J Build Rehabil (2016) 1:18
DOI 10.1007/s41024-016-0020-7

RESEARCH ARTICLE

Determination of time zero in high strength concrete containing superabsorbent polymer and nano-silica

T. A. Cunha[1] · P. Francinete[1] · M. A. Manzano[1] · L. A. Aidar[2] · J. G. Borges[2] · E. F. Silva[1]

Received: 30 June 2016 / Accepted: 21 November 2016 / Published online: 28 November 2016

Abstract The autogenous shrinkage is a phenomenon that occurs due to the appearance of tensile stresses in capillary pores. Inherent in the hydration process, not depending on external interference. In high strength concrete, autogenous shrinkage is most pronounced, due to the refinement of microstructure, the high cement content, presence of mineral addictions and low water/cement ratio, which interfere in the transport of water curing. In this context, Superabsorbent polymers (SAP) stand out for their ability to reduce or eliminate the autogenous shrinkage, because they absorb large amounts of water, which is subsequently released into the matrix, avoiding self-desiccation and the onset of tensile stresses (internal curing). However, studies show that SAP can reduce the mechanical strength, which can be compensated by addiction of Nano-silica (NS). In this paper, the effect of these additions in Time Zero (T_0) was evaluated. T_0 determines the time at which the material starts to behave as a solid, with the development of a rigid mineral skeleton to oppose the volumetric variations that occurs in the paste, which can lead to cracking, compromising esthetics, durability, and structures safety. The ultrasonic pulse velocity test performed the T_0, which measures the velocity of propagation of an ultrasonic wave through the material and is taken as the time when a sudden change occurs at this velocity. Nine blends were made containing SAP and NS, where it was found that SAP addition increases the T_0 (up to 11%), while NS decrease its value (in 55%).

Keywords Ultrasonic pulse velocity · Time zero · High strength concrete · High performance concrete · Superabsorbent polymer · Nano-silica

1 Introduction

In the 1970s, when the compressive strength of concrete reached some greater values than usual, it was legitimate to call this material as a high strength concrete (HSC). Produce concrete with suitable workability by using low water/cement (w/c) ratio, using super pozzolans as silica fume and metakaolin and high cement content is a complex task. The reason is that with the increase of compressive strength, the concrete properties are no longer controlled exclusively by the w/c ratio, essential parameter to usual concrete due to the porosity of the hydrated paste [1].

In HSC, the high cement content, the low w/c ratio and the highly reactive mineral admixtures cause a refinement of the pores due to the greater presence of hydrates, which densified microstructure and raise up water demand, increasing the self-desiccation and resulting in greater levels of autogenous shrinkage and cracking in these particular concrete [2].

1.1 Mitigating of autogenous shrinkage with SAP

The autogenous shrinkage is an independent deformation of the cement paste during hardening. In traditional concretes, autogenous deformation is ignorable when compared to the shrinkage during the drying process. In the HSC, the low water/binder (w/b) rate and the use of

✉ T. A. Cunha
thyalacunha@unb.br

[1] Post-Graduate Program in Structures and Civil Construction (PECC/UnB), University of Brasília, Brasília, Federal District, Brazil

[2] Civil Engineering Department (ENC/UnB), University of Brasília, Brasília, Federal District, Brazil

mineral addictions cause a significant drop in relative humidity inside the pores, during hydration, even sealed (phenomenon closely related to the change of moisture). This shrinkage results in the onset of tensile stresses which can result in the appearance of micro or macro cracks, impairing the quality and performance of the concrete structure. It is a phenomenon known since the middle of twentieth century, but its practical significance was only recognized in recent years [3]. By the mechanism of capillary depression, the autogenous shrinkage happens when, in a portion not completely saturated, the liquid phase is pulled by creating meniscus at the liquid–gas interface, which induces a negative pressure in the capillary walls, tending to bring it over. The answer to this compression is the macroscopic shrinkage, called autogenous shrinkage [4].

Since the 1990s, autogenous shrinkage techniques and mitigation strategies have been studied, highlighting the use of absorbents materials saturated with water able to promote internal curing. These materials are called internal curing agents because they act providing water to the capillaries as it advances the hydration of cement, avoiding the appearance of tensile stresses responsible for autogenous shrinkage [5].

One of these alternatives has been proposed by Jensen and Hansen [6]. It consists of the addition of superabsorbent polymer particles (Superabsorbent polymers—SAP) to the concrete. These SAP absorb huge quantities of water and subsequently releases it inside the paste by providing necessary water to the surrounding matrix and mitigating or even eliminating the self-desiccation.

Superabsorbent polymers are a group of synthetic polymeric materials that have the ability to absorb significant amount of fluid from the environment and retain that liquid within its structure without dissolving. They are mainly used for absorbing water and aqueous solutions. The SAP can present absorption of up to 5000 times its own weight. However, in dilute salt solutions, the absorption capacity of the commercial products is about 50 g/g [6]. In engineering, the SAP are mostly linked polyacrylates crossed by covalent bonds or copolymerized polyacrylates/polyacrylamides [7]. In Fig. 1 is shown a spherical particle of SAP in the dry and saturated states, and its molecular structure representation.

During the mixing of the concrete, the SAP absorbs a large amount of water and builds macro inclusions containing free water. This free water is consumed during the cement hydration, as the relative humidity decreases ($RH < 100\%$), promoting internal cure. Due to the small particle size, their high water absorption and a good distribution volume, SAP can be very effective in internal curing of HSC [9]. Results proving the effectiveness of this polymer in the mitigation of autogenous shrinkage can also be found in studies by Mechtcherine [9], Igarashi and Watanabe [10], Craeye and Schutter [11], among others.

However, several studies have found that the SAP, during the desorption process, leaving empty spaces in the cement paste, which end up harming the mechanical strength of these materials [5, 12–18]. The question to consider is to what extent such loss is admissible. To promote compensation for this loss of strength, the use of Nano-silica particles was proposed, once this material is recognized in the technical community due to its improved capacity of the mechanical properties.

1.2 Use of nano-silica

The growing interest in the use of mineral additions incorporated into the cementitious material is due to the fact that, in addition to saving energy and preserving natural resources, provides advantages to the final product. The advantages may be attributed to the increasing of technological properties, reducing of the clinker consumption, reduction in the environmental impact, besides reducing the CO_2 emissions from cement kilns [19, 20].

Nano-silica (NS) is considered a highly reactive pozzolanic addition that has entailed improvements in the strength of cementitious materials and increasing resistance to water penetration, which strongly influences the durability of concrete, being more effective than silica fume. In addition to providing the filler effect to improve the microstructure of concrete and mortar, also functions as an activator for the Pozzolanic reaction and as nucleation sites, contributing to hydration. This behavior leads to an improvement in the microstructure due to the refinement of the pores, which improves the mechanical properties [21].

According to Sobolev and Sanchez [22], the beneficial effects of Nano-particles on the microstructure and about the performance of cementitious materials can be explained by the following factors:

- When well dispersed, increase the viscosity of the liquid phase, helping in the suspension of cement grains and aggregate, and thus improving the resistance to the segregation;
- Fill the empty spaces that exist between the grains, making it a more dense mixture (filler effect);
- The Nano-silica act as crystallization centers during the hydration of cement, to accelerate;
- Promotes the formation of small and uniform groups of hydrated calcium silicate;
- Improve the transition zone, strengthening the link between aggregate and paste.

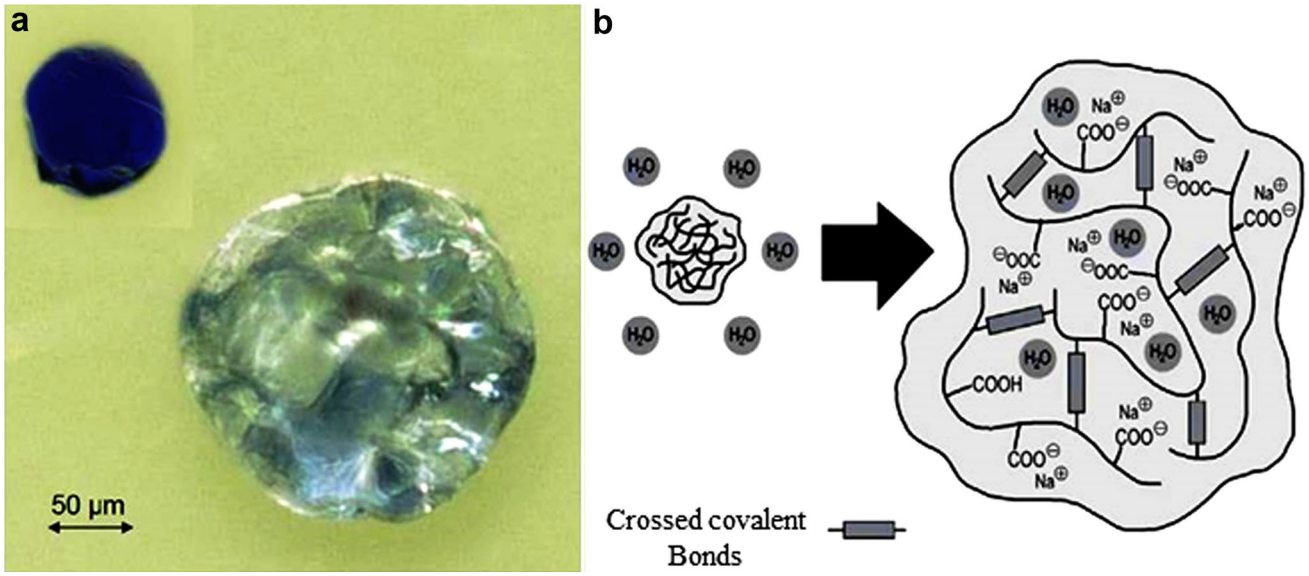

Fig. 1 **a** Dry and saturated SAP particle [8]; **b** representation of SAP based in polyacrylate [7]

1.3 Time zero

Time zero (T_0) is the interval time between the addition of water to the mixture and the time that the tensile stress become supported by the rigid skeleton formed in the concrete, characterizing the transition from the suspension state to the solid state. Some authors define this moment as "percolation threshold". T_0 is the duration time between the instant at which the water comes into contact with the cement until the moment in which the mixture develops a sufficiently rigid structure to resist the movement and allow transfer of tensile stress [4]. The solid grains of cement, previously isolated in the suspension phase, begin to make contact with each other as hydration products are being formed. These contacts are random, discontinuous about the volume and develop solid subsets continuously connected. The time at which the first path through the entire material is set is percolation threshold [4]. Figure 2 illustrates this phenomenon.

It is remarkable the existence of different T_0, which creates difficulty when compared results of separate surveys. Some theorists expressed the need for experimental determination of T_0 and the possibility of its use for the determination of the deformations that occur by autogenous shrinkage. Others believe that it can determine the starting time takes calculated by the normal paste, using the Vicat apparatus [16]. Although not standardized, the technique of Ultrasonic Pulse Velocity (UPV) for determining the transitional time between a fluid and a solid is increasingly used. This technique relate the change of the ultrasonic pulse velocity with the Time Zero and the hardening of mortar.

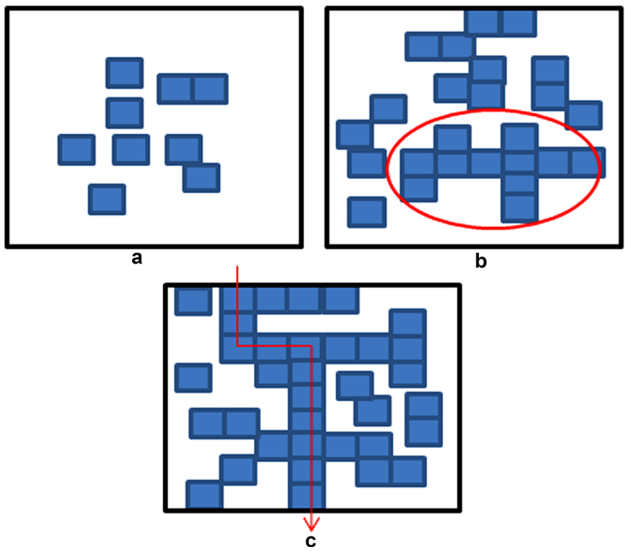

Fig. 2 Percolation threshold concept scheme: **a** hydrating events of the isolated products; **b** grouping the hydrates; **c** formation of the first mechanically switched path, which defines the percolation threshold [adapted, 4]

Numerous authors have reported an increase in the T_0 due to the addition of superabsorbent polymer cementitious materials. For them, the delay due to the SAP may be associated with increased cement flocculated particles, while the internal cure for the addition of water causes the seclusion of one particle to another [13, 15, 16, 23]. Although, the use of NS in cement pastes led to a considerable reduction in the T_0, caused by the increase in the velocity of hydration reactions [24]. The aim of this paper is to analyze the effect of these two additions at T_0 of high

strength concrete through the propagation of the ultrasonic wave technique.

2 Experimental program

2.1 Materials

Table 1 shows the properties of Portland cement and silica fume used in the manufacture of mixtures. This study uses high early strength cement, type CPV—ARI RS (CEM I). Silica fume is a national brand and non-densified. Both materials belong to the same manufacturing batch. Table 2 presents other relevant properties of Portland cement.

The fine aggregate used is natural, kind of washed sand of river, with fineness modulus of 2.6 and absorption of 0.3%. The particle size of the material fits in the optimal zone presented by ABNT NBR 7211: 2009 [25]. The superplasticizer (SP) used in this research was based on a polycarboxylate with normal setting time, a great efficiency water reducer classified as a third-generation class. It is a turbid liquid with 30% solids content.

2.2 Superabsorbent polymer

The superabsorbent polymer used in the study was provided by Professor Ole Mejlhede Jensen and developed at the Technical University of Denmark (DTU). It is the polymer based in an acrylic acid/acrylamide, with covalent crosslinks produced by the inverse suspension polymerization process [6]. The SAP has been specially developed for use in high alkaline environment, such as cement suspension. It was provided as a dry white powder, with spherical particles. In Fig. 3 is shown the size distribution of the studied SAP, obtained by laser granulometry method according the ERT 420.2-02:2012a, from EDANA [26], and an image of the dry particles obtained by optical microscope. Table 3 presents other relevant characteristics of this material.

2.3 Nano-silica

The nano-silica used in the research was chosen because of its physical and chemical characteristics, and considering the prior existence of supplier in Brazil. This is an aqueous solution and stabilized colloidal silica with 30% solid contents. NS amorphous particles have a negative surface charge, are discontinuous, slightly rough, spherical in shape and narrow particle size distribution. The dispersion is a translucent liquid, slightly more viscous than water, specially designed for use in concrete. Figure 4 shows the NS used by the transmission electronic microscopy (TEM) method. Other properties of the studied NS are shown in Table 4.

The NBR 5752: 2014 [30] describes the method for determining the performance index of Portland cement with other Pozzolans, at 28 days. As there is no specific standard for determining the Nano-silica performance index with Portland cement, applied the methodology of the performance index for the Metakaolin with Portland

Table 1 Chemical composition of Portland cement and silica fume used in this research (%)

Material	Chemical composition (%)									
	SO_3	MgO	SiO_2	Fe_2O_3	Al_2O_3	CaO	Free CaO	$CaSO_4$	Na_2O	K_2O
Cement	3.28	4.36	24.41	3.02	7.09	53.44	2.16	2.16	0.29	0.77
Silica Fume		0.49	93.55	0.16	0.15	0.37			0.26	0.85

Table 2 Density, specific surface, mechanical strength and other properties of Portland cement

Test method	Unit	Result	Limits by NBR 5733	Normative references
Density	g/cm^3	3.03	–	NBR NM 23:2001
Specific surface by Blaine	cm^2/g	5.723	≥3000	NBR NM 23:2001
Setting time				
Initial	h:m	03:00	≥01:00	NBR NM 65:2003
Final	h:m	04:10	≤10:00	NBR NM 65:2003
Normal consistency paste	(%)	32.8	–	NBR NM 43:2003
Autoclave expansion	(%)	0.1	–	ASTM C151
Compressive strength				
1 day	MPa	22.3	≥14.0	NBR 7215:1996
3 days	MPa	30.7	≥24.0	
7 days	MPa	39.5	≥34.0	

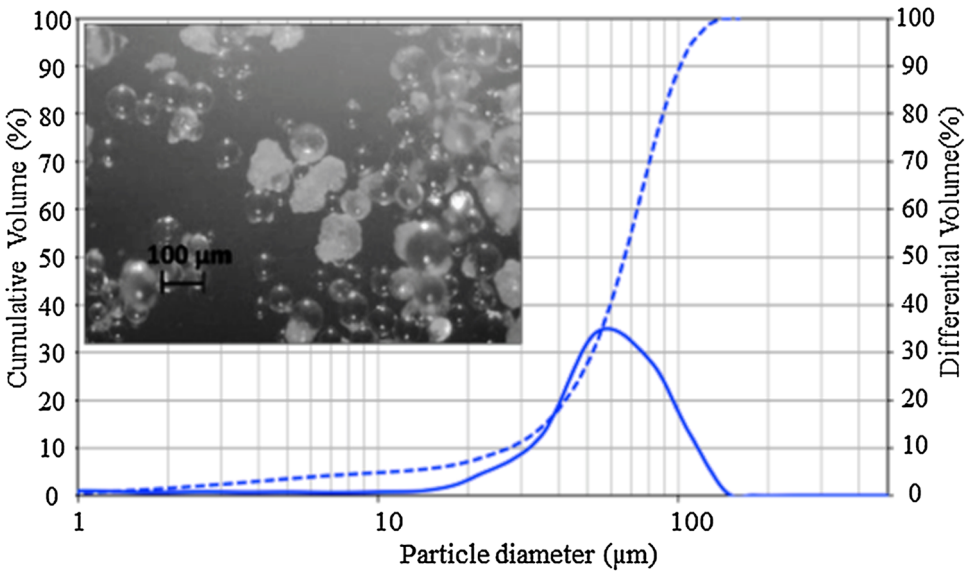

Fig. 3 Particle size distribution of the SAP studied and image of its particles in optical microscope [27]

Table 3 Properties of the studied SAP [28]

Property	Method	Results	References
Specific mass (g/ml)	Pycnometer	1.456	–
Absorption in aqueous environment (g/g)	Graduated cylinder	95.80	Jensen (2011)
	Optical microscope	80.30	–
Absorption in cementitious environment (g/g)	Slump-flow	15.00	Mönnig (2005)
Spherical particles composition	Scanning electron microscope (SEM)	C, O and Na	–
"Raspberry" particles composition		C, O, Na and S	
Particle size according the laser granulometry test	D10	27	ERT 420.2 (EDANA, 2002a)
	D50	66	
	D90	102	

cement in the standard NBR 15894: 2010 [31], changing the contents of additions. The performance index obtained by Andrade [29] is shown in Table 5. This test was conducted with the same Nano-silica used in this study, however, using the CPII-E-32 Portland cement (CEM II/B-S). It is observed that all mixes with addition of NS showed greater compressive strength than REF mixture after 28 days, showing that the addition of NS, even in small amounts, provides an increased compressive strength of mixtures. The pozzolanic reaction is the mainly reason for this behavior due the filler effect.

2.4 Studied mixtures

The experimental program is comprised of nine mixtures of high strength concrete, all with w/c ratio equal to 0.30. They are: a reference of mixture (REF), two mixtures containing 0.2 and 0.3% levels of superabsorbent polymer (SAP02 and SAP03), two mixtures containing 1 and 2% levels of Nano-silica (NS1 and NS2) and four mixtures containing the combination of these two additions (SAP02-NS1, SAP02-NS2, SAP03-NS1 and SAP03-NS2) as shown in Table 6. The content of superplasticizer (SP) for each mixture was experimentally determined in the Laboratory for Testing Materials at the University of Brasilia (LEM/UnB), in order to achieve a spread of 190 ± 10 mm, determined according to DIN 18555-2 [32], according to the TC's recommendations 225-SAP [33].

The composition of reference w/c ratio = 0.30 was suggested by TC 225-SAP [33] to carry out to the Round Robin tests and is presented in Table 2. The w/c ratio of 0.30 is usual for HSC.

2.5 Test methodology

2.5.1 Production of concrete

The script was based on TC 225-SAP [33] recommendations to carry out the Round Robin tests. The concrete was mixed on an inclined concrete-mixer with a capacity of

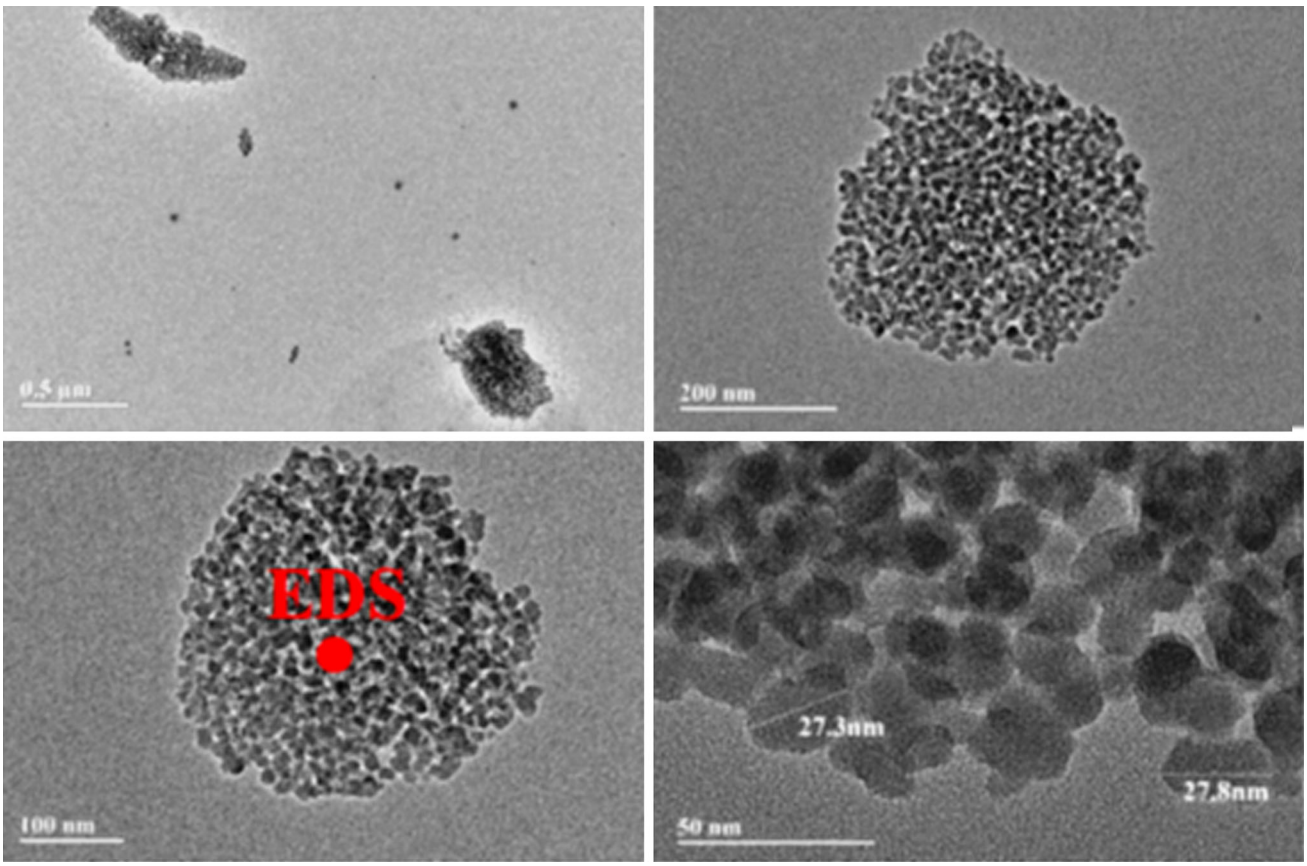

Fig. 4 Micrographs of Nano-silica applied in the research using transmission electronic microscopy [29]

320 L. First, the mixture of dried materials is performed, including the SAP, for 4 min. In parallel, the superplasticizer and the liquid NS was mixed with water. Then, it is added to the solution (water + NS + SP) to the dried materials already homogenized by mixing for 4 min. The concrete-mixer is then stopped to perform the scraping of material stuck on the edges and blades, and are then mixed for another 4 min.

2.5.2 *Fresh state tests*

The properties evaluated in the fresh state were spreading through the slump cone, by two different methods: according to DIN 18555-2/1982 [32] and according to ABNT NBR 13276/2005 [34]. It was also performed fresh density test of the mixtures, according to ABNT NBR 13278/2005 [35], the cone penetration test, according to ASTM C780/2007 [36] and the air content by the Pressure Method according to ABNT NBR NM 47/2002 [37].

Table 4 Properties of the colloidal nano-silica used in this program

Colloidal nano-silica properties	
Nano-silica content (%)	30.0
pH	10.5
Density (g/cm^3)	1.20
Na_2O content (%)	0.55
Particle size (nm)	3–40
Surface area (m^2/g)	80.0

2.5.3 *Test specimen to Ultrasonic Pulse Test (UPV)*

The dimensions of the test specimens were set on the basis of the transducer frequency, following the recommendations of RILEM NDT 1 [38], as shown in Table 7. The frequency of the transducer of the devices used was 54 kHz. The dimensions adopted were: cross section of 150 × 150 mm and length of 300 mm. The shape has a hole in each of its smaller sections with 50 mm in diameter.

The test specimens were cast in three layers compacted manually with 30 hits of the standard socket of the spreading test. Then the test specimens were sealed inside the shape with PVC film and adhesive tape, to prevent water loss, and then taken in a temperature-controlled room (21 ± 2° C) where were attached to the equipment for testing.

Table 5 The performance index of the nano-silica studied in this research according NBR 5752:2014 [29]

Mixture	Results at 28 days	
	Compressive strength (MPa)	Performance index
REF	36.05	100.00
NS1	37.15	103.05
NS2	39.23	108.82

Table 7 Natural frequency of the transducer according to the dimensions of the test specimens [38]

Distance to be traveled by the wave (mm)	Natural frequency of the transducer (kHz)	Minimum lateral width of the element (mm)
100–700	≥60	70
200–1500	≥40	150
>1500	≥20	300

2.5.4 Time zero experimental determination

According to Reinhardt [39], the first trials using the ultrasonic pulse to determine the T_0 of concrete were proposed by Casson and Domone in 1982. The authors used the method to show the influence of temperature and additives in the setting time. They also have a reasonable correlation between the derivative of the velocity of the ultrasonic pulse (relative to time) and the maximum velocity of the hydration reaction.

The methodology used to determine the T_0 was proposed by Silva [4], also using as a reference the standard ABNT NBR 8802:2013 [40]. The purpose of the test is to determine the velocity of propagation of an ultrasonic wave through the time necessary for it to travel a known distance. The test is performed within 48 h after molding, from the moment of addition of water. Figure 5 shows the equipment performing the test, whose methodology is described below [41]:

- Manufacturing the concrete with environment and constituent materials in temperature (21 ± 2° C);
- Assess the equipment using the reference bar that comes with the device with known transit time;
- Place a silicone gel layer on the faces of the transducers to ensure continuous contact with the concrete;
- Connect the receiver and transmitter in the existing holes in the sides of shape so as to face it internally, providing an arrangement with direct transmission of the electric pulse as a shock wave;
- Wrap the test specimen in a prismatic form, with section of 150 mm × 150 mm and length of 300 mm section;
- Cover the exposed surface with plastic wrap and adhesive tape, preventing the loss of water;
- Starts the acquisition data of UPV during the first 48 h after molding. The interval between readings is 3 min;
- Plot the curve UPV versus age of concrete;

Table 6 Mixtures produced in this research

Mixture	Dry materials (Kg/m^3)				Nano-silica				Water (Kg/m^3)			Superplasticizer (SP)	
	Cement	Silica Fume	Sand	SAP	Total content (%)	Total weight (kg/m^3)	NS pure content (%)	Pure weight (kg/m^3)	Water added	Water in NS	Curing water for PSA	Content (%)	Weight (kg/m^3)
REF	700	70	1340	–	–	–	–	–	210	–	–	2.6	18.2
SAP02	700	70	1340	1.4	–	–	–	–	210	–	21.0	3.0	21.0
SAP03	700	70	1340	2.1	–	–	–	–	210	–	31.5	3.2	22.4
NS1	700	70	1340	–	3.3	23.4	1	7	210	16.4	–	3.0	21.0
NS2	700	70	1340	–	6.7	46.7	2	14	210	32.7	–	3.5	24.5
SAP02-NS1	700	70	1340	1.4	3.3	23.4	1	7	210	16.4	21.0	3.2	22.4
SAP02-NS2	700	70	1340	1.4	6.7	46.7	2	14	210	32.7	21.0	3.5	24.5
SAP03-NS1	700	70	1340	2.1	3.3	23.4	1	7	210	16.4	31.5	3.5	24.5
SAP03-NS2	700	70	1340	2.1	6.7	46.7	2	14	210	32.7	31.5	3.9	27.3

1. Adopted the value of 15 g/g for the absorption of SAP in cementitious environment

2. The surface humidity of the sand was determined by Chapman Test

3. The SP content was experimentally determined to achieve the desired spreading

Fig. 5 Determination of the time zero test scheme (T_0) by the UPV method

Table 8 Properties in fresh state: results

Mixture	Addiction content (%)			Results of fresh state properties				
	SAP	NS	SP	Spreading (mm)		Cone penetration (mm)	Air content (%)	Density in the fresh state (g/ml)
				DIN	NBR			
REF	–	–	2.6	193	233	83	1.7	2.316
SAP02	0.2	–	3.0	193	225	80	2.4	2.257
SAP03	0.3	–	3.2	192	220	80	2.9	2.242
NS1	–	1	3.0	187	196	79	3.2	2.307
NS2	–	2	3.5	193	222	83	3.4	2.315
SAP02-NS1	0.2	1	3.2	188	206	78	3.3	2.270
SAP02-NS2	0.2	2	3.5	180	195	69	3.2	2.225
SAP03-NS1	0.3	1	3.5	198	210	81	3.8	2.258
SAP03-NS2	0.3	2	3.9	180	199	73	3.4	2.257

- The percolation threshold is assumed as the age of the concrete where there was a sharp increase in the UPV.

The time from the addition of water into the mixture until the beginning of data acquisition was approximately 1 h for all mixtures. This time was added at the determined T_0 in the ultrasound test.

3 Results and discussion

3.1 Properties in fresh state

The Table 8 shows the summary of the results of the various tests carried out in the fresh state.

The spreading values by DIN [32] were within the specified range (190 ± 10 mm) in all mixtures, by varying the admixture SP content and adding up the internal cure water. The results of the spreading determined by NBR 13276 [34] were determined for comparison purposes. The cone penetration results show a strong correlation with the tension leakage, a rheological property of the material. Angelim [42] considered as a fluid the mixtures that the spreading is greater than 69 mm. The results obtained in this study were greater than the minimum coating mortar consistency established by this author. Therefore, the mixtures studied in this research can be classified as very fluid. It was observed that the addition of SAP has an expressive influence on the air content (at the mix containing 0.3% of SAP, was an increase of 71% compared to the REF). The most presence of air bubble left in the matrix during the release process of the curing water by the SAP seems to justify this behavior, which can also affect the development of the mechanical properties [17]. Increasing the NS percent also caused increase in air content, which is in agreement with the results obtained by Senff et al. [43] According the authors, the presence of NS causes a decrease in density in the fresh state, which interferes with the air content.

There is a reduction in the density in the fresh state caused by the addition of SAP. This behavior can be explained by the greater air content caused by the polymer [5]. Also, the addition of the internal cure water for the

SAP, in amounts of 21 and 3.5 kg/m^3, for the mixtures containing 0.2 and 0.3% of SAP, respectively, may have contributed to this behavior. Mixtures containing only NS and hybrid mixtures showed no significant changes in this property.

3.2 Time zero

The UPV curve versus the time for the determination test for the time is shown in Fig. 6. Table 8 shows a summary of the results and their percentage related to the reference mixes.

The total time period considered for the execution of the test was 48 h, because after this period occurs the stabilization of the velocity readings. The graphs obtained at T_0 test may be associated with cement hydration stages. Immediately after mixing, the Phase 1 occurs, or pre-induction, lasting approximately 15 min. In Phase 2, called dormancy, the UPV readings start to be carried out, however, they are all zero (0 m/s). Phase 3 starts at the moment where there is a sudden change in velocity, called acceleration period, and corresponds to the first continuous path of connected mechanically grains, defining T_0. Phase 4, or deceleration period, is characterized by the increase values of velocity, but with a lower growth rate. In the Phase 5, or stabilization, the changes are minor, and the velocity tends to stabilize [44].

3.2.1 Effect of SAP

Note that the addition of the polymer causes an increase in the value of the T_0 of the mixtures, 4 and 11% for mixes SAP02 and SAP03, respectively. The setting time delay due to the SAP may be associated with an increase of the flocculated particles of cement, while the addition of water for internal cure causes the separation of the cement particles [15]. Dudziak and Mechtcherine [45] found that the addition of SAP affected the T_0 in ultra-high performance concrete (UHPC). They studied a content of 0.4% of a specific SAP and reported an increase in 1 h 40 min at T_0 regarding to the reference mixture, which represents approximately a 20% increase.

3.2.2 Effect of NS

The Nano-silica had reverse effect, since the T_0 decreased to 54 and 55% in the NS1 and NS2 mixtures, respectively. As NS is added to the mixture, the setting time is reduced, the heat release rate increases, the calcium hydroxide (CH) reacts with the NS and the mixtures are more consistent. The NS not only behaves as an agent to improve the microstructure, but also as an activator to accelerate the pozzolanic reactions [46]. It also acts as nucleation sites, promoting the acceleration of cement hydration reactions, which cause a considerable reduction at T_0. Moreover, it accelerates the consumption of C3S, the production of portlandite and homogeneous groups of C–S–H, thus favoring the appearance of the first solid path of grains mechanically connected [47].

Previous studies [48] noted that the increasing content of NS causes a significant decrease in the setting time, 61 and 37%, using concentrations of 1 and 2% of Nano-silica. This behavior is related to the acceleration of the hydration reactions, provided by high specific surface. The results show that it is possible to establish a relationship between T_0 and the beginning of the acceleration period of the cement hydration, since the decreasing of the setting time is related to a proportional decrease in the time to reach the maximum temperature.

It has not been established if the faster hydration in the presence of NS is due to its pozzolanic activity or to the high surface area. Furthermore, there is a greater presence

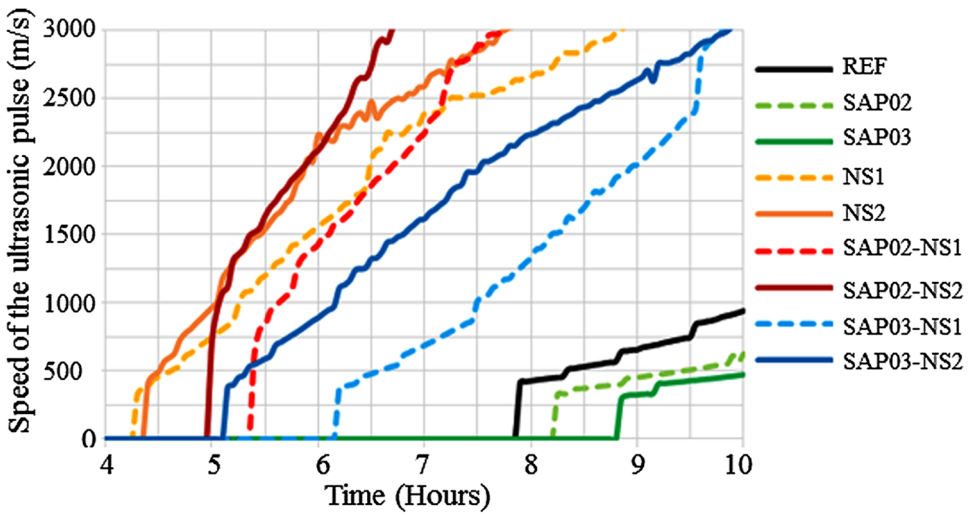

Fig. 6 UPV × time: determination of T_0 of the studied materials

Table 9 T_0 obtained by the ultrasonic pulse velocity (UPV)

Mixture	Time zero (T_0)	% Compared to REF	% Compared to SAP mixture	
			SAP02	SAP03
REF	7 h 54 min (474 min)	100		
SAP02	8 h 12 min (492 min)	104	100	
SAP03	8 h 48 min (528 min)	111		100
NS1	4 h 16 min (256 min)	54		
NS2	4 h 20 min (260 min)	55		
SAP02-NS1	5 h 24 min (324 min)	68	65	
SAP02-NS2	4 h 59 min (299 min)	63	60	
SAP03-NS1	6 h 11 min (371 min)	78		70
SAP03-NS2	5 h 07 min (307 min)	65		58

of calcium hydroxide (CH) in samples with NS. The rapid growth of CH crystals occurs at the end of the induction period and it suggests that the CH precipitation is related to the beginning of the acceleration phase and, consequently, the Time Zero [49].

3.2.3 Effect of SAP and NS combined use

Mixtures containing the two additions also showed a lower T_0, the NS effect being much more visible than the SAP effect. This behavior was expected, since the percentage reduction caused by the NS (around 45%) is much more evident than the increase promoted by SAP (8% on average). Mixtures containing both additions had a T_0 value well below those values shown for the REF (approximately 65% averaged for the four hybrid mixtures). This behavior is mainly due to the addition of the NS in these mixtures, because as stated above, the addition of NS reduces the T_0. Although, the hybrid mixes obtained better results than the mixtures containing only NS (increase of 14 and 24% for SAP02-NS1 and SAP03-NS1, compared with NS1 mixture, and increased by 8 and 10% for the SAP02-NS2 and SAP03-NS2, when related to the mixture NS2). This behavior leads to the conclusion that it appears that the addition of SAP in the presence of NS, had the same effect on the mixtures containing only SAP. In other words, the addition of SAP is able to increases T_0 even in mixtures containing NS addition.

4 Conclusions

About the method of the Ultrasonic Pulse Velocity (UPV) provides satisfactory results to determine the setting time of high strength concrete and are consistent with other studies performed previously.

The additions studied changed significantly some properties in the fresh state, it is necessary to also increase the superplasticizer content, which has a more pronounced effect for the mixture SAP03-NS2, where there was a 50% increase in the level of SP. Both additions also caused slight reduction in the density of the mixtures in the fresh state, which can be justified by the presence of empty spaces in the paste. The addition of SAP also influenced the air content, increasing it. The polymer used reached a 71% increase in this property, from the 0.3% level. The same behavior was observed from the addition of NS, which caused an increase of 100% of the mixture NS2. In the hybrid mixtures it was observed the same behavior, which can be explained by the increased number of empty spaces left by SAP, and also due to the reduction in the density of the mixture promoted by NS.

The effect of the two additions at T_0 validates previous research results, where it is found that the SAP increases Time Zero, while the NS cause reduction. The increasing of the T_0 caused by the SAP was around 11% of 0.3% content. The addition of NS reduced the T_0 by approximately 45% in both added contents. SAP's ability to increase the T_0 value was not influenced by the addition of NS, since the hybrid mixtures containing SAP and NS showed an increase of T_0 when compared with concrete containing only NS. This behavior can also be related to the high content of superplasticizer additive used (Table 9).

Therefore, it is concluded that the addition of superabsorbent polymers (SAP) causes an increase in the T_0 of the material; the addition of Nano-silica has the effect of decreasing the setting time of concrete.

Acknowledgements The authors thanks the University of Brasilia, by the opportunity. The Material Testing Laboratory (LEM/UNB) and Furnas Central Hydropower S.A., partnerships in this research. The National Council for Scientific and Technological Development (CNPq) and the Federal Institute of Education, Science and Technology of Goiás (IFG), for financial support. The Professor Jensen and DTU by providing the studied SAP and the other suppliers and partners.

References

1. Aitcin PC (1998) High-performance concrete, 1st edn. E&FN Spon, London
2. Lopes AN (2011) Mitigação da retração autógena em concretos de alta resistência contendo aditivo redutor de retração e seus efeitos na macro e microestrutura - Doctoral Thesis. Universidade Federal do Rio Grande do Sul, Porto Alegre
3. Lura P (2003) Autogenous deformation and internal curing of concrete - Doctoral Thesis. Delft University of Technology, Delft
4. Silva EF (2007) Variações dimensionais em concretos de alto desempenho contendo aditivo redutor de retração - Doctoral Thesis. Universidade Federal do Rio de Janeiro, Rio de Janeiro
5. Suarez ML (2015) Polímeros superabsorventes (PSA) como agente de cura interna para prevenir fissuração em concretos de alta resistência - Masters Dissertation. Universidade de Brasília, Brasília
6. Jensen OM, Hansen PF (2001) Water-entrained cement-based materials I: principles and theoretical background. Cem Concr Res 31:647–654
7. Friedrich SV (2012) Superabsorbent polymers (SAP). In: Mechtcherine V (ed) State of the art report of RILEM technical committee 225-SAP. Springer, France
8. Assmann A (2013) Physical properties of concrete modified with superabsorbent polymers - Doctoral Thesis. Stuttgart: Fakultät für Bau- und Umweltingenieurwissenschaften der Universität Stuttgart
9. Mechtcherine V, Dudziak L, Hempel S (2009) Mitigating early age shrinkage of ultra-high performance concrete by using superabsorbent polymers (SAP). In: Tanabe T et al (eds) Shrinkage and durability mechanics of concrete and concrete structures - CONCREEP-8. London
10. Igarashi S, Watanabe A (2006) Experimental study on prevention of autogenous deformation by Internal curing using super-absorbent polymer particles. In: Jensen OM, Lura P, Kovler K (eds) Pro changes of hardening concrete: testing and mitigation, vol 52. RILEM, France
11. Craeye B, Schutter G (2006) Experimental evaluation of autogenous shrinkage by means of a vertical dilatometer for concrete. In: Jensen OM, Lura P, Kovler K (eds) Pro changes of hardening concrete: testing and mitigation, vol 52. RILEM, France
12. Kumm TC (2009) Influência do emprego de polímeros superabsorventes nas propriedades de materiais à base de cimento Portland - Masters Dissertation. Universidade Federal de Santa Catarina, Florianópolis
13. Pereira DF, Matos VN (2011) Combate à retração autógena utilizando polímeros superabsorventes - Final Graduation Work. Universidade de Brasília, Brasília
14. Claro GP, Saraiva LM (2013) Contribuição ao estudo da retração autógena em concretos de alta resistência - Final Graduation Work. Universidade de Brasília, Brasília
15. Ordoñez SL (2013) Mitigação da retração autógena em microconcretos de alta resistência com adição de PSA e aditivo redutor de retração - Masters Dissertation. Universidade de Brasília (PECC), Brasília
16. Traldi CL, Aguirre LM (2013) PSA como agente de cura interna para prevenir fissuração devido à retração autógena - Final Graduation Work. Universidade de Brasília, Brasília
17. Manzano MR (2016) Estudo experimental de microconcretos de alta resistência modificados com polímeros superabsorventes - Doctoral Thesis. Universidade de Brasília, Brasília
18. Santos TAC (2016) Estudo da Adição de PSA e Nanossílica para melhorar propriedades de concretos de alta resistência - Masters Dissertation. Universidade de Brasília, Brasília
19. Neville AM (1996) Propriedades do concreto, 2nd edn. Pini, São Paulo
20. Mehta PK, Monteiro PJ (2008) Concreto: microestrutura, propriedades e materiais, 3rd edn. Ibracon, São Paulo
21. Gleize PJ (2007) Nanotecnologia e materiais de construção. In: Isaia GC (ed) Materiais de Construção Civil e Princípios de Ciência e Engenharia de Materiais, vol 2, 2nd edn. Ibracon, São Paulo
22. Sobolev K, Sanchez F (2010) Nanotechnology in concrete: a review. Constr Build Mater 24:2060–2071
23. Moraes BJ, Cerqueira CM (2014) Determinação do T_0 de microconcretos contendo polímeros superabsorventes utilizando a técnica do ultrassom - Final Graduation Work. Universidade de Brasília, Brasília
24. Kong D et al (2013) Influence of nano-silica agglomeration on fresh properties of cement pastes. Constr Build Mater 37:707–715
25. Associação Brasileira de Normas Técnicas (2009) NBR 7211: Agregado para concreto: especificação. ABNT, Rio de Janeiro
26. European Disposals and Nonwovens Association. ERT 420.2-02 (2002) Recommended test method: determination of content of respirable particles. EDANA, Belgium, p 2002
27. Manzano MAR et al (2016) Estudo da hidratação de pastas de cimento contendo polímero superabsorvente pela técnica da difração de raios-X. In: 58° Congresso Brasileiro do Concreto. Belo Horizonte, Ibracon
28. Manzano MAR et al (2015) Análise da caracterização de um PSA utilizado em materiais cimentício. In: Congresso Latino-Americano de Patologia da Construção – CONPAT 2015. Alconpat, Lisboa
29. Andrade DDS (2015) Microestrutura de pastas de cimento Portland com incorporação de nanossílica e adições altamente reativas - Doctoral Qualification. Universidade de Brasília, Brasília
30. Associação Brasileira de Normas Técnicas (2014) NBR 5752: Materiais pozolânicos - Determinação de atividade pozolânica com cimento Portland aos 28 dias. ABNT, Rio de Janeiro
31. Associação Brasileira de Normas Técnicas (2010) NBR 15894: Metacaulim para uso com cimento Portland em concreto, argamassa e pasta - Parte 1: Requisitos. ABNT, Rio de Janeiro
32. Deutsches Institut für Normung (1982) 18555-2: Testing of mortars containing mineral binders, freshly mixed mortars containing aggregates of dense structure (heavy aggregates), determination of consistence, bulk density and air content. DIN, Germany
33. Mechtcherine V, Reinhardt HW (2007) Application of superabsorbent polymer (SAP) in concrete construction: state of the art report technical committee TC-225-SAP. Springer, London
34. Associação Brasileira de Normas Técnicas (2005) NBR 13276: Argamassa para revestimento de paredes e tetos - preparo da mistura e determinação do índice de consistência. ABNT, Rio de janeiro
35. Associação Brasileira de Normas Técnicas (2005) NBR 13278: Argamassa para revestimento de paredes e tetos - determinação da densidade de massa e do teor de ar incorporado. ABNT, Rio de Janeiro
36. American Society for Testing and Materials (2014) C780: Standard test method for preconstruction and construction evaluation of mortars for plain and reinforced unit masonry. ASTM, Philadelphia
37. Associação Brasileira de Normas Técnicas (2002) NBR NM 47: Concreto - determinação do teor de ar em concreto fresco - método pressométrico. ABNT, Rio de janeiro
38. Réunion Internationale des Laboratoires et Experts des Matériaux (1972) NDT 1 - Testing of concrete by the ultrasonic pulse method. RILEM, Belgium
39. Reinhardt HW, Grobe CU, Herb AT (2000) Ultrasonic monitoring of setting and hardening of cement mortar: a new device. Mater Struct 33:580–583

40. Associação Brasileira de Normas Técnicas (2013) NBR 8802: Concreto endurecido - determinação da velocidade de propagação da onda ultrassônica. ABNT, Rio de Janeiro
41. Silva EF et al (2011) Técnica do pulso ultrassônico para determinação do T_0 de concretos contendo aditivo redutor de retração. In: 6° Congresso Luso-Moçambicano de Engenharia. Maputo
42. Angelim RR (2000) Influência da adição de finos calcários, silicosos e argilosos no comportamento de argamassas de revestimento - Masters Dissertation. Universidade Federal de Goiás, Goiânia
43. Senff L et al (2009) Effect of nano-silica on rheology and fresh properties of cement pastes and mortars. Constr Build Mater 23:2487–2491
44. Trtnik G, Gams M (2014) Recent advances of ultrasonic testing of cement based materials at early ages. Ultrassonics 54:66–75
45. Dudziak L, Mechtcherine V (2008) Mitigation of volume changes of ultra-high performance concrete by using superabsorbent polymers. In: Kassel: 2nd international symposium on ultra high performance concrete
46. Scrivener KL, Kirkpatrick R (2008) Innovation in use and research on cementitious material. Cem Concr Res 38:128–136
47. Aleen AS, Heikal M, Morsi WM (2014) Hydration characteristic, thermal expansion and microstructure of cement containing nano-silica. Constr Build Mater 59:151–160
48. Senff L (2009) Efeito da adição de micro e nanossílica no comportamento reológico e propriedades no estado endurecido de argamassas e pastas de cimento - Doctoral Thesis. Universidade Federal de Santa Catarina, Florianópolis
49. Björnström J et al (2004) Accelerating effects of colloidal nano-silica for beneficial calcium–silicate–hydrate formation in cement. Chem Phys Lett 392:242–248