



Styrene–butadiene latex modified calcium aluminate cement mortar



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ABSTRACT

This paper investigates properties of calcium aluminate cement (CAC) mortar modified with the styrene–butadiene–rubber (SBR) latex. This material may be advantageously applied as a rapid repair mortar. Mortar specimens were prepared with constant water-to-cement mass ratio; polymer solid content of latex was varied from 0% to 9%, and Li_2CO_3 was investigated as an accelerator. Specimens were treated at different curing conditions: 1, 7 days and transformation of metastable hydration products at 70 °C. The heat of hydration evolution of mortar specimens was measured by means of a self adopted isoperibol calorimeter.

The measurement results indicate that SBR latex improves workability of fresh state mortar and retards nucleation and growth of hydration products. Due to polymer coagulation process and co-matrix formation permeability, stiffness and compressive strength decrease while adhesion strength to old concrete substrate, and flexural strength increase with amount of added latex.

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1. Introduction

Calcium aluminate cement (CAC) is a special cement with many specific properties [1–7]. Mainly due to fast hardening and excellent resistance to chemical attack, CAC is advantageously used for repair work of highways, airport's runways, internal and external building surfaces. Furthermore, the CAC is the preferred cement for polymer composites due to its high water to cement stoichiometric requirement that chemically bonds higher portion of water in the latex and thus enables higher degree of polymer coagulation. Setting and hardening of CAC is primarily due to the hydration of CA (cement notation: C = CaO, A = Al_2O_3 , F = Fe_2O_3 , S = SiO_2 , H = H_2O), but other compounds also participate in the hardening process especially in long term strength development [1,7] and at higher temperatures of hydration. The CAC hydration is highly temperature dependent, yielding CAH_{10} as main products at temperatures less than 20 °C, C_2AH_8 [8] and AH_3 at temperatures about 30 °C, whereas C_3AH_6 and AH_3 at temperatures greater than 55 °C. CAH_{10} and C_2AH_8 are known to be metastable at ambient temperature and transform to more stable C_3AH_6 and AH_3 with consequent material porosity and permeability increment, and loss of strength. On the other hand, in the absence of sufficient water, these phases do not transform but dehydrate [8].

CAC harden rapidly with high early strengths even under low (near-freezing) temperatures [7], if protected from freezing prior

to initial set. The hydration process of other types of cements (e.g. Portland cement, PC) is greatly slowed or even stopped at such low temperatures. Furthermore, CACs are favorably used in cryogenic areas, such as the loading docks of liquid–gas plants, because of the excellent thermal shock resistance [5]. The rapid hardening characteristic of CAC makes it suitable to put a cement based lining (e.g. floor or highway and bridge deck repair patch [9,10]) back in service within a few hours. The ultra-rapid setting CAC based materials, which set within a few minutes, can be readily obtained by a very small addition of Li salts [11,12]. The acceleration of the setting and hardening process generally results in a reduction of the ultimate strength [11,12].

Properties of cement-based materials can be improved by addition of a polymer admixture [13]. Upon hydration, the resulting hardened material contains a continuous, interconnected matrix of coagulated polymer particles which fill up pores in cement matrix and improve the bonding between aggregates and cement paste. As a result of this co-matrix formation, polymer modified mortars have low permeability, good freeze–thaw resistance, relatively higher flexural strength and adhesion strength to old concrete substrate, which allow those materials to be advantageously employed as repair materials for concrete buildings, concrete bridges, highway covering materials and waterproof materials [13]. Styrene–butadiene–rubber (SBR) latex modified mortars have been used on highway bridges in the US over the past 35 years. It is generally known that the polymer modified PC based material is more durable than the conventional one. In the last two decades, SBR latex-modified (PC) mortars have been widely used as

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a repair materials for concrete and reinforced concrete structures because of their superior chemical as well as mechanical (e.g. frost attack, higher modulus of elasticity, higher tensile strength) resistance [13]. Polymer latex has been employed also in CAC based materials for making chemically resistant mortars, screeds and surface coatings [14]. Rubber latex modified CAC mortars are considerably more resistant than plain CAC mortars against dilute acid (pH >4), alkaline and oil (grease), and other chemical attack [14]. SBR is not resistant to oxidizing acids (e.g. nitric acid).

While the properties of different polymer latex-modified mortars based on ordinary (Portland) cements are widely reported in the literature, little is known on the polymer modification of the special CAC based materials. Systematic studies on the properties of the SBR modified CAC mortars are lacking in literature. Therefore, this paper presents the results on the effect of amount of added SBR polymer onto setting time, heat of hydration evolution, rheology, and physical and mechanical properties of a SBR latex modified CAC mortar.

2. Experimental

2.1. Materials

Commercial CAC (type ISTRA 40) was taken from a regular production of Calucem Pula, Croatia. The cement has the oxide mass fraction composition listed in Table 1. Physical properties of used cement are given in Table 2. The main compounds are CA and ferrite phase ($C_4AF-C_6AF_2$), with mayenite ($C_{12}A_7$), gehlenite (C_2AS) and β - C_2S as minor compounds. SBR latex with a 47% solid content, nonionic surfactant and antifoaming agent in the commercial composition was used. Mortars were prepared with distilled water and river sand with the size of 0–4.0 mm (100% passed 4 mm sieve). Analar grade Li_2CO_3 salt was used as an accelerator.

2.2. Specimen preparation

The sand-to-cement ratio for all specimens was 3 and (polymer solid)-cement ratios (p/c) were 0%, 3%, 6% and 9%. The amount of water in the latex emulsion was taken into account in the overall water-to-cement mass ratio which is fixed at 0.450. Li_2CO_3 accelerator was dissolved in freshly deionised water prior to mixing with cement with a mass fraction of 0.0045% relative to cement weight.

In order to reduce the amount of entrained air the following mixing method was used. First, cement and sand were mixed together in a standard laboratory planetary mixer (following ASTM C305-80) for 1 min at speed of 140 rpm. Then, the water was added into the mix and mixing process was continued for 2 min at the same speed. At last, latex was added and everything was mixed for another 2 min. Fresh mixtures were cast into prismatic molds ($40 \times 40 \times 160$ mm) and vibrated. Specimens were cured in mold for 24 h at 20 °C and 95% of relative humidity. In order to investigate properties of hardened CAC mortars with morphologically different hydration products, the aimed specimens were obtained according to a designed experimental hydration program shown in Table 3. The specimens were hydrated at 20 °C to obtain CAH_{10} as main hydration product. After 7 days of hydration (Table 3), the metatable hydration products were transformed to the stable ones (nominally C_3AH_6 and AH_3) by additional heating of

the specimens (sealed in plastic bags) at 70 °C in a thermostated water bath for 24 h.

2.3. Experimental methods

The consistency (fluidity) of the fresh state mortar was tested using the standard flow table test according to EN 1015-3. The test procedure involved placing the mold (60 mm in height, internal diameter: base 100 mm – top 70 mm) in the center of the flow table. A period of 15 s is allowed to elapse before the mold is removed, the table is jolted 15 times at a rate of one jolt per second. The mean diameter of the spread mortar is recorded.

Apparent density and air entrapment of mortars were determined following ASTM C185-08. The mortars were compacted (vibrated) into a measure of known volume and weighed. The air content is calculated from the measured apparent density of the mortar, the known densities of the constituents, and the mixture proportions. CAC and sand densities are determined according to the ASTM C 188-89.

Bending and compression test of hardened mortars were done as per EN 1015-11. The bending tests were performed on $40 \times 40 \times 160$ mm prisms, while the compression tests were carried out on two pieces of original prisms for each specimen. The standard molds were filled by placing on a vibrating table.

The open porosity was obtained from the measurements of the dry weight (W_D), the water saturated weight (W_{Sat}) and the sample volume (on broken halves of standard prisms by Archimedes method, W_{Arch}), according to the following equation:

$$P_{OPEN} = \frac{W_{Sat} - W_D}{W_{Arch}} \quad (1)$$

Drying of samples was achieved by using a vacuum pump for 1 day (at 0.5 mbar). Drying of samples by heating is not used because of the well known effect of the transformation reactions [1] that significantly modified the pore microstructure of CAC based material.

Ultrasonic modulus (E) for each specimen was determined by the following equations:

$$E \text{ (GPa)} = \frac{v^2 \rho}{K} \quad (2)$$

$$K = \frac{(1 - \nu)}{(1 + \nu)(1 - 2\nu)} \quad (3)$$

where ρ is the sample density, ($g \text{ cm}^{-3}$), ν the velocity of ultrasonic pulse propagation through the specimen (160 mm long), ($km \text{ s}^{-1}$), ν is the Poisson's coefficient.

The velocity of ultrasonic pulse propagation through the specimen was measured by TICO Proceq Testing Instruments with time resolution of 0.1 μs , voltage impulse of 1 kV, pulse repetition of 3 s^{-1} and frequency of 54 kHz.

Determination of adhesive strength of hardened mortar on concrete substrates was done as per EN 1015-12. This test method involves determining the maximum tensile stress applied by a direct load at right angles to the surface of the mortar. The substrate used was a PC based concrete panels with dimensions $550 \times 150 \times 50$ mm with a maximum aggregate size of 8 mm. The concrete panels were wood floated to provide a suitable surface and are more than 28 days old when testing was undertaken.

Table 1
Chemical composition (mass%) of investigated CAC.

CaO	Al ₂ O ₃	Fe ₂ O ₃	FeO	SiO ₂	TiO ₂	MgO	SO ₃	Na ₂ O	K ₂ O	Sum
37.95	38.00	13.11	2.77	4.23	1.59	0.65	0.20	0.14	0.18	98.82

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