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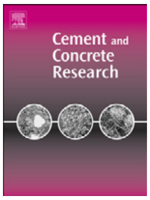

The influence of aminosilanes on macroscopic properties of cement paste

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ABSTRACT

In this work the authors present the results obtained by studying the influence of γ-aminopro-pyltriethoxysilane or $(CH_3CH_2O)_3Si(CH_2)_3NH_2$, (APTES), and *N*-β-aminoethyl-γ-aminopropyltri-methoxylsilane or $(CH_3O)_3Si(CH_2)_3NH(CH_2)_2NH_2$, (AEAPTES), on macroscopic properties of fresh and hardened cement pastes and mortars prepared from ordinary Portland cement. The mixing ability of aminosilane substances with water is an advantage in comparison to other types of organofunctional silanes when used as an admixture to the cement system. This enables direct blending with water and cement and homogeneous distribution of aminosilane molecules through the bulk of the cement material. The highly polar amine and alkoxide groups of aminosilane molecules exhibit strong chemical interactions with cement matrix which are reflected in modified macroscopic properties of the cement system. The effect of APTES and AEAPTES on (a) properties of fresh cement paste and mortar as workability, setting time, water/cement ratio, air content and density, and on (b) properties of hardened cement paste and mortar as compressive and flexural strength, was studied.

1. Introduction

Organofunctional silanes have an important role in the fast-growing field of advanced materials. They act as adhesion promoters, coupling agents, and surface primers [1]. The aminosilanes differ from the general organosilanes in carrying an aminofunctional group in the organic chain e.g. $H_2N–R–Si–(OR')_3$. The most widely used and studied aminosilanes are γ-aminopropyltriethoxysilane or $(CH_3CH_2O)_3Si(CH_2)_3NH_2$), (APTES), γ-aminopropyldiethoxymethylsilane or $(CH_3CH_2O)_2CH_3Si(CH_2)_3NH_2$), (APDEMS), and *N*-β-aminoethyl-γ-aminopropyltrimethoxylsilane or $(CH_3O)_3Si(CH_2)_3NH(CH_2)_2NH_2$), (AEAPTES) [1–3]. The amine group serves for the specific chemical reaction behavior and high reactivity of aminosilane molecules. The electron rich nitrogen atom of the amine group easily enters into hydrogen bonding interaction with hydrogen donating groups, such as hydroxyl groups or other amines. This makes aminosilanes mixable with water in all proportions and enables fast adsorption by hydrogen bonding of the amine group to the substrate surfaces rich with hydroxyl groups. In addition to this a hydrolysis of alkoxy groups (e.g. $–OC_2H_5$ or $–OCH_3$) to hydroxyl groups (–OH) and subsequent condensation reactions with hydroxyl groups of the substrate result in the siloxane covalent bond formation, which has been successfully used for coupling between mineral and organic phases in glass reinforced plastic composites for more than 30 years. The aminosilane-silica coupling has been used also for the reinforcement of natural and synthetic rubbers and elastomers [4]. In the last decade, the aminosilanes have been intensively applied in the broad field of oxide modification, where the aminosilane modified silica gel was the most widely used combination [5].

The use of organofunctional silanes in cementitious systems was restricted, so far, to the cement systems containing mineral admixtures as fumed silica [6,7]. The amino organofunctional silanes were introduced into the fumed silica and cement mix in two ways: (i) by coating the fumed silica particles with silane prior to mix it with the cement, and (ii) by adding the silane directly into the fumed silica cement mix [6]. The coating of fumed silica was accomplished by a 1:1 (by weight) mixture of AEAPTES and γ-glycidoxypropyltrimethoxysilane or $(CH_3O)_3Si(CH_2)_3OCH_2CHCH_2O$, (GLYMO). The amine group in AEAPTES served as a catalyst for the curing of epoxy and consequently binding of AEAPTES molecules with GLYMO molecules. The terminal alkoxy groups served for connection to the –OH functional groups on the surface of fumed silica particles. As described in ref. [6], the whole coating process was rather laborious, but the positive effect of silane coupling was clearly realized in better workability, decreased drying shrinkage, and better mechanical properties of tested cement paste. The use of silane as an admixture which was added directly into the cement mix involved slightly more silane material but less processing cost than with coating the fumed silica. The silane used as an admixture was aqueous amino vinyl silane, chosen due to its stability in aqueous environment. The final result of testing on cement paste showed similar positive effects as with coated fumed silica [6]. The aqueous amino vinyl silane was used also to improve the dispersion of steel fibers in cement mortar [7]. The results of testing the steel-fiber-reinforced mortars showed that use of amino vinyl silane as an admixture to the mortar improved the dispersion of the steel fibers, whereas, the use of silane as a coating on the steel fibers was found less effective [7]. The aminosilanes

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Table 1
Chemical composition of ordinary Portland cement, type CEM I 42,5 R determined according to procedures described in EN 196-2, 21

Parameters	(wt.%)	Demand of EN 197-1 (wt.%)
Loss after ignition (corrected)	1.40	≤5.0
SiO_2	20.84	–
Al_2O_3	5.25	–
Fe_2O_3	2.93	–
CaO	62.46	–
SO_3	2.91	≤4.0
S^{2-}	0.00	–
MgO	2.74	–
Na_2O	0.37	–
K_2O	0.72	–
MnO	0.09	–
Cl^-	0.01	≤0.10
Insoluble residue	1.68	≤5.0

Table 3
Physical properties of ordinary Portland cement, type CEM I 42,5 R determined according to EN 196-1

Strength (MPa)		Measured values (MPa)	Demand of EN 413-1 (MPa)	Expanded measurement uncertainty, *U*
Flexural	2 days	5.2	–	±0.6 MPa
	7 days	6.2	–	±0.7 MPa
	28 days	7.7	–	±0.8 MPa
Compressive	2 days	34.2	≥20.0	±1.2 MPa
	7 days	47.9	–	±1.6 MPa
	28 days	59.0	≥42.5≤62.5	±1.9 MPa

were used also as an admixture in polymer modified cement mortars where positive impact on bending strength and adhesion properties of mortars on concrete substrates was observed [8,9].

In this work the authors present the results obtained by studying the influence of APTES and AEAPTES aminosilanes on macroscopic properties of cement paste and mortar prepared from ordinary Portland cement. The properties of (a) fresh cement paste and mortar as workability, setting time, water/cement ratio, air content and density, and (b) properties of hardened cement paste and mortar as compressive and flexural strength, were examined.

2. Experimental

2.1. Raw materials

Cement pastes and cement mortars were prepared from ordinary Portland cement, type CEM I 42,5 R, produced by Lafarge Trbovlje, distilled water and CEN Reference sand. Chemical composition and physical–mechanical properties of CEM I 42,5 R, are presented in Tables 1, 2 and 3. All parameters were determined according to the standard procedures described in EN 196-1, 2, 3, 6, 21. The results complied with the demands of standard EN 197-1. The aggregate used for the preparation of standard mortar was a natural siliceous sand (CEN Reference sand) consisting predominately of rounded particles containing more than 98 wt.% of SiO_2. The particle size analysis of the sand presented in Table 4 showed that particle size distribution lay within the limits defined in the standard EN 196-1. Moisture content of the sand was less than 0.2 wt.% determined as the loss of mass after 2 h drying at 105 °C to 110 °C, expressed as a percentage by mass of the dried sample. The aminosilanes, (APTES and AEAPTES, Aldrich), used in this study were slightly viscous colorless transparent liquids.

2.2. Cement paste

Cement paste was prepared by mixing 500 g±1 g of cement and appropriate quantity of water in a turbine mixer (Toni Technik/ToniMIX) following the procedure described in standard EN 196-3. The volume of water was measured using the graduated cylinder to an accuracy of±1 ml. The aminosilanes were added to the cement paste as water solutions containing different amounts of hydrolyzed aminosilane molecules. The quantity of aminosilane in the cement paste ranged from 0.3 to 1.2 wt.% by mass of the cement. Preparation of cement paste was performed in the laboratory climate at 20±1 °C and relative humidity of about 55%.

2.3. Standard consistency

The water for standard consistency was determined on manual Vicat apparatus equipped with cylindrical plunger (effective length of 50±1 mm and diameter of 10.00±0.05 mm), following the procedure in standard EN 196-3. The release of the plunger and penetration into the paste was started 4 min±10 s after the zero time (the point after the addition of water from which the initial and final setting times were calculated). The scale reading which indicated the distance between the bottom face of the plunger and the base-plate, together with the water content of the paste expressed as a percentage by mass of the cement were recorded 5 s after penetration had ceased or 30 s after the release of the plunger, whichever was earlier. The test of normal consistency was repeated with pastes containing different water contents until one was found to produce a distance between plunger and base-plate of 6±3 mm. The water content of the paste was recorded to the nearest 0.5% as the water for standard consistency.

2.4. Setting time

The initial and final setting time was determined on the same Vicat apparatus equipped with appropriate steel needles and attachment as described in the standard EN 196-3. The needle for the initial set had length of 50±1 mm and diameter of 1.13±0.05 mm. The needle for determination of final setting time was shorter (effective length of 30± 1 mm and diameter of 1.13±0.05 mm) and equipped with ring attachment (diameter 5 mm) to facilitate accurate measurement of small penetrations. The penetration depth and the time were recorded when the penetration of the needle had ceased. The penetration test and recording of depth and time was repeated on the same specimen at

Table 2
Physical properties of ordinary Portland cement, type CEM I 42,5 R and corresponding cement paste determined according to EN 196-3, 6

Parameters	Measured	Demand of EN 197-1
Cement residue on 0.09 mm sieve (%)	0.9	–
Density (g/cm^3)	3.09	–
Specific surface — Blaine method (cm^2/g)	3525	–
Water for standard consistence (%)	29.4	–
Initial setting time (min)	170	≥60
Final setting time (min)	205	–
Soundness — Le Chatelier (mm)	0.4	≤10

Table 4
Particle size distribution of the CEN Reference sand

Square mesh size (mm)	Cumulative sieve residue (% mass passing individual sieve)
2.00	0
1.60	5±2
1.00	34±2
0.50	69±2
0.16	85±2
0.08	99±1