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Alkali-activated Ground Granulated Blast-furnace Slag Based Viscosity-modifying Agents

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Abstract

This paper studies the influence of VMAs on the rheological properties of Na_2CO_3 alkali-activated GGBS. Two commercial VMAs - PEO as a superplasticizer and EDTMP - were combined and mixed with the binder at different water to binder ratio (w/b = 0.35; 0.40; 0.45 and 0.50). The PEO dosage used was 0.3%, and EDTMP was 0.1% and 0.3%. The diameter of spread, viscosity and viscoelastic properties were investigated through a series of experiments. Results showed that, at high w/b, the workability of fresh paste increased with increasing EDTMP content in the binder. Moreover, EDTMP has decreased the viscosity when mixed at high fraction with PEO, while achieving a high-water reduction. Also, in the linearity region at SAOS, the elastic modulus exhibited stronger microstructure network of the system when lower EDTMP fraction was used at low w/b. The presence of PEO superplasticizer did not decrease the viscosity of the paste, while the EDTMP agent had a major effect on the superplasticizer efficiency at low w/b.

Keywords

Viscosity modifying agents, Fresh state properties, Rheology, Viscoelastic properties, Workability

Abbreviations

AAMs: Alkali-activated materials; EDTMP: Ethylene-diamino-tetra-methylen-phosphonic acid; G´: Elastic modulus; GGBS: Ground granulated blast-furnace slag; LVE: Linear viscoelastic; PCE: Polycarboxylate ether; PEO: Polyethylene oxide; SAOS: Small amplitude oscillatory shear; SEQ: Sequion D30; SUP: Supla P161; VMAs: Viscosity-modifying agents; w/b: Water/binder.

Introduction

Nowadays the cement industry is subjected to the short-term constraint to achieve a good workability necessary for the placement of the fresh concrete. The widespread use of admixtures makes it possible to formulate concretes with targeted workability and water reduction [1, 2]. Superplasticizers have demonstrated their fluidity efficiency towards cement binders. They have shown many advantages such as high-water reduction, high workability retention as well as low concentration is required [3, 4]. However, it is agreed that those admixtures are less efficient in AAMs [5-7]. AAMs are sustainable materials mostly made from industrial by-products to replace Portland cement because of their advantages such as low cost, high strength, good durability, and very low CO_2 emissions [8-11]. These materials can be made by mixing alkaline solution with a reactive solid aluminosilicate precursor such as fly ash, metakaolin, slags and other precursors [11-14]. However, the large-scale application of AAMs progresses gradually.

One of the limitations of the engineering application is the fresh-state properties of AAMs. When the alkali activator is added to the reactive aluminosilicate, dissolution of the precursor and the speedy formation of primary phases make the alkali activation mechanism more complex [15].

The fresh-state properties of Portland cement concrete can be modified and controlled by adding viscosity modifying agents such as superplasticizers. These admixtures can decline the water to cement ratio, promote targeted workability and retard initial setting time. Superplasticizers usually are adsorbed on the surface of cement particles, providing electrostatic repulsion forces and deflocculating flocs leading to the dispersion of cement particles. Hence, the workability of the fresh binder is improved [16]. However, the processing and functioning mechanism of superplasticizers towards AAMs are still difficult to understand and the need for more robust admixtures to meet desirable workability and mechanical performance are required.

Some studies highlighted the influence of VMAs on the fresh and hardened properties of GGBS blended cement. Gee et al. [17] have revealed the dominance of the chemical structure of PCE superplasticizers on the flowability and the strength performance of GGBS and fly ash blended cement. It was stated that an optimal charge density of VMAs can exhibit better conditions for electrostatic forces and steric hindrance in preventing flocculation and agglomeration of blended cement particles. In cementitious systems, the adsorption of VMAs onto the surfaces of the particles has significance for improving workability [18]. However, the quantitative and qualitative addition of VMAs to cementitious systems cannot be standardized due to differences in chemical structure and functional group interactions.

In this context, the purpose of this study is to try two different commercial VMAs with defined fractions and mixed with sodium carbonate alkali-activated GGBS. This work aims to examine the influence of VMAs, PEO as a superplasticizer and EDTMP, on the fresh properties of Na_2CO_3 alkali-activated GGBS at different w/b. The effect of the combined VMAs on the fresh-state properties of alkali-activated GGBS was investigated by the mini-slump test and the rheological measurements.

Materials and Method

Materials

The precursor used for this study includes GGBS was obtained from ECOCEM (France) with a median size distribution d_{50} = 11.37 µm and the chemical composition is reported in table 1. The mineralogical composition of GGBS was obtained with an X'Pert Pro diffractometer (Malvern-Panalytical) equipped with a Co anode X-ray source (40 kV, 40 mA) and an X'Celerator detector. The obtained XRD diffractogram (Figure 1) shows an entirely amorphous composition of GGBS.

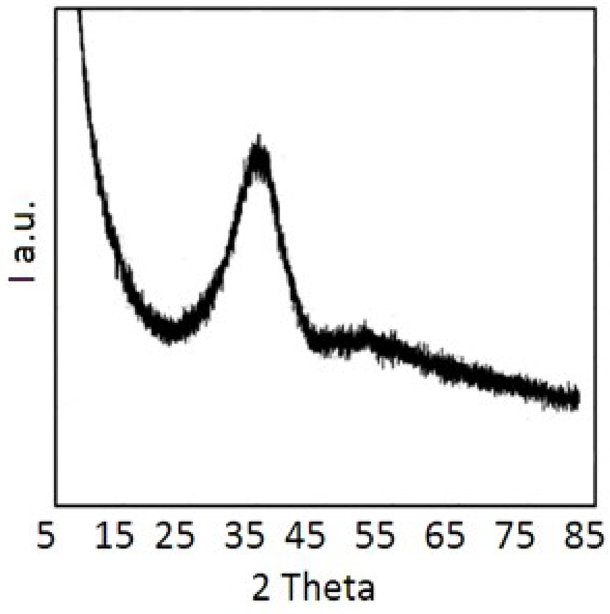

Figure 1: XRD diffractogram of GGBS.

The binder was prepared as one-part alkali-activated material by mixing GGBS with equimolar fractions of Na_2CO_3 and $Ca(OH)_2$ (91.5:5.0:5.3 wt.%) [19].

Two commercial VMAs were used: Supla P161 and Sequion D30 from Bozzetto S.p.A. (Italy). Supla P161 is a dispersing agent - superplasticizer with high yield for cement binders, its chemical composition is phosphonic acid PEO. Sequion D30 is not a plasticizer but a sequestering agent for detergent applications, its chemical composition is EDTMP. Both materials are very soluble in water. The technical data sheets are available on the manufacturers' website [20]. The molecular structures of these additives are illustrated in figure 2, and table 2 summarizes some characteristics of the two additives.

According to the development of such additives, they are classified into two categories:

- The first, Supla P161, contains a set of polymers with a more marked action. They are new generation polyphosphonic superplasticizers blended with PCE based superplasticizers characterized by carboxylic functional groups capable of modifying the hydration of the cement phases. These compounds allow the reduction of water content to be added to the mixtures to reach levels of workability without losing mechanical strength.
- The second, Sequion D30, is a sequestering agent for detergent applications often used as a component in many textile wet processing steps to remove metallic ions that interfere with the process.

PEO (SUPLA P161) belongs to the new generation of superplasticizers based on anionic hydrophilic polymers. It is

Table 1: Chemical composition of GGBS.

Na_2O	MgO	Al_2O_3	SiO_2	SO_3	K_2O	CaO	TiO_2	MnO	Fe_2O_3
0.2	7.4	10.7	36.2	1.0	0.5	40.9	0.7	0.3	0.7

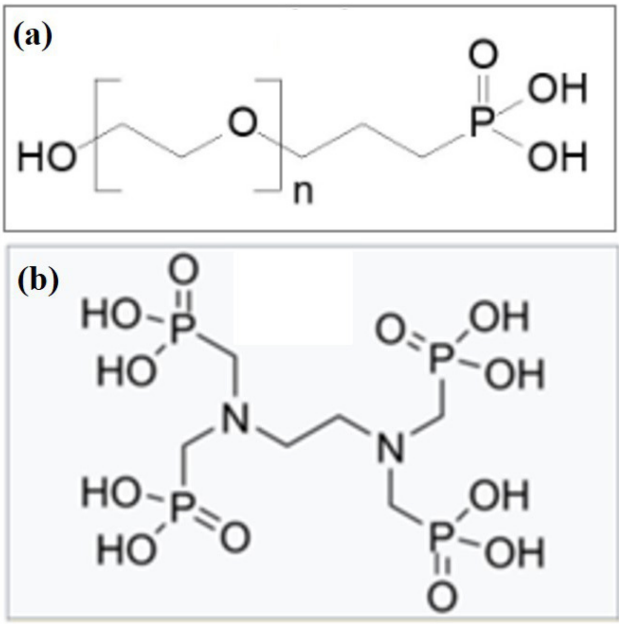

Figure 2: Molecular structure of **(a)** PEO-phosphonic acid and **(b)** EDTMP.

characterized with high dispersant efficiency and high maintenance of cement workability. The recommended dosage of this additive varies from 0.15% to 0.30% by weight on the cement as a basic material [20]. On the other hand, EDTMP (SEQUION D30) can be used as a sequestering agent for metal ions and help to disperse and suspend suspensions. Therefore, the two additives were combined and dispersed in deionized water before mixing with the binder at different w/b of 0.35, 0.40, 0.45 and 0.50. The addition of Supla P161 was a steady dosage of 0.3%, and Sequion D30 was 0.1% and 0.3%, as shown in table 3.

Methodology

The flow table test was used to determine the flowability of the binder based on different prepared admixtures with w/b of 0.5. The freshly mixed binder was placed inside the cone, and then the cone was lifted gently. Immediately, the spreading diameter was measured.

A new fresh paste was mixed in an IKA ULTRA TURRAX Tube Drive mixer for 3 min according to the target w/b (0.35; 0.40; 0.45 and 0.50). The rheological measurements were performed with a stress-controlled rheometer Anton Paar MCR92 equipped with a plate-plate system at a temperature of 20 ± 1 °C and a gap of 2 mm. The evaporation of water has been avoided thanks to a solvent trap. After pre-shearing at 100 s^{-1} shear rates for 30 s and a structure recovery at low oscillation (shear amplitude 10^{-4}% and frequency 1 Hz) for 120 s, the viscosity curves have been measured with a triangular procedure and logarithmic ramps of shear rates from 10^{-4} s^{-1} to 10^{-1} s^{-1} and back allowing 5 s measuring time per point.

The viscoelastic properties of the unbroken structure were examined by means of a series of SAOS experiments. A logarithmic ramp of shear strain amplitude from 10^{-3}% to 10^{1}% and a constant frequency of 1 Hz was applied to a new freshly paste subjected to the same pre-shear and structure recovery mentioned above. The results can provide significant information on the structural breakage of the system by identifying the critical shear strain and the limit of the LVE response. The findings were interpreted from the evolution of the G´ in response to the sinusoidal load input. The stress dependency of the structure was observed via stress amplitude sweeps at a constant frequency of 1 Hz.

Table 2: Some characteristics of the studied VMAs.

	SUPLA P161	SEQUION D30
Chemical compound	PEO	EDTMP
Density at 20 °C	1.10 g/cm³	1.31 g/cm³
Dry residue wt.	30%	31%
pH	7.0	7.0
Ionic charge	Anionic	Anionic
Appearance	Brown liquid	Yellow liquid

Table 3: Composition of different admixtures based on different VMAs dosages.

Code	Water (wt.%)	SUPLA (wt.%)	SEQUION (wt.%)
Water	100	-	-
0.3SUP/0.1SEQ	99.6	0.3	0.1
0.3SUP/0.3SEQ	99.4	0.3	0.3

Results and Discussion

Mini-slump test

The mini-slump test offers a quick overview of the yielding and workability of the paste. The measurements of the diameter spread are shown in figure 3. At high w/b 0.5, the addition of the admixtures has increased the workability of the fresh paste. The binder with water alone had a diameter of spread around 30 mm, and when the admixture (0.3% Supla) made with low fraction of Sequion (0.1%) the spreading diameter increased to 40 mm. However, by increasing the Sequion fraction (0.3%) in the admixture, the spreading diameter was

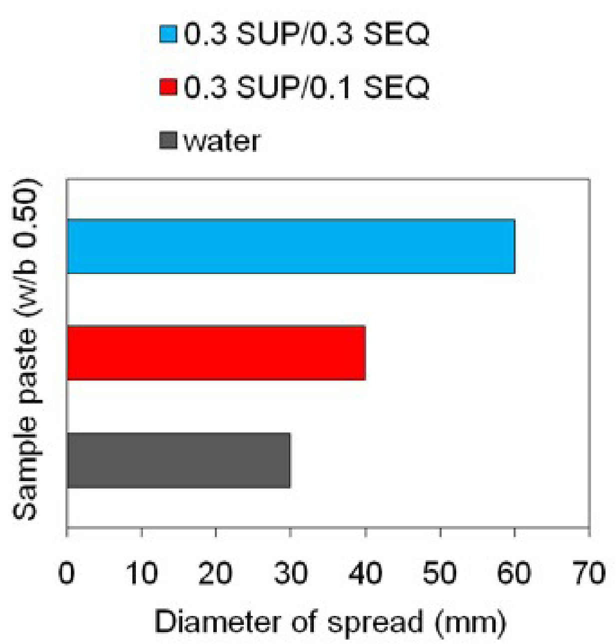

Figure 3: The mini-slump spread diameter for BBGS binder based on the admixtures (w/b 0.5).

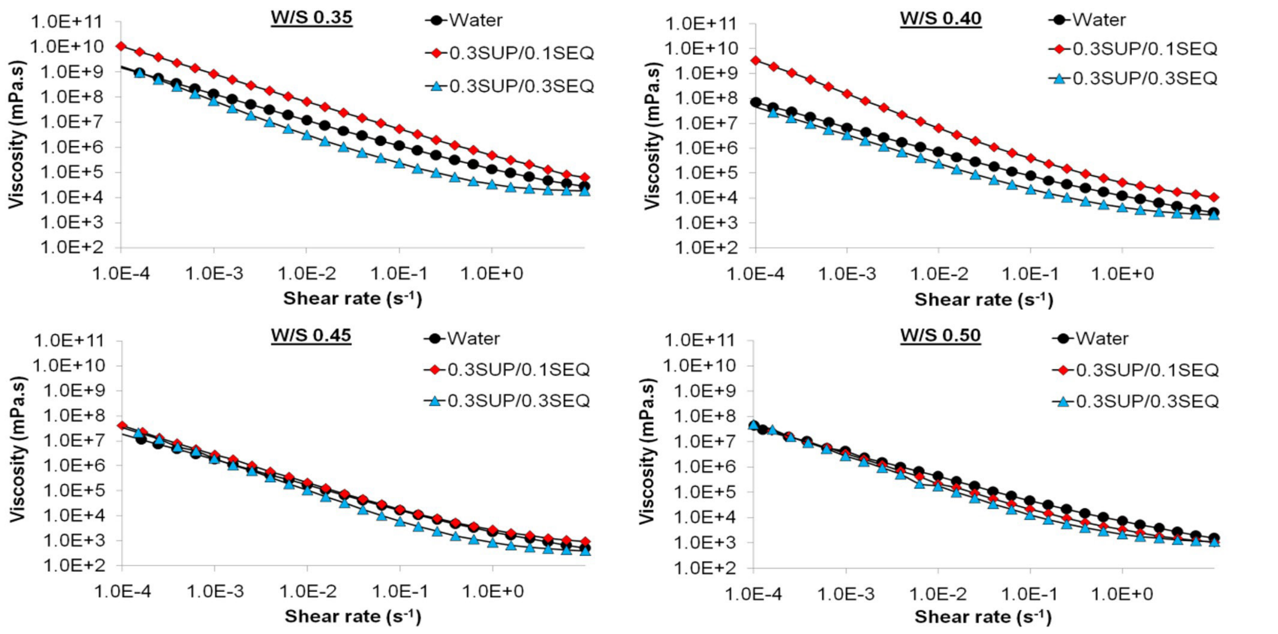

Figure 4: Viscosity curves for the binder with different admixtures at different w/b ratios.

extended to 60 mm. Therefore, increasing the Sequion content has a significant effect on the workability of the binder.

Viscosity curves

Figure 4 shows the viscosity curves for the binder mixed with different admixtures at different w/b ratios. The viscosity curves decrease when shear rates, w/b, and SEQ fraction increase. All samples showed a shear thinning behavior with decreasing viscosity by increasing shear rate. At lower w/b (i.e., 0.35 and 0.40), the admixture 0.3SUP/0.1SEQ has increased the viscosity of the binder. On the other hand, the admixture 0.3SUP/0.3SEQ showed the lowest viscosity at the same w/b ratios. The decrease in viscosity with the increase of shear rate and SEQ fraction explains the relative maintenance of low flow resistance during mixing, pumping, and casting of the fresh paste. Sequion has a much greater effect than Supla and it acts on the interfacial interactions between the binder particles and reduces the frictions between the suspensions. In other words, higher SEQ fraction leads to further dispersion ability of GGBS particles and minimizes agglomeration. The fraction and chemical structure of EDTMP has a significant effect that can act over the GGBS particles by applying electric charges and/or binding of lengthy polymer chains to the particle´s surface, creating a strong repulsion. This repulsion force can be the reason for lowering the viscosity and the G´ (see section below) of the cementitious system.

At higher w/b (i.e., 0.45 and 0.50), the curves showed a decrease in the viscosity by increasing the w/b ratio. This result is due to the increase of the mixed water content in the binder and thus, increasing the dispersion of the suspensions in the medium. Furthermore, at w/b of 0.5, it is worth mentioning that the mixed binders with the admixtures exhibited a slight decrease in the viscosity than the binder mixed with water only, which is linked to the action of the VMAs.

The viscoelastic properties were determined to evaluate the rigidification of blended mixtures and offer more information on the effect of different admixtures on the structure under oscillation mode.

Viscoelastic properties

Amplitude sweep: elastic modulus vs strain

The evolution of the G´ as a function of oscillation strain amplitude for binders with different admixtures at different w/b ratios is reported in figure 5. G´ for all samples at different w/b go steady (LVE region) by increasing deformation, before reaching the limit of LVE region. The decrease of G´ at different LVE regions with the increase of w/b for each binder is due to the decrease of the solid fraction of the suspensions. In other words, the increase of w/b leads to the dilution of the system overcoming the dispersion of the suspensions, thus weaker microstructure network. As can be clearly seen for w/b of 0.35, the elastic modulus for the binder with 0.3SUP/0.1SEQ dramatically increased (G´ = 2.15 x 10^7 Pa) compared to the one with water (G´ = 1.26 x 10^4 Pa) and reduced when 0.3SUP/0.3SEQ admixture is added (G´ = 8.73 x 10^4 Pa). The use of the admixture with lower Sequion content (0.3SUP/0.1SEQ) appears to rigidify the microstructure.

Except for the samples with 0.3SUP/0.1SEQ, all LVE regions showed a yielding – limit of linearity, at a critical strain less than 10^{-2}%. For the sample with 0.3SUP/0.1SEQ, the critical strain is shifted to higher values. This finding is clearly described in the following section. The different behavior of the binder with 0.3SUP/0.1SEQ may be assigned to the stiffening effect due to Supla (PEO). It has been shown that PEO superplasticizers have no effectiveness toward alkali-activated slags [21, 22].

Amplitude sweep: elastic modulus vs stress

Figure 6 shows the evolution of the elastic modulus as

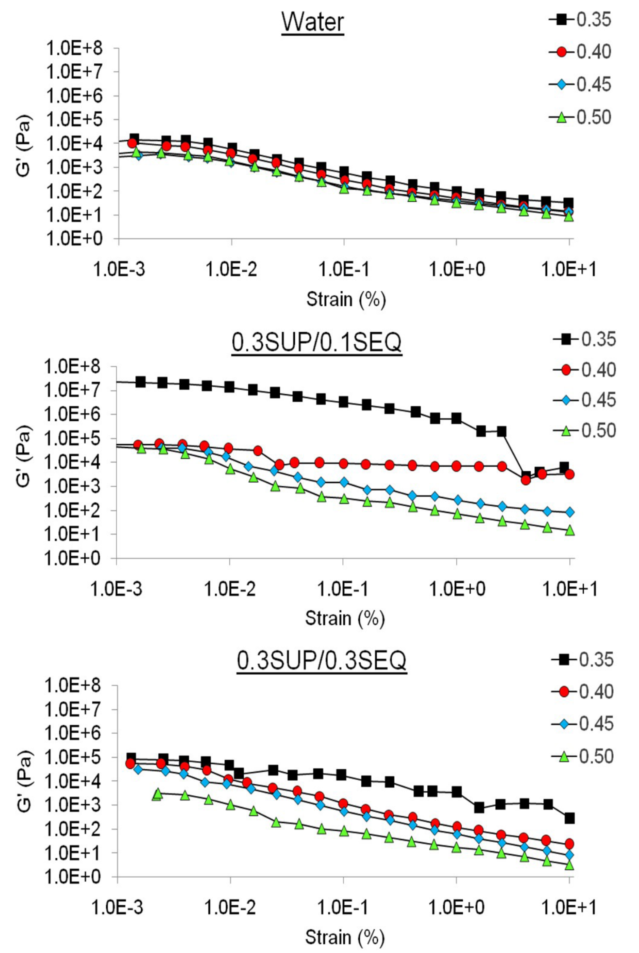

Figure 5: Elastic modulus (G´) vs oscillation strain amplitude for binders with different admixtures at different w/b ratios.

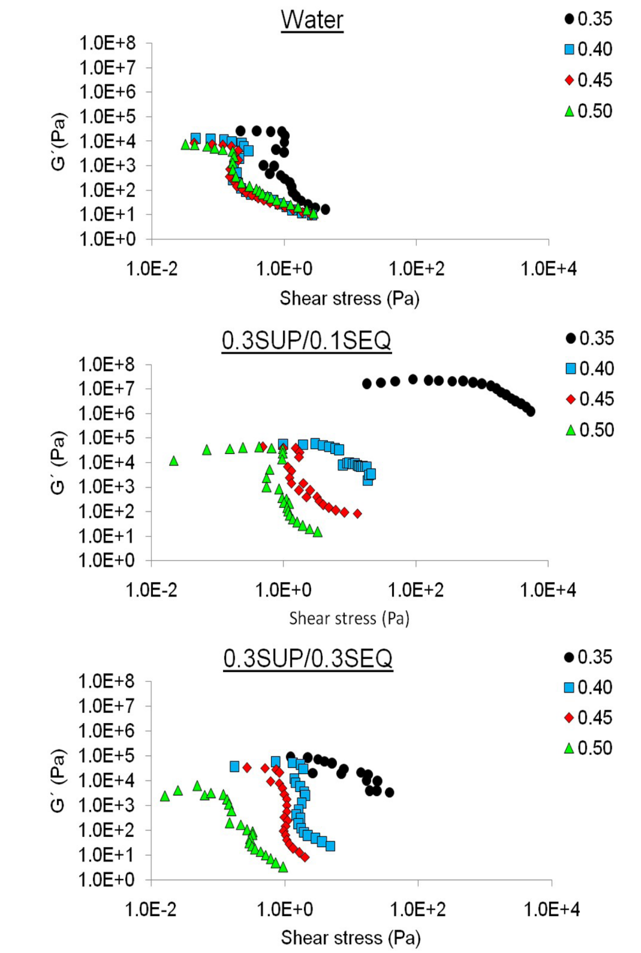

Figure 6: Elastic modulus (G´) vs oscillation stress amplitude for binders with different admixtures at different w/b ratios.

a function of stress amplitude for the binders with different admixtures at different w/b ratios. As can be seen, all samples showed a linear plateau followed by a drastic decrease with increasing stress. The limit of linearity is associated with the critical stress when the binder starts to yield. Samples with water showed critical stress values almost in the same range (≤1 Pa). However, the sample with 0.3SUP/0.1SEQ revealed higher critical stress values (~10^3 Pa). Besides, G´ at the LVE region for the same sample with w/b of 0.35 is dramatically increased to 1.84 x 10^7 Pa. This suggests that the admixture 0.3SUP/0.1SEQ has increased the rigidity of the binder structure. When 0.3SUP/0.3SEQ admixture is used, the critical stress and the corresponding G´ were reduced by increasing the SEQ fraction.

Conclusion

The workability of Na_2CO_3 alkali-activated GGBS can be improved by adding the VMAs in which it is grown by increasing the SEQ fraction. The tested flow spread at w/b of 0.5 resulted in the increase of the diameter of spread by adding different VMA admixtures to the GGBS mix. Higher SEQ fraction showed higher diameter of spread. However, these findings cannot be considered for lower w/b ratios. Higher w/b of 0.5 leads to fluidifying the fresh paste. Nevertheless, we cannot distinguish the effect of the VMAs on the microstructure network of the system because of the higher particle dispersion due to the higher mixing water. The rheological measurements have elucidated the behavior of the VMA admixtures on the fresh paste. The rheological properties such as viscosity and G´ were defined on fresh pastes with various w/b and VMAs fractions. According to the experimental findings, viscosity decreases when shear rates, w/b, and SEQ fraction increase. In general, as w/b and SEQ fraction grow, the elastic modulus decreases. Variation of SEQ (EDTMP) fraction has a significant influence on the rheological properties of alkali-activated GGBS. SEQ can be considered as a fluidifier and acts on the interfacial interactions between the GGBS particles. However, their action occurs at higher fraction (3 wt.% SEQ) when it is mixed with SUP (PEO). This latter has limited factor of dispersing ability in alkali-activated GGBS. PEOs are basic inorganic substances which have the purpose of fluidifying the fresh paste when they are added to cement binders. This type of superplasticizer is however less effective when mixed with alkali-activated materials. Since this work is focused on the rheological behavior, it is important to understand the types of VMAs, their chemical characteristics and the mechanisms of action in alkali-activated materials to guarantee workability and fresh properties before mixing, casting or pumping.

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Conflict of Interest

None.

References

1. Björnström J, Chandra S. 2003. Effect of superplasticizers on the rheological properties of cements. *Mater Struct* 36: 685-692. https://doi.org/10.1007/BF02479503
2. Puertas F, Santos H, Palacios M, Martínez-Ramírez S. 2005. Polycarboxylate superplasticiser admixtures: effect on hydration, microstructure and rheological behaviour in cement pastes. *Adv Cem Res* 17(2): 77-89. https://doi.org/10.1680/adcr.2005.17.2.77
3. Liu J, Yu C, Shu X, Ran Q, Yang Y. 2019. Recent advance of chemical admixtures in concrete. *Cem Concr Res* 124: 105834. https://doi.org/10.1016/j.cemconres.2019.105834
4. Sha S, Wang M, Shi C, Xiao Y. 2020. Influence of the structures of polycarboxylate superplasticizer on its performance in cement-based materials-a review. *Constr Build Mater* 233: 117257. https://doi.org/10.1016/j.conbuildmat.2019.117257
5. Palacios M, Puertas F. 2005. Effect of superplasticizer and shrinkage-reducing admixtures on alkali-activated slag pastes and mortars. *Cem Concr Res* 35(7): 1358-1367. https://doi.org/10.1016/j.cemconres.2004.10.014
6. Palacios M, Houst YF, Bowen P, Puertas F. 2009. Adsorption of superplasticizer admixtures on alkali-activated slag pastes. *Cem Concr Res* 39(8): 670-677. https://doi.org/10.1016/j.cemconres.2009.05.005
7. Puertas F, González-Fonteboa B, González-Taboada I, Alonso MDM, Torres-Carrasco M, et al. 2018. Alkali-activated slag concrete: fresh and hardened behaviour. *Cem Concr Compos* 85: 22-31. https://doi.org/10.1016/j.cemconcomp.2017.10.003
8. Shi C. 2003. Corrosion resistance of alkali-activated slag cement. *Adv Cem Res* 15(2): 77-81. https://doi.org/10.1680/adcr.2003.15.2.77
9. Madhuri G, Rao SK. 2018. Performance of alkali-activated slag concrete against sulphuric acid attack. *Asian J Civil Eng* 19: 451-461. https://doi.org/10.1007/s42107-018-0028-1
10. Aula M, Haapakangas J, Heikkila A, Iljana M, Kemppainen A, et al. 2012. Some environmental aspects of BF, EAF and BOF. Oulu: University of Oulu, Faculty of Technology, Department of Process and Environmental Engineering.
11. Shi C, Roy D, Krivenko P. 2003. Alkali-activated Cements and Concretes. CRC press, London.
12. Yang T, Yao X, Zhang Z, Wang H. 2012. Mechanical property and structure of alkali-activated fly ash and slag blends. *J Sustain Cem Based Mater* 1(4): 167-178. https://doi.org/10.1080/21650373.2012.752621
13. Kong DL, Sanjayan JG, Sagoe-Crentsil K. 2007. Comparative performance of geopolymers made with metakaolin and fly ash after exposure to elevated temperatures. *Cem Concr Res* 37(12): 1583-1589. https://doi.org/10.1016/j.cemconres.2007.08.021
14. Nikravan M, Firdous R, Stephan D. 2023. Life cycle assessment of alkali-activated materials: a systematic literature review. *Low Carbon Mater Green Constr* 1(1): 13. https://doi.org/10.1007/s44242-023-00014-6
15. Palacios M, Gismera S, Alonso MDM, de Lacaillerie JDE, Lothenbach B, et al. 2021. Early reactivity of sodium silicate-activated slag pastes and its impact on rheological properties. *Cem Concr Res* 140: 106302. https://doi.org/10.1016/j.cemconres.2020.106302
16. Sha S, Ma Y, Xiao Y, Xiao Z, Hui W, et al. 2021. Comparative study of PCE superplasticizers with different anchoring groups in low water-to-binder ratio cementitious material. *Constr Build Mater* 312: 125344. https://doi.org/10.1016/j.conbuildmat.2021.125344
17. Ng PG, Cheah CB, Ng EP, Oo CW, Leow KH. 2020. The influence of main and side chain densities of PCE superplasticizer on engineering properties and microstructure development of slag and fly ash ternary blended cement concrete. *Constr Build Mater* 242: 118103. https://doi.org/10.1016/j.conbuildmat.2020.118103
18. Winnefeld F, Becker S, Pakusch J, Götz T. 2007. Effects of the molecular architecture of comb-shaped superplasticizers on their performance in cementitious systems. *Cem Concr Compos* 29(4): 251-262. https://doi.org/10.1016/j.cemconcomp.2006.12.006
19. Ez-zaki H, Riva L, Bellotto M, Valentini L, Garbin E, et al. 2021. Influence of cellulose nanofibrils on the rheology, microstructure and strength of alkali activated ground granulated blast-furnace slag: a comparison with ordinary Portland cement. *Mater Struct* 54: 1-18. https://doi.org/10.1617/s11527-020-01614-5
20. Technical Data Sheets [http://www.bozzetto-group.com] [Accessed September 21, 2023]
21. Lu C, Zhang Z, Shi C, Li N, Jiao D, et al. 2021. Rheology of alkali-activated materials: a review. *Cem Concr Compos* 121: 104061. https://doi.org/10.1016/j.cemconcomp.2021.104061
22. Cheah CB, Tiong LL, Ng EP, Oo CW. 2019. The engineering performance of concrete containing high volume of ground granulated blast furnace slag and pulverized fly ash with polycarboxylate-based superplasticizer. *Constr Build Mater* 202: 909-921. https://doi.org/10.1016/j.conbuildmat.2019.01.075