Use of Aminosilane Coupling Agents in Cementitious Materials

Franc Švegl, Jerneja Šuput-Strupi*

Slovenian National Building and Civil Engineering Institute, Dimičeva 12, SI-1000 Ljubljana, Slovenia
Fax: (+386) 1 2804484; E-mail: franc.svegl@zag.si

Summary: The work presented in this paper has been focused on the evaluation of the influence of the addition of aminosilanes like γ-aminopropyltriethoxysilane (3-AMPS) on physical and mechanical properties of fresh and hardened polymer modified cement mortars (PMCMs), which contained also mineral fillers like fumed silica and blast furnace slag. The role of the aminosilane in cementitious system was to produce surface modification and covalent bonding among different inorganic phases of inorganic matrix (cement, aggregate, fumed silica) and strong chemical interaction between inorganic matrix and organic (polymer) phase of the mortar. The strong chemical bonding of inorganic matrix and polymer phase transformed composite mortar into cementitious material with more like monolithic structure. Mortars with the addition of aminosilanes showed improved physical-mechanical properties like bending strength, adhesion to concrete, and lower dry-shrinkage.

Keywords: aminosilanes; 3-AMPS; coupling agents; fumed silica; polymer mortars

Introduction

The repair of surface damaged concrete is usually accomplished with composite polymer modified cement mortars (PMCM's) consisting of series of constituents, which proportions determine mortars final properties. Nowadays is very popular to modify cement mortars with powdered acrylic or vinyl acetate based polymers and different types of fibers for reinforcement.[1,2] To achieve good performance of PMCM's a special attention should be devoted to ensure homogenous distribution of polymer powder and fibers in freshly prepared mortars. The addition of mineral fillers with pozzolanic activity, as fumed silica, blast furnace slag, and fly ash has significant effects on the physical and mechanical properties of cementitious materials. Fumed silica considerably improves compactness of cement based materials, which results in improvement of various properties like higher compressive strength, higher abrasion resistance, and lower

 DOI: 10.1002/masy.200550316

permeability of water and chemically aggressive substances. However, on the other hand, the negative influence of the silica fume is shown in increased drying shrinkage and lower workability of the fresh mortar or concrete.[3] An additional problem in designing of concrete and mortar mixtures containing mineral fillers poses rather low hydraulic activity of fumed silica and fly ash, which is much lower than that of Portland cement minerals.[4,5] To overcome these obstacles different organic admixtures are added to the fresh mortars, which predominately act as surface modifiers of cement and sand particles.[4] It has been shown that treatment of silica fume with mixture of Z-6020 and Z-6040 Dow Corning (Midland, MI) silane coupling agents improves physical and mechanical properties of fumed silica cement.[6] The basic idea of using silanes in cement based systems was taken from polymer composites where they serve as surface modifiers and coupling agents between polymer and mineral phase.[7,8] The use of aqueous amino silanes as an admixture to cement paste or cement mortar showed that they can completely substitute classical water-reducing agents with the additional improvement of workability, tensile and compressive strength, as well as some other physical and mechanical properties.[6,9-11] The combination of epoxy and amino silane coupling agents was successfully applied as an admixture to improve the degree of dispersion of carbon and steel fibers in fiber reinforced cement based composites.[1,2] The ability of aminosilanes to make covalent bridging between inorganic phases (e.g. cement, stone, fumed silica, slag) and strong chemical interaction between inorganic and organic phases (e.g. cement-polymer, fumed silica-polymer) to bind them together and form monolithic like structure makes them promising new type admixtures for cementitius materials. Concrete and mortars with the addition of aminosilanes are expected to show improved physical and mechanical properties such as lower water/cement ratio, higher flexural strength, better adhesion, lower shrinkage, better thermal conductivity, and better resistance to different sources of corrosion.

The main aim of this work was to evaluate the influence of the addition of water soluble γ-aminopropyl-triethoxysilane (3-AMPS) on physical and mechanical properties of fresh and hardened polymer modified cement mortars, which contained powder form ethylene-vinyl acetate (EVA) type polymer and mineral fillers like fumed silica and blast furnace slag. The laboratory testing of macroscopic physical and mechanical properties was accomplished according to the standard procedures for testing of mortars and cement (EN 1015, EN 1766, EN 196-1, and EN 196-3).

Experimental

Materials - The dry polymer modified mortar mixtures with different composition were prepared from Portland cement (CEM II/A-S 42,5 R, Cementarna Anhovo), fine quartz type aggregate, poly (ethylene-vinyl) acetate polymer (EVA), appropriate amount of fumed silica, and polypropylene fibers. The physical and mechanical properties, and chemical composition of Portland cement, CEM II/A-S 42,5 R, complied with the demands of standard EN 197-1. The fumed silica (FS) used was a dry uncompacted powder, which was applied as a partial replacement of cement by weight. The minimum content of SiO_2 in the fumed silica was 94 wt.%, the rest were iron and aluminum oxides. The polymer used for the modification of cement mortar was a milky-white powder of EVA having specific gravity of 1,150 g/cm^3 (20°C). The aminosilane coupling agent used as an admixture to PMCMs (up to 1 wt% to mass of cement) was liquid γ-aminopropyl-triethoxysialne (3-AMPS, Aldrich). The aminosilane was hydrolyzed prior the addition to cement based system at room temperature (at about 25°C) in highly alkaline environment and then polycondensed at elevated temperatures at 80°C for 4 hours to obtain colloidal solutions of pre-defined hybrid organic-inorganic particles or nanobuilding blocs (NBBs). Some of the mortars were reinforced with polypropylene fibers (PP) with the length of around 6 mm. Tensile strength of fibers was ranging between 540 to 750 MPa, their modulus of elasticity was around 3,400 MPa, the melting point was at 160°C and specific gravity was 0,91 g/cm^{-3}. A commercial melaminformaldehyde based superplasticizer (WRA) (ZETA PLUS, TKK Srpenica) powder was added to the mortar mixtures containing fumed silica to obtain a nominal slump or workability of around 160 mm.

Preparation of mortar - The fresh mortar mixtures with different formulation (Table 1) were prepared from dry premixed components in a stationary turbine mixer (Toni Technik/ToniMIX). The volume of the cementitious materials was held constant regardless of the aggregates and admixtures used. The water-cement ratios (w/c) ranged from 0,56 to 0,42. The mortars were mixed for 10 min. The sequence of batching and times of mixing were as follows: (i) mixing of dry mortar mixture (cement, coarse/fine aggregate, powder form admixtures, PP fibers and silica fume) for 2 min; (ii) adding water and mixing for 1 to 2 min; (iii) determining unit weight, slump, and air content; (iv) adding balance of water, and mixing for 2 min. The mass of the aggregate was determined in dry base, and the aggregate was then soaked in water for 24 h prior to mixing.

Preparation and curing of test samples for laboratory testing - Mortar prisms with dimensions 40 x 40 x 160 mm were molded for determination of compressive and flexural strength, and for determination of linear deformations. All the specimens were de-molded after curing in the chamber with relative humidity over 80% at 20 ±3 °C for 24 h. After de-molding, the prisms were cured under water at 20 ±3 °C for 3, 7, 28, and 90 days and for additional 7 days in air with 50 wt.% relative humidity prior to strength tests.

Testing of mechanical properties - The laboratory testing of compressive and flexural strength was performed in the Toni Technik/Toni Norm press. Measurements were accomplished according to the procedures described in standard EN 12190 and EN 196-1. The bonding strength of mortars with concrete plates with known characteristics was measured in a three point pull-off machine Josef Freundl Typ F15D EASY M.[11] Mortar samples were applied by hand in thickness up to 20 mm on standard reference concrete specimens prepared according to the procedure described in standard EN 1766. The method of test is by direct dolly pull-off using a circular dolly (diameter 50 mm) bonded to the surface of the applied mortar. The testing procedure is thoroughly described in standard EN 1542.

Specific heat - A Setaram Labsys DSC 131 Differential Scanning Calorimeter was used for measuring the specific heat of cement mortars containing polymer, silica fume and coupling agent. Sapphire was used as a reference material. The samples were taken from cured mortar prisms by cutting out small cylinders with diameter and height of around 3 mm. The sample weight was around 45 mg. The measurements were performed in the range from 25°C to 700°C at heating rate 10°C/min in Ar atmosphere (flow rate 10 ml/min).

Microstructural examination - Scanning electron micrographs of mortars were obtained on Jeol JSM-5500 LV scanning electron microscope at high or low vacuum. The cured prism samples of examined mortars were carefully fractured approximately at the middle of their length, applying minimum pressure to reduce the number of artificially generated cracks. The small cubic samples with dimensions 1 x 1 x 1 cm were prepared by cutting using an electric saw. Upon that some of the specimens were placed in plastic molds and vacuum saturated with low viscosity epoxy resin for 4 hours and subsequently placed in an oven set at 70°C to cure the epoxy. After the epoxy was fully cured, one face of the specimen was exposed by using a precision saw operated at low speed. The exposed face was ground and polished using cloth impregnated with diamond of successively finer sizes down to 0,25 μm. The exposed sample surface was coated with gold for examination under a scanning electron microscope equipped with an energy depressive X-ray analyzer.

Table 1. Mix proportions of dry powder mortars.

Mortar mixture	C/A*	EVA, wt. %**	Fumed silica, wt. %**	PP fibers, wt. %**	3-AMPS, wt. %**	WRA, wt. %**
CM	1/3	-	-	-	-	-
PM	1/3	5	-	-	-	-
PMA	1/3	5	-	-	0,6	-
PMSF	1/3	5	10	-	-	1,5
PMSFA	1/3	5	10	-	0,6	-
PMSFPPF	1/3	5	10	0,5	-	1,5
PMSFAPPF	1/3	5	10	0,5	0,6	-

* - C/A is a ratio between cement and aggregate.

** - All materials are expressed in wt. % with respect to the mass of cement.

CM - reference cement mortar containing only Portland cement CEM II/A-S 42,5 R and fine type quartz aggregate without any additives.

PM - polymer modified cement mortar.

PMA - polymer modified cement mortar containing 3-AMPS coupling agent.

PMSF - polymer modified cement mortar containing fumed silica filler and water reducing agent (WRA).

PMSFA - polymer modified cement mortar containing fumed silica and3-AMPS coupling agent.

PMSFPPF - polymer modified cement mortars containing fumed silica, PP fibers and water reducing agent (WRA).

PMSFAPPF - polymer modified cement mortars containing fumed silica, 3-AMPS coupling agent and PP fibers.

Results and Discussion

Workability – The workability of mortars was determined at constant water/cement ratio (w/c) of around 0,55 by the slump test described in the standard EN 1015-3. The results in Table 2 show that the addition EVA polymer increases the workability of mortar according to expectations and in agreement with the data from the literature.[12] The high demand for water of the fumed silica and resulting decrease of mortar workability was compensated by the addition of water reducing agent (WRA). The addition of 3-AMPS increases the workability of polymer modified mortar and even more of polymer modified mortar containing mineral admixtures such as fumed silica and blast furnace slag. The workability of mortars containing aminosilane (up to 0,6 wt.% by weight of cement) was better than the mix with as-received silica fume and water reducing agent (1,5 wt.% by the amount of cement). With coupling agent and water-reducing agent in the amount of 0,1 wt.% by the amount of cement, the workability was better as with mortars containing fumed silica and only water-reducing agent in the amount of 1,5 % by weight of cement. The results showed that it is possible to completely substitute superplasticizer (WRA) by an aminosilane additive. The high workability of mortars containing aminosilane can be explained by its hydrophilic nature due to the presence of amino and hydroxide groups.

Table 2. Properties of fresh mortars.

Mortar mixture	Slump, mm	Unit weight, kg dm^{-3}	Air void content, %
CM	132	2,17	5,1
PM	154	2,06	6,8
PMA	182	2,14	5,1
PMSF	155	2,01	9,1
PMSFA	188	2,19	4,2
PMSFPPF	175	2,04	6,9
PMSFAPPF	183	2,18	4,3

Air void content and density – The air void content and density of mortars were determined by the procedures described in standard EN 1015-6,7. The most pronounced increase in air-void content was observed by adding fumed silica to the mortar (Table 2). The accompanying effect is a decrease in density of fresh mortars. The addition of aminosilane decreased the air void content of mortars containing fumed silica for more than 100 %, which resulted in considerable increase of density of the fresh mortar mixtures. The explanation for this effect is in surface modification of cement and sand particles by aminosilane molecules, which enables strong chemical interaction between mineral-mineral and mineral-polymer phases resulting in more compact structure with less air entrapped in the solid matrix.

Mechanical properties – As shown in Figure 1 and 2 for mortars after 3, 7, 28, and 90 days of curing under water and 7 days in air, the compressive strength and bending strength are increased in early stage of hydration of the cement. A considerable decrease in compressive strength of polymer modified mortar, PM, was observed after longer time period (90 days). This shows the degradation of EVA polymer in highly alkaline environment of cement. The addition of fumed silica (10 wt.% by weight of cement) increased the compressive strength as expected.[13] The presence of 3-AMPS in polymer modified mortar improved the stability of EVA polymer and its performance with time. In general, the compressive strength was not much affected by the addition of aminosilane to the mortars (Figure 1). However, the bending strength of all mortars was considerably increased when 3-AMPS was present. The bending strength after 28 days for mortars containing 3-AMPS was increased for more than 60 % in comparison to reference cement mortar (CM). The addition of 3-AMPS to the mortars containing PP fibers (up to 0,5 wt. % to the mass of cement) improved the homogeneity in dispersing of fibers through the whole volume of the mortar, which resulted in additional improvement of bending strength. It is assumed that the hydrocarbon part in H_2N-CH_2-CH_2-CH_2- chain of 3-AMPS influenced the wettability of the PP fibers and that the chemical affinity of cementitious system to polypropylene was improved.

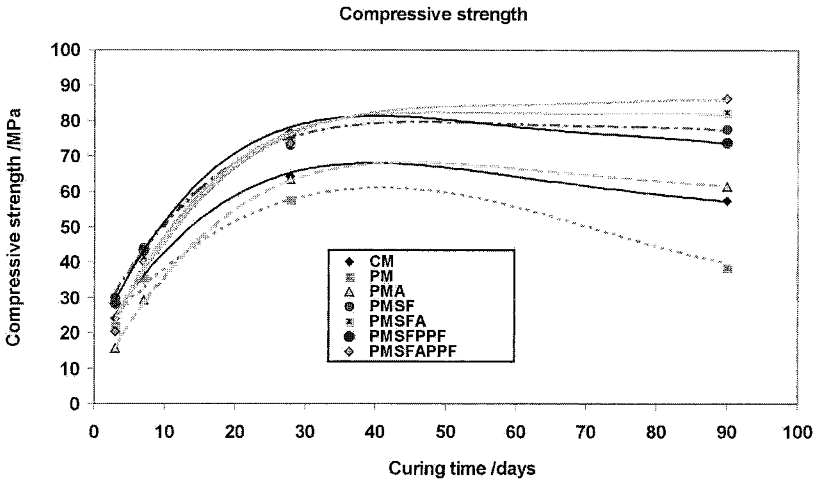

Figure 1. Compressive strength of mortars after 3, 7, 28, and 90 days curing under water and additional 7 days in air.

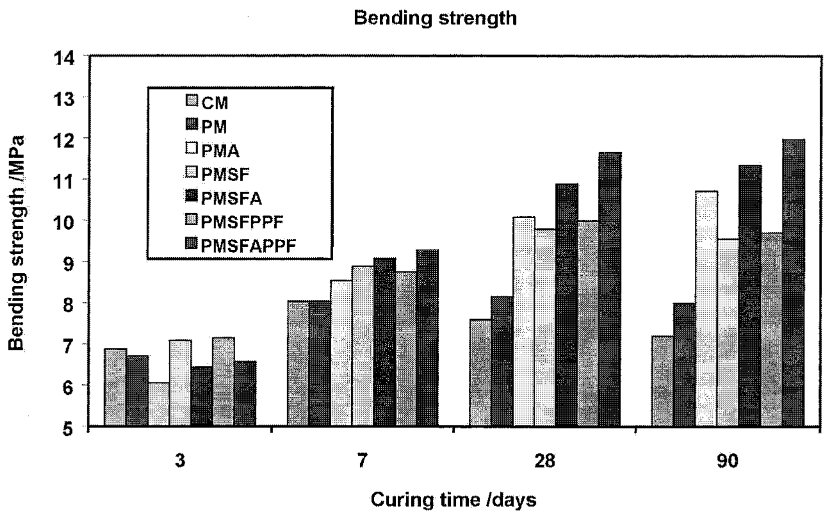

Figure 2. Bending strength of mortars after 3, 7, 28, and 90 days curing under water and additional 7 days in air.

Drying shrinkage – The results of the measurements of linear deformations of mortar prisms after drying in air for 28 days showed that the addition of EVA polymer and fumed silica reduced the drying shrinkage (Table 3). The addition of aminosilane has an additional beneficial effect on drying shrinkage by reducing linear deformations of prisms for more than 40 %. The formation of covalent chemical bonds of 3-AMPS at the interfaces of inorganic phases compensates stresses occurring due to different shrinkage characteristics of the mortars components.

Specific heat – The results of specific heat measurements by DSC of cement pastes modified with the same amount of additives showed that the addition of polymer and fumed silica increased the specific heat of mortars depending on the amount of added modifier (Table 3). When aminosilane was added to the cement paste the formation of the network of covalent bonding between particles of cement greatly contributes to the absorption of energy due to the increased amount of phonon vibrations. This resulted in considerable increase of specific heat, which was above 0,6 wt. % of added 3-AMPS to the mass of cement independent on the amount of added aminosilane.

Table 3. Linear deformations of mortars after 28 days drying in air and specific heat of cement pastes with the addition of polymer, fumed silica, and aminosilane.

Mortar mixture	Linear deformations, mm/m	Specific heat, J/g K
CM	-0,95	0,698
PM	-0,84	0,746
PMA	-0,67	0,883
PMSF	-0,90	0,921
PMSFA	-0,53	1,121
PMSFPPF	-0,74	0,933
PMSFAPPF	-0,45	1,119

Adhesion to concrete – The results of adhesion testing with pull-off method showed that the addition of fumed silica considerably improved the bonding properties of mortars to concrete substrate. This positive effect can be attributed to the fact that fine particles of fumed silica easily fill the pores of concrete even few millimeters into the bulk, which increased the contact surface area of mortar with concrete. The addition of the aminosilane coupling agent dramatically improved the adhesion of the mortars to concrete (Figure 3). This showed that 3-AMPS enabled even more efficient contact and stronger bonding between the particles of mortar and concrete substrate. The visual assessment of the type of failure categorized according to the standard EN 1542 showed that with all specimens containing silica fume and aminosilane cohesion failure in the concrete substrate (type A) occurred.

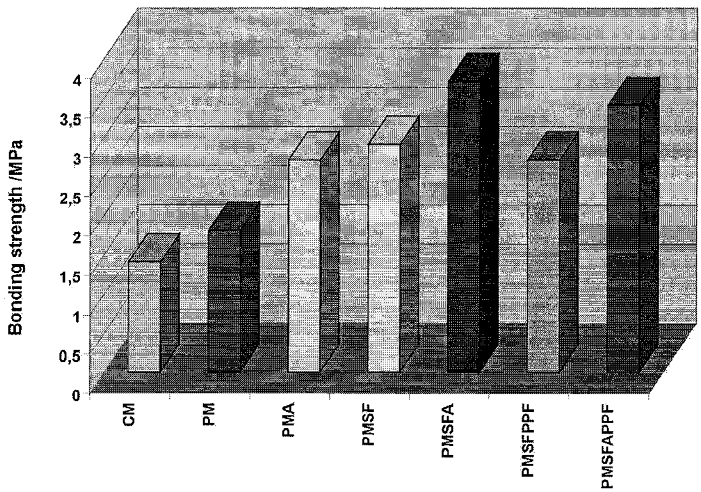

Figure 3. Pull-off results of mortars deposited on concrete panels obtained after 28 days.

Morphology - SEM micrograph of polymer mortar containing fumed silica (PMSF) (Figure 4a) showed rather compact structure with small cracks appearing between aggregate particles and cement matrix. From the SEM micrograph of the mortar containing fumed silica and aminosilane (PMSFA) (Figure 4b) it can be seen that almost all the voids and cracks disappeared. The borders between stone particles and cement phase are less distinct as with mortars without the addition of aminosilane. This indicates that coupling agent improved the adhesion between neighboring particles and bound them together into three-dimensional, dense, monolithic like structure.

(a) (b)

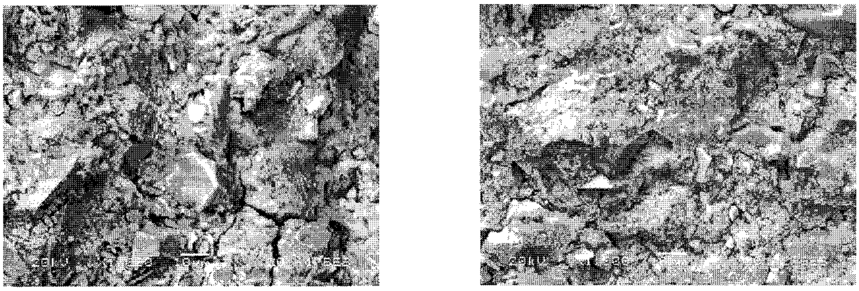

Figure 4. (a) SEM micrograph of the polymer mortar containing fumed silica (PMSF). (b) SEM micrograph of the polymer mortar containing fumed silica and aminosilane (PMSFA).

Conclusions

The incorporation of mineral fillers with pozzolanic activity as fumed silica had great positive impact on physical and mechanical properties of polymer modified cement mortars. An additional beneficial effect was obtained by introduction of aminosilane additives based on 3-AMPS. The introduction of aminosilanes as surface modifiers and coupling agent was a new approach in modifying of cementitious systems. The major impact of the addition of 3-AMPS was observed in improving bending strength, drying shrinkage and adhesion properties of mortars to concrete.

Acknowledgments

The authors gratefully acknowledge the financial support from Ministry of Education, Science and Sport, Slovenia. This work was accomplished in the scope of the project L2-4520.

[1] Y. Xu, D. D. L. Chung, *Cem. Cocn. Res.*, **1999**, 29 (5), p.773.
[2] J. Cao, D. D. L. Chung, *Cem. Cocn. Res.*, **2001**, 31, p.309.
[3] J. M. Gao, C. X. Qian, B. Wang, K. Morino, *Cem. Conc. Res.*, **2002**, 32 (1), p.41.
[4] F. Massazzana, M. Moranville-Regourd, P. Fidyestøl, R. Lewis, in *"Leas's Chemistry of Cement and Concrete"*, Ed. by P. C. Hewlett, 4th Edition, Arnold, 1998, Chapter 10-12, p.471.
[5] H. F. W. Taylor, *"Cement Chemistry";* Academic Press, London, 1990, Chapter 7, p.199.
[6] Y. Xu, D.D.L. Chung, *Cem. Conc. Res.*, **2000**, 30, p.1305.
[7] E. P. Plueddemann, *"Silane Coupling Agents"*, Plenum Press, New York, 1982, Chapter 3, p.49.
[8] A. V. Pocius, *"Adhesion and Adhesives Technology"*, Carl Hanser Verlag, Munich, 2002, Chapter 6, p.153.
[9] F. Švegl, J. Šuput-Strupi, *Proceeedings of the Worshop in Chemistry*, Maribor, Slovenia, 20-21 September **2001**, p.630.
[10] F. Švegl, J. Strupi-Šuput, S. Kadunc-Kodra, J. Grdadolnik, *Proceedings of the Workshop in Chemistry*, Maribor, Slovenia, 26. and 27. September, **2002**, p. 845.
[11] F. Švegl, J. Strupi-Šupput, *Proceedings EUROFILLERS 2003,* Alicante, Spain, 8-11 September, **2003**, p. 203.
[12] M. U. K. Afridi, Z. U. Chaudhary, Y. Ohama, K. Demura, M. Z. Iqbal, *Cem. Conc. Res.*, **1994**, 24, p.1199.
[13] Z. Bayasi, J. Zhou, *ACI. Mater. J.*, **1993**, 90, p.349.