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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

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%.

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

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

conveniently spaced positions for initial and final setting times each 10 and 30 min, respectively. The initial setting time was determined as a time measured from zero time to the moment when the needle stopped at distance 6±3 mm above the base-plate. The final setting time was recorded as a time passed from zero time to the point where the needle with the attachment penetrated only 0.5 mm into the specimen.

The total mass of moving parts on Vicat apparatus was 300±1 g. The Vicat mould with internal diameter of 75±10 mm of conical form (40.0±0.2 mm deep) was made of hard rubber. The base-plate was 3 mm thick plain glass. Testing of consistency and setting time of cement paste was performed in a humidity chamber (relative humidity ~100%) at 20±1 °C.

2.5. Preparation of fresh cement mortars

In general, fresh cement mortar mixes used in this study were prepared (a) at constant w/c=0.42 ratio and (b) at constant workability measured as flow table spread, FTS=150 mm. Further, for each type of mortar one batch was prepared with the intrinsic air-void content (Table 5) and another batch was prepared with adjusting the air-void content to the constant value of about 5±1% using nonionic antifoaming agent (AGITAN 731).

(a) A batch of fresh cement mortar mix prepared at constant ratio w/c=0.42 was consisting of 450±2 g of cement, 1350±5 g of CEN Reference sand and 189±1 g of water. The neat or reference cement mortar was modified with aminosilanes which were added to the mortar mix as water solutions containing different amounts of hydrolyzed aminosilane molecules in the range from 0.3 to 1.2 wt.% by mass of the cement. Mixing of each batch of mortar was performed in a turbine mixer (Toni Technik/ToniMIX) following the procedure described in the standard EN 196-1.

(b) A batch of cement mortar mix with constant FTS was prepared by adjusting the amount of water added to the mixture (w/c ratio) in a way to reach the workability of fresh mortar resulting in the FTS of 150±10 mm. No superplasticiser or other rheology modifier was added to the mortar mix. A batch of reference cement mortar at constant FTS was consisting of 450±2 g of cement, 1350±5 g of CEN Reference sand and appropriate amount of water. Mixing and the addition of aminosilanes were performed following the same procedure as described above.

2.6. Air-void content of fresh mortars

The air-void content of fresh mortar was determined by pressure method as described in standard EN 1015-7. The values for air-void content were recorded to the nearest 0.1%. The air content of the mortar was calculated as the mean value from the two individual values determined for each mortar test sample rounded to the nearest 0.5%.

2.7. Bulk density of fresh mortar

The bulk density of fresh mortar was determined by weighing following the standard procedure described in standard EN 1015-6. The filling and compaction method for fresh mortars was applied. The bulk density of fresh mortar was calculated as the mean value of two measurements rounded to the nearest 10 kg/m^3.

2.8. Workability of mortars

The workability of mortars was measured by the flow table spread (FTS) of a defined test sample when placed on a flow table, with the spread being achieved by a set number of jolts, whereby the platen of the table was raised slightly and then dropped back to the resting position. The method used in this work is thoroughly described in standard EN 13395-1. The workability of mortars was determined in the laboratory

Table 5
Compressive and flexural strength of mortars modified with different amounts of aminosilanes

Aminosilane		APTES					AEAPTES				Exp. uncertainty of measurement, *U*=*ku*
Amount of aminosilane in wt.% to the mass of cement		0	0.3	0.6	1.0	1.2	0.3	0.6	1.0	1.2	
w/c=0.42		const.					const.				
FTS (mm)		124	137	149	156	160	142	155	170	171	±5 mm
Air-void (%)		5.1	6.0	6.1	7.3	8.3	6.3	7.7	10.4	11.4	±0.5%
Compressive strength (MPa)	1 day	26.6	–	–	–	–	–	–	–	–	±1.9 MPa
	2 days	28.4	20.8	15.0	11.2	8.3	17.2	11.7	8.4	5.2	±1.2 MPa
	3 days	30.4	27.3	25.7	23.8	15.8	26.8	24.7	18.8	9.8	±1.5 MPa
	7 days	43.3	41.3	40.5	38.4	36.4	42.5	39.5	37.7	35.4	±1.6 MPa
	28 days	56.4	58.4	60.3	59.1	58.3	60.7	61.8	62.3	58.1	±1.9 MPa
Flexural strength (MPa)	1 day	5.2	–	–	–	–	–	–	–	–	±0.6 MPa
	2 days	5.9	4.0	3.2	2.2	1.5	3.9	2.9	2.5	1.6	±0.6 MPa
	3 days	6.6	4.9	4.0	3.4	2.3	4.8	3.8	3.2	2.2	±0.7 MPa
	7 days	7.1	6.1	5.7	5.3	4.7	6.3	5.9	5.7	4.1	±0.7 MPa
	28 days	8.2	8.7	9.4	9.6	9.0	9.0	9.7	10.6	8.8	±0.8 MPa
FTS ~150±5 mm		Const.					const.				
w/c		0.51	0.44	0.42	0.41	0.40	0.39	0.36	0.36	0.37	
Air-void (%)		4.7	6.4	6.6	7.2	7.3	5.8	6.9	8.2	8.6	±0.5%
Compressive strength (MPa)	1 day	28.2	–	–	–	–	–	–	–	–	±1.9 MPa
	2 days	33.1	22.8	19.2	15.0	12.4	16.2	13.6	6.9	3.7	±1.2 MPa
	3 days	42.0	28.5	25.1	23.4	18.4	25.0	20.4	19.8	14.6	±1.5 MPa
	7 days	47.5	41.6	35.7	34.3	30.3	43.1	41.9	40.6	33.6	±1.6 MPa
	28 days	58.6	60.1	60.9	62.0	57.8	60.3	62.3	63.6	57.0	±1.9 MPa
Flexural strength (MPa)	1 day	5.8	–	–	–	–	–	–	–	–	±0.6 MPa
	2 days	6.3	4.8	3.6	2.8	2.0	4.3	3.9	3.1	1.8	±0.6 MPa
	3 days	7.5	5.3	3.9	3.5	2.5	5.4	4.7	4.0	2.4	±0.7 MPa
	7 days	7.9	6.1	5.6	5.5	4.3	7.3	6.8	6.5	4.8	±0.7 MPa
	28 days	8.6	9.3	9.7	10.2	9.1	9.3	10.6	11.3	9.1	±0.8 MPa

U=*ku* — expanded measurement uncertainty of the method, where *k*=2 — which for Normal distribution corresponds to coverage probability of approximately 95% and *u* represents the standard uncertainty of the method determined according GUM [19].

climate at relative humidity ~55% and 20±1 °C. Two samples from the same batch were tested 15±5 min after preparation of the mortar. Prior testing, the mortar was remixed for a period of 20±2 s.

2.9. Preparation of mortar specimens for strength determination

Mortars samples for determination of compressive and bending strength were prepared in the form of prisms with dimensions 40 mm×40 mm×160 mm. Specimens were molded immediately after the preparation of the fresh mortar mix and then put and kept in a humidity chamber (relative humidity ~100%) at 20±1 °C for 24 h prior de-molding. Further conditioning was carried out by keeping the prisms in a humidity chamber (relative humidity ~100%) at 20±1 °C for another 7 days and then under normal laboratory conditions (relative humidity ~55% and 20±1 °C) for 21 days before strength determination. The laboratory testing of compressive and flexural strength was performed on Toni Technik/Toni Norm press equipped with appropriate adapters. Detailed description on the preparation of standard cement mortar and test specimens, conditioning of prisms and determination of strength as applied in this work is described in standard EN 196-1.

3. Results and discussion

3.1. Properties of fresh cement paste and mortars

3.1.1. Standard consistency

The results showing the penetration depth of the plunger versus water added to reach the standard consistency of the cement paste are presented in Fig. 1. A comparison of the data obtained for cement pastes modified with aminosilanes with those of neat cement paste revealed that aminosilane molecules considerably influence the penetration of the plunger already at small amounts of water added to the cement (below 50 ml). When fitting the curves through the data points in Fig. 1 the exponential relations between penetration of the plunger and water content were obtained. These results are consistent with macroscopic observations for cement pastes modified with organic admixtures obtained by conventional rheology measurements [10].

The results showing the quantity of water added to reach the standard consistency versus concentration of the aminosilane admixed to the cement paste are presented in Fig. 2. The water content needed to reach the standard consistency of cement paste containing 0.3 wt.% of AEAPTES was found to be 27.1±0.5% (w/c=0.271), which is about 2% less as with the neat cement paste (29.4% or w/c=0.294). Slightly higher amount of water (27.9% or w/c=0.279) was needed to reach the standard consistency of the cement paste modified with 0.3 wt.% of APTES. The plasticizing and water reducing properties of aminosilanes were even more clearly realized when higher amounts (up to 1.2 wt.%) of aminosilanes were added. With both aminosilanes the amount of water needed to reach the standard consistency of cement paste was decreasing with an increase in the amount of aminosilane in the cement paste.

3.1.2. Setting time

The results presenting the setting time of neat cement paste and modified cement pastes containing different amounts of APTES and AEAPTES are shown in Fig. 3. The initial setting time of cement paste containing 0.3 wt.% of APTES with one amino group was more than six times longer as with the neat cement paste. The setting of cement paste containing 0.3 wt.% of AEAPTES molecules with two amino groups was even longer. In general, the setting of cement pastes containing aminosilanes was strongly delayed in comparison with neat cement paste, and this trend was dependent on the amount of aminosilane. The results of measurements presented in Fig. 3 showed that the beginning and end of stetting decreased considerably with an increase in the concentration of aminosilane up to 1.0 wt.% to the mass of cement. At higher amounts of aminosilanes the trend was opposite. Nevertheless, the effective time ($t_{\mathrm{eff}}=t_{\mathrm{final}}-t_{\mathrm{initial}}$) needed for setting of cement expressed as a difference between final (t_{final}) and initial (t_{initial}) setting time was increasing with an increase in the amount of aminosilane (Fig. 3). These results were similar to findings published in the literature about the influence of polymers on the properties of normal Portland cement paste [10–13]. In later case, the reason for delay in setting of cement was attributed to the inhibition of hydration processes of cement minerals by surfactants such as alkylbenzene sulfonates and caseinates contained in latexes. Rheology studies on PVAC-modified concrete by Zivica [14] revealed that the hydration of cement was inhibited by the adsorption of the surfactants on the binder surface. When using the aminosilanes as cement modifiers the electron rich nitrogen atom of the amine group may enter into a

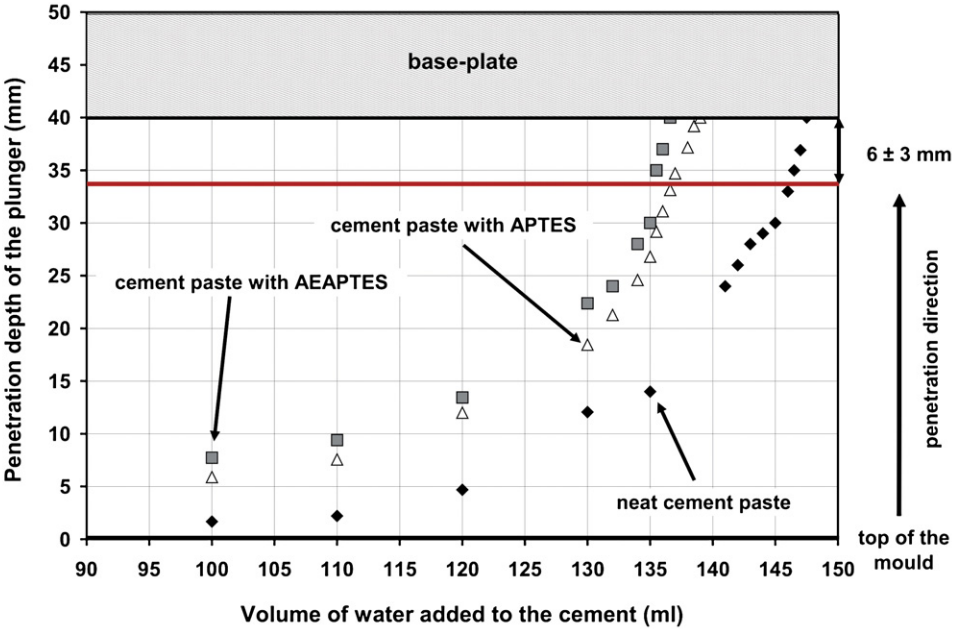


Fig. 1. Penetration depth of the plunger versus water added to reach the standard consistency of the cement paste.

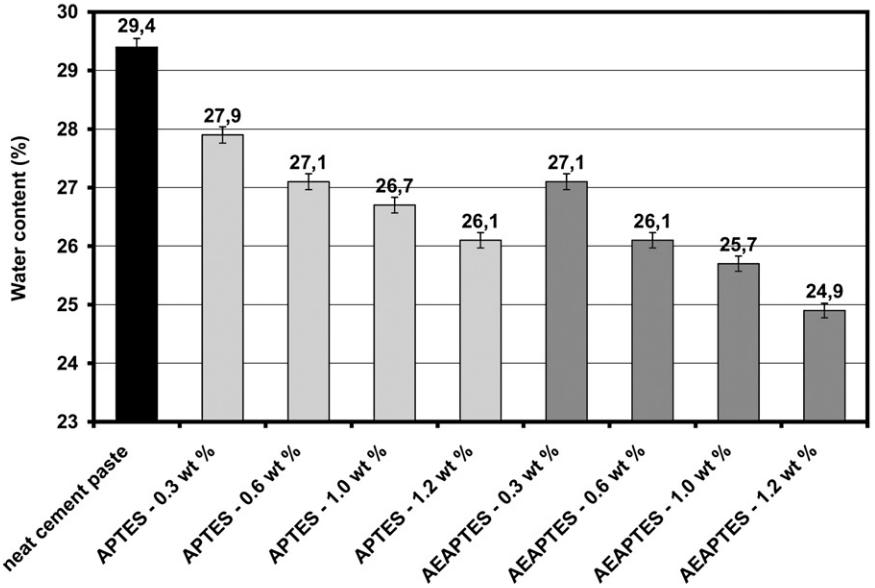


Fig. 2. Quantity of water added to reach the standard consistency versus concentration of the aminosilane admixed to the cement paste.

strong hydrogen bonding interaction with hydrogen donating groups on the surface of the binder particles [5]. This enables, similar as with surfactants, strong adsorption of aminosilane molecules on the surface of the cement particles and delays setting of cement. Additionally, deprotonated hydroxyl groups resulting from hydrolysis of alkoxy groups (e.g. $–OC_2H_5$ or $–OCH_3$) attached to the silicon atom may also strongly interact with cement particles through hydrogen bonds and through the formation of oxo bridges (Si–O–Si) between aminosilane molecules and cement matrix. The latter is a result of oxolation condensation reaction (Eq. (1)) in which an oxo bridge is formed between two silicon centers [15,16].

$$\equiv \mathrm{Si}-\mathrm{OH}+\mathrm{HO}-Si\equiv \rightarrow \equiv \mathrm{Si}-O-Si\equiv +\mathrm{H_2O} \tag{1}$$

The oxolation reaction may influence the nature of the hydration processes of cement phases. An important source of inhibition for setting of cement by aminosilanes may also be the presence of alcohol [17] which is a byproduct of the hydrolysis of aminosilane molecules in water (Eq. (2)):

$$\equiv \mathrm{Si}-\mathrm{OH}+\mathrm{H_2O} \rightarrow \equiv \mathrm{Si}-OR+ROH \tag{2}$$

However, the last source of inhibition was not possible to prove with the experiment. The experiment was carried out by adding quantitative amounts of ethanol, as it is expected to be released by hydrolysis of aminosilane molecules, to water used for the preparation of the cement paste (around 1% by the mass of water — depending on the amount of aminosilane used for modification of the cement paste). The measurements of setting time of cement pastes did not show meaningful influence of ethanol on the setting processes of cement. However, the direct addition of ethanol into water does not represent the same conditions as present when hydrolysis of aminosilane molecules is taking place.

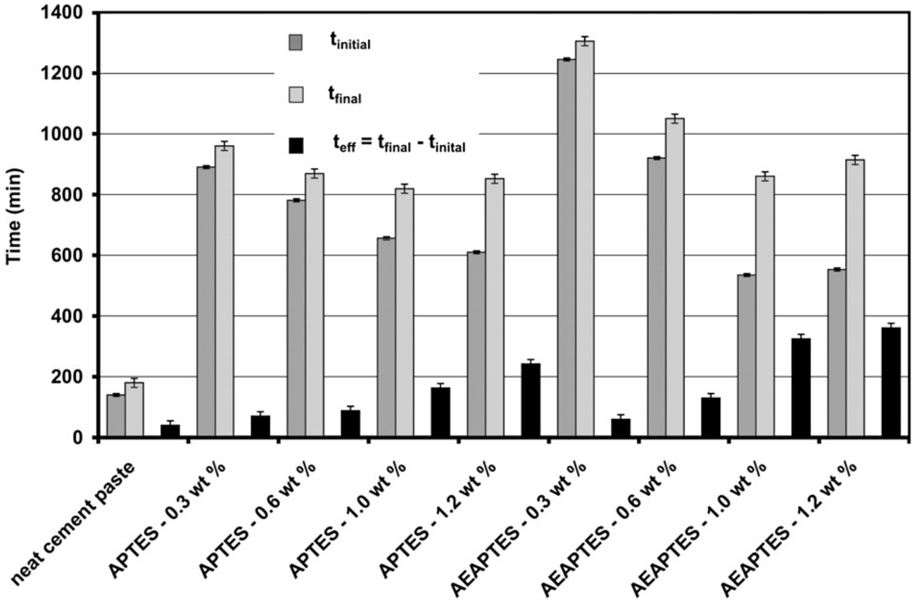


Fig. 3. Setting time of neat cement paste and modified cement pastes containing different amounts of APTES and AEAPTES.

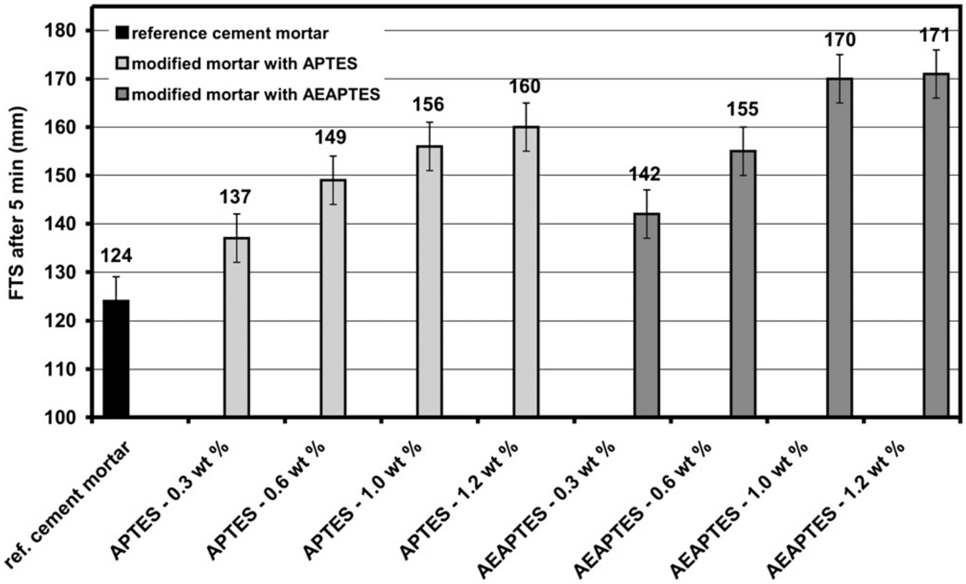


Fig. 4. Flow table spread (FTS) of mortars prepared at constant w/c = 0.42.

3.1.3. Workability, air-void content and density of fresh mortars

The workability of fresh mortar mixes was evaluated using the flow table spread test. The use of commercial superplasticizers to attain high workability of cement mortars at low w/c ratios was avoided. The results presented in Fig. 4 show FTS for mortars prepared at constant w/c = 0.42. As can be seen there are considerable differences in workability between unmodified cement mortar and aminosilane modified mortars. According to expectations the workability was increasing with raising the concentration of aminosilanes in the mortar mix from 0.3 to 1.2 wt.%. The highest value for FTS of about 170 mm was measured at concentrations above 1.0 wt.% of AEAPTES to the mass of cement. The results obtained by measuring the change in FTS of mortar with time, as presented in Fig. 5, showed that FTS is varying with the square root of time. The AEAPTES in concentration of 1.0 wt.% retained the FTS of mortar above 110 mm for more than 3 h. In general the effect of aminosilanes on workability of mortars was more pronounced with AEAPTES, which correlates well with the two highly hydrophilic amino groups in the structure of AEAPTES. The APTES contains only one amino group.

The results showing the air-void content and density dependence of modified mortars on concentration of AEAPTES are presented in Fig. 6. The air-void content of mortars modified with AEAPTES was increasing linearly with the concentration of AEAPTES and the density was correspondingly decreasing. Quite similar results were obtained also for mortars modified with APTES (Table 5). In general, the results of air-void content and density of mortars prepared at constant w/c and constant FTS showed that aminosilanes entrain air in the mortar which results in decrease of density. The highest content of air-voids (above 11%) was measured in mortars containing more than 1.0 wt.% of AEAPTES aminosilane. The density of mortars after the adjustment

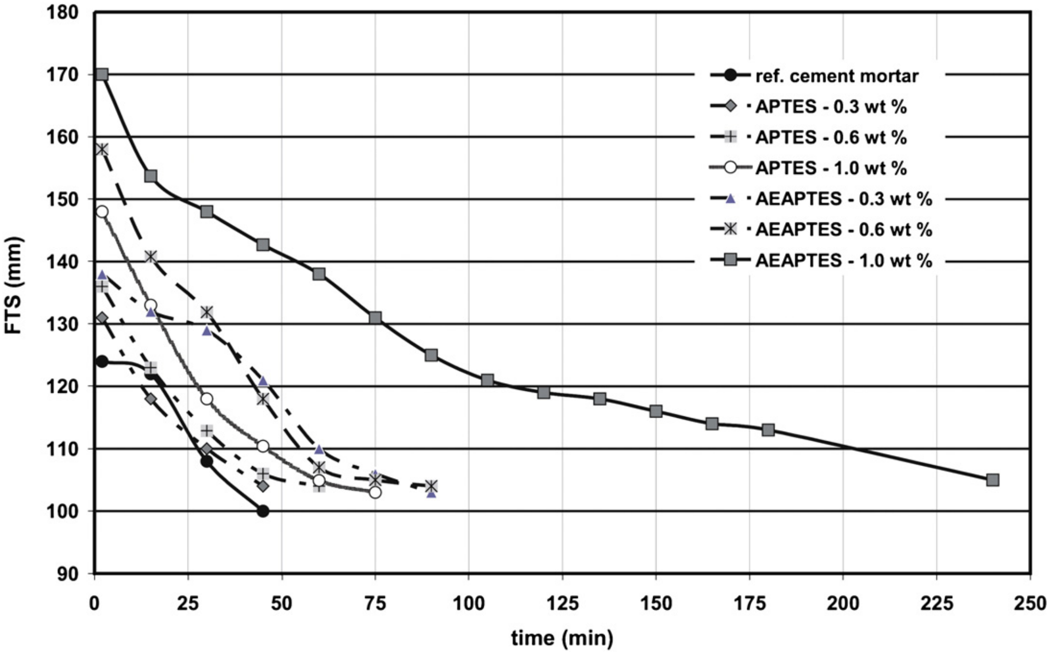


Fig. 5. Time dependence of flow table spread (FTS) for mortars prepared at constant w/c = 0.42 containing different amounts of APTES and AEAPTES aminosilane, respectively.

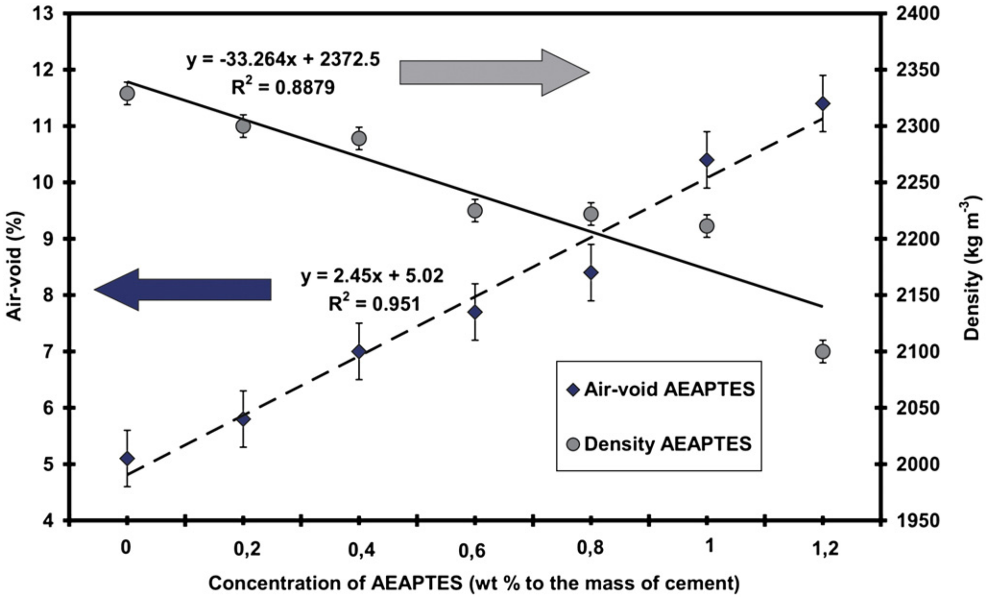


Fig. 6. Air-void content and density dependence of modified mortars on concentration of AEAPTES.

of air-void content, with the addition of small amount of antifoaming agent (0.5 g per whole batch of mortar) to the value of around 5%, was comparable to the value obtained for unmodified cement mortar.

3.2. Properties of hardened mortars — compressive and flexural strength

The complete results of compressive and flexural strength measurements on prisms of all types of mortars tested in this work are presented in Tables 5 and 6. The results in Table 5 show strength of mortars prepared without the adjustment of air-void content in the fresh mortar mix. The results in Table 6 present strength of mortars where air-void content was adjusted to the value of about 5% by adding an antifoaming agent. In general, the aminosilane modified mortars showed different strength development with time as compared to unmodified cement mortars.

a) Compressive and flexural strength of mortars with constant w/c
   As shown in Fig. 7a and b, the addition of APTES aminosilane to the cement mortar with constant w/c ratio of 0.42 exhibited negative influence on the development of compressive and flexural strength in the early age of hydration of cement. This effect was even more pronounced with mortars modified with AEAPTES aminosilane

Table 6
Compressive and flexural strength of mortars (constant air-void content 5 ± 1%) modified with different amounts of aminosilanes

Aminosilane		APTES					AEAPTES				Expanded uncertainty of measurement, $U=ku$
Amount of aminosilane in wt.% to the mass of cement		0	0.3	0.6	1.0	1.2	0.3	0.6	1.0	1.2	
w/c = 0.42		const.					const.				
Air-void ~ 5 ± 0.5%											
FTS (mm)		124	139	153	162	173	144	162	181	185	±5 mm
Compressive strength (MPa)	1 day	28.2	–	–	–	–	–	–	–	–	±1.9 MPa
	2 days	33.7	18.8	15.9	12.4	9.8	17.7	12.3	8.0	4.8	±1.2 MPa
	3 days	35.2	22.7	21.5	17.7	15.7	27.3	25.5	21.2	9.9	±1.5 MPa
	7 days	46.0	41.0	38.7	38.2	35.8	40.2	39.6	36.5	34.8	±1.6 MPa
	28 days	57.8	58.9	59.8	61.1	58.4	60.9	62.6	64.0	58.6	±1.9 MPa
Flexural strength (MPa)	1 day	4.8	–	–	–	–	–	–	–	–	±0.6 MPa
	2 days	5.3	3.7	3.0	2.6	1.7	4.0	3.4	2.2	1.6	±0.6 MPa
	3 days	6.2	4.7	3.8	3.5	2.4	4.8	4.0	3.6	2.5	±0.7 MPa
	7 days	7.2	6.3	5.7	5.5	4.5	6.5	6.3	6.0	4.1	±0.7 MPa
	28 days	7.8	8.6	9.3	9.9	8.5	8.9	9.5	10.0	8.5	±0.8 MPa
FTS ~ 150 ± 5 mm		const.					const.				
Air-void ~ 5 ± 0.5%											
w/c		0.51	0.43	0.41	0.39	0.37	0.40	0.38	0.37	0.38	
Compressive strength (MPa)	1 day	30.5	–	–	–	–	–	–	–	–	±1.9 MPa
	2 days	37.0	24.4	21.9	17.1	14.5	20.5	14.5	9.2	4.4	±1.2 MPa
	3 days	44.7	31.2	29.0	24.8	20.0	28.0	21.8	20.6	10.8	±1.5 MPa
	7 days	49.9	43.1	38.8	38.0	31.5	45.7	43.3	42.4	35.7	±1.6 MPa
	28 days	59.7	60.9	62.3	63.6	58.5	61.5	63.7	65.2	59.4	±1.9 MPa
Flexural strength (MPa)	1 day	5.4	–	–	–	–	–	–	–	–	±0.6 MPa
	2 days	6.2	4.4	3.8	3.0	1.8	4.1	3.5	2.5	1.7	±0.6 MPa
	3 days	6.8	4.7	4.0	3.6	2.3	5.5	4.8	3.6	2.3	±0.7 MPa
	7 days	7.9	6.3	5.8	5.7	4.6	7.4	7.2	6.7	4.9	±0.7 MPa
	28 days	8.9	9.4	9.8	10.3	9.2	9.7	10.9	11.5	9.7	±0.8 MPa

$U=ku$ — expanded measurement uncertainty of the method, where $k=2$ — which for Normal distribution corresponds to coverage probability of approximately 95% and u represents the standard uncertainty of the method determined according GUM [19].

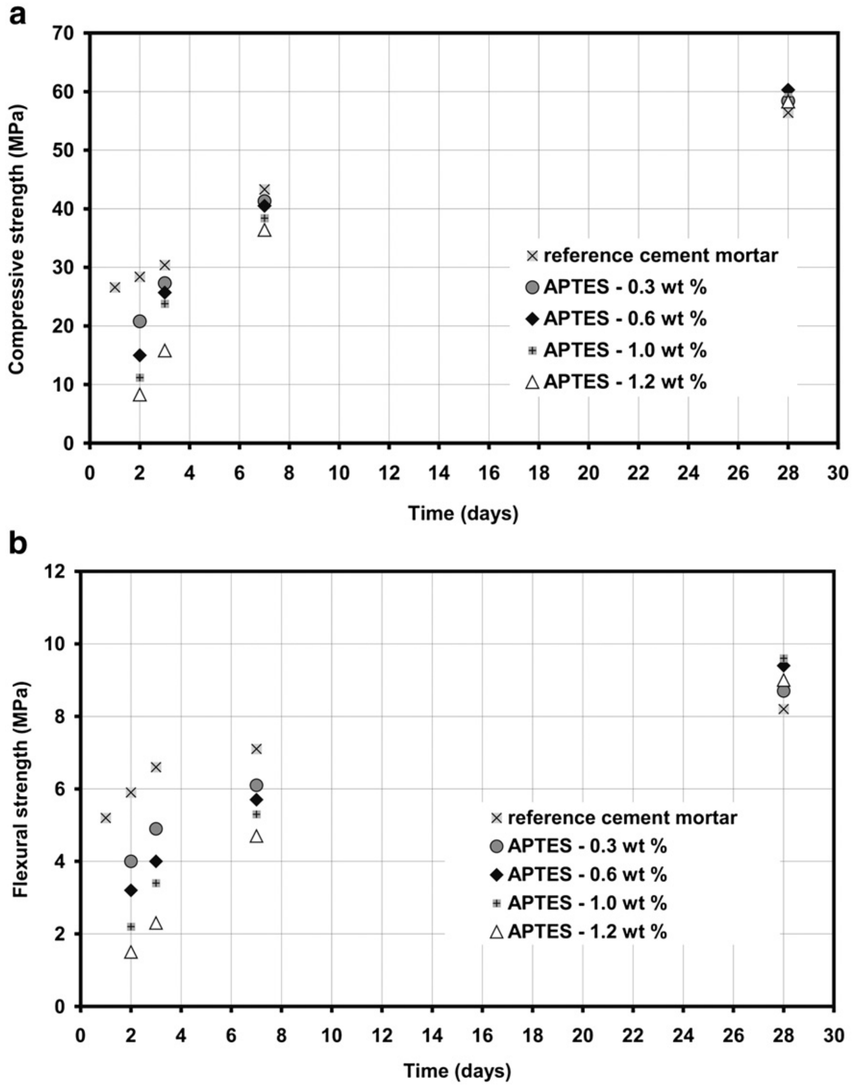


Fig. 7. (a) Compressive strength of mortars modified with different amounts of APTES prepared with constant w/c = 0.42 factor. (b) Flexural strength of mortars modified with different amounts of APTES prepared with constant w/c = 0.42 factor.

containing two amino groups. Slow strength development in the early age can be directly related to the retarding effect of aminosilanes observed by measurements of setting of cement (Fig. 3). For all modified mortars the strength after 1 day of curing was too low to be determined precisely with our measuring equipment. The compressive and flexural strength of aminosilane modified mortars measured after 2 and 3 days, and even after 7 days of curing was considerably lower as with neat cement mortar. However, during further curing, the strength development turned to the favor of modified mortars. Both, compressive and flexural strength of all aminosilane modified mortars determined after 28 days of curing surpassed the value for neat cement mortar (Tables 5 and 6). The analysis of data showed that the turning point in strength from negative to positive with respect to the values of neat cement mortar occurred in the time period between 14 and 24 days, depending on the amount and type of aminosilane added to the mortar.

b) Compressive and flexural strength of mortars with constant FTS
The compressive and flexural strength development of mortars with constant FTS (Fig. 8a and b) exhibited similar patterns as with mortars prepared at constant w/c ratio, but more than 10% higher values. The main reason for higher strength was lower w/c ratio due to the plasticizing effect of aminosilane molecules. When adding APTES or AEAPTES less water was needed to reach desired workability of mortars with FTS of about 150 mm (Tables 5 and 6). The positive effect of aminosilane on workability of fresh cement mortars resulted in high flexural strength determined after 28 days of curing. Measured values for flexural strength of modified mortars with constant FTS were considerably higher as for mortars with constant w/c ratio (Tables 5 and 6). The highest value for 28 days flexural strength of about 11.5 MPa was measured for mortar mix, which was modified with 1.0 wt.% of AEAPTES aminosilane.

It is important to note that compressive and flexural strength of all modified mortars determined after 28 days of curing exhibited higher values as with reference cement mortar in spite of increasing amount of air-void content in the fresh mortar mix (Fig. 3 and Table 5). As presented in Table 6, the strength of mortars prepared with constant w/c or constant FTS, which air-void content was adjusted to about 5%, exhibited only slight increase in comparison to mortars with the initial air-void content presented in Table 5. Analysis of these results showed that air entrainment into fresh mortar mix did not substantially influence the strength of modified mortars after 28 days of curing. This finding was quite different from the experience with other air-entraining agents published in the literature [18], which showed that an increase in air-void content resulted in considerable loss of strength.

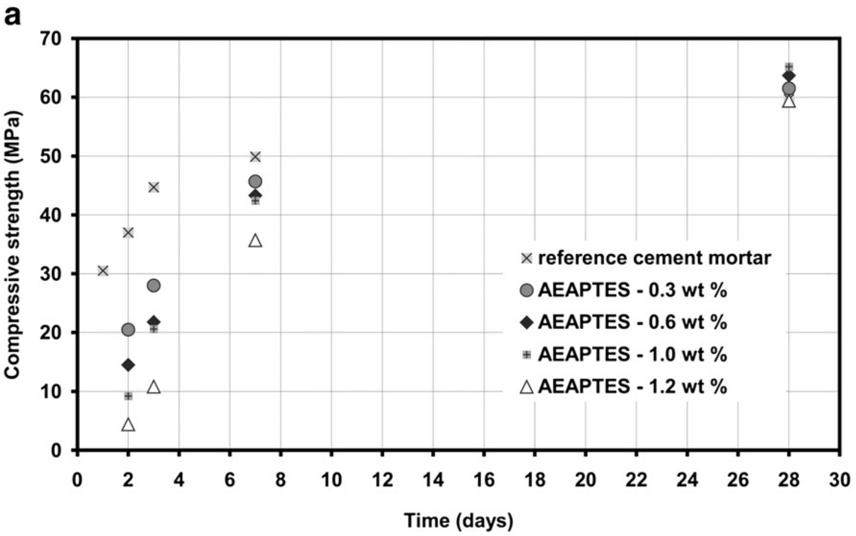
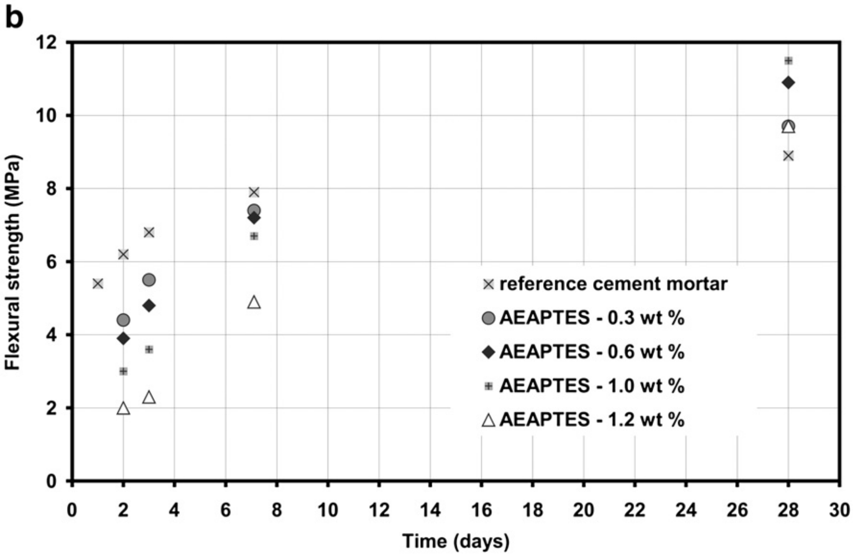


Fig. 8. (a) Compressive strength of mortars modified with different amounts of AEAPTES prepared with constant flow table spread (FTS ~150 mm). (b) Flexural strength of mortars modified with different amounts of AEAPTES prepared with constant flow table spread (FTS ~150 mm) and constant air-void content of about 5.0%.



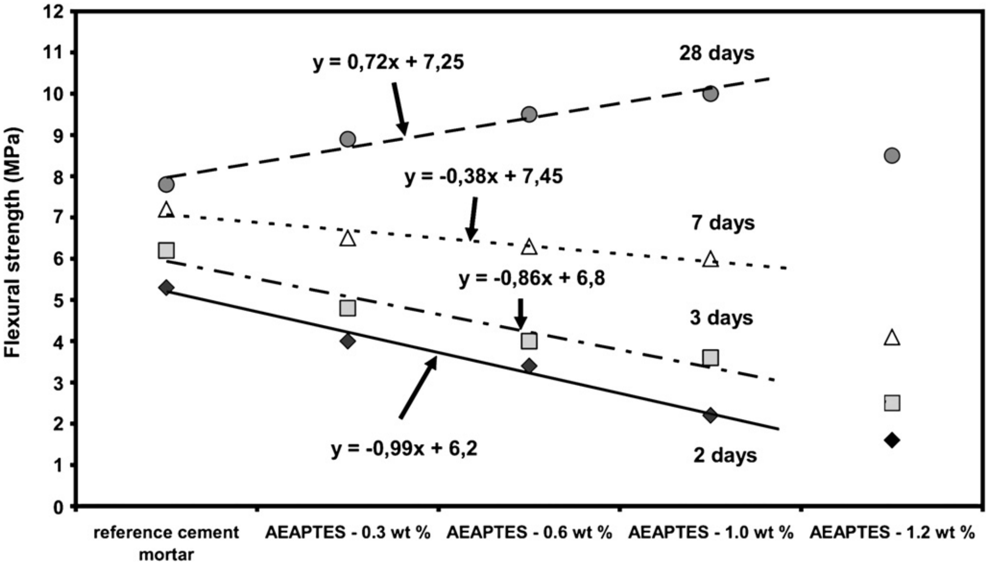


Fig. 9. Linear relations between flexural strength measured after 2, 3, 7 and 28 days and concentration of AEAPTES aminosilane added to the mortars which were prepared at constant flow table spread (FTS ~150 mm) and constant air-void content (~5%).

The plots in Fig. 9 show linear relations between flexural strength of mortars modified with AEAPTES measured after 2, 3, 7 and 28 days of curing and the amount of aminosilane in the range from 0 to 1.0 wt.% of AEAPTES. The slope of the line is an indicator for the influence of aminosilane concentration on flexural strength development during curing of mortars. As shown in Fig. 9, the transition from negative to positive influence of AEAPTES aminosilane concentration on flexural strength development of modified mortars with constant FTS is presented with an increase of slope from negative value of −0.99 for 2 days flexural strength up to positive value of about 0.72 for 28 days flexural strength.

The benevolent influence of aminosilanes on 28 day strength of mortars is related to the key function of the silanol and amino groups attached to the aminosilane molecular skeleton. The silanol and amino groups strongly interact with the cement gel which is formed as the hydration product of Portland cement. The results of compressive and flexural strength support the mechanism of strong chemical interaction between aminosilane species and inorganic phases of the cement system.

4. Conclusions

The aminosilanes as APTES and AEAPTES containing one and two amino groups, respectively, strongly interact with mineral phases of the cement system. The results of this study showed that aminosilanes when added to the cement system strongly influence different macroscopic properties of fresh and hardened cement mortars:

- workability of cement mortar, by improving the workability;
- water demand of cement, by decreasing the w/c factor;
- setting of cement, by strongly retarding the hydration processes;
- compressive strength, by delaying the early strength development and increasing the compressive strength after 28 days of curing for more than 5% in comparison to reference cement mortar;
- flexural strength, by delaying the early strength development and considerably increasing the flexural strength measured after 28 days of curing for more than 20% in comparison to the reference cement mortar.

Although, already small amounts of aminosilanes considerably improve workability, lower the w/c factor and show positive effect on long term flexural strength, the main challenge for the future remains to overcome the retardation in setting if cement, before they can be a useful product for the modification of cementitious materials. The positive effect on flexural strength after 28 days of curing constitutes an encouragement to solve the retardation issue.

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