



The fresh properties of nano silica incorporating polymer-modified cement pastes

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HIGHLIGHTS

- A new mixture incorporating both nano silica particles and polymer latexes in cement mixtures have been studied.
- Flowability, hydration heat development and surface adsorption of particles on cement grains were investigated.
- The studied fresh properties are influenced by both of the admixtures.
- The interaction between the two admixtures is specifically evaluated.

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ABSTRACT

Nano silica and polymers are both recognized for causing certain changes to the properties of cement mixtures in both fresh and hardened states, through different mechanisms. While each of these admixtures have individually different influences on those mixtures, incorporating both in a single mix might result in interesting observations, which are the focus of this research. The fresh properties of nano silica incorporating polymer-modified mixtures are investigated in terms of flowability, hydration heat properties, and surface adsorption of the particles. Two types of polymer and three sizes of nano silica colloids are incorporated in cement paste mixtures. It is observed that when introducing both nano silica and polymer, a competitive interaction is likely to occur between them, causing certain changes in the behavior of the resulting mixtures in the investigated fresh properties. Considering surface adsorption, one of the polymers shows a stronger surface adsorption, which explains its remarkable influence on the studied properties of hydration reaction and flowability, compared to the other polymer.

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1. Introduction

To improve the performance of concrete in different conditions, modification of the cement paste phase through incorporating different admixtures is a popular method [1]. Two of the best known modifications are done through incorporating silica fines (micro- and nano-silica), and polymers in the mixes. Silica fines are usually employed as cement replacement by certain percentages, and cement-polymer mixtures are categorized into the three groups of polymer-modified (or polymer cement) concrete (PMC or PCC), polymer concrete (PC), and polymer-impregnated concrete (PIC) [2,3]. In this paper, the application of nano silica and polymers, and their possible interaction in a cementitious medium have been investigated, focusing on the fresh state properties of flowability

and hydration heat development. Observations reveal the interesting role of each of these admixtures and their interactions on the tested properties.

Nano silica and polymers induce different changes in the fresh state of cement mixes [4,5]. The setting time of cement mixes is shortened significantly when nano silica particles are incorporated in the mixtures; smaller average particle sizes are more influential on shortening the setting time, compared to the larger ones [6–8]. Moreover, polymer modification also influences the setting time of cement mixes. The general view is that, regardless of type, polymers prolong the setting time due to their physical and possibly chemical interaction with the cement particles. In ACI 548.3R-03, it has been reported that cement mixes modified by styrene butadiene rubber (SBR) latex show prolonged setting time compared to the conventional concrete mixes [9]. In other investigations, well-known polymers like ethylene vinyl acetate, as well as SBR latex were also observed to prolong the initial setting time significantly, however through different mechanisms [10–12].

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Considering the hardening time and hydration activity, again the general view is a delayed hardening peak and less activity (lower peak in calorimeter diagrams), when polymers are incorporated in the mixes [13–15]. Chemical explanations for this observation refer to the interaction between the polymer and Ca^{2+} as the product of cement hydration, reduction of CH in the structure and a lower delayed hydration activity, while physical explanations refer to the effects of polymers surfactants, and adsorption of polymers on the surface of cement particles [16,17]. Introducing nano silica leads to an increase in pozzolanic activity and hydration acceleration, confirmed by several studies [4,6,18,19]. Significant reduction in CH amount is reported by incorporating nano silica in the cement mixes [8]. Additionally, when nano silica particles are incorporated, by introducing an additional large surface area to the mixes, water demand is increased remarkably; the larger the surface area (smaller particles), the higher the demand for water or superplasticizing agents [4,6,20–22]. On the other hand, regarding the influence of polymers on flowability, in some papers, they are considered improvers, mainly due to the polymer particles acting like ball bearings, increasing the flowability [13]. SBR latex is reported to have significant improving effects on mortars, measured in flow table test [9]. Conversely, ethylene vinyl acetate (EVA) latexes may not be effective on the flowability of mortar mixes [10]. Furthermore, the initial condition of the mix, and the mixing procedure were observed as important factors on the effect of incorporating this polymer [17,23,24].

The focus of this study is to investigate the fresh state properties of nano silica-polymer-cement composites. Flowability, hydration heat development and surface adsorption of these mixes were evaluated by flow table, quasi-adiabatic calorimeter, and zeta potential testing devices. In order to evaluate the results statistically, a full factorial design method was followed to design the experiments and analyze the results.

2. Experimental studies

2.1. Materials properties

One type of cement was mixed with colloidal silica and polymer latexes, in different percentages. Portland cement CEM I PC 42.5 with specific weight of 3.14 g/cm^3 was employed throughout the experiments; Table 1 shows the chemical composition of the employed cement.

Three different nano silica colloids with different average particle sizes, commercially called Cembinder 8 (C8), Cembinder 17 (C17), and Cembinder 75 (C75) from AkzoNobel, with the densities of 1.1, 1.1 and 1.05 g/cm^3 respectively, were introduced in the mixes. The two type of polymer, added at a fixed amount of 10% by weight of cement were DARAWELD T (polyvinylacetate and Vinylacetate- dibutylmaleate) with solid percentage of 37% pH of 4 and density of 1.5 g/cm^3 , and Lipaton (carboxylated styrene-butadiene copolymer), with solid percentage of 47%, PH of 10 and density of 1.2 g/cm^3 . In this paper, the former is referred as P1 and the latter is P2. The amount of both nano silica and polymers were designed based on their solid percentages. Fig. 1 shows the particle size distribution and properties of nano silica colloids and cement, tested in Malvern Zetasizer and Mastersizer respectively.

2.2. Testing procedure

To produce the mixes, cement, water and the corresponding polymer latex were first mixed together and then, the nano silica colloid was added to the mixture. This mixing order was followed throughout the experiments aiming to minimize the flocculation caused by the nano particles. To determine the flowability and consistency of the mixtures flow table test device described in ASTM Standard of C 230/C 230 M was employed [25]. Reported in percentage, it shows the change in the base diameter of the poured sample, after 25 drops of the flow table.

To investigate the hydration process, a quasi-adiabatic calorimeter was employed. Paste samples of 100 g were poured in the containers of the calorimeter and the change in their temperature was recorded for at least 24 h, giving out the diagrams of temperature-time. The surface adsorption of polymer and nano silica particles on the cement hydration products were determined through zeta potential measurement, for 15 min after mixing.

Stat-Ease Design Expert software was employed throughout the design of the experiments and evaluation of the results; in total, 12 mixtures were prepared, as summarized in Table 2. In order to keep the W/B (water/binder) ratio constant at 0.4, water adjustments were made in all the colloidal nano silica added mixtures.

Two-level full factorial model was followed to design the mixtures of this study. Water to binder ratio and the total binder (cement + nano silica) were kept constant throughout the experiments. Independent variables were the applied percentages of nano silica and polymers. The two levels of each of the polymers were 0 and 10%, and the levels of nano silica colloids were 0 and 1% for Cembinder 8 and Cembinder 17, and 0 and 0.5% for Cembinder 75. These percentages are in terms of solid contents to the cementitious materials.

In the first part, to eliminate the superplasticizer demand in the mixtures, although they are necessary at the presence of nano particles, the incorporating percentages of nano silica were kept at a low level of 0.5 and 1%, depending on the size of them. However, in another set of samples, some mixtures were also produced by incorporating 0.6% superplasticizer with the density of 1.06 g/cm^3 (Sika Viscocrete 3050), to understand the influence of superplasticizer on the hydration process of these mixtures.

3. Results and discussions

3.1. Flow table test analyses

The flow table results are given in Fig. 2. No superplasticizer was used in the mixtures of this part of the study. It is shown that although the percentage of incorporating nano silica is relatively low, their negative effect on the flowability is remarkably pronounced, especially at smaller average particle sizes (e.g. C75). Having nano particles even at low amounts, increases the total surface area remarkably, which then increases the water demand, or making it essential to employ superplasticizer [6,10,22,27–29].

Considering the influence of different latexes, different outcomes can be observed. In the first group of columns in Fig. 2, when P1 latex is added to the plain paste (C), flowability is reduced, unlike P2, which increased the flowability remarkably. This difference might be explained based on the different interactions of the

Table 1
Chemical Composition of the employed cement.

SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	SO_3	Cl^-	Loss ignition	K_2O	Na_2O
19.1	3.24	4.85	61.86	2.02	2.63	–	2.9	–	–

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