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The influence of cellulose derivatives on water structure in gypsum

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HIGHLIGHTS

- Water structure in gypsum at different setting state was presented.
- Differences between surface and fracture of gypsum pastes were identified by FTIR.
- Cellulose derivatives modifiers retard the gypsum setting process.
- The model of supramolecular structure of gypsum with polymer addition was proposed.

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ABSTRACT

In this study the influence of cellulose derivatives modifiers: 2-hydroxyethyl methylcellulose (HEMC), hydroxypropyl methylcellulose (HPMC) and hydroxypropyl cellulose (HPC) on the gypsum setting process and their respective changes in water arrangement were analysed. IR spectroscopy revealed the differences in the water structure between the surface and the fracture of gypsum samples. In comparison to pure gypsum, the setting process is slower in the presence of cellulose derivatives as the hydrophilic polymer partially traps the water molecules. Through the comparison of IR, SEM, DSC and micromechanical measurements supramolecular model of gypsum structure containing cellulose derivatives which stabilized water clusters was proposed.

1. Introduction

Gypsum plaster, $CaSO_4{\cdot}2H_2O$ (also known as dihydrate) is one of the oldest building materials. It is used widely as indoor building material because of its numerous advantages: easy fabrication, low price, aesthetics, environmental friendliness, fire resistance, etc. [1]. Calcium sulfate dihydrate can be found in nature as a sedimentary rock or it can be produced by carrying out different industrial processes. Commercially available materials are hemihydrate sulfate ($CaSO_4{\cdot}0.5H_2O$), which are obtained as a result of mechanical (fragmentation) and thermal (calcination) treatment of gypsum rocks [2]. The process of setting and hardening of gypsum binder is based on the reaction with water, resulting in the hydration of hemihydrate to dihydrate [2]. Generally, four steps in the process of setting hemihydrate sulfate can be distinguished [2–5]:

1. Dissolution of the hemihydrate in water,
2. Formation of crystallization nuclei of dihydrate,
3. Growth of dihydrate crystals (hydration and crystallization),
4. Interconnection of dihydrate crystals.

Gypsum is characterized by short setting time and large increase in volume during binding process (up to a few percent) [2]. In modern building materials, such as cement or gypsum, additives play an important role in the creation of tailored properties. This can include elongation or reduction of gypsum hydration or hardening time, regulation of ability to water retention, plasticity or fluidity. Through the introduction of natural polymers (to a few percent) morphological structure of gypsum and its effectiveness in water retention is modified [3–4]. This feature is essential to the prevention of overheating as the bound water is removed through rising temperatures the fire resistance of gypsum increases. Currently, cellulose ethers dominate the market as admixtures for gypsum due to their advantageous properties: solubility in water, cost-effectiveness, and environmental compatibility. The following cellulose ethers are the most commonly used in the building sector: hydroxyethyl methylcellulose (HEMC),

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hydroxypropyl methylcellulose (HPMC) and hydroxypropyl cellulose (HPC) [6–8].

Cellulose is a polysaccharide in a form of linear homopolymer constituted of anhydroglucose units with β-1,4-linkages (Fig. 1). Due to its strong intra- and intermolecular hydrogen bonds, it is insoluble in water [9]. However, through esterification or etherification cellulose's solubility in water can be significantly improved. These modifications are performed by substitution of the C-2, C-3 or C-6 -OH groups of an anhydroglucose unit (see Fig. 1).

The main purpose of this study is to clarify the mechanisms of the phenomena responsible for the changes in the water structure during the gypsum setting caused by cellulose derivatives. In literature, there is a lack of detailed and systematic knowledge on the impact of the presence of polymer additives, as cellulose derivatives, on the water retention in gypsum. This knowledge is indispensable for design gypsum with desirable properties. In this study IR spectroscopy was used to examine samples of hydrated gypsum and to investigate the kinetics of gypsum setting process. To investigate the morphological properties of gypsum samples, Scanning Electron Microscopy (SEM) was applied. To evaluate the FTIR-ATR data, the analysis of setting process was carried out also by Differential Scanning Calorimetry (DSC) and micro-mechanical analysis (Supplementary Section).

2. Experimental

2.1. Materials

Commercially available gypsum (hemihydrate calcium sulfate of β form) supplied by Dolina Nidy (Poland) was used in this study. The gypsum fulfilled the requirements of norm PN-EN 13279-1:2009 [11]. Amount of calcium sulfate ($CaSO_4$) in gypsum was 90.98 wt%. Others components: $CaCO_3$ – 2.79 wt%, SiO_2 – 1.62 wt%, montmorillonite – 3.07 wt%, illite – 0.79 wt%, chlorite – 0.16 wt%. The following cellulose derivatives were used: 2-hydroxyethyl methylcellulose (HEMC), hydroxypropyl metyl cellulose (HPMC) and hydroxypropyl cellulose (HPC). Cellulose derivatives were supplied by Sigma-Aldrich and their detailed characteristics are available at the appropriate safety data sheets (methyl 2-hydroxyethyl cellulose HEMC, No. 93802; (hydroxypropyl)methyl cellulose HPMC, No. H9262; hydroxypropyl cellulose HPC, No. 191884). Standard samples of calcium sulfate crystals (selenite – calcium sulfate dihydrate; bassanite - calcium sulfate hemihydrate; anhydrite) were purchased by Geological Museum of University of Lodz.

2.2. Sample preparation

The samples with 1 or 2 wt% of cellulose derivatives (such as HEMC, HPMC and HPC) were prepared. The cellulose derivatives were dissolved in distilled water at 20.0 °C and stirred on a magnetic stirrer at 300 rpm for 8 h in a sealed vessel. Before use, colloidal solutions of the polymers were left to stand for 24 h at room temperature in order to obtain a homogeneous solution. Then, they were added to gypsum powder (hemihydrate calcium sulfate) in amount to get proper water to gypsum weight ratio (w/g) and planned polymer concentration 1 or 2% by weight (to pure gypsum) and were intensively mixed using mechanical stirrer for 30 s. Different amount of distilled water were added to prepare initial gypsum pastes: w/g was equal to 0.54 or 1.00. Next, initial mixtures were poured out into the rubber frames and left for one week to dry under normal conditions. All hydrated gypsum samples had shape of rectangular blocks with dimensions of 5 cm × 2 cm × 0.5 cm (length/width/height).

Gypsum samples for investigations of setting process were prepared in the same manner. After pouring the hemihydrate mixture into the rubber molds the appropriate measurements started immediately. For the FTIR-ATR measurements, gypsum samples were prepared as follow: first, the outer layer ("skin") of gypsum was removed and then the bulk material was taken out of the mold cavity and placed directly onto the diamond crystal of ATR accessory and measured. All prepared samples used in the research are presented in Table 1.

2.3. Methods

2.3.1. Scanning electron microscopy

SEM observations were made on fracture of gypsum samples after at least one week of setting. The samples of hydrated gypsum with 1 wt% of HEMC were examined by SEM model 1430 VP (LEO Electron Microscopy Ltd., England) using variable vacuum mode 50 Pa and microscope equipped with a BSE detector. The acceleration voltage was equal to 10 kV.

2.3.2. IR spectroscopy

The absorption spectra in the middle IR range (4000 cm^{-1}–525 cm^{-1}) were recorded using Nicolet Fourier-Transform iS50 (Thermo Scientific). The attenuated total reflection (ATR) accessory with a diamond crystal was applied. All measurements were performed at (20.5 ± 0.5) °C. The FTIR-ATR spectra of hydrated gypsum, with 2 wt% of cellulose derivatives, were recorded for surface and fracture of each gypsum sample with a resolution of 2 cm^{-1} with an average of 128 scans.

During the analysis of setting process the FTIR-ATR spectra were registered immediately, after mixture preparation and at various times in a range of 3 min to 30 h with a resolution of 2 cm^{-1} and with an average of 16 scans per sample. For each measurement, some material was removed from the surface to reveal new data. Moreover, the baselines were extracted from the spectra. Next, the deconvolution of selected regions of interest were done using Peak Fit (Systat Software, Inc.) software. In the investigations of the setting kinetics, the most noticeable differences were observed between R_1 and $G_{1\ HPMC}$ so these results are thoroughly analyzed in the manuscript. Upshots of setting process obtained for gypsum with HEMC ($G_{1\ HEMC}$) and HPC ($G_{1\ HPC}$) additives are presented in the Supplementary Section.

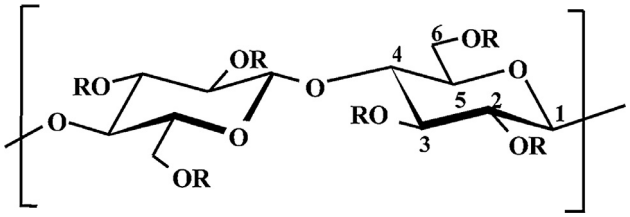

Fig. 1. Structure of cellulose derivatives (R = H for cellulose and R = H, CH_3, $-CH_2-CH_2OH$ or $-CH_2CH_2CH_2OH$ for HEMC and HPMC respectively, and R = H or $-CH_2-CHCH_3OH$ for HPC) [10].

Table 1
Samples of gypsum mixtures with 2 wt% of cellulose derivatives used in the study of FTIR-ATR.

Water to gypsum ratio [w/g]	Polymer additives	Abbreviation
0.54	–	$R_{0.54}$
0.54	HEMC	$G_{0.54\ HEMC}$
0.54	HPMC	$G_{0.54\ HPMC}$
0.54	HPC	$G_{0.54\ HPC}$
1.00	–	R_1
1.00	HEMC	$G_{1\ HEMC}$
1.00	HPMC	$G_{1\ HPMC}$
1.00	HPC	$G_{1\ HPC}$