CMC} = 1$, in the sense that we have defined it, necessarily implies zero porosity.

$$P(\alpha_{CMC}) = A + B \cdot \alpha_{CMC} + C \cdot (\alpha_{CMC})^2 \tag{5}$$

The elastic modulus was then expressed as a function of a unique variable α_{CMC}:

$$E(\alpha_{CMC}) = (1 − A) \cdot E_{Ap−V} + (E_{CMC} − (1 + B) \cdot E_{Ap−V}) \cdot \alpha_{CMC} − C \cdot E_{Ap−V} \cdot (\alpha_{CMC})^2 \tag{6}$$

As a direct result of Eq. 6, a parabolic function was used to model the relationship between the elastic modulus and the volume fraction of CMC ($E = f(\alpha_{CMC})$). With the parameters A′, B′ and C′ determined and reported in Fig. 8a, this model seems appropriate and leads to three equations (Eqs. 7, 8, 9) that resolve the two unknown moduli $E_{Ap−V}$ and E_{CMC}:

$$A' = (1 − A) \cdot E_{Ap−V} \tag{7}$$

Table 3 Mass and volume composition of the composite cements, respectively, obtained from experimental data and estimations

|	Estimated total weight loss	Weight fractions ($f_{m(CMC)} + f_{m(Ap-V)} = 1$)		Volume fractions ($\alpha_{void} + \alpha_{CMC} + \alpha_{Ap-V} = 1$)		
		$f_{m(CMC)}$	$f_{m(Ap-V)}$	P ($=\alpha_{void}$)	α_{CMC}	α_{Ap-V}
C−2CMC−d	0.11	0.02	0.98	0.88	0.00*	0.12
C−10CMC−d	0.10	0.11	0.89	0.66	0.06	0.28
C−20CMC−d	0.09	0.22	0.78	0.55	0.14	0.31
C−30CMC−d	0.08	0.33	0.67	0.59	0.18	0.23
C−50CMC−d	0.06	0.53	0.47	0.24	0.49	0.27

* The estimated volume content for C−2pCMC is 0.004
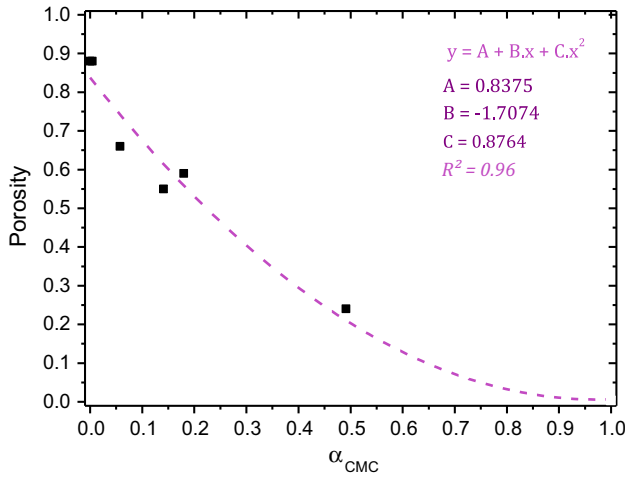
Fig. 7 Evolution and modelling of composite cements' porosity (*P*) according to their volume fractions of CMC

$$B' = E_{CMC} - (1 + B) \cdot E_{Ap-V} \tag{8}$$

$$C' = -C \cdot E_{Ap-V} \tag{9}$$

Because Eqs. 7 and 9 are not equivalent, two mathematical solutions can be established: (1) $E_{Ap-V} = 3.0$ GPa and $E_{CMC} = 3.3$ GPa; (2) $E_{Ap-V} = 4.2$ GPa and $E_{CMC} = 2.5$ GPa. Figure 8b compares these two solutions with the experimental results. Solution (2) is not admissible from a physical point of view: it is unlikely that the elastic modulus of composite cements decreases from a certain content of CMC. Solution (1), however, shows a good correlation with the experimental results and appears physically relevant. This estimation of the elastic moduli of the mineral and organic phases ($E_{Ap-V} = 3.0$ GPa; $E_{CMC} = 3.3$ GPa) of the composite cements does not intend to determine a "real" quantitative value: it is a consequence of a series of approximations, particularly the real densities of the different phases which would require a finer assessment. However, this gives us two interesting pieces of information about these cements. First, the elastic
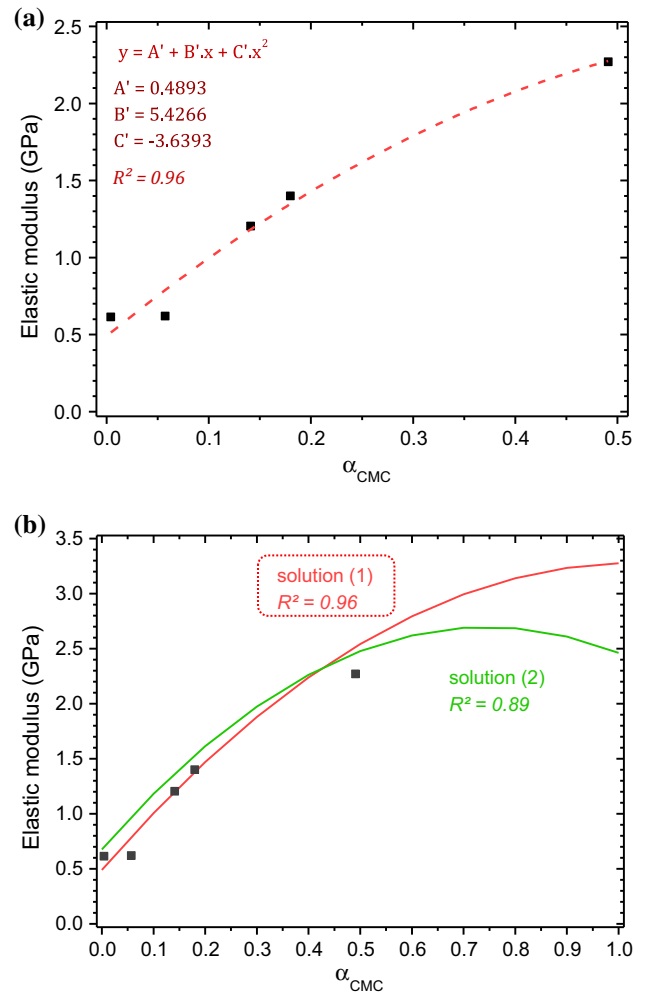

Fig. 8 Expression of the elastic modulus $E = f(\alpha_{CMC})$: **a** parabolic regression from experimental data; **b** mathematical solutions after resolving the full system

moduli of both the organic and inorganic phases appear to be of the same order of magnitude and therefore cannot on their own explain such an important dependence of the composite elastic modulus on the polysaccharide (CMC)

content. Data from the literature on TTCP-monetite cements tend to confirm the weak influence of the polysaccharide on the elastic modulus of the composite cement: the addition of 0.25–1.5 wt% hydroxypropyl methylcellulose [26] or 3.3–7.0 wt% lead to chitosan [27] did not show a significant change in the elastic modulus of the cements. So this conclusion implies a key role of porosity, whose reduction drastically improves the composite mechanical strength. Secondly, the Voigt model initially used does indeed appear to be appropriate, which supports the hypothesis of a long-range interaction of the polymer from a mechanical point of view within the material, which is thus similar to an entangled network intimately mixed with the mineral matrix. The interaction between these two phases would be even more important as carboxyl groups of the CMC are likely to form strong ionic bonds with calcium salts, especially apatite precipitated in situ [28, 29].

Composite materials and heterogeneity

The modellisation of the composite cement's Young's modulus as a function of the content of CMC demonstrates that the porosity is the main factor explaining an important increase of the elastic modulus together with the content of CMC introduced. Nevertheless, it could not explain the initial loss of this parameter, and of the compressive strength or energy at maximum stress between the mineral cement C-REF and the composite cements C−2pCMC and C−10pCMC, whose porosity is equivalent or even lower. However, the heterogeneity caused by the addition of a new phase (i.e. CMC) into the system could be a source of weakening of the mechanical properties by favouring, for example, the initiation of cracks. Considering the overall results, it seems that there is competition between this induced heterogeneity and the inherent superior mechanical properties, in terms of compressive strength, of the polysaccharide compared to the mineral phase. As shown in the schematic diagram in Fig. 9, this competition could explain the initial loss of compressive strength, which is then offset by the addition of a higher content of CMC. There must be a minimum polysaccharide content to allow organisation as a 3D entangled network, and our results suggest that this minimum must be a CMC content of around 10–20 wt% in our system. Indications regarding the volume distribution of the polymer are important, especially in view of the behaviour of composite cement once it has been implanted in a bone site: the arrangement of the CMC in the mineral matrix may indeed play a role in the chemical degradation and/or resorption of material by the osteoclast cells and by the chemical processes involved in bone regeneration.
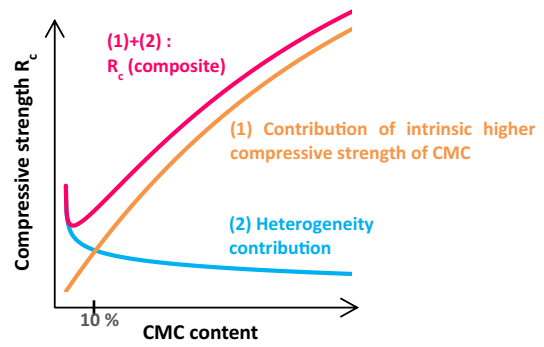
Fig. 9 Schematic diagram illustrating the probable competition between the source of heterogeneity and better compressive strength of CMC compared to the mineral phase

Conclusion

This study highlights the determining role of the introduction of a hydrophilic polysaccharide such as CMC in $CaCO_3$–CaP cement formulation and of the compressive test conditions (dried or wet samples) in the mechanical characteristics (elastic modulus, compressive strength, strain and energy at maximum stress) of the composite materials. Whatever the composition, the compressive strength of the wet samples was low (under 3 MPa) but the gain observed in the dried samples (up to ca. 86 MPa) was encouraging and might be extrapolated to wet conditions if we were to use a less hydrophilic polysaccharide. By combining experimentation and a simplified model for dried composites we showed: (i) the key role of porosity, whose decrease with increasing CMC content improves the composite mechanical strength, and (ii) that there must be a minimum CMC content in the composite formulation to allow organisation of an entangled mineral–organic network and thus to observe the enhancement of the composite mechanical properties. The composite materials presented in this study showed interesting properties in terms of cohesion, ductility and toughness, thanks to the entangled polymeric network, which could prevent the release of mineral particles into the body fluids, after implantation, which might have dramatic consequences.

Compliance with ethical standards

Conflict of Interest   The authors declare that they have no conflict of interest.

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