

Evaluation of Polycarboxylate Ethers that can Mitigate the Detrimental Effects of Clay Content of Sand on Concrete Workability and Strength

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Clay tolerant superplasticizers can enable the use of low quality, clay containing aggregates and also alleviate the need for washing clay containing sand used in concrete fabrication, thereby promoting sustainable concrete production. Previous studies considered specific aspects of polycarboxylic ether (PCE) superplasticizer molecular design which influence their clay tolerance. In this study, the effect of a combination of various aspects of PCE molecular design on their clay tolerance was investigated. The aim of the study was to determine PCE structural differences that are more tolerant to clay contamination of sands used in concrete making. The objective was to evaluate the effectiveness of six recently developed proprietary PCEs with varying molecular designs in concretes fabricated with clay containing sands sampled from three South African quarries. The PCEs were evaluated by their ability to retain good workability and compressive strength in concretes fabricated using a standard laboratory clay free sand and high clay content sands from the three quarries. Workability was evaluated through slump flow tests and the compressive strength was evaluated through 24 h and 28 d compressive strength tests. Incorporation of an acrylic based PCE with low side chain graft ratio and long side chain lengths in the concretes resulted in a higher initial slump flow of at least 200 mm at 5 min, indicating relatively good workability, which however deteriorated rapidly in concretes made with the clay contaminated sands. Unexpectedly, the 28 d compressive strengths of concretes fabricated with higher clay content sands were found to be comparable to the compressive strengths of concretes made with the clay free standard sand when three of the PCEs were used. High compressive strength in the concretes fabricated with the sand containing the most clay was accomplished by incorporating a PCE with very high molecular weights, very long side chain lengths and a low graft ratio.

1. Introduction

Superplasticizers are polymeric dispersants that reduce cement inter-particle forces and disperse cement particles evenly in concrete mixes (Halim et al., 2017). Their use enables fresh concrete to be more workable using less water. They can enhance concrete setting time, its pore structure and compressive strength (Zheng, 2018). Superplasticizers enable the formulation of concrete with a reduced environmental impact.

Polycarboxylic ethers (PCEs) are superplasticizers that have been used extensively as admixtures for concrete since their introduction in the 1980s. They are co-polymers with a comb-like structures. PCEs are composed of anionic backbones mostly polymerized from monomers that contain carboxylic groups, and non-ionic polyethylene oxide side (PEO) chains attached to the backbone through ester, amide or ether linkages (Flatt and Schober, 2012).

The dispersion of cement particles by PCEs is achieved through adsorption of the PCEs onto the cement surfaces (Flatt and Schober, 2012). Studies have shown that steric repulsion caused by the non-adsorbing side chains of the PCEs was the dominant dispersion mechanism of PCEs during cement hydration (Uchikawa et al., 1997).

Poor incompatibility between PCEs and clays has been widely reported. Clay minerals can be present in aggregates used in concrete mixes as impurities. In the study by Ng and Plank (2012) it was observed that

PCEs adsorbed chemically and physically on to clays more than 100 times than on cement. The competitive adsorption of PCEs between clays and cement has been identified as the cause for incompatibility (Gao et al., 2018). The effectiveness of PCEs have been shown to drastically deteriorate in the presence of the clay mineral montmorillonite (MMT) compared to other types of clay minerals (Lei and Plank, 2014). The presence of MMT in aggregates drastically reduces the dispersing ability of PCEs and slump retention of fresh concrete. Several approaches have been suggested to mitigate the detrimental effects of clay on the effectiveness of PCEs, including molecular design of new PCEs with modified chemical structures (Liu et al., 2017).

Studies have been conducted on some specific aspects of PCE molecular design which influence their clay tolerance. Lei and Plank (2012) synthesized clay tolerant PCEs that had alternative side chains to the conventional PEO side chains which are known to induce the high clay affinity of PCEs. They also proposed varying the lengths of the alternative side chains as a viable solution. Ng and Plank (2012) studied the MMT clay tolerance of methacrylic acid based PCEs with varying graft ratios. To the best of the authors' knowledge, the effect of a combination of various aspects of PCE molecular design such as the PCE backbone, grafting ratio, length of side chains and molecular weight on their clay tolerance and the resulting workability and mechanical properties of the concrete in which they are applied is yet to be reported on.

The aim of this study was to determine PCE structural differences that are more tolerant to clay contamination of sands used in concrete making, with respect to slump retention ability (workability) and mechanical properties of concrete. The objective was to evaluate the effectiveness of six recently developed PCEs with varying molecular design in concretes fabricated with clay containing sands sampled from three quarries in South Africa. The sand clay content was quantified using the methylene blue test. X-ray diffraction was used to confirm the presence of MMT. The PCEs were assessed by their effect on concrete workability and compressive strength.

2. Theory

The enhancement of the workability of cementitious systems by PCEs is dependent upon their effective adsorption on cement particles and their ability to function as dispersants through electrostatic and steric repulsion effects. Winnefeld et al. (2007) showed that the adsorption of PCEs on onto cement particles is promoted by higher PCE charge densities. The PCE charge density increases with the number of free carboxylic groups, which in turn increases with a decrease in side chain length and side chain density. It is also known that in the aqueous phase at the high pH of cementitious systems, acrylic acid based PCEs will develop a higher charge density compared to methacrylic based PCEs (Flatt and Schober, 2012).

The effectiveness of PCEs in dispersing cement particles is hampered by their preferential adsorption onto clay particles. This adsorption was shown to occur through PEO side chain intercalation into interlayer space of the aluminosilicate layers and electrostatic attraction of the PCEs on to clay surface (Ng and Plank, 2012). These phenomena are dependent on the PCE dosage added, amount of PEO side chains available for intercalation, and anionic charge density of the PCE which promotes surface adsorption through electrostatic attraction (Ng and Plank, 2012). A delicate balance of PCE molecular properties could possibly mitigate the clay intolerance that can arise from clay contaminated aggregates.

3. Materials and methods

3.1 Materials

The experimental work in this study involved the preliminary evaluation of the clay tolerance of six recently developed PCEs through their effectiveness on workability and mechanical properties of concretes fabricated with clay contaminated sands from three different quarries. These PCEs were based on either acrylic or methacrylic backbones and they had varying graft ratios, side chains length and molecular weights. As discussed in the theory section, these properties influence the effectiveness of the PCEs.

The cement used in the study was masonry cement supplied by AfriSam, Roodepoort, South Africa with code MC CEM I 42.5N. The six PCEs evaluated in this study were supplied by Chryso (Johannesburg, South Africa). Their characteristics are given in Table 1. The PCEs are differentiated by their molecular structures, their estimated ability to either give slump retention or water reduction (Table 1). Clay free sand (clean standard laboratory sand) and clay containing sand from three different quarries in South Africa; Kimberly, Vaal and Wadeville was used in the study.

The particle size fraction (0-0.6 mm) of clay free sand (clean standard laboratory sand) was replaced in a micro concrete mix design by clay containing sand from the three different quarries. The particle size fraction 0-0.6 mm is known to contain most of the clay in sand. The clay content of this particle size fraction of the clay containing sands was determined using the methylene blue test. Quantitative X-ray diffraction (XRD) analysis was conducted on the clay containing sands to determine the types of clays from each quarry. The XRD analysis was conducted using a PANalytical Aeris diffractometer with PIXcel detector and fixed slits with Fe filtered Co-

K α radiation using a back loading preparation method. The phases were identified using X'Pert Highscore plus software. The relative phase amounts (weight %) were estimated using the Rietveld method.

Table 1: PCE Characteristics

PCE	Polymerization	Graft ratio	Side chain length	Molecular weight	Water reduction	Slump retention
A1	Acrylic	High	Medium	Medium	Low	Long
A2	Acrylic	Medium	High	Low	Medium	Medium
B3	Acrylic	Low	High	Low to medium	High	Low
B4	Methacrylic	Low	Very high	Very high	Very high	Low
P5	Methacrylic	Very low	Very high	High	Very High	Thixotropic
B6	Methacrylic	Low	Medium	Very low	Medium	Medium

3.2 Micro concrete mix design

Micro concrete was prepared by pre-wetting the sand fractions with particle sizes 0-0.6 mm, 0.6-1.2 mm, 1.2-2.4 mm and 2.4-4.8 mm with a portion of batch water. A mortar mixer was used to mix these components for one minute at low speed using a mortar mixer. The cement portion was added and mixed for one minute at high speed along with batch water. The PCEs were incorporated into micro-concrete mix designs at predetermined dosages of 0.198 % volume of PCE per cementitious weight content in the concrete mix design and mixed for two minutes at high speed. The mini slump flow was measured from this fresh concrete mix.

3.3 Slump flow test

The rheological properties of the micro-concrete design were evaluated using the slump flow test according to the test method ISO –TC71. The slump flow gives an indication of how long the concrete mix will last before slump loss during transportation. It therefore gives a measure of the workability of the concrete. A mini slump cone was placed in the centre of a demarcated circle on a clean, glass surface with a slight damp sheen. The slump cone was filled with fresh concrete and smoothly lifted vertically in one movement. When the concrete stopped flowing, the diameter of the flow circle (slump flow diameter) was measured at two locations to give the slump flow diameter as an average of the two in millimetres. The slump flow was measured at 30 min intervals up to 2 h. The target slump flow was 320 mm.

3.4 Mechanical properties

On completion of the slump flow test, the concrete was used to prepare compressive strength test specimens. Prism moulds were used to form 40x40x160 mm³ compressive strength test specimens. The temperature used for casting was 25 °C. The moulds were placed in a humidity chamber for 24 h. Thereafter, the specimens were demoulded, marked and submerged in a curing water bath set at 23 °C. The strength evaluation was done after aging for 24 h and 28 d. Before each test, the specimens' surfaces were dried with a dry cloth after removing them from the curing bath. The compressive strength test was performed on a King Test Auto 2,000 kN according to the ASTM-EN196 test method. Three specimens were evaluated for each test and the average reported.

4. Results and discussions

4.1 Clay content of the sands

The methylene blue values (MBV) given in Table 2 confirm that that the standard laboratory sand was a fairly clean, clay free sand. Table 2 shows that the sands from the three quarries had MBV of more than 1, therefore they can be classified as very dirty sands. The MMT weight content of the sands determined using quantitative XRD is also given in Table 2. A linear correlation was observed between the MBV and the MMT content.

Table 2: Filler sand methylene blue values and smectite content

Filler sand type	Methylene blue value (MBV), mm	Montmorillonite content, wt.%
Standard sand	0.20	-
Vaal sand	3.00	0.62
Wadeville sand	6.25	1.25
Kimberly sand	7.25	1.79

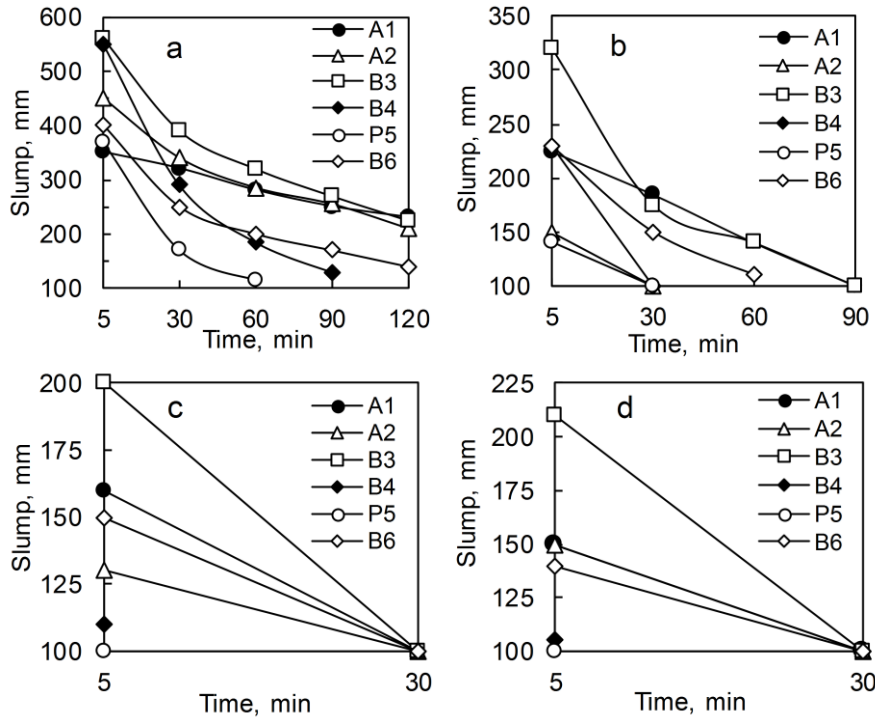


Figure 1: Slump flow of concrete fabricated using (a) Standard laboratory sand, (b) Vaal sand, (c) Wadeville sand and (d) Kimberly sand

4.2 Slump flow

Figure 1 shows that the PCE B3 enabled higher slump retention for a longer period in the concrete fabricated from the standard laboratory sand compared to any of the other PCEs. This PCE B3 also consistently produced higher slump flows at 5 minutes, in concretes fabricated with the clay containing sands, compared to the rest of the PCEs. The PCEs A1 and A2 also maintained relatively high slump flows beyond 30 min in the standard sand, compared to the PCEs B4, P5 and B6. The target slump flow for ready mix concretes is 320 mm. The PCEs A1, A2 and B3 achieved this slump flow when the standard laboratory sand was used for close to 60 min. As the MBV increased, the slump flow deteriorated.

The structure of the best performing PCE with respect to the slump flow, PCE B3, was given in Table 1 as an acrylic based PCE with low graft ratio of the side chains and long side chains.

4.3 Compressive strength

Figure 2 shows that the 24 h compressive strength of the concrete fabricated with the relatively clay free standard sand was higher for all the concrete mixes made with the various PCEs, compared to the compressive strength of the concrete fabricated with the clay containing sands. The variation in the 24 h compressive strength of the concrete fabricated from the standard sand with the different PCEs can be inferred to arise from the different molecular structures of the PCEs. Strength development in concrete is related to the cement hydration reactions (Atarashi et al., 2015). PCEs are known to interfere with the cement hydration reactions and retard strength development, particularly the early stage strength (Atarashi et al., 2015). Incorporation of the PCE B4 in the concrete fabricated with the clay free standard sand resulted in the highest 24 h compressive strength. This suggests that this PCE with a lower graft ratio, long side chains and lower to medium molecular weight had a lower cement hydration retarding effect.

The 24 h compressive strength of the concretes was also observed to decrease with an increase in the MBV. This apparently confirms that the compressive strength decreases with an increase in the clay content, which is in agreement with previous studies (Norvell et al., 2007). The cohesive interaction between clay surface coatings on sand grains is known to be weak electrostatic forces (Fernandes et al., 2007). The deterioration of the compressive strength of the concrete in the presence of clay is thought to be because of the interference of clay particles with the bond between the sand particles and cement paste (Fernandes et al., 2007). Adsorption of the PCEs on the clay surfaces also diminishes the PCEs available to efficiently deflocculate the cement particles in the cement paste. As a result, there is a higher water demand, which deteriorates strength (Alsadey, 2015).

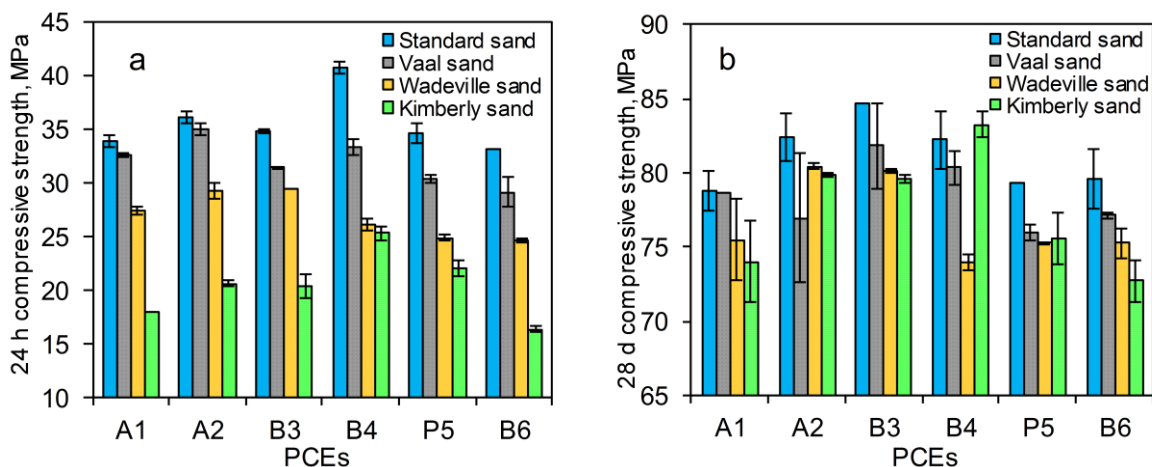


Figure 2: (a) 24 h compressive strength and (b) 28 d compressive strength of concretes fabricated with the various sands and PCEs

Figure 2 also shows the 28 d compressive strength of the concrete fabricated with the standard laboratory sand and sands from the different quarries incorporated with the different PCEs. As expected, the compressive strength of the concretes fabricated from all the sands was higher than the 24 h compressive strength due to the continued hydration of cement. Figure 2 also shows that the 28 d compressive strength of the concrete fabricated using the standard sand was highest, regardless of which PCE was used, with the exception of the concrete which contained the PCE P5. The 28 d compressive strength of the concrete fabricated with the Vaal sand, which had a lower MBV and clay content compared to the sands from the other quarries, had, slightly lower compressive strength compared to the concrete fabricated from the standard laboratory sand. The compressive strength values of this concrete followed the trend exhibited by the concrete fabricated with the standard laboratory sand, with the exception of the concrete with the PCE A2. The decrease in the compressive strength with MBV is not apparent in the 28 d compressive strength.

The highest 28 d compressive strength from the concrete fabricated with the standard sand was observed when the PCE B3 was used. In the concrete fabricated with sand which had the highest MBV and clay content, Kimberly sand, incorporation of the PCE B4 resulted in highest 24 h and 28 d compressive strengths. From Table 1, the PCE B4 differed from the PCE B3 which showed good performance in the clay free sand based concrete. The PCE B3 was acrylic based, with long side chains, high molecular weight and high water reduction ability compared to the methacrylic based PCE B4 that had very high molecular weights, very long side chain lengths and very high water reduction capacity. However, they both had low graft ratios.

It was expected that the 28 d compressive strength of the concretes would vary with the MBV in a similar fashion as the 24 h compressive strength shown in Figure 4, that is, to deteriorate with an increase in clay content, as was observed in previous studies (Norvell et al., 2007). This was not the case as Figure 4 attests. When the PCE B4 was used in the concrete fabricated with the sand with the highest clay content, Kimberly sand, it resulted in 28 d compressive strength comparable to the highest strength obtained with the clay free standard sand. The PCEs A2 and B3, also resulted in a relatively higher compressive strength in the clay contaminated sands, compared to any of the other PCEs.

Besides the dependence of strength development in concrete on the cement hydration reactions, it also strongly depends on porosity of the cement paste (Fardis et al., 1994). The pore structure resulting from the use of superplasticizers in cement pastes and distribution of components in the mix has been observed to impact on the strength developed (Puertas et al., 2005). Although the pore structures of the concretes fabricated in this study using the various PCEs with different molecular structures have not yet been analyzed, it is possible that they influenced the compressive strength. It is also possible that MMT clay contributed to the initial retardation of hydration reactions (hence the initial deterioration of compressive with an increase in MMT clay content at 24 h) but somehow these reactions accelerated at a later stage. This would however be in contradiction with the observations of Atarashi et al. (2015), which showed that MMT clay had no role in cement hydration reactions in the presence of PCE type superplasticizers. It is also possible that, the PCEs which enabled the increase in strength were able to disassemble the flocculated cement particles and release entrapped water, thereby promoting further hydration and resulting in increased compressive strength (Alsadey, 2015).

5. Conclusions

This study evaluated the effectiveness of six recently developed polycarboxylate ether (PCEs) superplasticizers through their ability to retain good workability and compressive strength in concretes fabricated using standard laboratory clay free sand and high clay content sands from three quarries. Although none of the PCEs considered was able to maintain the workability (320 mm slump flow) desirable for ready mix applications over the desired 2 h slump retention window, the study showed that an acrylic acid based PCE with low side chain graft ratio and long side chain lengths can be used to attain high initial slump flows of at least 200 mm in concretes made with clay containing sands. This PCE can be used a sacrificial PCE, in combination with other superplasticizers. This aspect will be the focus of future research work. The early stage 24 h compressive strength of the concretes was shown to be dependent on the clay content. However, unexpectedly, the 28 d compressive strengths of concretes fabricated with higher clay contents were found to be comparable to the compressive strengths of concretes made with the clay free standard sand when three of the PCEs were used. The study showed that a high 28 d compressive strength of close to 85 MPa can be accomplished in a concrete fabricated with the sand containing high clay content by incorporating a methacrylic acid based PCE with a low graft ratio, very high molecular weights and very long side chain lengths. The mechanism by which this unexpected high compressive strength is attained needs to be determined by further studies through calorimetry.

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