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Research Article

Physical and Mechanical Properties of Cement Grouts Mixed with Different Super Plasticisers

Costas A. Anagnostopoulos and Christos Echonomidis
Department of Civil Engineering, School of Technological Applications, Alexander Technological Educational Institute of Thessaloniki, 57400 Thessaloniki, Greece

Abstract: The use of super plasticisers in microfine or regular cement-based grouts has become of vital importance in advanced professional grouting practices. These super plasticisers play an important role in the production of more durable grouts with improved rheological characteristics. This report presents a laboratory study of the effects of a new-generation Polycarboxylate Super Plasticiser (PCE) on the rheological properties, mechanical strength, final setting time and bleeding of cement grouts in comparison to that of a polynaphthalene (SNF) and a modified Lignosulfonate (MLS) superplasticisers. The experiments were conducted using different super plasticiser dosages with cement grouts proportioned with a water to cement ratio (w/c) of 0.33, 0.4 or 0.5. The results showed that grouts with PCE had higher viscosity, slightly increased bleeding and longer setting times compared with the SNF admixture. However, the PCE improved the final strength, especially for grouts with a w/c ratio of 0.4 and 0.5 and decreased the yield stress. Among the three super plasticisers, MLS had the less effect on improving the different properties of the grouts.

Keywords: Grouts, lignosulfonate, polycarboxylate ether, sulfonated naphthalene formaldehyde

INTRODUCTION

Cement-based grouts are widely used in many construction domains (Nonveiller, 1989), such as grouting of soil or rock, injecting cracks in massive concrete structures or masonries, coating pre-stressed cables, stabilising ground near tunnels (Stille and Gustafson, 2010), fixing reinforcing elements (e.g., cables) in pre-stressed concrete structures or rock pre-stressing anchors and rehabilitating old defective masonries in historical buildings (Yeon and Han, 1997; Baltazar *et al*., 2012). The strength of a grout is important whenever the purpose of the grouting is to strengthen the ground or an existing concrete structure. The ratio of water to cement (w/c) is the most significant factor that affects the strength of the grout. Consequently, the use of grouts with low w/c ratios necessitates the addition of a superplasticiser to obtain the appropriate rheological properties of the suspension so that grouts are able to flow sufficiently in boreholes, formation pores and rock joints and ensure grouting effectiveness. Superplasticisers belong to the most common admixtures used in the production of concrete with high workability, excellent slump retention, high strength and durability. Particularly, superplasticisers have the following advantages:

- They reduce water demand up to 30% when added during the preparation of concrete and the resulting water/cement ratio significantly increases both initial and final strength
- They improve workability significantly without the need of additional water when added to the ready-mixed concrete
- They contribute to better hydration of cement
- They facilitate compaction of concrete, reduce segregation and bleeding and improve pumpability
- They reduce setting shrinkage (crack prevention) and creeping
- They improve water impermeability, resistance to carbonation and chloride ion attack, freezing and thawing durability and adhesion between steel and concrete
- They are compatible with all types of Portland cement.

Currently, the most widely used superplasticisers are sulfonated naphthalene formaldehyde (SNF) condensates, Modified Lignosulfonate (MLS) and a new-generation Polycarboxylate-Based Dispersants (PCE) composed of comb-like copolymers with grafted chains of polyethylene oxide. The dispersion mechanism of the SNF superplasticiser occurs because

Corresponding Author: Costas A. Anagnostopoulos, Department of Civil Engineering, School of Technological Applications, Alexander Technological Educational Institute of Thessaloniki, 57400 Thessaloniki, Greece

the adsorption of the superplasticiser anionic polymers can convey a net negative electrical charge to the surface of the cement particles, which induces repelling forces between neighbouring cement particles and causes increased dispersion (Plank and Hirsch, 2007; Kim *et al*., 2000). However, the dispersion mechanism of a PCE superplasticiser is mainly attributed to steric forces, which are dominant for a copolymer and consist of one main linear chain with lateral carboxylate and ether groups (Uchikawa *et al*., 1997; Puertas *et al*., 2005; Yamada *et al*., 2000). Steric forces provide a higher dispersive action compared to electrostatic forces (Collepardi, 2005). For a MLS superplasticiser, the dispersion may be attributed to a combination of electrostatic repulsion and steric hindrance effect (Kauppi *et al*., 2005). According to Ramachandran *et al*. (1998), although lignosulfonate based superplasticisers consisted of linear molecular structures, the steric effect is caused by the cross-linked molecules taking up a relatively large volume on the surface of cement particles. Despite numerous studies have been conducted concerning the use of both dispersion mechanism admixtures for the production of concrete or mortar (Zhang *et al*., 2010; Montes *et al*., 2012; Golaszewski, 2012; Parra *et al*., 2011), there is minimal information available on the effect of the different types of superplasticisers on various physical and mechanical properties of cement grouts, which are directly related to the effectiveness of the grouting operation.

The overall goal of this study was to investigate the effect of a PCE, SNF and MLS dispersant on the rheological properties, setting time, strength development and bleeding of cement grouts made with different w/c ratios and superplasticiser dosages, in order to improve the knowledge about the use of such admixtures in cement grouting technology.

MATERIALS AND LABORATORY METHODS

The experiments were conducted using a common type of Portland cement (CEM II 42.5 N, according to EN 197-1 (2000)), various w/c ratios of 0.33, 0.4 and 0.5 and three types of High-Range Water Reducers (HRWR). A polynaphthalene-based superplasticiser, a modified lignosulfonate and a polycarboxylate ether-type superplasticiser (main chain consisted of a copolymer of methacrylic acid with lateral carboxylate and ether groups) were selected as HRWRs. All superplasticisers are commercial products with the trade name Adium 110 (PCE), Sikament 150 (MLS) and Sikament 240 (SNF). The first one is distributed by Isomat SA and the others are distributed by Sika AG. Their properties are presented in Table 1. The HRWR dosages (by cement mass) are summarised in Table 2. The water content of the superplasticisers was accounted for to maintain a constant w/c ratio. The w/c ratios and dosages of the superplasticisers were varied to maintain proper setting times and bleeding values, which are proposed by the European Standard EN 12715 (2000) and grouting practices, as discussed more thoroughly in the following sections.

All grouts were mixed using a three-blade paddle high rotating mixer suggested in ASTM C 938-80 (1993). This high-shear mixing regime was used to ensure the complete dispersion of the cement particles. The addition of the superplasticiser in the grout was performed using the delayed addition method. Particularly, after 5 min of stirring cement and distilled water in the mixer and 2 min of static hydration, the appropriate dosage of superplasticiser was added into the grout. Then, an additional mixing sequence was performed for a total time of at least 2 min. The selection of this method for preparing superplasticised grout is because the delayed addition of superplasticiser in cement suspensions significantly enhances the efficacy of its dispersing power in comparison to the direct addition (Fernàdez-Altable and Casanova, 2006; Chiocchio and Polini, 1985; Uchikawa *et al*., 1995; Aiad *et al*., 2002; Flatt and Houst, 2001). In the latter case, a higher quantity of superplasticiser becomes entrapped (adsorbed) in the early-forming hydrate products of tricalcium aluminate (C_3A) and consequently, loses a part of its dispersing action. A detailed study by Uchikawa (1994) depicted the comparison between the effects of direct addition and delayed addition of superplasticiser on the adsorption of the superplasticiser and the fluidity of the grout. By using electron spectroscopy, the study measured the thickness of the hydrates formed on a polished clinker surface, which was immersed into a solution of SNF superplasticiser. In the case of simultaneous

Table 1: Properties of superplasticisers used in the study

	Polycarboxylate ether	Sulfonated naphthalene formaldehyde	Modified lignosulfonate
Aspect	Slightly yellow	Dark brown	Dark brown
Specific gravity	1.05	1.2	1.16
pH	6.3±0.5	6-8	8-11
Chloride ion content	Chloride free	Chloride free	Chloride free
Solid content	40%	40%	38
Molecular mass	44,000 g/mol	16,000 g/mol	30,000 g/mol
Recommended dosage (% by cement weight)	0.6-1.4	0.5-2	0.6-1.2

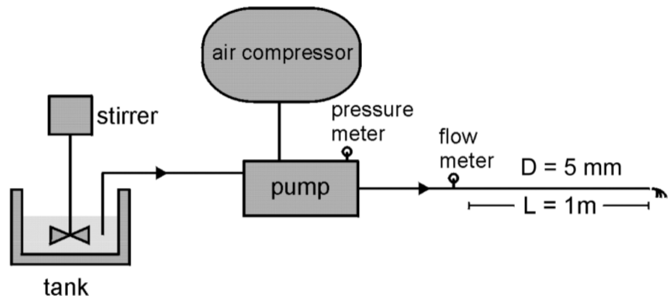


Fig. 1: Device for pumping grouts through capillary tube

Table 2: Dosages of superplasticisers on various grouts

Proportion	MLS (%)	SNF (%)	PCE (%)	Designation
w/c = 0.5	0.5	0.5	0.5	G_1
	0.75	0.75	0.75	G_2
	1	1	1	G_3
	1.25	1.25	1.25	G_4
w/c = 0.4	0.75	0.75	0.75	G_5
	1	1	1	G_6
	1.25	1.25	1.25	G_7
	1.5	1.5	1.5	G_8
w/c = 0.33	1.25	1.25	1.25	G_9
	1.75	1.75	1.75	G_{10}
	2.25	2.25	2.25	G_{11}
	2.75	2.75	2.75	G_{12}

superplasticiser addition, the adsorbed hydrate layer thickness of tricalcium silicate (C_3S) and C_3A was approximately 50 and 300 nm, respectively. When the addition of the superplasticiser was delayed, the thickness of the adsorbed hydrates was 20 nm for both C_3S and C_3A. This result corresponded to the thickness of the adsorbed polymer, which indicated that the molecules were not overgrown.

The grout setting time was investigated by conducting Vicat needle tests according to ASTM C 953-87 (2010a).

The strength development was measured from unconfined compression tests on cubic specimens with an edge of 50.8 mm that were performed 3, 7 and 28 days after grout preparation. The storage and curing of specimens were conducted using suggestions provided by ASTM C 942-86 (2010c) and ASTM C 109-92 (2012), respectively. Particularly, immediately upon completion of moulding, test specimens were placed in a moist room with a temperature of 23°C and relative humidity of 95%. After 24 h of curing, the specimens were demoulded and immersed in saturated limewater in a storage tank until required for testing. A BETA 5 loading machine (FORM+TEST PRÜFSYSTEME) with a maximum capacity of 3000 KN was used for compression testing at an axial strain of 0.1%/min. The elastic modulus was determined from the linear section of the compressive stress-strain curve. Each of the reported compressive strength and elastic modulus values correspond to the average value of at least three specimens that have strength values deviate no more than 10% from the average value of all tested specimens made from the same grout mixture.

Bleeding was investigated by conducting sedimentation tests according to ASTM C 940-89 (2010b).

The rheological flow curves and viscosities of the superplasticised grouts were determined using a capillary tube viscometer recording the shear stress-shear rate relationship (Ashikhmen and Pronima, 1986; Shizhu and Ping, 2012; Mannheimer, 1991). The capillary viscometer method was selected instead of the classical rotational viscometer method, which is commonly used, because it is necessary to determine the flow properties of the grouts under conditions similar to those in situ and evaluate the test results in such a way that reliable data are obtained (Anagnostopoulos, 2006; Widmann, 1996; Bair, 2012). Another advantage of the capillary viscometer, which was taken into account for this choice, is the functional dependence of shear stress on shear strain in a wide range of these variables in contrast to the limited shear rate range of rotational viscometers. The rheological measurements were completed between 10 and 12 min after the initial contact of cement with water.

To conduct the rheological experiments, a pipe-flow facility was constructed (Fig. 1). This facility consisted of a mixing tank (capacity of 100 l) with a high speed rotating stirrer, air operated double diaphragm pump, air compressor, pressure and flow meters and a test section consisting of 1-m-long capillary plastic tube (internal diameter of 5 mm) with smooth interior walls. The grout was allowed to flow through this small diameter pipe each time under the desired steady pressure. The shear stress τ and shear rate $\dot{\gamma}$ were calculated by considering the Hagen-Poiseuille law as follows:

$$\tau = \frac{\Delta P}{L} \cdot \frac{R}{2} \tag{1}$$

$$\dot{\gamma} = \frac{4 \cdot Q}{\pi \cdot R^3} = \frac{4 \cdot V}{R} \tag{2}$$

where,

ΔP = The pressure drop across the capillary tube
R and L = The inner radius and length of the capillary tube, respectively
Q = The volumetric flow rate of the grout
V = The mean velocity of the grout

The Herschel-Bulkley model was used to fit the shear stress-shear rate values (Larrard *et al*., 1998; Jayasree and Gettu, 2008; Nguyen *et al*., 2011; Yahia and Khayat, 2001). This model is given by the form:

$$\tau = \tau_o + \kappa \cdot \dot{\gamma}^{\,n} \tag{3}$$

where,
τ_o = The yield stress
k = The consistency
n = A constant that indicates the rheological behaviour of the mixture

The mixture behaves as a shear thickening fluid when n>1 and as a shear thinning fluid when n<1. It should be noted that the inherent limitation of the capillary viscometer assumes the flow to be laminar for the application of Eq. (1) and (2). In fact, by using the following equation of Metzner and Reed, the Reynolds number for all tested grouts were found to fluctuate between 1 and 940, which is significantly lower than 2000 and indicates that the flow was laminar.

The Reynolds number (N_{Re}) for non-Newtonian fluids is defined as follows:

$$N_{Re} = \frac{D^n \cdot V^{2-n} \cdot \rho}{\kappa \cdot 8^{n-1}} \tag{4}$$

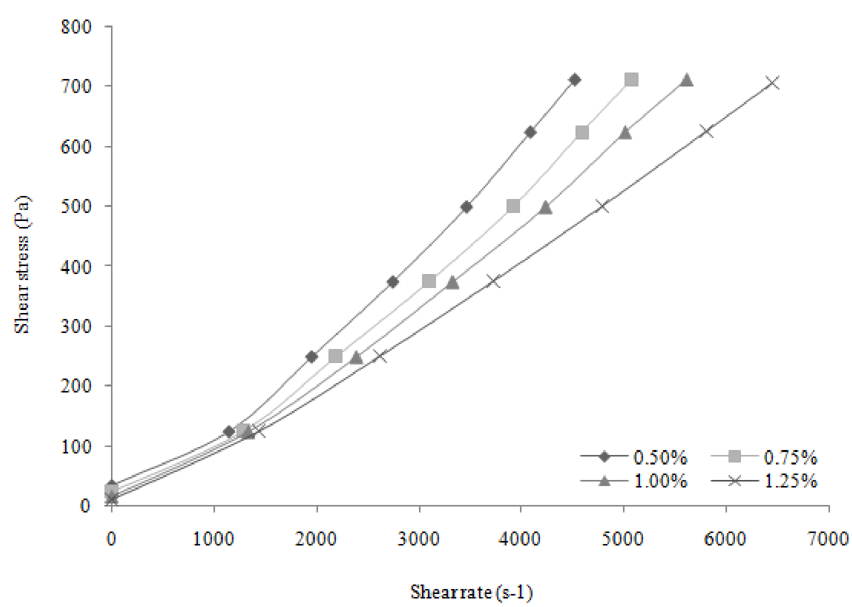
where,
D = The diameter of the pipe
ρ = The density of the grout

The yield stress of a particular grout was calculated using Eq. (1) after estimating the minimum pressure value required to start the flow condition.

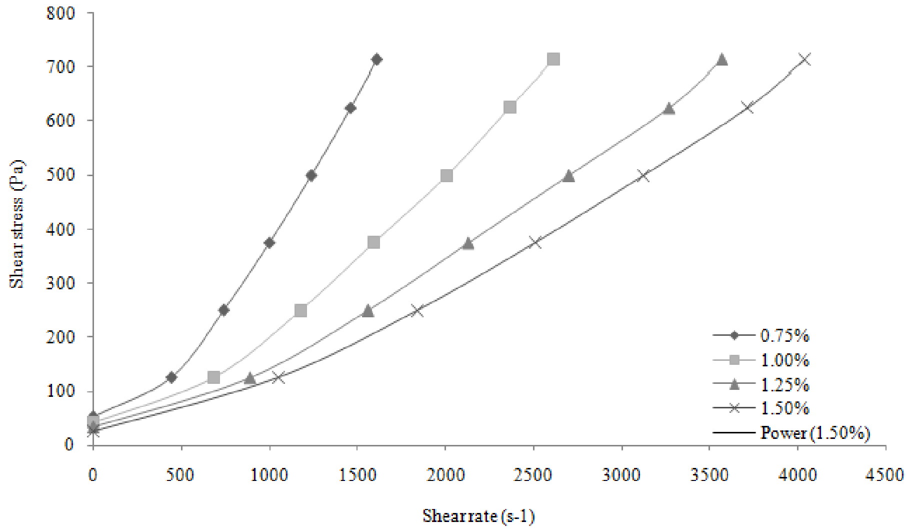
For the reliability of the test results, each of the reported yield stress-shear rate values correspond to the average value of at least three measurements that have values deviating no more than 1% from the average value of the total measurements.

RESULTS AND DISCUSSION

The influence of the w/c ratio, superplasticiser type and dosage on the rheological properties of grouts can be studied in plots of the variation of shear rate as a function of shear stress applied to the grouts. Flow curves of the examined grouts containing MLS, SNF or PCE superplasticisers are depicted in Fig. 2 to 4, respectively. It was determined that the relation between the shear stress-shear rate data is well represented by Herschel-Bulkley's equation for all grouts. The correlation coefficients R^2, which were obtained from non-linear regression analysis, are nearly equal to unity. Table 3 summarises the model parameters and R^2 values of the various grouts. The flow curves show that the rheological behaviour of the grouts was strongly shear thickening regardless of the type of superplasticiser (Cyr *et al*., 2000), which resulted in the viscosity enhancement with an increase



(a)



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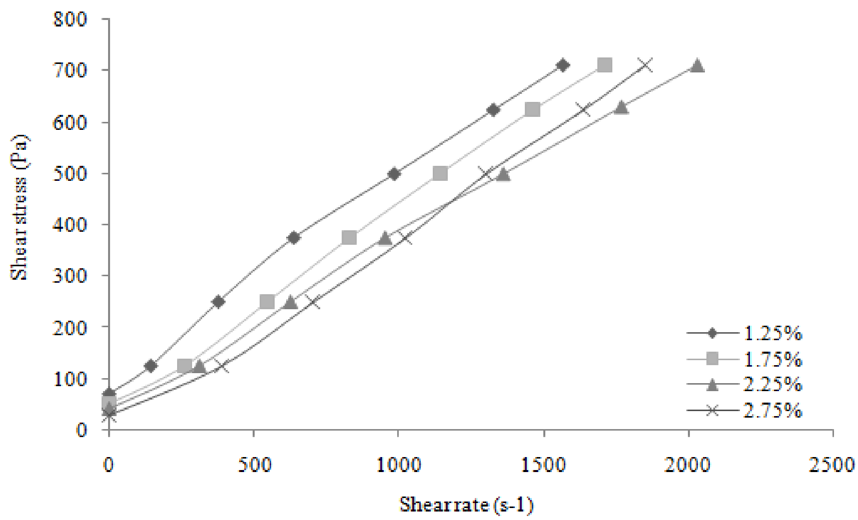
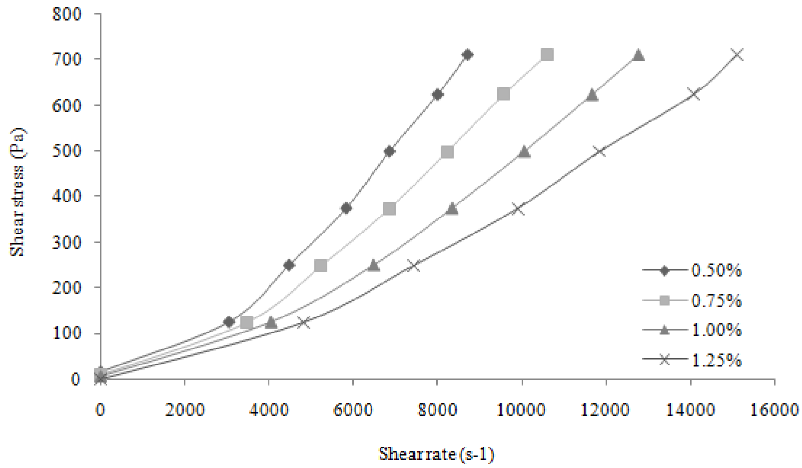


(c)

Fig. 2: Flow curves of grouts containing MLS super plasticiser, with w/c ratio of (a); 0.5 (b); 0.4 (c); 0.33

in the applied shear stress. An exception is the case of a 0.33 w/c grout made with low dosage (1.25%) of MLS or SNF which exhibited shear thinning response and Bingham behaviour (n values of about 1) when proportioned with 1.75 and 2.25% doses of the same superplasticiser. The shear thickening behaviour can be justified by considering the order-disorder transition theory of Hoffman (1998), who supported that an easy flowing state, where the particles are ordered into layers, shifts at a critical shear rate to a disordered state where this ordering is absent. This less-ordered structure dissipates a significant part of the applied energy to generate the suspension flow due to collisions between particles. Less effective energy is available; hence, the viscosity increases. In fact, the experiments indicated that as the shear rate increased, the grout apparent viscosity ($\mu = \tau/\dot{\gamma}$) exhibited an increasing tendency. For example, a 0.5 w/c grout made with a SNF dosage of 1% appeared to have viscosity values ranging from 0.03 to 0.05 Pa s as the shear stress increased from 125 to 715 Pa. In the case of grouts superplasticised with 1% PCE and MLS, the viscosity values ranged from 0.07 to 0.1 Pa s and from 0.09 to 0.12 Pa s, respectively. Moreover, it is possible that the increase in shear rate enhances the disorder, not only between the cement particles but also within the polymeric chains of the superplasticiser, which leads to desorption of a part of the polymer in the free liquid. Consequently, this part of the polymer could increase the grout viscosity according to Hoffman's theory whereas the local lack of adsorbed polymer could lead to a partial flocculation of cement particles. This



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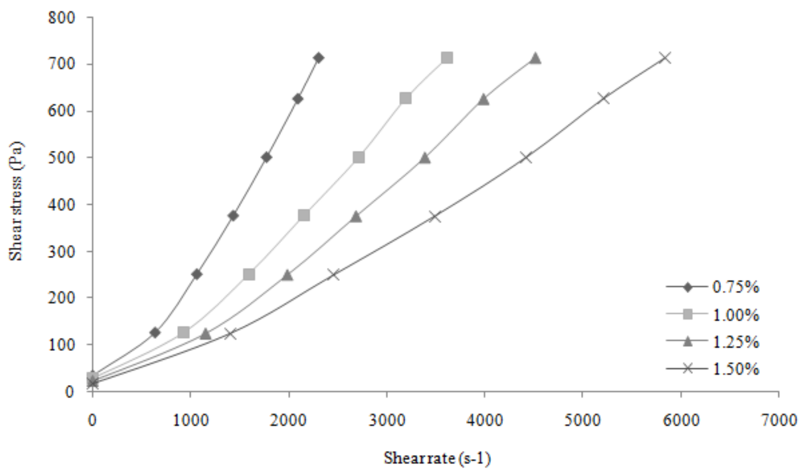

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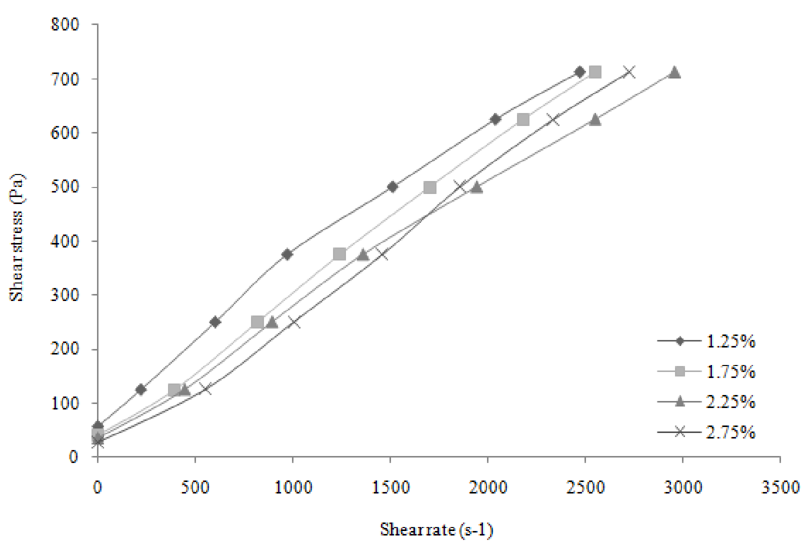
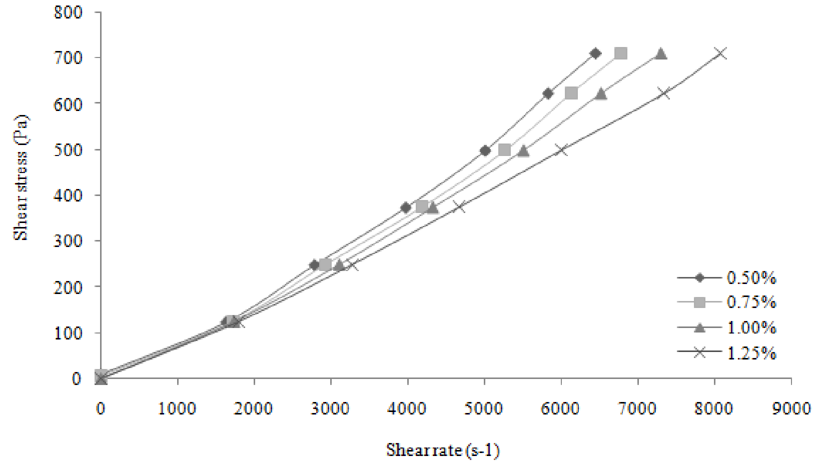


(c)

Fig. 3: Flow curves of grouts containing SNF super plasticiser, with w/c ratio of (a); 0.5 (b); 0.4 (c) 0.33



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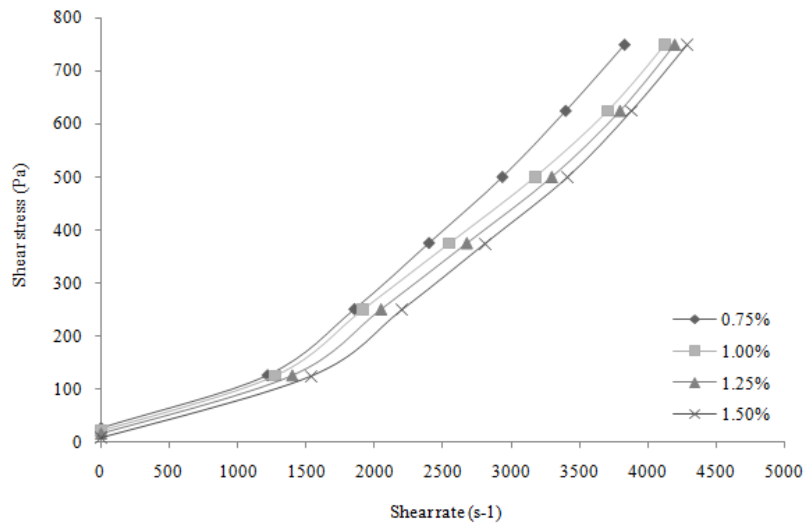

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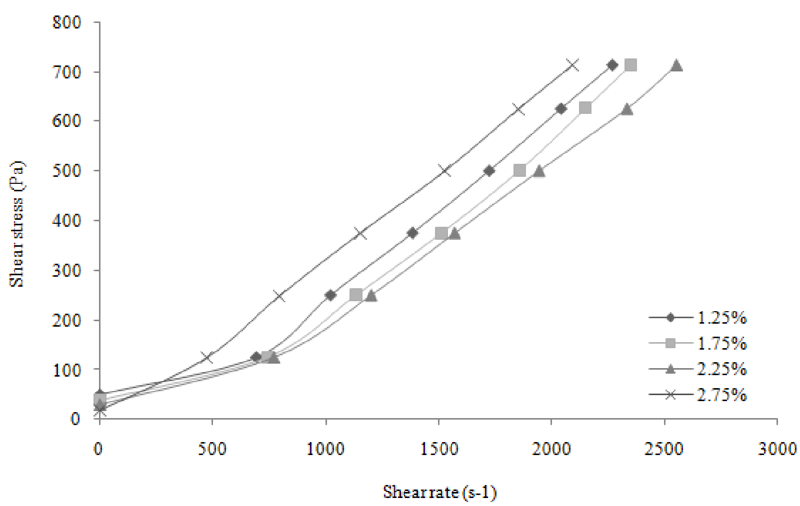

(c)

Fig. 4: Flow curves of grouts containing PCE super plasticiser, with w/c ratio of (a); 0.5 (b); 0.4 (c) 0.33

Table 3: Herschel-Bulkley model parameters and R^2 for different grouts

	MLS			SNF			PCE		
Designation	κ	n	R^2	κ	n	R^2	κ	n	R^2
G_1	0.005	1.40	0.98	$2.4 \cdot 10^{-5}$	1.66	0.99	0.006	1.32	0.98
G_2	0.006	1.36	0.99	$6.9 \cdot 10^{-5}$	1.54	0.99	0.007	1.30	0.99
G_3	0.011	1.28	0.99	0.0004	1.54	0.99	0.013	1.23	0.99
G_4	0.021	1.19	0.99	0.0004	1.48	0.99	0.022	1.15	0.99
G_5	0.006	1.57	0.99	0.007	1.48	0.99	0.001	1.62	0.99
G_6	0.006	1.47	0.99	0.009	1.37	0.99	0.002	1.54	0.99
G_7	0.009	1.37	0.99	0.008	1.35	0.99	0.001	1.63	0.99
G_8	0.005	1.42	0.99	0.009	1.29	0.99	$7 \cdot 10^{-4}$	1.71	0.99
G_9	0.92	0.89	0.99	0.902	0.84	0.99	0.004	1.55	0.98
G_{10}	0.277	1.05	0.99	0.221	1.02	0.99	0.002	1.63	0.99
G_{11}	0.35	1.03	0.99	0.327	1.05	0.99	0.006	1.49	0.99
G_{12}	0.099	1.18	0.99	0.093	1.13	0.99	0.091	1.17	0.99

Table 4: Yield stress of different grouts obtained from rheological experiments

	Yield stress (Pa)		
Designation	MLS	SNF	PCE
G_1	35	15	11
G_2	24	10	6
G_3	17	5	0
G_4	12	0	0
G_5	52	33	25
G_6	42	28	21
G_7	34	24	15
G_8	25	18	8
G_9	70	57	50
G_{10}	50	42	38
G_{11}	41	35	30
G_{12}	30	27	20

hypothesis explains the observation that the thicker grouts with a w/c ratio of 0.33 containing a superplasticiser dosage of 2.75% appeared to be more viscous than the grouts with a lower content of 2.25% superplasticiser, when subjected to high shear stress or even under the whole range of shear stresses as in the case of PCE.

Generally, the test results indicate that both μ and τ_o significantly increased as the w/c ratio decreased, despite the addition of significantly higher dosages of superplasticisers. In particular, it is observed that the lowest τ_o values were obtained for PCE grouts, whereas the addition of MLS resulted in the highest τ_o values, for all w/c ratios and admixture contents (Table 4). However, grouts proportioned with PCE appeared to be more viscous compared to the grouts obtained with SNF for all w/c ratios and admixture contents. Also, among the three superplasticisers, MLS had the less effect on fluidizing the grouts. For example, when the shear stress increased from 125 to 715 Pa, the viscosity values of the thicker grout (w/c = 0.33) containing the maximum PCE dose of 2.75% ranged from 0.26 to 0.34 Pa s; however, in the case of SNF and MLS, the viscosity values ranged from 0.22 to 0.26 Pa s and from 0.32 to 0.38 Pa s, respectively. These results are in agreement with the results reported by Yahia (2011), which demonstrated that grouts with a low w/c ratio containing a superplasticiser acting by a steric effect exhibited high shear thickening response and viscosity compared to those acting by an electrostatic effect. The lower τ_o values for grouts made with PCE can be attributed to the higher dispersive action of PCE molecules due to the steric hindrance effect that results from the extension of their grafted chains away from the surface of the cement particles (Uchikawa *et al*., 1997; Yoshioka *et al*., 2002). The higher viscosity values of PCE grouts compared to the ones of grouts made with SNF can be explained according to the clustering theory of Brady and Bossis (1985). This theory stated that hydrodynamic clusters are composed of compact groups of particles formed when hydrodynamic forces are sufficient to drive particles into contact. Under these conditions, the increase in shear rate leads to an increase in the viscosity as the clusters became larger and larger. It is possible that the long polycarboxylate-ether chains of PCE under shearing promote the formation of these clusters, which in turn entraps additional water and results in a higher inter-particle friction that causes an increment in the viscosity of the system (Zhang *et al*., 2010; Yahia, 2011).

Table 5 summarises the final setting time of the various grouts used in the tests. The final setting time is of great importance to the grouting practice; a short setting time (less than 4 h) can damage equipment and a long setting time (higher than 24 h) can delay execution of the process and, consequently, the grouting efficiency (Perret *et al*., 2000). The setting times obtained for all grouts ranged between 6 to 22.5 h. In general, the setting time increased as the superplasticiser dosage increased, a fact that is attributed to the retardation mechanism of superplasticisers. The degree of retardation varied with the type and dosage of the admixture. MLS had stronger retarding effect compared with the PCE and SNF. Zhang *et al*. (2010) noted similar observations. The difference in the setting times between the three types of superplasticisers can be due to the different retardation mechanism. Jolicoeur and Simard (1998) suggested that the retardation caused by SNF is mainly due to the adsorption of its molecules on nucleating hydrate particles, which inhibit the development of

Table 5: Final setting time and bleeding of grouts used in the tests

Designation	Setting time (h) SNF	PCE	MLS	Bleeding (%) SNF	PCE	MLS
G_1	7.5	8	10	1.87	2.4	1.1
G_2	10	11	13	3.59	4.1	1.4
G_3	12	13.5	15.5	4.12	4.7	2.3
G_4	15	17.5	20	4.85	5.2	3.1
G_5	6	7.5	9	1.66	1.82	0.8
G_6	8.5	10	11.5	1.83	2.64	1.22
G_7	11	13	14.5	3	3.52	1.91
G_8	14.5	16.5	17	4.2	4.9	2.44
G_9	6.5	9.5	10	2.17	2.72	1.45
G_{10}	9	12	13.5	2.39	3.22	1.52
G_{11}	11	17	19	3.64	4.2	2.06
G_{12}	12.5	20	22.5	4.38	5.3	2.71

Table 6: Development of compressive strength of grouts used in the tests

	Compressive strength (MPa)								
	MLS			SNF			PCE		
	Curing time (Days)			Curing time (Days)			Curing time (Days)		
Designation	3	7	28	3	7	28	3	7	28
G_1	14.4	19.1	24.6	21.2	27	36.1	21.6	27.9	39.8
G_2	15.2	20.2	26.6	23.4	28.9	38.7	31.2	36.2	44
G_3	13.6	18.7	27.1	25.6	30.8	40.5	33.6	38	45.5
G_4	12	17.2	27.5	28.9	33.5	42.2	30.9	42	47
G_5	19.3	25.3	30.3	24.1	33.1	43.3	33.6	40.4	49.4
G_6	24.1	26.6	31.5	28.1	34.3	46	37.4	46.5	54.5
G_7	28	27.2	35.6	32.3	38.7	47.3	38.3	50.2	56.2
G_8	25.7	27.8	39.4	35.1	42	48.5	40.2	53.2	58.6
G_9	30.2	35.4	44	40.7	45	55.8	41.3	48.5	58.3
G_{10}	28.5	37.6	47.6	49.2	53	60.6	43.2	51.6	62.4
G_{11}	23.9	39.4	50.3	52.1	54	63.2	45.3	52	66.7
G_{12}	19.2	41	52.2	48.2	56.6	64.5	44.2	55.4	69.4

Table 7: Development of elastic modulus of grouts used in the tests

	Elastic modulus (GPa)								
	MLS			SNF			PCE		
	Curing time (Days)			Curing time (Days)			Curing time (Days)		
Designation	3	7	28	3	7	28	3	7	28
G_1	1.68	2.7	3.16	2.36	2.83	4.63	2.7	3.1	4.77
G_2	1.76	2.8	3.32	2.46	2.95	4.82	3.75	3.94	4.95
G_3	1.56	2.68	3.44	2.52	3.1	4.92	3.93	4.2	5.08
G_4	1.08	2.62	3.52	2.63	3.3	4.97	3.25	4.5	5.16
G_5	2.02	3.14	3.51	2.56	3.32	5.08	4	4.46	5.2
G_6	2.08	3.05	3.6	2.64	3.58	5.12	4.21	4.68	5.35
G_7	2.15	3.11	3.82	2.82	3.7	5.18	4.3	4.92	5.43
G_8	2.1	3.20	4.12	2.94	3.9	5.25	4.33	5.2	5.58
G_9	2.25	3.40	4.31	3.46	3.84	5.44	4.45	5.2	5.62
G_{10}	2.54	3.55	4.52	3.64	4.37	5.65	4.53	5.34	5.75
G_{11}	2.48	3.62	4.67	4.1	4.6	5.67	4.62	5.47	5.89
G_{12}	1.86	3.7	4.76	3.77	4.89	5.71	4.6	5.61	5.95

hydration products. However, Uchikawa *et al*. (1997) observed that an interaction between PCE molecules and Ca^{2+} ions occurs, which results in lowering the Ca^{2+} concentration in the system and hinders the solid phase hydration and hydration products growth. For MLS, it is believed that the retardation is caused by a complexity of various mechanisms of retardation such as adsorption, complexation, precipitation and nucleation (Zhang *et al*., 2010).

According to cement grouting practices, the use of thick stable cement suspensions is compulsory to obtain maximum filling of voids or other spaces that cannot be obtained with the performance of unstable grouts due to their significant bleeding (Houlsby, 1988; Mirza *et al*., 2013). European Standard EN 12715 (2000) characterises a suspension as stable if it has a bleed capacity of up to 5%. The bleed capacity values of all tested grouts are demonstrated in Table 5. All grouts appeared to be stable with a bleed capacity lower than 5%, except a few cases of PCE grouts, which showed bleeding near to or slightly higher than 5%. In general, the bleed capacity was more pronounced for grouts proportioned with PCE, which is clearly due to the higher dispersive action of PCE molecules leading to less water trapped in the cement mixture.

Table 6 and 7 show the unconfined compressive strength and elastic modulus development of the various grout mixtures. An inspection of the results indicates that the early strength, especially after 3 days of curing, is affected by the superplasticiser dosage as well as the w/c ratio. In general, the strength exhibited an increasing tendency over time, which resulted in significantly higher strength values. This tendency was strongly dependent on the superplasticiser dosage and type. After 3 and 7 days of curing, MLS superplasticised grouts appeared to have significantly lower strength values than the ones obtained with PCE and SNF admixtures. In the case of PCE superplasticised grouts with a w/c ratio of 0.5 and 0.4 and despite the extension in setting time caused by PCE, the strength at the early stages (3 and 7 days) was higher compared to that with SNF. Puertas *et al*. (2005) performed conduction calorimetry and microstructural studies on the effect of a polycarboxylate admixture on the hydration of Portland cement pastes and determined that these results could be attributed to the strong retarding effect of PCE on the initial cement hydration reactions at very early stages (less than 2 days); nonetheless, this effect is offset in later stages where the reactive processes and reaction speed increase. Uchikawa *et al*. (1995) used X-ray photoelectron spectroscopy to report similar conclusions. In contrast, grouts with w/c ratio of 0.33 containing 1.75 to 2.75% PCE attained lower compressive strength with respect to the corresponding grouts incorporating SNF. The strong retardation of the development of the early compressive strength caused by PCE can be attributed to the high dosage of this superplasticiser.

From Table 6 and 7, it is observed that the grouts with MLS had much lower final strength (28 days) compared with those of the corresponding ones with PCE and SNF, a fact indicating the limited dispersive action of MLS that determines the cement hydration reactions. Among the SNF and PCE superplasticisers, PCE resulted in higher final strength values for all w/c grouts, especially for grouts with a high w/c ratio. For example, the addition of 0.75% PCE in grouts with a w/c ratio of 0.5 resulted in higher compressive strength and elastic modulus values of 14 and 3%, respectively, compared to the values of SNF. However, grouts with a w/c ratio of 0.33 containing 1.75% PCE appeared to have a compressive strength and elastic modulus increase of 3 and 1.7%, respectively. Thus, it can be noted that the incorporation of SNF or PCE results in similar final strength of extremely thick grouts. It appears that the presence of high PCE content in dense suspensions causes disperse-phase aggregation (Han *et al*., 2011). The increase in the solid fraction results in a reduced distance between neighbouring cement particles that favours interaction and entanglement of PCE chains, which is likely assisted by a fraction of non-absorbed (excess) polymers. The formation of such groups of particles enveloped by long polymers can change the local osmotic balance and trap additional water otherwise used to hydrate the system (Yahia, 2011).

CONCLUSION

In this study, the rheological properties, mechanical strength, bleeding and setting time of thick grouts with three types of superplasticisers of different dispersive mechanisms were investigated. By considering the data and results developed in this comprehensive laboratory study, the following conclusions can be noted:

- Regardless of the superplasticiser type, dosage and w/c ratio, all the grouts exhibited a shear thickening behaviour. The shear thickening response can be attributed to the formation of clusters when hydrodynamic forces overcome repulsive interparticle forces as the shear rate increases. Particles interact through clustering using lubrication and frictional forces. The difficulty of particles to flow around each other results in a higher rate of energy dissipation and an increase in viscosity. Another possible explanation in which lubrication hydrodynamics forces are not included is that shear forces drive particles sufficiently close to overcome a repulsive energy barrier; hence, the formation of clusters occurs. The shear thickening is presumed to be a temporary aggregation in a short-range attraction due to van der Waals forces.
- Addition of MLS resulted in much higher viscosity values and τ_o values than those made with SNF and PCE. The new generation of polycarboxylate superplasticiser acting by steric effect resulted in a decrease in τ_o but an increase in viscosity compared to the SNF acting by electrostatic effect. This result can be explained by the fact that the dispersive mechanism of PCE is more effective and consequently, less force is needed to drive particles in motion. However, the presence of the PCE polymer chains in the solution appear to promote cluster formation, especially in the case of high solid concentration, which results in greater viscosity of the grout.
- All the types of superplasticisers retarded grouts setting. However, the degree of retardation varied with the type and dosage of the admixture. The MLS had stronger retarding effect compared with the SNF and PCE superplasticisers.
- The higher dispersive action of PCE releases more entrapped water into the solution. This phenomenon resulted in a slightly increased

bleeding of grouts proportioned with PCE but remained at low acceptable values.

- Grouts proportioned with MLS had much lower early and final strength values compared with those of the corresponding ones with PCE and SNF. Among the SNF and PCE superplasticisers, PCE resulted in higher final strength values for all w/c grouts, especially for grouts with a w/c ratio of 0.4 and 0.5, whereas the more retarding action of PCE did not adversely affect the early strength. However, high doses of PCE in thick grouts (w/c = 0.33) reduced the early strength development and the final strength increment was limited. This low final strength improvement may be due to the formation of local groups composed of entangled polymer and cement particles leading to the entrapment of additional water otherwise used for hydration reactions.

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