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Improvement on mechanical strength and water absorption of gypsum modeling material with synthetic polymers

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Abstract

α- or β-Calcium sulfate hemihydrate (α-H or β-H) are commonly used to make gypsum model for ceramics manufacture as modeling material. Unlike construction gypsum, gypsum model urges both high mechanical strength and water absorption. In this experiment, synthetic polymers were investigated on their effect on the properties of hardened gypsum pieces, focusing on the structure–function relationship. Four sulphur polycarboxylates were designed and synthesized for a comparison study with some commercial polymers. It was found that all assayed sulphur polycarboxylates could maintain or improve water absorption of the hardened gypsum pieces made from β-H, but only the one without carboxyl group led an increase of the mechanical strength; the more hydrophilic polymers enhanced the mechanical strength and water absorption even at a ratio of water to hemihydrate (W/H) as high as 0.7. The results suggest that keeping sulphur and vinyl alcohol residues in the molecular will be a promising design for polymer structure applied in gypsum modeling material.

Keywords: Calcium sulfate hemihydrate; Gypsum; Polycarboxylate; Mechanical strength; Water absorption

1. Introduction

α-Calcium sulfate hemihydrate (α-H) or β-calcium sulfate hemihydrate (β-H) are commonly used as construction materials and modeling materials. Construction materials such as cement or gypsum usually require strong mechanical strength and lower water absorption, which is not difficult to realize since strong mechanical strength does not conflict with lower water absorption. However, gypsum used as modeling material requires strong mechanical strength especially bending strength but high water absorption, which is very different from what construction gypsum prefers. The challenge is that the strength and water absorption are contradictory to each other in a same hardened gypsum piece. Except careful choosing the gypsum formula, i.e., the ratio of α-H to β-H [1], using additives [2] like polymers can improve the strengths and alternate the water absorption; but so far, except countable experiences coming from industry, there are very few reports can be adapted to understand how the functional groups in molecular structures of the additives affect the strengths and water absorption.

Gypsum models such as models for ceramics manufacture are normally made from either α-H or β-H or both. In industry, α-H has been admixed with cheaper β-H to form the gypsum modeling material for higher strength and better water absorption, since α-H provides high strength but weak water absorption while β-H does reversely [3]. As a matter of fact, α-H has same molecular structure with β-H but differs from the crystal structures, which may induce the differences in the mechanical strength and water absorption. α-H consists of well-formed transparent idiomorphic crystals with sharp crystal edges whereas β-H consists of flaky particles made of small

Abbreviations: AA, acrylic acid; APEP, alkenyl methyl polyoxyethylene polyoxypropylene ether; APS, ammonium persulphate; α-H, α-calcium sulfate hemihydrate; β-H, β-calcium sulfate hemihydrate; MA, maleic anhydride; *N*-MAM, *N*-hydroxymethyl acrylamide; PC, polycarboxylates; PEG, polyethylene glycol; PAM, polyacrylamide; PVA, polyvinyl alcohol; SMS, sodium methylallyl sulfonate

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crystals [3]; hence β-H requires more water than the α-H does in order to obtain a paste of standard consistency because it has much higher specific surface area. Therefore, theoretically β-H needs to work in a high ratio of water to hemihydrate (W/H) that induces weak mechanical strength.

Polymers have been used to alternate the mechanical properties of cement [4–7] or cement-gypsum product [7,8]. Recently, polymers such as polycarboxylates, polysaccharides and other natural or synthetic polymers have been noticed because of their effects on the rehydration of gypsum [9], water retention capacity [10] on gypsum plaster; or their adsorption and dispersion characteristics [11] on calcium sulfate hemihydrates. Some natural polysaccharides, such as dextrin, starch and cellulose did not affect setting times of the gypsum [9], while 0.025 wt% of carboxymethylcellulose (CMC) can increase the initial and final setting time without significantly affecting the mechanical strength of the hardened pieces. Methyl hydroxypropyl cellulose (MHPC) was found to decrease the water retention capacity significantly in gypsum plaster with higher dosages to attain water retention values comparable to those in cement [10]. Sulfonated melamine formaldehyde (SMF) and polycarboxylate (PC) were found to increase 38% and 25% of bending strength in 2 h at the optimum dosages of 0.5 wt% and 0.3 wt%, respectively [12]. SMF accelerates early hydration, while PC decelerates it, they both allow similar maximum water reductions, giving a more compact structure and a decrease in the total pore volume and average pore diameter, and thus leading to higher strengths in the hardened plasters [12].

However, systematical studies on the structure–functional relationship of polymers are still insufficient, less has been devoted to accurate determination except few reports [13]; hence data from different groups are difficult to compare. In addition, although using the mixture of β-H and α-H is a common industrial protocol, but there still lacks knowledge of relevance between mechanical properties and composite of the hemihydrates and even the water/ hemihydrate ratio dependence. Moreover, there are few researches towards to the structure–function relationship of the polymers [9,13,14], which is far more lagging behind what in Portland cement and concrete research. Specifically, it hardly found reports about polymer performance on β-H.

From the countable literatures, we have noticed a fact that polymers can alternate the morphology of β-H to that of α-H [3], which implies a possibility to use polymer to modify β-H, to obtain stronger mechanical strength with a lower water/ hemihydrate ratio for its workability, meanwhile and the most important, do not decrease the water absorption of the hardened piece, which is very important for modeling material.

Therefore, in this experiment, to contribute knowledge to the effect of polymer structures especially the essential functional groups on gypsum properties, to verify how the polymers affect the mechanical strength and water absorption of gypsum, to study possibility of using β-H instead of the blending hemihydrates for lower cost, several commercial synthetic polymers and designed synthetic polycarboxylates were investigated on their effects on properties of hardened gypsum made from β-H and α-H, respectively. Meanwhile, the effect of composites of hemihydrates and W/H on the gypsum properties was also disclosed.

2. Materials and methods

2.1. Chemicals

α-Calcium sulfate hemihydrate and β-calcium sulfate hemihydrate (98%) were provided by Yingcheng hechang gypsum products company (Hubei, China). Ammonium persulphate (APS), NaOH, maleic anhydride (MA), acrylic acid (AA), and polyethylene glycol (PEG) were purchased from Sinopharm chemical reagent company. *N*-hydroxymethyl acrylamide (*N*-MAM) was purchased from Tianjin chemical reagent research institute. Sodium methylallyl sulfonate (SMS) was from Taichang Xinmao district polyester chemical company. Alkenyl methyl polyoxyethylene polyoxypropylene ether (APEP, molecular weight 2400) was from Liaoning Oxiranchem, Inc. Polyacrylamide (PAM, 95%) was from Wuxi Fengmin environmental science and technology development company. Polyvinyl alcohol (PVA, 99%) was from Shanghai Kaidu industrial development company.

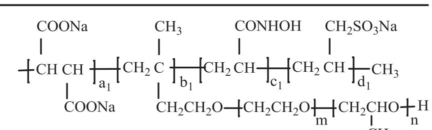
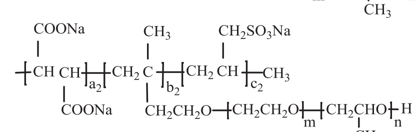
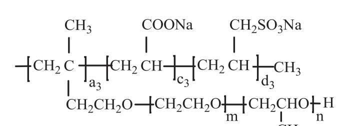
Four sulphur polycarboxylates (PC) were synthesized in our lab as described in methods (Section 2.2.1).

2.2. Methods

2.2.1. Preparation of the polycarboxylates

Polycarboxylates (PC) (Table 1) were synthesized with monomers in the following molar ratios: PC-1 (APEP:MA:*N*-MAM:SMS = 8:20:20:5), PC-2 (APEP:MA:SMS = 8:20:5), PC-3 (APEP:AA:SMS = 8:20:5), PC-4 (APEP:*N*-MAM:SMS = 8:20:5). Briefly and typically, PC-3 was prepared with aqueous phase radical polymerization with APS (final concentration was 0.6 wt%) as the initiator. SMS and APEP

Table 1
Structures of the synthetic polycarboxylates.

Polymer	Structure
PC-1	
PC-2	
PC-3	
PC-4