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Rheological properties of grouts with viscosity modifying agents as diutan gum and welan gum incorporating pulverised fly ash

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Abstract

This investigation was undertaken to evaluate the influence of the dosage of the second generation of viscosity modifying agent (diutan gum) on fluidity and rheological parameters of cement-based materials grout compared to welan gum. All grouts were made with 0.40 water-to-binder ratio (W/B). The fresh properties of control grouts made without any viscosity modifying agent (VMA) and with superplasticizer (SP) were compared to those of grouts made with 0.02, 0.04, 0.06 and 0.08% diutan gum by mass of binder. Similar mixes made with welan gum were compared to those containing diutan gums. The effect of admixtures on fluidity and rheological parameters are discussed in this paper. The effect of the replacement of cement by pulverised fly ash (PFA) was also investigated. Grouts with replacements of PFA of 5, 13 and 20% by mass were used with the same W/B. Similar control grouts and mixes incorporated different dosages of PFA made with welan gum were made in order to compare the fluidity and the rheological parameters to the previous grouts made with diutan gum.

The results show that the increase of the dosage of diutan gum and welan gum for a given dosage of SP increases significantly the yield value, the apparent and plastic viscosity and reduces the fluidity. With an increase in dosage of SP, the apparent viscosity at low shear rate decreases dramatically than that at high rate of shear rate due to the pseudo-plastic rheology of the grouts containing VMA. Both VMAs exhibited high apparent viscosity values at low shear rates which were attributed to the entanglement and intertwining of VMA polymer chains at low shear rate and association of water between adjacent chains. For a given dosage of VMA, diutan gum showed a high apparent viscosity than welan which could be attributed to the molecular weight and to the long-side chain of diutan gum leading to greater entanglement and intertwining. For any given dosage of SP, the diutan gum exhibited higher yield value and plastic viscosity than welan gum. Diutan gum grouts demonstrate a greater yield value and apparent and plastic viscosity than welan gum for control and PFA grouts. The replacement of cement by PFA resulted in a reduction of yield value and an increase in plastic viscosity.

Keywords: Diutan gum; Mini-slump; Plastic viscosity; Rheology; Viscosity modifying agent; Yield value; Welan gum

1. Introduction

Cement-based grouts are widely used in injection grouting of cracks in massive structures since their physical and mechanical properties can be easily controlled. The rheological behaviour of special cement grouts intended for the underwater sealing of cracks in dams, offshore structures, massive foundations, or fissures in rock can be enhanced by the incorporation of a viscosity modifying agent (VMA) [1–3]. Grouts containing VMA are also used for filling post-tensioning ducts, where it is important to ensure high resistance to sedimentation and bleeding, hence ensuring corrosion protection of stressed tendons [2]. VMAs are also used in grouts for the repair of deteriorated structures by injection.

VMAs are relatively new admixtures used to enhance the cohesion and stability of cement-based systems [3–11]. Such VMAs are water-soluble polysaccharides that enhance the water retention capacity of grout [4–11]. The use of VMAs increases the yield value and plastic viscosity of cement-based grout at constant water-to-cement ratio. VMAs are highly effective to control bleeding as the long-chain molecules of VMA adhere to the periphery of water molecules, thus it adsorb and fix part of the mix water which increase the yield value and plastic viscosity of cement-based grout [4,12]. Molecules in adjacent

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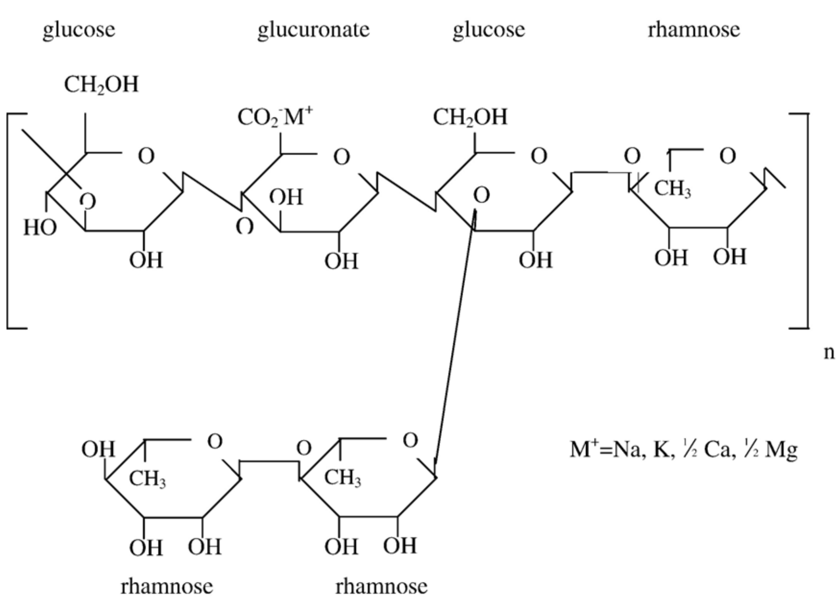
polymer chains develop attractive physical forces, block further water migration and cause the formation of a viscous gel. At low rates of shear and especially at high concentrations, the polymer chains can also intertwine and entangle which result in an increase in the apparent viscosity [4]. Several researchers have related the improvement in rheological properties and the performance of cement-based grout to the addition of superplasticizer (SP) and VMA [4–12]. Most VMA solutions are pseudo plastic (shear thinning) which means that increased shear rate causes a progressive decrease in apparent viscosity. This is due to the alignment of polymer chains along the flow lines [3]. The degree of pseudo-plasticity varies for different types of polymer solutions [13].

Diutan gum (DG) and welan gum (WG) are both high molecular weight, microbial polysaccharides produced by aerobic fermentation. They are anionic polymers and their performance is influenced by the presence of SP. Without the presence of SP, the biopolymer's anionic nature will cause them to have a tendency to adsorb out of the mix water onto the surface of cement [14] and with the presence of SP, it prevents this phenomena. The chain structure of diutan gum is different to the welan gum. Diutan gum had two-rhamnose side chain compared to welan gum which had only one rhamnose and one mannose (Fig. 1). The molecular length of diutan gum is up to 3 times longer than welan gum, which the molecular weights of diutan and welan gum are about 2.88 to 5.18 million Daltons and 0.66 to 0.97 million Daltons, respectively [15]. Welan gum is a long-chain biopolymer with sugar backbones substituted with sugar side chain. It is efficient in maintaining high viscosity in alkaline solution with a high concentration of calcium ions even at high temperature [15,16]. Diutan and welan gums are compatible with cement hydration products. It is believed that the molecules' side groups sterically shield carboxylate (COO) groups on the backbone, and prevent cross-linking by calcium ions. The longer side-chain of diutan may offer a more effective shielding of the carboxylic acid function on the molecular backbone, than that achieved with welan's shorter side-chain [16]. These biopolymers can be used to control bleeding and prevent segregation as the long-chain molecules of the polymer adhere to the periphery of water molecules, thus adsorbing and fixing part of the mix water and thereby expanding. As a consequence of the water retention, the yield value and viscosity of the cement-based materials increase. Molecules in adjacent polymer chains can also develop attractive forces, thus further blocking water migration and causing the formation of viscous gel. At low shear, and especially at high concentrations, the polymer chains can intertwine and entangle, resulting in an increase in the apparent viscosity [16,17].

2. Scope of the investigation

The objective of this study is to characterise the fluidity measured by mini-slump and the rheological parameters of diutan gum and to evaluate the influence of the dosages of diutan gum and SP on the fresh properties and the rheological parameters of grouts made with 0.40 W/B. The effect of the replacement of cement by PFA by 5, 13 and 20% (by mass) is also investigated with the variation of the dosages of diutan gum and SP. Similar control grouts and mixes made with different percentages of PFA and welan gum were investigated in order to



→ 3) β-D-Glcp-(1→4)-β-D-GlcpA-(1→4)-β-D-Glcp-(1→4)-∞-L-Rhap-(1→
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Fig. 1. Molecular structure of diutan gum [15].

Table 1
Chemical and physical properties of PFA and cement

	OPC	PFA Part 1
SiO_2 (%)	20.8	50
AL_2O_3 (%)	5	30
Fe_2O_3 (%)	3.2	7
CaO (%)	63.7	2.3
MgO (%)	2.6	1.2
K_2O (%)	–	1.1
Na_2O (%)	–	0.08
TiO_2 (%)	–	1.1
SO_3 (%)	–	0.4
Chloride (%)	–	<0.03
Free CaO (%)	1.6	–
LOI (%)	0.65	5.9
Na_2O eq. (%)	0.39	–
Moisture content	–	NIL
Water requirement (%)	–	94
Strength factor	–	0.85
Bulk density	–	1.2–1.7 g/cm^2
Specific density	3.15	2.2
Compressive strength — 28 days (MPa)	62	60.7
Particle density (kg/m^3)	–	2029
Specific surface area (m^2/kg)	385	5.8 *

* % retained on a 45 ìm sieve; BS 3892 Part 1: 1997.

compare the fluidity and the rheological parameters to diutan gum grouts.

3. Experimental programme

In the first phase, the test program consisted of evaluating the effect of the concentration of diutan gum and SP on the fluidity and the rheological parameters of the cement grout. This was carried out for grouts made with and without diutan gum to isolate the effect of VMA. All grouts were prepared with a W/B of 0.40, corresponding to high-performance cement-based materials. In this study, all grouts were prepared to determine the mini-slump, the yield value and the plastic viscosity using a co-axial viscometer.

The second part of this investigation consists of comparing the fresh and rheological properties of grouts made with diutan gun to similar mixes made with welan gum. The influence of the replacement of cement by PFA at 5%, 13% and 20% (% by mass) and SP on fresh and rheological parameters was also investigated for both VMAs.

4. Materials, proportions and testing procedures

4.1. Materials and mix proportions

The grout mixes investigated in this study were prepared with Standard CEM I 42.5N Ordinary Portland cement (OPC) and PFA. OPC and PFA used conformed to the BS EN197-1 and BS 3892, Part 1 and their chemical and physical properties are shown in Table 1. The relative density of PFA was 2.2.

A superplasticizer produced on the basis of modified polycarboxylic ether was used as aqueous solution with a solid content of 30% and specific gravity of 1.05. SP was used from 0.75% to 1.47% (by mass of binder). Diutan gum was supplied by Kelco-crete which an anionic polysaccharide developed specifically for use with cementitious materials and is a natural high molecular weight gum produced by carefully controlled aerobic fermentation. The repeating unit is comprised of a six sugar unit. Fig. 1 presents the structure of the diutan gum. Welan gum, which is a high molecular weight, microbial polysaccharide, was also provided by Kelco-crete. The diutan and welan gums were supplied in a powder gum and were used from 0.02% to 0.08% (by mass of binder).

4.2. Testing procedures

In total, 26 mixes were tested for OPC grouts and 21 mixes for PFA grouts. All grouts were prepared in a 5-litre planar-action high-shear mixer. The mixing tap water had a temperature of 16±1 °C, which was measured before mixing started. The VMA was mixed with cement. The SP was added to the water and mixed together. Mixing time was measured from when the binder (the first solid component) was added into the mix of water and SP. Finally, all components were mixed for 7 min from the start of measuring time. The grout temperature following the end of mixing was maintained at 20±2 °C.

Following the end of mixing, the properties of fresh cement grout were measured. The following tests of fresh cement grout carried out (the numbers in brackets show the range of times when the individual tests start after finishing mixing): mini-slump test (1–2 min) and coaxial cylinder rotation viscometer (4–10 min).

The mini-slump test is based on the measurement of the spread of slurry placed into a cone-shaped mould (Fig. 2). A PVC plate and a cone, which has a lower inner diameter of 38.1 mm, an upper inner diameter of 19 mm, and a height of 52.7 mm were used in the flow test of grout. The cone is placed into the center of the PVC plate, and, immediately after mixing, the sample is filled into the cone. The cone is then vertically lifted to let the grout flow freely. Finally, the diameters at four right-angle positions are measured when the grout stops flowing, and the average diameter of four measurements is recorded.

The viscosity of the cement grout is determined using a coaxial rotating cylinder viscometer (smooth cylinders, no serration) that enabled the determination of the apparent viscosity at different shear rates. The test is contained in the annular space between an outer cylinder (rotor) with radius of 18.415 mm and a bob with radius of 17.245 mm and height of 3.80 cm. The rotor and the bob

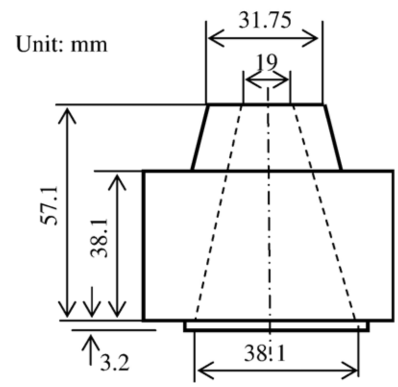

Fig. 2. Mini-slump test.

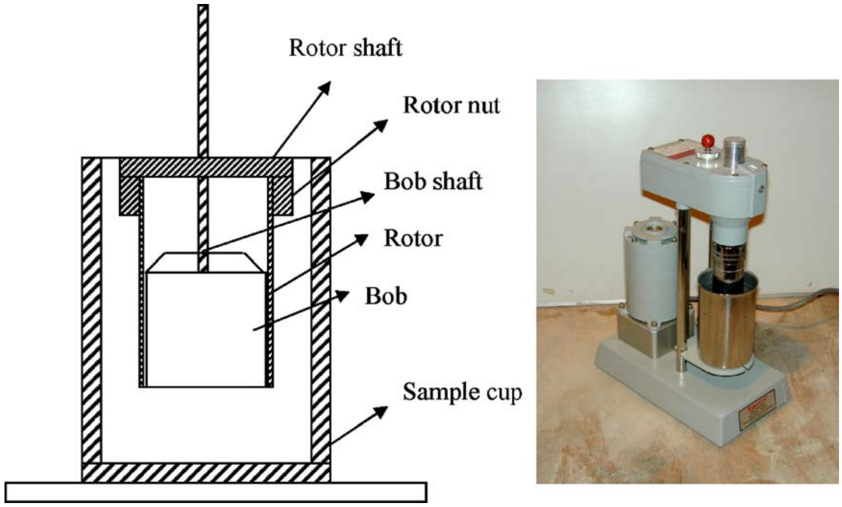

Fig. 3. Coaxial rotating cylinder viscometer.

are plunged into a cup which contains 350 ml of sample (Fig. 3). Viscosity measurements are made when the outer cylinder, rotating at a known speed, causes a viscous drag to be exerted by the fluid. This drag creates a torque on the bob, which is transmitted to a precision spring where its deflection is measured and then compared with the test conditions and the instrument's constants. The measurement is made in stepwise for 12 speeds of rotor from 0.9 rpm to 600 rpm (0.9, 1.8, 3, 6, 30, 60, 90, 100, 180, 200, 300, 600) when the values of viscometer reading = θ are recorded. The value of shear stress = τ (Pa) is calculated by including k_1 = torsion constant of spring per unit deflection (N cm/degree), k_2 = shear stress constant for the effective bob surface (cm^{-3}) and k_3 = shear rate constant [s^{-1}/rpm] [12].

The speed of the rotor was increased step by step from 0 to 600 rpm and the reading on the viscometer with increasing rotating speed was recorded. The reading of θ was taken when the needle in the viscometer was stabilised, or 30 s after the change of speed in cases when the needle has not stabilised which was caused by the thixotropy of the cement grout. The time of reading θ was in general between 5 to 10 s as maximum.

The yield value measured using co-axial cylinder is largely independent of rotational speed and which the concept of water-rich slip layer, with solids concentration lower than bulk materials, forms during the testing [18]. Saak et al. [18] found that the yield stress measured with the vane rheometer was twice the value using the smooth-walled concentric rheometer. The effect of slippage on the rheological parameters was also reported in the literature [19,20] and which at the solid wall, a reduction of the suspension density during the shearing test takes place due to the geometric difficulty of the arrangement of particles and the particle migration from high shear rate [19]. Results from Saak et al. [18] showed that the influence of slip was more pronounced as the concentration of solids increases. It was reported also that if the material of the wall cannot be able to disperse particles, the dispersing product tends to form a layer that acts as lubricant, therefore a slippage along the wall forms particularly at low shear rate [11]. Nehdi and Rahman [19] investigated the effect of smooth and serrated parallel plates, and smooth and vaned coaxial cylinders on the rheological parameters of cement grouts and they concluded that the surface roughness of the shearing wall was an important factor on these properties. In this study, the effect of the slip wall was not considered and also the shear rates which are fixed by the co-axial viscometer, but all experimental variables of testing were maintained similar. Other models such as Herchel-Bulkely,

Table 2
Summary of test results of grouts made with 100% C

Mix	SP (%, binder)	WG (% binder)	Mini-slump (mm)	μ_3 (Pa · s)	μ (Pa·s)	τ_0 (Pa)
1	0.30	0	103	1.10	–	–
2	0.75	0	121	0.80	0.18	4.8
3	1.00	0	123	0.70	0.13	2.2
4	1.20	0	126	0.70	–	1.8
5	0.75	0.04	78	1.80	0.55	18.4
6	0.93	0.04	81	2.60	0.45	10.7
7	1.29	0.04	89	2.50	0.39	9.3
8	1.38	0.04	90	1.80	0.38	7.5
9	1.00	0.06	70	2.71	0.51	14.6
10	1.30	0.06	72	2.61	0.44	13.7
11	1.38	0.06	78	2.20	0.43	12.5
12	1.47	0.06	84	2.10	0.41	11.8
13	1.29	0.08	60	3.01	0.47	16.3
14	1.38	0.08	64	2.91	0.44	15.6
15	1.47	0.08	65	2.71	0.42	13.2

Mix	SP (%, binder)	DG (% binder)	Mini-slump (mm)	μ_3 (Pa · s)	μ (Pa·s)	τ_0 (Pa)
16	0.75	0.04	84	5.81	0.67	23.7
17	0.93	0.04	88	4.71	0.60	18.9
18	1.29	0.04	98	4.50	0.56	16.9
19	1.38	0.04	91	4.31	0.54	14.7
20	1.00	0.06	77	4.91	0.73	19.4
21	1.30	0.06	84	4.81	0.73	19.1
22	1.38	0.06	86	4.71	0.71	18.7
23	1.47	0.06	92	3.31	0.67	13.8
24	1.29	0.08	77	5.00	0.79	18.6
25	1.38	0.08	82	4.80	0.73	18.8
26	1.47	0.08	89	4.58	0.70	14.7

μ_3 : apparent viscosity at 5.1 s^{-1}.

Table 3
Summary of test results obtained for grout mixes containing PFA and made with diutan gum and welan gum

PFA (%)	SP-VMA (%)	Mini-slump (mm)	μ_3 (Pa.s)	Experiemental shear stress (Pa) at various shear rate (s^{-1})										
				1.5	3.1	5.1	10.2	51.1	102	153	170	306	340	510
5%	0.30–0.0	101	1.20	3.1	4.1	6.1	8.2	22.0	35.3	47.0	48.5	75.1	81.2	117.5
13%	0.75–0.0	125	0.70	1.5	2.6	3.6	4.1	11.8	21.0	29.6	31.2	53.1	56.7	85.8
20%	1–0.0	136	0.50	1.0	2.0	2.6	3.6	13.8	26.6	36.8	41.4	63.9	74.1	124.2
	Diutan gum													
5%	0.75–0.02	94	1.50	12.8	16.4	20.4	26.6	46.5	66.9	82.8	86.4	96.1	129.3	150.2
	1.0–0.04	83	2.10	12.3	16.9	23.0	32.7	53.1	85.3	116.5	123.2	–	–	–
	1.2–0.06	67	2.71	14.3	19.9	26.6	35.3	50.1	76.1	102.7	109.4	146.7	–	–
13%	1–0.02	101	1.10	12.8	17.4	22.0	29.1	45.5	69.0	91.0	94.5	123.7	131.3	153.3
	1.3–0.04	98	1.30	13.3	17.9	23.0	31.2	52.6	82.8	109.4	112.9	153.3	–	–
	1.38–0.06	76	2.10	14.3	18.9	24.5	34.7	62.3	102.7	133.9	140.5	–	–	–
20%	1.3–0.02	113	0.90	8.7	11.8	14.3	19.9	34.2	53.7	71.0	76.1	111.9	114.0	139.0
	1.38–0.04	93	1.40	13.3	17.9	22.0	30.1	52.6	85.3	111.9	116.5	–	–	–
	1.47–0.06	80	1.90	14.3	19.4	25.0	33.2	58.8	94.0	124.2	131.3	–	–	–
	Welan gum													
5%	0.75–0.02	88	4.01	5.1	6.1	7.7	10.7	30.1	47.5	62.9	67.5	80.2	88.4	130.4
	1.0–0.04	86	4.51	9.2	10.2	10.7	13.3	36.3	57.7	76.1	79.7	94.5	100.7	137.5
	1.2–0.06	83	5.21	13.3	13.8	13.8	15.8	38.8	63.4	78.7	81.8	100.7	111.9	142.1
13%	1–0.02	85	4.31	3.1	4.1	5.6	8.7	27.6	47.5	65.4	68.0	94.0	101.2	140.5
	1.3–0.04	92	4.51	4.1	5.1	6.6	9.2	28.6	48.0	64.4	69.0	98.1	104.8	147.7
	1.38–0.06	83	4.81	9.2	10.2	10.7	13.8	35.3	58.8	77.2	88.4	111.4	118.6	151.8
20%	1.3–0.02	100	2.81	2.0	3.6	4.6	7.7	24.0	42.9	60.3	64.4	99.6	104.2	148.7
	1.38–0.04	90	4.31	4.6	5.6	7.2	10.2	31.7	54.7	74.6	80.2	100.7	112.4	–
	1.47–0.06	88	4.91	7.2	8.2	9.7	14.3	36.3	58.3	78.2	84.3	105.8	119.6	–

Casson, Sisko and Williamson were reported in literature and used in comparative studies of rheological models for pseudoplastic grouts [19,21].

In this study, the upcurve was chosen for the final evaluation for better description of rheological behaviour of the grouts including a structural breakdown phenomenon of inner forces among particles [10,11].

The values of yield stress and plastic viscosity are obtained from the mathematically modified Bingham model [12], which is described by the equation:

$$\tau = \tau_0 + \mu_p \dot{\gamma} + c\dot{\gamma}^2$$

Where τ_0 is the yield stress (Pa), μ_p is the plastic viscosity (Pa · s), $\dot{\gamma}$ is the shear rate (s^{-1}), and c is a constant. The value of the constant c is mostly about 10^{-3} and less, which is much smaller than the value of the plastic viscosity μ_p and the yield stress τ_0, and for this reason this constant is considered to be equal to zero.

5. Test results and discussion

The results of all grouts made with diutan gum and welan gum for grouts prepared with OPC and PFA are summarised in Tables 2 and 3, respectively. An example of the rheological parameters measured using the co-axial viscometer of the control mix and grouts made with 0.04% of diutan gum and welan gum at 0.75% of SP is shown in Fig. 4.

5.1. Comparison of the rheological behaviour between diutan gum and welan gum of control mix

Fig. 5 presents the comparison of the apparent viscosity of diutan gum and welan gum at different dosages of VMA ranged from 0.04% to 0.08% with fixed dosage of SP of 1.38% (by mass of binder), and no-VMA mix. The graphics show that the effect of the dosage of diutan and welan gums on increasing the pseudoplastic behaviour or shear thinning compared to the control grout without VMA which was almost Newtonian at the same dosage of SP 1.38%. Both VMAs exhibited high apparent viscosity values at low shear rates which were attributed to the entanglement and intertwining of the VMA polymer chains at low shear rate and association of water between adjacent chains. Reduction in the viscosity of the VMA grouts was observed when the shear rate increased and due to a partial realignment of the polymer chains in the direction of flow and dislodge of the intertwined chains, thus the resistance of the mix is decreased to undergo deformation. The apparent viscosity was then reduced with an apparent enhancement of the fluidity at high shear rate.

The comparison between both VMAs showed that diutan gum was more pseudoplastic and exhibited greater viscosity at low shear rate than welan gum at the same dosages of VMA and SP. This difference can be attributed to diutan's gum molecular weight and molecular length which diutan gum is longer up to 3 times than welan gum [15]. These results confirm data obtained by Phyfferoen et al. [16]. The higher viscosity of the diutan gum which had high molecular weight may also be attributed to higher water retention. The factors that influence flow are described by Dracy's Law which the flow rate is inversely proportional to fluid viscosity. Therefore, diutan gum increased the viscosity of the matrix and will improve the water retention. Pourchez et al. [22] reported that the higher molecular weight of cellulose ethers, the higher water retention obtained. It was also reported that diutan gum used in grout made with W/C = 1 had less bleed water after 24 h compared to welan gum [16]. Further experiments on water retention of diutan are required using for

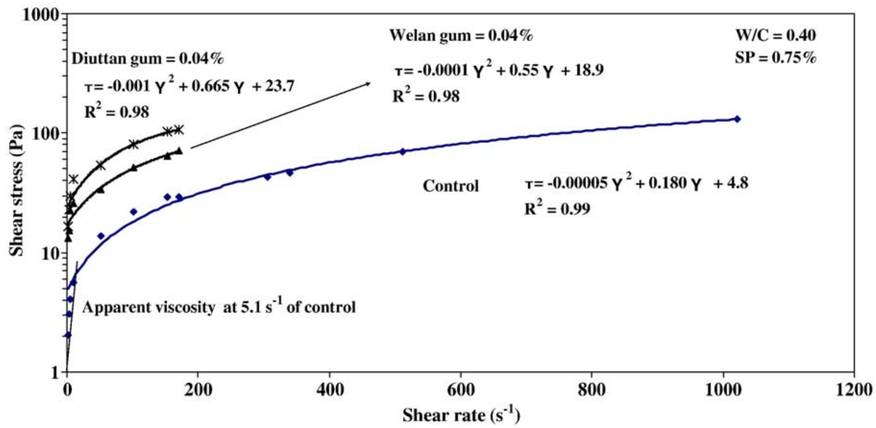

Fig. 4. Rheological parameters measured using a co-axial viscometer of the control mix and grout made with 0.04% of diutan and welan gums (SP = 0.75%).

example forced (pressure) bleeding with a Baroid filter. It can be seen that at low rate of shear, the viscosity could be similar to welan gum grout by using lower dosage of diutan gum (up to 50%).

5.2. *Effect of dosages of diutan gum, welan gum and SP on mini-slump of control mix*

Fig. 6 presents the variation of the results of mini-slump of the grouts made with 100% C, and diutan gum and welan gum with the dosage of SP. Three dosages of VMA were tested, 0.04%, 0.06% and 0.08%. As expected, the increase in the dosage of SP resulted in an increase of mini-slump for a similar dosage of VMA and the increase of VMA led to a reduction in the mini-slump. For a similar dosage of SP, adding VMA resulted in a significant decrease in the fluidity. For example, for grout made with 1% SP, adding diutan gum at a concentration of 0.04% resulted in the reduction of the mini-slump from 123 mm to 90 mm and to 83 mm for welan mix, respectively.

For the control grout without VMA, the increase of dosage of SP was more significant from 0.30% to 0.75%, and the mini-slump was similar between 0.75% and 1.2% (121 mm vs. 126 mm) which indicated the saturation point. However, among the grouts made with welan gum, the grouts with 0.04%, 0.06% and 0.08% had similar mini-slump when the SP dosage were increased from 0.75% to 1%, 1% to 1.3%, and 1.38% to 1.47%, respectively. For grouts with diutan gum, similar consistency was observed for the mixes made with 0.06% of diutan gum and 1.3% and 1.38% of SP. For all dosages of VMAs, it was noted that the grouts made with diutan gum had better fluidity than those made with welan gum. For example, for the mix containing 0.04% of VMA, to assure a mini-slump 88 mm, welan gum grout required 1.3% of SP instead of only 1% of SP for diutan gum grout.

The results from Fig. 6 indicated that with lower SP content, grout which contained diutan gum could assure similar fluidity to grout made with welan gum. This can be attributed to the lower charge density of diutan gum which resulted in a reduction tendency to adsorb out onto the hydration cement products compared to welan gum. These results confirm the findings by Phyfferoen et al. [16].

5.3. *Effect of dosages of diutan gum, welan gum and SP on the apparent viscosity at low shear rate of the control mix*

The influence of the increase in the dosage of SP on apparent viscosity at low shear rate of 5.1 s^{-1} for grouts made with various VMAs dosages of diutan gum and welan gum is shown in Fig. 7. Adding 0.04% of diutan gum or welan for both dosages of 0.75% and 1% of SP resulted in an increase in the apparent viscosity at low shear rate compared to similar mix grouts without any VMAs. The increase in the dosage of both VMAs increases the apparent viscosity at low shear rate for any given dosages of SP. The increase in the pseudo plastic behaviour in the presence of VMAs compared to similar mixes without any VMAs is attributed to the polymer chains of VMAs which

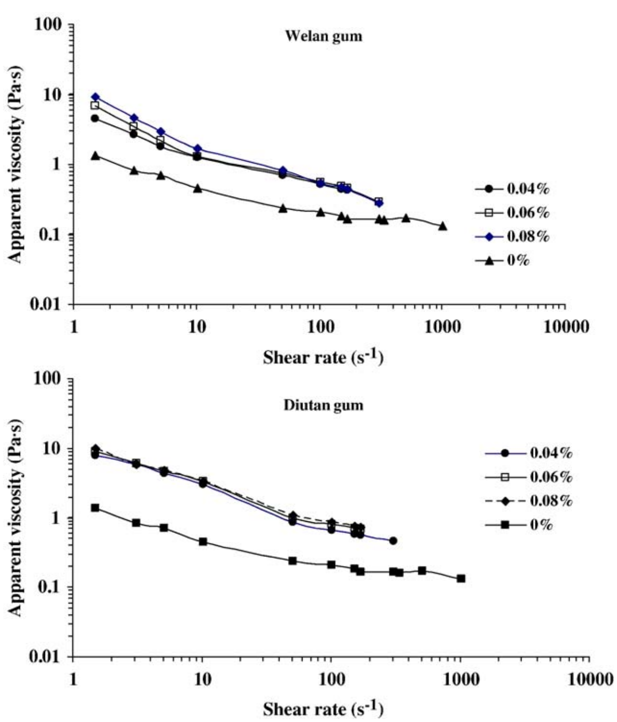

Fig. 5. Comparison of variations in apparent viscosity vs. shear rate of welan gum and diutan gum at different percentage of VMA with SP = 1.38%.

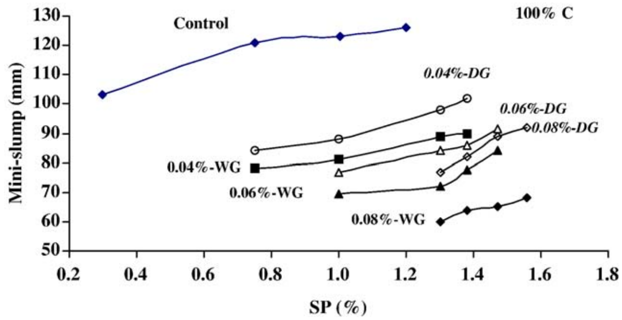

Fig. 6. Variations of mini-slump vs. SP for diutan and welan gum (grout made with 100%C and W/B = 0.40).

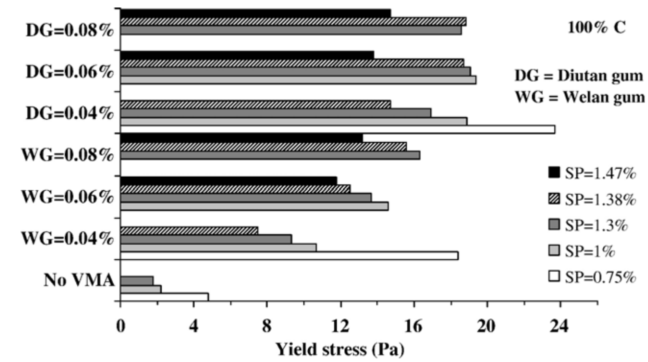

Fig. 8. Variations of yield value with dosages of SP and diutan and welan gums (grout made with 100% C and W/B = 0.40).

entangle and intertwine thus resulting in an increase in apparent viscosity, especially at low shear rate. For any given dosage of VMAs, the increase in SP led to a reduction of the apparent viscosity for both diutan gum and welan gum. It was noted that the apparent viscosities at low shear rate of 5.1 s^{-1} of all grouts containing diutan gum were higher than those made with welan gum. For example, grouts made with 1% of SP, the grouts containing 0.04% and 0.06% diutan gum exhibited apparent viscosities at low shear rate of 4.7 Pa·s and 4.9% Pa·s compared to 2.6 Pa · s and 2.7 Pa·s, respectively. At low dosages of SP of 0.75% and 1%, the apparent viscosities at low shear rate of diutan gum were more than twice than those for similar grouts made with welan gum. At the same dosage of VMA, the diutan gum exhibited higher apparent viscosity at low shear rate than welan gum which is attributed to the long-side chain of diutan gum which resulted in greater entanglement and intertwining.

5.4. Comparison of yield value and plastic viscosity between diutan gum and welan gum of the control mix

Figs. 8 and 9 present the yield value and the plastic viscosity results of grouts made with 100% C and three dosages of VMA at 0.04%, 0.06% and 0.08% for a dosage of SP ranged between 0.75% and 1.47%, respectively. For any given dosage of diutan gum or welan gum, the increase in the dosage of SP resulted in a reduction of yield value and plastic viscosity. Similarly for no-VMA mix, the increase in dosage of SP led to a reduction in yield value and plastic viscosity. For any given dosage of SP, the introduction of VMA (diutan gum or welan gum) resulted in significant increase in yield value and plastic viscosity. For example, for grout containing 1.38% of SP, the increase in the concentration of diutan gum and welan gum from 0.04% to 0.06% resulted in an increase of yield value from 14.7 Pa to 18.7 Pa and 7.5 Pa to 12.5 Pa, respectively. For the plastic viscosity, the increase was from 0.38 Pa·s to 0.43 Pa·s, and 0.54 Pa·s to 0.71 Pa·s for diutan gum and welan gum, respectively. In the case of no-VMA grouts, for example the incorporation of 0.04% diutan gum at dosages of 0.75%, 1% and 1.3% of SP resulted in an increase of 4.9 times, 8.6 times and 9.4 times in yield value, respectively. Such an increase was 3.8 times, 4.9 times and 5.2 times in the case of welan gum. Adding 0.04% of diutan gum with 0.75% and 1% SP to no-VMA grout resulted in an increase in plastic viscosity of 270% and 250%, respectively, and 200% and 160% in the case of adding welan gum at the same dosages. At 0.04% of VMAs, it appears that the yield stress and plastic viscosity reduced significantly when the dosage of SP increased from 0.75% 1.3%, and up to this dosage, the yield stress and viscosity decreased slightly.

The comparison between the results of yield value and plastic viscosity of diutan gum and welan gum indicates that the grouts containing diutan gum led to greater values of the rheological parameters than those of welan gum. The highest viscosity of diutan gum can be attributed to the highest diutan's molecular weight which resulted in more water retention. The higher molecular weight, the higher water retention obtained [22]. These results on viscosity are in agreement with some results of Phyfforeon et al. [16]. Further investigation on water retention of diutan gum is required. It can be concluded that to

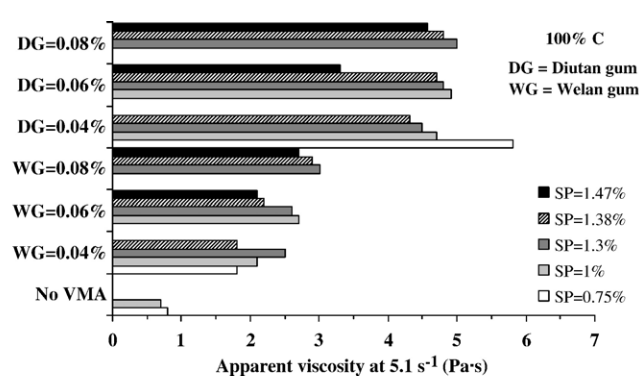

Fig. 7. Variations of apparent viscosity at 5.1 s^{-1} with dosages of SP and diutan and welan gums (grout made with 100% C and W/B = 0.40).

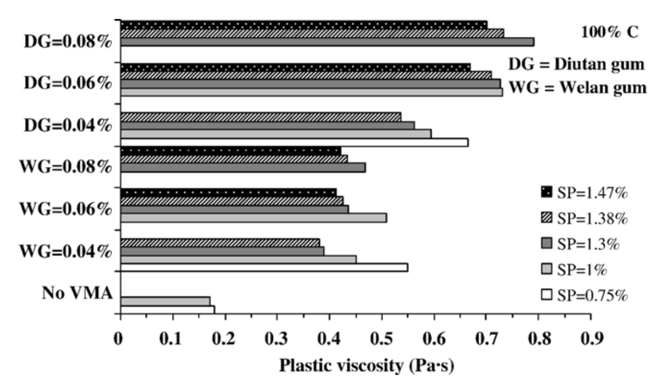

Fig. 9. Variations of plastic viscosity with dosages of SP and diutan and welan gum (grout made with 100% C and W/B = 0.40).

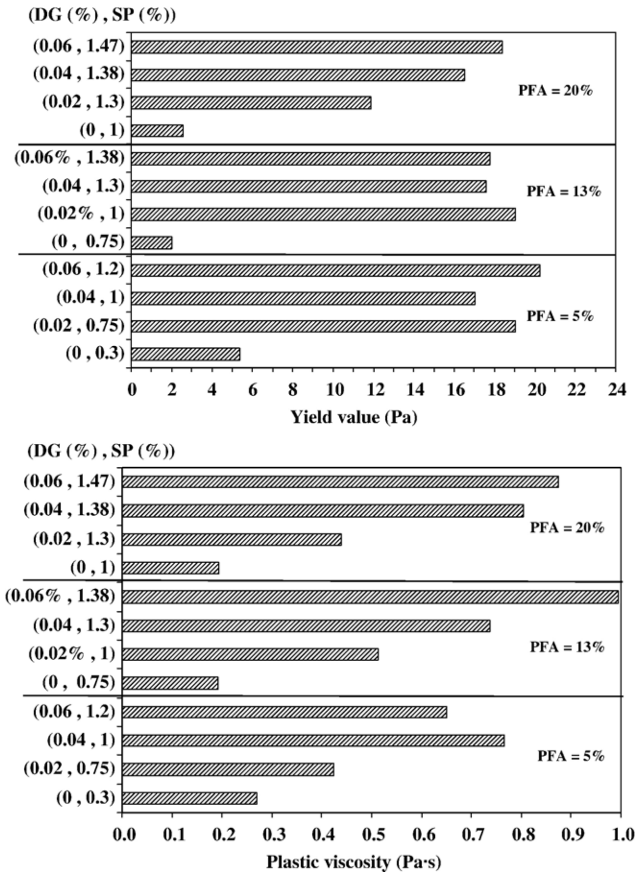

Fig. 10. Variations of yield value and plastic viscosity with dosages of PFA, SP and diutan gum (W/B = 0.40).

achieve a similar yield value and plastic viscosity, diutan gum required lower dosage than welan gum.

5.5. *Effect of PFA on rheological parameters of grouts made with diutan gum and welan gum*

The mini-slump of grouts made with fixed W/B (0.40) and with 5% PFA, 13% PFA, and 20% PFA at various combinations of diutan gum-SP or welan gum-SP are presented in Table 3. The dosage of SP required to secure a given fluidity is related to the dosage of VMA. For a given dosage of VMA, the increase in dosage of SP enhances fluidity which is reflected in an increase of the mini-slump. The mini-slump values of no-VMA grouts increased when the dosages of PFA and SP increased. The PFA improves the fluidity because the spherical shape of PFA led to a reduction of the friction forces among the particles of cement, playing the role of 'ball bearing effect' and easily roll over one another as reported in literature [23,24]. For grouts made with diutan gum and welam gum, the mini-slump results varied between 67 to 113 mm, and 88 to 100 mm, respectively.

The results of yield value and plastic viscosity for diutan gum and welan gum grouts with different percentages of PFA are compared in Figs. 10 and 11, respectively. The replacement of cement by 5%, 13%, and 20% PFA led to a reduction of the yield value for any given dosages of VMA and SP. Therefore, the replacement of cement by PFA at level 20% significantly reduced the yield value, and these results confirm the data reported by Sonebi [25] investigating self-compacting concrete and Ferraris et al [26] working on paste and concrete without VMA. Ferraris et al. [26] reported that the highest reduction in yield value was found at 12% PFA as replacement of cement in grout made with W/C ratio of 0.35 and 0.44% SP and without VMA. The reduction of yield value can be attributed that the replacement of cement by PFA improves the contact between the particles of cement by ball bearing effect and reduce the friction forces [22,23] and therefore, the applied shear stress needed to initiate flow of grout reduced. The spherical shape of PFA also minimises the particle's surface to volume ratio, resulting in low fluid demands, and out of all 3 dimensional shapes, a sphere gives the minimum surface area for a given volume [27]. A higher packing density was obtained with spherical particles as compared to crushed particles in a wet state and which resulted in lower water retention with spherical particles, and therefore lower water demand for a specific fluidity [28]. A stronger dependence of fluidity (defined as the inverse of value of viscosity) on the average particle size was reported with an optimum value [28]. For example, for the grout made with 0.04% of welan gum and 1% of SP, the replacement of cement by 5% PFA resulted in a reduction of yield value from 10.7 Pa to 8 Pa, and from 9.3 Pa to 6.3 Pa with 13% PFA and

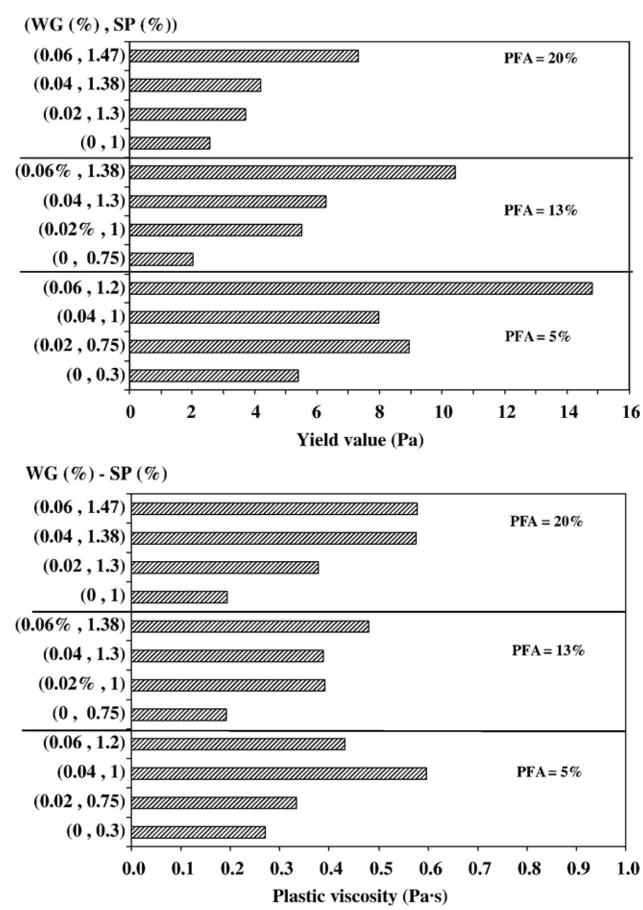

Fig. 11. Variations of yield value and plastic viscosity with dosages of PFA, SP and welan gum (W/B = 0.40).

1.3% of SP compared to the control mix. With 20% PFA, the reduction of yield value was from 7.5 Pa to 4.2 Pa using 1.38% of SP. However, the incorporation of PFA for grouts using diutan gum resulted in the slight reduction of yield value. For example, the grouts made with 0.06% of diutan gum and 1.38% SP, using 13% of PFA led to a reduction of yield value from 18.7 Pa to 17.8 Pa, and in the case of 20% PFA with 1.47% SP, the yield value decreased from 18.8 Pa to 18.4 Pa. Park et al. [29] worked on cement paste without VMA and found that the yield value decreased at 10% PFA replacement of cement and started to slightly increase at 20% and 30%, which suggested that at some level of around 20% of PFA, the yield stress began to increase. At a high level of replacement of cement by PFA, this increase of yield value due to the higher amount of unburned carbons from the PFA [29] in the grout might lead to a reduction of workability linked to the adsorption of SP [30].

The results from Figs. 10 and 11 show that the incorporation of 5% PFA, 13% PFA and 20% PFA led to a slight increase of the plastic viscosity compared to similar grout mixes made with 100% C for any given combination of VMA–SP. For example with grout mix made with 5% PFA, 0.04% diutan gum and 1% SP, the plastic viscosity was 0.77 Pa·s compared to 0.60 Pa·s for grout made only with OPC, and in the case of welan gum, the incorporation of 5% PFA resulted in an increase of plastic viscosity from 0.45 Pa · s to 0.60 Pa·s.

For all replacements of cement by PFA, the results showed that the diutan gum grouts exhibited high yield values than welan gum for any given combination of VMA and SP. For a dosage of 0.04% of VMA, using diutan gum increase the yield value up to 2.7 times than the grout containing similar dosage of welan gum and SP. The increase of the yield value of the grouts containing diutan gum was more important for high replacement of cement by PFA compared to the grouts made with welan gum. For example, for grout made with 20% PFA and 0.06% of VMA, adding diutan gum resulted in 4.2 times increase in yield value compared to similar grout made with welan gum and in 1.7 times increase with 13% PFA mix. Similarly, the use of diutan gum resulted in an increase of plastic viscosity compared to welan gum grouts for any given dosages of SP and PFA. For dosage of VMA of 0.04% and 13% PFA, diutan gum grout containing 1.3% SP had a plastic viscosity of 0.74 Pa·s compared to 0.39 Pa·s for welan gum grout. With 20% PFA and similar dosage of VMA and using 1.38% SP, the diutan gum grout exhibited higher plastic viscosity compared to welan gum grout (0.80 Pa · s vs. 0.58 Pa·s).

6. Conclusions

Based on the above results, the following conclusions can be draw:

– Using diutan gum and welan gum led to an increase in the pseudoplastic behaviour and the shear thinning increased with their dosages compared to the control grout without VMA due to the entanglement of the chains polymers and association of water between adjacent chains. Therefore, the apparent viscosity increased especially at low shear rates. At high shear rate, the entangled chains dislodge and align in the direction of the flow and then the apparent viscosity decreased which led to an enhancement of the fluidity.
– For a similar dosage of SP, adding diutan gum or welan gum resulted in a major reduction in fluidity, and vice versa, for any given dosages of VMA, an increase in dosage of SP led to an improvement of fluidity.
– For fixed dosages of VMA and SP, the diutan gum grouts exhibited better fluidity than the welan gum grouts. A lower charge density of diutan gum results in a reduction tendency to adsorb out onto the hydration cement production and grout could assure similar fluidity to that of welan gum with lower SP content.
– Diutan gum was more pseudoplastic and exhibited greater viscosity at low shear rate of up to 5 s^{-1} than welan gum at the same dosages of VMA and SP. This difference can be attributed to diutan's gum molecular weight and which is attributed to the long-side chain of diutan gum leading to greater entanglement and intertwining.
– The incorporation of SP led a reduction in apparent viscosity, thus improving the fluidity and reduced the yield value due to the action of dispersion of SP by limiting or suppressing agglomeration among the cement particles [31]. For a given dosage of SP, the increase in diutan gum or welan gum dosages resulted significantly in an increase in yield value and plastic viscosity. For both VMAs used at a dosage of 0.04%, the increase of dosage of SP from 0.75% to 1.3% led to an important reduction of yield value and plastic viscosity compared to other dosages of 0.06 and 0.08%.
– Diutan gum had higher yield value and plastic viscosity compared to similar grout with welan gum for any given dosage of SP. Thus, to achieve similar rheological behaviour, lower dosage of diutan gum could be used and also SP compared to welan gum grout. The highest viscosity may be attributed to the highest diutan's molecular weight and to greater water retention. Further research on water retention of diutan gum is required.
– Adding 0.04% VMAs, the yield value of diutan gum grout was increased by 4.9 to 9.4 times with SP ranged from 0.75% to 1.3% compared to no-VMA grout, while using welan gum, the increase of yield value was slightly lower (3.8 to 5.2 times). For the same dosage of VMAs, the plastic viscosity was increased by 2.5 to 2.7 times with diutan gum, and only 1.6 to 2 times with welan gum.
– For any given dosages of diutan gum or welan gum and fixed dosage of SP, the incorporation of PFA at different percentages of 5%, 13% and 20% resulted in a reduction in yield value and an increase in plastic viscosity. This reduction can be attributed to the ball bearing effect of PFA between the particles of cement enhancing the contact of cement particles by reducing the friction forces [23,24]. The increase of yield value of grouts with diutan gum was more important with high replacement of cement by PFA compared to that containing welan gum.
– With welan gum grout, the highest replacement of PFA, the greater a reduction of yield value. With diutan gum gout, the incorporation of PFA led a slight reduction in yield value compare to welan gum.

References

[1] A.C. Houlsby, Construction and design of cement grouting, A guide to Grouting in Rock Foundation, Ed. John Wiley and Sons, 1990.442 pp.
[2] K.H. Khayat, A. Yahia, P. Duffy, High-performance cement grout for post-tensioning applications, ACI Materials Journal 96 (4) (1999) 471–477.
[3] K.H. Khayat, Viscosity-enhancing admixtures for cement-based materials — an overview, Cement and Concrete Composites 20 (2–3) (1998) 171–188.
[4] K.H. Khayat, A. Yahia, Effect of welan gum—high-range water reducer combinations on rheology of cement grout, ACI Materials Journal 94 (5) (1997) 365–372.
[5] V.A. Ghio, P.J.M. Monteiro, L.A. Demsetz, The rheology of fresh cement paste containing polysaccharide gums, Cement and Concrete Research 24 (2) (1994) 243–249.
[6] V.A. Ghio, P.J.M. Monteiro, O.E. Gjørv, Effects of polysaccharide gums on fresh concrete properties, ACI Materials Journal 91 (6) (1994) 602–606.
[7] T. Kawai, Non-dispersible underwater concrete using polymers, Marine Concrete, International congress on Polymers in Concrete, Brighton, UK, Chapter 11.5, 1987.
[8] T. Kawai, T. Okada, Effect of superplasticizer and viscosity-increasing admixture in properties of light-weight aggregate concrete, ACI SP-119 (1989) 583–604.
[9] M. Sonebi, Factorial design modelling of mix proportion parameters of underwater composite cement grouts, Cement Concrete Research 31 (11) (2001) 1553–1560.
[10] M. Sonebi, Experimental design to optimize high-volume of fly ash grout in the presence of welan gum and superplasticizer, Materials and Structures 35 (250) (2002) 373–380.
[11] M. Nehdi, M.-A. Rahman, Effect of geometry and surface friction of test accessory on oscillatory rheological properties of cement pastes, ACI Materials Journal 101 (5) (2004) 416–424.
[12] K.H. Khayat, A. Yahia, Simple field tests to characterize fluidity and washout resistance of structural cement grout, Cement, Concrete and Aggregates 20 (1) (1998) 145–156.
[13] C.B. Skaggs, W.G. Rakitsy, S.F. Whitaker, Applications of rheological modifiers and superplasticizers in cementitious systems, ACI Publications SP-148 (1994) 191–207.
[14] A. Phyfferoen, C.B. Skaggs, Optimizing the use of welan gum in cementitious and gypsum-based systems, ConChem Proceedings, Verlag für chemische Industrie, H. Ziolkowsky, Augsburg, 1997, pp. 193–202.
[15] N. Sakata, S. Yanai, M. Yoshizaki, A. Phyfferoen, H. Monty, Evaluation of S-657 biopolymer as a new viscosity-modifying admixture for self-compacting concrete, in: K. Ozawa, M. Ouchi (Eds.), Proceedings of the 2nd International Symposium on Self-Compacting Concrete, Tokyo, Japan, 2001, p. 229–23.
[16] A. Phyfferoen, H. Monty, B. Skaggs, N. Sakata, S. Yanai, M. Yoshizaki, Evaluation of the biopolymer, Diutan gum, for use in self-compacting concrete, in: S. Shah, J. Daczko, J. Lingscheit (Eds.), Conference Notes of First North American Conference on the Design and Use of Self-Consolidating Concrete, USA, 2002, pp. 141–146.
[17] K.H. Khayat, M. Saric-Coric, Effect of welan gum—superplasticizer on properties of cement grouts, Sixth CANMET/ACI International Conference on Superplasticizers and Other Chemical Admixtures in Concrete, ACI SP-195, Nice, 2000, pp. 249–268.
[18] A.W Saak, H.M. Jennings, S.P. Shah, The influence of wall slip on yield stress and viscoelastic measurements of cement pastes, Cement and Concrete Research 31 (2) (2001) 205–212.
[19] M. Nehdi, M.-A. Rahman, Estimating rheological properties of cement pastes using various rheological models for different test geometry, gap and surface friction, Cement and Concrete Research 34 (11) (2004) 1993–2007.
[20] J.R. Van Waser, J.W. Lyons, K.Y. Kim, R.E. Colwell, Viscosity flow measurement, Interscience Publishers, New York, 1963, p. 214.
[21] A. Yahia, K.H. Khayat, Analytical models for estimating yield stress of high performance pseudoplastic grout, Cement and Concrete Research 31 (5) (2001) 731–738.
[22] J. Pouchez, A. Peschard, P. Crosseau, R. Guyonnet, B. Guilhot, F. Vallée, HPMC and HEMC influence on cement hydration, Cement and Concrete Research 36 (2) (2006) 288–294.
[23] T. Termkhajornkit, T. Nawa, H. Ohunuma, Effects of properties of fly ash on fluidity paste, Cement Science Concrete Technology 55 (2001) 163–169.
[24] V.S. Ramachandran, Concrete Admixtures Handbook, Properties, Science and Technology, Noyes Publications, Park Ridge, NJ, 1995.
[25] M. Sonebi, Applications of statistical models in proportioning medium strength self-compacting concrete, ACI Materials Journal 101 (5) (2004) 339–346.
[26] C.F. Ferraris, K.H Obla, R. Hill, The influence of mineral admixtures on the rheology of cement paste and concrete, Cement and Concrete Research 31 (2) (2001) 245–255.
[27] G. Polya, G. Szego, Isoperimertic in quality in mathematical physics, Princeton Uni. Press, Princeton, NJ, 1951.
[28] E. Sakai, S. Hoshimo, Y. Ohba, M. Daimon, The fluidity of cement paste with various types of inorganic powders, Proceedings of 10th Int. Congress on the Chemistry of cement, Sweden, 1997, p. 2ii002 Amarkai AB, Sweden (8 pp.).
[29] C.K. Park, M.H. Noh, T.H. Park, Rheological properties of cementitious materials containing mineral admixtures, Cement and Concrete Research 35 (5) (2005) 842–849.
[30] M.A. Akgerman, M. Zardkoohi, Adsorption of phenolic compounds of fly ash, Journal Chemical Engineering Data 41 (1996) 185–187.
[31] R.J. Flatt, Towards a prediction of superplasticized concrete rheology, Materials and Structures 37 (269) (2004) 289–300.