



Research paper

Effect of the mix composition with superplasticizer admixture on mechanical properties of high-strength concrete based on reactive powders

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Abstract: This paper outlines effect of the mix composition on mechanical properties of high-strength concrete based on aggregate size like in of Reactive Powder Concrete (RPC) but without fiber reinforcement. The main purpose which guided the authors choosing proportion of water and superplasticizer (SP) was to achieve a similar consistency in the test slump for various concrete mix. Test results for 3 groups of superplasticizers, designated as D – with chemical base – acrylic polymer, V – with chemical base – polycarboxylate ether, P – with chemical base – modified polycarboxylates, two cement groups, designated as Cem A – with fineness Blaine 3980 cm²/g, Cem B – with fineness Blaine 4430 cm²/g and 2 types of aggregate: basalt and granite were presented. After curing for 1, 7 and 28 days samples were tested for compressive strength and flexural tensile strength. The article also presents the study of the elemental composition and structure of the SP with the use of the SEM electron microscope. The amount of solid particles in the SP was also determined by the water vaporization. The assumption of the paper was to maintain the consistency of the mixture at the S2 level according to the Eurocode standard. The paper proposes a method based on SEM analysis in order to select a superplasticizer with the best ductility parameters, and the best results of the compressive and flexural tensile strength of concrete samples were obtained. The best results for compressive strength after 28 days are obtained for concrete series with the polycarboxylate ether superplasticizer and modified polycarboxylate ether superplasticizer in combination with the use of type A cement and it is greater than for the concrete series with type B cement by 11.7%.

Keywords: concrete design, high strength concrete, superplasticizers type, superplasticizer ductility, reactive powder concrete

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1. Introduction

The effect of the mix composition on the mechanical properties is just as important as in the other concrete mixture, especially in Reactive Powder Concrete (RPC). RPC consists of a special concrete where the microstructure is optimized by precise gradation of all particles in the mix to yield maximum density. It uses extensively the pozzolanic properties of highly refined silica fume and optimization of the Portland cement chemical composition to produce the highest strength hydrates. This type of concrete is the material with superior properties like high compressive strength, flexural and tensile strength. RPC can come in two variants: without – or with fibers adding, [1]. The first (without fibers) or the second (with fibers) type of RPC may achieve the compressive strength to 230 MPa or to 810 MPa, respectively, depending on the curing conditions, for various temperatures in the range of 20–400°C and compacting pressure in the range of 0–50 MPa [1]. In the concrete technology, steel, glass, basalt, carbon, aramid and other fibers, e.g. from recycling car tires, are used, [2–5]. RPC due to very good mechanical properties are used, among others, to build special civil engineering structures, nuclear power plants, marine and military infrastructure, blast resistance structures, high pressure pipes [6]. Further advantages of RPC concretes are the low maintenance costs of the building throughout its life cycle [7], because RPC has a good durability due to its low porosity nature and dense microstructure [8]. RPC concrete production with high fluidity is dependent on superplasticizer type, due to low water – to cement – ratio and high fine content.

The study of the effect of SP on various parameters of fresh and hardened concrete is widely described in the literature. In article [9] the authors presented the results of the research on the influence of SP type on the mechanical performance of the concrete made with fine recycled concrete aggregates. It was shown that using SP improves the parameters investigated. The effect of the type of superplasticizer was also presented in relation to the microstructure and properties of fresh cement pastes in paper [10], to workability retention and initial setting time of cement paste [11], fresh properties and compressive strength of self-compacting concrete [12]. Article [12] shows that the polycarboxylate based superplasticizer gave more workability and higher compressive strength than the naphthalene sulphonate based SP. In the works [13–16], the authors also studied, among others, the effect of SP types in relation to packing density and flowability, flexibility, strength and durability, plastic shrinkage or pore structure. Positive effect of different types of SP in all works was shown. In article [16] investigations have shown that the pore structure clearly depends on the superplasticizer added to the concrete mix.

Important aspects when designing and manufacturing RPC concrete are also optimized mix design and curing conditions [17], the proper order of SP addition to the remaining components of the mixture, grain size and fine aggregate type [18, 19]. In paper [17], the authors indicated that modification of the cure treatment consisting in the maturation of samples in water at different temperatures, finally resulted in an increase in compressive strength about 174%.

In the paper [20] the results of tests on the influence of the SP type on compressive strength was shown. In this research three types of superplasticizers were used: aqueous solution of acrylic polymer, aqueous solution of sulfonated melamine-formaldehyde con-

densate and aqueous solution of sulfonated naphthalene – formaldehyde condensate. It was found that acrylic polymer admixture performed better than the others. They were the old types SP used in the 90's.

From the literature review above, one can see that there is a need to conduct research on the use of modern superplasticizers which, in combination with the other parameters listed above, will allow the design and construction of new quality RPC concrete.

The literature does not provide many studies concerning the comparison of the effect of the properties of commonly available new generation superplasticizers on the mechanical parameters of concretes based on the RPC technology, including concerning the checking of the influence of SP for various material combinations of aggregate. The recent research presented in [21] show that ensuring good interaction of superplasticizers with various types of cement is still problematic in many cases, and most of the available articles refer to the SP of older technologies.

These facts motivated the authors to undertake research aimed to determine the influence of a new generation superplasticizers on strength parameters in various research formulas and to determine at which material combinations of aggregate the best results will be achieved.

The scope of the work includes tests of 10 concrete mixes made of the base of 2 cement types with 2 different Blaine active surface ratios, with the use of 2 types of aggregate: basalt and granite, and – first of all – using 3 types of superplasticizer admixtures with different chemical bases. The basic assumption of the concrete mixes preparation was to maintain the consistency of the mixture at the S2 level according to the Eurocode standard.

The paper presents the results of tests on the compressive strength and the flexural tensile strength of concrete and the ductility, expressed as the strength ductility coefficient of the flexural tensile strength to the compressive strength of the concrete.

Moreover, the study on the elemental composition and the content of solid particles in the superplasticizers, are presented in the paper. The SEM analysis of superplasticizers structure was carried out indicating the ductility of this structure. It was also demonstrated that the observed ductility of the SP structure is convergent with the strength ductility coefficient.

The best combination of concrete mix components, i.e. the type of cement and aggregate with superplasticizer admixture, was indicated in terms of concrete strength properties.

2. Experimental program

2.1. Materials

The cements used in this study was CEM I 52,5 R – SR5 from two different manufacturers. Cement 1 with the compressive strength of the cement as measured on ISO mortar 70.0 MPa and fineness Blaine 3980 cm²/g was marked Cem A, Cement 2 with the compressive strength of the cement as measured on ISO mortar 61.0 MPa and fineness Blaine 4430 cm²/g was marked Cem B.

Microsilica was used as the reactive material. Microsilica with an average particle size d_{50} of 0.15 μm was used. Chemical compositions of cement A, cement B and microsilica (MS) are shown in the Table 1. The chemical compositions of the used powders were determined by X-ray fluorescence (XRF); the uncertainties of the laboratory measurements δ of chemical compounds for individual materials are also presented in the Table 1.

Table 1. Chemical compositions of Cem A, Cem B and microsilica (MS)

Chemical composition	Cem A (mass %)	$\pm\delta\text{C}$ (mass %)	Cem B (mass %)	$\pm\delta\text{C}$ (mass %)	MS (mass %)	$\pm\delta\text{MS}$ (mass %)
CaO	67.42	0.003	57.8	0.002	0.10	0.067
SiO ₂	22.56	0.022	36.8	0.025	96.2	0.012
Al ₂ O ₃	2.69	0.249	2.8	0.235	–	–
Fe ₂ O ₃	0.19	0.067	0.3	0.081	0.50	0.029
K ₂ O	0.03	0.090	0.2	0.074	1.30	0.025
SO ₃	2.10	0.037	3.26	0.42	0.20	0.161
CaCO ₃	–	–	–	–	–	–
MgO	–	–	–	–	1.70	0.675

The properties of superplasticizers types used in the mixture are shown in the Table 2.

Table 2. Properties of superplasticizers types

SP mark	SP type	Chemical base	Density (g/cm ³)	Alkali content
D	Highly efficient water solution based on acrylic polymer	Acrylic polymer	1.07	< 3.0%
V	Highly efficient based on polycarboxylates	Polycarboxylate ether	1.08	< 0.8%
P	Highly efficient based on polycarboxylates	Modified polycarboxylate ether	1.07	< 4.0%

The elemental compositions and the content of dry material content in the superplasticizers are presented in the Table 3.

The elemental compositions of the SP used were determined by Scanning Electron Microscopy (SEM), (Quanta 250 FEG SEM, FEI, Hillsboro, OR, USA), associated with Energy Dispersive X-ray spectroscopy detector (EDS-EDAX, LLC, Mahwah, USA), and with an accelerating voltage of 30 kV.

The content of solid particles in the SP was determined by weighing the samples after vaporization of the water in a vacuum furnace for 10 days at a temperature of 70°C. The SP samples contained of 200 ml water suspension and had the weight of D – 210.2 g, V – 203.7 g, P – 205.2 g, respectively.

Table 3. Elemental compositions of the superplasticizers

SP mark	Chemical composition	Weight (%)	Atomic (%)	Net int.	Error (%)	Dry material content (%)
D	C	68.5	74.76	682.2	5.36	25.2
	O	29.87	24.48	137.93	11.19	
	Na	0.95	0.54	27.69	14.62	
	P	0.91	0.38	56.54	7.29	
	S	0.24	0.1	18.73	17.12	
V	C	67.19	73.45	1091.05	4.73	34.8
	O	31.35	25.74	228.43	10.53	
	Na	1.48	0.85	45.49	11.48	
	P	0.12	0.05	14.60	20.49	
	S	0.06	0.02	7.05	39.92	
P	C	68.06	74.15	1935.94	4.67	35.9
	O	30.93	25.34	401.95	10.27	
	Na	0.55	0.32	27.79	14.95	
	S	0.46	0.19	104.72	5.26	

2.2. Mix design and methods

In this study, the modified Funk and Dinger model, following the Andreasen and Andersen model, was used in the design of concrete mixes:

$$(2.1) \quad P(D_i) = \frac{(D_i^n - D_{\min}^n)}{(D_{\max}^n - D_{\min}^n)} \cdot 100\%$$

where: (D_i) is the cumulative percentage of the i -th fraction lower than D_i , D_i^n is the granulation of the calculated fraction (μm), D_{\min} is the granulation of the minimum fraction (μm), D_{\max} is the granulation of the maximum fraction (μm), n is a constant exponent as the distribution coefficient depending on the type of concrete (composites).

As presented in the literature, different types of concrete can be designed using Equation (2.1), by applying different values of the constant $n = 0.23$, which is determined by the proportions of the fine and coarse particles.

The design of the granular structure of the RPC concrete used in our study was made according to the compressible packing model (CPM) developed by de Larrard and modified

by authors, [18, 19]:

$$(2.2) \quad f_{Lt} = \frac{k_k k_{fr} k_{sz} k_t f_{cem}}{\left[1 + \frac{1.4 \cdot \frac{W}{C + 0.22m_s}}{1.4 - 0.4 \cdot \exp\left(-11 \cdot \frac{m_s}{C}\right)} \right]^2}$$

where: f_{Lt} is the compressive strength at the time of t days (MPa), f_{cem} is the strength of the cement as measured on ISO mortar (MPa), $\frac{W}{C + 0.22m_s}$ is the total amount of water included in the all mixture elements (including the water in the SP) relative to the amount of cement with 0.22 microsilica fume amount, $\frac{m_s}{C}$ is the ratio of the microsilica fume to cement.

In Equation (2.2), new correction factors have been introduced.

– the aggregate coefficient:

$$(2.3) \quad k_k = 3.0 + \frac{\rho_B - B_s}{\rho_B}$$

where: B_s is the amount of binders and aggregates lower than 0.2 mm in size per kg in 1 m^3 of the concrete, and ρ_B is the bulk density of all the aggregates in the sample (kg/m^3).

– the reinforcing-fiber coefficient:

$$(2.4) \quad k_{fr} = \exp^{0.034\rho_s}$$

where: ρ_s is the percentage ratio of steel-fiber mass to the mass of the cement (%), hereinafter $k_{fr} = 1.0$ for $\rho_s = 0.0$ is taken.

– specimen shape and size coefficient:

$$(2.5) \quad k_{sz} = 1.06 \quad \text{for cube } 100 \text{ mm}$$

(for another shapes and sizes, see Table 2 in paper [19]).

– the sample curing time coefficient:

$$(2.6) \quad k_t = \left[1 - \exp\left(-\left(\frac{t - 0.9}{3}\right)^{0.6}\right) \right]$$

where: t is the sample curing time (days).

Equation (2.2) expresses a modification of a non-standard design procedure. This procedure makes it possible to compare the results obtained on the basis of standard procedures, assuming constant parameters, e.g. regarding the composition of the mixture. Detailed information on the UHPC concrete design methodology based on the RPC technology is included in [19]. The original methodology was developed by de Larrard in 1992 [22], and then it was improved, among others, by the authors [2, 23, 25–31].

Table 4. Mix recipes RPC concretes

Superplasticizer type	D		D		V		V		P		P		Control granite / basalt
	granite		basalt		granite		basalt		granite		basalt		
Cement type	A	B	A	B	A	B	A	B	A	B	A	B	A / B
Mix mark (SP-AggrCem)	D-GA	D-GB	D-BA	D-BB	V-GA	V-GB	V-BA	V-BB	P-GA	P-GB	P-BA	P-BB	R
Cement	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Microsilica	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22
Aggregate 0.125–0.25 mm	0.89	0.89	0.89	0.89	0.89	0.89	0.89	0.89	0.89	0.89	0.89	0.89	0.89
Aggregate 0.25–0.5 mm	1.45	1.45	1.45	1.45	1.45	1.45	1.45	1.45	1.45	1.45	1.45	1.45	1.45
Water	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38
W/C	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.4
SP	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.00
Cone slump test	S2	too dense	too dense	too dense	S2	S2	too fluid	S2	S2	S2	S2	too dense	too dense

Concrete mixes based on Cem A and Cem B were designed according to formulas (2.1) and (2.2) with the use of fine basalt and granite aggregates, as well as microsilica as a reactive material. Two types of aggregates was used, one was a basalt with the fraction 0.125–0.5 mm and the other one was the granite with this same fraction. One type of the microsilica was selected as an high active pozzolanic material in this study ($\text{SiO}_2 = 96.1\%$).

Mix recipes of the designed concretes are shown in the Table 4. The table shows the proportions of the individual components to the amount of cement, where the reference value of 1.0 is equal to an amount of cement equal to 630 kg/m^3 .

Due to the fact that the superplasticizer was not used in the control samples, the samples could not be properly compacted and the structure of rolled concrete was obtained. In the control samples (marked as R), the amount of water was used as the sum of the water and 70% of superplasticizer mass added in other recipes. An average value of the amount of solids in the superplasticizer was assumed to be 30%. The consistency of the concrete mix was tested using the cone slump method, in accordance with EN 12350-2 [32].

The flexural tensile strength of $40 \times 40 \times 160 \text{ mm}$ samples was obtained on formula:

$$(2.7) \quad f_{ct,fl} = \frac{3 \cdot F \cdot l}{2d_1 d_2^2}$$

where: F is the maximum load (N), $l = 120 \text{ mm}$ is the distance between the supporting rollers, $d_1 = d_2 = 40 \text{ mm}$ are the lateral dimensions of the specimen.

2.3. Curing Conditions, Mixing Procedure and Mechanical Properties

The mixing was executed under laboratory conditions with dried aggregates and powder materials. The room temperature was maintained at around 20°C during mixing and testing. The mixing procedure:

- All powders and sand fractions was added into the mixer for dry mixing in time 60 s, (at low speed);
- Around 90% of water and all SP admixture was added into the mixer and mixing for 360 s, (at low speed);
- Around 10% of water was added into the mixer and mixing for 120 s, (at high speed).

The samples were prepared in the form of cubes $100 \times 100 \times 100 \text{ mm}$ and beams $40 \times 40 \times 160 \text{ mm}$. The six samples of each type were made. After 24 h, the samples were disassembled and cured in water at 20°C in accordance with EN 12390-2:2009 [33]. After curing for 1 day, 7 and 28 days, the samples were tested for average compressive strength f_{cm} , in accordance with the standard EN 12390-3:2009 [34], using a MEGA 6-3000-150 (Form+Test, Riedlingen, Germany) hydraulic press.

The strength ductility coefficient was introduced as the proportion of the flexural tensile strength to the compressive strength of the concrete:

$$(2.8) \quad \alpha_t = \frac{f_{ctm,fl}}{f_{cm}}$$

where: $f_{ctm,fl}$ is the average flexural tensile strength.

The similar interpretation of the material ductility measure was used by the authors of the papers [35–37].

2.4. SEM analysis

The samples of the superplasticizers were subjected to a vacuum drying process in a BMT VacuCell device (Watertown, USA) at 20°C, and then sprayed with a 5.14 nm layer of gold using a Leica ACE 600 high-vacuum sputtering machine (Wetzlar, Germany). As a result, the coefficient of secondary electron emission as well as the electrical and thermal conductivity of the tested samples was improved.

The microstructure of superplasticizers were observed by Scanning Electron Microscopy (SEM) was used (Quanta 250 FEG SEM, FEI, Hillsboro, OR, USA). SEM images were acquired using a backscattered detector (ETD-BSE, FEI, Hillsboro, OR, USA) with an accelerating voltage of 5 kV for and 10 kV.

3. Results and discussion

3.1. Mechanical properties

The main purpose which guided the authors choosing water and SP was to achieve a similar consistency in the cone slump test. More recipes have been tested, whereas in the publication only those that obtained the assumed value in the slump test about 10 cm were included. The results of the cone slump test are shown in the Table 5. The table shows the results for the mix – design meeting the criteria of class S2 in the cone slump test. The results of a series of R showed no slump in the test. In the Fig. 1 the average compressive strength results for samples made according to the recipes listed in the Table 4 were presented. The compressive strength of 100 × 100 × 100 mm samples was obtained.

Table 5. Results of the cone slump test

Series	D-GB	V-GB	V-GA	V-BB	P-GA	P-BA	P-GB	R
Slump test result (mm)	91.0	95.0	102.0	97.0	96.0	93.0	95.0	0.00

The highest compressive strength after 1 day was obtained for the V-BB series samples. After 7 days, the greatest compressive strength was obtained in samples of the V-GA and V-BB series. However, after 28 days, the greatest compressive strength was obtained in the V-GA series. The early strength results was greatly influenced by fineness Blaine, which for cement marked as B was 4430 cm²/g and was about 11.3% larger than for cement type A. We can notice that the V superplasticizer allowed to obtain the highest early compressive strength, after 1 and 7 days. However, after 28 days the compressive strength was similar and differed by max. 14% except for the V-GA series, which was 108.5 MPa.

In the early maturation period, after 1 day, the average compressive strength of concrete series made with the polycarboxylate ether superplasticizer (type V) is of 27.6% higher

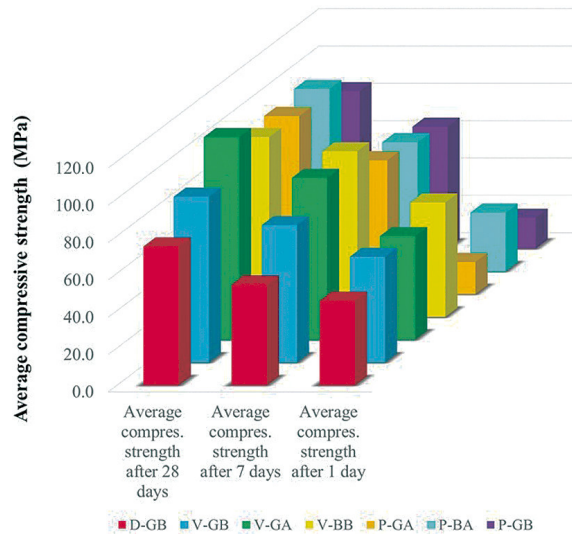


Fig. 1. Average compressive strength f_{cm} after 1, 7 and 28 days

than the strength of concrete series made with acrylic polymer superplasticizer (type D), while using the modified polycarboxylate ether superplasticizer (type P) as much as 166.4% higher. This fact indicates that the modified polycarboxylate ether superplasticizer delays both setting time and process of compressive strength increasing, as well.

After 7 days of maturation, the compressive strength for the concrete series made with polycarboxylate ether superplasticizer (V) is of 53.7% higher than for the concrete series made with the acrylic polymer, and of 20.8% higher than for the concrete series made with the modified polycarboxylate ether superplasticizer (P).

The best results after 28 days are obtained for the V and P superplasticizer. The best results after 1 and 7 days are obtained for the V superplasticizer and series P-BA (cement type A with basalt aggregate). The best early results are obtained for the cement type B and SP type V. The best results were achieved for the V-type superplasticizer with the highest amount of sodium element (Na) as well as with a SP with large amount of solid particles content.

In the Fig. 2 the average flexural strength results for samples made according to the recipes listed in the Table 2 were presented.

For average flexural tensile strength, the best results were obtained in the V-GA and V-BB series of 8.2MPa and 7.9MPa, respectively. In turn, the highest strengths after 7 days were obtained for the series P-BA = 15.5 MPa, and V-GB, V-GA in both cases at 13.7 MPa. After 28 days, the highest strengths were obtained in the V-GA (18.0 MPa), P-BA (17.2 MPa), and V-GB (17.0 MPa) series samples for which the difference in result was only 5%. In the early maturation period, after 1 day, the average tensile strength of the concrete series made with the polycarboxylate ether superplasticizer (V) is greater by 212.0% than for the concrete series made with acrylic polymer superplasticizer (D),

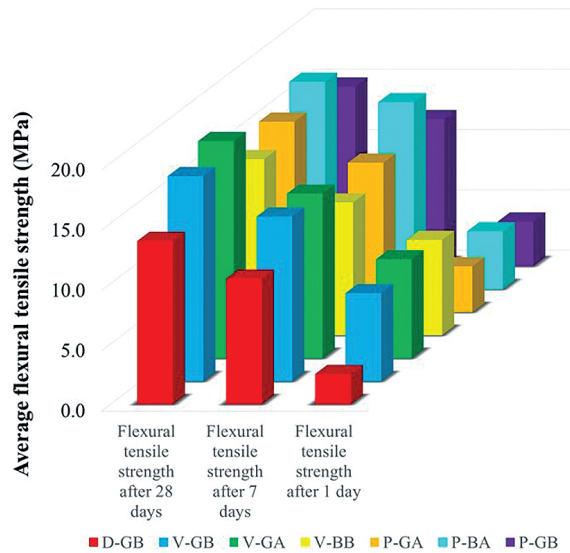


Fig. 2. Average flexural tensile strength $f_{ctm,fl}$ after 1, 7 and 28 days

and is greater by 190.2% than for the concrete series with the modified polycarboxylate ether superplasticizer (P). The use of a V-type superplasticizer resulted in significantly acceleration of the tensile strength increase.

After 7 days of maturation, the tensile strength of the concrete series made with the polycarboxylate ether superplasticizer (V) is of 123.1% greater than for the concrete series made with the acrylic polymer superplasticizer (D), while it is of 3.5% less than for the concrete series made with the modified polycarboxylate ether superplasticizer (P).

After 28 days of maturation, the tensile strength of the concrete series made with the polycarboxylate ether superplasticizer (V) is greater than for the concrete series made with the acrylic polymer superplasticizer (D) series by 22.4%, and greater than for the concrete series made with modified polycarboxylate ether superplasticizer (P) by 4.2%. In the Table 6 results of the compressive and flexural tensile strength after 1, 7 and 28 day with standard deviation σ and coefficients of variation V are shown.

In the Fig. 3, strength ductility coefficient α_t after 1, 7 and 28 days was presented.

The highest compressive strengths were achieved after 1, 7 and 28 days, while the tensile strength after 7 and 28 days was lower than the highest by approx. 15.0%.

The best values of the strength ductility coefficient α_t was obtained:

- after 1 day for the P-GB and P-GA series, respectively 22.4% and 22.1%;
- after 7 days for the V-GB and D-GB series, respectively 19.1% and 18.1%;
- after 28 days for the P-BA and D-GB series, respectively 22.4% and 19.3%.

In the paper [38], the authors compared the influence of the type of superplasticizer in the slump test and the compressive strength of concrete samples during 1, 7 and 28 days. The 8 types of superplasticizers based on poly – acrylic's and poly – methacrylic's were considered. In the slump test analysis, it was found that the best results were obtained

Table 6. Results of the compressive and flexural tensile strength after 1, 7 and 28 days

	28 days			7 days			1 day		
	Compressive strength [MPa]	σ [MPa]	V [%]	Compressive strength [MPa]	σ [MPa]	V [%]	Compressive strength [MPa]	σ [MPa]	V [%]
D-GB	74.4	4.0	3.8	54.0	3.0	2.9	45.3	4.5	4.0
V-GB	88.8	1.4	1.6	73.6	1.6	1.9	56.6	1.7	2.0
V-GA	108.5	2.0	1.8	86.7	2.2	2.4	55.5	2.3	2.7
V-BB	96.3	4.8	5.0	88.7	4.7	5.2	61.3	5.0	5.4
P-GA	95.4	1.6	1.4	71.7	1.9	1.7	17.2	1.9	2.2
P-BA	97.7	1.9	1.7	69.1	2.2	1.9	31.4	2.3	2.0
P-GB	84.3	1.4	2.8	65.3	1.6	2.9	16.5	1.8	3.0
	Flexural tensile strength [MPa]	σ [MPa]	V [%]	Flexural tensile strength [MPa]	σ [MPa]	V [%]	Flexural tensile strength [MPa]	σ [MPa]	V [%]
D-GB	13.5	0.8	5.9	10.4	0.6	5.8	2.5	0.5	5.6
V-GB	17	0.1	0.8	13.7	0.5	3.3	7.3	0.5	3.7
V-GA	18	0.4	2.4	13.7	0.5	3.3	8.2	0.5	3.6
V-BB	14.6	0.9	4.2	11.0	0.8	4.0	7.9	0.7	3.9
P-GA	15.8	0.5	2.2	12.4	0.6	3.5	3.8	0.6	3.6
P-BA	17.2	0.4	2.0	15.5	0.5	2.2	4.8	0.5	2.6
P-GB	14.9	0.4	3.3	12.2	0.4	3.5	3.7	0.5	3.7

with Poly-Methacrylic acid based superplasticizers. In the presented research a similar superplasticizer (i.e. marked as D) was used, but it's using gave the lowest results compared to superplasticizers marked as V and P, see Table 5. The D-type superplasticizer obtained a result lower than the average of the other superplasticizers in the cone fall test by approx. 5.5%. It should also be emphasized that in paper [38] this type of SP obtained results is higher than the others by 10.0–27.0%. The development of superplasticizer technology allowed the use of new, more efficient chemical compounds, which was proved in the presented study on an example of SP types V and P.

The paper [38] presents the influence of the type of superplasticizers on the compressive and tensile strength and the different influence of the same type of superplasticizer on the indicated properties. As the authors of [38] shown, the best results were achieved for a superplasticizer based on a chemical composition similar to SP type D.

In the paper [9], Two types of superplasticizer were used: a current one hence forth called SP 1, whose chemical basis is lignosulfonate, with additions; a high-performance

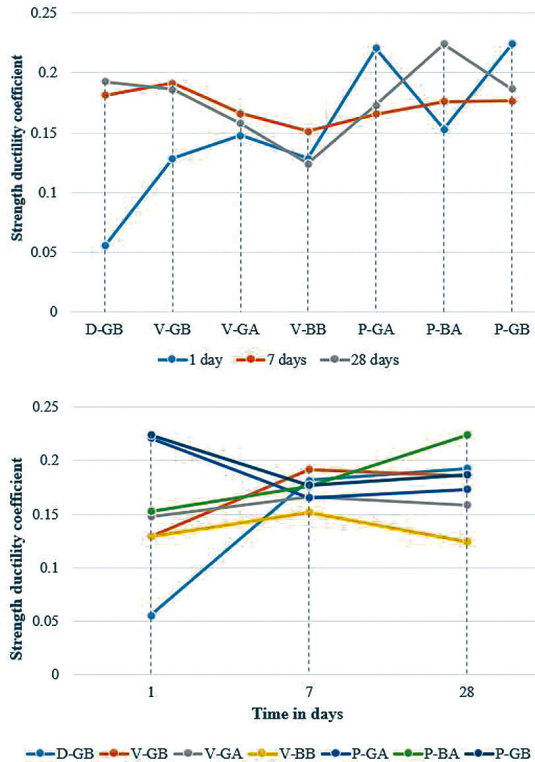


Fig. 3. Strength ductility coefficient α_t after 1 day, 7 days and 28 days

superplasticizer, henceforth called SP 2, whose chemical basis is a combination of modified polycarboxylates in an aqueous solution. It was found that in terms of improvement linked to the superplasticizers, mixes with SP 1 performed worse than those with SP 2 (20.7% against 33.0%). Which is consistent with the results obtained in the research, because the SP2 in [9] is similar to the V and P types used in this study.

3.2. SEM study

The liquid samples of superplasticizers were evaporated in accordance with the previous information until they obtained a solid consistency. In the case of the P superplasticizer, taking SEM images required gold sputtering, because the sample became more fluid after a few seconds under the influence of the impulse. Figure 4 shows SEM images for 3 types of superplasticizers of magnifications 1000 \times , 10 000 \times and 30 000 \times . Figure 4a shows a superplasticizer based on acrylic polymers, type D. The image shows the structure homogeneity and ductility of the superplasticizer. That create links between the components of the concrete, surrounding its individual components. Figure 4b shows an SP type P based on polycarboxylate ether. A more compact structure forming lumps at the edges is visible.

Figure 4c shows a modified polycarboxylates SP, type V, where also the formation of ductile connections between the formed areas of evaporated SP can be observed.

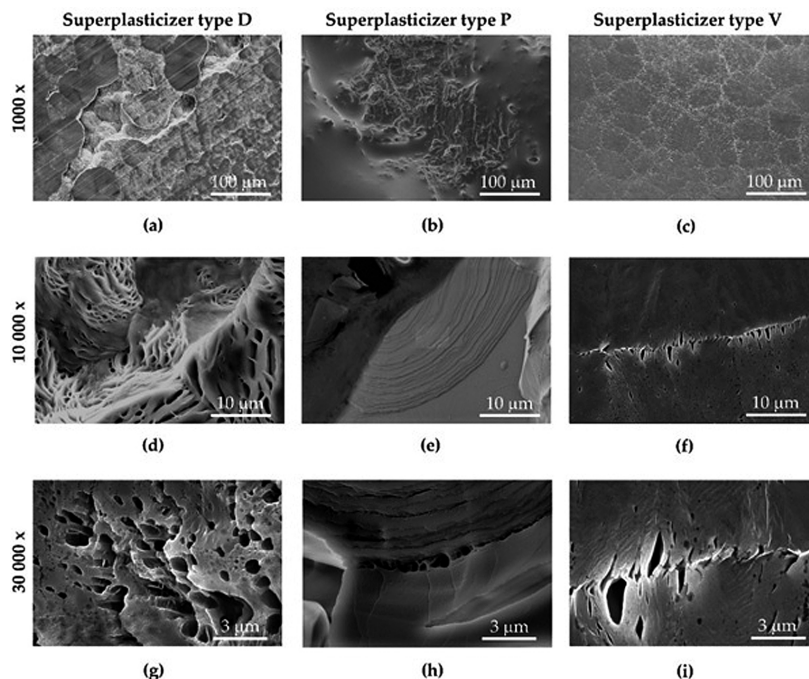


Fig. 4. SEM sectional images for superplasticizers type D, type P, type V in various magnifications

Based on SEM drawings, measurements of the size of SP fields of separated formation of ductile connections between the formed areas were made. The D type SP has area dimensions in the range 33.93–109.3 μm , while for the V type SP it ranges from 112.0–184.5 μm . These facts may indicate greater flexibility of the V type superplasticizer. In the case of the P type superplasticizer at 1000 \times magnification, no visible connections were observed. This type of superplasticizer is the most homogeneous and ductile.

Images of magnification 10000 \times are shown in the Fig. 4d–4f. We can notice a diverse structure of superplasticizers. SP type D has an openwork structure, Fig. 4d. Fig. 4e shows the superplasticizer layers that are formed and the method of forming its flow in the form of contour lines. On the other hand, Fig. 4f shows the connections between V type SP grains more clearly. Similar conclusions are shown in the Fig. 4g–4i at magnification 30000 \times .

The results of the SEM analysis of superplasticizers for the adopted observation scale have not been hitherto presented in the literature. As a result of the SEM analysis, it is possible to conclude about the stability of the structure system, the formation of interfacial connections and ductility, typical for each superplasticizer.

The paper [39] presents the effect of naphthalene-based and polycarboxylic acid superplasticizers on the properties of sulfoaluminate cement paste. The authors in the study

used SEM to analyze the cement paste, which confirmed significant changes in the morphological structure of ettringite. The paper [40] presents SEM images for samples made for various W/C ratios and during 14 and 28 days for hardened concrete. The analyzes included in the study took into account the SP admixtures, but without their detailed analysis. The paper [41] presents the use of fluorescence microscopy from superplasticizers in cementitious systems. Both articles found a significant influence of the type of SP on the structure of concrete. In paper [42] three types of superplasticizers, namely, S1(Naph), S2(Ethe), and S3(Este) were used as water-reducing admixtures in order to follow the effect on compression and fluidity. It was found that as the solids content increases, the cemented tailings backfills (CTB) samples with higher dosage of superplasticizer have a lower rate of decrease in fluidity. Higher solid content contributes to higher ultimate compressive strength of CTB samples, especially at 28 days curing time, what was also noticed in the presented studies.

4. Conclusions

The innovativeness of the work results from the analysis of the influence of new generation superplasticizers on the properties of concretes made with modern cements CEM I 52.5R with high CA3 content and very high standard characteristic strengths and variable fineness, using a combination of different aggregates.

Based on the above experimental results, the following conclusions can be drawn:

- The best results for compressive strength after 28 days are obtained for concrete series with the polycarboxylate ether superplasticizer and modified polycarboxylate ether superplasticizer in combination with the use of type A cement and it is greater than for the concrete series with type B cement by 11.7%.
- The concrete with the acrylic polymer superplasticizer (D) achieves the lowest compressive after 7 and 28 days and tensile strengths, which is related to its openwork structure visible in the SEM analysis. Similar results of the strength parameters of modified polycarboxylate ether (P) and polycarboxylate ether (V) superplasticizers correspond to their compact structures in the SEM analysis.
- The best value of the strength ductility coefficient after 7 and 28 days were obtained for the acrylic polymer superplasticizer (D).
- The best results in strengths properties can be obtained on the mixture proportioning using cement type A and basalt aggregate. The concretes with cement type A achieved the greater strengths with the of modified polycarboxylate ether superplasticizer (P), and the greater strengths with basalt aggregate with the polycarboxylate ether superplasticizer (V) and modified polycarboxylate ether superplasticizer (P).
- The best values of the strength ductility coefficient for all samples were obtained for the modified polycarboxylate ether superplasticizer (P) for which the best results for compressive strength and flexural tensile strength were obtained, considering them together. This fact confirms the correlation between the higher level of structural plasticity and homogeneity of the superplasticizer (P) found in the SEM analysis

with the higher values of the strength ductility coefficient for concrete samples obtained with using of this superplasticizer.

- The best superplasticizer type in this paper is modified polycarboxylate ether superplasticizer (P).
- The alkali content in SP has no significant effect on the ductility and the strength parameters obtained.

In the case of RPC concretes, a very important aspect is the use of aggregate with a low content of powder fractions, because these are properly, close to optimal filled with cement and microsilica.

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Wpływ składu mieszanki z domieszką superplastyfikatora na właściwości mechaniczne betonu o wysokiej wytrzymałości na bazie proszków reaktywnych

Słowa kluczowe: beton wysokowytrzymałościowy, beton z proszków reaktywnych, ciągliwość superplastyfikatora, projektowanie betonu, rodzaj superplastyfikatora

Streszczenie:

W artykule zamieszczono wpływ składu recepturowego betonu na jego właściwości mechaniczne. Badaniom poddano betony wysokowytrzymałościowe bazujące na proszkach reaktywnych, ale bez wykorzystania dodatkowego zbrojenia rozproszonego. Głównym założeniem autorów było uzyskanie klasy konsystencji S2 dla wszystkich receptur uwzględnionych w artykule. Betony zaprojektowano posługując się zmodyfikowaną procedurą de Larrarda opartą na modelu CPM (concrete packing model). W metodzie tej wprowadzono dodatkowe współczynniki uwzględniające ilość włókien zbrojenia rozproszonego, rodzaj i kształt formy próbek badawczych, czas, w którym wyznaczana jest wytrzymałość oraz współczynnik kruszywowy uwzględniający ilość frakcji poniżej 0,2 mm w mieszance betonowej. W badaniach uwzględniono dwa rodzaje kruszywa: granitowe i bazaltowe, dwa rodzaje betonu oznaczonych jako Cem A o powierzchni właściwej Blaina 3980 cm²/g i Cem B o powierzchni właściwej Blaina 4430 cm²/g oraz 3 rodzaje superplastyfikatorów oznaczonych jako D – z chemiczną bazą polimeru akrylowego, V – z chemiczną bazą eteru polikarboksylianowego i P – z chemiczną bazą zmodyfikowanego eteru polikarboksylianowego. Dla wszystkich wykonanych serii próbek badawczych wykonano test opadu stożka. Wyniki wytrzymałości betonów na ściskanie

i rozciąganie przedstawiono dla serii próbek badawczych spełniających kryterium klasy konsystencji S2. Określono współczynnik ciągliwości wytrzymałościowej jako proporcję wytrzymałość betonu na rozciąganie przy zginaniu w stosunku do wytrzymałości betonu na ściskanie. Przedstawiono wyniki współczynnika ciągliwości dla średnich wytrzymałości wszystkich serii próbek badawczych po 1, 7 i 28 dniach.

W artykule przedstawiono również badanie składu pierwiastkowego odparowanego superplastyfikatora z wykorzystaniem analizy SEM. Przedstawiono zdjęcia odparowanych i przygotowanych próbek superplastyfikatorów w celu określenia, który z SP ma największą ciągliwość, tzn. największe wymiary jednorodnych obszarów pomiędzy powstałymi pęknięciami. Wskazano na jakościową zgodność wyników opartych na współczynniku ciągliwości wytrzymałościowej i ciągliwości struktury superplastyfikatorów obserwowanej na podstawie analizy SEM.

W wyniku przeprowadzonych badań i analiz stwierdzono, że zastosowanie superplastyfikatora typu P pozwala uzyskać największe wytrzymałości betonu na rozciąganie przy zginaniu oraz wytrzymałości betonu na ściskanie przy zachowaniu założonej klasy konsystencji S2. Podkreślić należy również, że metodyka projektowania betonów UHPC oraz RPC z założenia uwzględnia domieszkę superplastyfikatora.

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