

## Performance of new viscosity modifying admixtures in enhancing the rheological properties of cement paste

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Viscosity modifying admixtures (VMAs) are water-soluble polymers that increase the viscosity of mixing water and enhance the ability of cement paste to retain its constituents in suspension. The use of VMA along with adequate concentration of high-range water reducer (HRWR) can ensure high deformability and adequate workability leading to better resistance to segregation of such a concrete. Commonly used VMA in cement-based materials include polysaccharides of microbial or starch sources, cellulose derivatives and acrylic-based polymers.

Mixture containing VMA exhibits shear-thinning behavior whereby apparent viscosity decreases with the increase in shear rate. Such mixture (paste, mortar or concrete) is typically thixotropic where the viscosity buildup is accelerated due to the association and entanglement of polymer chains of the VMA at a low shear rate that can further inhibit flow and increase viscosity.

The investigation by authors was carried out to evaluate the performance of four different types of new VMAs whose properties are given in the Table: 1 based on various tests of rheological properties, fluidity, segregation and washout resistance of the cement pastes. A series of tests using viscometer to obtain rheological data such as yield stress and apparent and plastic viscosity along with minislump and washout tests were carried out to determine the robust mixture proportions for the cement pastes incorporating various dosages of superplasticizer (SP) and VMA. Rheological properties and consistency of cement paste play an important role in controlling the rheology and consistency of concrete.

Table 1: Chemical and physical properties of VMA

	VMAs				
	A	B	C	D	COM
Total solid(%)	80.7	80.2-81.4	80.4-81.6	82.1	42.5
pH	4.9	4.9	4.8	4.8	7.0
Specific Gravity	1.42	1.42	1.42	1.42	1.21
Viscosity (cP) 26°C	81,000	81,000	54,000	25,000	-
Viscosity (cP) 60°C	2500	2500	1600	1000	-

Four novel polysaccharide-based VMAs in liquid form classified as A-D and a known commercial VMA widely used in Canada and designated in this paper as "COM" were also used to perform a comparative study. The chemical composition of COM is a proprietary secret and it is composed of a combination of SP and VMA. The percentages of VMA and SP were calculated based on total solid content. New VMAs are soluble in water and dispersed homogeneously to create robust mixtures.

### Fluidity tests:

The minislump tests on paste were designed to study the performance of novel form of VMAs. This test could also be used for studying the cement/SP compatibility. The proportions for the cement paste mixes identified as Series 1-4 are summarized in Table 2. The variable parameters in the mixes were VMA and SP contents. Investigations on pastes with COM suggested that the addition of SP was necessary to generate slump flows comparable with those of new VMAs. Even then, higher dosages of COM were necessary in the pastes to generate slump flows comparable with those of new VMAs.

Table 2: Mix design of paste for minislump tests

	VMAs		
	A, B, C or D	COM	Control
W/c	0.45	0.45	0.45
VMA (%C)	0.25	0.25	0
	0.50	0.37	
	0.75	0.62	
SP(%)	0.25	0.25, 0.75	0.25, 0.75
Number of mixes	12	6	2

### Washout tests:

The mix proportions of the cement pastes used to investigate washout mass loss are presented in Table 3. These pastes were used to determine the effect of VMA-SP combination on washout mass loss.

Table 3: Mix design of pastes for washout and rheological tests

	Washout Tests		Rheological Tests
	VMA Type A-D, COM	Control	VMA Type A-D, Com
W/C	0.45	0.45	0.45
VMA (%C)	0.025	0	0.025
	0.050		0.075
	0.075		
SP (%)	0.25, 0.5, 0.75	0.25, 0.5, 0.75	0.25
Number of mixes	45	3	10

## Tests on rheological properties of cement pastes:

The purpose of using VMA in cement-based pastes is to improve the stability (bleeding) and rheological properties (viscosity, cohesion and internal friction or bond) to enhance the penetrability and flow characteristics. Ten paste mixes shown in Table 3 were used. The mixing sequence was similar to that used in minislump test. The rheological measurements of paste were conducted by using a commercially available digital Brookfield viscometer (Model RVDV-II) equipped with disc spindles at normal room temperature of about 22-25°C.

## Test results and discussion

### Fluidity of pastes:

Fig. 2 compares the influence of different types of VMA by showing typical variation of minislump diameter with time for pastes. The fluidity of new VMA pastes is much better than the control mix without VMA and commercial VMA COM. The minislump value (Fig. 2) in VMA pastes ranges between 127 and 132 mm at 0 min compared with 116 mm in control paste (0% VMA). To achieve similar fluidity at a particular dosage of SP (0.25% in Fig. 2), the paste needed much higher commercial VMA COM (about 0.37% compared with only 0.05% of new VMAs in Fig. 2). A number of trial paste mixes using different dosages of COM were tested to verify this conclusion. The minislump value also decreases with the increase of time. The minislump value decreases from a range of 127-132 mm to a range of 93-98 mm in new VMA pastes, from 130 to 82 mm in COM paste and from 118 to 65 mm in control paste (Fig. 2) within 2 h. This clearly indicates a better fluidity retaining capacity for pastes with the combinations of new VMA-SP than the COM-VMA and the control. The requirement of lower dosages to achieve satisfactory fluidity and better fluidity retaining capacity with time can be very useful in developing a satisfactory and cost-effective SCC with new VMAs. Fig. 3 shows the influence of dosages of Type a VMA and time on the fluidity of the paste. The slump value increases with the increase of dosages of VMA in the mixes. Similar phenomena were also observed in pastes with other new VMAs. All VMAs (with Type A marginally better) prove to be quite effective in all the paste mixes and shows better results compared with commercial VMA COM.

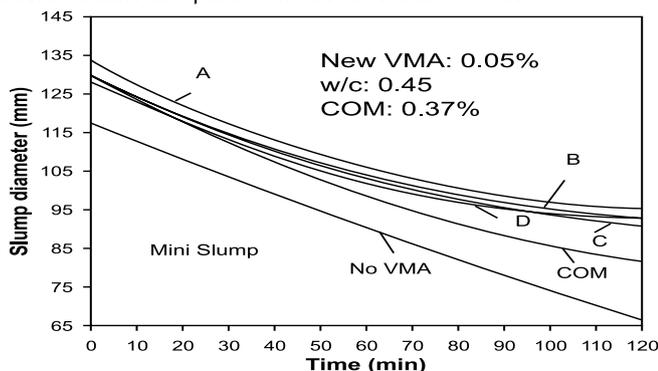


Figure 2 : Effect of type of VMA on the slump of paste (SP=0.25%)

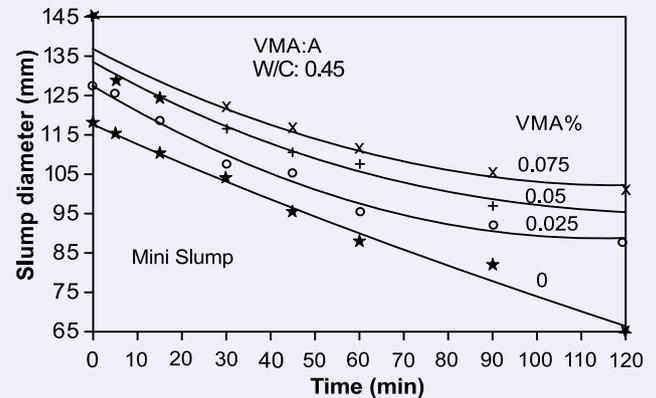


Figure 3 : Effect of VMA content on the slump diameter of paste (SP=0.25%)

### Washout resistance of pastes

Typical washout resistances of paste with VMAs A and B and COM are compared with those of control paste without VMA in Fig. 4. For similar dosages of VMA and SP, washout resistances of new VMAs A and B are found to be better than the commercial COM and control pastes. Washout mass losses were higher in COM pastes (ranges between 12.6% and 14.9%) compared with VMA Types A (ranges between 6.7% and 12.4%) and B (ranges between 7.5% and 13%) pastes. The washout resistance of the control paste was similar to that of COM pastes. Improvement in washout resistance was not observed in pastes with COM compared with control pastes for the SP-VMA combinations of dosages used in this study. VMA Types A and B pastes are found to have similar washout resistances. Similar behavior was also observed in pastes with VMAs C and D. These results are similar to those obtained by Khayat and Yahia in their investigation on the combination of Welan gum-HRWR. Washout resistance improves with increasing concentration of VMA coupled with a greater content of SP to maintain the desired fluidity. Therefore, by adjusting the combination of VMA-SP, a washout-resistant paste with adequate fluidity can be obtained. The increase in the dosage of SP in paste disperses the cement grains and increases the amount of free water in the system. The higher SP dosage may be the cause for no improvement in washout resistance of pastes with COM compared with control paste. As COM is a combination of SP and VMA, the actual SP content in the COM paste is higher than the pastes with new VMA. This leads to the higher washout mass loss in pastes with COM (Fig. 3). The combined addition of SP and VMA can improve both fluidity and washout resistance. The improvement in washout resistance is due to the enhancement in the degree of water retention by the VMA, whereby some of the free water made by the addition of SP can be physically adsorbed by hydrogen bonding onto polymer molecules of the VMA. Furthermore, some of the VMA polymer becomes adsorbed onto cement grains along with the imbibed water, resulting in further retention of suspended cement particles. The use of VMA increases the viscosity of the paste, which reduces the rate of sedimentation of cement grains, thus resulting in highly stable paste even at elevated fluidity levels.

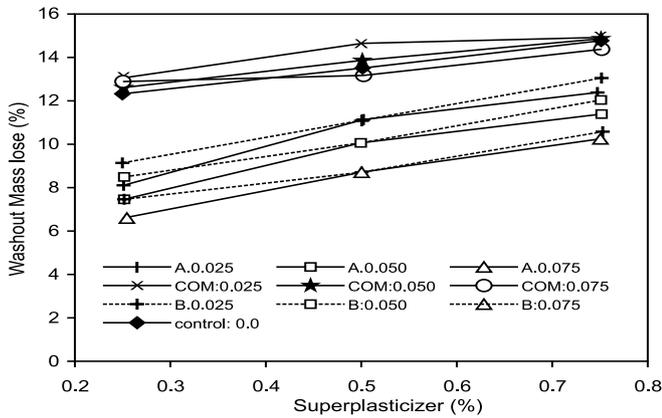


Figure 4 : Washout mass loss of paste

## Rheological properties of pastes

The variation of apparent viscosities with shear rate for pastes with 0.025% and 0.075% of various VMAs at 15 and 30 min is shown in Fig. 5 and Fig. 6. Apparent viscosity decreases with the increase of shear rate. The apparent viscosities of pastes with Types A and B VMA are found to be higher than those of the other VMAs including commercial COM. The apparent viscosity is also increased with the increase of the dosages of VMA from 0.025% to 0.075% as can be seen from the typical graphs shown in Fig. 7 and Fig. 8 for Types A and B VMA. For any given concentration of SP (0.25% in the current study), the increase in VMA content should increase the viscosity at both high and low shear rates, and this was observed in the study (Fig. 7 and Fig. 8).

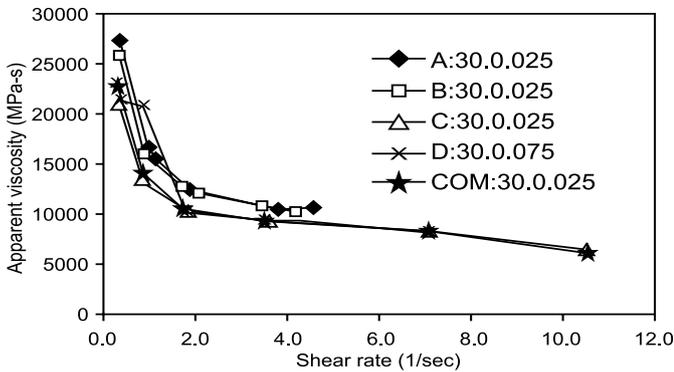


Figure 5 : Variation of apparent viscosity with types of VMA 1

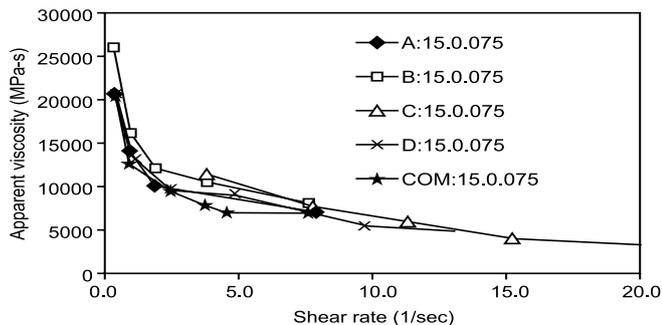


Figure 6 : Variation of apparent viscosity with types of VMA

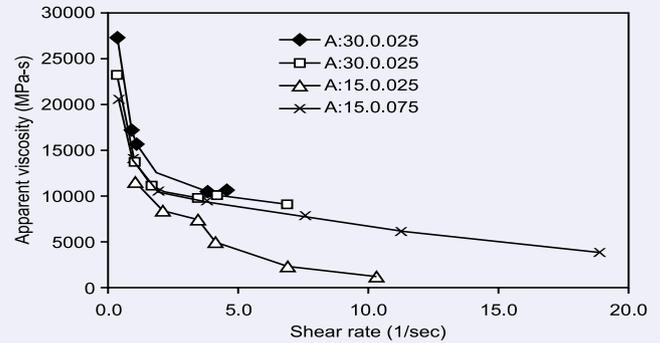


Fig. 7 : Variation of apparent viscosity with time and dosages of VMA

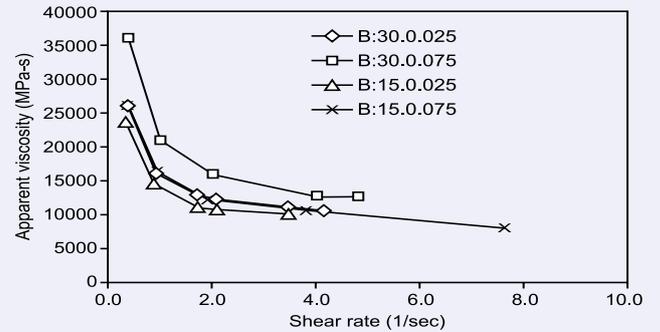


Fig. 8. Variation of apparent viscosity with time and dosages of VMA

The apparent viscosity of paste with 0.025% of Type A VMA is increased from 1500 MPa s at 10 s<sup>-1</sup> to 11,500 MPa s at 1.5 s<sup>-1</sup> compared with 7000 MPa s at 10 s<sup>-1</sup> and 20,500 MPa s at 1.5 s<sup>-1</sup> in paste with 0.075% Type A VMA (Fig. 7). Similar behavior is also observed in pastes with Type B VMA (Fig. 8).

This can be attributed to the fact that the degree of water retention and the free water needed to lubricate the paste increases with the dosage of VMA that acts on the aqueous phase. The addition of VMA also increases the degree of pseudo plasticity or shear thinning of cement paste regardless of the concentration of SP. Pastes with VMA exhibit high apparent viscosities at low shear rates and significantly lower viscosities at greater shear rates. For the same dosage of SP, the use of VMA results in a greater apparent viscosity at low shear rate than at high shear rate (Fig. 5, Fig. 6, Fig. 7 and Fig. 8).

The increased pseudo plastic response in the presence of VMA is believed to be because the polymer chains of the VMA entangle or associate, resulting in an increase in apparent viscosity, especially at low shear rate. With the increase in shear rate, the entangled chains dislodge and align in the direction of flow, thus decreasing the resistance of the grout to undergo deformation. The apparent viscosity is then decreased with an obvious improvement in flowability at high shear rate regimes.

The effect of the increase in the concentration of VMA on viscosity depends on the shear rate. For a given concentration of SP, the increase in the dosage of VMA is more effective in increasing viscosity at low shear rate than that at high shear rate (Fig. 5 and Fig. 6).

Fig. 9 compares the yield stress of pastes with different dosages and types of VMA. The yield stress is decreased with the increase of dosages of VMA from 0.025% to 0.075%. The yield stress, viscosity and apparent viscosity values are affected by the combination of dosages of VMA and SP. It is then important to find out the combinations of dosages of VMA and SP to secure a stable paste with required fluidity and rheological properties. This can be achieved by testing trial mixes with various combinations of dosages of SP and VMA as illustrated in this study.

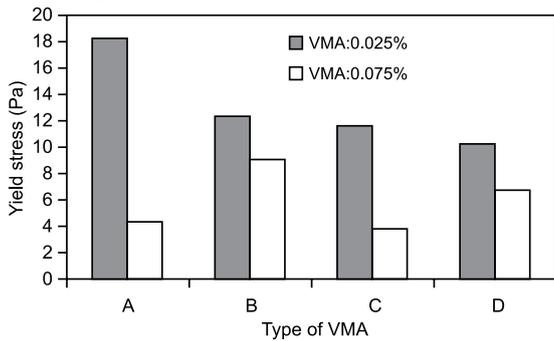


Figure 9 : Variation of yield stress with VMA concentration

Fig. 10 shows a typical variation of viscosity of paste with time (elapsed between mixing and testing) for various types of VMA. Viscosity is found to increase with the increase of elapsed time. This can be attributed to the hydration of cement with time that made the paste stiffer as time progresses. This also indicates somehow that the new VMAs are not inhibitors for the cement hydration.

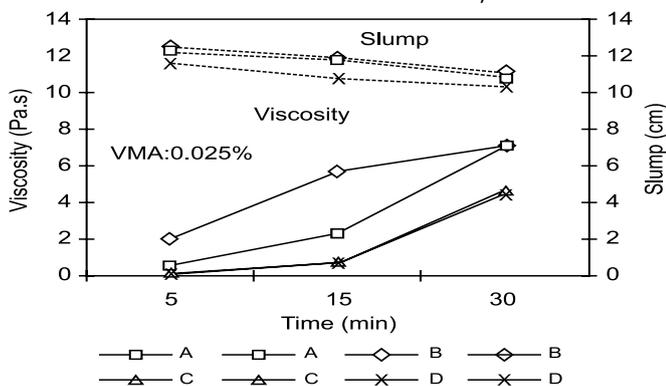


Figure 10 : Viscosity and slump as a function of time and types and dosages of VMA.

The performance of Types A and B VMA is found to be better than the other VMAs for similar dosages of VMA and SP used in this study.

Figure 10 shows a typical variation of viscosity and slump diameter with time. The viscosity increases and the slump value decreases with time. It can be seen that an increase in the viscosity of the paste reduces the flowability. The increases in Types A and B VMA content from 0.025% to 0.075% can increase the viscosity in wider range than the other VMAs (Fig. 7 and Fig. 8). This justifies the suitability of Types A and B VMA and the need of finding an optimum dosage that can develop adequate viscosity to ensure an optimum flowability.

## Conclusions

The performance of four different novel VMA designated as Types A-D compared with a commercial VMA designated as "COM" was investigated. The influence of various dosages and types of VMA in addition to the dosages of SP on fluidity, viscosity, yield stress and washout resistance of cement pastes made with a W/C of 0.45 was studied. Based on the results presented in this paper, the following conclusions can be derived:

1. Minislump value increases with the increase of dosages of VMA from 0.025% to 0.075% for a fixed dosage of SP. Minislump value decreases with the increase of elapsed time between mixing and testing, somehow indicating that the hydration of the cement pastes is not inhibited. Based on investigation, all new VMAs prove to be quite effective (with Type A marginally better) in enhancing the consistency of all the paste mixes, showing better flowability compared with commercial VMA COM.

2. The apparent viscosity of the cement paste is increased with the increase of dosages of VMA from 0.025% to 0.075%. The viscosity of Types A and B VMA is found to be higher than other new VMAs and commercial COM particularly at low shear rate of up to  $5 \text{ s}^{-1}$ . Viscosity of the pastes also increases with the increase of elapsed time between mixing of paste and testing. Based on viscosity data, Types A and B VMAs are found to be more efficient than other new VMAs and would provide better rheological properties.

3. The washout resistance is enhanced by the increase in VMA dosage and reduction in SP content. However, with a proper use of VMA-SP combination, highly flowable yet washout-resistant mixtures can be secured. Washout resistance of Type A, B, C or D VMA is found to be higher than that of commercial VMA COM for similar dosages of VMA-SP combination.

4. The minislump test results correlate roughly with the yield stress of the cement paste even if there is a scatter of data. General trend shows a decrease in yield stress of the paste with the increase in slump. This suggests that a correlation between rheological properties and consistency of paste can be achieved with sufficient test data.

5. A correlation between viscosity and minislump of paste shows a decrease in minislump with the increase in viscosity of the paste.

6. Based on the current investigation, cement pastes with 0.05% of either Type A or Type B VMA would provide better rheological properties at W/C of 0.45 and SP content of 0.25%.

7. The conclusions reached based on the tests on paste in the selection of type and dosage of new VMA (in this case, VMA Types A or B) could be used in the development of a SCC with satisfactory properties, and research is now focused in that direction. The future research will also validate the prediction of the influence of VMA on SCC rheology based on that on the rheology of cement paste.