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Incorporation mode effect of Nano-silica on the rheological and mechanical properties of cementitious pastes and cement mortars

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Abstract. Previous research indicates that the inclusion of nanosilica (NS) modifies the properties of the fresh and hardened state, compared to the traditional mineral additions. NS decreases the setting times of the cement mortar compared to silica fume (SF) and reduce of required water while improving the cohesion of the mixtures in the fresh state. Some authors estimate that the appropriate percentage of Nano-silica should be small (1 to 5% by weight) because of difficulties caused by agglomeration to particles during mixing, while others indicate that 10% by weight, if adjustments are made to the formulation to avoid an excess of self-drying and micro cracks that could impede strength. For this purpose, the present work aim to see the effect of the introduction mode of the nanosilica on the rheological and physic mechanical properties of cement mortars. In this study, NS was used either powdered with cement or in solution with the superplasticizer (Superplasticizer doped in nanosilica). Results show that the use of nanosilica powder (replacing cement on the one hand) has a negative influence on the rheological parameters and the rheological behavior of cementitious pastes. However, the introduction of nanosilica in solution in the superplasticizer (SP) was significantly improved the rheological parameters and the rheological behavior of cementitious pastes. Indeed, more the dosage of NS-doped SP increases more the shear stress and viscosities of the cementitious pastes become more fluid and manageable. A significant reduction of shear stress and plastic viscosity were observed that due to the increase in superplasticizer. A dosage of 1.5% NS-doped SP gave adequate fluidity and the shear rate was lower.

1. Introduction

The nanotechnology of nano-structured materials develops with an astronomical speed and gains from days to day new fields of application [1-5]. It is the potential to be the key to a whole new world of today's industry, especially the production of building materials. Among the most important in the global economy, the latter is one of the major contributors to global warming by greenhouse gas (GHG) emissions and, on the other hand, is energy intensive and far from being an example of sustainable development because of the continued depletion of natural resources. The increase in energy prices and environmental requirements require a different understanding of the composition of concretes, while maintaining the same performances [5-7]. One of the possible solutions to be envisaged to mitigate this environmental and economic problem is the sustainable development of the mortar which would save not only the natural resources and the energy but also the protected environment by reduction of the wastes.

In this regard, nanotechnology helps to make concrete an intelligent material designed by the incorporation of Nano-sized substitute such as nanoparticles (NP), which is a superior and economical experience of the hour. The mastery of the science of the infinitely small makes it possible to better understand and control, at the atomic scale, the Nano-modification of cement-based materials as well as their influence on the behaviour and properties of mortar and concrete. The fresh state, the rheological functionality and the hydration process of cement paste which play an important role in the determination of the concrete structure and also on the mechanical properties and the durability [6-11]. Nanosilica is a very effective pozzolanic material. They are very fine glassy particles, about 1000 times smaller than the average cement particles [2-3]. It forms an excellent mixture with cement to improve the overall quality of the cementitious matrix to a great extent. It behaves on a scale not only as a filler to improve the microstructure, but also as an activator to promote the pozolanic reaction. Rapid and accelerated hydration is recorded in NS-containing cement pastes, but it has not yet been established whether this is due to chemical reactivity (pozzolanic activity) or high surface area. The pozzolanic reaction results in a reduction in the amount of calcium hydroxide in the concrete and reduces the price time, porosity, water absorption and permeability. It accelerates the dissolution of C-S and the formation of C-S-H with inverted activity proportional to the size and destination of nucleation sites for C-S-H. NS by their size can fill the spaces between the C-S-H gel particles, acting as a Nano-filler material [8-12].

Previous research indicates that the inclusion of nanosilica (NS) modifies the properties of the fresh and hardened state, compared to the traditional mineral additions. NS decreases the setting times of the cement mortar compared to silica fume (SF) and reduce of required water while improving the cohesion of the mixtures in the fresh state. Some authors estimate that the appropriate percentage of Nano-silica should be small (1 to 5% by weight) because of difficulties caused by agglomeration to particles during mixing, while others indicate that 10% by weight, if adjustments are made to the formulation to avoid an excess of self-drying and micro cracks that could impede strength. For this purpose, the present work aim to see the effect of the introduction mode of the nanosilica on the rheological and physic mechanical properties of cement mortars.

2. Experimental Study

2.1. Materials used

The ordinary Portland cement CEM II (42.5N type) was used in this work and it is conformed to ENV norm. The Nano-silica (NS) used is manufactured by EVONIK INDUSTRIE named AEROSIL 200 (Figure 1). It is a white amorphous powder having a silica content of 99.8% and a specific surface area of 200 m2/g with particle size about 12 nm (table 1). The chemical and physical characteristics of NS are given in Table 1. A polycarboxylate type (SP) is used as superplasticizer to ensure some workability. For mortar mixes, natural sand (S) with a maximum size of 5 mm is used in this study.

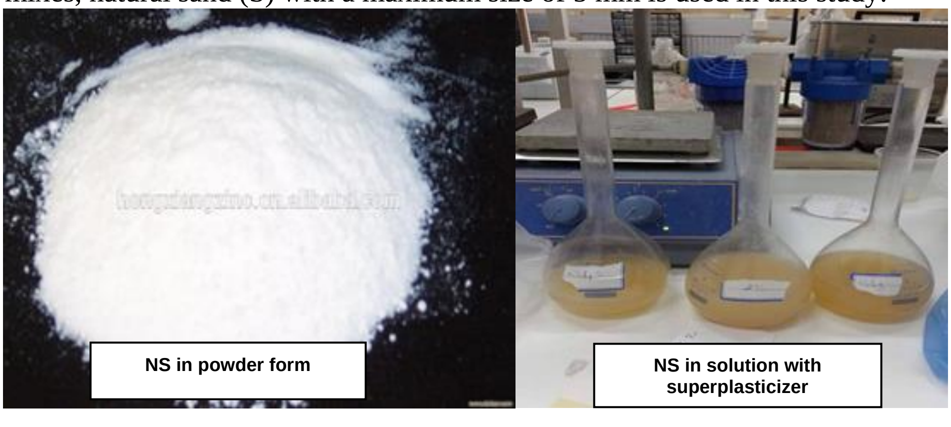


Figure 1 Nano-silica (NS) used in this work; Image obtained by SEM for Nano-silica (NS).

Table 1 Chemical composition and physical properties of cementitious materials.

Items	Chemical composition (%)	
	Ordinary Portland Cement OPC	Nano-silica NS
SiO_2	17.3	99.8
Al_2O_3	5.54	0.05
Fe_2O_3	2.80	0.005
CaO	59.34	–
MgO	1.84	–
SO_3	2.51	–
K_2O	0.54	–
Na_2O	0.25	–
P_2O_5	0.09	–
TiO_2	0.30	0.003
L.O.I	2.29	1.00
Specific gravity	3.15	-
Avg. particle size SSA (cm^2/g)	3700	200.10^4

2.2. Details of cement paste and mortar mixtures

The study was divided into two parts. Firstly, the work involves studying the effect of nanosilica in powder (2, 4, 6 and 8%.wt of cement) and solution (0.7, 1.3 and 2.8%.wt of SP) on the rheological behaviour of cementitious pastes. The saturation point is the dosage above which the superplasticizer has no effect on the rheological properties of cement paste was evaluated. This study part was carried by AR 2000 rheometer (Table2). Second work part was realized on the cement mortars with same content of NS in two cases (in powder and in SP-solution). The Control Mortar (CM) was prepared according to the European standard EN 196-1 (Table3). After, NS was used in powder form by cement substitution (2, 4, 6 and 8%.wt of cement) and used in solution with superplasticizer (0.7, 1.3 and 2.8%.wt of SP).

Table 2: Mixtures details of studied cement pastes

	NS in Solution [%]	NS in powder [%]	PC [%]	Water [g]	SP [%]	E/C
PC2NS	-	2	98	40	0,70	0,4
PC4NS	-	4	96	40	1,30	0,4
PC6NS	-	6	94	40	3,00	0,4
PC8NS	-	8	92	40	3,50	0,4
PC-NS0,7	0,7	-	100	30	0,50	0,3
PC-NS1,3	1,3	-	100	30	1,00	0,3
PC-NS2,8	2,8	-	100	30	1,50	0,3
PC-NS3,2	3,2	-	100	30	2,00	0,3

The cement mortars were mixed in a rotary kneader. Nanoparticles are not easily dispersed evenly because of their high surface energy. As a result, the mixing was carried out as follows; the nano-silica particles were stirred with the mixing water at high speed for 1 min. After, the cement was added to the mixer and mixed at medium speed for another 1 min. Then, the superplasticizer has been added and stirred at high speed for 30 s. Finaly, the sand was added gradually, then mixed for 2 min 30 s at high speed.

Table 3: Mixtures details of cement mortars

	NS in Solution [%]	NS in powder [%]	PC [g]	Water [g]	Sand [g]	SP [%]	E/C
M0	0	0	450	225	1350	0	0,5
MNS2	-	2	441	225	1350	0,70	0,5
MNS4	-	4	432	225	1350	1,30	0,5
MNS6	-	6	423	225	1350	3,00	0,5
M-NS0,7	0,7	-	450	180	1350	0,50	0,4
M-NS1,3	1,3	-	450	180	1350	1,00	0,4
M-NS2,8	2,8	-	450	180	1350	1,50	0,4
M-NS3,2	3,2	-	450	180	1350	2,00	0,4

2.3. Test Methods:

Rheological study: the rheological tests are performed on several series of cement paste samples for two studies cases of Nanosilica adding. The superplasticizer dosage is determined by testing the saturation point. Rheology tests were performed at 20 °C using a rheometer AR2000 (Figure2) equipped with a valve rotor speed imposed according to the following: presheared to 50 s-1 for 60 s followed by a rest period of 30s, then a linear ramp increasing rate of 0-435 s-1 is applied through the rheometer (Figure3). The flow curves were analyzed and modeled by the software Rheology Advantage Data Analysis (Version-V4.021/TA-Instrument).

Figure 2 : Rheometer AR2000 used for rheological study.

Figure 3 : Mexing of cement pastes with NS.

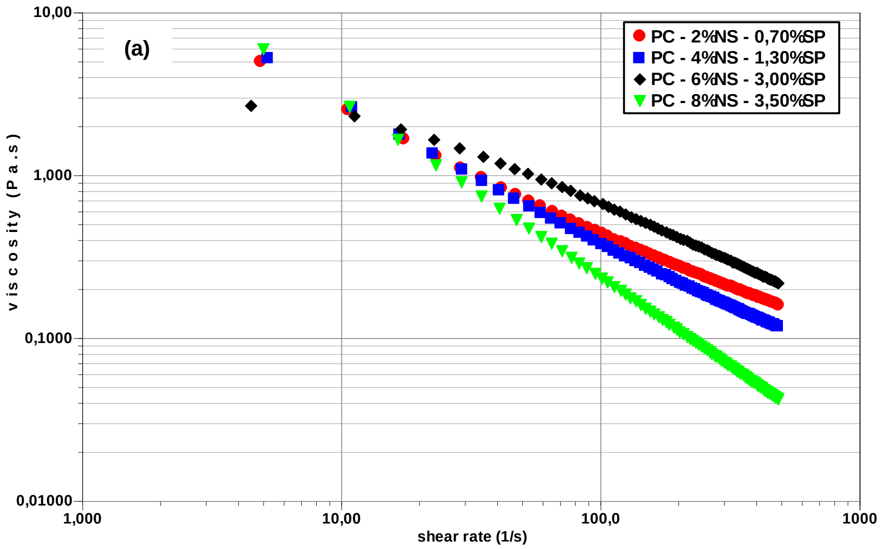
Flexural and Compressive Strength: After mixing, for each mixture, specimens of 4×4×16 cm were prepared for in accordance with ASTM specification. The test specimens were demolded after 24 h and then cured in water. The compressive strengths of cement mortar specimens were tested at 2 and 28 days of curing times by using a uniaxial hydraulic compression machine under a load control rate of 0.20 MPa/s. Three-point bending tests were carried out on prismatic samples according to ASTM C348 [13]. Half samples were subjected to compressive stress by using a hydraulic press with a capacity of 3000 KN according to ASTM C349 [14].

3. Results and discussions

3.1. Effect of Nanosilica in powder form:

Rheological study: Figure 4a and 4b show the evolution of main rheological parameters (plastic viscosity and shear stress) of nanosilica-based cementitious pastes at various superplasticizer dosages as a function of shear rate. According to the results obtained, it is clearly observed that the nanosilica (as powder adding) is more viscous which requires an extra dose of superplasticizer. However, at a higher rate of fluidity and the rate of high nanosilica causes an excess of superplasticizer.

The rheogram of figure 4b shows also the shear stress evolution of cementitious pastes based on different dosing of nanosilica and different dosage of superplasticizer. It is clear that according to these results, the nanosilica (NS) has increased shear stress and the superplasticizer has significantly reduced this stress. However, it is noted that the higher the NS dosage increases the higher the shear stress increases the pasta requires more superplasticizer to become fluid and flow at low shear stresses. We also note above 4% NS, the superplasticizer dosage has doubled [12, 15-16].



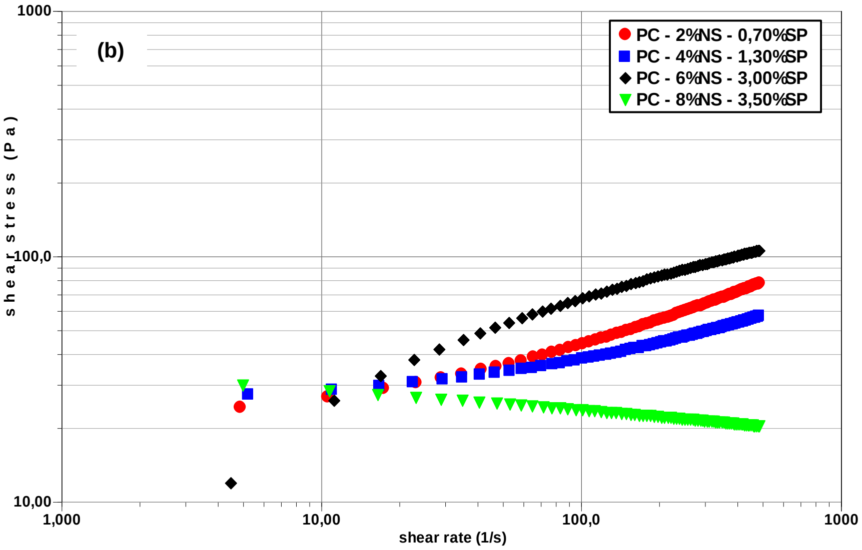


Figure 4: Evolution of main rheological parameters (plastic viscosity (a) and shear stress (b)) of nanosilica-based cementitious pastes.

Rheological behavior: The flow curves of cementitious pastes are shown in **Figure 5**. From the rheograms, all the cementitious pastes show a non-Newtonian flow. Indeed, it is clear that these pastes represent a flow threshold that means that they have a non-Newtonian behavior. According to several researchers found that the behavior of these types of pasta follows the pattern of Herschel Bulkely that depicted in the figure. It is noted that beyond 4% of NS, the behavior of the pasta changes and causes a rheological instability.

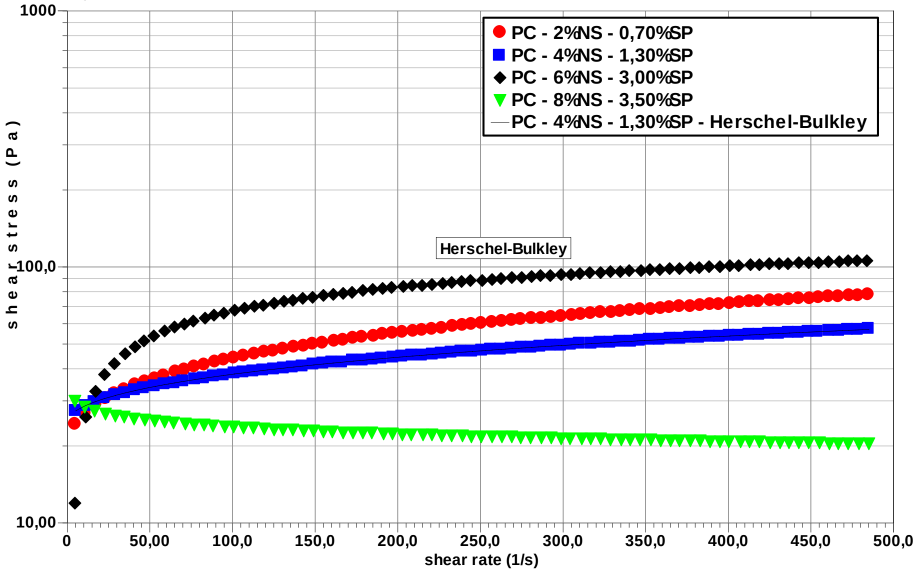


Figure 5: Rheological behavior of studied cement pastes containing NS in powder form.

3.2. Effect of Nanosilica in superplasticizer solution:

Rheological study: Figure 6a and 6b shows the variation in plastic viscosity of nanosilica (NS) -based superplasticizer (NS) -based cementitious pastes as a function of shear rate. According to the results obtained, it is clearly seen that SP doped with NS makes cementitious pastes more fluid. Indeed, the higher the SP dosage increases the viscosity of the cement paste decreases and beyond the high shear rates the viscosity of the cement pastes become constant. However, cementitious pulps with 1.5% NS-doped SP are more fluid and the shear rate is lower [12].

Figure 6b shows the variation of the shear stress as a function of NS-doped SP dosing of cementitious pastes. For all cementitious pastes studied, a significant reduction in shear stress was observed as a function of the increase in SP. This is reflected by the deflocculating and dispersive effect of SP. Indeed, in the presence of water, the SP adsorbs on the surface of the cement particles, causing electrostatic and steric inter-particle repellent effects. This results in the dispersion of the grains and the water retained in the flocculates is released, thus increasing the fluidity. It should also be noted that the saturation dosage obtained for these pastes is of the order of 1.5% of SP doped with NS.

Rheological behaviour: Figure 7 shows the flow curves of the cementitious pastes based on different dosages of the superplasticizer doped with nanosilica. According to the rheograms, these pastas also show a non-Newtonian flow, characterized by a flow threshold and which follows the model of Herschel Bulkely. It is observed that the higher the dosage of the doped superplasticizer, the more the pasta becomes more fluid. Above 1.5% of the SP doped with NS, the effect is not important, which corresponds to the saturation point.

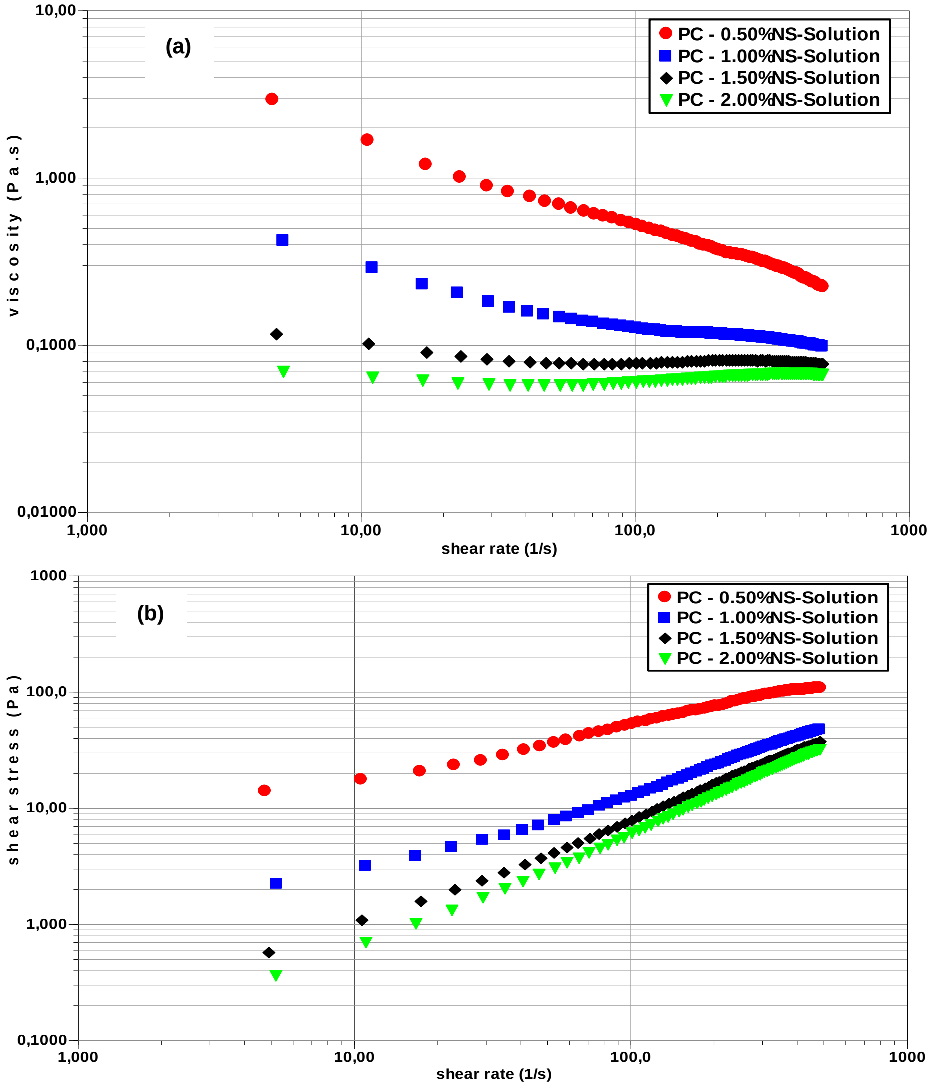


Figure 6: Evolution of main rheological parameters (plastic viscosity (a) and shear stress (b)) of nanosilica-based cementitious pastes containing NS in superplasticizer solution.

It was noted that a significant reduction in shear stress and plastic viscosity, due to the increase of the superplasticizer. This is reflected by the deflocculating effect of SP. Indeed, in the presence of water, the SP adsorbs on the surface of the cement particles, causing electrostatic and steric inter-particle repellent effects. This results in the dispersion of the grains and the water retained in the flocculates is released, thus increasing the fluidity [15-17].

3.3. Mechanical strength

The evolution of the compressive and flexural strength of nanosilicate (NS) -based mortars is given in the figure 7. According to these results, it was noted that the strength development of all mortars according to curing age is an increasing function, because the resistance (compression or flexural) increases according to age. This is explained by the effect of hydration of clinker minerals contained in the cement used. The values of resistance recorded at 28-days are in order of 57 MPa and 9 MPa respectively for compressive and flexural strength. Regarding the effect of cement substitution by NS, a slight decrease in the compressive strength of the mortars was observed and that the introduction of NS powder, causing the reduction of resistance.

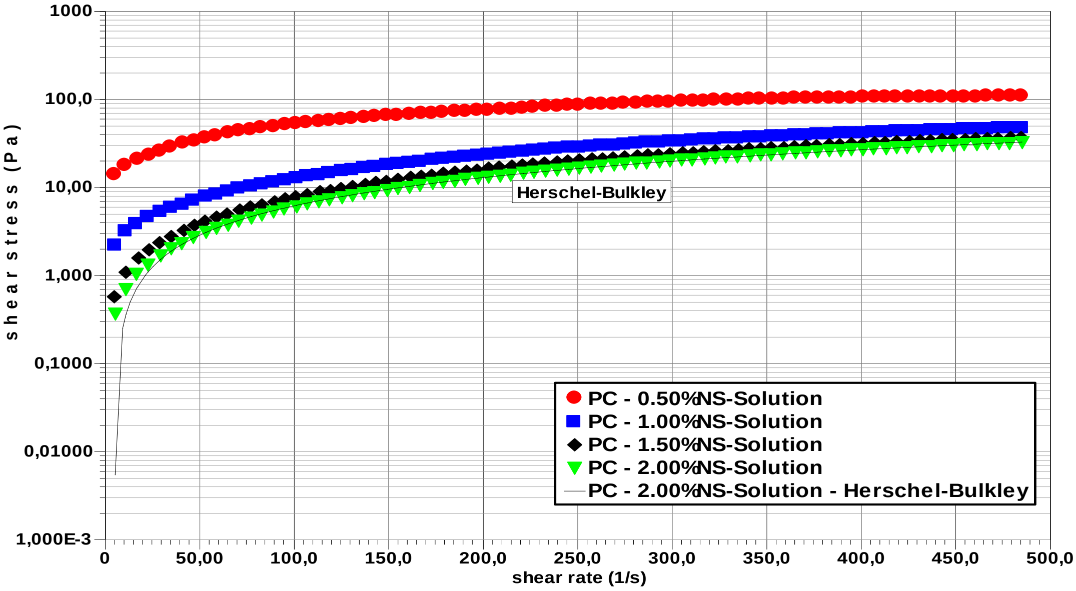


Figure 7: Rheological behavior of studied cement pastes containing NS in superplasticizer solution.

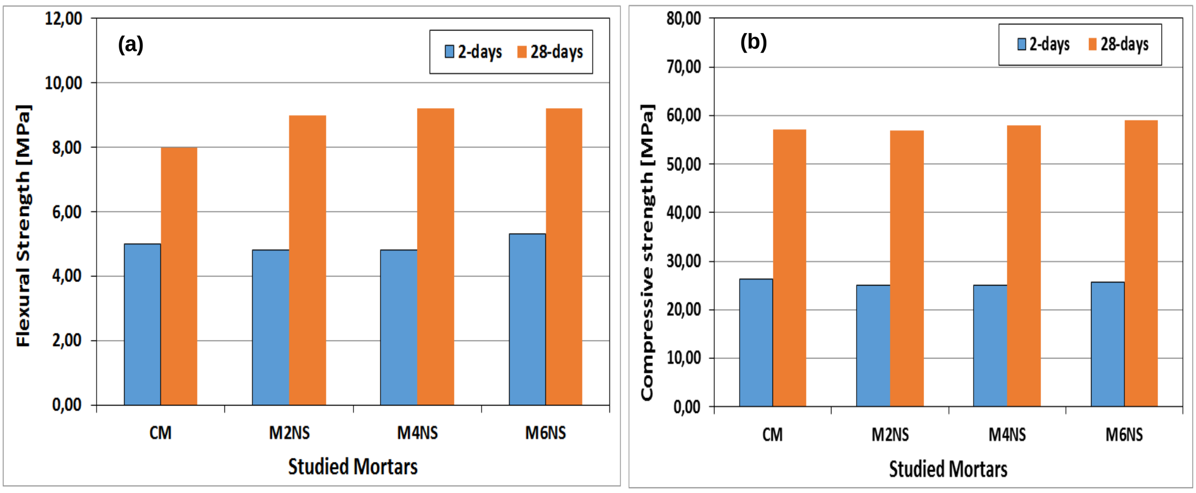
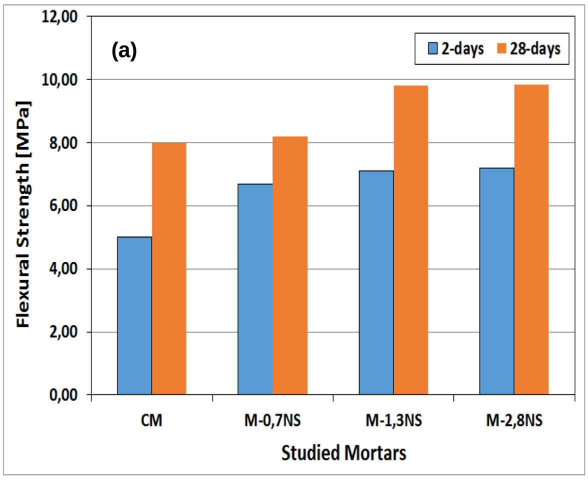


Figure 8: Mechanical Strength of studied mortars based on NS in powder form
(a) Flexural strength (b) Compression Strength.



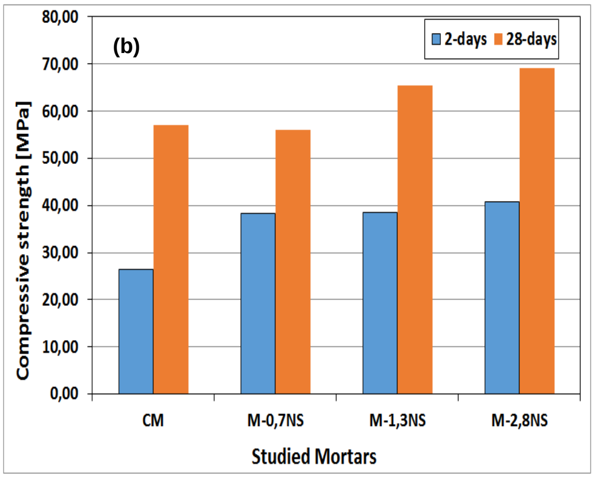


Figure 9: Mechanical Strength of studied mortars based on NS in superplasticizer solution (a) Flexural strength (b) Compression Strength.

It should be noted that during the implementation of the mortars was difficult what influenced on the resistance of the mortars [18-21]. Use up to 6% NS powder, which may have a mortar with a compressive strength of 55MPa.

The results of the mechanical tests (compressive and flexural strength) of NS-doped SP-adjuvanted mortars are presented in Figure 8. We observe that the evolution of mechanical resistance as a function of curing age is an increasing function. Indeed, the resistance (compression or flexion) increases with age. This is reflected by the effect of hydration of clinker minerals contained in the cement used. Strength values recorded at 28days are of the order of 70 MPa and 10 MPa respectively for compressive strength and flexural strength. Regarding the effect of NS-doped superplasticizer, a considerable improvement in the compressive strength of the mortars was observed and the adjuvanted mortars obtained having higher strengths than the control mortar. However, a slight decrease in compressive strength was recorded for the SP1.29% NS mortar, followed by an increase in the higher strength. This is shown the beneficial effect of a NS-doped superplasticizer [19-23].

4. Conclusion

The aim of study was to explore of the effect of introduction mode of the nanosilica on the rheological and physic mechanical properties of cement mortars. It can be concluded that:

Using of NS in powder form: As a result, the use of nanosilica powder (replacing cement on the one hand) has had a negative influence on the rheological parameters and the rheological behavior of cementitious pastes. Indeed, the higher the cement substitution rate by NS increases the shear stress and the viscosity increases, the more cementitious pastes become more viscous and the handling difficult. From the point of view of mechanical properties, it should be pointed out that the more the substitution of cement by NS in powder increases the more the implementation of the mortars become more difficult which has influenced the resistance values.

Using of NS in superplasticizer solution: The introduction of nanosilica in solution in the superplasticizer significantly improved the rheological parameters and the rheological behavior of cementitious pastes. Indeed, the higher the dosage of NS-doped SP increases the lower the shear stress and the viscosity, the more the cementing pastes become more fluid and manageable. It was noted that a significant reduction in shear stress and plastic viscosity, due to the increase in superplasticizer. A dosage of 1.5% NS-doped SP gave adequate fluidity and the shear rate was lower. This assay can be considered as saturation point assay. The effect of SP doped with NS seems very beneficial on the mechanical strengths of the mortars. As a result, the use of the nanosilica in solution in the superplasticizer has considerably improved the resistance of the mortars compared to the control mortar. The values of resistance recorded at 28days are of the order of 70 MPa and 10 MPa respectively for compressive strength and flexural strength. This is shown the beneficial effect of a NS-doped superplasticizer.

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