INFLUENCE OF ANTI-FOAMING ADMIXTURE AND POLYCARBOXYLIC SUPERPLASTICIZER TYPE ON FRESH AND HARDENED PROPERTIES OF SELF-COMPACTING MORTAR

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A b s t r a c t

Research results proved, that some type of superplasticizers (SP) show air-entraining functioning. In order to counteract the excessive air-content in self-compacting mortar the anti-foaming admixtures (AFA) can be applied. Verification of the influence of type, amount and introduction manner of AFA and two type of polycarboxylic SP on air-entrainment, rheological properties and stability of the self-compacting mortar are described in the paper. The research results showed, that the SP and AFA type influence significantly investigated properties of fresh mortars. The hardened properties of the mortars were also investigated. Research results showed, that the AFA type does not influence significantly compressive strength of mortars. The compressive strength of mortars incorporating AFA is similar to mortar with "non air entraining" SP. Moreover, AFA increases significantly the flexural strength of mortar. SEM (*Scanning Electron Microscopy*) research results showed clearly that admixtures type influence significantly SCC microstructure and values of porosity structure parameters investigated according to EN 480-11.

S t r e s z c z e n i e

Wyniki badań wykazały, że niektóre rodzaje superplastyfikatorów (SP) wykazują się działaniem napowietrzającym. W celu przeciwdziałania powstania nadmiernej zawartości powietrza w samozagęszczalnej zaprawie można stosować domieszki przeciwpieniące (AFA). Podjęto badania celem weryfikacji wpływu rodzaju, ilości oraz sposobu dozowania AFA oraz dwóch rodzajów polikarboksylowych SP na napowietrzenie, właściwości reologiczne i odporność na segregację samozagęszczalnych zapraw. Rezultaty badań dowodzą, że rodzaj AFA i SP wpływa istotnie na badane właściwości świeżej zaprawy. Badano także właściwości stwardniałych zapraw. Wyniki badań wykazały, że rodzaj AFA nie wpływa znacząco na wytrzymałość na ściskanie zapraw. Wytrzymałość zaprawy wykonanej z udziałem AFA jest podobna do wytrzymałości zaprawy wykonanej z „nienapowietrzającego" SP. Ponadto wyniki badań dowiodły, że AFA bardzo istotnie wpływa na wytrzymałość na zginanie zapraw. Wyniki analizy SEM udowodniły, że rodzaj domieszki ma zasadnicze znaczenia dla mikrostruktury SCC i wartości parametrów struktury porowatości według EN 480-11.

Keywords: **Anti-foaming admixtures (AFA); Superplasticizer (SP); Workability; Air-content; Compressive strength; Flexural strength; SEM; Porosity structure parameters.**

1. INTRODUCTION

In case of self-compacting concrete, air entrainment of the concrete mix as well as adequate values of porosity structure parameters are problematic issues of the concrete mix self compaction [7], [14], [17]. Considerable fluidity of self-compacting concrete mix, air bubbles, presented in air entrained concrete mix, can be unstable because of floating and coalescence of air bubbles or fading of bubbles diameter less than 0.10 mm [2], [3], [4], [9].

Moreover, on the basis of different tests concerning self-compacting concrete mixtures, the authors found out too high air content in concrete volume, which was the result of high range of water reducer (SP) presence [7], [14], in spite of meeting the criteria [1].

The molecules of SP should also modify the surface of solid particles in order to keep its hydrophilic character. The air bubbles can adhere only to hydrophobic surfaces.

Superplasticizers belong to widely understood group of surface-active substance. Most of the superplasticizers molecules are elongated, asymmetric, have red and blue poles, and because of this a constant dipolar moment. One part of the molecule is usually positively charged hydrophobic hydrocarbon group, another part is negatively charged hydrophilic group. Anion, placed at the end, is directed towards liquid phase, causing repellent effect (Fig. 1). This effect is connected with hydrophilic acting of superplasticizer.

Depending on the chemical base of superplasticizers, they can produce different effects in the concrete mix (Fig.1) [5],[6],[10],[11]:

- Creating "grease" layer on the cement and grains of micro-filler, decreasing internal friction of concrete mix (SMF – sulfone melamine-formaldehygenic resin),

- Surrounding grains of cement with negative charge, causing their mutual repulsion (SNF – sulfone naphtelene-formadelhygenic resins), the type of superplastcicizer dictates the value of molecules dispersion force, whose measure is jeta surface potential, with the value increase of this potential, the force of molecules dispersion increases,

- Decreasing of surface water tension in relation to cement and micro-fillers (MLS – modified lime or sodium lingisulfones; other products are: copolymers of formic acid with naphtylic-sulfone acid,

copolymers of methacrylate acid with sodium salt or polyethylene glycol),

- Sterole – they create long chains of polymer, physically precluding the cement grains to approach each other (new-second-generation of fluxing admixtures; substances from the polycarboxylants group (pc), copolymers of acryl acid with acrylate (CAE) and not acryl resins (CLAP)). Such work results in a situation where admixtures of new generation function "preventively" – instead of smashing already formed cement grains agglomerates, they do not allow their forming.

The presence of listed functional groups (oxygen in form of etheric group (-0-), hydroxyl group (-OH) and carboxyl group) produce water surface tension decrease, producing flocculation of associated molecules and increase in moisture content of not only grains of cement but also the whole mineral framework [5].

In the superplasticizers group there are ones that show only dispergation functioning not decreasing surface tension. They are, f.e.: hydrocarboxylen acid salts, sulphonic melamine-formaldehygenic resins, formaldehygenic picodensats salts of beta-naphtalensulphonic acid [5].

As the author shows in his publication [6], air bubbles formed by hydrophilic surface active compounds should not adhere to cement and grains of aggregate, being uniformly dispersed in concrete mix (Fig. 2). Moreover, according to the author [5] these bubbles are slightly bigger than those formed as a result of air-entraining admixture functioning, but their stability is lower. Air bubbles formed as a result of air-
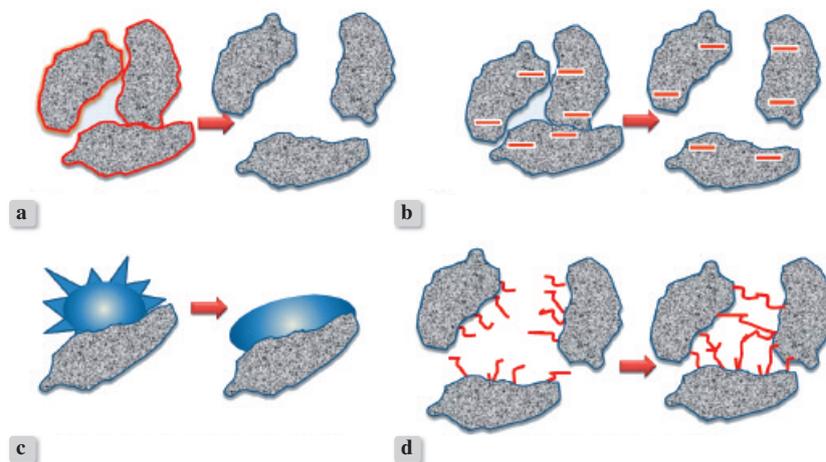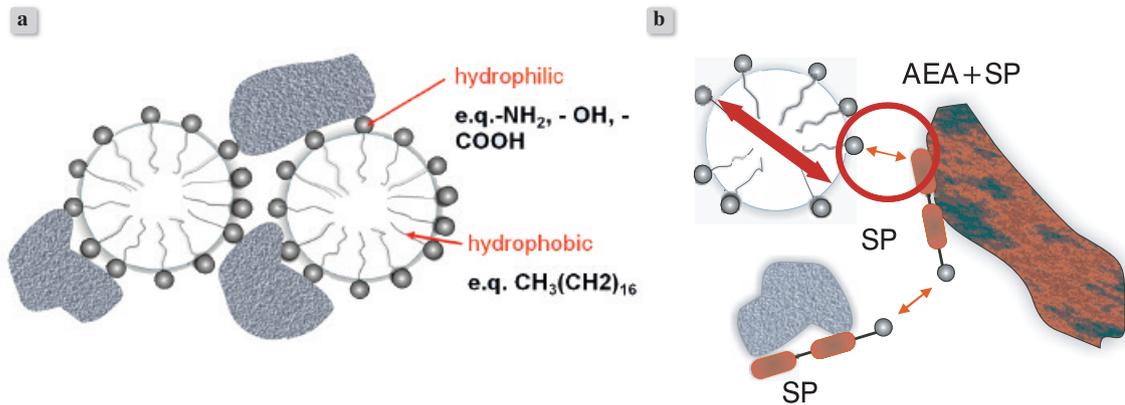

Figure 1.
Types of superplasticizer action: a) creating "grease" layer b) surrounding grains of cement with negative charge, c) decreasing surface water tension d) long chains of polymer, physically precluding the cement grains to approach each other [11]
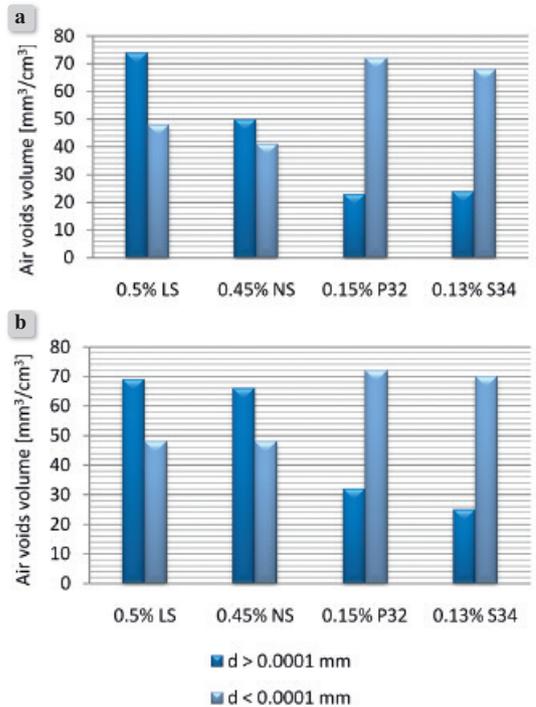
Figure 2.
a) adsorption of the flux molecules framework in the grains of cement and the negative effect of the anion final group; b) diagram of arrangement of cement –water and aggregate–cement-water arrangement, with the use of air-entraining mean (surface active anion substance) [6]

entraining admixtures functioning, reach the size of $20 \div 250$ μm. Moreover, they adhere to the surface of particles of cement (Fig. 2b). During hardening of concrete, formed pores are not fulfilled with the products of hydration, because C-S-H gel can form only in water. From the point of view of freeze-resistance of concrete it would be the best if the air voids were of $0.05 \div 0.10$ mm diameter and they are located in the volume of paste in spacing of $0.15 \div 0.20$ mm from each other. Although the problem of critical value of pores spacing in freeze-resistant concrete, depending on its type, is still taken into consideration [10].

The type of superplasticizer according to [12] is crucial regarding the size and proportions of air pores participation, gained as a result of its functioning, although the time of concrete hardening is of no importance for further changes of these proportions (Fig. 3). With the use of polycarboxylen superplasticizers, the air pores characterize with smaller diameters than pores formed as a result of lingosulphonic or naphthalene superplasticizers functioning.

Results of researches [11] presented in Table 1, prove that new superplasticizers generations show air-entraining functioning, which was proved by the

Figure 3.
The influence of naphthalene superplasticizer (β-NS), refined lignin sulfonate (LS) and polycarboxylate (P34, S34) on the structure of concrete porosity (a) 28 days of curing , (b) 91 days of curing [12]

Table 1.
The influence of superplasticizer type on the concrete mix air-entrainment [11]

SP	LS	SNF	SMF	New Generation SP	
				PCP	AAP
Air volume	++	+	0	++	++

Where: LS – Lignosulfian, SNF – Sulfonated Naphtalene Formaldehyde Condensate, SMF – Sulfonated Melamine Formaldehyde Condensate, PCP – PolyCarboxylate Polyoxyethylene, AAP – Amino Phosphonate Polyoxyethylene
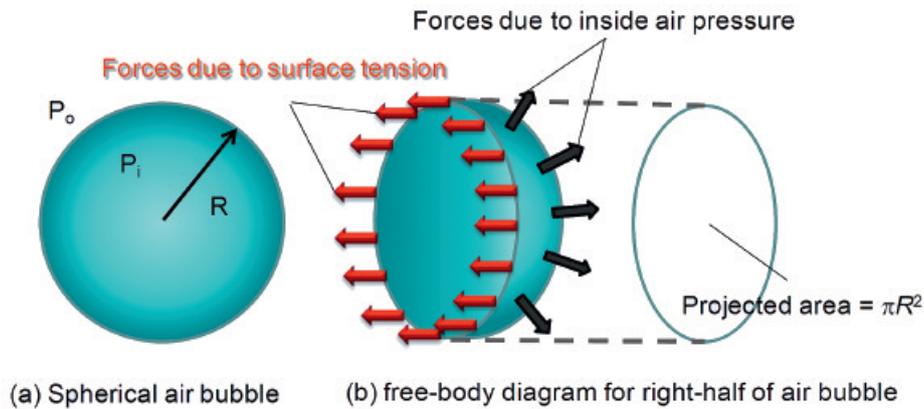
Figure 4.
Surface tension and air pressure forces acting on air bubble [8]
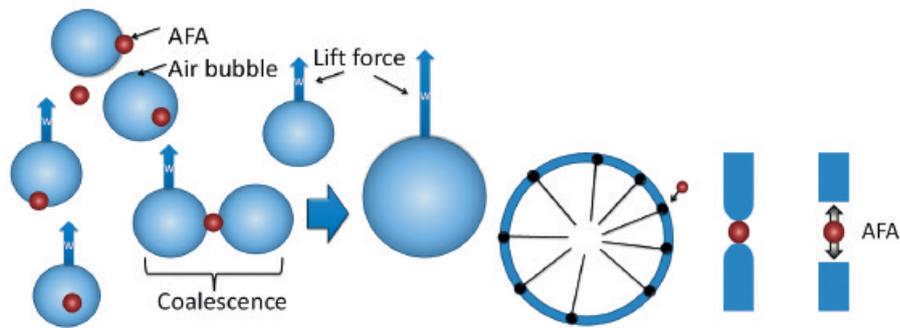

Figure 5.
Stages of an anti-foaming admixture action mechanism

research results carried out by the authors. The research results showed that excessive air-entrainment is caused – mostly – by the decrease of surface tension of liquid phase in paste by the PCP superplasticizer.

Whereas the results of certain researches [8] prove that some new SP generations have air-entraining ability. The research results showed that excessive air-entrainment in concrete mix is mostly generated by some high water range reducers decreasing surface tension of liquid phase in paste (Fig 4).

In order to prevent the presence of the excessive air-entrainment, the SP should not only be compatible with cement, but also do not create air-entraining effect in the paste. To counteract the excessive air-entrainment and air bubbles formation the anti-foaming admixtures (AFA) can be applied.

Components and their proportions used in the anti-foaming admixtures, as in SP, are known only to the producers. These ingredients could be mineral oils, silicone oils, organic modified silicones, hydrophobic constant molecules (silica, waxes, higher fatty acids soaps, alcohols and fatty acids), emulsifiers, polyalcohol, alcohol derivatives of organic compounds. Mixes of active components mentioned above could have a synergetic effect. Unfortunately, high price and insufficient recognition of influence on the fresh mix and concrete properties do not promote wider use of the anti-foaming admixtures.

The mechanism of anti-foaming admixture functioning may be explained in the following way. The active components are distributed around air bubbles, displacing surfactant molecules. As a result, the thickness of the lamella wall built of surfactant leads to its
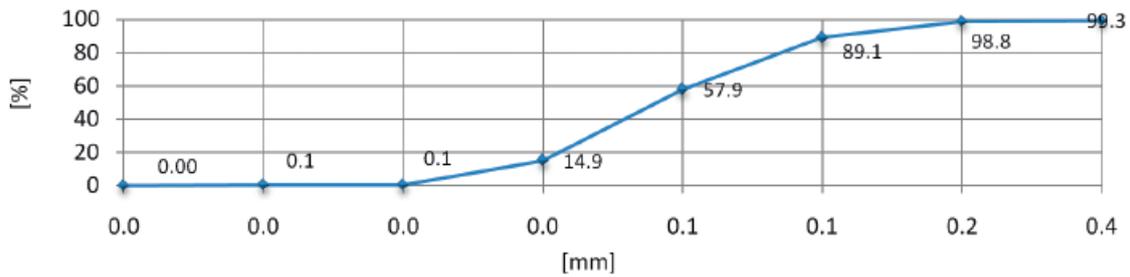
Figure 6.
Curve of sand grading

Table 2.

Mix composition of mortars (*M*); cement CEM II B-S 32.5 R: 744.3 [kg/m^3], w/b = 0.40; sand (Fig. 6): 1224.5 [kg/m^3]

Series	w^1/b	SP [%m.C]	SP type	AFA [%m.C]
M0		-	-	-
M2			PCE*	0.00
M2-a				2.21
M2-a1				4.42
M2-b				
M2-c	0.40	0.77		2.21
M2-d			PCE	
M2-d1				4.42
M2-d2				1.11
M2-e				2.21
M2-f				
M3	0.41	0.56	PCE**	0.00
M3-f				2.21

* *SP* based on polycarboxylic ether (PCE),
** *SP* based on polycarboxylic ether (PCE) (another type than *),
^{1}water + admixtures liquid part

destabilization and in effect to the bubble fracture or coalescence (Fig. 5).

Hence, the mechanism of AFA functioning is not well-known, as well as effectiveness in decreasing the air content in fresh mix and its influence on fresh mix properties and on properties of hardened concrete. Unfortunately, we do not know, what the best type of AFA decreasing air-volume in mortar is. So, it is advisable to carry on proper tests verifying the influence of anti-foaming admixtures type on air-entrainment, rheological properties and stability of self-compacting concrete mix mortar effect of the moment of AFA introduction should be defined, as well.

2. MATERIALS AND METHODOLOGY OF THE RESEARCH

The composition of mortar is presented in Table 2 and Table 3. The w/b ratio of mortars was kept at a constant level. The value of w/b of mortars corresponds to the values of average used self-compacting concrete with a compressive strength of less than 60 MPa.

Author's research results showed that when the flow diameter of mortar is higher than 26 cm and time flow is less than 6 sec., the concrete mix is self-compacting. Thus, the dose of SP and AFA (given in Table. 2) was determined because of the required diameter and time flow of mortars.

The effectiveness of anti-foaming admixture depending on its type and SP type (Table 2) was investigated in tests of flow and air-entrainment of mortar according to the EN 1015-3:2000/A2:2007 and EN 1015-7:2000 codes, respectively.

The process of mixing of the mortars started with dry

Table 3.
AFA components

Symbol	AFA based on:
a	froth breaker on the PDMS basis/ silicone oil/ hydrophobic silica
b	froth breaker on the basis of mineral oil or amidol wax
c	froth breaker on the basis of alcohol derivative of saturated fatty alcohol, mineral oil and PE wax
d	fiakyl derivative of saturated fatty alcohol/mineral oil/PE and amidol wax
e	alkoxyl derivative of fatty alcohol, 100%
f	polyalcohol

Table 4.
Investigated properties of fresh mortars

Series	Air-volume Ac, [%]	Flow diameter, after 20 min, [mm]	Flow time T after 20 min, [s]
M0	4.0	-	-
M2	12.0	26.0	4
M2-a	3.0	29.9	6
M2-a1	3.0	27.0	6
M2-b	5.2	36.3	5
M2-c	3.8	39.1	4
M2-d	3.4	37.0	6
M2-d1	3.4	34.0	6
M2-d2	4.0	32.0	6
M2-e	5.4	30.6	6
M2-f	2.8	36.0	5
M3	3.0	29.5	5
M3-f	2.2	31.0	4

ingredients (Fig. 6 and Table 2). Then the SP and next the anti-foaming admixture of particular types (Table 2) were added. The mixing of mortars components was carried out in accordance with the procedure of EN 197-1/2002 code. Mortar *M* type, containing SP, was consolidated by shaking. The mortar was laid in three layers in the container which is the part of the apparatus for the air content by volume testing.

Each layer was shaken before laying another one. After 20 minutes when effectiveness of SP is the highest, the air-entrainment and mortar flow were measured. To assess AFA influence on the time relating workability loss of the mortar, the assessment of paste flow was measured after 20 and 60 minutes, counting from the time of components mixing.

The properties of the mortars were described by compression and flexural strength tested according to EN 1015-11:2001 + A1:2007 code. All tests of hard-

ened mortars were carried out after 28 days on 4x4x16 cm mortars blocks curing in 20°C water.

The microstructure of SCC made of M2, M2-f, M3 mortars were described by SEM (*Scanning Electron Microscopy*). Values of porosity structure parameters of SCC made of M2 and M2-f were investigated according to EN-480-11.

3. RESEARCH RESULTS AND THEIR DISCUSSION

Table 4 presents test results on fresh mortars. It was noticed, that different type of SP, with the same PCE base, produced radically different volume of air in mortars (see *M2* and *M3*). In case of consolidated mortars without admixtures (*M0*), 4% of air volume was observed. The mortar with air-entraining SP contained even about 12% of air volume. Both mortars were considered as a reference for assessment of AFA effectiveness.

Research results (Table 4) showed that c type AFA result in higher flow diameter of mortar, but contains 3.8% of air (higher than AFA type *f*).

According to research results in Table 4, AFA type f (on the basis of polyalcohol) is most effective in decreasing air-content and increasing mortar flow diameter without its segregation.

As it was mentioned earlier, after exceeding some quantity of AFA, there is no further reduction of air-volume in mortar and SCC. Only improvement of the fluidity of the mortar was observed (compare *M2-d, M2-d1, M2-d2*, Table 3).

Fig. 7 and Fig. 8 present tests results of the fresh mix containing anti-foaming admixture preparation technology. In one case, the admixture was introduced immediately after SP addition. In the other case, admixture was introduced 20 minutes after starting the process of mixing and SP addition. The tests results prove that the time of anti-foaming admixture introduction is not essential for the effectiveness of decreasing the air-entrainment of the mix. This conclusion is very important because the application of anti-foaming admixtures may be used in order to:

– prevent the excessive air-entrainment of mix (introducing anti-foaming admixture with air-entrained SP),

– decrease existing air content (produced by air-entrained SP) in fresh mix.

The tests results presented in Fig. 7 and 8 show that the moment of anti-foaming admixture introduction influences significantly the diameter and flow time of the fresh mix. In order to achieve the highest fluxing of mix, the anti-foaming admixture should be introduced as fast as it possible.

In Table 4 the test results of mortars are presented. It was noticed, that anti-foaming admixtures (except for e AFA type) improve significantly compressive strength of mortars. Moreover, the compressive strength of mortars incorporating AFA (except for e AFA type) is similar to mortar strength with "not entraining" SP.

The research results (Table 5) showed, that AFA increases the flexural strength of mortar in comparison with mortar without AFA and air-entraining or not air-entraining SP.
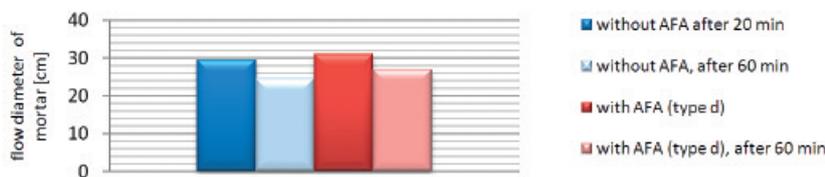

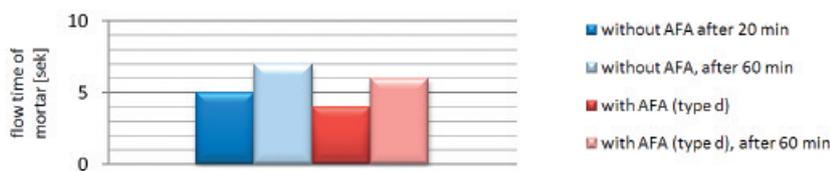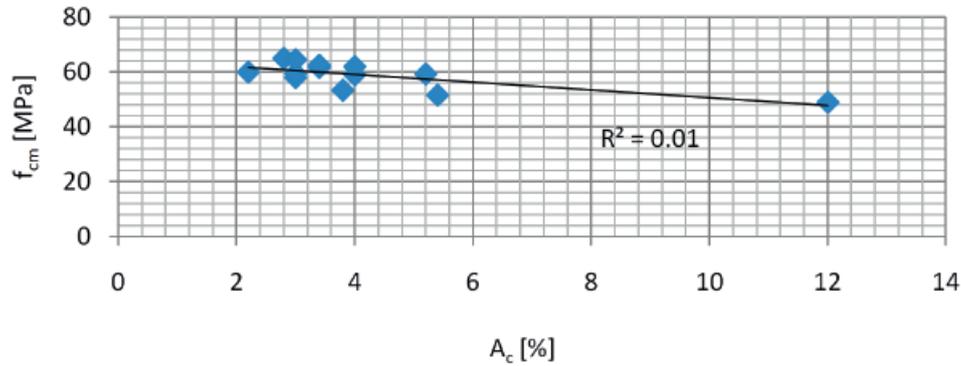**Figure 7.**
The influence of AFA on flow diameter of mortars

Figure 8.
The influence of AFA on mortars flow time

Figure 9.
**The relationship between air-volume in mortar and its compressive strength**

Table 5.
Properties of hardened mortars

Series	f_{cm} [MPa]	f_{ct} [MPa]
M0	59.0	6.3
M2	49.0	5.4
M2-a	58.0	12.0
M2-a1	59.5	12.0
M2-b	59.3	11.7
M2-c	53.4	11.3
M2-d	61.7	11.9
M2-d1	62.5	10.5
M2-d2	62.0	10.4
M2-e	51.6	9.9
M2-f	65.0	11.0
M3	64.5	5.5
M3-f	60.0	11.8

In Fig. 9 the relationship between air-volume in fresh mortar and compressive strength is presented.

The research results suggest that apart from summarize air-content in mortar, the values of porosity structure parameters of mortars and its microstructure, obtained by different admixtures, have greater influence on compressive strength and flexural strength of mortars. In order to verify this thesis, the author carried out another research: SEM and analysis of porosity structure parameters (according to EN 480-11) of SCC made of mortars investigated in the paper.

SEM (*Scanning Electron Microscopy*) research results carried out by author investigated the influence of "air-entraining" SP, "non air-entraining" SP and AFA on structure of SCC made of the mortar analyzed in the paper. Figures 10÷12 show these results. It is clearly visible that admixtures influence significantly SCC microstructure. Admixture generates different
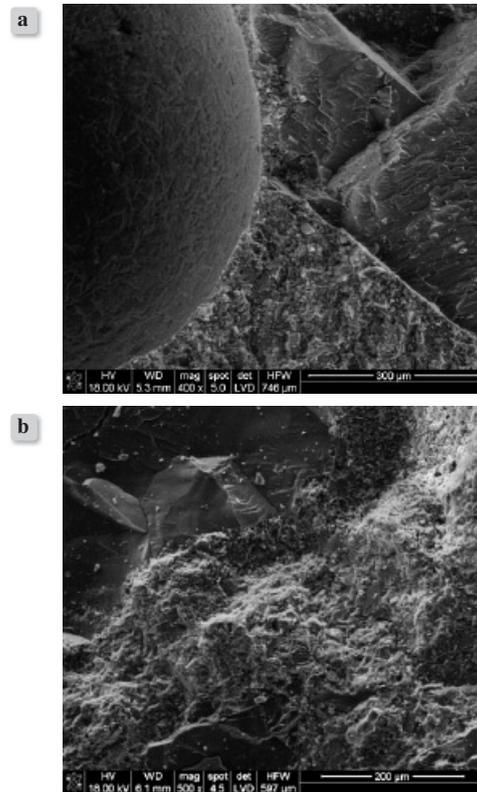
Figure 10.
SEM research results of SCC for "non air-entraining" SP (PCE): a) no air void; b) CSH phase

porosity, CSH structure and contact zone in SCC.

There are no visible large air voids in Fig. 10. This is the result of "air-entraining" PCE SP application. The CSH phase is homogeneous and compact. The cement paste tightly encloses the aggregate. No calcium hydroxide was observed.
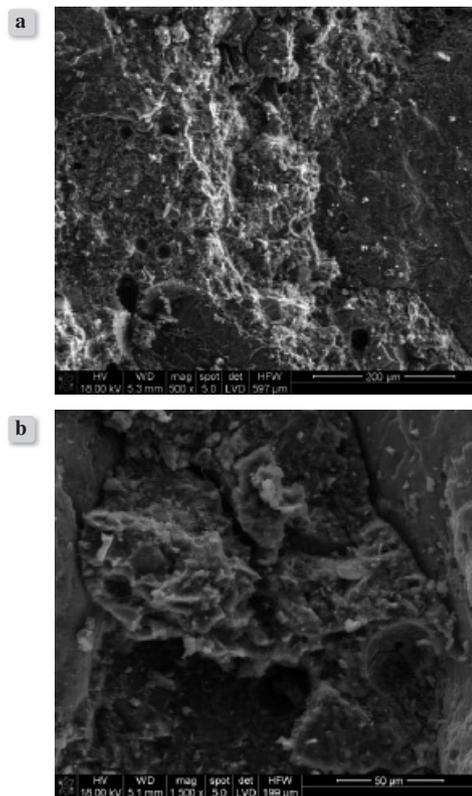
Fig. 11 presents the effect of "air-entraining" PCE SP application on quality of SCC structure. This struc-

Table 6.
The values of concrete porosity parameters

Symbol	A [%]	α [mm^{-1}]	$\overline{L}$ [mm]	A$_{300}$ [%]
SCC made of M2	3.64	10.8	0.71	0.29
SCC made of M2-f	1.79	18.3	0.39	0.68
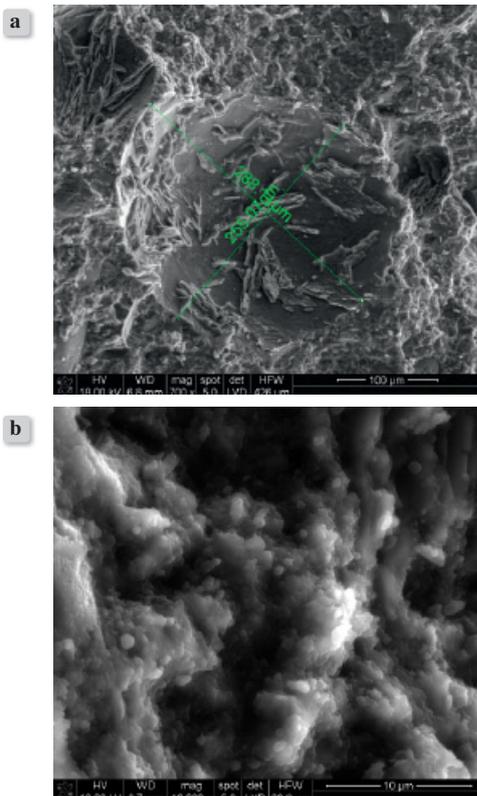
Figure 11.
SEM research results of SCC for "air-entraining" SP (PCE): a) air void; b) CSH phase

Figure 12.
SEM research results of SCC for "air-entraining" SP (PCE) and AFA: a) air void; b) CSH phase

ture is the most amorphous. There are a lot of large pores in SCC structure (with diameter higher than 560 μm).

Moreover, a lot of calcium hydroxide (its hexagonal structure) overgrowing the air voids was observed.

Structure of SCC with AFA and "air-entraining" PCE SP is less heterogeneous than structure of SCC with "air-entraining" PCE SP (compare Fig. 10 and 12). Moreover, no calcium hydroxide was fund in SCC structure.

Research results according to EN 480-11 are presented in Table 6 and in Fig. 13. This research proved that AFA generate positive change of values of porosity structure parameters. Value of air void space factor

(L) is smaller, when SP and AFA are incorporated. Moreover, air void volume with diameter smaller than 300 μm (A$_{300}$) is almost two times bigger. The specific surface of air voids (α) is higher where AFA is used. These changes are very positive in respect of SCC frost-resistance.

Research results presented in the paper proved that admixtures have significant influence on properties of self-compacting mortars. The influence of investigated admixture on durability of self-compacting concrete made of mortars analyzed in the paper will be presented in the next publications.
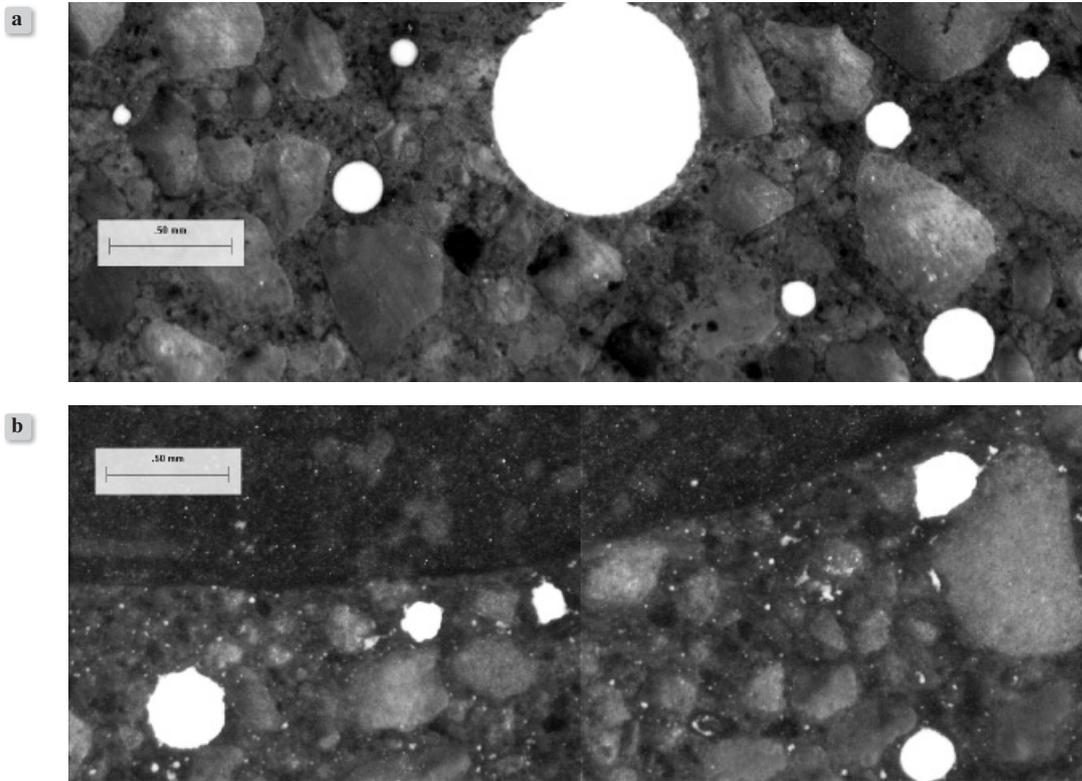
Figure 13.
Porosity structure of (a) SCC made of M2, (b) SCC made of M2-f

4. CONCLUSIONS

In the scope of carried out tests the following conclusions can be drawn:

- Some of the new generation SP based on polycarboxylic ether produces excessive air-entrainment of self-compacting mortar. Two types of PCP high range water reducers produce different air-content in mortar. Thus, it is difficult to predict the effect of SP type on air-content in mortar.

- Test results of mortars showed that AFA made on the basis of polyalcohol reduce the air entrainment and improve mortar workability most effective.

- The effectiveness of AFA depends on its dosage. Exceeding some AFA saturation, there is no further reduction of air content in mortars. Only improvement of the mortar fluidity is still evident.

- It should be emphasized, that the mortar containing AFA, despite of considerable fluidity, does not undergo segregation, different than in the case of mortars with no AFA with similar degree of fluidity (produced by higher amount of SP). Moreover, test results prove that mortars with AFA keep initial consistency for longer time in comparison with

mortar with SP only.

- Anti-foaming admixture type influence significantly compressive strength of mortars. The compressive strength of mortars incorporating AFA is similar to mortar with "non air entraining" SP.

- All of the AFA type increases significantly the flexural strength of mortar. The most influence on this mechanical parameter has a AFA made of polyalcohol.

- SEM (*Scanning Electron Microscopy*) research results showed clearly that admixtures type influence significantly SCC microstructure.

- AFA has positive influence on values of porosity structure parameters. Air void factor is smaller, when SP and AFA is applied. Moreover, air void volume with diameter smaller than 300 mm and specific surface of air voids are almost two times bigger.

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