Rheological Characterization of Cement-based Materials Pastes Containing Diutan Gum and Limestone Powder

M. Sonebi
Queen's University Belfast, Belfast, Northern Ireland, UK

Abstract: The aim of this paper is to characterize the effect of the dosages of diutan gum and limestone powder (LSP) on the workability and the rheological behaviour of grouts and compare the results to similar grouts made with ordinary Portland cement and welan gum with 0.40 water-to-cementitious materials ratio (W/CM). The fresh properties of reference grouts made without any viscosity modifying agent (VMA) and with superplasticizer (SP) were compared to those of grouts made with 0.04, 0.06, and 0.08% diutan gum by mass of CM. The effect of replacement of cement by limestone powder at 12%, 29% and 45% (by mass) was also investigated. The results showed that for any given dosage of SP, the increase in the dosages of diutan and welan gum led to an increase in yield stress, apparent and plastic viscosities, and to a reduction of fluidity. For both reference and LSP mixes, diutan gum grouts exhibited a greater yield stress, apparent viscosity and plastic viscosity than welan gum grouts. The apparent viscosity at low shear rate decreases dramatically than that at high shear rate when the dosage of SP increases which attributed to the pseudoplastic characteristics of these mixes containing VMA. The incorporation of LSP resulted in a significant decrease of yield stress and a slight reduction of plastic viscosity.

1. Introduction

VMAs are polymer chains used to enhance the cohesion and stability of cement-based materials. Such VMAs are water-soluble polysaccharides that enhance the water retention capacity of grout [1-7]. The use of VMAs increases the yield stress and plastic viscosity of cement-based grout at constant water-to-cementitious ratio. VMAs are highly effective to control bleeding and segregation as the long-chain molecules of VMA adhere to the periphery of water molecules, thus it adsorb and fix part of mix water which increase the yield stress and plastic viscosity of cement-based grout [1-7]. Molecules in adjacent 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 [2]. Several researchers have related the improvement in rheological properties and the performance of cement-based grout to the addition of VMA and superplasticizer and [1-7]. 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 alignment of polymer chains along the flow lines [1, 2, 8]. The degree of pseudo-plasticity varies for different types of polymer solutions [9].

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 [9] 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 compare to welan gum which had only one rhamnose and one mannose. 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 [10]. 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 [10].

2. Material, proportions and testing procedures

2.1 Materials and mix proportions

Standard CEM I 42.5N Ordinary Portland cement and limestone powder were used to prepare the grouts. The grading of LSP produced from carboniferous limestone of a very high purity was 98% < 45 μm and 25% < 5 μm, and LSP was finer than cement. The relative density of the limestone powder was 2.65.

SP 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 0.8% to 1.56% (by mass of CM). Diutan gum and welan gum were supplied by Kelco-crete which an anionic polysaccharides 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 units. The diutan and welan gums were supplied in a powder gum and were used from 0.02% to 0.08% (by mass of CM).

2.2 Testing procedures

All grouts were prepared in a 5-litre planar-action high-shear mixer. The mixing tap water had a temperature of 16 ± 1ºC, which was measured before mixing started. The VMA was mixed with cement and SP was added to the water and mixed together. Finally, all components were mixed for seven minutes from the start of measuring time. The grout temperature following the end of mixing was maintained at 20 ± 2ºC.

The mini-slump test is based on the measurement of the spread of slurry placed into a frustum mould. A PVC plate and a frustum, 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 rheological parameters were evaluated using a co-axial cylinder rheometer. 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 are plunged into a cup which contains 350 ml of sample. The measurement is made in stepwise for 12 speeds of rotor from 0.9 rpm to 600 rpm. The shear stress was taking after 20 sec of rotation at each speed. In this study, the upcurve was chosen for final evaluation for better description of rheological behaviour of the grouts by assuming a polynomial behavior and neglecting the second order value which is insignificant. The polynomial law modified Bingham model [8] ensures a better fit than the traditional linear (Bingham model).

3. Test results and discussion

3.1 Comparison of the variation of apparent viscosity of diutan and welan gums with OPC mix (100% C)

Fig. 1 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 1.4% (by mass of CM), and mix without VMA of 100% C mix (made only with OPC). The curves 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 almost Newtonian. 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. Reduction in the viscosity of 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 the intertwined chains dislodge, 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.
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 [10]. It may be attributed to higher water retention of diutan gum. These results confirm some results obtained on water solutions [11]. The higher weight molecular of VMA is the higher water retention will be obtained [12]. 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.

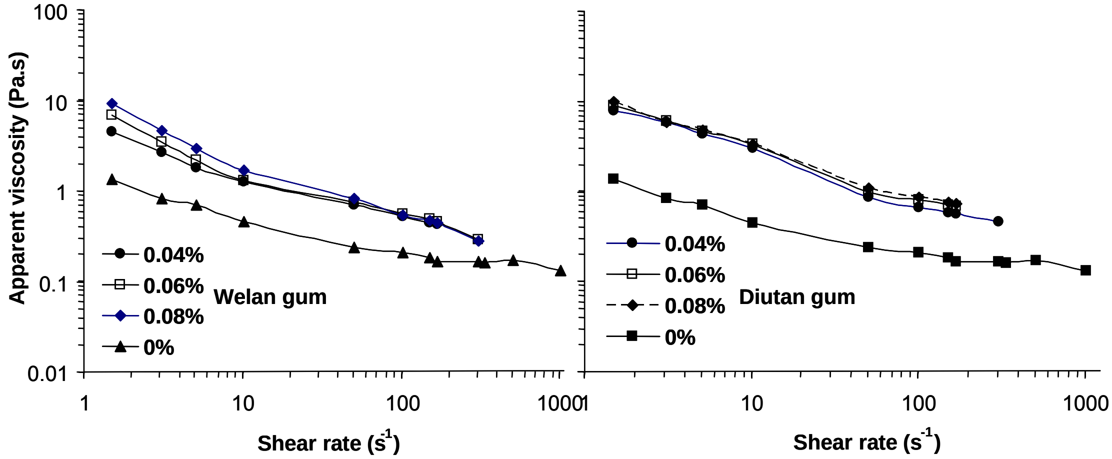

Fig. 1. Comparison of variations in apparent viscosity vs. shear rate of welan gum and diutan gum grouts at different % of VMA (100% C, SP = 1.4%

3.2 Effect of diutan gum, welan gum and SP on fluidity of OPC mix

Fig. 2 presents the variation of the results of mini-slump of the grouts made with only OPC (100% C mix), and diutan gum and welan gum vs. the dosage of SP. Three dosages of 0.04%, 0.06% and 0.08% VMA were tested. As expected, the increase in the dosage of SP resulted in an increase of mini-slump for similar dosage of VMA and the increase of VMA led to a reduction in mini-slump. For 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 and welan gum at concentration of 0.04% resulted in a reduction of mini-slump from 123 mm to 90 mm and to 83 mm, respectively.

The increase of dosage of SP was more significant from 0.3% to 0.8% for 100% C mix without VMA, and the mini-slump was similar between 0.8% and 1.2% (121 mm vs. 126 mm) which indicated the saturation point was reached. 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 increase from 0.8% to 1%, 1% to 1.3%, and 1.4% to 1.5%, respectively. For grouts with diutan gum, similar consistency was observed for mix made with 0.06 % of diutan gum and 1.3% and 1.4% 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 grout 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.

Fig. 2 indicated that with lower SP dosage, the grout 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 [11].

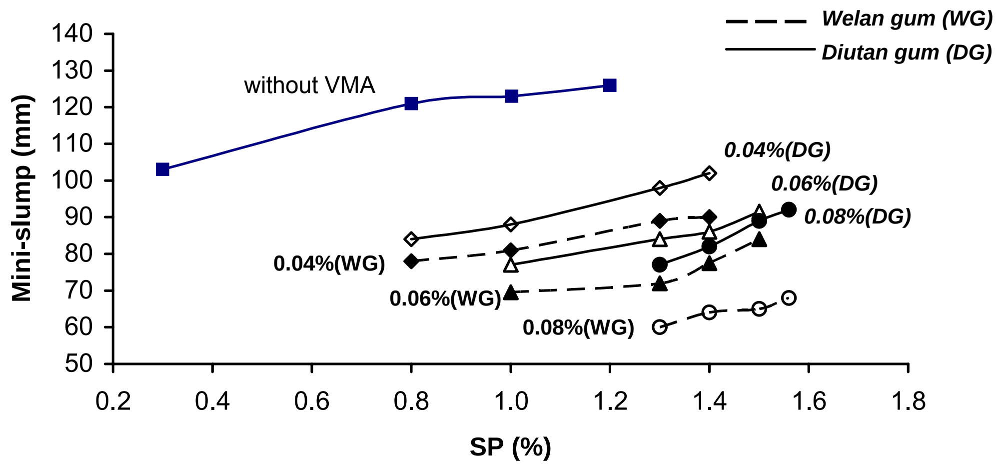

Fig. 2. Variations of mini-slump vs. SP for diutan and welan gum (grouts made with 100%C and W/CM = 0.40)

3.3 Variation of apparent viscosity at low shear rate of 100% C mix

The effect 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 dosages of diutan gum and welan gum is shown in Fig. 3. Adding 0.04% of diutan gum or welan for both dosages of 0.8% and 1% of SP resulted in an increase in the apparent viscosity at low shear rate compared to similar 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 pseudoplastic behaviour in the presence of VMAs compared to similar grouts without any VMAs is believed to the polymer chains of VMAs 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 and 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 0.8% 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 it is believed to the long-side chain of diutan gum resulted in greater entanglement and intertwining.

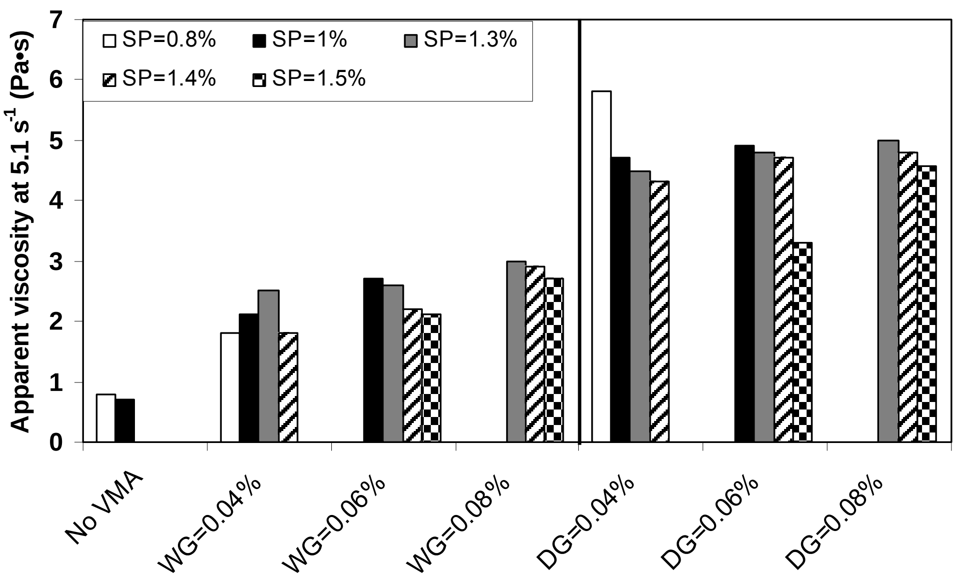

Fig. 3. Variations of apparent viscosity at 5.1 s^{-1} vs. diutan and welan gums and SP (100% C and W/CM = 0.40)

3.4 Comparison of yield stress and plastic viscosity between diutan gum and welan gum of control mix (100% C)

Figs. 4 and 5 present the yield stress 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 dosage of SP ranged between 0.8% to 1.5%, respectively. For any given dosage of diutan gum or welan gum, the increase in the dosage of SP resulted in a reduction of yield stress and plastic viscosity. Similarly for no VMA grout, the increase in dosage of SP led to a reduction in yield stress and plastic viscosity. For any given dosage of SP, the introduction of VMA (diutan gum or welan gum) resulted in significant increase in yield stress and plastic viscosity. For example, for grout containing 1.4% 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 stress 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 dosage of 0.8%, 1% and 1.3% of SP resulted in an increase of 4.9 times, 8.6 times and 9.4 times in yield stress, 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 0.8% and 1% SP to no VMA grout resulted in an increase in plastic viscosity of 270% and 250%, respectively, and 200% and 160% in case of adding welan gum at the same dosage. At 0.04% of VMAs, it appears that the yield stress and plastic viscosity reduced significantly when the dosage of SP increased from 0.8% 1.3%, and up to this dosage, the yield stress and viscosity decreased slightly.

The comparison between the results of yield stress 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. It can be attributed to the diutan's molecular weight and high pseudo-plasticity [11] and water retention. The increase of molecular weight led to improvement of water retention [12]. Thus, to achieve a similar yield stress and plastic viscosity, diutan gum required lower dosage than welan gum.

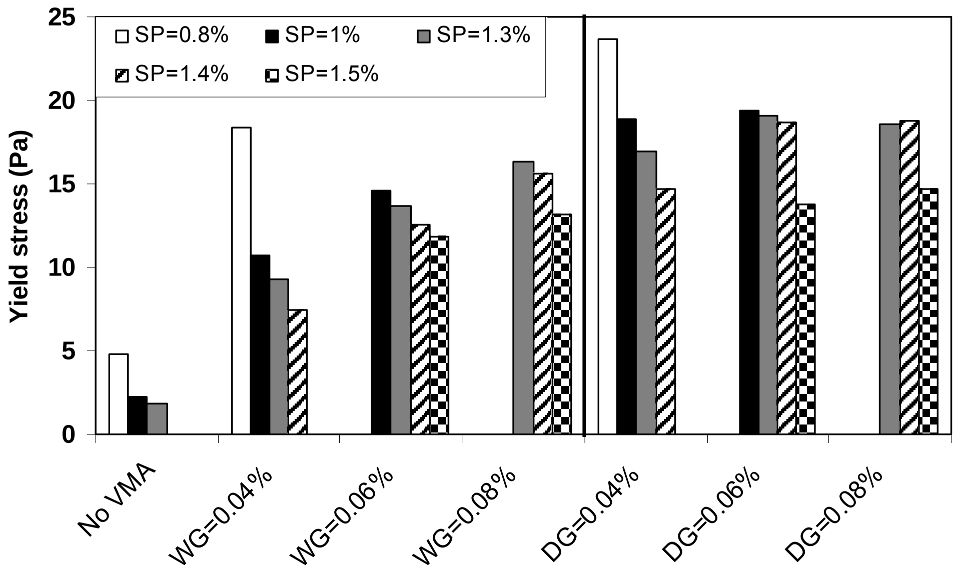

Fig. 4. Variations of yield stress with dosages of SP and diutan and welan gums (100% C, W/CM = 0.40)

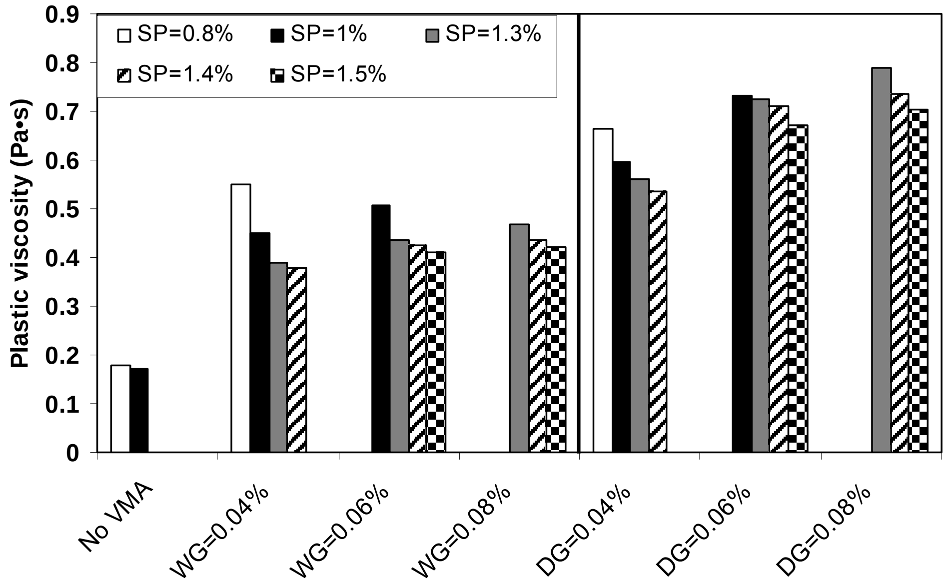

Fig. 5. Variations of plastic viscosity with dosages of SP and diutan and welan gum (100% C, W/CM = 0.40)

3.5 Effect of limestone powder on rheological parameters of grouts made with diutan gum and welan gum

The mini-slump values of no-VMA grouts increased when the dosages of LSP and SP increased. For grouts made with diutan gum and welam gum, the mini-slump results varied between 78 and 112 mm, and 83 to 134 mm, respectively. In general, the replacement of welan gum by diutan gum for all replacement of LSP mixes resulted in reduction of fluidity from 5 to 31% (increase of yield stress). The results of yield stress and plastic viscosity for diutan gum and welan gum grouts with different percentage of LSP are compared in Figs. 6 and 7, respectively. For example, for the grout made with 0.04% of welan gum and 1% SP, the replacement of cement by 12% LSP resulted in a reduction of yield stress from 10.7 Pa to 7.3 Pa, and from 9.3 Pa to 6.8 Pa with 29% LSP and 1.3% of SP compared to reference mix. With 45% LSP, the reduction of yield stress was from 7.5 Pa to 3.3 Pa using 1.4% of SP. However, the incorporation of LSP for grouts using diutan gum resulted in slight increase or/decrease of yield stress depending of the percentage of LSP. For example, the grouts made with 0.06% of diutan gum and 1.4% SP, using 29% of LSP led to an increase of yield stress from 18.7 Pa to 20 Pa, and in case of 45% LSP with 1.5% SP, the yield stress decreased from 18.8 Pa to 16.4 Pa. This can be attributed to the packing effect or packing density of paste related to the shape and particle size distribution and the percentage of LSP which influenced the fluidity (yield stress) [13].

The results from Figures 6 and 7 show that the incorporation of 12% LSP, 29% LSP and 45% LSP led to a decrease of the plastic viscosity compared to similar grouts made with 100% C for any given combination of VMA-SP. For example with grout made with 12% LSP, 0.04% diutan gum and 1% SP, the plastic viscosity was 0.46 Pa·s compared to 0.60 Pa·s for grout made only with cement, and in case of welan gum, the incorporation of 12% LSP resulted in a slight reduction of plastic viscosity from 0.60 Pa·s to 0.56 Pa·s. These results confirm the data reported by the authors [14] which for given W/CM, SP and welan gum dosages, the partial replacement of cement by LSP in grout or mortar resulted in an improvement of workability and a reduction of yield stress and plastic viscosity.

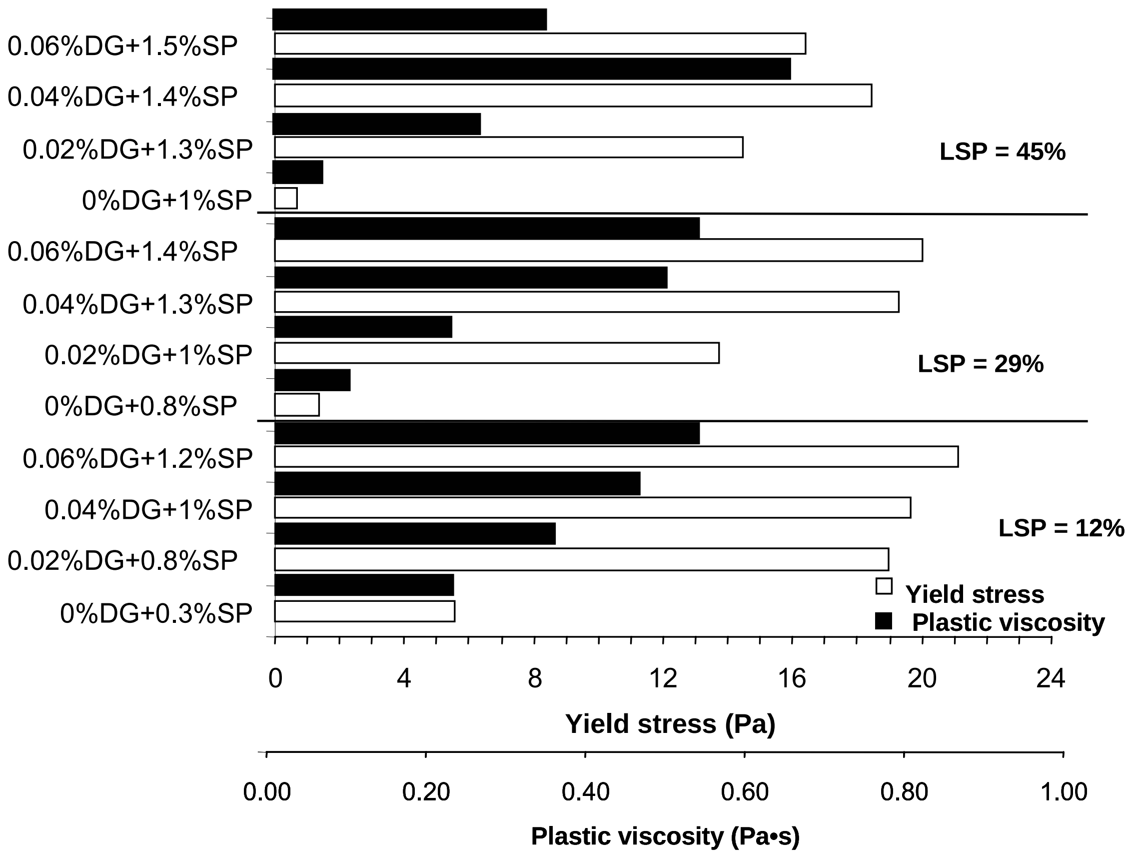

Fig. 6. Variations of yield stress and plastic viscosity with dosages of LSP, SP and diutan gum (W/CM = 0.40)

For all replacements of cement by LSP, the results showed that the diutan gum grouts exhibited high yield stress than welan gum for any given combination of VMA and SP. For dosage of 0.04% of VMA, using diutan gum increase the yield stress up to 2.8 times than the grout containing similar dosage of welan gum and SP. The increase of the yield stress of the grouts containing diutan gum was more important for high replacement of cement by LSP (45%) compared to the grouts made with welan gum. For example, for grout made with 45% LSP and 0.04% of VMA, adding diutan gum resulted in 5.6 times increase in yield stress compared to similar grout made with welan gum and in 2.8 times increase with 29% LSP mix. In general, the use of diutan gum resulted in an increase of plastic viscosity compared to welan gum grouts particularly with 29 % and 45% LSP replacement expected for 0.02% diutan gum and 1% SP. With 12 % LSP, the comparison of plastic viscosity of diuan gum grout to welan gum resulted in an increase of the viscosity only for mix with 0.06%. Further experiments may be required to determine the exact limit of the replacement of LSP which contribute to enhancing the particle distribution of the powder skeleton, thus reducing interparticle frictions and ensuring a better packing density.

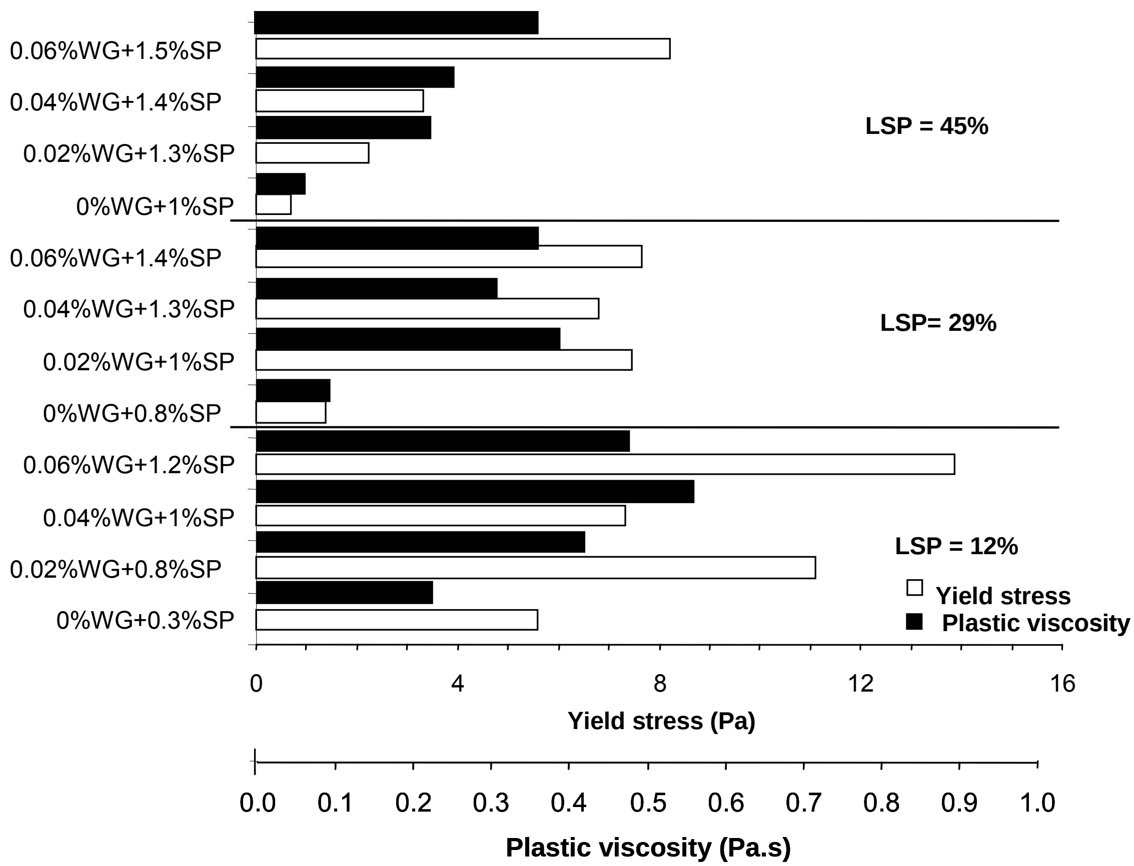

Fig. 7. Variations of yield stress and plastic viscosity with dosages of LSP, SP and welan gum (W/CM = 0.40)

4. Conclusions

Based on the results presented in this paper, the following conclusions appear to be warranted:

- Adding diutan gum and welan gum led to an increase in the pseudoplastic behaviour and the shear thinning increased with their dosages compared to the reference grout without VMA which can be attributed to the entangle of chains polymers and the 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 similar dosage of SP, increasing the dosage of diutan from or welan gum 0.02% to 0.08% resulted in a major a reduction in fluidity, and vice versa, for any given dosages of both VMAs, 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 believed to the long-side chain of diutan gum leading to greater entanglement and intertwining.
- Grouts made with diutan gum had higher yield stress 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.
- For any given dosages of diutan gum or welan gum and fixed dosage of SP, the incorporation of LSP resulted in a reduction in yield stress and plastic viscosity. This reduction can be attributed to better packing density of the system and reducing interparticle frictions [15].
- For all replacements of cement by LSP, the results showed that the diutan gum grouts exhibited high yield stresses than welan gum for any given combination of VMA and SP.

References

[1] 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.
[2] 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.
[3] V.A., Ghio, P.J.M, Monteiro,.L.A., Demsetz, The rheology of fresh cement paste containing polysaccharide gums, Cement & Concrete Research 24(2) (1994) 243-249.

[4] M., Sonebi, M., A., Tamimi, P.J.M., Bartos, Application of factorial models to predict the effect of anti-washout admixture, superplasticizer and cement on slump, flow time and washout resistance of underwater concrete, Materials and Structures 33(229) (2000) 317-323..

[6] M., Sonebi, Factorial design modelling of mix proportion parameters of underwater composite cement grouts, Cement Concrete Research 31(11) (2001) 1553-1560.

[7] 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.

[8] 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.

[9] 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.

[10] A., Phyfferoen, C.B., Skaggs, Optimizing the use of welan gum in cementitiuous and gypsum-based systems. In ConChem Proceedings, Verlag für chemische Industrie, H. Ziolkowsky, Augsburg (1997) 193-202.

[11] A., Phyfferoen, H., Monty, B., Skaggs, N., Sakata, S., Yanai, M., Yoshizaki, Evaluation of the biopolymer, Diutan gum, for use in self-compacting concrete. Conference Notes of First North American Conference on the Design and Use of Self-Consolidating Concrete, Ed. Shah, S, Daczko, J., Lingscheit, J., USA, 2002, pp. 141-146.

[12] Pouchez, J., Peschard, A., Crosseau, P., Guyonnet, R., Guilhot, B., Vallée, F, HPMC and HEMC influence on cement hydration, Cement and Concrete Research 36(2) 2006 288-294.

[13] E., Sakai, S., Hoshino, Y., Ohba, M., Daimon, The fluidity of cement paste with various types of inorganic powders, 10th Int. Congress on the Chemistry of cement, Sweden, 1997, 2ii002, 8 pp.

[14] L., Svermova, M., Sonebi, P.J.M., Bartos, Influence of mix proportions on rheology of cement grouts containing limestone powder. *Cement, Concrete and Composites*, 25(7) 2003 737-749.

[15] R.J., Flatt, Towards a prediction of superplasticized concrete rheology. Materials & Structures 37(269) (2004) 289-300.