



Microstructural formation of gypsum by setting in the presence of hydroxypropyl methylcellulose (HPMC)

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Abstract

The role of a polymer as a retarder additive is to enhance workability of the gypsum paste by modifying its setting process and to improve its properties. The study focuses on the influence of water-soluble cellulose derivative hydroxypropyl methylcellulose (HPMC) on the setting kinetics as well as on the properties and the microstructure of gypsum. The influence of HPMC (used in mass fractions of up to 1.5%) on the kinetics of crystallization/hydration of hemihydrate calcium sulfate was investigated by heat flow measurements using differential scanning calorimetry (DSC). To describe the experimental results, the Avrami equation was used and its parameters n and K were determined. The hydration/crystallization process was modified by the presence of the polymer. As a result, the K value decreased, but $n \approx 2.5$ pointed to the three-dimensional diffusion-controlled mechanism. The morphology studies involved porosity measurements. Mechanical properties of the gypsum plaster composites were examined using the bending strength test and correlated with the sample microstructure.

Keywords Gypsum composite · Hydroxypropyl methylcellulose · Porosity · Mechanical properties · DSC

List of symbols

E	Young's modulus (Pa)
K	Values of crystal growth rate constant (min^{-1}) ^{n}
n	Avrami parameter (–)
p	Porosity (%)
P	Pressure (Pa)
t	Time (min)
T	Temperature (°C)
X	Degree of hydration/crystallization (–)
σ	Bending stress (Pa)
w	Mass fraction (%)
η	Dynamic viscosity (Pa s)
w/g	Water to gypsum mass ratio (–)

Subscripts

a	Acceleration stage
i	Induction
p	Polymer
max	Maximum

Introduction

Certain information is available on the effect of water-soluble polymers on the microstructural formation of cementitious materials [1–3]. During the hydration of calcium sulfate hemihydrate, calcium sulfate dihydrate (gypsum plaster) is formed. The hydration reaction is driven by higher solubility of the hemihydrate in water compared with gypsum. Three steps can be distinguished in the hydration reaction: the dissolution of hemihydrate yielding a partially saturated gypsum solution, the nucleation and growth of gypsum crystals and the final formation of solid material through the entanglement of gypsum needle-like crystals.

The water to gypsum ratio w/g is always well above the stoichiometric mass ratio of 0.186 [4]. A greater water content increases the fluidity of the paste and workability of the material but also results in greater porosity after complete drying. The solidification of the plaster and the hydration reaction can be monitored in various ways, but the calorimetric measurements are the most popular [4, 5]. The morphological microstructure forming in the hydration process can be controlled by the water to gypsum ratio and the additives added to the plaster. They directly influence both the strength of the gypsum material and its thermal conductivity [6, 7].

Previous results also proved the influence of other water-soluble polymers on the setting induction time, the rate of

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hydration as well as certain mechanical and thermal properties of the final product. The cellulose derivatives are found to be suitable retardant additives for the modification of gypsum setting [2, 8].

The purpose of the study was to find the correlation between the gypsum microstructure (porosity) and its modification by water-soluble hydroxypropyl methyl cellulose applied in small doses up to 1.5% of the gypsum mass.

Materials and methods

Beta-calcium sulfate hemihydrate was used in the study. It was supplied by Nida Manufacture (Poland) and had the following composition: calcium sulfate hemihydrate—90.98%, CaCO_3 —2.79%, SiO_2 —1.62%, montmorillonite—3.07%, illite—0.79%, chlorite—0.16% (manufacturer data).

The hydration reaction was investigated using a water to gypsum (w/g) mass ratio of 0.6–1.0.

The polymer, i.e., hydroxypropyl methylcellulose (HPMC), was dissolved in water and added to the sample in quantities from 0.5 to 1.5% of the initial hemihydrate sample mass. HPMC ($\eta = 80 \div 120 \text{ Pa s}$) was supplied by Sigma-Aldrich. The mixture was stirred mechanically for 30 s in order to obtain homogeneous paste. The samples were prepared and examined according to the PN-86 B-04360 norm (Plasters. The methods. Physical characteristic determination).

The induction period and the rate of setting were measured using a Vicat's device (with needle).

Differential scanning calorimetry (Melter FP-90) was used to study the energetic effects in the hydration process under isothermal conditions at 30 °C. The composite

Fig. 1 **a** Heat evaluation versus time in hydration process and **b** degree of hydration/crystallization X versus $t - t_i$ for pure gypsum and gypsum modified by HPMC $w_p = 1\%$, $w/g = 0.74$, t_i —induction period

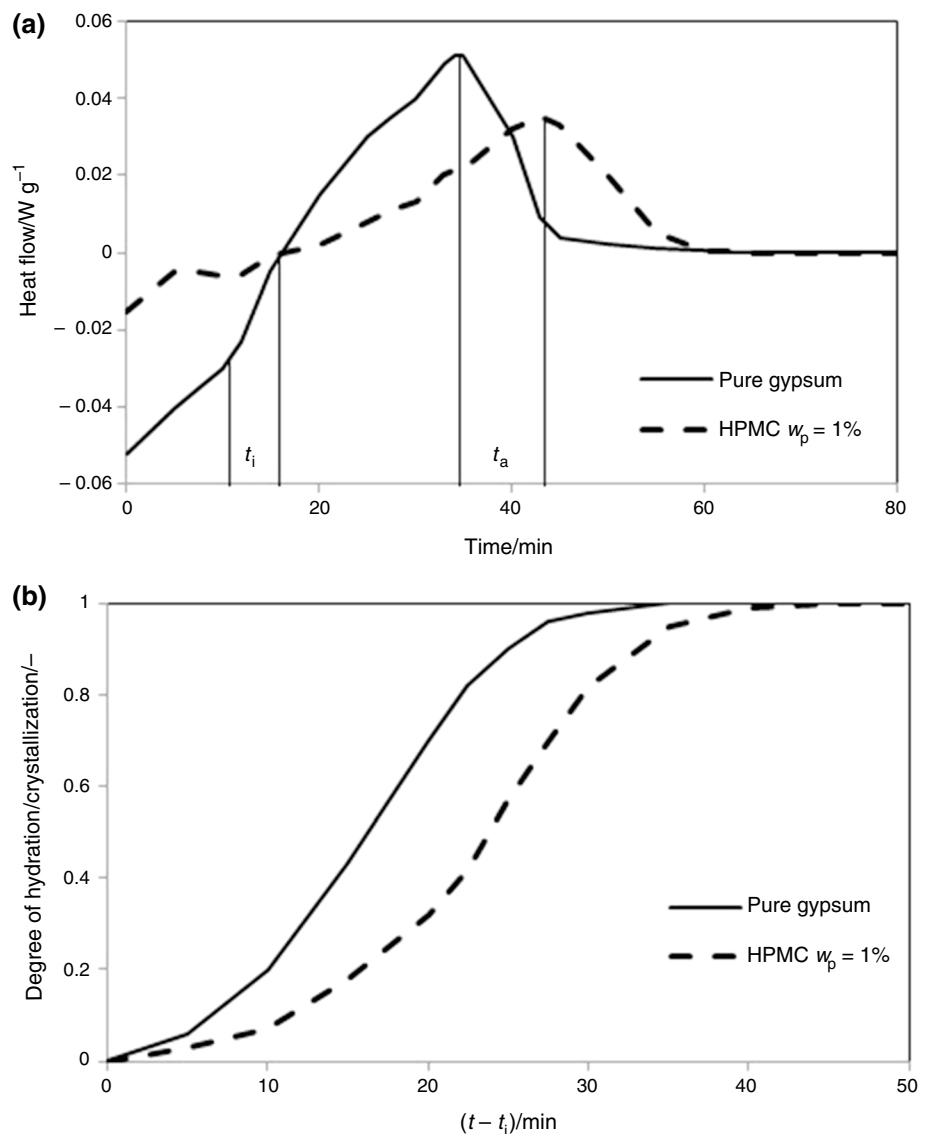
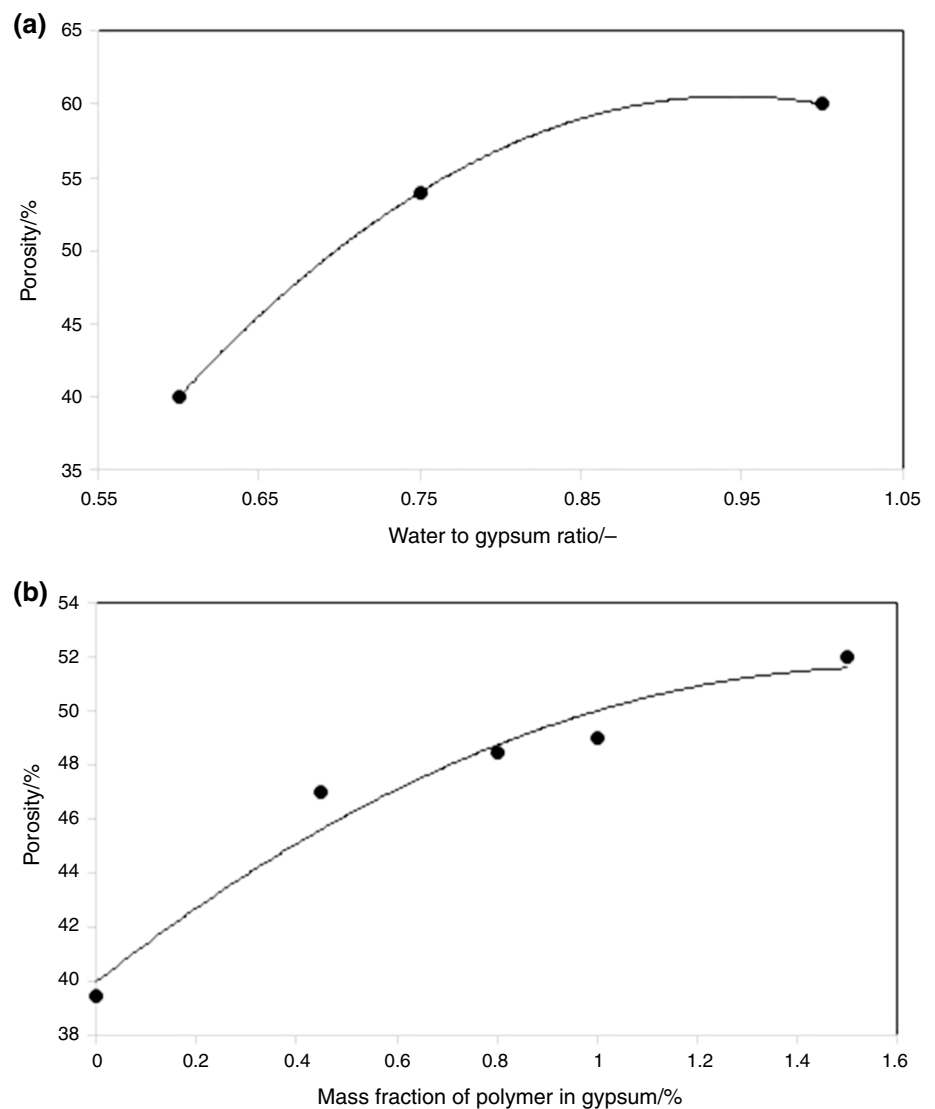


Fig. 2 Porosity of gypsum sample a) versus w/g ratio and b) HPMC content (mass fraction w_p) $w/g = 0.6$



gypsum paste was mixed before inserting in the measuring unit. The mass of sample was approximately 10 mg.

The porosity measurements were taken using a mercury porosimeter AutoPore IV model 9500. The maximum pressure required to intrude mercury into the pores was 2000 MPa (the contact angle was equal to 130° for the intrusion and 104° for the extrusion). The measurements were taken at 25°C with a mercury surface tension of 0.485 Nm^{-1} .

The mechanical bending test to determine the flexural Young's modulus E and the maximum stress value σ_{max} was carried out using an Instron (3345 Instron USA) apparatus. The samples for the bending tests were prepared by spreading the gypsum paste into rubber molds ($50 \times 18 \times 5$ mm in size) attached to glass plates. The samples were examined at least 1 week after the setting. The measurements were taken three times. The examined samples had different water to gypsum ratios (from 0 to 1.0) and different polymer contents

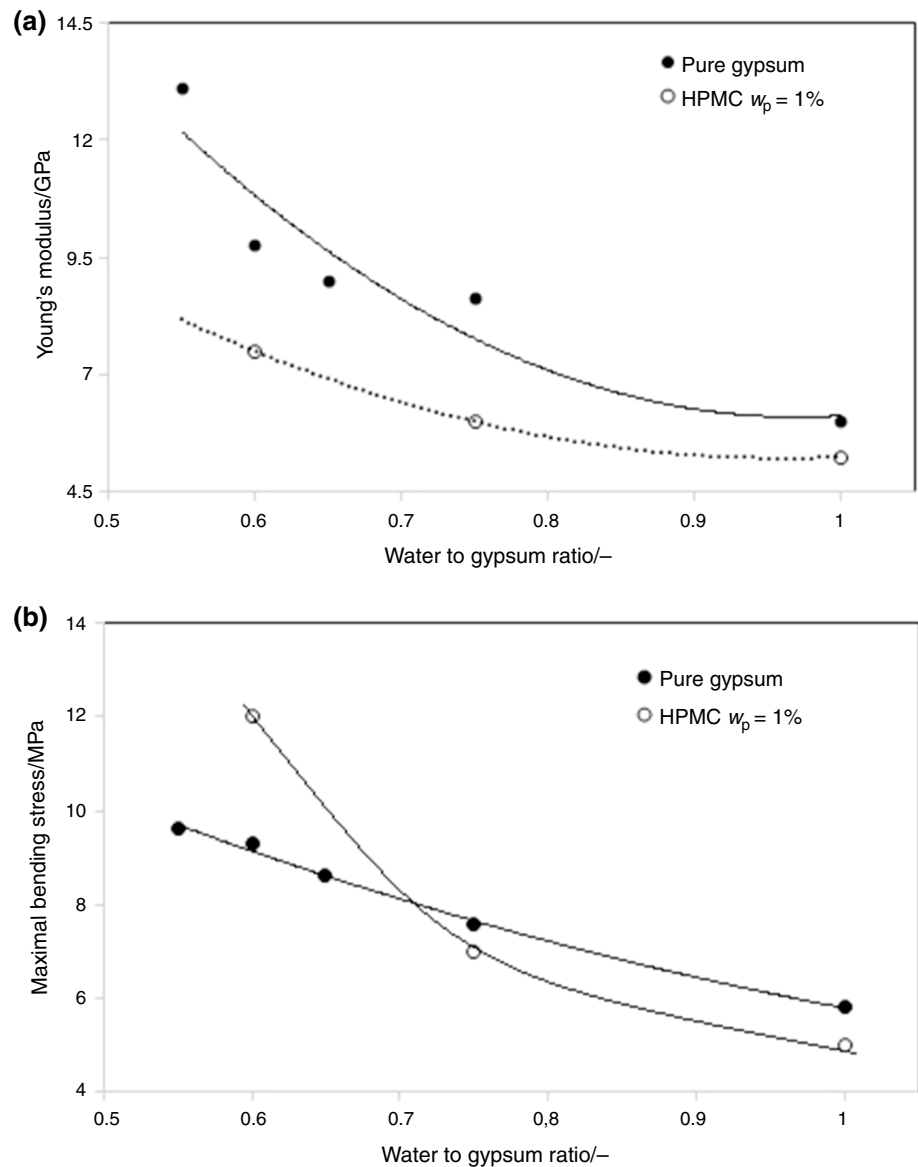
(from 0 to 1% of the gypsum mass). The most representative results have been chosen to summarize the study.

Results and discussion

Kinetics of gypsum crystallization/hydration

The kinetics of gypsum crystallization/hydration was investigated using DSC measurements. The heat generated in the setting/hydration process is presented in Fig. 1a both for pure gypsum and gypsum modified with HPMC (an example is given for $w_p = 1\%$). It can be noticed that the induction period (t_i) of the acceleration stage (t_a) is longer than $5 \div 8$ min when HPMC is used. Moreover, the rate of the dehydration process is slowing down, as illustrated by the broader heat release curves having lower maximum values.

Fig. 3 Dependence of **a** Young's modulus and **b** maximal bending stress σ_{\max} versus water/gypsum ratio (w/g)



In the same figure (Fig. 1b) the integral curves $X=f(t-t_i)$ are shown.

The Avrami [9] Eq. (1) where X is a degree of hydration/crystallization:

$$X = 1 - e^{-K(t-t_i)^n} \quad (1)$$

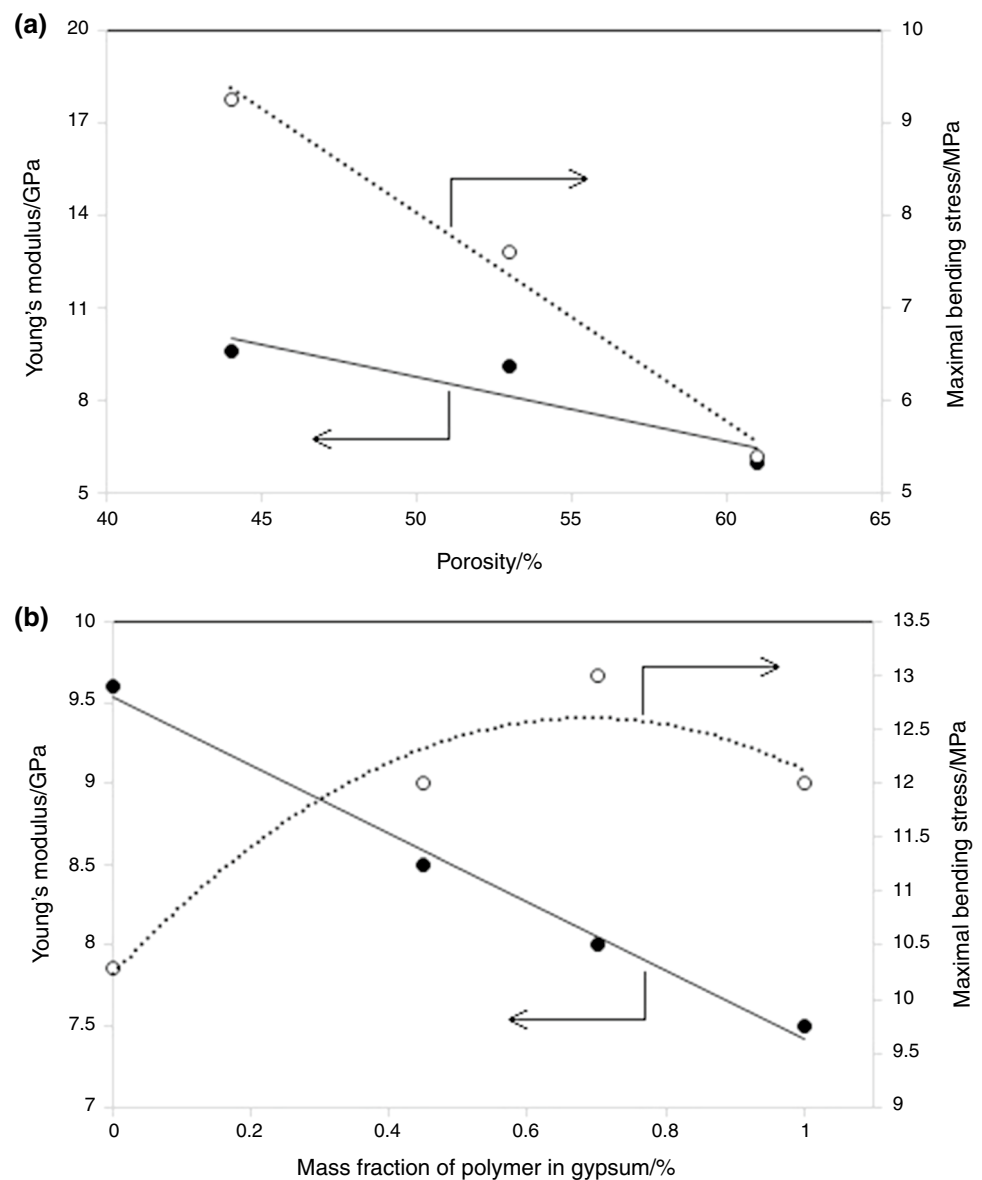
was used to determine the values of parameter K and n by fitting to the experimental data: $K=4.7 \times 10^{-4} (\text{min}^{-1})^n$ $n=2.25$ for modified gypsum and $K=1.77 \times 10^{-3} (\text{min}^{-1})^n$ $n=2.1$ for pure gypsum.

K is a complex rate constant that involves both the rate of crystal nucleation and their growth. The values of n and K describe the hydration/crystallization of calcium sulfate

hemihydrate. The value of $n \approx 2.5$ means that the growth process is three dimensional, controlled by diffusion, and the K value decreases approximately 30 times due to the presence of the polymer. A similar result was obtained for gypsum modified with HEMC [5] and chitosan [10].

Several explanations can be found in the literature [11–22] for the retardation in gypsum (or cement) hydration in the presence of organic compounds such as: nucleation control, disturbance in the crystal growth, decrease in ion mobility [4]. The water-soluble polymers such as cellulose ethers contain numerous hydroxyl groups which are able to form hydrogen bonds with oxygen ions on the surface of anhydrous materials (absorption).

Fig. 4 Dependence of Young's modulus E and maximal bending stress σ_{\max} of gypsum **a** on porosity (pure gypsum) and **b** gypsum with polymer content w_p ($w/g=0.6$)



Porosity

Figure 2 shows the porosity of pure gypsum dependent on the w/g ratio (a) and the polymer content at constant $w/g=0.6$ (b).

Increasing porosity of gypsum (volume fraction of pores) with increasing w/g (pure gypsum) and polymer content (w_p) is presented in Fig. 2a and b. At $w/g=0.6$ the increase in porosity is the greatest and equal to approximately 10% for the sample containing 1% polymer. In the sample with a greater w/g ratio, the polymer presence makes the material much less porous ($\sim 3\%$).

Polymers can take part in the creation of stronger bridges between gypsum monocrystals in the decelerative stage of hydration and after removing the excess free water. Only up to 20% of water is used in the formation of dihydrate

crystals. The rest is removed as free water during drying, which results in the creation of pores. When a water-soluble polymer is used as an additive, its strong affinity to water helps to make swell structures, and in the ensuing drying process a thin layer of polymeric film is created inside the pores [1, 3]. The presence of polymer inside the pores changes the microstructure of gypsum, and an increase in porosity can be observed after removing the excess water from the swollen polymer. Therefore, the properties of the material are changed.

Mechanical results

The results of mechanical tests (E —Young's modulus and maximum bending stress σ_{\max}) are shown in Figs. 3 and 4. Figure 3a and b shows plots of E and σ_{\max} versus the w/g

ratio, while Fig. 4a and b shows plots of E and σ_{\max} versus the porosity and the content of polymer w_p in modified gypsum at $w/g = 0.6$.

The maximum bending stress describes a force applied to the sample while bending. The value of σ_{\max} depends on the porosity of the material and increases with w/g . Cellulose ethers cause a few percent increase in water retention in the system containing gypsum [8, 18]. Therefore, it is proposed that two different types of pores (of different origin) exist in the material. One type is empty capillary pores created during drying as a result of removal of free water (not consumed by the hydration), while the other type is pores filled by the polymer which is still swollen. It has been observed that during drying of cellulose ethers the samples lose nearly 10% of their mass. The presence of polymers causes the structure of the material to be modified, but the formation of hydrogen bonds between the polymer active groups and the gypsum surface is also possible. It increases mechanical strength and decreases the elastic modulus of the composite material resulting in a more flexible morphological structure. According to the mechanism of hemihydrate hydration, a polymer cannot be built into the crystal structure of dihydrate calcium sulfate, but it can form a film layer in the interconnecting parts of the gypsum plaster. It has been noticed that the presence of polymer additives changes the gypsum crystalline structure (lower rate of nucleation and more narrow crystals of dihydrate). More data collected for various values of w/g using HEMC can be found elsewhere [2, 3].

Conclusions

The paper discusses the setting of calcium sulfate hemihydrate and the mechanical properties of the hardened gypsum plaster, both pure and modified by a small amount of HPMC. The experimental results are shown in figures and can be summarized as follows:

1. It has been established that the acceleration stage of hydration up to the maximum rate is controlled by the rate of crystal nucleation and their growth. The calorimetric tests show that the presence of HPMC retards setting (hardening) of calcium sulfate hemihydrate. Not only the induction period of the process is extended, but also the rate of hydration is slowed down (Fig. 1). The complex K parameter of hydration/crystallization was calculated, and its value was shown decreasing when the polymer was added to the sample. Therefore, the nucleation rate of the dihydrate crystals in the composite material containing the polymer is lower.
2. It has been shown that the porosity of the material increases both with increasing w/g (initial water to gypsum ratio) and increasing w_p (mass fraction of polymer)

present in the system (Fig. 2). It results in strong water retention caused by the polymer, which subsequently modifies the pore structure during drying. A change in pore distribution has also been observed (increased fraction of pores smaller than $1 \mu\text{m}$).

3. The porosity is correlated with the mechanical properties of the gypsum plaster, defined by the elastic modulus E and the maximum bending stress σ_{\max} . Both E and σ_{\max} decrease with increasing w/g ratio (Figs. 3, 4a).

However, the presence of the polymer in the gypsum material increases the maximum bending stress σ_{\max} and decreases the Young's modulus (Fig. 4b). It seems that the polymer molecules are incorporated in spaces between single crystals of calcium dihydrate in the interconnected parts of gypsum, improving its mechanical properties [3].

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