CHITOSAN APPLIED FOR GYPSUM MODIFICATION

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Abstract

In order to improve the properties of gypsum materials, including workability, mechanical strength and ability to retain water, various admixtures (also polymers), known as plasticisers, have been applied. These polymers can be soluble in water, such as cellulose and starch ethers, or unsoluble applied in a form of dispersion up to 5% of weight fraction. The admixtures are added into initial water and mixed with hemihydrate calcium sulphate in a proper ratio. In the hydration process of the hemihydrate into dehydrate, a crystallisation process leading to gypsum setting occurs.

In the present work, a chitosan sample of DD=85% in two forms was applied: dissolved in 1% acetic acid and as a water dispersion in the weight fraction up to 1% of the gypsum matrix. The water to gypsum ratios of 0.6 or 0.74 was applied. The influence of chitosan on the rate of setting and kinetics of crystallisation of gypsum was investigated and discussed. The morphological structure of the resulting gypsum sample was examined using SEM microscopy.

In the presented results, chitosan in the form of a 1% dispersion was a setting retardant and it changed the morphological structure of gypsum. However, mechanical tests showed a decrease of bending strength. When chitosan was applied as a biomaterial, the chitosan content in the composite was equal to 10%, and thus a compressing strength increased. The presence of PVA (polyvinyl alcohol) in the gypsum matrix caused a small effect on gypsum setting in contrast to PVAc (polyvinyl acetate), which is a good admixture for both cement and gypsum [2,3].

Keywords: chitosan/PVA, gypsum, setting time, mechanical properties, morphology.

1. Introduction

One of the oldest building materials exploited by mankind is gypsum plaster ($CaSO_4 \cdot 2H_2O$). Gypsum plasterboard is used widely as an indoor building material because of its easy fabrication, fire resistance, low price, environmental friendliness and aesthetics [4]. In wallboard production, the control of setting times is very important.

Hemihydrate calcium sulphate dissolves in water, forming Ca^{2+} and SO_4^{2-} ions, which forms dihydrate crystals with water that precipitate from the solution. In this proces, three stages are distinguished:

1) dissolution
2) hydration, i.e. binding to water
3) precipitation of $CaSO_4 \cdot 2H_2O$ crystals [5,6].

However, the rapid setting of gypsum gives no possibility of preparing its paste in substantial amounts [7]. In order to ensure convenient application, the time period from preparation of the low viscosity paste until hardening of the gypsum must be long [8]. Therefore, polymers are used as additives to cement or gypsum for longer setting times as well as for better workability and good mechanical properties [7–10]. In the present tests, we have used chitosan and polyvinyl alcohol (PVA). The effect of the addition of these polymers is dependent on the dosage. This is caused by increased entanglement and crosslinking between chains in a calcium-rich system (interaction between polymer and gypsum particles).

2. Materials and methods

2.1. Materials

Gypsum (calcium sulphate hemihydrate) supplied by Dolina Nidy (Poland) was used in this study. The gypsum meets the requirements of PN-EN 13279-1:2009 and contains calcium sulphate hemihydrate 90.98%. Other components: $CaCO_3$ – 2.79%, SiO_2 – 1.62%, montmorillonite – 3.07%, clays – 0.79%, chlorite – 0.16%. Distilled water was used for mixing gypsum with admixtures, and 1% acetic acid was used to dissolved chitosan.

The polymer additives were polyvinyl alcohol supplied by Sigma-Aldrich (M_w=72,000 g/mol) and chitosan supplied by Heppe, manufactured to 85% deacetylation degree (M_w=200,000 g/mol).

2.2. Preparation and samples

The following samples were prepared to use in calorimetry, setting time, mechanical and morphological studies: gypsum without admixtures and gypsum with different contents of polymers. Various amounts of water were added: the water to gypsum ratios were 0.6–0.74. Samples were prepared according to standard PN-86 B04360 (Plasters. The methods. Physical characteristic determination).

Polymers were dissolved in distilled water or used as dispersant. Admixtures in appropriate amounts were first dissolved in distilled water at room temperature. Then, the composition with gypsum powder was vigorously mixed for 30 seconds using a mechanical stirrer. Admixtures used as dispersants were added to gypsum powder, then mixed with appropriate amounts of water using a mechanical stirrer for 30 seconds.

Table 1 presents the composition characteristics of the samples.

Table 1. Composition characteristics of the samples under study

Sample	Water/gypsum (w/g) ratio
Gypsum without admixtures	0.54; 0.6; 0.67; 0.7
Chitosan 1% used as dispersant	0.54; 0.6; 0.67; 0.7
Chitosan 0.5% used as dispersant	0.6
Chitosan 0.25% used as dispersant	0.6
Chitosan 0.25% dissolved in 1% acetic acid	0.6
Acetic acid 1%	0.6
PVA 1% used as dispersant	0.54; 0.6; 0.67; 0.7
PVA 0.5% used as dispersant	0.6
PVA 0.25% dissolved in water	0.6
PVA 0.5% dissolved in water	0.6
PVA 1% dissolved in water	0.54; 0.6; 0.67; 0.7

2.3. Setting, DSC, mechanical and morphological studies

The rate of setting time was carried out at room temperature using a Vicat's device (Master, Italy).

The hydration/crystallisation process was performed using isothermal calorimetry. The quantity of gypsum paste (mg) was placed in the calorimeter. The instrument was maintained in a constant controlled temperature of 30°C. The heat flow was recorded for up to 2 hours, after which time, the heat flow becomes very low. The cumulative heat proportional to the degree of hydration was calculated with reasonable accuracy. Differential scanning calorimetry (DSC) (model METTLER FP90) was used for the study.

Mechanical bending test of flexural stress was carried out using Instron 3345 (Instron, USA). Samples were prepared for the bending test by spreading gypsum plaster into special rubber molds attached to the glass plates. Before the experiment, the entire mold was smeared with oil. Mold dimensions were 50 mm/18 mm/5 mm. The tests were repeated three times for every sample. The applied samples were set for 48 hours at room temperature. The study was conducted according to standard PN-86 B-04360 (Plasters. Test methods. Physical characteristic determination.).

Scanning electron microscope (SEM) model 1430 VP (LEO Electron Microscopy Ltd, England) was applied to make microphotographs of gypsum fractures after mechanical flexural tests. Variable vacuum mode 50 Pa, detector BSE was used.

3. Results and discussion
3.1. Setting results

The setting of material is a transition period during which the physical state of material changes from paste to solid. This transformation occurs as a result of the development of hydration products (dehydrated calcium sulphate), which causes rigid connections between hydrating grains. It is usually characterised by two points in the

hydration process, namely initial and final setting time. The development of connected hydration product which reflects the transition of the material state was measured by the penetration resistance technique (Vicat needle test). The beginning of the setting period was estimated as the first inflection point on h = f(t) (where h is the height of the needle) on the figures below. The time of setting was measured as the time of the intersection of straight line on the h = f(t) curve. The time from the onset of the experiment to the beginning of the setting period is known as the induction period [4].

Figures 1–5 show the setting process of the chosen samples.
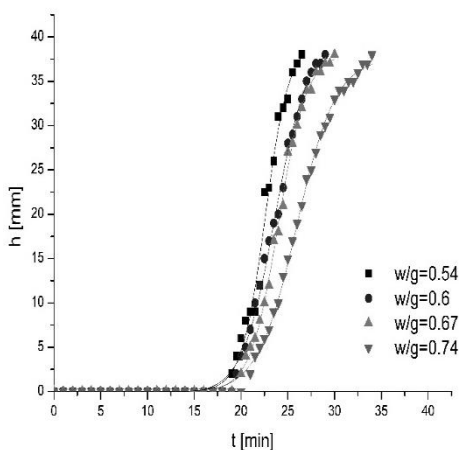
Figure 1. The setting process of hemihydrate hydration dependent on w/g. Samples without admixtures (h – level of needle).
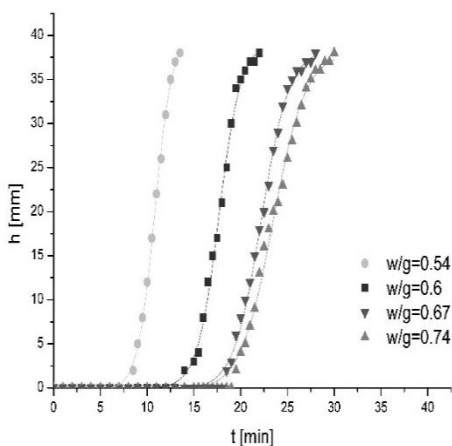
Figure 2. The setting process of hemihydrate hydration dependent on w/g. Samples with 1% chitosan used as dispersant.
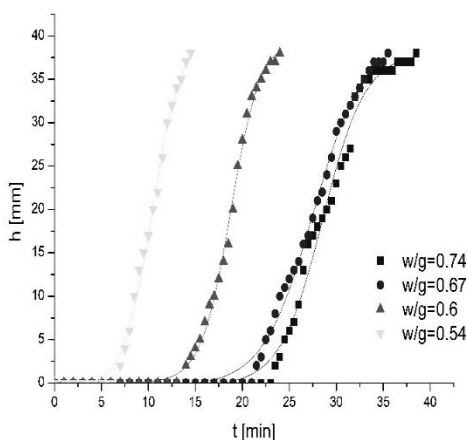

Figure 3. The setting process of hemihydrate hydration dependent on w/g. Samples with 1% PVA used as dispersant
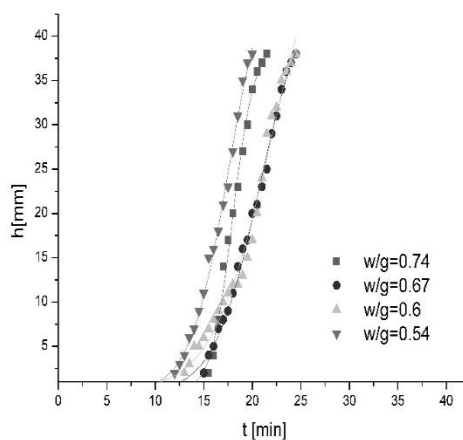
Figure 4. The setting process of hemihydrate hydration dependent on w/g. Samples with 1% PVA dissolved in water

Measurements of the setting time is highly dependent on the water to gypsum ratio. With increasing amounts of water in mortar, induction time is delayed. Due to using different polymers as additives with different w/g ratios, the induction time varies for the samples. The dependence is shown in Figure 5.
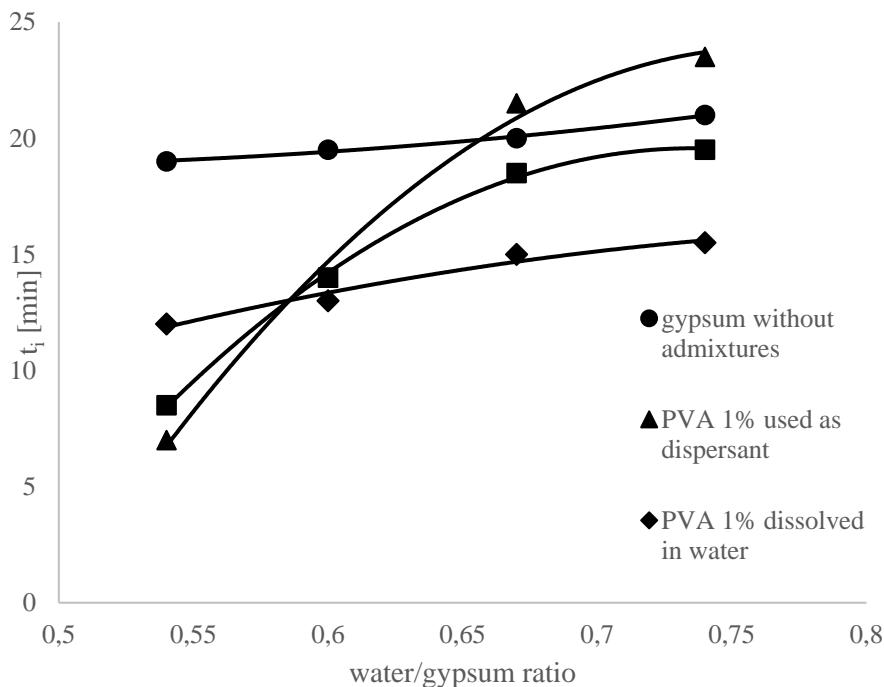

Figure 5. Dependence of induction period of setting t_i on the water/gypsum ratio for various gypsum samples containing 1% admixture.

3.2. DSC results

The hydration/crystallisation process of gypsum without admixtures and with admixtures was conducted by DSC research. Figures 6 and 7 show isothermal process thermograms. The hydration/crystallisation process occurs faster in the case of gypsum sample without admixtures.
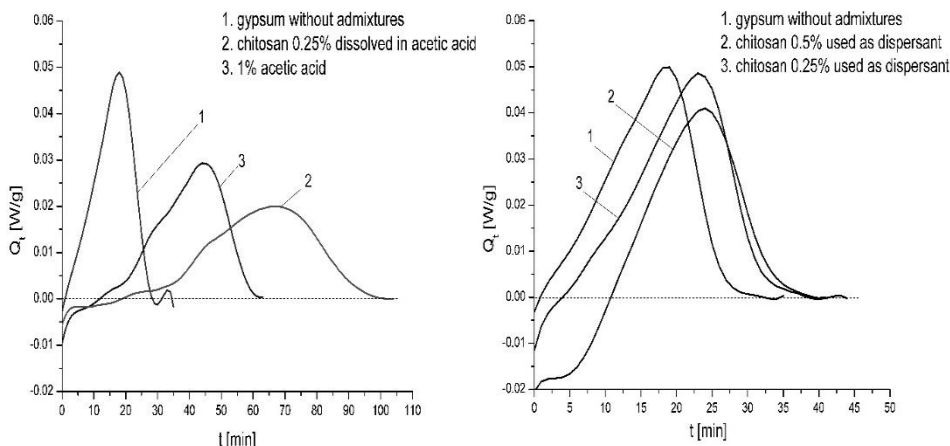
Figure 6. Calorimetric heat flow curves for gypsum without admixtures with chitosan used as dispersant and with 1% acetic acid and dissolved in acetic acid chitosan. The w/g ratio is 0.6

The kinetics of the transformation of the amorphous phase to the crystalline phase was analysed by the Johnson-Mehl-Avrami (JMA) model, assuming that the equation for the degree of transformation is expressed as follows:

$$X(t) = 1 - \exp(-K(t-t_i)^n)$$
$$X(t) = dH/H_t$$

where:
t is the time of hydration, and t_0 corresponds to the length of the induction period, K is a parameter depending on the rate for the nucleation process, n is the Avrami coefficient depending on the mechanism, size and type of nucleating growth, H_t – total heat flow
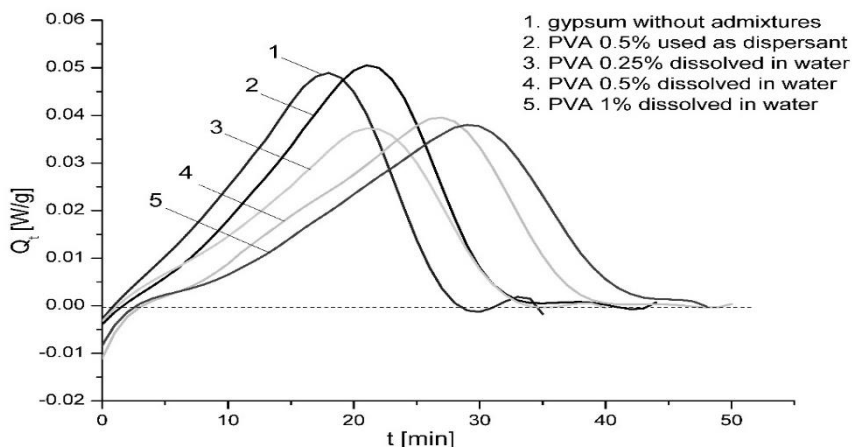

Figure 7. Calorimetric heat flow curves for gypsum without admixtures and with PVA 0.25–1% used as dispersant or dissolved in water. The w/g ratio is 0.6

171

The degree of transformation crystallisation X(t) as a function of time is presented in Figure 8.

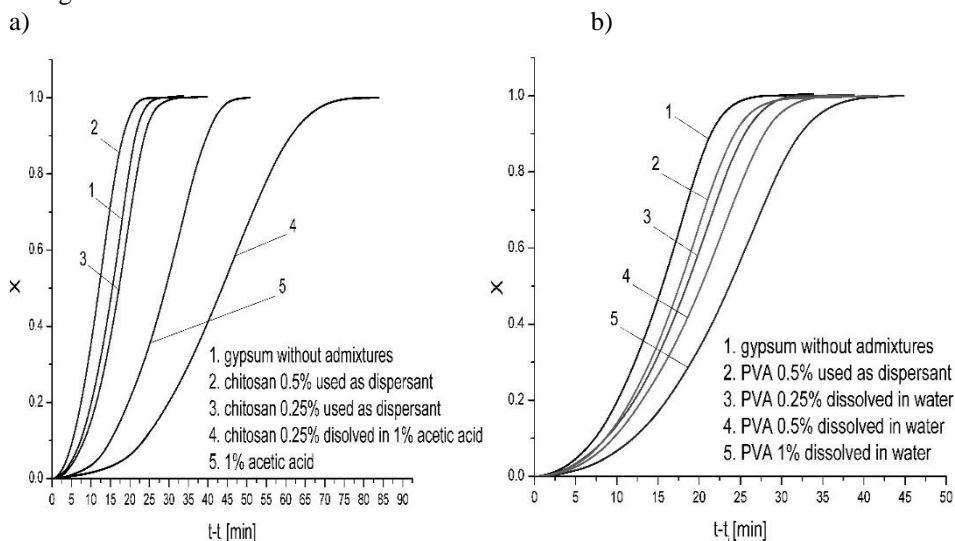a)   b)

Figure 8. Degree of crystallinity (transformation) X (integrated curves) versus time t-ti a) for samples without admixtures, with 1% acetic acid and with chitosan used as dispersant or dissolved in 1% acetic acid; b) for samples without admixtures and with PVA 0.25–1% used as dispersant or dissolved in water. X = dH/H$_t$ (H$_t$ – total heat flow). The w/g ratio is 0.6

The results of the obtained Avrami's parameters are presented in Table 2.

Table 2. Obtained Avrami's parameters for various samples

Sample	Avrami's parameter n	Avrami's parameter K [(1/min)^n]
Gypsum without admixtures	2.20	0.0015
Chitosan 0.5% used as dispersant, deacetylation degree 85%	2.15	0.0031
Chitosan 0.25% used as dispersant, deacetylation degree 85%	2.31	0.0009
Chitosan 0.25% dissolved in acetic acid, deacetylation degree 85%	2.05	0.0002
1% Acetic acid	2.33	0.00025
PVA 0.5% used as dispersant	2.26	0.0010
PVA 0.25% dissolved in water	2.23	0.0009
PVA 0.5% dissolved in water	2.24	0.0007
PVA 1% dissolved in water	2.32	0.0004

Avrami's equation parameters were determined on the basis of calorimetry. The n coefficient obtained was 2–2.5 and it sets out the process as a diffusion control two-dimensional crystal growth. The used additives caused a decreasing K value and decreasing nucleation rate [Table 2]. In most cases, dispersant additives have a lower impact on hydration/crystallisation kinetics.

The error of n and K calculation did not exceed 10% (fitting of crystallisation curve).

3.3. Mechanical tests

The results of the mechanical tests studied by checking the dependence between maximal bending stress for samples without additives and with polymer additives are shown in Figures 9 and 10.

The value of bending stress increased for samples with polyvinyl alcohol used both as dispersant and dissolved in water. This results from a change in the sample's morphological structure and modification of its porosity. Using chitosan as additives decreased the value of bending stress. A similar dependence can be observed by increasing the water/gypsum ratio: the bending stress value decreased with increasing water/gypsum ratio (increasing porosity). The statistical error of the σ_{max} measurement is close to 10% (few tests for every samples).
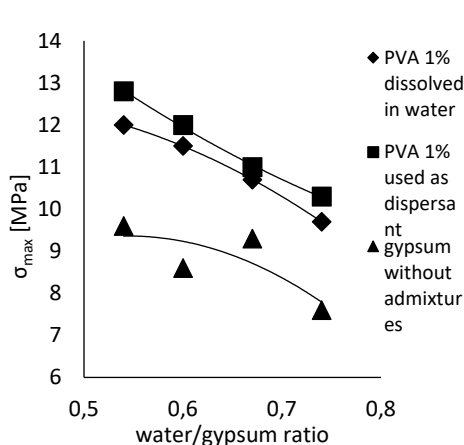

Figure 9. Bending stress σ_{max} versus w/g for samples: with 1% PVA dissolved in water and used as dispersant and without admixtures
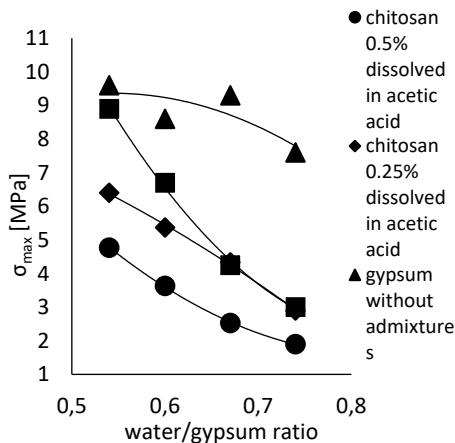
Figure 10. Bending stress σ_{max} versus w/g for samples: with 0.25% and 0.5% of chitosan dissolved in water; with 0.5% of chitosan used as dispersant and without admixtures

3.4. Morphology – Scanning electron microscope

SEM microphotography was used to observe the crystal structures of the samples. Figures 11 and 12 present a comparison of the sample without admixture with a sample with 1% of chitosan used as dispersant. In both samples, the w/g ratio was equal to 0.74.

Application of chitosan as an additive leads to the formation of thinner elongated dihydrate calcium sulphate crystals.
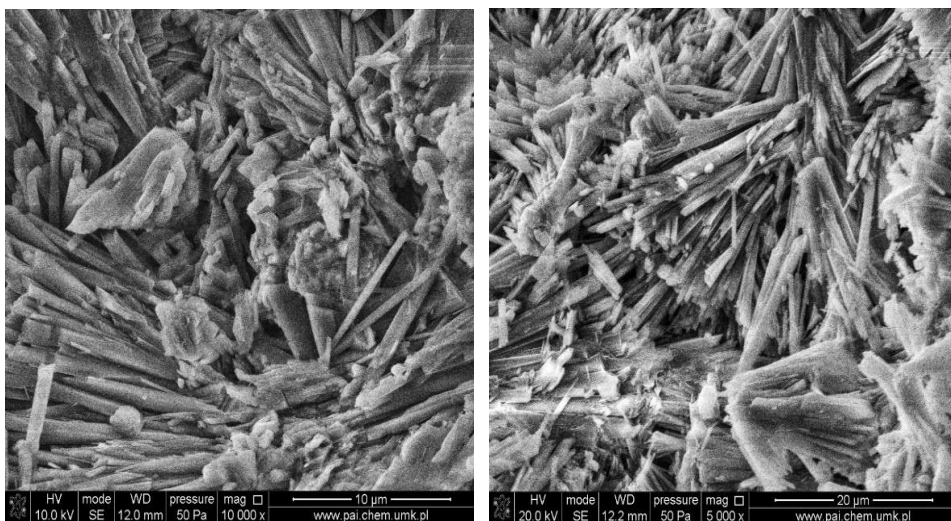

Figure 11. Gypsum without admixtures, w/g=0.74

Figure 12. Gypsum with 1% chitosan, w/g=0.74

4. Conclusion

It was found, as before [2,11,12], that the presence of a small amount (~1%) of water soluble polymers (cellulose derivatives) has an influence on gypsum hydration kinetics. In the case of the presented results, chitosan in the form of 1% dispersion was a setting retardant and it changed the morphological structure of gypsum [3]. However, the mechanical tests showed a decrease in the bending strength. In the case of chitosan applied as a biomaterial in previous work [13], the chitosan content in the composite was 10%, and thus the compressing strength increased. The presence of PVA (polyvinyl alcohol) in the gypsum matrix caused a small effect on gypsum setting in contrast to PVAc (polyvinyl acetate), which is good admixture for both cement and gypsum [1,2].

Future work will be continued for water soluble chitin derivatives as dibuthyl chitin and chitosan ethers.

5. *Acknowledgements*

6. References

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