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Effect of treatment temperature on the early hydration characteristics of superplasticized silica fume blended cement pastes

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Abstract

In this investigation, two mixes were used: ordinary Portland cement (OPC) and a blended cement prepared with the partial substitution of OPC by 10 mass% silica fume (SF). The setting and hardening characteristics were monitored by the aid of electrical conductivity as a function of curing time. The shear stress and electrical conductivity were studied at different temperatures, namely, 20, 35, 45 and 55 °C. As the temperature increases, the shear stresses decrease with the increase of shear rate. The height of electrical conductivity peaks of superplasticized cement pastes increases due to the increase of the paste fluidity. In the presence of 1.0% polycarboxylate (PC), the electrical conductivity of cement pastes decreases from 1 to 28 days. PC retards the hydration of cement pastes. The presence of PC extended the setting times of cement pastes at 35 °C than at 20 °C due to the increase in the adsorption capacity at this temperature. PC extends the dormant stage of the hydration process and delays the onset of the accelerating stage, without affecting its rate.

Keywords: Blended cement; Silica fume; Temperature; Rheology; Electrical properties; Polymer

1. Introduction

When Portland cement is mixed with water, its four crystallographic phases start to hydrate. The reaction of tricalcium aluminate (C_3A) and ferrite phase (C_4AF) predominates at early ages of hydration. The reaction of calcium silicate phases (C_3S and β-C_2S) predominate from about the time of initial set onward, forming calcium silicate hydrates and $Ca(OH)_2$. Ettringite is the usual product in the early ages of the hydration of Portland cement.

The electrical conductivity of cement pastes can give an indication of the initial hydration of the cement pastes and early formation of hydration products [1]. Electrical conductivity is an important parameter to study the hydration process of cement pastes at early stages [2]. Hansson and Hansson [3] discussed the factors that control electrical conduction in cement-based materials, such as concentration and mobility of ions in the pore solution, porosity and pore size distribution. A high water/cement ratio leads to a greater ability to conduct electricity. Morsy [4] studied the effect of temperature on the electrical conductivity of blended cement pastes.

Superplasticizers are now widely used in the production of concrete with excellent workability. Superplasticizers improve the fluidity of concrete by dispersing the cement particles in the paste. High-performance concrete (HPC) that includes the high-strength and the high-fluidity concrete can be produced with superplasticizers [5]. Sodium salts of formaldehyde condensates disperse the cement particles by electrostatic repulsion, which results from the adsorption on cement surfaces.

Polycarboxylic acid (PC) with graft chains disperses cement particles with the help of the steric hindrance effect, which results from the extension of their graft chains away from the surface of cement particles. Recently, a new type of superplasticizers has been developed. This superplasticizer is contrived to activate both of the preceding two effects. These dispersing mechanisms are also predicted from interparticle forces theoretically calculated from potential energy [6–9]. Therefore, it is important to understand how superplasticizers are adsorbed on each cement component mineral for controlling the fluidity of cement paste.

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The rheological or flow properties of concrete, in general, and of HPC, in particular, are important because many factors, such as ease of placement, consolidation, durability and strength, depend on the flow properties. Concrete that is not properly consolidated may have defects, such as honeycombs, air voids and aggregate segregation. Such an important performance attribute has triggered the design of numerous test methods. Generally, the flow behavior of concrete approximates that of a Bingham fluid. Therefore, at least two parameters, yield stress and viscosity, are necessary to characterize the flow. The rheological (flow) properties of concrete are important for the construction industry because concrete is usually put into place in its plastic form [10,11].

This work aimed to study the effect of different curing temperatures, namely, 20, 35, 45 and 55 °C, on the rheological and electrical properties of superplasticized blended cement pastes containing 10 mass% silica fume (SF).

2. Experimental

The materials used in this investigation were ordinary Portland cement (OPC) provided from Helwan Portland Cement, Egypt, and SF from Ferro-Silicon Alloys (Edfo-Aswan), Egypt. Table 1 shows the chemical oxide composition of OPC and SF. The specific surface areas of OPC and SF are 0.3154 and 20 m^2/g, respectively.

The phase composition of Portland cement was calculated from Bogue's equations, as shown in Table 2. The superplasticizer used is a commercial PC supplied from Cairo International Development Center, Fosroc, Egypt, as a liquid form with 35% solid content.

Blended cement was prepared with partially substituted OPC with 10 mass% SF. The blend was mixed in a porcelain ball mill with four balls for 6 h to assure complete homogeneity.

2.1. Rheological measurements

Two mixes were made of OPC cement pastes and OPC containing 10 mass% SF (blended cement) admixed with different dosages of the PC superplasticizer at a constant W/C ratio of 0.30. The mixing was done at a speed of 120 rpm for 3 min, continuously. Exactly 50 g of each mix was transported to the Rheotest cell, as described in an earlier publication [12]; the ratio of radii of measuring tube and measuring cylinder (R/r) was 1.24. The test begins exactly after 6.5 min from contact of cement and water, including the mixing time. The shear rate was measured in the range from 3 to 146 s^{-1}.

Table 1
Chemical oxide composition of OPC and SF (mass%)

Chemical composition (mass%)	OPC	SF
SiO_2	21.05	96.10
Al_2O_3	5.45	0.52
Fe_2O_3	3.42	0.70
CaO	63.41	0.21
MgO	2.09	0.48
SO_3	2.39	0.10
Na_2O	0.18	0.31
K_2O	0.09	0.49
L.O.I	1.90	1.14
Blaine surface area (m^2/g)	0.3154	20

Table 2
Phase composition of Portland cement clinker

Phase composition (mass%)	OPC
C_3S	50
C_2S	23
C_3A	8.6
C_4AF	10.4

2.2. Electrical conductivity measurements

In electrical conductivity measurements, the test cell was of the coaxial type, which included concentric inner and outer electrodes mounted on an insulated base plate [12–14]. The electrodes were polished before the experiments. The cement pastes were prepared by dissolving the PC superplasticizer within the quantity of water required to produce a constant workability (the required water of standard consistency). The cement pastes were placed in the space between the electrodes, and the cell was kept in a cabinet chamber at 100% relative humidity during the test period. The electrical conductivity was measured under three different temperatures: 20, 35 and 55 °C. The measurements began exactly 3 min after mixing with water (0 time) up to 28 days. The electrodes were connected to an RLC meter, Model SR 720, operating at 1 kHz for resistance measurements.

3. Results and discussion

3.1. Rheology

Figs. 1 and 2 show the effect of OPC and 10 mass% substitution of OPC by SF on the obtained shear stress values of cement pastes at different shear rates. The maximum shear stresses were 208 and 371.8 Pa, respectively. It is clear that the addition of SF in cement pastes leads to increases in shear stress values. Increase of the shear stress values is an indication that the apparent viscosities of the cement paste increase.

The effect of different temperatures on the rheological properties of OPC and blended cement pastes were investigated. The rheological properties were determined at different temperatures, in absence or presence of 1.0 mass% PC. The effect of temperature on plain and superplasticized pastes on the loss of fluidity is important to know the limitation during transportation and placement, and the

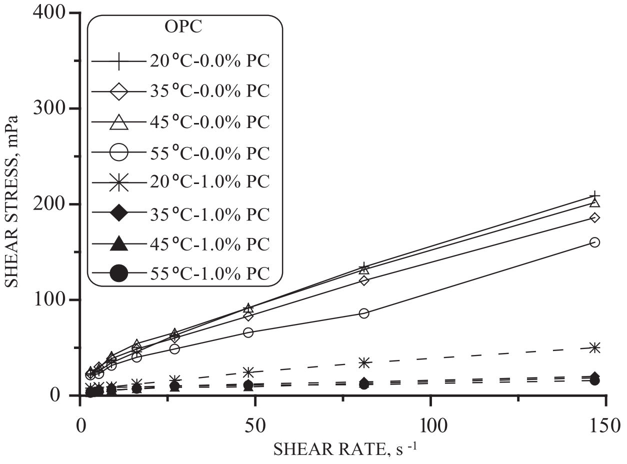

Fig. 1. Shear stresses–shear rate of OPC pastes in the absence and the presence of 1.0 mass% PC at 20, 35, 45 and 55 °C.

properties of the fresh concrete can change considerably and their compositions have to often compensate for these effects. The shear stress decreases as PC is added. This is due to the adsorption of the PC superplasticizer on the surface of the cement particles, causing a creation of negative charges on the cement particles. This leads to an electrostatic repulsion of cement grains with each other and a lubricating effect on the mix, as well as steric hindrance between the side branches of the PC, which increase the interparticle distance and give the high fluidity [8]. As the temperature increases, the shear stresses decreases with the increase of shear rate. The increase of temperature results in a sharp decrease of the shear stresses of cement pastes. The decrease of the shear stress of the pastes with the addition of the superplasticizer is higher than that of the specimens without superplasticizer. Kasai-Tetsurou [15] found that the increase of temperature changes the adsorption capacity of superplasticized cement pastes, which enhances the paste fluidity.

3.2. Electrical conductivity

Figs. 3–6 show the electrical conductivity-time curves of the neat and superplasticized cement pastes up to 24 h. Two conductivity peaks were obtained during the initial hardening of cement pastes. The first conductivity peak takes place within 0.5–1.5 h. The first maximum of conductivity peak is due to the initial hydrolysis of cement pastes. The ions produced are Ca^{2+}, OH^{-}, SO_4^{2-} and alkali ions; these act as charge carriers, leading to a rapid increase in the conductivity. Once the concentration of these ions in the solution becomes very high, ionic association starts. These ions get adsorbed or precipitated with the formation of calcium silicate hydrate (C-S-H), and ettringite as well, due to the formation of electrical insulating layer around the cement grains, leading to a decrease in the mobility of these ions; hence, the electrical conductivity decreases again. The second appears within 2–6 h. The second maximum peak is due to an increase in the number of ions and internal pressure development around the cement grains due to ettringite-monosulphate transformation [16]. In the transformation, 2 mol Ca^{2+} and SO_4^{2-} ions are produced, leading to an increase in the electrical conductivity (the second peak).

When cement is in contact with water, Ca^{2+} ions go into the solution and then adsorb at the surface, which becomes positively charged. PC gets in the solution and it adsorbs over the surface cement grains, leading to block the hydration. Because PC has a depressive effect, it increases the workability of the paste, and during this, the solution diffuses inside the cement through the polymer coating. In the presence of PC, it appears that only a few number of Ca^{2+} ions go into the solution and it does not become supersaturated with respect to $Ca(OH)_2$. The dissolution of Ca^{2+} ions increases with time and accordingly increases the conductivity. The increase continues until the Ca^{2+} ions becomes saturated with respect to $Ca(OH)_2$. As the amount of admixture increases, the conductivity maximum becomes more broad with a lower intensity and shifted to a longer time.

On increasing the curing temperature, the rate of initial hydration of cement phases and the rate of formation of hydration products are increased. Consequently, the initial electrical maxima conductivity will be shifted to a shorter hydration time, and the later decrease in electrical conductivity values gets more sharper, as shown in Figs. 3–6. The crossing of the conductance-time curves indicates that the mobility and the concentration of ions are increased. The variations of electrical conductivity as a function of PC dosages at 20, 35 and 55 °C were monitored up to 24 h. The addition of PC decreases the electrical conductivity of cement pastes. The PC can disperse the flocculent structure of cement particles, and the required water of standard consistency (mixing water) can be decreased [17]. The electrostatic repulsion is reported to play a role in the dispersing mechanism associated with PC. The PC has, besides its negatively charged group, a steric hindrance due to longer side chains present in its polymer molecules, which leads to enhance the paste workability [18].

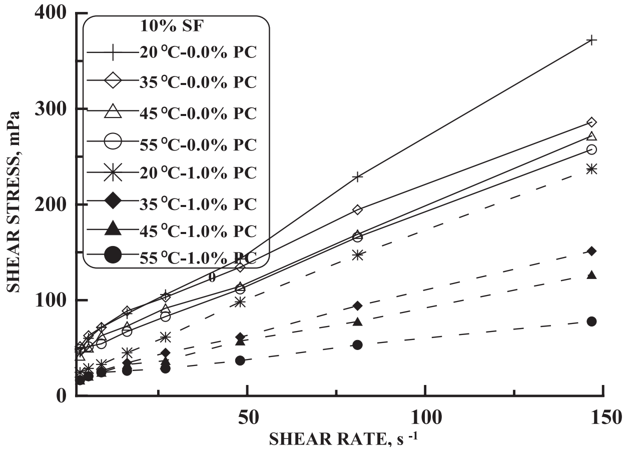

Fig. 2. Shear stresses–shear rate of blended cement pastes in the absence and the presence of 1.0 mass% PC at 20, 35, 45 and 55 °C.

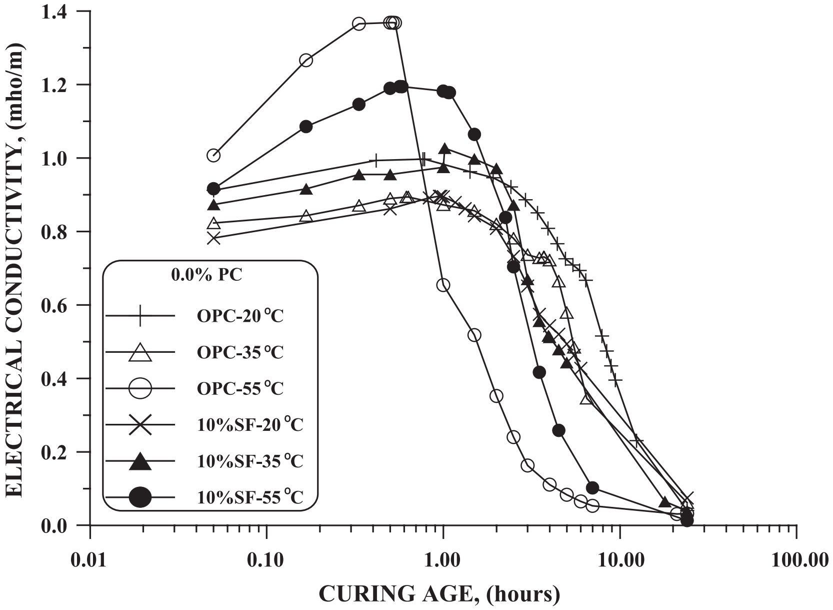

Fig. 3. Electrical conductivity of plain OPC and blended cement pastes at 20, 35 and 55 °C in the absence of PC.

PC contains –COO$^-$ groups, which can react with Ca^{++} ions liberated from cement hydration, forming [R-COO]-Ca-[OOC-R] on the surface of the C-S-H gel or Ca(OH)$_2$ crystals; the interweaved net structure consists of ion bonded large molecular system bridged by means of Ca (OH)$_2$ [19]. PC inhibits the growth of hydrates [17]; this is due to the shifting and broadening of the peaks of electrical conductivity to a longer hydration time. On increasing PC dosages, the second peak due to monosulphte formation appeared. The transformation of ettringite to monosulphate was delayed in the presence of SF within the cement pastes. This may be attributed to the formation of a protective film of C-S-H gel around the ettringite particles.

The SF-blended cement undergoes a sharp decrease in the electrical conductivity during hydration periods. This result is mainly attributed to the decrease in the number of released ions during the hydration of OPC and the degree of consumption of the free Ca(OH)$_2$ released during the hydration of OPC as a result of interaction with SF, leading to the formation of C-S-H [20].

The increase of the treatment temperatures (35 and 55 °C) leads to an increase in the height of electrical conductivity peaks of superplasticized cement pastes. This is due to the increase of the paste fluidity due to the change of the adsorption capacity of the superplasticizer, as mentioned before [15].

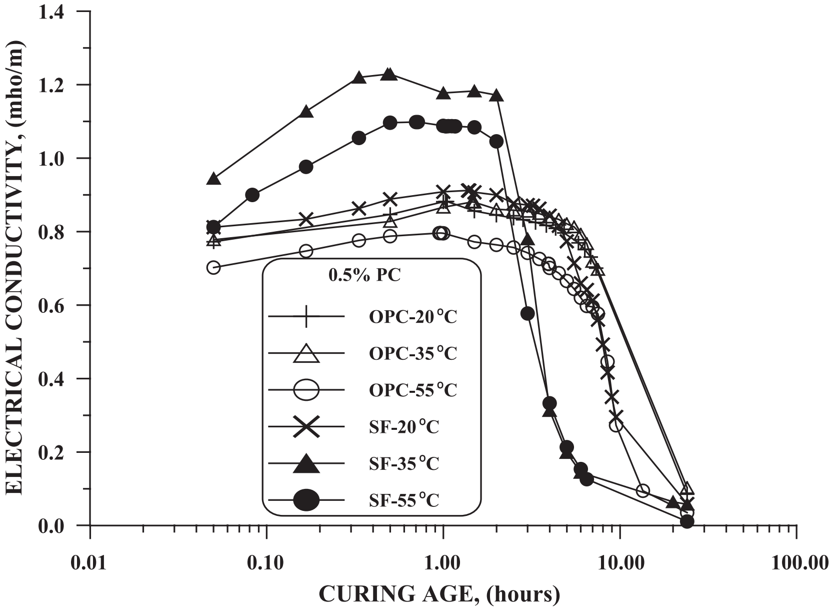

Fig. 4. Electrical conductivity of OPC and blended cement pastes at 20, 35 and 55 °C in the presence of 0.5% PC.

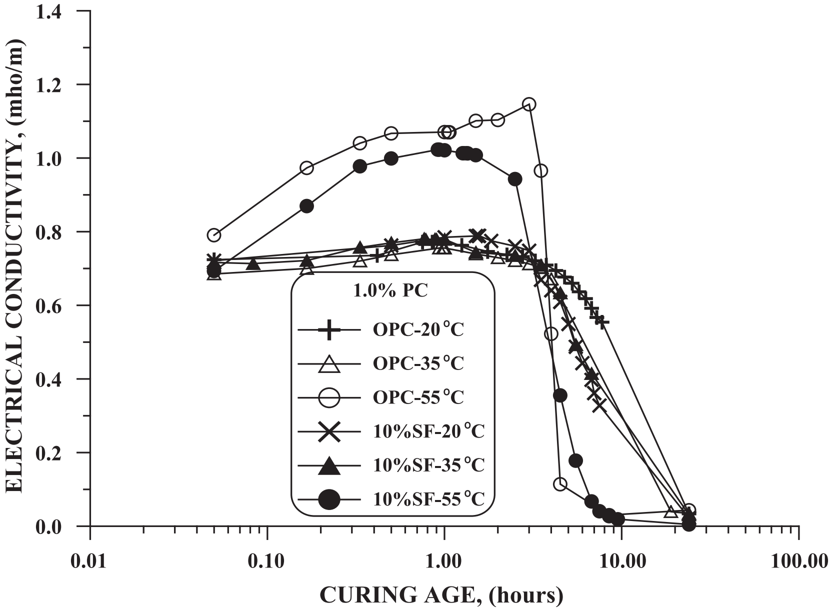

Fig. 5. Electrical conductivity of OPC and blended cement pastes at 20, 35 and 55 °C in the presence of 1.0% PC.

Fig. 7 illustrates the effect of treatment temperatures and curing ages on the variations of the electrical conductivity for the plain and superplasticized cement pastes from 24 up to 672 h (28 days). The electrical conductivity of OPC and blended cement pastes decreases with curing time, and, at 20 °C, the electrical conductivity of OPC pastes at 1 day exhibited a higher value than of the SF cement pastes. The SF-blended cement pastes undergo a sharp decrease in electrical conductivity during the period from 24 to 672 h (28 days). This is attributed to the pozzolanic reaction of SF, which reacts with the formed lime from the hydration of OPC phases forming additional C-S-H. In presence of 1.0% PC, the electrical conductivity of OPC and blended cement pastes decreases; this is due to the formation of more amounts of hydration products within the pore system.

The electrical conductivity of cements during hydration evaluates the microstructural characteristics of cement materials. The application of electrical resistance measurements has been widely studied by many authors as a useful method for monitoring the initial hydration of OPC [14,21]. In view of the increasing use of pozzolanic materials in hydraulic binders, there is great interest in designing a rapid and efficient method to evaluate their reactivity. Electrical measurements are used to characterize the response materials,

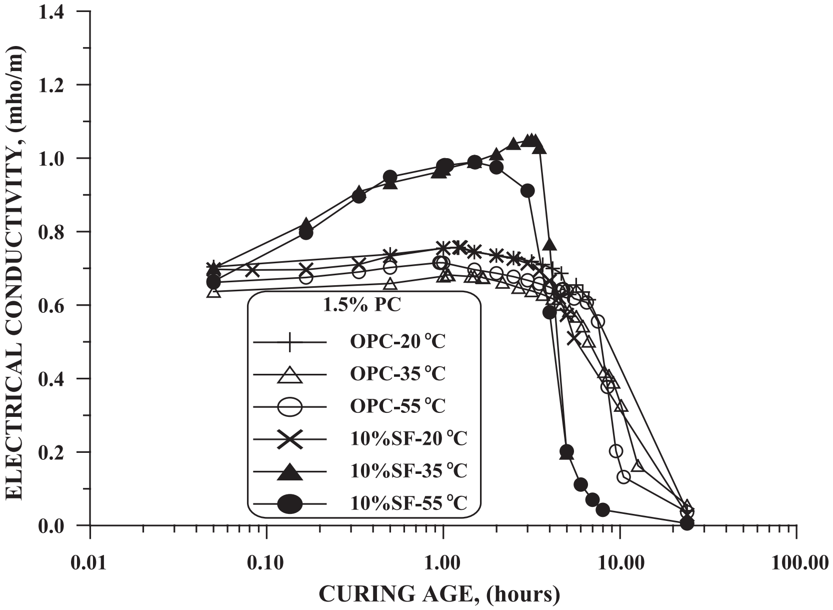

Fig. 6. Electrical conductivity of OPC and blended cement pastes at 20, 35 and 55 °C in the presence of 1.5% PC.

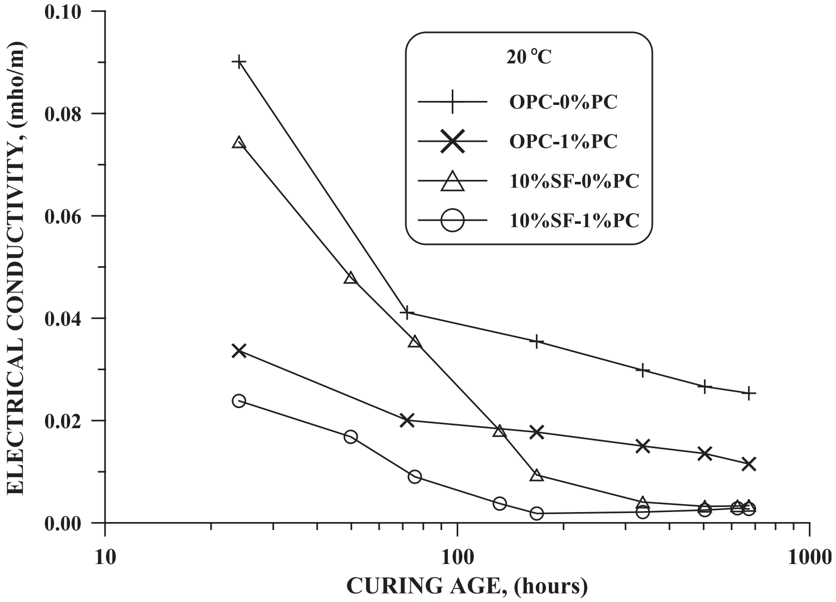

Fig. 7. Electrical conductivity of OPC and blended cement pastes at 20 °C of plain and 1.0% PC.

such as ionic conductors' semiconductors, pore structure and changes in ionic concentrations within the pore fluid [22].

Fig. 8 represents the electrical conductivity of OPC and blended cement cured at 35 °C during the periods from 24 to 672 h (28 days). It clear that the electrical conductivity of the blended cement pastes shows a sharp decrease from 24 up to nearly 100 h and then tends to a constant value. On the other hand, the conductivity of OPC pastes (plain and superplasticized) decreases up to 14 days (336 h), then, they show an increase in their conductivity values. This may be due to the formation of the hydrogarnet phase. The increase of temperature (55 °C) causes an increase in the rate of formation of hydration products, and consequently, the conductivity shows a sharp decrease (Fig. 9).

3.3. Initial and final setting times

Fig. 10 shows the initial and final setting times of OPC and blended cement pastes. The initial and final setting times of cement pastes were measured from the electrical conductivity-time curves [13]. The partial replacement of OPC by SF extended the initial and final setting times (20 °C). The properties of both fresh cement pastes are affected by hot weather conditions. The fresh concrete will set in a shorter

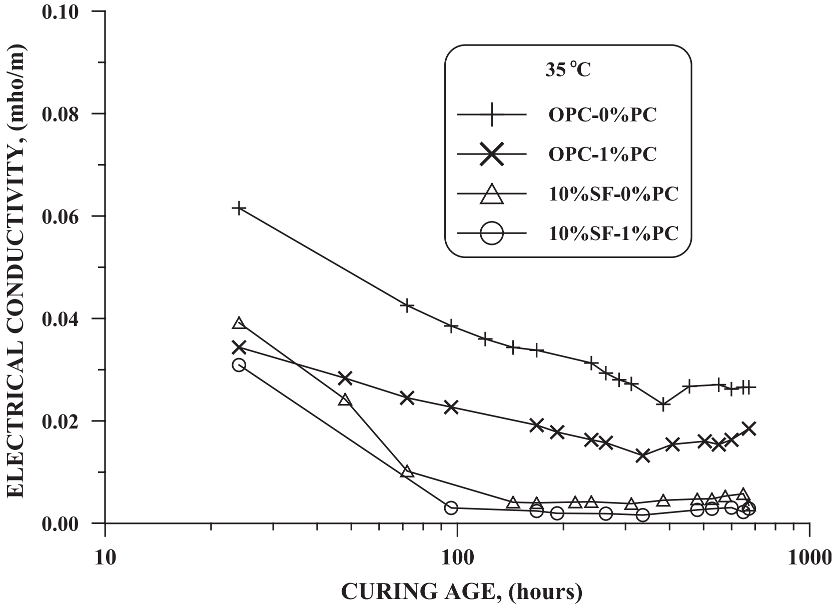

Fig. 8. Electrical conductivity of OPC and blended cement pastes at 35 °C of plain and 1.0% PC.

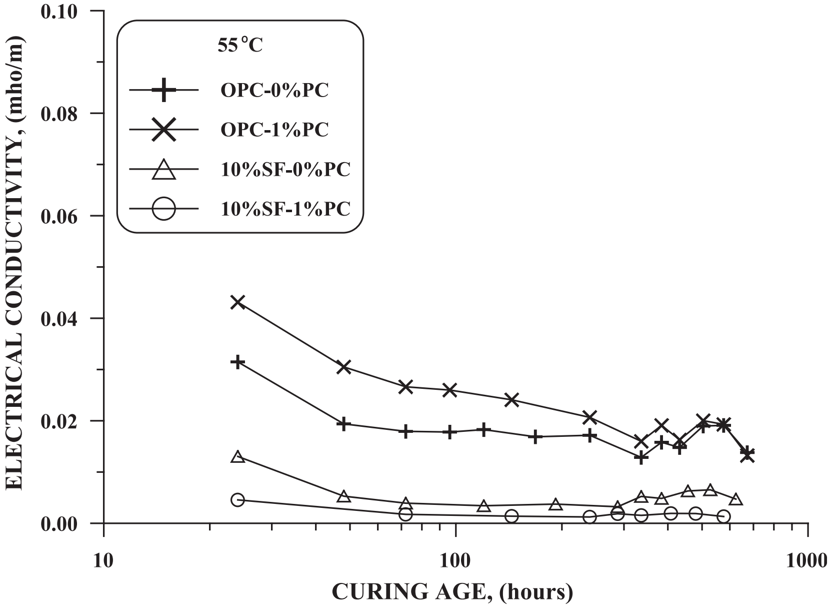

Fig. 9. Electrical conductivity of OPC and blended cement pastes at 55 °C of plain and 1.0% PC.

time as compared with normal conditions. The quick setting decreases the workability during handling, consolidating and finishing. The general trend in the results indicates that both of the initial and final setting times decrease as the curing temperature increases. Obviously, this may be due to the increased rate of hydration with temperature, mostly at early ages. The degree of hydration is controlled by the density and thickness of the calcium silicate hydrate layer around the cement grains. It was shown that the initial and final setting times of plain OPC shorten with the treatment temperature increased, as well as blended cement pastes. In the presence of 1.0% PC, the setting times of cement pastes at 35 °C were extended than at 20 °C; this may be due to the adsorption capacity of PC, which increases at this temperature. The PC superplasticizer causes the formation of a semipermeable membrane on the surface of the cement grains and may react with a component to form a precipitate on the cement particles, imparting low-permeability coating on the grains and thus slowing further hydration. Evidently, the extension of setting of blended cement is longer than the setting of OPC.

4. Conclusions

1. The addition of SF in cement pastes leads to an increase in shear stress values. The decrease of the shear stress of the cement pastes made with a superplasticizer is higher than those made without the superplasticizer. As the temperature increases, the shear stresses decreases with the increase of shear rate.
2. At 20 °C, the electrical conductivity of OPC pastes exhibited higher conductivity value than the did the

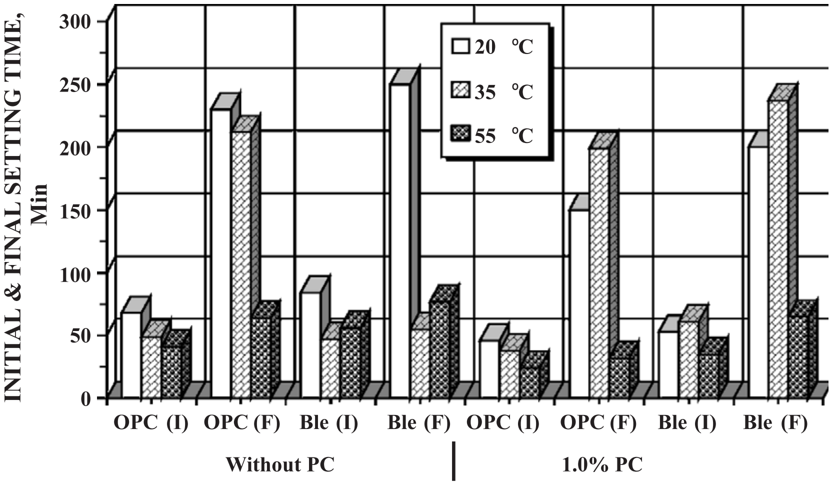

Fig. 10. Initial (I) and final (F) setting times of plain and superplasticized OPC and blended (Ble) cement pastes with 1.0% PC.

SF-containing cement pastes. As the treatment temperature increases (35 and 55 °C), the height of the electrical conductivity peaks of the superplasticized cement pastes increases, due to the increase of the paste fluidity. In the presence of 1.0% PC, the electrical conductivity of cement pastes decreases from 1 to 28 days.

3. The partial replacement of OPC by SF extended the initial and final setting times at 20 °C. PC retards the hydration of cement pastes. The presence of 1.0% PC extended the setting times of cement pastes at 35 °C than at 20 °C, due to the increase in the adsorption capacity at this temperature.

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