



Cape Peninsula
University of Technology

**EFFECT OF POLYCARBOXYLATE SUPERPLASTICISER ON THE ADSORPTION
AND RHEOLOGY OF SELF-COMPACTING CONCRETE PASTE**

by

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ABSTRACT

Self-compacting concrete (SCC) is a concrete which can compact by its own weight without the need of manual intervention. In order to achieve the desired workability without increasing the content of water within self-compacting concrete systems, superplasticisers (SP) are generally used as admixtures and added into the cement systems. These chemical admixtures are adsorbed onto the surface of cement particles and disperse agglomerated particles which release entrapped waters, resulting in an increase in fluidity. These admixtures however react differently depending on cement compositions and can develop compatibility issues with the cement used. It is more rational to investigate the flow behaviour of self-compacting concrete on paste scale since, SP-cement interactions within concrete systems occur normally at paste level.

The aim of this research was to investigate the effectiveness of a modified superplasticiser obtained by blending two different polycarboxylate SPs at different proportions, on the rheology of three CEM II cements with distinct chemical and physical characteristics.

An Anton Paar MCR51 rotational rheometer with roughened parallel plates was used to determine the rheological properties of cement pastes and a mini-slump test was used to determine the cement workability by considering their yield stress developments. The total organic carbon (TOC) approach was used to determine the adsorption of SP on cement particles using the depletion method. The effectiveness of the modified SP products was determined by comparing their adsorption behaviour and induced rheological performances in cement paste systems.

It was found that SPs with greater molecular weight and longer side chains easily adsorb on cement particles, thus improving the repulsion phenomenon within the cement system that in its turn improves the fluidity of the overall systems. It is thus possible to tailor rheological performances of SCC using modified SP based on SPs with different molecular structures. The desired fluidity would therefore be achieved by fine-tuning the proportion of SP with molecular weight and longer side chains within the SP blend.

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NOMENCLATURE

Constants

Symbol	Meaning (units)
A	Calculated absorbance
Area _{ES} ¹⁶⁴⁰	Area of the ester groups of peak 1640 cm ⁻¹
Area _{ET} ¹⁰⁸⁰	Area of the ether groups of peak 1080 cm ⁻¹
A _s	Maximum adsorbed amount of PCE at saturation
b	Thickness of the adsorption layer, in nm
E _b	Electron binding energy, eV
E _k	Photoelectron kinetic energy after the photoelectron has gone through the adsorption layer, eV
F	Orthogonal measurement
G	Gibbs free energy
H	Entropy
hν	Electron energy, eV
I (b)	Photoelectron intensity after it has gone through the adsorption layer
I _o	Initial photoelectron intensity
k	Adsorption equilibrium constant
K	Consistency index, Pa.s ⁿ
M	Main chain/backbone
N ²	Square of the ionic charge of the SP admixture
P	Mean length of the ether side chains
PCE _(Ads)	Concentration of adsorbed PCE
PCE _(Sol)	Concentration of PCE within the solution at adsorption equilibrium
P _o	Baseline, (%)
P _T	Transmittance, (%)
R	Average spread diameter (m)
S	Ethylene oxide side chain
S	Enthalpy
S _{sc}	Surface area (m ²)
SSP	Sulphate sensitivity
T	Temperature, °C
V	Volume (m ³)
X	Units of ethylene oxide per side chain (S)
Y	Repeating trunk chain units with regards to (M)

Greek letters

Symbol	Meaning (units)
τ_y	Shear stress (Pa)
$\dot{\gamma}$	Shear rate (1/s)
λ	A parameter fixed at 0.003, this parameter takes into account the liquid-vapor interfacial energy and the wet angle
μ	Bingham plastic viscosity (Pa.s)
ρ	Density (kg/m ³)
Γ	Relative flow area ratio
τ	Yield stress (Pa)

Terms and concepts

Term	Explanation
C ₂ S	Dicalcium silicate
C ₃ A	Tricalcium aluminate
C ₃ S	Tricalcium silicate
C ₄ AF	Tetracalcium aluminoferrite
Clinker	Product of fusing together clay and limestone as the first stage in the manufacture of Portland cement
Flow curve	A graphical representation of the behaviour of flowing materials in which shear stress is related to shear rate
Flow-ability	Property of fresh concrete, mortar or cement paste describing their ability to flow
Fluidity	The quality of being fluid or free-flowing
Fresh	Refers to cement paste or concrete that has been recently mixed and is still fluid
Hydration	The combination of water with any substance such as lime or minerals, which is responsible for the alteration of minerals in weathering; the formation of hydrated lime; the setting of cement, and so on
Paste	A mixture of cement and water
Rheometer	Device used for the measurement of rheological properties over varied and extended range of conditions

Term	Explanation
SCCP	Self-compacting concrete paste
Setting	The transition from fresh cement paste to hardened cement paste
Shear rate	The rate of change of shear strain with time
Shear stress	The component of stress that causes successive parallel layers of material to move in their own planes relative to each other
Workability	Property of fresh concrete or mortar that determines the ease and homogeneity with which it can be mixed, placed, consolidated and finished
Yield stress	The stress that needs to be overcome to allow the material to flow

CHAPTER ONE

1.1 Background and Motivation

Self-compacting concrete (SCC) is concrete that can compact itself without the need of vibration or techniques such as 'poking'. To achieve this, the cement mixture needs to be fluid enough to be able to flow between steel reinforcement and complex formwork without showing signs of bleeding or segregation whilst compacting itself at the same time. This can be achieved by using a mix which includes admixtures such as superplasticisers (SP) (Kauppi et al., 2005; Li et al., 2020).

Cement paste within SCC is primarily responsible for adhesions between aggregates within a concrete mixture, therefore investigating the rheological properties of the binder on a paste scale (a mixture of cement and water) can provide a better understanding of the effect that these superplasticisers have on SCC.

Polycarboxylate-based (PCE) superplasticisers are one of the admixtures used within the construction industry which have an effect on the rheological properties of self-compacting concrete (SCC) by improving the fluidity of the cement paste through steric hindrance or electrostatic phenomena. SPs enhance the fluidity of concrete mixtures at very low w/c ratios which improves the workability of concrete mixtures at reduced mixing water. This is the reason why polycarboxylate-based SPs are amongst the most preferred admixtures (Chen et al., 2020).

This research investigated the effect of a blended PCE SP on the rheology of three cements with differences in chemical composition. The modified SP which was used for all the experiments consisted of a blend of two different SPs with distinct molecular structure and function: SP-A and SP-B which were blended at ratios (SP-A/ SP-B) of 10%/90%; 30%/70%; 40%/60%; 50%/50%; 60%/40%; and 80%/20%.

SP-A is described as having a high negatively charged polymer with a non-ionic backbone consisting of long thin side chains. This allows it to have a strong affinity towards the surface of the cement particle through electrostatic adhesion.

SP-B is described to have a lower negatively charged polymer with a non-ionic backbone consisting of shorter and thicker side chains. This allows for a slower adhesion to the cement particle.

The effectiveness of these SPs with respect to the workability loss of cementitious materials depends on their rate and degree of adsorption on cement particles within a given mixture. This behaviour has been associated to the type and physiochemical properties of the cement used (Cheah et al., 2020; Prince et al., 2003).

1.2 Research Problem

The effect of modified polycarboxylate-based SPs on the rheological behaviour of fresh self-compacting cement paste (SCCP) is not well known.

1.3 Research Question

Can a modified polycarboxylate-based SP (as a reagent of two different SPs blended at different proportions) improve the rheological properties of cement paste?

1.4 Objectives and Outcomes

The aim of this research was to investigate the effectiveness of a modified SP on the rheology of cement paste. This effectiveness was observed by assessing the yield stress development of corresponding cement pastes. Three different cements were used (with different chemical compositions) and their fresh properties were measured. Next, the adsorption of blended SPs at different proportions on these cements was evaluated. Finally, it was attempted to establish a relationship between the rheological performances and adsorption behaviour of the SP for each cement paste.

The research objectives were as follows:

- To modify two individual SPs by blending them at different proportions to obtain product SPs.
- To determine the rheological parameters of each cement paste with these product SPs.
- To assess the adsorption behaviour of product SPs on each cement paste.

To determine this, the following outcomes were investigated:

- The relationship between the degrees of adsorbed SP and the yield stress development (loss of workability) of each cement paste.
- The impact of the product SP on the yield stress/viscosity of each cement paste.
- The relationship between the degrees of adsorbed SP and the physiochemical properties of each cement paste.

1.5 Significance

This research helps understanding how the blending of polycarboxylate-based admixtures influences the efficiency of the superplasticiser. The finding on blended SP cement interactions at paste scale could possibly be extended to concrete level for industrial use. This can help admixture companies produce more efficient products by blending polycarboxylate SP in order to limit their production costs.

1.6 Delineation

This study did not determine the effects of bleeding and segregation of the cement paste. The focus was to observe on the effect of a blended SP on the rheological behaviour and adsorption of the cement paste.

1.7 Methodology

The experiments were conducted at paste scale using three CEMII 42.5N cements produced at different factories which were plasticised with a blended polycarboxylate SP at optimum dosage. The total organic carbon content was used to calculate the adsorption and the rheological tests were done on an Anton Paar MCR 51 rotational rheometer and a mini-slump cone at the Flow Process and Rheology Centre laboratories of the Cape Peninsula University of Technology.

1.8 Organisation of research

Chapter 2: literature review

This chapter reviews the literature pertaining to SCCP and the effectiveness of the SP admixture to enhance the fluidity of cement paste systems. This chapter also revises factors that influence SP adsorptions and the role of hydration products in the interaction between cement and chemical admixtures.

Chapter 3: Methodology

This chapter presents the methodology used to determine the characteristics of the materials, and introduces the test methods and procedures deployed to solve the research question and meet the objectives.

Chapter 4: results

The data obtained experimentally through the methodology discussed in chapter 3 are presented in this chapter. Both the rheological and the adsorption results are presented in this section.

Chapter 5: Discussion

The results presented in chapter 4 are discussed in detail in this chapter. The rheological and adsorption results are discussed and analysed in order to identify a relationship between the interactions.

Chapter 6: Conclusion

This section summarises the outcomes of this research and presented the conclusions reached and recommendations for further research are proposed.

CHAPTER TWO: LITERATURE REVIEW

2.1 Introduction

The use of high performance concrete with low water/cement ratios has become very popular in the concrete industry. One way of achieving this is to introduce superplasticisers (SPs) to the concrete mixture, although many concerns have been raised with regard to factors that can hinder the performance of these SPs in the mixture. One major example was the compatibility of the chemical composition of cement and the SP admixtures (Prince et al., 2003). The way in which admixtures affect cement can be unpredictable due to many factors (Ferrari et al., 2011).

Workability is the term used to define the ease at which fresh concrete can flow and be handled (Ferrari et al., 2011). Superplasticisers are known to improve the workability of concrete mixtures by increasing the fluidity without increasing the water content. It is this phenomenon which makes SPs the preferred admixture used amongst many viscosity modifying admixtures to produce SCC within the construction industry (Kreppelt et al., 2002; Sun et al., 2020; Zingg et al., 2008a).

High strength concretes can be achieved by reducing water contents in the concrete mixture (Plank et al., 2008a). Modified lignosulphonates (LS) and sulfonated naphthalene formaldehyde (SNF), are the first generation SPs which were used to improve the rheological properties of fresh concrete. Although new superplasticisers are available such as polycarboxylate-type SPs, the first generation SPs are still widely used in industry (Kauppi et al., 2005; Ma et al., 2020; Yousuf et al., 2017). According to Plank et al. (2008a), the polycondensate admixtures which are composed of poly-naphthalene sulfonate (BNS) and poly-melamine sulfonate (PMS), are more efficient than the lignosulfonate SPs.

The new generation of SP used in the industry is the polycarboxylate-based (PC) type which is known to increase the fluidity of a concrete mixture by dispersing agglomerated cement particles, releasing the entrapped water molecules, which results in a more fluid mixture. Polycarboxylate-based SPs are defined by the length and thickness of the backbone and the side-chains which can have different effects on the cement rheology. How these polycarboxylate-based SPs effect the rheology of a concrete mixture when PC admixtures are blended together is not fully understood, which allows for further research (Cheah et al., 2020; Ferrari et al., 2017; Kreppelt et al., 2002).

2.2 Self-compacting concrete

Self-compacting concrete (SCC) is a type of concrete that minimises laborious compacting through “poking” and vibrating of the fresh concrete during placing, by allowing the concrete mixture to compact itself by its own weight (Kauppi et al., 2005). The two essential characteristics of SCC (it should have a yield stress that is low enough to allow it to pass through steel reinforcement; and a viscosity which is able to homogeneously suspend aggregates without presenting signs of segregation or bleeding) can be achieved by introducing superplasticisers within the concrete mix (Zingg et al., 2008b).

Superplasticisers like polycarboxylate-based SP, when added to concrete, disperse the agglomerated cement particles which entrap the water molecules, which allows the concrete mixture to flow without the addition of more water.

2.2.1 Cement composition

In cement chemistry, making use of long chemistry terms has brought forth the need for a shorter cement notation in order to easily identify the minerals and compounds involved (Ma et al., 2014). The cement nomenclature used in cement chemistry is as follows:

- **C**=> CaO
- **S**=> SiO₂
- **A**=> Al₂O₃
- **F**=> Fe₂O₃
- **S**=> SO₃
- **H**=> H₂O
- **N**=> Na₂O

Portland cement is composed of four reactive phases namely:

- **C₃A** => Tricalcium aluminate
- **C₃S**=> Tricalcium silicate
- **C₂S**=> Dicalcium silicate
- **C₄AF**=> Tetracalcium aluminoferrite

How these phases react when hydrated is what makes Portland cement a very complex material (Liu et al., 2015). There are four main mineral phases that cement clinker is composed of: two calcium aluminate phases which are C₃A and C₄AF, and two silicate phases which are known as belite, C₂S, and alite, C₃S. Out of the four main phases, the C₃A and the C₃S (alite) phases were found to be more reactive than the C₄AF and the C₂S (belite) phases because of

their immediate reaction with the water molecules (Kreppelt et al., 2002). The physical appearance of alite is defined as being a pseudo- hexagonal shape with an angular appearance, while belite can be defined as being more rounded with a lamellar structure. These grains (alite and belite) are both embedded within a mixture of C_3A and C_4AF also known as the interstitial phase (Kreppelt et al., 2002). The interstitial phase of a cement particle may contain gypsum, CaO (free lime) and alkali sulfate (Hanehara and Yamada, 1999). The composition of the main phases within Portland clinker are not clearly defined, but are rather modified by the compounds within the solid solution such as potassium and sodium oxides or with minority elements such as Fe^{3+} , Si^{4+} and Mg^{2+} . These minority elements play a role in the polymorphism of the clinker components which has an ultimate effect on the reactivity of the cement (Alonso and Puertas, 2015).

2.2.2 Cement clinker

Portland cement consists of four main minerals, $Ca_3Al_2O_6$, $C_4Al_2Fe_2O_{10}$, Ca_3SiO_5 and Ca_2SiO_4 . For convenient naming of these minerals, they can be further abbreviated to C_3A , C_4AF , C_3S and C_2S (Wesselsky and Jensen, 2009; Yoshioka et al., 2002). These are the four main phases of cement clinker: two calcium aluminate phases which are C_3A and C_4AF , and two calcium silicate phases, alite C_3S , and belite, C_2S (Jolicoeur and Simard, 1998; Kreppelt et al., 2002). The alite (C_3S), which can be depicted as an angular hexagonal shape grain, and belite (C_2S), which takes the form of a more rounded grain, are embedded into the interstitial phase which consist of the aluminate phases, C_3A and C_4AF . Figure 2.1 shows a scanning electron microscope (SEM) image of the alite (dark angular) and belite (light rounded) phases embedded into the interstitial phase (Kreppelt et al., 2002).

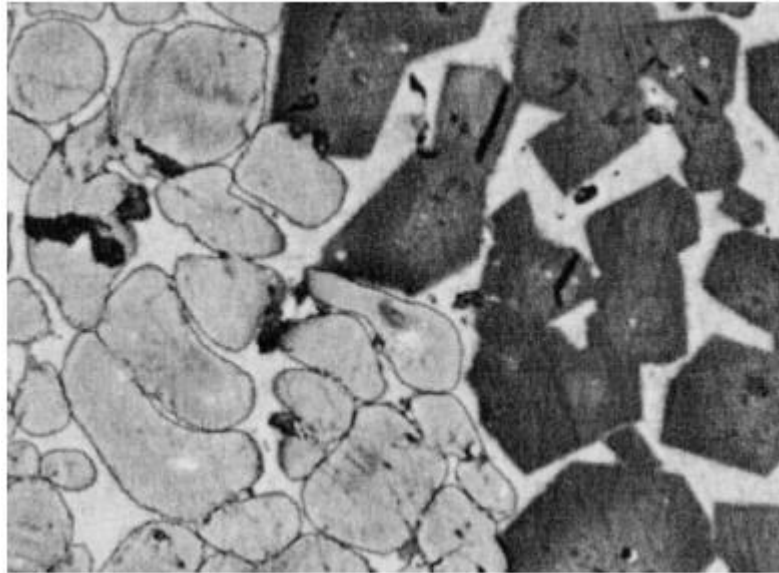


Figure 2.1: Reflected light micrograph of a polished clinker section that depicts prismatic particles known as alite (right of image, dark grey), and round particles known as belite (left of image, grey) which are embedded into the interstitial phase (bright) (Kreppelt et al., 2002)

2.2.3 Cement chemistry and reactions

Cement hydration is a complex chemical and physical process that involves a constant release of heat making it the prime focus of researchers' studies when it comes to understanding the behavior of this complex material (Kong et al., 2016).

The minor phases such as $\text{CaSO}_4 \cdot x\text{H}_2\text{O}$, K_2SO_4 , Na, etc., make Portland cement a multi-component system comprising many inorganic materials. As the mineral phases make contact with water, the relative reactivity process usually follows $\text{C}_3\text{A} > \text{C}_3\text{S} > \text{C}_2\text{S} \approx \text{C}_4\text{AF}$, however the absolute reactivity is dependent on the crystal structure and the degree of metal ion substitution within the phases. The reaction of the C_3A phase and its relative hydration products play a major role in the early hydration process of the cement system. The hydration of aluminates (C_3A) in the presence of sulfate ions governs the early hydration behavior (0-1 hour) of the cement mixture. The hydration of the silicate phases (C_3S), however, is responsible for the early strength development.

The reaction between the aluminate phase and the sulfates produces the hydration products, ettringite (AFt) and monosulfoaluminate (AFm). The hydration process of the cement, from the addition of water, to the setting and curing phases, can be described in 5 stages:

1. The initial hydration process (approximately 0-15 min)
2. The induction period also known as the lag phase or the dormant phase (approximately 15 min-4 hours)
3. The acceleration and setting phase (approximately 4-8 hours)

4. The deceleration and hardening period (approximately 8-24 hours)
5. The curing period (approximately 1-28 days)

Initially as water makes contact with the cement, components such as KSO_4 , Na, and $\text{CaSO}_4 \cdot \text{H}_2\text{O}$, which are easily soluble, are released and dissolved within the aqueous solution. The simultaneous release of Ca^{2+} and OH^- ions from the reactive surfaces of the aluminate and silicates phases is increased through the process of hydrolysis (Jolicoeur and Simard, 1998). The solution concentration of the aluminate and silicate phases will continue to increase as the pH rises, but it will still remain in orders of magnitude lower compared to the Na^+ , OH^- , K^+ , SO_4^{2-} , and Ca^{2+} ionic species, even at maximum concentrations. The Na^+ , OH^- , K^+ , SO_4^{2-} , and Ca^{2+} ionic species, whether it be through selective solubilisation (incongruent) or complete solubilisation (congruent), are known to be the most important phenomena upon water-cement contact. The release of Ca^{2+} ions is the reaction that affects the adsorption of polycarboxylate-based SP as this allows the negatively charged SP to adsorb onto the Ca^{2+} ions which surrounds the cement particle (Jolicoeur and Simard, 1998).

The incongruent solubilisation and surface hydrolysis processes produce intermediate amorphous hydration products which in a thin layer, coat the aluminate sites as the initial relative reaction, though the formation of C-S-H gels can also form upon the active silicate sites (Jolicoeur and Simard, 1998).

2.2.4 Purpose of the hydration products and how it forms

The performance of cement paste and SP can directly be linked to the hydration characteristics of the cement making hydration one of the key phases in understanding this complex material (Liu et al., 2015). These hydration products can take the form of either:

- Ettringite - $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$
- Monosulfate aluminate - $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 13\text{H}_2\text{O}$
- Calcium hydroxide - $\text{Ca}(\text{OH})_2$

The formation of ettringite prevents further dissolution of Ca^{2+} ions by covering the surface of the cement particles. These needle-like hydration products slow down the hydration process. That is why the hydration products formed in the early stages of hydration are known to give the cement mixture its first form of strength, stability and structure (Prince et al., 2003). The amount of calcium sulfate added to the clinker dictates the formation of ettringite. Calcium sulfate can take the form of:

- Gypsum

- Hemihydrate
- Synthetic calcium sulfate
- Natural anhydrite

Out of the different forms of calcium sulfate, natural anhydrite was found to have the lowest dissolution rate (Prince et al., 2003). The formation of the ettringite is more dependent on the dissolution rate and nature of the sulfate ions at the solid-liquid interface rather than on the specific surface area of the minerals. Despite the presence of gypsum, large amounts of alkali-sulfate can cause the ettringite not to easily crystallise, which is the reason why sulfate plays such a crucial role in the rheological behavior of cement systems. A deficiency of SO_4^{2-} with respect to $\text{Al}(\text{OH})_4^-$ can enhance the formation of monosulfate aluminate, which can later transform into ettringite when sufficient sulfate ions are reached (Prince et al., 2003).

The hydration of the interstitial phase is influenced by the lime-saturation ratio and by the amount of ions present in the mixing water after the addition of water. Small ettringite crystals form in the presence of high ion concentration and cover the unreacted interstitial phase which then in return slows down the hydration reaction rate. Large ettringite crystals (large needles) are formed when the ion concentration is too low, which results in the continuous growth of hydration products within the interstitial phase causing the cement paste to experience a rapid “flash” setting also known as pseudo-setting. This phenomenon makes the formation of ettringite an essential condition to slowing down the reaction rate of the hydration products and in controlling the rheological properties of a fresh cement paste (Ferrari et al., 2011; Hanehara and Yamada, 1999).

2.2.5 Setting of cement paste

The hydration of the aluminate phase occurs within one hour from the cement particle’s first contact with water and involves the hydration of C_3A , C_4AF and Alite (C_3S). The hydration of the aluminate phase is highly influenced by the concentration of Ca^{2+} , SO_4^{2+} and OH^- ions within the mixing water and the concentration of those ions are dependent on the amount of gypsum, f-CaO (free lime) and alkali sulfate within the cement. The stiffness that the cement paste experiences within the first hour after the addition of water is a product of the accelerated hydration within the interstitial phase (growth of ettringite crystals and CSH). After that phase is complete, the further setting of the paste relies on the further hydration of alite (Hanehara and Yamada, 1999). It is also believed that there is a correlation between the amount of Ca^{2+} ions released into the liquid phase and the setting time. As the concentration of Ca^{2+} ions reaches a stable and constant value, initial setting of the cement paste is experienced (Hanehara and Yamada, 1999).

2.2.6 Hydration of C₃A

The hydration of the C₃A phase is essential for controlling the workability of cement suspensions as it produces the hydration product ettringite (Aft) which covers the reactive sites of the cement particle (Zingg et al., 2008b). The chemical reaction and synthesis of C₃A and ettringite is as follows:

Synthesis of C₃A

- $3\text{CaCO}_3 + \text{Al}_2\text{O}_3 \Rightarrow 3\text{CaO} \cdot \text{Al}_2\text{O}_3 + 3\text{CO}_2$

Synthesis of ettringite

- $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$

It was observed by Ferrari et al. (2017) that ions such as Ca²⁺ and Al³⁺ were being substituted within the structure of the C₃A phase. Cubic, monoclinic and orthorhombic polymorphs stabilise when the Na⁺ ion gets taken up within the C₃A structure. There are a series of eight hollow rings (Al₆O₁₈)¹⁸⁻ each consisting of 6 AlO₄ compounds interconnected across the Ca²⁺ ions within the crystalline structure of cubic C₃A. To maintain the electrical neutrality of the structure, the central cavity of (Al₆O₁₈)¹⁸⁻, which is empty in pure C₃A, needs two sodium atoms as Na⁺ replaces the Ca²⁺ atom (Alonso and Puertas, 2015).

2.2.7 Low water equals high strength

The term fresh concrete is given to a concrete mixture that has been freshly mixed and is still in its plastic state, and has not yet started its strength development phase. The key attributes of self-compacting concrete are its ability to flow into moulds and into formwork, around reinforcement, and being able to compact itself, leaving a smooth finish without segregation (Banfill, 2011). Adding more water to the fresh mixture to achieve this desired fluid state can however affect the strength and durability of the concrete mixture by creating pores within the concrete, ultimately weakening the hardened product. This gave rise to the use of water-reducing admixtures to maintain a desired flow with very low water content. This results in an increase in strength and durability which improves the quality of the concrete (Banfill, 2011).

Lowering the water content of a cement mixture results in a reduction in permeability and absorption into the hardened cement matrix which prevents the penetration of aggressive agents of the environment from corroding and damaging the steel reinforcement (Banfill, 2011). According to the literature, a W/C ratio as little as 0.29 is sufficient to hydrate all the cements particles (Liu et al., 2017a; Qian et al., 2018). With the aid of PCE SP, the release of the entrapped water molecules is sufficient for the hydration of all the cement particles, even

at a low w/c of 0.29, as the dispersing force of the SP enhances the water to cement contact (He et al., 2017a).

2.2.8 Surface area of the mineral phases

The specific area and weight of alite was found to represent more than 50% of the clinker produced from Portland cement (Hanehara and Yamada, 1999). However despite the size of the C_3S , C_3A which only represents 5-15 w.t% of the cement particle, is the most reactive phase when hydrated and is a major constituent for the determinant of the hydration products through the release of Ca^{2+} . This makes C_3A a major component effecting the rheology of concrete, mortar and cement paste (Alonso and Puertas, 2015).

The flow of cement paste decreases as the C_3A content and specific surface area increases; due to the growth of hydration products. The content of C_3A and the cement specific surface S_{sc} have an influence on the performance of certain admixtures such as a PCE. The general performance of SP's decrease when there is an increase in the Na_2O_e and C_3A content, as well as when there is an increase in the cement specific surface. The increase in Na_2O_e and C_3A content within a fresh cement paste as well as the cement specific surface S_{sc} also increases the yield stress over time which is related to the formation of hydration products. It was reported that a C_3A content of just 12% within a fresh mortar mixture is known to increase the yield stress tenfold compared to analogical mortars which only contain a C_3A content of 2%. This increase in the hydration products affects the performance of a PCE SP by decreasing the amount of free water that is available for fluidising the mixture, instead, it is used to create abundant hydration products. The increase in hydration products also increases the rate of adsorption by consuming much more SP due to the affinity the PCE SP has towards the positive sites of the hydration products. This leaves less SP available within the mixture for further fluidising (Gołaszewski, 2012).

2.2.9 Strength development of concrete

The mechanical strength gained by a fresh cement paste in the early stages of hydration is subject to a combination of hydration products namely, ettringite (AFt), calcium monosulfoaluminate hydrate (AFm), alumina and ferrite gels, forming a network of hydration products across the cement particles connecting and bonding to other adjacent cement particles within the system (Ma et al., 2014). It is believed that cement systems that are rich in C_3S release more silicate, calcium and hydroxide ions within the solution which help form portlandite and C-S-H hydration products within the cement paste. This subsequently produces a much stronger paste due to the abundance of these hydration products forming an

interconnected network between the adjacent hydrating cement particles (Yousuf et al., 2017). The strength development of a fresh cement mixture is directly linked to the yield stress of the material. As the solid content of the cement mixture increases due to the growth of the hydration products, so does the improvement of the mechanical performance of that cement mixture as can be observed by the yield stress development (Ouattara et al., 2017).

2.2.10 Does SP affect the formation of hydrates?

Ettringite, as one of the initial hydration products, will form in the presence of sulfate ions as well as in the presence of SP. SP does not affect the formation of the ettringite crystallisation, although it does change the shape of the hydration products from a needle like appearance to short, large crystals (Prince et al., 2003).

2.2.11 Organo-mineral phase

Monosulfatealuminate hydrate (C_4ASH_{12}) and C_4AH_{19} are hydration products of C_3A which are capable of taking up admixtures such as SP within its layered double hydroxide- type laminar structure. It was observed through XRD measurements that the formation of the organo-mineral phase can occur in the presence of an polycarboxylate-based admixture, although the organo-mineral phase can lead to a reduced fluidising effect by lowering the admixture's affinity towards the silicate phases and by reducing the amount of admixture available in the suspension (Alonso and Puertas, 2015; Dalas et al., 2015b).

Where the polycarboxylate-based admixtures adsorb depends greatly on the SO_4^{2-} / C_3A molar ratio. Polycarboxylate-based admixtures can adsorb between the layers of the aluminate hydrates, C_2AH_{13} or C_2AH_8 , at low sulfate concentrations (a SO_4^{2-} / C_3A molar ratio of 0.1-0.35); however at high sulfate concentrations (SO_4^{2-} / C_3A molar ratio of 0.7-2), PCE was found not to be adsorbed between the layers of the main hydration products, ettringite and monosulfoaluminate (Alonso and Puertas, 2015).

Depending on the molar ratio, Alonso and Puertas (2015) discovered that in the presence of sulfates, ettringite formation is favoured over the formation of the organo-mineral phase. In that case PCE will have to compete with the sulfate ions for adsorption sites onto the C_3A phase whose reaction form AFt and AFm phases, because of the affinity the sulfate ions have towards the aluminate sites

2.2.12 Effect of calcium sulfate as a setting regulator

The hydration of C_3A without the addition of soluble sulfates brings forth the formation of C_4AH_{19} , C_2AH_8 and C_3AH_6 which are calcium aluminium hydrates responsible for the instantaneous setting of the cement paste also known as flash setting. The addition of calcium sulfate to the clinker as a setting regulator can be used to prevent this quick hardening effect. The reason for this instantaneous setting is the abundant formulation of hydration products such as ettringite ($C_6AS_3H_{32}$), also termed AFt, alongside fluctuating quantities of calcium monosulfoaluminate hydrates (C_4ASH_{12}), also termed AFm (Alonso and Puertas, 2015).

Without the addition of calcium sulfates, the reactivity of C_3A declines rapidly as Na^+ gets taken up within the structure. The reason why cubic C_3A is known as the most reactive polymorph is the interaction it has with water, leaving vacant positions within its structure; however C_3A reactivity can decline as Na^+ fills those vacant positions resulting in a denser structure which in return reduces the reactivity of the cubic C_3A . The polymorphs with high content of Na^+ within its structure are less reactive within water and subsequently produce fewer hydration reactions. The addition of sulfates however has a reverse effect on the reactivity of polymorphs as the higher amounts of Na_2O content within the C_3A result in greater sulfate reactivity. C_3A is known to be the phase within clinker to be highly attractive to SP, which is why the reaction that the C_3A has with the sulfates, impacts the effectiveness and performance of the admixtures (Alonso and Puertas, 2015).

2.2.13 The effect of SP on the retardation of cement hydration

The polycarboxylate-based admixture will continue to adsorb until it has saturated the surface of the cement particles resulting in a cement mixture which is highly fluid. This maximum fluidity was found to have a great influence on the hydration kinetics causing the cement system to experience a retardation effect (Zhang and Kong, 2015). The retardation effect that the cement hydration process experiences due to the inclusion of SP, can be related to the following:

- The SP could be hindering the diffusion of the ions due to adsorption at the cement solution interface.
- The precipitation and nucleation of the hydration products could be hindered by the complexation bonding from the $-COO^-$ onto the Ca^{2+} ions within the aqueous solution.
- The effective dispersion of the cement particle caused by the influence of the SP can have an effect on the morphology and growth kinetics of the hydration phases.

The retardation effect that the cement system experiences is related to the adsorption of the SP, and to the fact that higher amounts of adsorption can lead to an increased retardation

effect with regards to the cement hydration process. In cases where the adsorption has reached saturation, abundant or unadsorbed carboxylic and sulfonic groups which remain within the aqueous medium, can extend the retardation period which delays the cement system from setting. The effect of unadsorbed polycarboxylate-based admixture and the mechanism behind the reason for the retardation effect remains unanswered. However, understanding and correlating the theoretical literature, can result in the production of new and improved SPs with efficient performance (Zhang and Kong, 2015).

2.3 Superplasticisers

The first generation plasticisers represented by sulfonated naphthalene formaldehyde (SNF) and by modified lignosulphonates (LS), were widely used in industry due to their significant improvement of the rheological properties of fresh concrete mixtures (Kauppi et al., 2005). It is only with the invention of the poly- condensate admixtures that the term superplasticisers started to be commercially used in industry. SPs were composed of poly-condensate admixtures which was mainly represented by poly naphthalene sulfonate (BNS) and poly melamine sulfonate (PMS). These SP's were known to be far superior with regards to efficiency compared to plasticisers using sulfonated naphthalene formaldehyde (SNF) and lignosulfonate (LS) technology (Kauppi et al., 2005; Ma et al., 2020; Plank et al., 2008b). Currently the most popular SP used within industry is the sulfonate formaldehyde polycondensate (NSF) and the polycarboxylate (PCE) SPs (Chomyn and Plank, 2020; Zhang and Kong, 2015). The effectiveness of SP on cement suspensions and how they can affect the fluidity can be divided into three sections:

- How the SP adsorbs onto the surface of the cement particle as well as the hydration products.
- How the SP integrates itself within the layers of the hydration products such as C-S-H and AFm.
- And the unadsorbed SP remains within the aqueous phase.

What varies between the different SPs available in industry is the dispersing ability they produce, which is closely linked to their adsorption behaviour, as this is their driving force (Zhang and Kong, 2015). One of the distinct differences between NSF SP and PCE SP is their adsorption mechanism. NSF SP makes use of electrostatic forces to adsorb itself onto the surface of the cement particle, where PCE SP makes use of electrostatic forces through its attraction to the cement particle by its $-\text{COO}^-$ group, and through the complex bonding between the Ca^{2+} ion released from the cement particle and the $-\text{COO}^-$ group of the PCE SP. The dispersing ability of NSF SP is related to its high charge density which increases its adsorption

ability. This then homogenises the surface charge of the hydrating cement particles, creating the electrostatic force which induces a repulsive force, dispersing the cement particles within the medium (Zhang and Kong, 2015). Polycarboxylate-based SP has both a lower charge density, and a lower adsorption amount compared to the NSF SP; however it displays far more dispersing ability due to the introduction of an additional steric through the side chains, which delivers a higher dispersing ability (Zhang and Kong, 2015).

2.3.1 Polycarboxylate-based superplasticisers

In the 1980's a new SP was invented by Nippon Shokubai together with Nippon Master Builder Technologies. This new SP consists of poly-ethylene oxide (PEO) side chains that are grafted onto a polycarboxylate-based main chain or backbone (Plank et al., 2008b; Yu et al., 2016). The performance of this new SP is highly dependent on factors such as the main chain length, side chain length and the side chain density, which all contribute to the dispersion of cement particles by inducing a negative charge onto the cement particle (Ferrari et al., 2011; Plank et al., 2008b).

One of the methods of evaluating the dispersing capability of a SP is to assess the fluidity of the cement paste. Polycarboxylate-type SP is known as one of the most indispensable materials when it comes to producing a concrete with high strength and high flowability due to its superior dispersing ability of the cement particles (Chen et al., 2020; Kong et al., 2016; Plank et al., 2008b; Yamada et al., 2001).

2.3.2 Architecture of polycarboxylate-based superplasticisers

Polymers are defined by their designation which describes the trunk chain length, length of side chains as well as the charge density of the polymer. Plank et al. (2010) make use of the designation SX-MY to describe the structure of the polycarboxylate-based SP. They further explain that (X) which represents the units of ethylene oxide per side chain (S), and (Y), which is calculated from (M), represents the repeating trunk chain units with regards to (M). (Y) Also describes the quantity of side chain per macromolecule as well as the length of the main chain. (M) Can be determined by using gel permeation chromatography (GPC). Polymers are differentiated by the ratio between the side chain and trunk length. Figure 2.2 depicts the image of a typical example of a comb like structure of these polymers. As can be seen by the image labelled S7-M31, the trunk chain (M), with 31 units, is much longer than that of the side chains (S), with only 7 units, portraying a worm or brush/comb like polymer. Whereas in Figure 2.2 the image labelled S34-M13, which has a trunk chain of 13 units, is much shorter than that of

the side chains which has 34 units per side chain, resulting in long side chains. The designation S34-M13 depicts a polymer shape resembling a star (Plank et al., 2010).

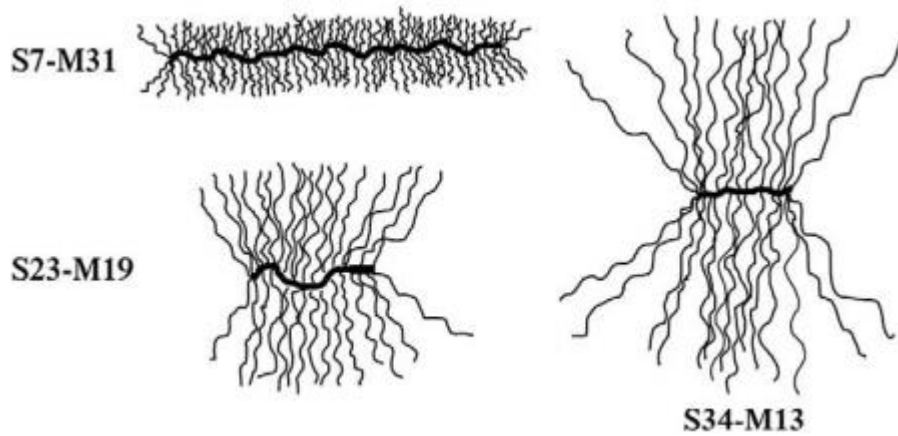


Figure 2.2: Schematic illustration of the molecular architecture of PCEs (Plank et al., 2010)

The longer the side chain lengths of a PCE SP are, the more the dosage of the SP is required to reach a saturated adsorption onto the cement particle (Plank et al., 2010). In theory, PCE SP with longer side chains should enhance the rheological properties by increasing the fluidity of a concrete mixture because of the longer side chains inducing a higher steric repulsion between the cement particles. This is not the case as polymers with longer side chains provide poor adsorption abilities because of its low charge density. However polymers with shorter side chains adsorb much more effectively onto the cement particle, which can be the result of its higher charge density hence enhancing the flow properties of cement (Ferrari et al., 2011). Figure 2.3 represents the chemical structure of a typical polycarboxylate-based SP. The (n) section represents the backbone or the trunk chain that subsequently gets attached to the surface of cement particle (C_3A and C_4AF), and the (m) section represents the grafted side chains.

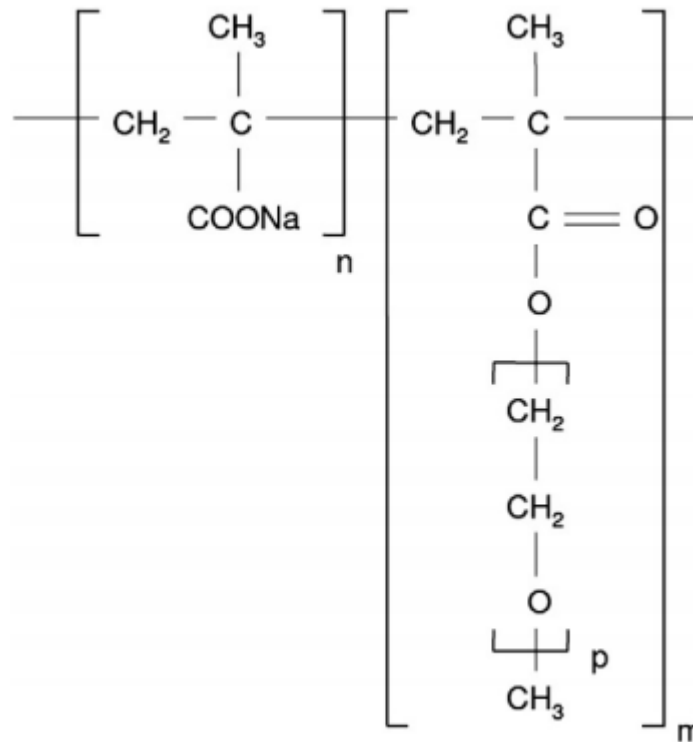


Figure 2.3: Chemical structure of a polycarboxylate superplasticiser (Ferrari et al., 2011)

2.3.3 Modifying the chemical structure

The effect of the molecular structure of PCE on the hydration behaviour of Portland cement is not fully understood (Kong et al., 2016). The influence that different densities of carboxylate groups of PCEs have on the hydration behaviour of cement paste is related to the retardation effect that the cement paste experiences (Kong et al., 2016). The carboxylic groups have a major influence on the retardation effect because of their strong interaction and affinity towards the calcium ions that are released within the medium. The steric position as well as the amount of carboxylic groups along the polymer trunk play a significant role in the binding capabilities onto the calcium ions through the calcium chelate complexes onto the various compositions. It is for this reason that the anionic charge as well as the adsorption behaviour can be affected by the polymer architecture of the polycarboxylates within the cement pore solution (Plank and Sachsenhauser, 2009). The reduction of the anionic charge (which is the reaction in which electrons are gained and valence is reduced, often through the removal of oxygen or the addition of hydrogen) is much stronger with PCE with a high content of carboxylic groups compared to the polymer containing low concentrations of carboxylic groups. The steric accessibility of the $-\text{COO}^-$ functionalities is an acceptable explanation for this phenomenon (Plank and Sachsenhauser, 2009).

The reduction of the anionic charge density can become stronger as the amount of Ca^{2+} bonding to the $-\text{COO}^-$ groups increase. This bonding onto the $-\text{COO}^-$ groups can be an explanation for the decrease in the effective anionic charge of a PCE within the cement pore solution. The cement pore solution is a fluid that possesses a high ionic strength due to counter-ion condensation on polyelectrolytes. Divalent (e.g. Ca^{2+}) and monovalent (e.g. Na^+) cations within the cement pore solution are attracted to the backbone of the PCE through electrostatic forces. They then surround the anionic backbone of the PC with a cloud of counter-ions which can be an explanation for the decrease in effective anionic charge. The attraction between the cement surface and the dissolved PCE are affected by the counter-ions present in the cement pore solution and can also be said to have an impact on the adsorption behavior (Plank and Sachsenhauser, 2009).

2.3.4 Changing the architecture of SP to enhance workability

The chemical structure of a PC based SP is flexible and allows for the modification of its structure to enhance its efficiency. The slump flow loss and the workability can be controlled by modifying the chemical structure of a PC-based SP. The modification of the chemical structure of a PC-based SP was generally focused on the main backbone length, side chain length, degree of backbone polymerisation, the charge density and the composition of the functional groups. However, when the aim is to improve workability, then some will argue that the focus should be directed at modifying the bond structure of the PC-based admixture. The general structure of all the PC polymers includes a polyoxyethylene (POE) group and a carboxylate group. The polyoxyethylene side-chains are grafted onto the acrylic backbone and are connected to the main chain by an ester bond. The drop in slump loss and the retardation of the setting time can be related to the ester bond between the side-chain copolymers and the main chain backbone within the structure of the PC-based SP. These side chains are bonded to the main chain by an ester bond which loses its stability at alkali ambient due to hydrolysis. Hydrolysis is a reaction where the ester bond is cleaved by an alkali group. This reaction causes a decrease in the amount of attached side-chains, which is attached onto the backbone of the main chain by producing a corresponding carboxylate and alcohol bond. This subsequently has an effect on the workability of the cement system as it decreases the side-chains needed for the steric repulsion (Felekoğlu and Sarıkahya, 2008).

Another method for improving the workability of a PCE SP is to make changes within the structure related to the changes to the ionic groups as well as to the oxyethylene side chains. The steric effect can be enhanced by allowing simultaneous adsorption of side groups and the backbone chain onto the cement surface. This can be achieved by replacing the hydrophobic methoxy groups ($-\text{O}-\text{CH}_3$) present within the side chain with the oxyethylene groups ($-\text{O}-\text{CH}_2-\text{CH}_2-$) or with the hydrophilic hydroxyl group ($-\text{OH}$). The hydrophilic chains of polyoxyethylene

experience hydration within the aqueous medium where hydrogen bonds are formed between the hydrogen atoms within the water molecules and between the oxygen atoms of the ether groups, changing the volume, the spatial arrangement and the length of the SP's chains which cause rapid hydration of these side chains due to the higher hydrophilicity, subsequently enhancing the steric hindrance effect of the PCE SP (Janowska-Renkas, 2013; Lin et al., 2021). The efficiency of PCE SPs can be enhanced and controlled by the following:

- Making changes to the hydrophilic nature of the polymer(which is measured as the ratio of ethers to esters), increases the hydrophilicity which in return increases the efficiency.
- The increase in concentration of the neat polymer form within the mother substance increases the efficiency.
- Increasing the weight-average molecular weight (Mw) of the polymer increases the efficiency.

2.3.5 Dispersing force

SPs have been used for the last 40 years to improve the flow ability of a cement system by dispersing the cement particles within a cement system (Kauppi et al., 2005). The fluidity of concrete can be improved by the dispersing of the cement particles within a cement system and this can be achieved by adding SPs to the concrete mixture to achieve this effect (Yoshioka et al., 2002). One of the key ways in which SPs increase the workability of a concrete mixture is by dispersing agglomerated particles of cement without increasing the water to cement ratio (Flatt and Houst, 2001).

How a SP reacts with certain properties of cement is believed to hinder the dispersing force which causes instability in the cement system. Reports have shown that the alkaline sulfate content within the cement has an effect on the dispersing ability of the polycarboxylate SP (Yamada et al., 2001). The polycarboxylate SP adsorbs onto the surface of the cement particle, creating an adsorption layer which is related to the dispersing force of the cement. The adsorption layer which consists of PEO chains is associated to the steric thickness which causes the hindrance effect that repels the particles. The decrease in steric size causes a decrease in the hindrance effect and the dispersing force of the polycarboxylate SP (Yamada et al., 2001).

It was also discovered by Flatt and Houst (2001) that the effectiveness of the dispersion force of a SP is related to the width of the adsorbed layer. Workability can only be improved once addition of the polymer reaches the optimum amount to induce a steric layer that can prevent

agglomeration (Flatt and Houst, 2001). The steric hindrance effect is caused by the PEO graft chains which are protracted away from the surface of the cement particle, which is the main contributor in the dispersion of the cement particles (Felekoğlu and Sarıkahya, 2008; Yoshioka et al., 2002). Li et al. (2005) suggested that if the adsorbing ability and electrostatic repulsion force was simultaneously increased, this would also increase and improve the dispersion ability of a cement system. Plank et al. (2010) agree with this suggestion by mentioning that the amount of adsorbed graft chains onto the cement particle plays an essential role in increasing the steric hindrance effect or the electrostatic repulsion, thus enhancing the dispersing ability.

The dispersing force of PCs is governed by the adsorption of the PC onto the cement particle and the hindrance effect caused by the protruding side chains within the aqueous medium. As the backbone of the PCE adsorbs onto the surface of the cement particle, the PEO side chains disperse other cement particles by creating an adsorption layer around the cement particle, increasing the steric thickness. This then increases the hindrance effect; decreasing the size of the steric will decrease the dispersing force of the PCE (Flatt and Houst, 2001; Yamada et al., 2001).

2.3.6 Steric hindrance effect of polycarboxylate-based superplasticizer

Polycarboxylate-based SP is an admixture that is very popular in the construction industry because it allows concrete to be produced with low w/c ratios without decreasing the workability of the mixture, which in return increases the strength of the concrete. This phenomenon has resulted in extensive studies on how this admixture can be enhanced (Li et al., 2005; Plank et al., 2008a).

Many of the studies on polycarboxylic-based SPs are related to the performance and the effects of the polyethylene oxide (PEO) chains within the molecular structure. It is previously believed that when it comes to the deflocculating of the cement particles through dispersion, the dominant role of this effect would be played by the steric hindrance over the electric repulsion. The main reason for the steric hindrance effect is the width of the slipping layers which is caused by the PEO side chains (Li et al., 2005). The polyelectrolytes generate a repulsive force by adsorbing onto the solid-liquid interface, resulting in a reduction of the adhesion force between the cement particles within close proximity (Kauppi et al., 2005).

The term used to describe how polyelectrolytes disperse cement particles within a system is referred to as electrosteric stabilisation. As the PCE SP adsorbs onto the solid-liquid interface

of a cement particle, it encourages inter-particle forces which are related to both steric and electrostatic forces (Kauppi et al., 2005).

2.3.7 Side chains inducing steric hindrance and density charge group

PCE SPs with longer PEO side chains were found to increase the fluidity of a concrete mixture, and lower the plastic viscosity and shear yield stress; however PCE SPs with higher degrees of backbone polymerisation and with shorter PEO side chains were found to have a better adsorption ratio at the same dosage as those with longer side chains. Although SPs with lower degrees of backbone polymerisation displayed a lower adsorption ratio compared to SPs with higher degrees of backbone polymerisation, the dispersing strength of the SPs with lower degrees of backbone and longer side chains were found to be far superior per adsorption amount (Ferrari et al., 2011; Sha et al., 2020; Yamada et al., 2000).

PCE SPs make use of a steric repulsion mechanism to disperse the cement particles within the medium after the charged backbone adsorbs onto the hydrating cement particle. The electrostatic interaction between the SP and the cement particle is determined by the anionic charge density of the macromolecules of the PCE. This electrostatic interaction has a great influence on the adsorption behaviour and the dispersing power. It is expected that the PCE molecule with the highest anionic charge will display a higher degree of adsorption until it reaches a saturation point where the adsorption rate plateaus. This anionic charge, which has a great influence on the adsorption behaviour, can be calculated by a chemical formula which correlates the anionic charge density with the dispersive force of the PCE molecule (Plank and Sachsenhauser, 2009).

This approach however does not account for the significant effect the high concentrations of calcium ions within the pore solution have on the anionic charge density of the PCE. The entropy changes that influence PCE adsorption is a derivative of the immobilised macromolecule which adsorbs itself onto the cement surface, simultaneously releasing ions and water molecules within the pore solution. It is this exchange process by enthalpy and entropy that can describe the adsorption behaviour of PCE. The entropy change is dependent on the number of ions and H₂O molecules that desorb from the surface as well as the molecular weight of the PCE, whereas the enthalpy contribution is dependent on the electrostatic attraction forces between the PCE SP and the surface of the cement particle. Adsorption can be identified by making use of the Gibbs free energy equation where a negative resultant Gibbs free exchange energy value is an indication that adsorption has occurred (Plank and Sachsenhauser, 2009).

$$\Delta G = \Delta H - T \cdot \Delta (\Delta S)$$

2.1

where G is the gibbs free energy, H is the entropy and S is the change in enthalpy. Polyelectrolyte titration can be used to determine the anionic charge density of a PCE SP. With this in mind, calculating the theoretical anionic charge of a PCE SP is possible with a highly alkaline cement pore solution, given that the COO^- are the only functionalities present. The theoretical charge density can be calculated with the following equation:

$$\text{Anionic charge density of polymer (eq/g)} = \frac{n_{\text{COO}^-}}{M_u} \quad 2.2$$

Where M_u represents the molar mass of a repeating unit within the polymer chain, and n_{COO^-} represents the amount of COO^- functionalities per reiterating unit (Chomyn and Plank, 2019; Plank and Sachsenhauser, 2009). The methacrylic acid and the methacrylate ester molar ratio, which is present within the polymer, corresponds to n_{COO^-} . An increase in the ester content within a polymer usually results in a decrease in the anionic charge density of the PCE molecules. For example, the anionic charge of 17PC6 is found to be more when compared to 17PC1.5 because it contains more methacrylic acid than the latter. An increase in side chain length also brings an increase in anionic charge density which indicates that the theoretical anionic charge density is not always best for predicting the adsorption behavior of a PCE (Plank and Sachsenhauser, 2009).

2.3.8 Steric hindrance vs electrostatic repulsion

When comparing the different dispersing mechanisms of an SP, one has to compare the effectiveness between dispersing through the steric hindrance effect or electrostatic repulsion force. As mentioned before, the first generation SPs such as sulphonated naphthalene formaldehydes (SNF) and polynaphthalene sulphonates (PNS), and the second generation SPs known as sulphonated melamine formaldehydes (SMF) and polymelamine sulphonates (PMS), make use of the electrostatic repulsive force as the main dispersing mechanisms (Ouattara et al., 2017). These first and second generation SPs adsorb onto the surface of the cement particle through electrostatic attraction by adsorbing onto the positive sites on the cement particle and through complexion bonding onto the Ca^{2+} ions (Ouattara et al., 2017).

The third generation SP is a polyacrylate SP which consists of a main backbone polymerised by a carboxylic acid group also known as polycarboxylates. Grafted onto the backbone are

ethylene glycol side-chain copolymers which protrude away from the backbone in the shape of a comb. The dispersing mechanism used by the third generation SPs is steric hindrance which is defined as the repulsive force between the groups which are positioned on the same side of the double bond. This mechanism alongside electrostatic repulsion forces is used by PCE to disperse cement particle agglomeration within the suspension medium (Ouattara et al., 2017). The PMS and PNS SP that make use of the electrostatic repulsive forces are more dependent on the cement composition as over-dosage could affect the stability of the material, unlike PCE which makes use of steric repulsion as its main dispersing force. PCE is the preferred high range water reducer (HRWR) in the concrete industry because of its effectiveness at low dosages and because the steric hindrance effect was found to be far more effective and stable than SPs that make use of electrostatic repulsion as their primary dispersing mechanism (Chen et al., 2020; Ma et al., 2020; Ouattara et al., 2017).

2.3.9 Incompatibility between SP and cement

The purpose of SPs in SCC is to improve the workability of the fresh concrete mixture by increasing the flow properties of the system. This phenomenon is governed by the dispersing force of the SP which was found to vary between different cements and SPs. The reason for the unpredictability of the dispersing force of the SP is described by many authors as being related to incompatibility between the SP and cement (Ferrari et al., 2017; Hanehara and Yamada, 1999; Ma et al., 2014, 2020; Prince et al., 2003; Sun et al., 2020; Yamada et al., 2001; Zingg et al., 2009). The interaction problems experienced between the cement and admixture can be classified into two groups:

- Adsorption of the SP onto the cement particle is hindered due to the competitive adsorption between the admixture and sulfate ions, and
- Problems caused by the effect that the admixture has on the reaction rate of the hydration products of cement (Hanehara and Yamada, 1999).

Previous research by Ferrari et al. (2017) has shown that one of the solutions to solving the cement and SP incompatibility, more specifically, cement and PCE incompatibility, is to increase the gypsum content to up to 7% w.t. However in order to avoid durability issues, the calcium sulfate addition should not surpass a dosage corresponding to 2.60% w.t of SO₃ (Ferrari et al., 2017). Nevertheless the solution of adding more gypsum to mitigate PCE and cement incompatibility is subject to the type of PCE used.

2.3.10 The effect of sulfate on other SP e.g. PNS

Not only does the introduction of SP admixtures affect the fluidity of a cement paste mixture, it also has an effect on the hydration process itself. How C_3A reacts with the soluble sulfates within the medium determines the compatibility between an admixture and cement; however not all admixtures are sensitive to the variations in concentration of soluble sulphates within the medium (Alonso and Puertas, 2015). Adding more gypsum to the clinker will not enhance the adsorption ability of poly-naphthalene sulphonates (PNS) at the surface of the cement particle, although it was observed that the addition of up to 7% w.t of gypsum to the clinker improved the fluidity of the cement paste (Ferrari et al., 2017). The fluidising effect of SNF SP's decreases as the C_3A/Ca_2SO_4 ratio in the cement increases (Gołaszewski, 2012). PCE based SPs were found to be much more sensitive to the concentration of soluble sulphates due the molecular structure of the polymer compared to the naphthalene- based SP, which was found to be less sensitive to the concentration of soluble sulfates (Alonso and Puertas, 2015). With this known, there still remain many unknowns about the effect of competitive adsorption between the soluble sulphates, the effect the structure of the admixture has on adsorption in the presence of soluble sulfates and the adsorption of SP admixtures onto the various C_3A polymorphs (Alonso and Puertas, 2015).

2.3.11 Sulphate sensitivity

Where there is a rise in sulphate concentration, there is also a decline in SP consumption/adsorption. The discovery made by Alonso and Puertas (2015) was that the competitive adsorption intensity of the PCE admixtures was much less than that of the sulphates onto the C- C_3A sites when the C/E ratio of the PCE admixture was low. Sulphates are much more attracted to O- C_3A than the admixtures are, compared to C- C_3A . When the O- C_3A content of OPC is higher, the amount of admixture adsorbed onto the silicate phases is greater which improves its effectiveness at low admixture dosages for a given fluidity. To determine how a PCE admixture will perform in the presence of sulphate, the following equation can be used to calculate the sulphate sensitivity:

$$SSP = P / N^2 , \quad 2.3$$

where the mean length of the ether side chains (P) is directly proportional to the sulphate sensitivity (SSP) and inversely proportional to the square of the ionic charge of the SP admixture (N^2) (Alonso and Puertas, 2015).

2.3.12 Alkaline sulphate in cement effects dispersing of PCE

Authors including Yamada et al. (2001) state that the dispersing force of PCE can be highly affected by the alkaline sulphate concentration within the composition of cement (Yamada et al., 2001). The alkaline sulphate ions within the aqueous phase affect the dispersing ability of the PCE by adsorbing competitively onto the positive sites on the cement surface. The higher the sulfate concentration, the lower the PCE adsorption; this ultimately affects the dispersing force which subsequently affects the fluidity of the cement mixture (Yamada et al., 2001). According to Flatt and Houst (2001), cements with low-alkali content consume more SP than those with higher alkali content; however they display poorer workability than the latter, which can be related to the hydration products formed allowing for more adsorption sites.

2.4 Rheology

Rheology can be defined as the study of the deformation and flow of matter. Rheological testing is used to define the structural response of a material which is governed by the frictional force between the internal particles of that material. Rheological testing in terms of SCC is useful in understanding the principals involved in enhancing the fluidity of cement-based material containing a superplasticiser (Xie and Kayali, 2016).

The rheological properties can also be referred to as the flow properties of a material and are best defined by parameters such as viscosity, shear stress and yield stress. Adsorbed PCE SP causes cement particles to disperse within the suspension medium and this effect causes the cement paste to experience increased fluidity by releasing entrapped water molecules. The increased fluidity within the cement paste can be defined by rheological parameters (i.e. yield stress, and plastic viscosity) and these parameters are best evaluated by means of flow tests and a rheometer (Cho and Suh, 2005; He et al., 2019; Yamada et al., 2000). These rheological parameters are used to investigate the behaviour of the internal structure of a fresh cement mixture in order to characterise the workability and mixability for further modification (He et al., 2019).

The fluidity and the workability of a cement mixture is dependent on the availability of free water within the cement mixture (Liu et al., 2017b). Two of the key parameters when defining rheology of a suspension are the viscosity and yield stress. The yield stress can be defined as the minimum amount of pressure needed to initiate the flow of a material, and viscosity is defined as the frictional resistance that exists between two layers of a fluid (Ouattara et al., 2017). There are two flow properties which can sufficiently describe the flow behavior and

workability of a fresh concrete mixture: the yield stress and the plastic viscosity (González-Taboada et al., 2017).

- Yield stress can be defined as the stress needed to initiate the flow (static yield stress); or the stress needed to maintain the flow; or the stress remaining after shearing (dynamic yield stress) (Fernández-Altable and Casanova, 2006).
- Plastic viscosity can be defined as the increase of the shear stress and the continuous increase of the shear rate once the static yield stress has been exceeded.

Understanding these rheological parameters provides a fundamental and quantitative way to describe the behavior of fresh SCC (González-Taboada et al., 2017).

The flow curve test (FCT) is one of the methods used to determine the dynamic yield stress and plastic viscosity of a fresh concrete mixture by measuring the relationship between the shear rate (flow curve) and shear stress, and then fitting those parameters to an appropriate rheological model (Chen et al., 2020; González-Taboada et al., 2017). A typical example of a flow curve can be seen in Figure 2.4.

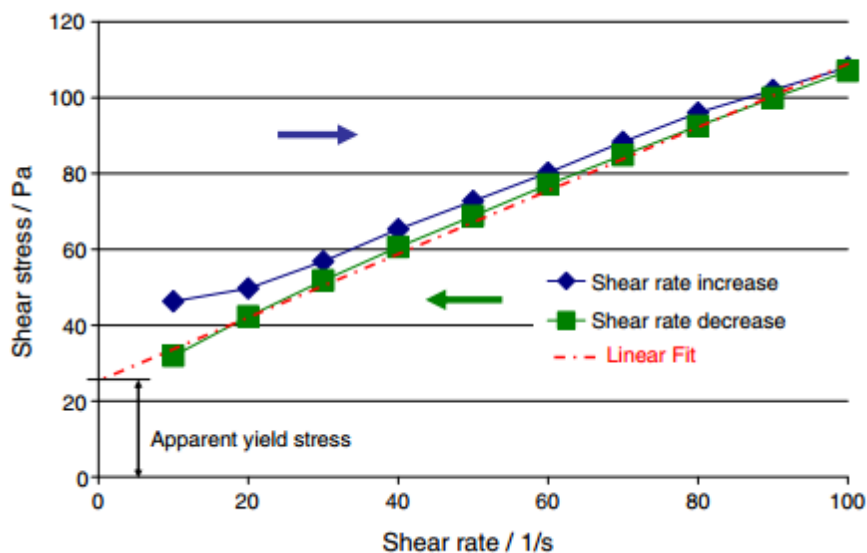


Figure 2.4: Typical example of a flow curve (Ferrari et al., 2011)

Shear rate can be defined as the rate of deformation that a material experiences within shear mode and is expressed as the differential of shear strain to time (Xie and Kayali, 2016). The unit used to define the shear rate is sec^{-1} or s^{-1} .

2.4.1 Bingham model

Since the 1970s the Bingham model has been used to determine the rheological properties of concrete (Banfill, 2011). Concrete technology is set around the basic principles of appropriately mixing gravel, sand, crushed rock, water and cement within its appropriate portions to create a material that once set, can withstand a load because of its strength and durability properties. From this phenomenon it was observed that the water/cement ratio is inversely proportional to the strength of the hardened concrete. In order to improve the workability of the concrete mixture, a higher water content is required, which however reduces the strength of the hardened concrete by creating pores within the hardened concrete matrix (Banfill, 2011).

The yield stress can be calculated by using a simple rheological model known as the Bingham model:

$$\tau = \tau_y + \mu \cdot \dot{\gamma} \quad \text{Bingham} \quad 2.4$$

Where τ_y is the shear stress (Pa), τ is the yield stress (Pa), μ is the plastic viscosity of Bingham model (Pa.s), and $\dot{\gamma}$ is the shear rate (1/s) (Alonso et al., 2013; Erzengin et al., 2018; González-Taboada et al., 2017; He et al., 2017a; Janowska-Renkas, 2013; Zingg et al., 2009).

The shear stress and shear rate results measured by a rheometer are used to develop a flow curve (which is a ratio between the measured shear stress and shear rate). This is fitted to the Bingham model in order to determine the yield stress and plastic viscosity of the material (Alonso et al., 2013; Bey et al., 2014; Chen et al., 2020; Hot et al., 2014; Li et al., 2020).

The Herschel-Bulkley model is well known for its ability to describe the rheological behaviour of a viscoelastic material. The Herschel-Bulkley model is defined by yield stress (τ), a flow behavior index (n) and a consistency index (K). When the flow index (n) is 1, then it is the Bingham model – equation 2.13 (Ouattara et al., 2017; Zhang et al., 2020).

$$\tau = \tau_y + K\dot{\gamma}^n \quad \text{Herschel-Bulkley} \quad 2.5$$

There have been attempts by researchers to modify the Bingham model by combining the principles of the Bingham model and the Herschel-Bulkley model and then trying to use this

second order Taylor development of the Herschel-Bulkley model to better describe the low estimations of the yield stress. However, it is recommended to keep the rheological model as simple as possible as in the case of the Bingham model as it gives the easiest description of the plastic viscosity and the yield stress (González-Taboada et al., 2017).

2.4.2 Rheology of cement paste

There are many rheological methods used in understanding and characterising the flow properties of cement suspensions. However using conventional rheometers to characterise the rheological behavior of a fresh concrete mixture can become difficult because of the coarse granular nature of the concrete with an aggregate size of up to 20 mm. This is why empirical methods such as slump tests related to the yield stress are more commonly used to determine the rheological properties of a concrete mixture (Banfill, 2011). Understanding the rheological behaviour at a paste scale can help model the behaviour of the concrete (including the aggregate) and deliver a better understanding of the microstructural behaviour of a cement mixture, although linking cement paste to concrete has its problems related to the introduction of the aggregate and the effect it has on inter-particle reactions. Trends can help predict optimised concrete mixtures, although a link between cement paste and concrete rheology is yet to be determined. The workability properties of a fresh cement paste are characterised by the kinetics of its hydration phases. Reversible flocculation of cement compounds is the term given to fresh cement suspensions to define the rheology of fresh cement paste, and it is highly governed by the hydration and surface properties of the cement particle (Gunnellius et al., 2014).

The filling ability which is also referred to as unconfined flowability or deformability, is defined as the ability of fresh concrete to fill formwork by encapsulating the reinforcement, and its ability to flow around obstacles by undergoing change within its shape, not with the assistance of mechanical consolidation, but by its own weight and through gravity (González-Taboada et al., 2017).

The passing ability, which is similar to the filling ability previously mentioned, refers to the ability of a fresh concrete mixture to flow around obstacles and through narrow spacing within the formwork without causing blockage or aggregate segregation and without the assistance of mechanical vibration (González-Taboada et al., 2017).

The resistance to segregation which is also referred to as the stability of the fresh concrete mixture is defined as the ability of a fresh concrete mixture to maintain its homogeneous state while distributing its various constituents through the reinforcement and into the formwork

(González-Taboada et al., 2017). The stability characteristics of SCC can be defined in Table 2.1 as dynamic stability and static stability:

Table 2.1: The stability characteristics of SCC

Dynamic stability	Dynamic stability refers to the ability of a fresh concrete mixture to resist separation of its constituents during transport and while it is flowing and spreading into the formwork.
Static stability	Static stability refers to the ability of a fresh concrete mixture to resist bleeding and segregating while it is still in its plastic state and while it is static, especially after casting.

The term thixotropic liquid can be given to a material like SCC because through chemical reactions it displays a decrease in its fluidity (workability) over time as well as displaying shear thickening while retaining a yield stress. It is for this reason that yield stress measurements are taken after the breakdown of the structure within the fresh mixture to avoid the effects of thixotropy (González-Taboada et al., 2017). The thixotropic phenomenon in fluid materials such as SCC paste transpires when the shear stress or shear rate loops in a response to the material recovering its initial viscosity after the material has been sheared or the application of the strain. This is a property which helps define the internal structure of the material (Fernández-Altale and Casanova, 2006). The thixotropic phenomenon is also defined as the restoration of the initial structural state at rest, after the gradual loss of cement paste viscosity during the shear process over a period of time. The thixotropic property of a cement paste is estimated by its time dependency behavior during the measurement (Migabo, 2015:20)

Workability can be defined as the ease with which a fresh concrete mixture can be mixed, the ease with which it can be handled and placed, and the ease with which it can consolidate itself and still remain in a homogenous condition (González-Taboada et al., 2017). One of the empirical methods used to determine the workability of a fresh concrete mixture is to observe its slump value; however the slump value is not always consistent in describing the workability of certain fresh concrete mixtures. The reason for this is that two fresh SCC mixtures can be observed to display identical slump flow values; however when their filling abilities are compared, they then display completely different flow capabilities. The reason for the difference in the flow behaviour is that flow cannot be described by a single parameter (González-Taboada et al., 2017).

2.4.3 Mini-slump test

In the 1920s, Abram saw the need to control and characterise this behaviour of the fresh concrete by introducing the slump test. The slump test and its relative, the flow table test, are among many empirical single-point tests (over 100) developed since the 1920s to help characterise the constituents of fresh concrete and are used worldwide for quality control and in the development of specifications. Abram established that a fresh concrete mixture poured into an open conical mould can retain its shape once the cone is lifted due to the yield stress that the concrete mixture possesses and that the dimension (diameter and height) recorded from this shape can be used to estimate the yield stress value of the cement system (Banfill, 2011).

Yield stress is used to describe the resistance a fresh concrete mixture has to flow. Many authors have made use of a mini-slump cone/flow cone to determine the rheological behavior of a low viscosity cement paste (He et al., 2017b; Li et al., 2005; Prince et al., 2003; Tan et al., 2017; Xiao et al., 2007; Yamada et al., 2000). The typical dimensions of this mini-slump cone/flow cone used to analyse the flow behaviour of a cement paste are a bottom diameter of 60 mm, a top diameter of 30 mm and a height of 60 mm (Yamada et al., 2001; Yousuf et al., 2017). The relative flow area ratio determined by Equation 2.6 can be used to evaluate the flow behaviour of a low-viscosity cement paste (Yamada et al., 2001).

$$\Gamma = F^2/50^2 - 1 \quad 2.6$$

(Γ) describes the relative flow area ratio and (F) is the mean orthogonal measurement of the spread. This empirical method (slump cone test) is a simple procedure for determining the yield stress of a low-viscosity cement paste, yet it was found in the literature that this method can be insensitive in the low (Γ) range; however in particular cases it is still used to determine the rheological behaviour of a cement paste by shear yield stress (Yamada et al., 2000).

The mini-slump test is best known for its ability to determine the plasticising (dispersing) effect (Chen et al., 2020; Cho and Suh, 2005; He et al., 2019; Lin et al., 2021; Ouattara et al., 2017; Plank et al., 2008b). This test generally makes use of a mini cone or mini-slump and a plate which can either be glass or metal. The cement mixture is poured into the cone from the top opening and is then allowed to stand for a few seconds before the cone is carefully and slowly lifted up vertically to avoid the effects of inertia. An average of two measurements is then taken of the resulting spread at a 90° angle from the initial measurement. This average value is then

used as the spread value (Dalas et al., 2015b; Lin et al., 2021; Plank et al., 2008b; Shu et al., 2016). Not only can the mini-slump test be used to obtain the material density dependent slump value, it can also be used as a functional rheological tool when it comes to determining intrinsic property such as the yield stress (Dalas et al., 2015b; Liu et al., 2017b; Plank et al., 2008b). This makes the mini-slump a suitable empirical test for measuring low viscosity cement mixtures (Plank et al., 2008b). Previous studies proved that there is a relationship between the slump and the yield stress. The slump measurements can be used to determine the yield stress by making use of the following equation (Dalas et al., 2015b):

$$\tau_y = \frac{225\rho g V^2}{128 \pi^2 R^2 \left(1 + \frac{225}{128\pi} \sqrt{3VR^{-3}}\right)} - \lambda \frac{R^2}{V} \quad 2.7$$

Where:

τ_y = Yield stress (Pa)

ρ = Paste density (kg/m³)

R = Average spread diameter (m)

λ = A parameter fixed at 0.003, this parameter takes into account the liquid-vapor interfacial energy and the wet angle

V = Volume of the cone (m³)

The λ coefficient can be neglected in spreads smaller than 35 cm as the effects of surface tension becomes useless and negligible when compared to the effect of the plastic yield stress (Roussel et al., 2005).

2.4.4 Rheometer

The slump test is used to investigate the apparent flow behavior of a cement paste; however a rheometer can be utilised to investigate the microstructural response to an external mechanical force. A rheometer utilises a rotating tool to apply the external shearing force to measure the deformation and plastic flow which is used to define rheological parameters of a sample (Xie and Kayali, 2016).

A rheometer, an instrument commonly used for determining the rheology of a cement paste, consist of a rotating tool consisting of two stainless steel parallel plates, one fixed and one rotating, or with a fixed rotating bob or paddle inside a cylindrical cup that shears the sample in order to determine its rheological properties. These tools mentioned above are commonly

utilised in the literature to determine the variations in shear to determine the yield stress and viscosity of fresh cement-based samples (Erzengin et al., 2018; Ferrari et al., 2011; Xie and Kayali, 2016; Zingg et al., 2009, 2008b) .

A concentric plate is lowered onto a fixed plate, leaving a gap between 0.6 mm to 1 mm (depending on the particle size) to measure the rheological parameters of a sample through shearing (Xie and Kayali, 2016; Zingg et al., 2009, 2008b). The rotational speed or torque required to break the inter-particle forces of a cement paste to induce flow can be observed by measuring the shear rate and the shear stress. Ferrari et al. (2011) used a rheometer with concentric cylindrical geometry to measure the shear stress of a cement paste by presetting the shear rate which was increased from 10 s^{-1} to 100 s^{-1} and then back down from 100 s^{-1} to 10 s^{-1} , to record a flow curve as can be seen in Figure 2.4. above. Hot et al. (2014) used a similar shear rate ramp 10 s^{-1} to 100 s^{-1} for a total of 200 s up and from 100 s^{-1} to 10 s^{-1} for 200 s and used the returning ramp to determine the viscosity and yield stress values. The yield stress and viscosity can be determined from this flow curve by extrapolating the parameters from the return curve and then using these rheological parameters to describe the flow properties of a cement paste by utilising the Bingham or the Herschel Buckley model. A similar procedure was followed by various authors (Fernández-Altable and Casanova, 2006; Ferrari et al., 2011; He et al., 2019; Zingg et al., 2009) where a hysteresis loop was used at a ramp from 1 s^{-1} to 100 s^{-1} for 200 s and back down from 100 s^{-1} to 1 s^{-1} for 200 s. Prior to testing, pre-shearing at 100 s^{-1} was done for 1 minute (He et al., 2019; Zingg et al., 2009).

Mixing time used to homogenise the cement paste mixture varies between researchers (2 minutes to 5 minutes) (Fernández-Altable and Casanova, 2006; Xie and Kayali, 2016). However it is the time after mixing and before testing that is a concern when obtaining accurate yield stress results. It was found in the literature that inter-particle forces and agglomerates caused by the network of hydration products causes the cement paste to experience a 'false set', which is recorded as the initial yield stress of the sample. The cause of the "false set" effect can be related to the reaction involving only the sulfates, or only reacting half way. As a solution to this exaggerated high initial yield stress caused by the 'false set' effect, He et al. (2019) and Zingg et al. (2008a) suggested that a pre-shearing of $50\text{-}100 \text{ s}^{-1}$ is required to break these agglomerates prior to testing in order to produce accurate yield stress results.

2.5 Adsorption

In order to determine the dispersing effect of a SP, a comparison needs to be made after the adsorption has taken place on the cement particle to effectively classify the SP in use (Yamada et al., 2000).

2.5.1 Adsorption measurements

One of the methods of measuring adsorption of a PCE SP on to a cement particle is to use a total organic carbon analyser (TOC) (Ferrari et al., 2011; He et al., 2019, 2017b; Ma et al., 2014; Plank et al., 2008b; Winnefeld et al., 2007; Yamada et al., 2001, 2001; Zhang et al., 2020; Zingg et al., 2009, 2008b). Yoshioka et al. (2002) used a total organic carbon analyser to measure the mass of the adsorbed superplasticisers on the component minerals of cement. Li et al. (2005) measured the adsorption of a concrete mixture by comparing the reduced amount of PCE SP, before and after mixing, within the aqueous phase by making use of a TOC analyser.

It is the portion of non-adsorbed PCE SP at equilibrium which remains in the solution after extraction that is measured by the TOC analyser (Plank et al., 2010). Tan et al. (2017) however found that it was not easy to produce accurate results for PCE SP utilising the TOC analyser and that extra precautions should be applied such as extracting the data during the early stage of hydration in order to differentiate between SP which adsorbed to the cement particle, and SP which have been consumed by the hydration products.

2.5.2 Adsorption or consumption

The solution depletion method is the most common method used to determine the amount of PCE adsorbed onto the cement particles through total organic carbon analysis (Flatt and Houst, 2001). Using the term consumed rather than adsorbed, best describes the interaction as it becomes hard to distinguish between SP being adsorbed or SP being consumed using the depletion method. The reason for this is that the solution depletion method cannot determine the concentration of SP adsorbed, although it gives us a close enough estimation which can be further used to quantify and understand the dispersing effects of SP.

2.5.3 Factors that have an effect on adsorption

Flatt and Houst (2001) indicated that one of the factors relating to the difference in the workability of cements produced with the same clinker can be the result of the grinding aid used. The grinding aid was found to have an influence on the adsorption of the SP onto the

cement particles. In their study they discovered that the grinding history of cement has a significant influence on the adsorption of a polysulfonate-polycarboxylate SP onto the surface of the cement particle. Even without the addition of an SP, it was found that the yield stress of a cement suspension decreased by 25% because of the effect of the grinding aid used (Flatt and Houst, 2001).

In order to be able to control the fluidity of a cement system, one first has to understand how SPs are adsorbed onto the component minerals of cement. The adsorption of the SP onto these component minerals is not done uniformly as the SP is more attracted to the aluminate phases, C_3A , C_4AF , hence more superplasticiser gets adsorbed onto the C_3A , C_4AF phase than the calcium silicate phase (Yoshioka et al., 2002).

Li et al. (2005) discovered that more adsorption takes place on the cement particles compared to that of fly-ash purely because of the higher quantity alkalinity and C_3A mineral within cement. The magnitude and the range in which adsorption has an influence is related to many coinciding parameters such as ionic strength, the degree of detachment of the polyelectrolyte backbone and the net surface charge (Kauppi et al., 2005).

2.5.4 The effects of sulphate ions on adsorption

The concentration of sulfate ions within a cement paste was found to have an effect on the adsorbing performance of the polycarboxylate SP on to the cement particle surface. It is the high concentration of sulfate ions within cement in the aqueous phase that decreases the adsorption because of the competitive adsorption of the polycarboxylate SP and the sulfate ions onto the cement particle (Yamada et al., 2001). The portion of the polycarboxylate SP that adsorbs onto the surface of the cement particle is the carboxylic group, and it is this carboxylic group that is being prevented from adsorbing due to competitive adsorption between dissociated carboxylic groups and the sulfate ions (Yamada et al., 2001).

2.5.5 The effect of the adsorption layer of the PC

The effectiveness of a PCE SP is dependent on its dispersing ability which is caused by the electrostatic forces of the adsorbed SP repelling the cement particles within the medium as well as the steric hindrance effect caused by the protruding side-chains of the PCE SP. Generally it is believed that the dispersing ability of a PCE SP increases with the increasing amount of PCE being adsorbed onto the surface of the cement particle. The dispersing ability is also more affected by the adsorption layer than by the adsorption amount, although the adsorption amount is the initial reason for the effectiveness of the dispersing effect (Shu et al.,

2016; Tan et al., 2016). The intensity of a photoelectron (the electron ejected from the surface of a material by the photoelectric effect) is much less after it has gone through the double layer, which means that the thickness of the adsorption layer can decrease the intensity of photoelectron. The thickness of the PCE adsorption layer onto the cement particle surface can be determined by the decrease in the intensity of photoelectron (Tan et al., 2016). They used x-ray photoelectron spectroscopy (XPS) data of silicon to determine the thickness of the adsorption layer by applying the following equations:

$$I(b) = I_0 \exp[-b/\lambda(E_k)] \quad 2.8$$

$$\lambda(E_k) = 49 E_k^2 + 0.11 (E_k)^{1/2} \quad 2.9$$

$$E_k = hv - E_b \quad 2.10$$

Where:

I_0 : the initial photoelectron intensity

$I(b)$: photoelectron intensity after it has gone through the adsorption layer

b : thickness of the adsorption layer, in nm

E_k : photoelectron kinetic energy after the photoelectron has gone through the adsorption layer, eV

E_b : electron binding energy, eV

hv : electron energy, eV

It has been reported by Dalas et al. (2015b) and Tan et al. (2016) that the dispersing ability is enhanced as the thickness of the adsorption layer increases. This is due to the increase in the steric hindrance caused by the thicker adsorption layer which improves the dispersing ability within a multicomponent SP system. This is why it is believed that the adsorption amount may not be the only decisive factor for enhancing the dispersing ability, but that the adsorption layer is more important and plays a greater role in the dispersing ability of the SP system (He et al., 2019; Stecher and Plank, 2020). Shu et al. (2016) and Tan et al. (2016) have reported cases where there was an increase in the dispersing effect in PC systems that produced low amounts of adsorption; the reason for the increase in dispersing ability can be related to the increase in the thickness of the adsorption layer. As the backbone of the PCE adsorbs onto the active adsorption points on the surface of the cement particle, the protruding side chains form complexes with the Ca^{2+} which increase the adsorption layer and subsequently improve this dispersing ability. The reason for the cases where the low adsorption amounts produce better dispersing ability is related to the long side chains of PEO which extend into the medium and increase the adsorption layer allowing for efficient dispersion of the SP system. Shu et al.

(2016) and Tan et al. (2016) have reported that the Ca^{2+} can form complex bonding with several carboxyl groups which create a multi-layer also known as a double layer (Shu et al., 2016; Tan et al., 2016).

It has been argued that it is not easy for PCE to establish a multiple adsorption layer because the long side chains of PEO of the PC that are adsorbed extend into the medium separating the different PCE molecules from each other. In addition to that, the distance between the un-adsorbed PCE in the solution and the adsorbed PCE are too far apart to be connected by the Ca^{2+} ion, and that PCE adsorption is more in accordance with the Langmuir monolayer adsorption (Tan et al., 2016). The linearised form of the Langmuir adsorption model can be applied to determine the adsorption constant and to analyse adsorption differences between PCE SPs and cement mixtures (Shu et al., 2016). The Langmuir adsorption model can be written as follows:

$$\frac{\text{PCE}_{(\text{Sol})}}{\text{PCE}_{(\text{Ads})}} = \frac{1}{A_s \cdot k} + \frac{1}{A_s} \cdot \text{PCE}_{(\text{Sol})} \quad 2.11$$

Where:

- A_s = represents the maximum adsorbed amount of PCE at saturation
- $\text{PCE}_{(\text{Sol})}$ = is the concentration of PCE within the solution at adsorption equilibrium
- $\text{PCE}_{(\text{Ads})}$ = is the concentration of adsorbed PCE
- k = represents the adsorption equilibrium constant

2.5.6 The effect of SP adsorption on the rheological properties

PCE SP is known to have an affinity towards a certain kind of cement mineral, thus does not adsorb evenly across the surface of the cement particle. The cement compounds that have the highest degree of adsorbed SP are the C_3A and the C_4AF , compared to the belite (C_2S) and the alite (C_3S). The fluidity of a cement mix is increased as a result of an even adsorption of the SP on the surface of a cement particle, as a result, requiring less admixture to obtain this effect (Hanehara and Yamada, 1999; He et al., 2017a; Zingg et al., 2008b).

The higher C_3A content of cement also has an influence on the physical properties of a cement paste by having an effect on the yield stress and viscosity as a result of more SP being

adsorbed onto the aluminate phase (Zingg et al., 2009). Figure 2.5 depicts a schematic illustration of PCE SP adsorbed onto the surface of a cement particle.

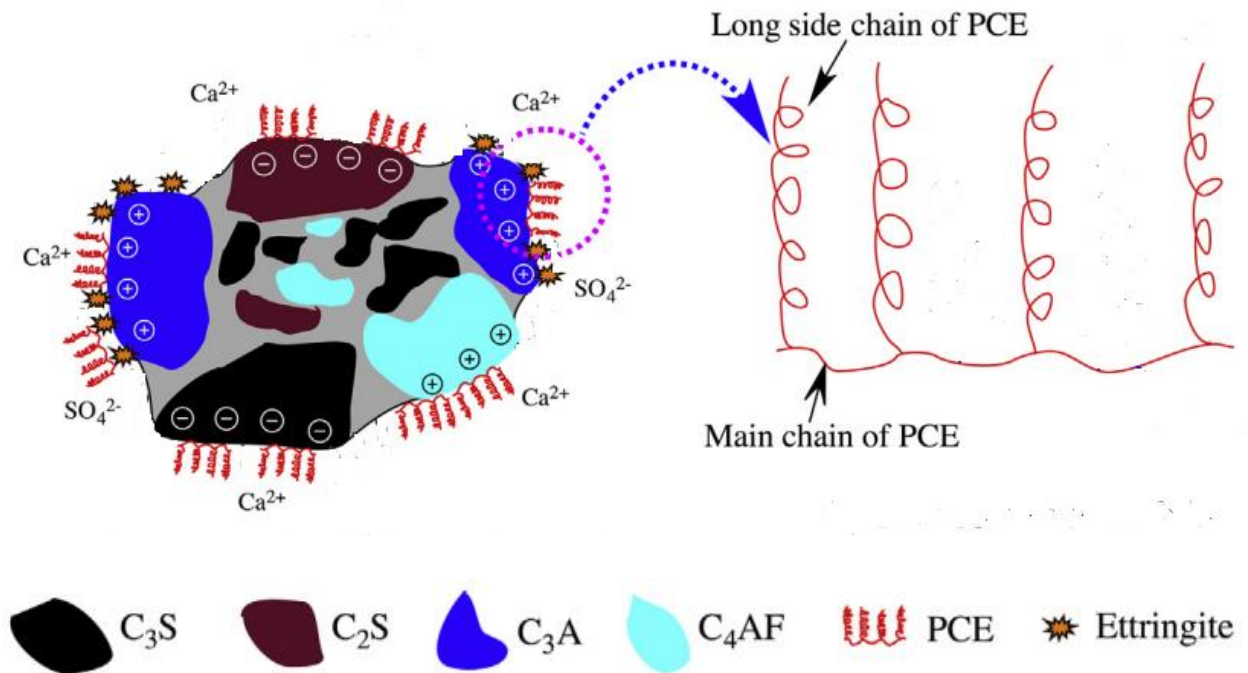


Figure 2.5: Schematic illustration of the dispersion model of PCE (Tan et al., 2017)

Hanehara and Yamada, (1999) discovered that delaying the addition of SP until after the water has been added to the mix, improves the rheological properties of concrete. This delayed addition of SP increases the flow value of a cement paste compared to the simultaneous addition of SP. Some researchers have concluded that this is the effect of more SP being adsorbed onto the hydration products (ettringite) (Liu et al., 2015; Tan et al., 2017; Zingg et al., 2009).

It is the positively charged phase that adsorbs the negatively charged trunk chain of the PCE SP. As more SP effectively adsorbs onto the surface of the cement particle, makes it become negatively charged. The cement particles then repel one another due to the reaction caused by like charges, releasing trapped water molecules, and resulting in more water being made available to increase fluidity. The hydration reactions of the four main clinker phases are affected by the presence of SPs which in return effects the rheological behaviour of the cement system (Kreppelt et al., 2002).

As the SP gets adsorbed onto the cement particle, it disperses the cement particles within the suspension medium by electrostatic or steric repulsion effects. This dispersing effect caused by the steric repulsive forces is what improves the fluidity of a cement paste by releasing

entrapped water from the flocculated cement grains, thus allowing these free water molecules to act as a lubricant between the cement particles resulting in an increase in workability. The polyethylene oxide (PEO) side chains of the PCE are responsible for the steric forces that cause the fluidising effect. It can be concluded from the literature that the dispersion of cement particles strongly influences the rheological behaviour of a cement paste (He et al., 2017a; Liu et al., 2015; Ma et al., 2014; Winnefeld et al., 2007; Zingg et al., 2008a).

2.5.7 Previous research on blended materials

The blending of material may result in improved results or it may retard the system depending on how the properties of the materials used react with each other. Alonso et al. (2013) investigated the compatibility between a PCE SP and a blended cement paste by comparing the effect it has on fluidity. They fitted the Bingham model to the flow curves to determine the yield stress (y-intercept, τ_0) and the plastic viscosity (the slope, μ) of the blended cement paste with the added SP. They also used the total organic carbon content to determine adsorption through the depletion method, and concluded that it was not easy to differentiate which cement had the highest adsorption within the blend because of the different mineral compositions within each cement. It was discovered that the adsorption of the PCE SP was highly dependent on the optimum sulphate content within the system, as this is required in order for it to react with the C_3A to form ettringite.

Li et al. (2011) observed the effect of two retarders on the fluidity of a paste containing an aminosulfonic-based SP and reported that competitive adsorption took place between the sodium gluconate (SG) and citric acid (CN) and aminosulfonic acid-based (AS) SPs when added to the same system. There was a decrease in adsorption of AS retarder when SG retarder was added to the same paste as more SG retarder competitively occupied the available adsorption sites. The same reduction in adsorption was observed by AS when CN was added to the paste. The SG and CN SP were found to desorb some of the AS SP from the adsorption sites within its respective mixtures. This decrease in adsorption of AS, reduced the dispersive capabilities of the AS SP due to the lack of available adsorption sites (Li et al., 2011).

It is suggested that when PC molecules are compared, it is best to do so with polymers that have a similar structure or general composition especially when comparing simultaneous adsorption and the effectiveness thereof. However when polymers with different lengths of side chain are compared, using the anionic charge density to differentiate them is preferred as adsorption is highly linked to the anionic charge density of the polymer. Therefore if more than

one additive is present within a mixture, the order of adsorption of those polymers will depend on their relative anionic charge density per mole (Plank and Winter, 2008).

Yoon and Kim, (2018) utilised a mini-slump cone test to evaluate the fluidity of a cement paste consisting of three PCE SPs and reported that a mixture incorporating multiple SP admixtures upon the mixing process produced an increased slump loss. In industry, two agents are blended together to produce a marketable brand of high-range water-reducing agents (HRWRA) based on findings of relevant slump loss, as reported above (Yoon and Kim, 2018).

Bey et al. (2014) observed the competitive adsorption between a viscosity enhancing agent derived from methyl- hydroxyl- ethyl cellulose (CE) and a polycarboxylate SP (PCE), by evaluating their effect on the rheological behaviour of a cement paste in relation to their adsorption capabilities, when both polymers were added to the cement paste simultaneously. They used a constant dosage of 0.3 bwoc for both CE and PCE and fitted flow curves to the Bingham model to determine the influence of the polymers on the yield stress and the viscosity of the cement paste. The TOC was determined by the depletion method to correlate the adsorption to the rheological results obtained and it was concluded from the investigation that the competitive adsorption between the two polymers prevented most of the CE polymer from adsorbing to the cement surface. This allowed the unadsorbed CE polymer remaining in the medium to contribute to increasing the fluidity of the cement paste (Bey et al., 2014).

The influence of 8 PCE SPs on the fluidity of a cement paste which contained silica-fume was investigated by Matsuzawa et al. (2019). The aim of the investigation was to observe the effect of the non-adsorbing SP on the adsorption and fluidity of the silica fume cement paste. The SPs used all had different molecular structures differentiated only by side chain length and by the amount of COO⁻ units in their main chain. However the average molecular weight of all the SP used was approximately 10 000 g/mol. The first SP was added to the paste with subsequent dosages of the second SP being added after the adsorption of the first SP had reached surface saturation. The fluidity was determined by a rotational viscometer and the adsorption was determined using a total organic carbon analyser, by using the depletion method. It was concluded that the SP-containing higher COO⁻ units had higher adsorption amounts and that the effect of the non-adsorbed SP depended on the molecular structure of the SP as the steric hindrance caused by the longer side chains had a greater effect on increasing the fluidity. However, SP with shorter side chains can still aid in increasing the fluidity by intercalating between particles (Matsuzawa et al., 2019).

When there are several admixtures of the same chemical structure present within a mixture, the admixture with the highest anionic charge is preferably adsorbed first and in a higher

amount, the admixture with the lowest anionic charge density remains within the mixture awaiting an opportunity to adsorb onto the surface of the cement particle as the initial adsorbed admixture gets consumed by the hydration products (Plank and Winter, 2008). The effects of non-adsorbed polymers in a system where there are multiple polymers with different molecular structures that are competitively competing for adsorption sites are not yet fully understood (Matsuzawa et al., 2019).

2.6 Conclusion

The chemical composition and the compounds in cement react differently with certain admixtures (Ferrari et al., 2011). SPs improve the workability of a cement mixture by increasing the fluidity without adding additional water to the mix, thus making SPs the most preferred admixture in the construction industry with regards to SCC (Kauppi et al., 2005; Kreppelt et al., 2002; Yousuf et al., 2017).

Polycarboxylate-type (PCE) SP is one of the key additives when it comes to producing a SCC with high strength because it reduces the water/cement ratio and because of its superior dispersing ability of the cement particles (Plank et al., 2008a; Yamada et al., 2001).

Polymers are defined by their designation which describes the trunk chain length, length of side chains as well as the charge density of the polymer. The performance of the PCE SP is highly dependent on parameters such as the main chain length, side chain length and the side chain density, which all contribute to the dispersion of cement particles by inducing a negative charge onto the cement particle. It is the positively charged interstitial phase (C_3A , C_4AF) that adsorbs the negatively charged trunk chain of the SP. As more SP effectively adsorbs onto the surface of the cement particle, it causes it to become negatively charged. It is this negative charge that causes the cement particles to repel each other, releasing water molecules trapped between the cement agglomerates, thus improving fluidity (Ferrari et al., 2011; Plank et al., 2008b).

PCE SP is known to have an affinity towards a certain kind of cement compound thus it does not adsorb evenly across the surface of the cement particle. The cement compound that has the highest degree of adsorbed SP is C_3A and C_4AF , compared to belite (C_2S) and alite (C_3S). The fluidity of a cement mix is increased as a result of an even adsorption of SP on the surface of a cement particle, as a result requiring less admixture to obtain this effect (Hanehara and Yamada, 1999; He et al., 2017b; Zingg et al., 2008b).

The higher C₃A content of cement also has an influence on the physical properties of a cement paste by having an effect on the yield stress and viscosity as a result of more SP being adsorbed onto the aluminate phase (Zingg et al., 2009).

As the SP is adsorbed onto the cement particle, it disperses the cement particles within the suspension medium by electrostatic or steric repulsion effects.

The dispersion of cement particles strongly influences the rheological behaviour of a cement paste (He et al., 2017b; Liu et al., 2015; Ma et al., 2014; Winnefeld et al., 2007; Zingg et al., 2008a).

The fluidity of a concrete paste can be improved by the dispersing of the cement particles within a cement system. This can be achieved by adding SPs to the concrete mixture to achieve this effect (Li et al., 2020; Yoshioka et al., 2002).

Many authors have made use of a mini-slump cone/ flow cone to determine the rheological properties of a low viscosity cement paste (Chen et al., 2020; He et al., 2017b; Li et al., 2005; Lin et al., 2021; Prince et al., 2003; Tan et al., 2017; Yamada et al., 2000; Zhang et al., 2020).

However, the rheometer was found to be the most commonly used for this and better describes the shearing forces within a cement paste that encourages the flow of a material (He et al., 2019; Hot et al., 2014).

One of the latest SPs in industry is the polycarboxylate-based type SP, yet no extensive research can be found focusing specifically on the effects it has on hydration and rheology of cement paste (Ferrari et al., 2017; Kreppelt et al., 2002; Sha et al., 2020).

It is clear from the literature that an investigation into the strength and type of PCE adsorption of different cement pastes is needed to better understand this relationship (Winnefeld et al., 2007; Zhang et al., 2020; Zingg et al., 2008a).

3 Chapter Three: Research Methodology

3.1 Introduction

This chapter discusses the methodology followed to answer the research question and reach the set objectives, and explains the research design, the research methodology as well as the

characterisation of the materials. The instruments used and the procedures followed in order to meet the objectives are also discussed.

3.2 Research design

This research investigated the effect of the interaction between two different polycarboxylate-based SPs which were blended at different proportions to improve the rheological properties of cement paste. The SP dosage was determined experimentally by observing the change in yield stress. An optimum SP dosage of 0.25%, by weight of cement, was used for all the tests. The rheological results were determined by using a rheometer and the mini-slump test was used to determine the workability loss in terms of yield stress. The total organic carbon content was used to determine the adsorption results in order to find a correlation between the rheological parameters; of cement pastes and the SP adsorption behaviour. A comparison was undertaken between the results of the different cements and a conclusion was drawn based on the effect of these SP blends on the rheological properties of the three cements.

3.3 Research methodology

This study was apportioned into four phases.

3.3.1 Phase 1

Phase 1 consisted of modifying the SP as a reagent of two different SPs by mixing them at predetermined ratios where SP-C will indicate x% of SP-A in the product SP and the difference is y% of SP-B fraction. Note that these proportions are based on the optimum dosage that was determined in previous experiments as explained in section 3.2. The two reactant SPs (SP-A and SP-B) were blended together by weight at predetermined ratios and the product was SP-C.

3.3.2 Phase 2

Phase 2 determined the effect that blended SPs have on the rheological behaviour of cement pastes by assessing their rheological parameters (yield stress and viscosity).

3.3.3 Phase 3

Phase 3 determined the loss of workability of each cement paste by measuring the orthogonal mean of the spread over time by utilising a mini-slump cone. This test was used to confirm the workability loss as determined by measuring the yield stress at different resting times of the cement pastes.

3.3.4 Phase 4

Phase 4 determined the degree of adsorbed SP of each blended SP by measuring the concentration of SP in the solution before and after mixing it with the cement paste by using a total organic carbon (TOC) analyser.

3.3.5 Experimental matrix

The experimental matrix is presented in figure 3.1

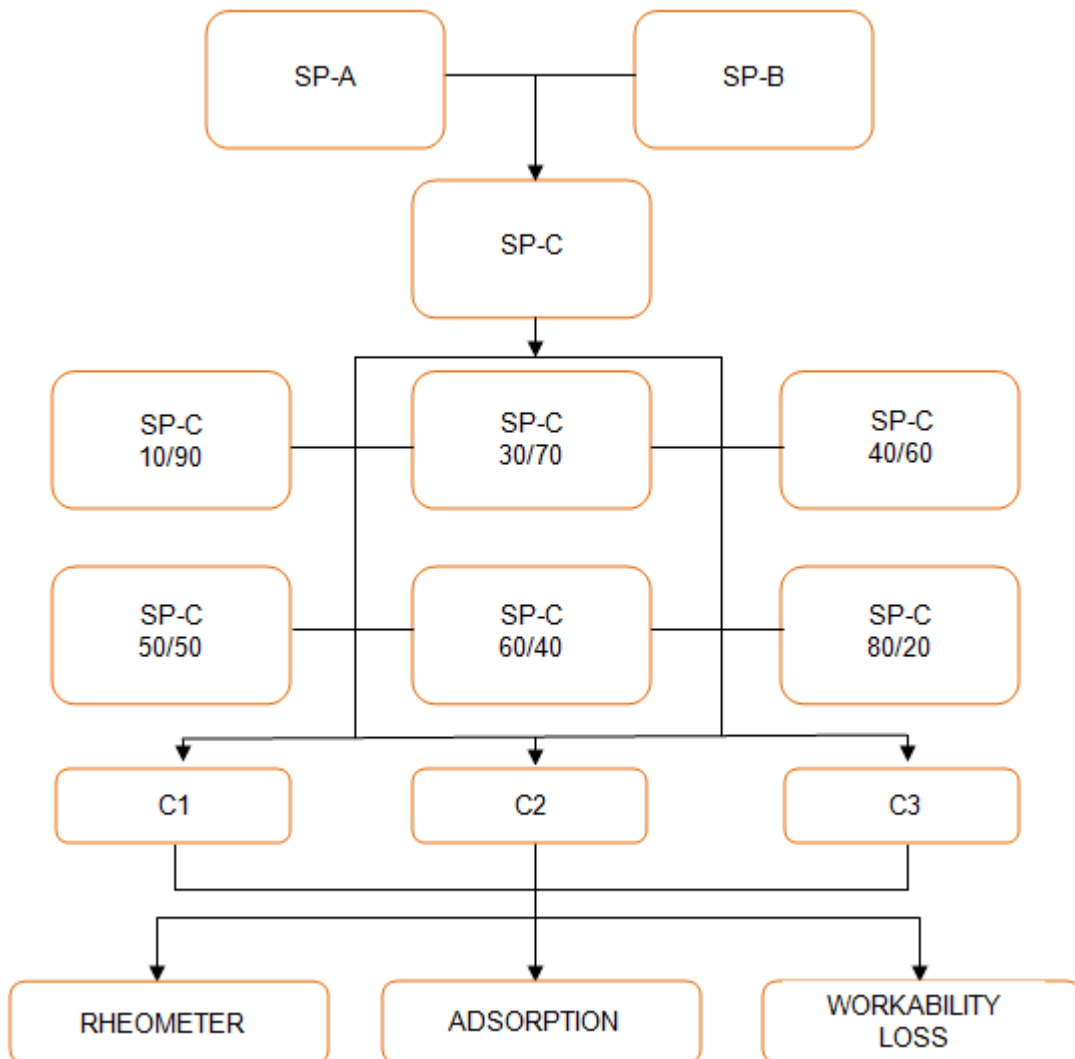


Figure 3.1: Experimental matrix of project

3.3.6 Research instruments

This section describes the equipment used and the procedures followed. The rotational rheometer is used in cement technology to measure the rate of shear of the fluid layers of low viscosity cement paste in order to produce flow curves. These flow curves were used to determine the rheological properties of the cement paste such as the viscosity and yield stress (Erzengin et al., 2018; He et al., 2019). This assisted in observing how the blended SP affects the fluidity of a low viscosity cement paste. The mini-slump cone was used to measure the spread of the cement paste over time. This test determined the loss of workability of the fresh cement paste. The TOC was determined by a TOC analyser which measured the adsorption of the blended SP on to the cement particle. The adsorption can be determined by measuring the total organic carbon remaining in the solution after adsorption.

Rheometer

An Anton Paar MCR51 rheometer was used for the experiments. The rheometer has a fixed plate which was fitted with a 50 mm diameter parallel steel plate attachment roughened on the surface of the plate to prevent slipping, and the gap between the two plates was 0.6 mm (Xie and Kayali, 2016; Zingg et al., 2009, 2008b).

The rheometer was used to determine the rheological properties of the fresh cement paste by making use of the hysteresis loop measuring technique. The hysteresis loop consists of two curves of shear stress measurements which start at a low shear rate and end at higher shear rates, and then decreases back to the lower shear rate. Measurements were recorded at 10 intervals going up and down, with test duration of 150 s for each cycle totalling 300 s for all the tests (15 s per measuring point). Before the start of each test, the cement samples were pre-sheared at a shear rate of 50 s^{-1} for 10 s to break down any agglomerates that could have formed at the start of the measurement. The down curve flow was then fitted to the Bingham model to determine the yield (Chen et al., 2020; He et al., 2019; Li et al., 2020).

Method

The following method was performed for each test related to the rheometer:

- 100 g of cement powder was weighed on a digital scale.
- 45 g of distilled water was weighed but varied and was adjusted w.r.t the percentage of SP used.
- The SP was added to the distilled water by using a syringe at a percentage w.r.t the weight of the cement (Chen et al., 2020; He et al., 2019; Lin et al., 2021).

- The distilled water (with SP) was added to the cement powder and was immediately mixed for exactly two minutes before adding the sample to the rheometer for measurement.
- The sample was trimmed and covered with a sample protection cell in order to prevent it from losing water through evaporation during the experiment.
- The temperature controlling bath attached to the rheometer was used to maintain the temperature at 25°C (Chen et al., 2020; Erzenin et al., 2018; Zhang et al., 2019).
- The sample was first pre-sheared at 50 s⁻¹ for 10 seconds in order to break down any agglomerates or network of hydrates in the time it took to prepare the sample.
- Hysteresis loops were obtained by applying a shear rate from 0.1 s⁻¹ to 100 s⁻¹ and then back down from 100 s⁻¹ to 0.1 s⁻¹ measuring 10 points up and 10 points down spending 15 seconds per measuring point, which totaled to a measuring time of 300s.

Mini-slump

The mini-slump test was used to determine the loss of workability of a fresh cement paste by measuring the orthogonal diameter of cement paste spread at different intervals of time. Fresh cements were prepared according to the same procedure for all experiments. The fresh cement paste was poured into the top opening of the cone and allowed to settle for 30 seconds. Thereafter, the cone was slowly and vertically lifted, nullifying thus the inertia effect for reproducibility of the experiment (Liu et al., 2017a, 2017b). The time was recorded the moment the cone was completely lifted and the spread came to a complete stop. The orthogonal measurement of the diameter was recorded and the mean diameter was then used, with the time it took the spread to come to a stop to calculate the yield stress value (Zhang et al., 2020, 2016; Zhu et al., 2018). The volume of the cone was calculated from the dimensions in Figure 3.2.

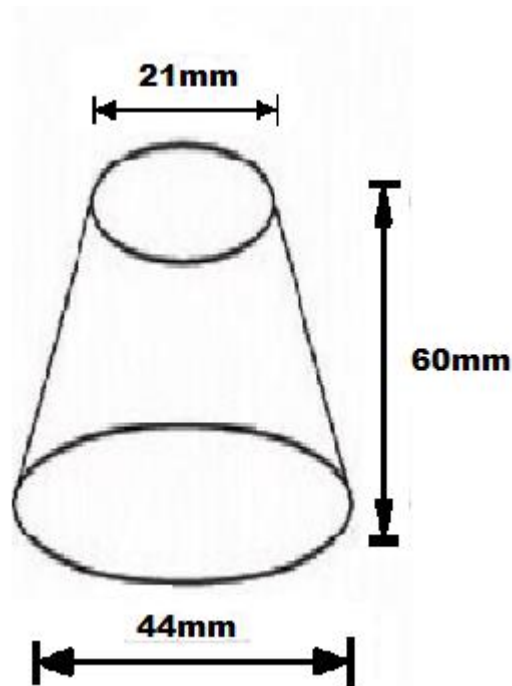


Figure 3.2: Dimensions of the mini-slump cone

The mean diameter of the spread and the final spread time including the volume of the cone were used to determine the yield stress by using Equation 2.7 (Qian et al., 2018; Tian et al., 2019; Yang et al., 2019). This procedure conforms to the test procedure DIN 1164 and is in accordance to the Chinese standard GB/T 8077-2012 (2012) (Chen et al., 2020; Chomyn and Plank, 2019; Dalas et al., 2015a, 2015b; Lange and Plank, 2016; Lin et al., 2021, 2019; Marchon et al., 2019).

Total Organic Carbon experimental procedure

The Hach DR1900 spectrometer was used for the TOC analysis. The objective of this experiment was to determine the amount of polycarboxylate-based superplasticiser that adsorbed onto the cement particles. As the adsorption reached saturation, un-adsorbed SP remained in the medium and assisted with fluidity. The aim of this experiment was to determine the amount of SP before and after adsorption through the depletion method (Bessaies-Bey et al., 2016; Erzenin et al., 2018; Hot et al., 2014; Lange and Plank, 2016; Liu et al., 2014; Marchon et al., 2019; Qian et al., 2018; Yang et al., 2019; Yoon and Kim, 2018; Zhang et al., 2017; Zingg et al., 2009).

Sample preparations

- SP was mixed with water before adding the wet mixture to the dry cement.
- The fresh paste was mixed for 2 minutes to ensure that everything was fully homogeneous (He et al., 2019; Lu et al., 2017).
- The fresh paste was immediately transferred to the centrifuge tube at a predetermined volume to ensure consistency.
- The cement paste was centrifuged at 3000 - 8000 rpm for 5 minutes to separate the solids from the liquids (Chen et al., 2020; Erzengin et al., 2018; He et al., 2019; Hot et al., 2014; Li et al., 2020; Liu et al., 2014; Lu et al., 2017; Yang et al., 2019; Zhang et al., 2018, 2017).
- The supernatant was removed with a glass syringe and the sample was stored in a glass vial, tube or container.
- The sample was then diluted with deionised water to meet the reading range of the instrument.

Sample dilution

The sample was diluted 5 x (5-fold: sample was diluted by a factor of 5) to reach the reading range of the TOC analyser (Plank and Winter, 2008). The following steps were followed to complete the 5-fold dilution:

- 2 mL of the sample was added to a 100 mL volumetric flask
- 8 mL of deionised TOC-free water was added to the sample (2 mL sample + 8 mL of deionized water) and homogenised with a stirrer bar for 5 minutes

The test procedure was done according to method 10128 from the Hach DR 1900 manual, and the depletion method was followed to determine the adsorption of the SP.

3.3.7 Materials characterisation

This section explains the different materials used for the investigation. The chemical analysis of the cement and SP helps to define the characteristics of the materials.

Cement characterisation

The chemical analysis was done by X-Ray Fluorescence Analysis (XRF) to determine the oxide composition of the cements used.

The chemical analysis showing the oxides of the cements used in this investigation is presented in Table 3.1.

SPs are more attracted to the positive surface of the cement particle C₃A on entering the medium therefore increasing the adsorption to the cement particle. The oxides which spontaneously formed the C₃A compound consisted of Al₂O₃ and CaO. The chemical oxides in Table 3.1 show that Cement 3 had a higher percentage of Al₂O₃ (4.47%), and Cement 1 had the lowest percentage of Al₂O₃ (3.07%). Cement 2 had the highest percentage of CaO (65.66%), and Cement 1 presented the lowest percentage of CaO (63.46%). Cement 1 had the lowest percentages of Al₂O₃ and the lowest percentage of CaO when compared to the other cements. It was assumed to present lower adsorption when compared to the other cements, although C₃A is formed spontaneously.

The alkali content in cement is responsible for increasing the pH of the pore water allowing more ions to be released. An increase in alkali equivalent content (Na, K) of cement can lead to a delay in the final setting time. The alkali equivalent can be calculated by the following equation:

$$\text{Na}_2\text{O}_{\text{eq}} = \text{Na}_2\text{O} + 0.685 \text{K}_2\text{O} \quad 3.1$$

The cement with the highest alkali equivalent is Cement 2 (0.64%), compared to Cement 1 (0.62%) and Cement 3 (0.21%) which had the lowest alkali equivalent.

Table 3.1: Cement oxides of each CEM II cement

Chemical Oxides (%)	Cement		
	Cement 1	Cement 2	Cement 3
SiO ₂	22.6	19.9	20.2
Al ₂ O ₃	3.07	4.14	4.47
Fe ₂ O ₃	4.83	2.89	3.06
Mn ₂ O ₃	0.09	0.06	0.67
TiO ₂	0.39	0.24	0.28
CaO	63.46	65.66	63.72
MgO	1.52	0.90	2.62
P ₂ O ₅	0.08	0.12	0.05
SO ₃	2.51	2.46	3.53
Cl	0.00	0.00	0.00
K ₂ O	0.49	0.70	0.22
Na ₂ O	0.28	0.16	0.06

LOI	1.45	3.05	1.99
Total	100.8	100.3	100.9

The physical properties of the cement used in this investigation are tabulated in Table 3.2

Table 3.2: Physical properties of the cement used

Physical Testing	Cement			
	Cement 1	Cement 2	Cement 3	
Relative Density	3.09	3.15	3.12	
Specific Surface, cm ² /g	3800	4300	4100	
Standard Consistency, %	28.0	27.6	28.0	
Initial Set	Min	180	130	100
Final Set	Min	195	150	120
32 µm Residue, %	15.6	23.2	9.5	
45 µm Residue, %	5.3	10.3	2.2	
90 µm Residue, %	0.2	0.8	0.1	
212 µm Residue, %	0.0	0.1	0.0	

From the physical properties presented in Table 3.2 it was observed that Cement 2 has the highest specific surface area. Higher specific surface area will show fine cement which might require a higher quantity of SP for optimum adsorption or more SP to cover the adsorption areas of the cement particle.

Sulphate adsorbs to the surface of the cement particle and can reduce the adsorption of the SP. The SO₃ content being more dominant in Cement 3 (3.53%) could present inconsistencies in SP adsorption when compared to the latter cements.

Superplasticiser characterisation

The SPs used for this project were named SP-A and SP-B, which are two PCE polymers used for different applications in industry. SP-A which is used in the premix industry for SCC, and SP-B which is used in industry for ready-mix SCC, were both prepared by radical polymerisation and are based on methacrylic acid MPEG-methacrylate. The molecular weights of the two polymers as received from the supplier were as follows:

- **SP-A** = 42 000 (g/mol)
- **SP-B** = 40 000 (g/mol)

A comparison between SP-A and SP-B can be observed in Table 3.3 followed by the characterisation of the PCE SP used for this investigation.

Table 3.3: Characteristics of Superplasticiser

Characteristics	SP-A	SP-B
Consistency	Liquid	Liquid
Colour	Amber	Amber
Density according to ISO 758 (g/cm ³)	1.08 ± 0.02	1.07 ± 0.02
Dry content according to EN 480-8 (%)	30.5± 1.5	30± 1.5
Chlorides soluble in water according to EN 480-10 (%)	<0.1	<0.1
Alkali content (Na ₂ O equivalent) according to EN 480-12 (%)	<3	<2.5

SP-A is described as a highly negatively charged polymer with a non-ionic backbone consisting of long thin side chains which result in a strong affinity towards the surface of the cement particle through electrostatic adhesion, ensuing high mechanical resistance for shorter periods.

SP-B is described as a lower negatively charged polymer with a non-ionic backbone consisting of shorter and thicker side chains, resulting in a slower adhesion to the cement particle providing moderate mechanical resistance for longer periods.

These descriptions can be confirmed by using a method used by Janowska-Renkas, (2013) where the hydrophilicity of the side chains are used to describe the efficiency of the polymer to increase the fluidity of a cement paste. According the Janowska-Renkas (2013), the longer the side chains of the polymer, the higher the hydrophilicity of the polymer resulting in an increase of the efficiency of the polymer (Sha et al., 2020). The long side chains are also linked to a higher molecular weight of the polymer, resulting in a stronger affinity towards the cement particle and an increase in fluidity due to the improved steric hindrance provided by the long side chains.

The hydrophilicity can be determined by using the method described by Janowska-Renkas, (2013) where the ratio of the hydrophilic oxyethylene ether groups (O-CH₂CH₂) and the hydrophobic ester groups (O=C-O-CH₂), are used to define the hydrophilicity of a polymer.

Figure 3.3 presents the infra-red spectrum of the polymers SP-A and SP-B at a wavelength range (spectral range) of 4000 cm⁻¹ to 900 cm⁻¹, displaying the aliphatic, carbonyl and ether groups.

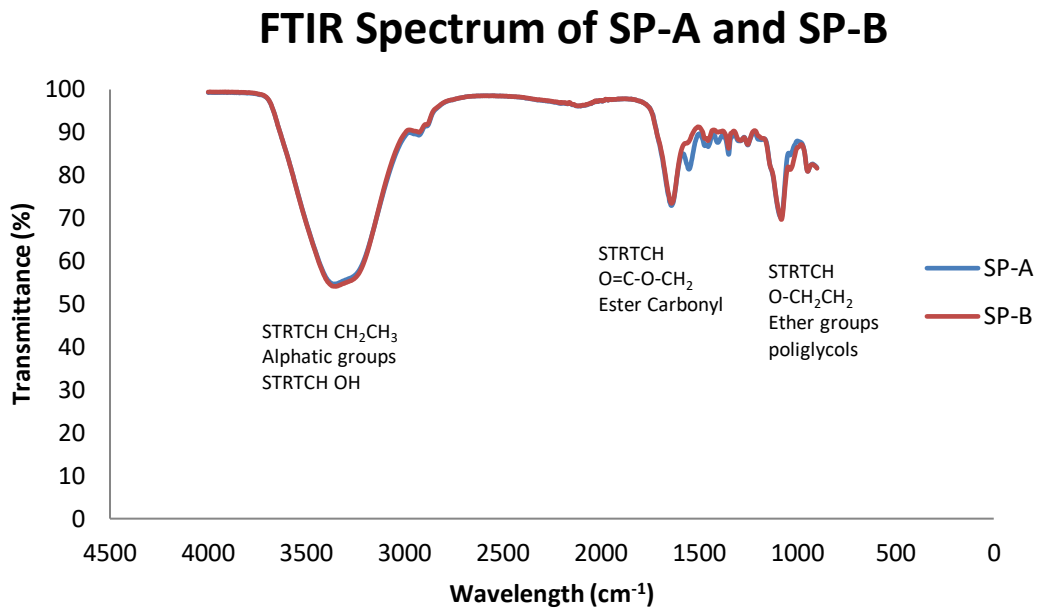


Figure 3.3: Infra-red spectrum of SP-A and SP-B (4000 cm⁻¹- 900 cm⁻¹)

Figure 3.4 presents the Infra-red spectrum of SP-A and SP-B at a spectral range of 2000 cm⁻¹ to 900 cm⁻¹.

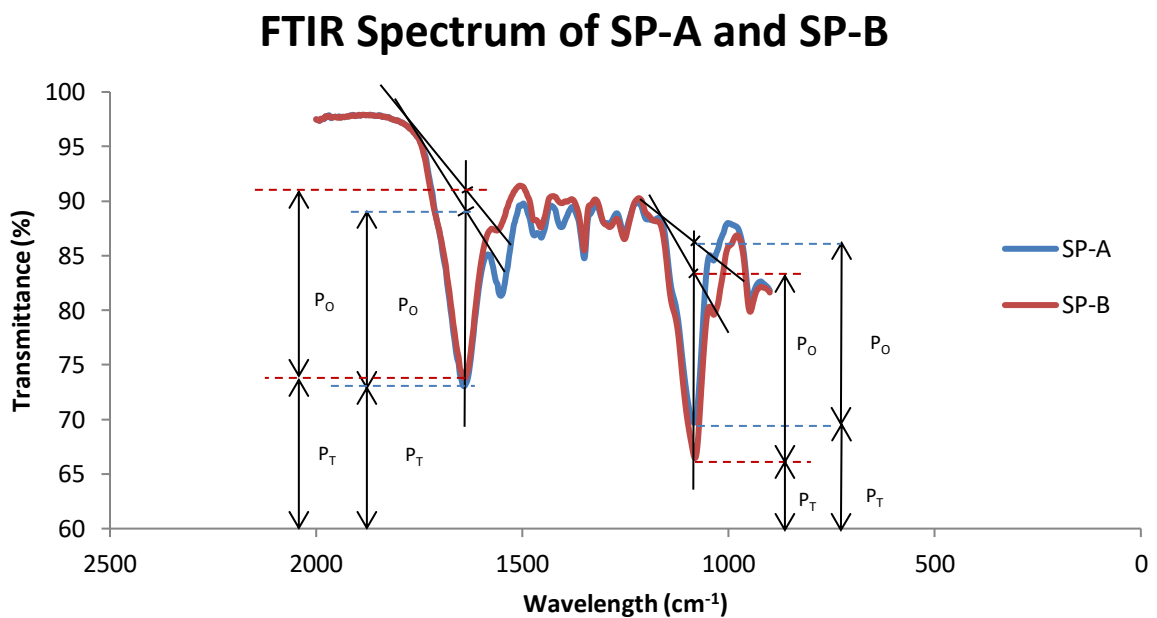


Figure 3.4: Infra-red spectrum of SP-A and SP-B (2000 cm⁻¹- 900 cm⁻¹)

This spectral range used in Figure 3.4 will be used to determine the hydrophilicity of the polymers as this range provides the clearest distinction of the two peaks in discussion.

Method 1

In order to use the method described by Janowska-Renkas, (2013), the absorbance was calculated from the transmittance as described below. The absorbance which is related to a relative baseline, established for the absorption band, can be used to define the hydrophilicity of the side chains of the PCE SP.

$$A = -\log \frac{P_T}{P_0} \quad 3.2$$

Where A is the calculated absorbance, P_0 (%) is the baseline (initial intensity) and P_T (%) is the transmittances.

SP-A

$$A = -\log \left(\frac{73}{89} \right) = 0.086 \text{ (First peak } 1640 \text{ cm}^{-1} \text{ Ester group)}$$

$$A = -\log \left(\frac{70}{86} \right) = 0.089 \text{ (Second peak } 1080 \text{ cm}^{-1} \text{ Ether group)}$$

$$\text{Hydrophilicity of SP-A } (A_{ET}^{1080} / A_{ES}^{1640}) = \frac{0.089}{0.086} = 1.035 \quad 3.3$$

SP-B

$$A = -\log \left(\frac{74}{91} \right) = 0.09 \text{ (First peak } 1640 \text{ cm}^{-1} \text{ Ester group)}$$

$$A = -\log \left(\frac{67}{83} \right) = 0.093 \text{ (Second peak } (1080 \text{ cm}^{-1} \text{ Ether group)}$$

$$\text{Hydrophilicity of SP-B } (A_{ET}^{1080} / A_{ES}^{1640}) = \frac{0.093}{0.09} = 1.033 \quad 3.4$$

With the calculations above it was determined that the hydrophilicity of the side chains of SP-A were greater than that of SP-B which can be interpreted as a prediction that SP-A will have a greater effect in increasing the fluidity of cement pastes.

Method 2

This method followed the same procedure in determining the hydrophilicity of the side chains (Ether groups/Ester groups), but instead of using the ratio in absorbance peaks to determine the hydrophilicity, the area of the peak was used instead.

SP-A

- $\text{Area}_{\text{ES}}^{1640}$ of peak $1640 \text{ cm}^{-1} = 715.79 \text{ \%T.cm}^{-1}$
- $\text{Area}_{\text{ET}}^{1080}$ of peak $1080 \text{ cm}^{-1} = 1023.68 \text{ \%T.cm}^{-1}$

$$\text{Area}_{\text{ET}}^{1080} / \text{Area}_{\text{ES}}^{1640} = 1023.68 / 715.79 = 1.43 \quad 3.5$$

SP-B

- $\text{Area}_{\text{ES}}^{1640}$ of peak $1640 \text{ cm}^{-1} = 1899.57 \text{ \%T.cm}^{-1}$
- $\text{Area}_{\text{ET}}^{1080}$ of peak $1080 \text{ cm}^{-1} = 910.28 \text{ \%T.cm}^{-1}$

$$\text{Area}_{\text{ET}}^{1080} / \text{Area}_{\text{ES}}^{1640} = 910.28 / 1899.57 = 0.479 \quad 3.6$$

Hydrophilicity = SP-A > SP-B

The areas under the peaks that were considered for the calculation above where the ratio between the hydrophilic Ester groups and the hydrophobic Ether groups of the PCE structure were used to determine the hydrophilicity of the side chains. It can be seen that Method 2 confirms the results obtained from Method 1 which established that SP-A has a greater hydrophilicity compared to SP-B, which translates to SP-A being more efficient in increasing fluidity. This validates the information received from the suppliers about the two polymers.

3.3.8 Data analysis

The results obtained from the TOC analysis were tabulated indicating the percentage differences of the SP in the solution before and after adding it to the cement paste. The difference between the percentages gives an indication of the degree of adsorbed SP which can be used to understand the rheological behaviour of cement pastes. The depletion method was used to determine the adsorbed SP. It uses the amount of SP remaining in the solution after adsorption has taken place within the solution.

The results obtained from the rheometer were recorded as a flow curve. Rheological parameters were extrapolated from the flow curve by using the Bingham model to determine the yield stress and viscosity of the cement paste.

The results obtained from the mini-slump cone test gave an indication of the loss of workability of the cement paste and the spread measurement were tabulated with respect to the ratio of SP used, the concentration of SP and cement.

3.4 Conclusion

Rheological parameters were measured on an Anton Paar MCR51 rheometer. The SP optimisation was done by observing the yield stress development over a range of SP dosages. The optimum dosage was therefore the percentage of SP which with further increase in SP, did not affect the yield stress value for a given cement mixtures. This exercise was done for all three cements used.

The blended SP which was used for all the experiments consisted of a mixture of SP-A and SP-B blended together at ratios (SP-A / SP-B) of 10% / 90%; 30% / 70%; 40% / 60%; 50% / 50%; 60% / 40% and 80% / 20%. The rheological properties were determined by using the rheometer to observe the effect of the blended SP on the rheological behaviour of three different cements using the Bingham model.

The mini-slump test was used to determine the effect the blended SP had on the loss of workability of the three cements. The adsorption of the SP onto the cement was determined by using the depletion method, which can be described as determining the amount of SP left in the solution after adsorption has occurred, to determine the amount of SP adsorbed onto the cement. The amount of SP within the solution was used to observe the adsorption by determining the TOC content within the solution after adsorption occurred.

The adsorption results was correlated with the rheological data collected from the rheometer and the workability loss data collected from the mini-slump test to provide a better understanding of the relationship between the adsorption of the SP and the rheological properties of cements produced at different plantations.

The different compositions and properties within the different cements were observed which can provide an understanding on the change in rheological behaviour as it was discovered in the literature that the different compositions within the cements can have an effect on the adsorption and dispersing ability of the SP.

4 Chapter Four: Results

4.1 Introduction

The objective was to study the effect of a blended SP, which is made up of fractions of two different SPs, on three CEM II cements with different chemical and physical properties. Chemical admixtures such as SPs are used to increase the flowability of concretes by reducing the yield stress. The objective was to study the effect of two SPs blended at various ratios. The TOC test was done in order to determine the adsorption of the SP onto the cement particle. The results in this section are presented in graphs and analysed in order to observe a trend produced by the fractions of the blended SP.

4.1.1 Optimisation of SP-A and SP-B

The effect of a blended superplasticiser on three different CEM II cements is not fully understood. The SPs were blended by combining two different SPs (SP-A and SP-B) at different ratios to determine the effect of the modified SP on the three cements.

The blending of the SP had to take place at the individual optimum dosage of the reactants. This dosage was obtained by observing the yield stress performance over a range of different SP dosages. The optimum dosage was that at which the yield stress was not affected by further increase in SP dosage.

The SP dosages were varied from 0% to 0.8% at a rate of 0.1%. Optimisation was done by observing the change in the yield stress trend in order to observe the point where no further noticeable change occurred as the additional amount increased from 0.1% to 0.8%. This change in the trend identified the change point within the yield stress results and was chosen as the optimum dosage. It was determined that 0.25% by weight of the cement was used for all the mixtures. The method mentioned above is presented in Appendix A.

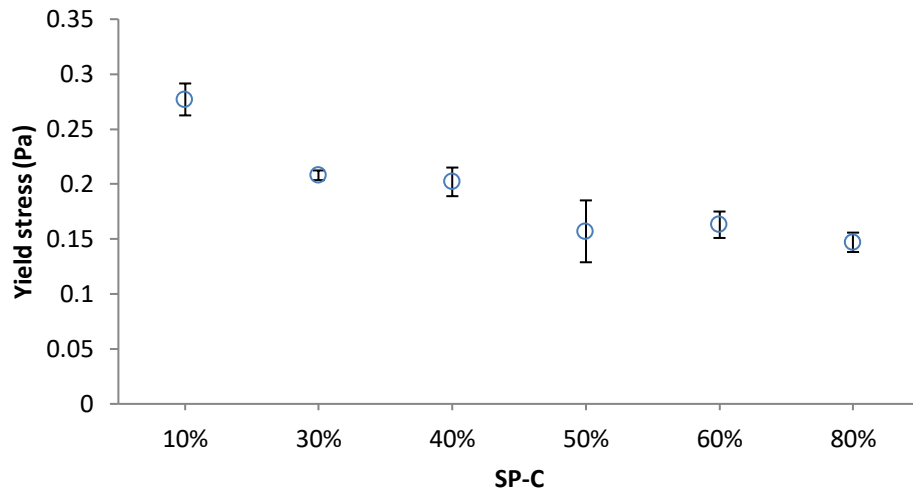
4.2 Effect of blended SP on the cement paste yield stress

The individual SPs were optimised and then blended at different fractions in order to study the effect of the product on cement paste rheology. The blended SPs affected the cement paste mixture by reducing the yield stress as the SP-A content within SP-B increases. Observing the reduction in yield stress helped in understanding the effect of the blended SP on the cement paste. The results were collected by placing a cement paste sample in the rheometer, and then the yield stress was obtained by using the Bingham modal.

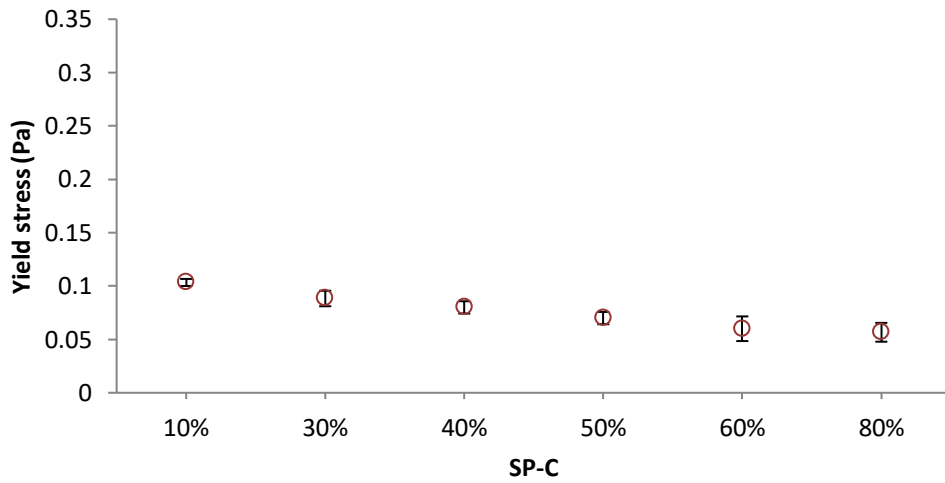
The yield stress results indicate the stress needed to initiate flow within a cement paste mixture. SP reduces the yield stress which results in an increased flowability of the cement paste mixture.

The effect of the blended SP on the yield stress of the cement pastes is presented in Figure 4.1.

a)



b)



c)

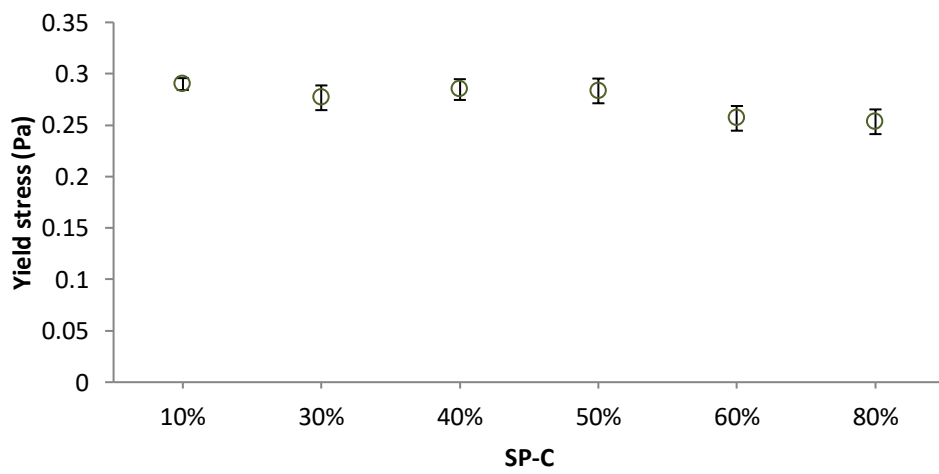


Figure 4.1: Yield stress (Pa) of Cement 1 (a), Cement 2 (b) and Cement 3 (c) with SP-C expressed in fraction of SP-A at optimum dosage of 0.25%

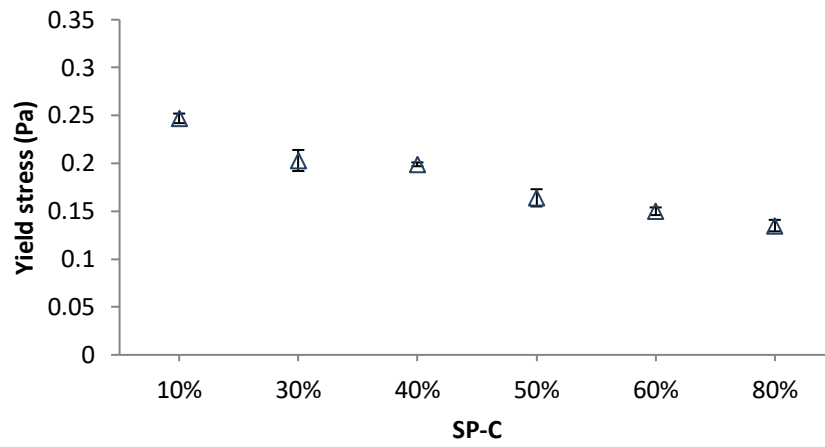
It is shown in Figure 4.1 (a), (b) and (c) that the combination of the two polymers effectively reduced the yield stress of the cement pastes. There was a 46% reduction in yield stress for Cement 1, a 40% reduction for Cement 2 and a 14% reduction for Cement 3 as the SP-A fraction within SP-B increased.

Effect of blended SP on the cement paste workability

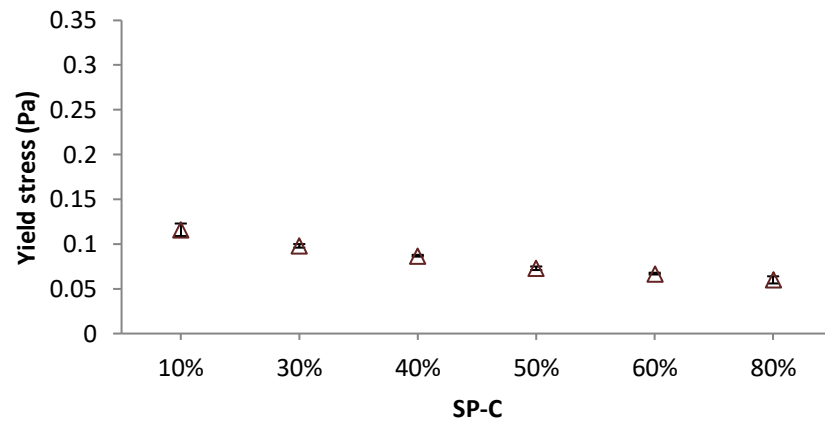
The mini-slump test was used to determine the workability of a cement paste mixture which is expressed in terms of yield stress. This section of the study presents the similarities in yield stress results obtained between the rheometer and the mini-slump test.

The mini-slump test was used to determine the yield stress values of the three cements with the addition of SP-C. Figure 4.2 (a), (b) and (c) presents the yield stress values for Cement 1, Cement 2 and Cement 3 respectively, determined by the mini-slump test with the addition of SP-C at 0.25%.

a)



b)



c)

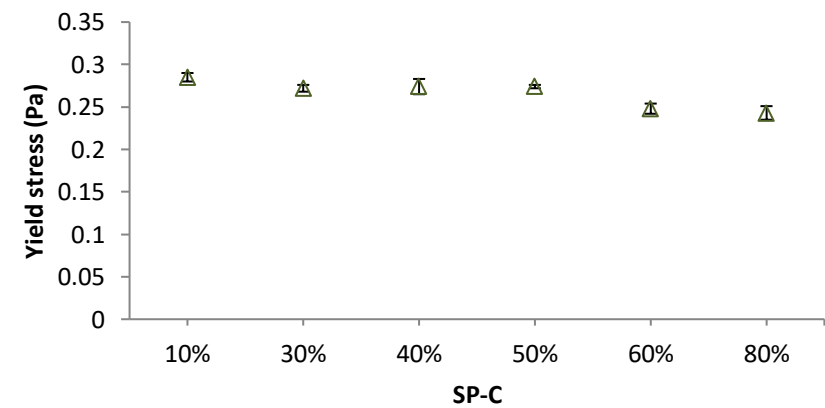


Figure 4.2: Yield stress (Pa) of Cement 1 (a), Cement 2 (b) and Cement 3 (c) determined by the mini-slump test with SP-C expressed in fraction of SP-A at optimum dosage of 25%

The yield stress values obtained using the mini-slump test can be seen to follow a similar trend when compared with the yield stress obtained using the rheometer.

Looking at Figure 4.2, it can be seen that increasing the SP-A fraction in SP-C at optimum dosage strongly affected Cement 1 and Cement 2. Their yield stress values were decreased by approximately 40% whilst that of Cement 3 only by 17%. Similar effect and trends were observed on the rheometer measurements.

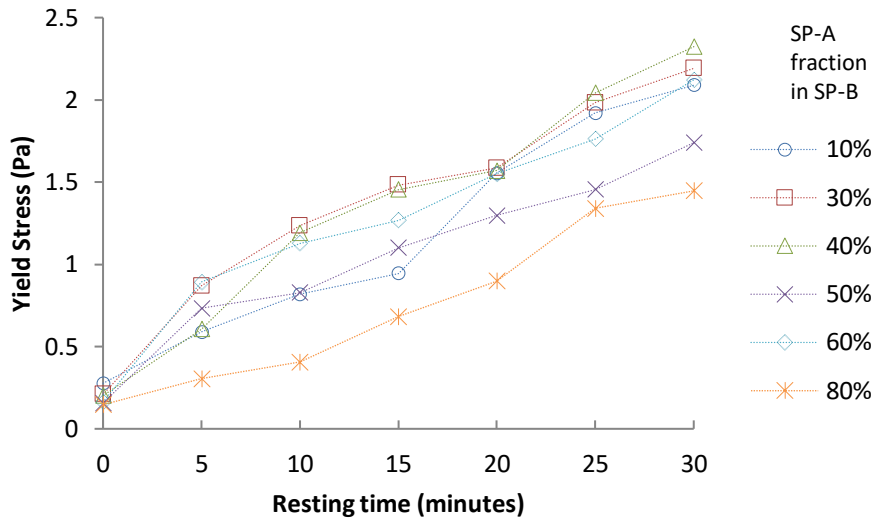
This trend would probably be an indication of the superior dispersing ability of SP-A within the SP blend. The greater the concentration of SP-A in the mixture the greater the reduction of the yield stress.

4.2.1 Yield stress development over time

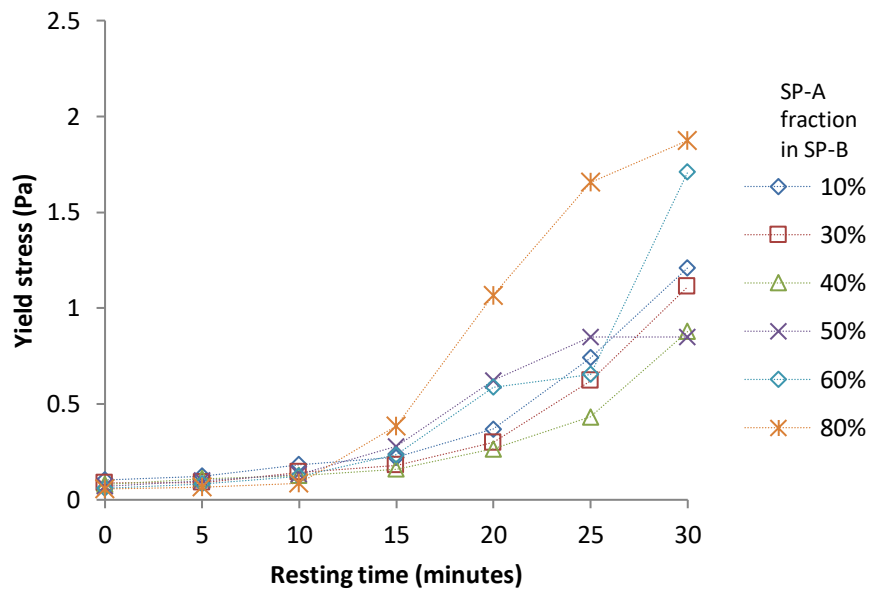
The effectiveness of SP-C on the workability loss is assessed by measuring the yield stress over time of each cement with each blended SP-C at optimum dosage of 0.25%. Cement is a time dependent material as the workability and flowability is reduced as the cement mixture ages. SPs are thus introduced to extend the workability time by ensuring tailored flowability properties of cement paste.

The yield stress development can be observed in Figure 4.3 (a) for Cement 1, (b) for Cement 2, and (c) for Cement 3, where the yield stress values were measured over 30 minutes at 5 minute intervals.

a)



b)



c)

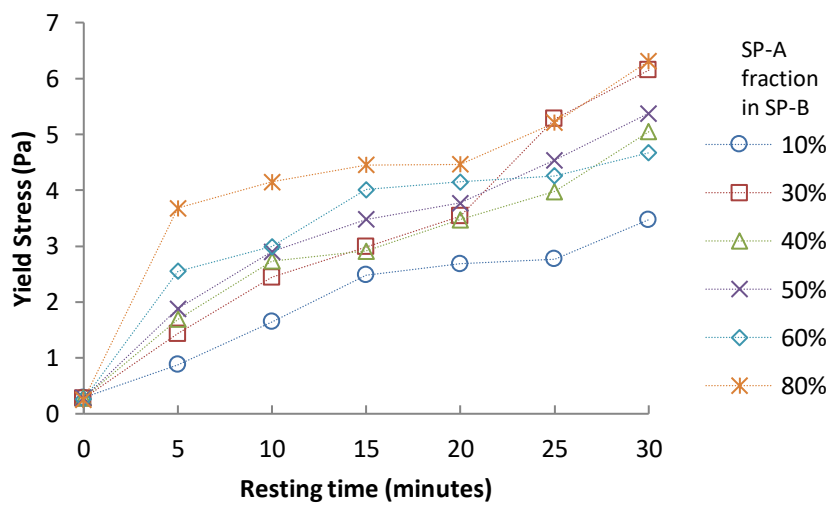


Figure 4.3: Development of yield stress over time of (a) Cement 1, (b) Cement 2 and (c) Cement 3 with SP-C at optimum dosage over 30 minutes

From Figure 4.2, it can be observed that the yield stress of each cement increases by 90% over 30 minutes resting time. The trend of Cement 2 shows a delay in the yield stress development up until 15 minutes after which the yield stress can be seen to significantly increase. This delay in strength development could be explained by the higher alkaline content in Cement 2 that favours the release of ions altering the hydration process of aluminate and gypsum phases as described in section 3.3.8.

4.3 Effect of blended SP on the cement paste viscosity

This section of the work displays the effect of SP-C on the viscosity of a cement paste mixture. The testing of the viscosity with the addition of SP-C at 0.25% was done using the rheometer and the results are presented in Figure 4.4 (a) for Cement 1, (b) for Cement 2 and (c) for Cement 3.

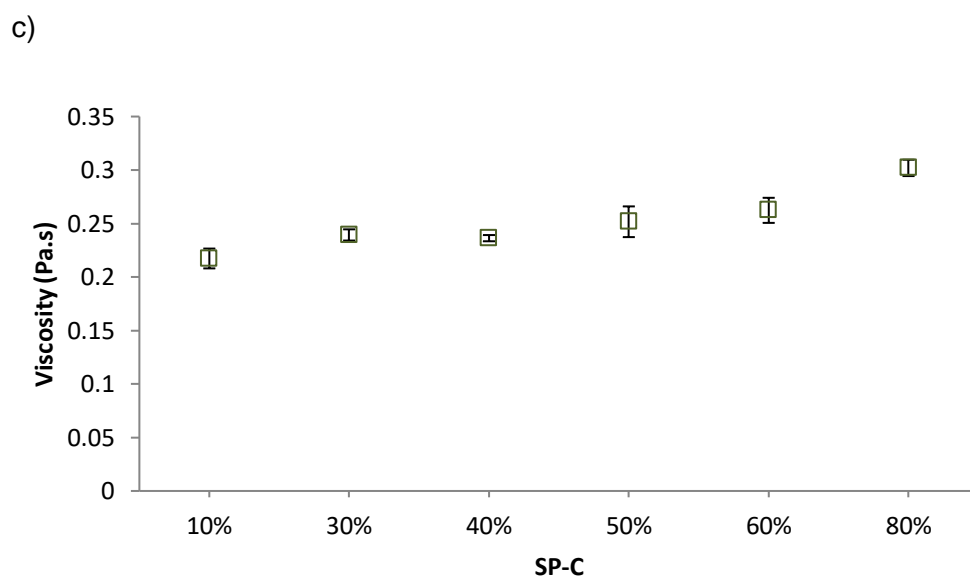
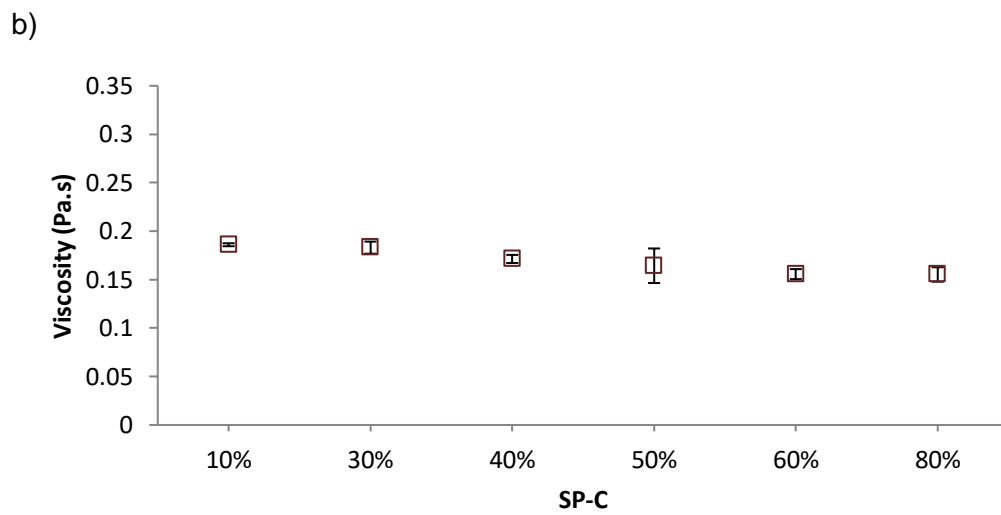
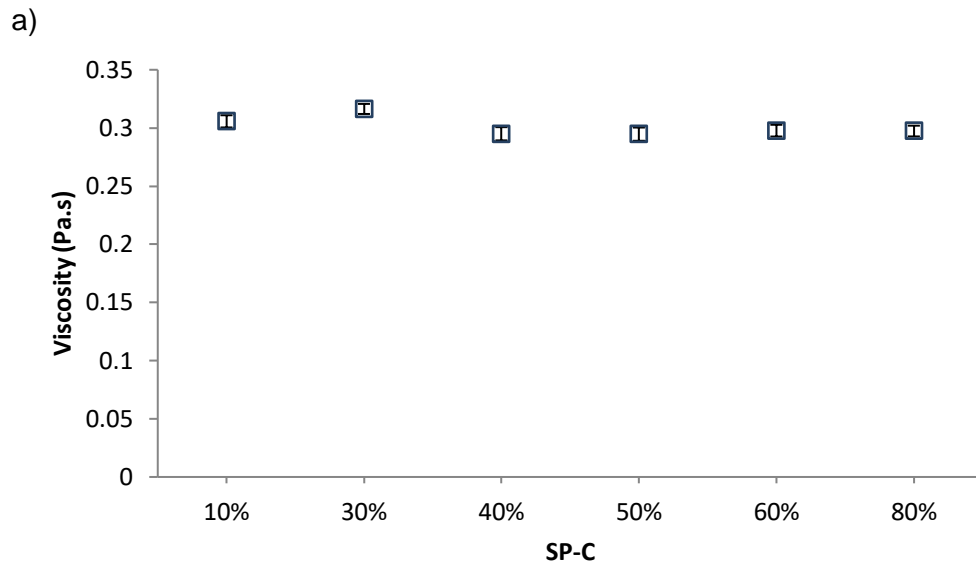


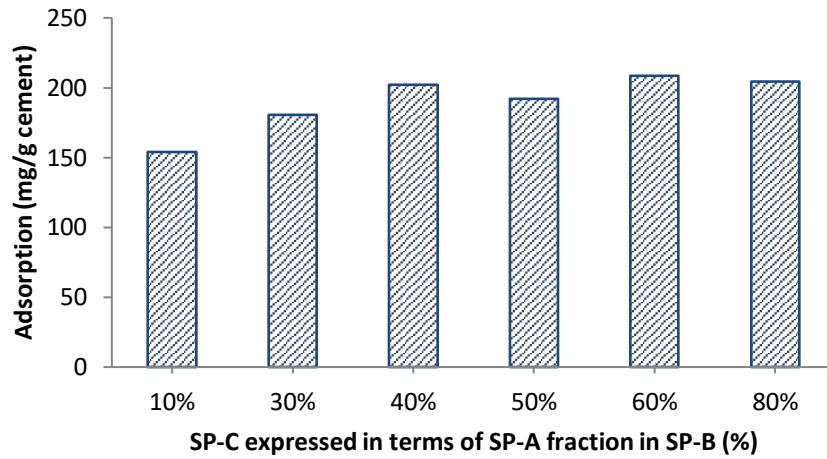
Figure 4.4: Viscosity (Pa.s) of Cement 1 (a), Cement 2 (b) and Cement 3 (c) with SP-C expressed in fractions of SP-A at optimum dosage of 0.25%

It can be seen from Figure 4.4 that there was a 6% and 16% decrease in the viscosity of Cement 1 and Cement 2 respectively, as the SP-A fraction within SP-B increased. However, a different trend can be observed for Cement 3 as there was a 27% increase in viscosity as the SP-A fraction in SP-C increased.

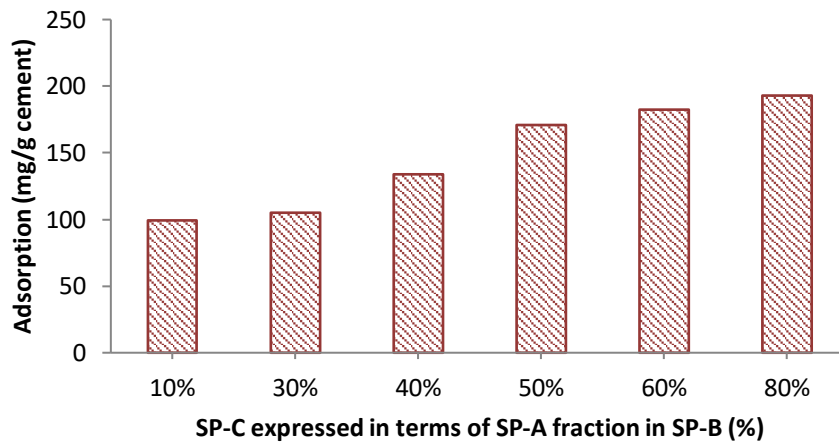
4.4 Effect of blended SP on the cement paste adsorption

Superplasticisers are added to cement mixtures with the purpose of reducing the yield stress. In order to achieve this, the polymer would have to adsorb on to the surface of the cement particles, increasing the steric hindrance effect and dispersing the cement particles from each other (Lin et al., 2019). Observing the trend of adsorption of SP-C onto the cement particles helps in understanding the behaviour of blended PCE SPs added to the same system.

This section discusses the results obtained using the TOC analysis (in mg/g of cement) of the three cements with the addition of SP-C at optimum dosage and are presented in Figure 4.5 (a) for Cement 1, (b) for Cement 2, and (c) for Cement 3.



b)



c)

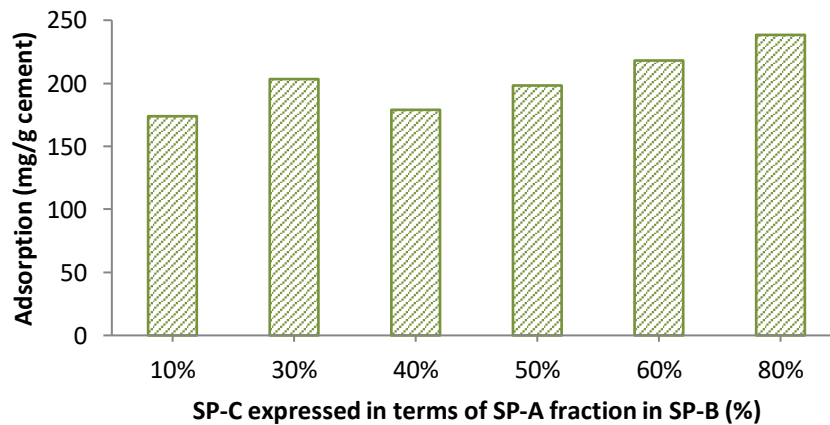


Figure 4.5: Adsorption (mg/ g cement) of the SP-C at 0.25% to Cement 1 (a), Cement 2 (b) and Cement 3 (c)

A change in trend 25% can be observed for Cement 1 as the adsorption amount increases following the increase of the SP-A fraction within SP-B. A similar trend can be observed for

Cement 2 (a) and Cement 3 (b) of 49% and 27% respectively, where the adsorption of SP-C increases as the SP-A fraction within SP-B increases.

It can be seen from these results that when two PCE admixtures are blended together and added to cement mixtures, the interaction between the polymers causes the polymer with the highest molecular weight to adsorb first allowing the latter unadsorbed polymer admixture to wait for an opportunity to adsorb onto the available adsorption sites as it remains in the medium. The un-adsorbed polymer gets adsorbed onto the hydration products (organo-mineral) as the initially adsorbed polymer is consumed by the forming hydration products (Bey et al., 2014).

These adsorption results indicate that the polymer with the highest molecular weight has a stronger affinity towards the adsorption sites when the two admixtures are simultaneously added to the cement paste mixture (Chen et al., 2020; Sha et al., 2020).

5 Chapter five: Discussion

5.1 Introduction

The yield stress and viscosity were determined to help understand the effect of SP-C on the rheological properties of SCC paste. The adsorption was determined by TOC analysis to help correlate the effect of the SP-C fractions on the rheological properties of the cement paste with the adsorption of the SP onto the cement particle. A summary of the results is presented below in order to assist in comparing the trends to better understand the effect of a blended SP within the same cement paste system.

5.1.1 The effect of SP-C on the yield stress of SCC paste

Determining the effect of SP-C on the yield stress of a cement paste helped in understanding how a blend of PCE SPs affects the yield stress of a cement paste, because the yield stress of a cement paste mixture indicates the point where flow is initiated. A summary of the yield stresses which were determined by the rheometer are presented in Figure 5.1.

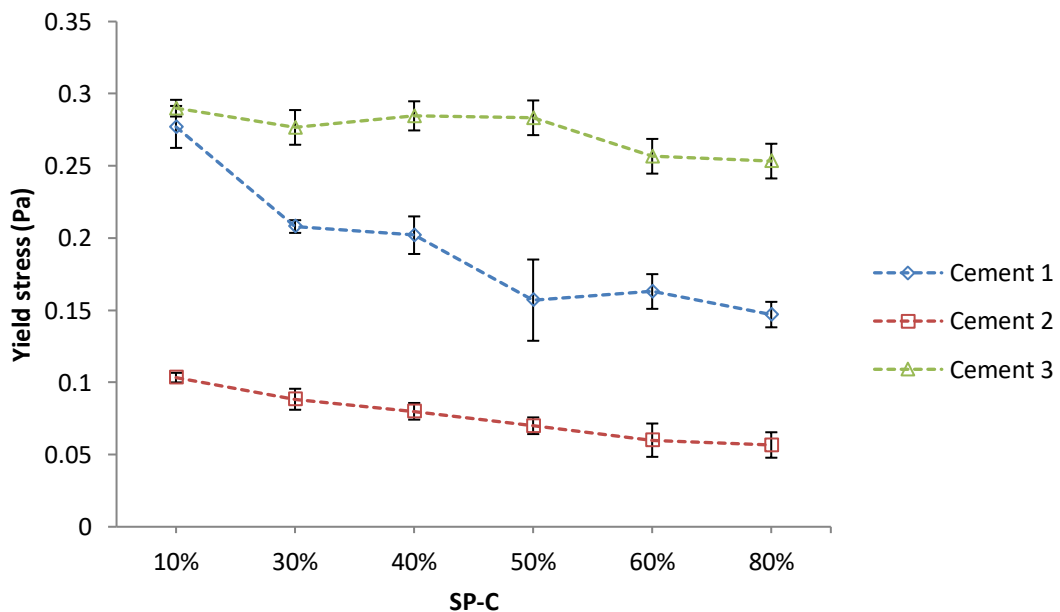


Figure 5.1: Summary of the yield stress (Pa) of Cement 1, Cement 2 and Cement 3 with SP-C expressed in fraction of SP-A at optimum dosage of 0.25%

All three cements in Figure 5.1 present different yield stress values, indicating the difference in cement properties. SP-C does not have much effect on Cement 3 up to 50% SP-A. This affects the yield stress of the cement at higher fractions of SP-A. However, with Cement 1, SP-

C continuously reduces the yield stress values at low fractions of SP-A. Above 50% SP-A the yield stress values are not affected any longer. However, lower yield stress values are achieved at these proportions. A slight decrease of yield stress values was observed in the presence of Cement 2 with the increase of SP-A fraction within SP-C.

A PCE SP containing longer side chains such as SP-A performs much better with regards to increasing fluidity than a PCE SP with shorter side chains. The longer side chains provide a larger steric hindrance which ultimately disperses the cement particle more effectively compared to the shorter side chains such as SP-B (Alonso et al., 2013; Lange and Plank, 2016; Zhang et al., 2017). Polymers which are not involved in the initial absorption also contribute to the dispersing of the cement particles and increase fluidity (Lange and Plank, 2016; Matsuzawa et al., 2019; Yoon and Kim, 2018).

A PCE SP possessing a higher anionic charge density due to having longer side chains or by having a thicker backbone (main chain) or more COO⁻ units, is known to have a stronger affinity to the cement surface allowing it to adsorb first and have priority at those sites (He et al., 2019; Matsuzawa et al., 2019; Zhang et al., 2017; Zingg et al., 2009). The increased organic carbon within the polymer weight, results in an increase in the adsorption capabilities (Lin et al., 2019). According to Plank et al. (2010), PCE admixture consisting of longer side chains and a low anionic charge can be a solution to the negative effects of intercalation and the prevention of the consumption of the admixture to produce organo-mineral phases.

5.1.2 Correlation between the yield stresses determined through the rheometer and mini-slump test

In this study the yield stress was determined on using two methods, by a rheometer, and by a mini-slump test. The results obtained from the two methods agreed and displayed similar trends for all cements with SP-C.

The yield stress determined by the mini-slump is plotted in Figure 5.2 as a function of the yield stress determined by the rheometer to determine a correlation between the two methods used.

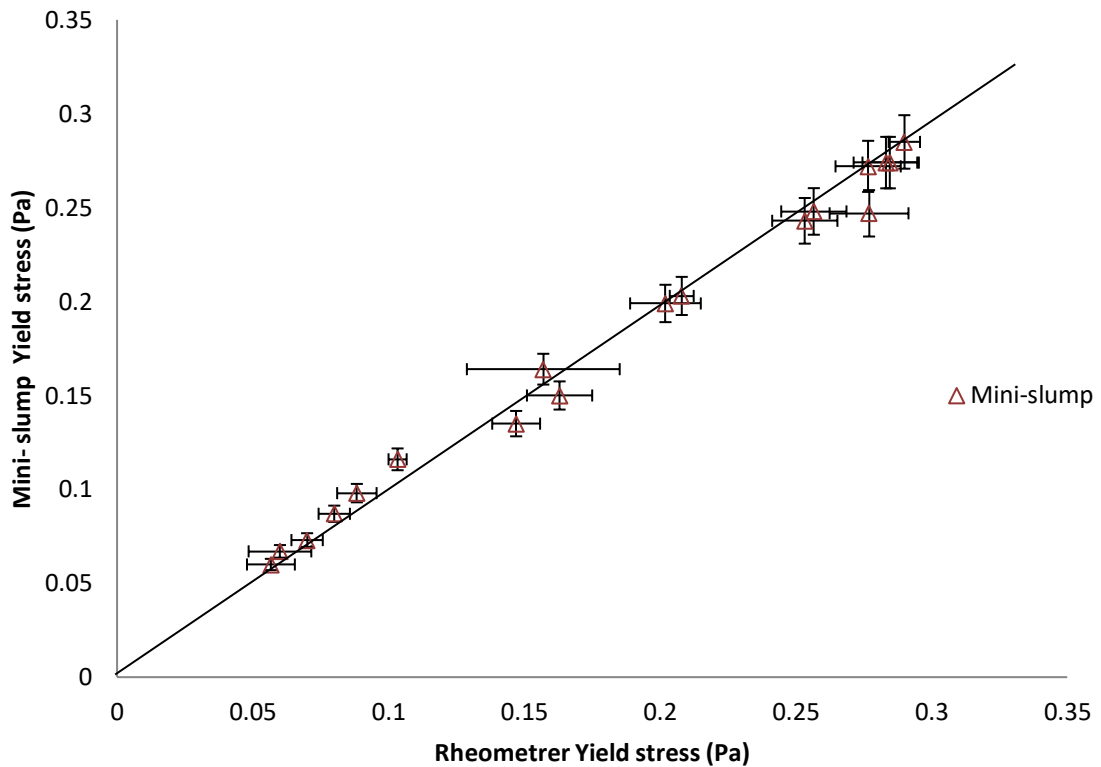


Figure 5.2: Correlation between the yield stresses determined using mini-slump test and rheometer with the blended SP at optimum dosage with different proportions of SP-A and SP-B, on Cement 1, Cement 2 and Cement 3

It can be seen from Figure 5.2 that the yield stress results measured from the rheometer and from the mini-slump tests are similar and have a strong correlation (Dalas et al., 2015b). This strong correlation has been published in the literature (Dalas et al., 2015b; Hot et al., 2014).

This evidence increases confidences in using mini-slump flow experiment as a rapid test to assess the rheological behaviour of cement mixtures for quick adjustments on sites deprived of sophisticated instruments.

5.2 The effect of SP-C on the plastic viscosity of SCC paste

A summary of the effect of SP-C on the plastic viscosity of Cement 1, Cement 2 and Cement 3, determined using the rheometer, can be observed in Figure 5.3.

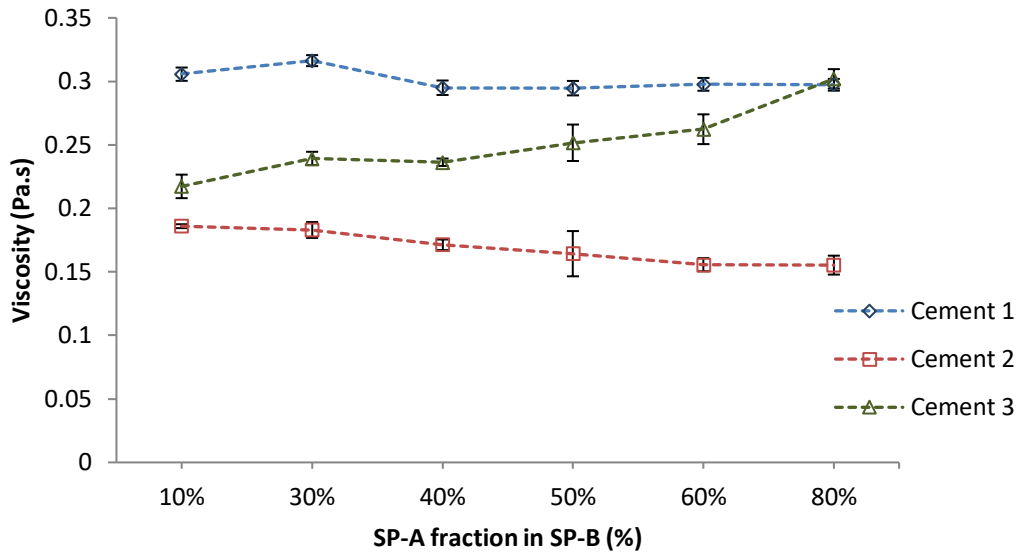


Figure 5.3: Summary of the plastic viscosity (Pa.s) of Cement 1, Cement 2 and Cement 3 with the addition of SP-C at 0.25%

It can be observed that the viscosity value for Cement 3 increased as the SP-A fraction within SP-B increased more than 50%. This increase could be caused by polymer entanglement, although the viscosity values of Cement 1 and Cement 2 remained fairly constant, showing that the optimum dosage was effective for all mixes at optimum dosage since the yield stress values were constant at further dosage, and the corresponding viscosity also remained constant.

5.3 The effect of SP-C adsorption on SCC paste

A summary of the effect of the SP blend on the adsorption on Cement 1, Cement 2 and Cement 3 is presented in Figure 5.4.

Adsorption

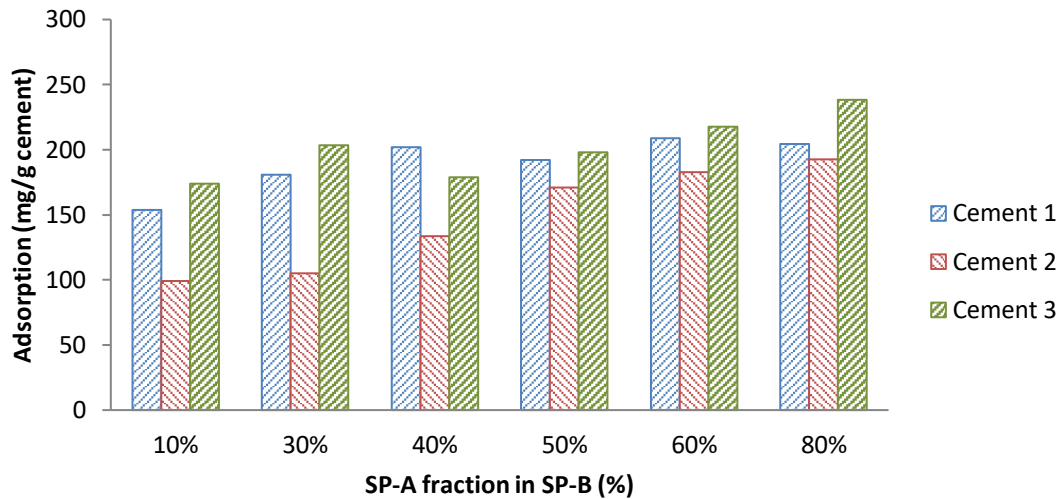


Figure 5.4: Summary of the adsorption (mg/g cement) of SP-C at 0.25% on Cement 1, Cement 2 and Cement 3

Cement 1 is coarser (and would therefore adsorb less SPs), but has low sulphate and alkali equivalent concentrations. The favourable dissolution of Ca-ions from the low concentration of alkali, allows therefore the soft adsorption of SP on the cement without any competitiveness of sulphate ions.

Cement 2 is finer (and would therefore adsorb more SP), but this is prevented by the presence of higher sulphate ions in which adsorption is even favoured due to higher alkali content that slows down the adsorption of SP on the cement particles. This has accentuated a low fraction of SP-A responsible for SP-C hydrophilicity.

Cement 3 is finer and expected to adsorb more SP. The higher adsorption of SP-C on Cement 3 is justified by the fact that sulphate ions lack Ca-ions to interact with due to the low alkali content in the cement, allowing the possibility of the SP-C rather to be adsorbed on the cement particle.

The ratio between the sulphate content and aluminate content is one of the key parameters in regulating the accelerator reaction (Herrera-Mesen et al., 2019). According to Alonso et al. (2013) a sulphate/C₃A ratio of 0.7-2.0 is sufficient for the growth of ettringite and monosulphaluminate hydration products, and prevents the production of organo-mineral phases. A ratio lower than 0.7 means that the sulphate content is not sufficient to react with the C₃A bringing forth the production of organo-mineral phases that are formed by the consumption of large amounts of admixture (Herrera-Mesen et al., 2019). This consumption of

the admixture to form organo-mineral phases has been confirmed in the literature by (Erzengin et al., 2018; Plank et al., 2010; Zhang et al., 2020). This phenomenon can be used to explain the difference observed between the SP admixture blends and the different cements used. This is explained by the low production of ettringite which means that the first indication of structure formed by ettringite within the cement matrix could not be formed, displaying the appearance of a low yield stress cement.

SP-A can be observed to have preference over SP-B for adsorption sites by not allowing further adsorption of SP-B due to electrostatic repulsion between the negative adsorption layer and the remaining SP-B within the medium. The increase in adsorption can be related to the increase of the free water available within the medium for the production of the hydration products, allowing more adsorption sites available as the initially adsorbed SP is consumed (formation of organo-mineral phase). This allows the un-adsorbed SP an opportunity to adsorb onto the hydration products reducing the remaining amount within the medium (Alonso et al., 2013; Flatt and Houst, 2001; Zhang et al., 2020).

Inorganic anions which possess a higher charge density such as phosphate, carbonate and sulphate, are known to hinder the adsorption capabilities of a polycarboxylate SP with a low anionic charge density within the main chain of the polymer, a phenomenon known to reduce the achievable flowability of the cement mixture (Plank and Winter, 2008). An additional factor influencing adsorption next to the anionic charge is the free energy change process. This process is described as the electrostatic interaction which takes place between the SP and the cement surface, expressed as the adsorption enthalpy (ΔH); and the entropy change (ΔS) is the result of the adsorption of the SP as the anions and water desorb from the cement particles (Plank and Winter, 2008). Thus an increase in adsorption of an SP can be achieved by a lower entropic loss upon adsorption which is related to the dense molecule conformation within the water phase (Plank and Winter, 2008). The adsorption process is described by Dalas et al. (2015a) as being in dynamic equilibrium, which is best explained as the exchange of one or two anchoring functions such as carboxylates, with an anion such as sulphate or hydroxide within the double layer. This phenomenon is also described as the process of competitive adsorption between the polyelectrolytes and the anions (Dalas et al., 2015a).

The interaction that takes place between organic admixtures is very sensitive and dependent on their molecular structure. The sulphate ions present have a stronger affinity towards the cement particle and have the potential to desorb the carboxylic groups at the surface of general PCE adsorption (Bessaies-Bey et al., 2016). However when the adsorption competitors are multiple polymer admixtures within a system (polymer/polymer competition), the delicacy of the competitive adsorption revolves around the entropic and enthalpic contributions of the

competitors. Therefore it can be said that the competitive adsorption is not only dependent on the physical properties such as the affinity the admixture has towards the cement particles and the chemical structure of the admixture, but more dependent on the surface coverage and the availability of those adsorption sites (Bessaies-Bey et al., 2016; He et al., 2019; Li et al., 2020; Qian et al., 2018). Competitive adsorption can be divided into three main regimes (Bessaies-Bey et al., 2016):

- The first regime describes a scenario where competitive adsorption between the molecules and polymers is not observed because they all adsorb equally when there is low surface coverage.
- In the second regime, at equilibrium or at intermediate surface saturation, all the organic admixtures compete against each other for available adsorption sites with the admixture that has the highest affinity towards the cement particle occupying most of the adsorption surfaces leaving fewer residual sites for the remaining species.
- The third regime is described as the species with the strongest affinity (strongest adsorption) fully saturating the adsorption sites leaving the un-adsorbed species remaining in the fluid.

Additives possessing a higher anionic charge density will in some cases prevent the adsorption of an admixture which has a lower charge density when placed in the same system; this is the same behaviour that was observed with the SP blends of this study where there was an increase in adsorption of the SP-C fractions which consisted of more of the SP-A content within the blend (Plank and Winter, 2008).

6 Conclusion

6.1 Summary

In this investigation two PCE SPs, which were different in side chain length (one long and one short) and different in average molecular weight (a difference of 2000 mol/g), were blended together at fractions (SP-A fractions within SP-B) and expressed as SP-C. This investigation evaluated the effect of adding this blended SP to three cement pastes, which had different chemical compositions, to study the effect of the product on cement paste rheology.

The rheological properties were described by the yield stress and viscosity results, and the workability of the cement pastes was determined by observing the spread flow of the cement pastes over time. The SP adsorption was determined using a TOC analyser and was calculated through the depletion method as described in the literature.

It was found that Cement 1, which was coarser and had a lower sulphate and alkali equivalent concentration, favoured the dissolution of Ca-ions from the low alkali content. This allowed for the soft adsorption of SP on the cement without any competitiveness of sulphate ions.

Cement 2 which was finer, had a higher concentration of sulphate ions whose adsorption was further favoured by the higher alkali content, which slowed down the adsorption of the SP and was further accentuated by a low fraction of SP-A responsible for SP-C hydrophilicity.

Cement 3 was even finer and was expected to adsorb more SP. The higher adsorption of SP-C on Cement 3 was justified by the low concentration of sulphate ions which lacked sufficient Ca-ions to interact with due to the low alkali content in the cement, resulting in more SP-C adsorption on to the cement particles.

It is suggested that in order for admixture companies to more efficiently blend PCE SPs, they should blend polymers with short side chains as the results show that the polymer with short side chains performs better than the polymer with the longer side chains. The majority of the blend should consist of a short chained polymer with a higher molecular weight, as this polymer will adsorb first to the cement surface. Once the adsorption has saturated the surface of the cement particles, the remaining polymer within the medium will continue to increase the fluidity through its steric hindrance effect. A polymer with short side chains performs better compared to a polymer with longer side chains. The former improves the fluidising efficiency and also increase profit, as low molecular weight polymers are more cost-effective to produce (longer side-chains increase the molecular weight which can increase the production cost). According

to the literature, the PCE that displays superior dispersion capabilities should contain long side chains as this extends the hydration period much more than short and medium length side chains. Further it should have a high charge density, but a short main chain or backbone (Sha et al., 2020).

Blending polymers has resulted in an increase in viscosity without increasing the yield stress which can be a solution for aggregate segregation and bleeding.

It is common practice for PCE SPs to be blended by the suppliers in order to achieve the desired rheological behaviour (Cheah et al., 2020). This study helps to better understand the behaviour of a blended PCE SP on the rheology of SCCP to help improve the design of SCC applications within concrete technology and engineering.

Having two PCE SPs with the same molecular structure, and only different in weight, can be effectively used in SCC design as the PCE SP with the higher molecular weight adsorbs first to the cement particles. This gives the remaining PCE SP with the lower molecular weight an opportunity to adsorb to the cement particles through continuous adsorption, or increase the fluidity within in the medium through electric repulsion forces (Chen et al., 2020; He et al., 2019; Sha et al., 2020).

The process of blending PCE SPs can lead the development of effective and more efficient products. Being able to improve the percentage of residual PCE remaining in the medium after the initial PCE has adsorbed can effectively be used in the design of SCC for controlling the fluidity behaviour of a concrete mixture (Chen et al., 2020).

6.2 Recommendations for further studies

It is recommended that further studies should be done on observing the effect of a blended SP on the rheology of self-compacting concrete to study the effect of SP adsorption at concrete level. Further studies can be done on observing the effect of a blended SP on the rheology of cement paste where the blended SPs have the same structure, yet are different in molecular weight, in order to study the effect.

A study focusing on explaining the chemical interactions responsible for the product SP adsorptions on cement particles would be of great interest to understand in full the effectiveness of blended SP.

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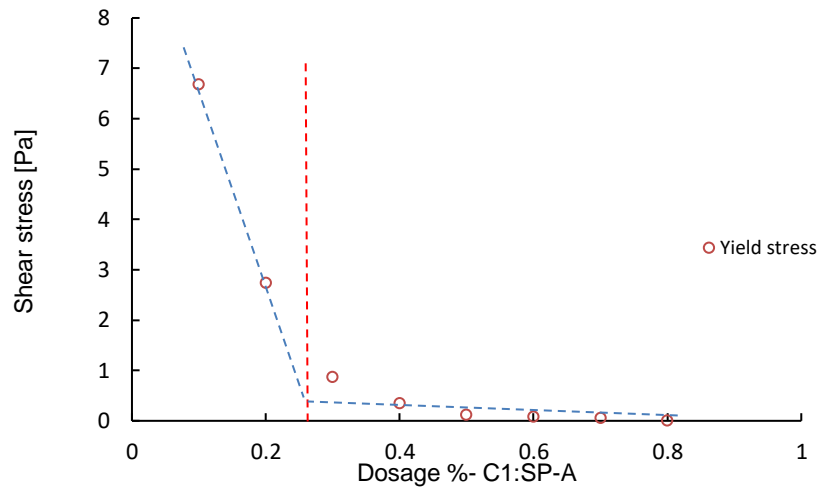
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7 Appendix A: Optimisation

a)



b)

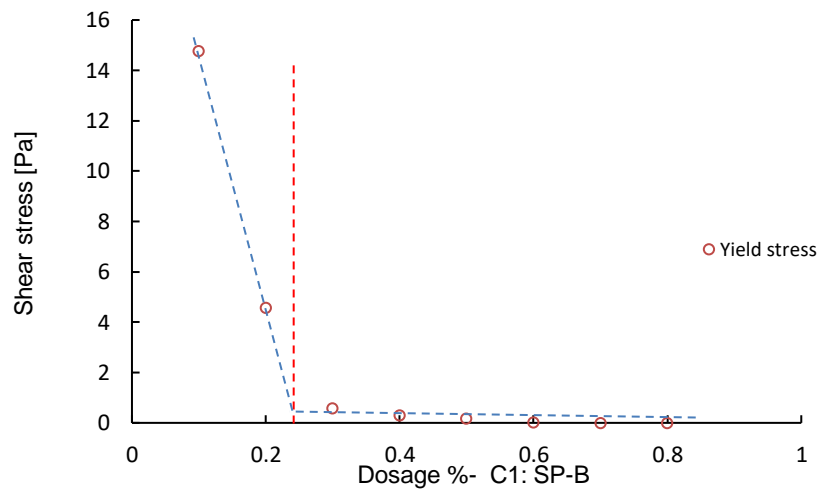


Figure A.1: Optimisation of Cement 1 with SP-A (a) and SP-B (b)

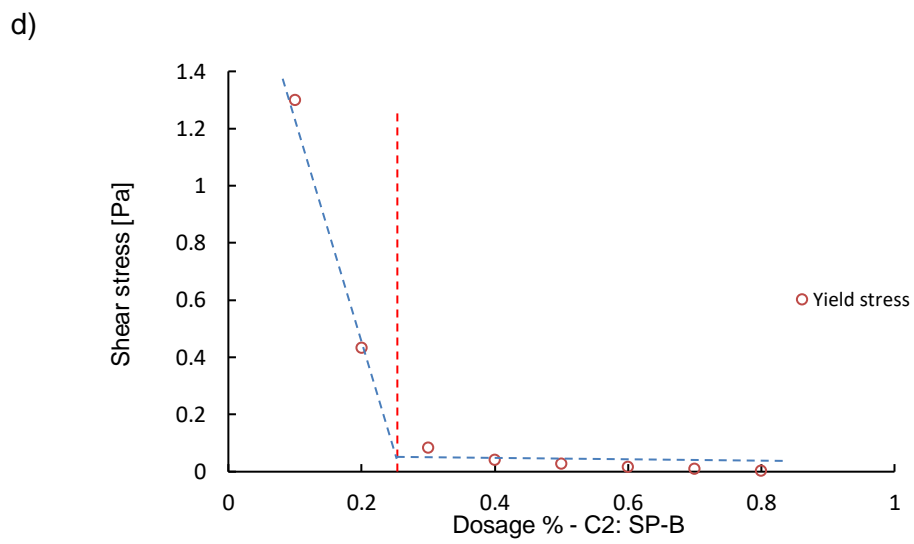
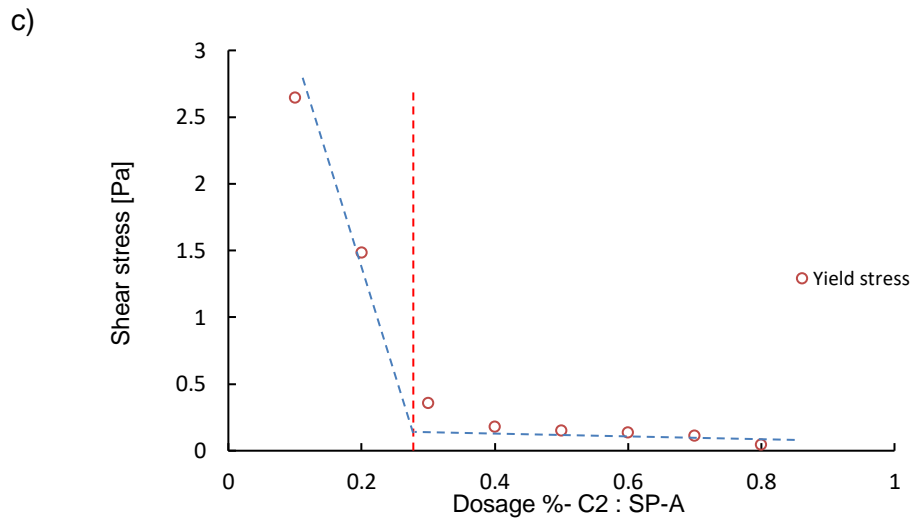
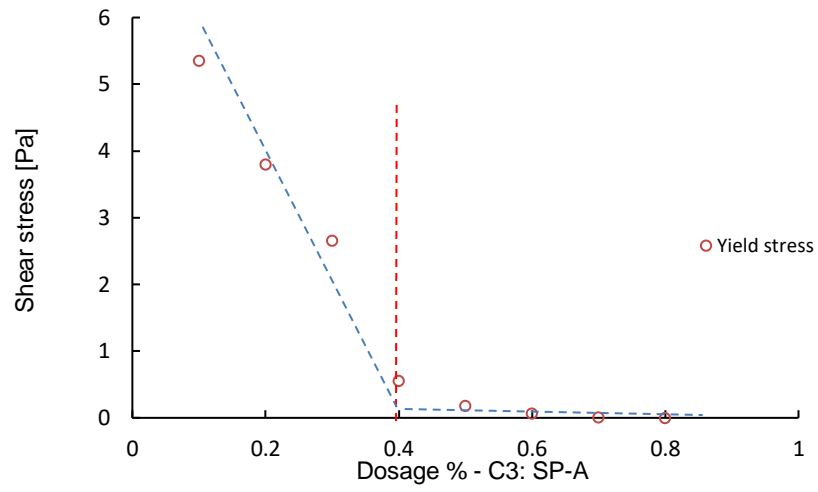


Figure A.2: Optimisation of Cement 2 with SP-A (c) and SP-B (d)

e)



f)

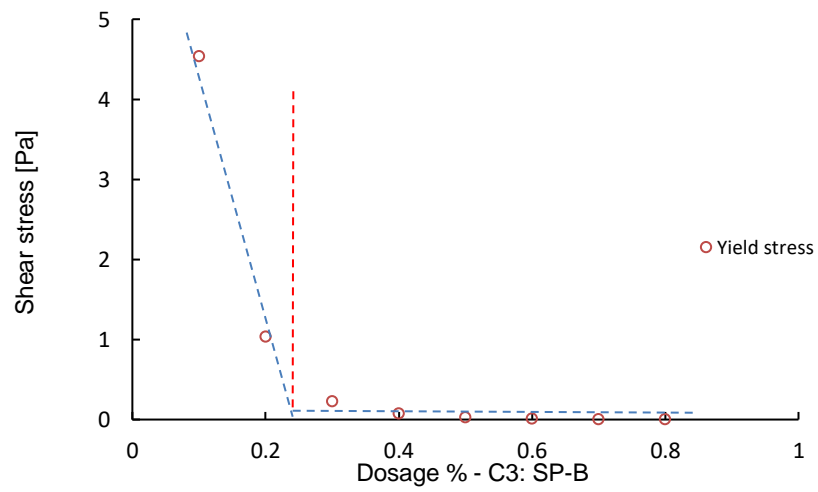


Figure A.3: Optimisation of Cement 3 with SP-A (e) and SP-B (f)

8 Appendix B: Rheometer results

Table B.1: Rheometer results of Cement 1

Cement 1		
SP-A fraction in SP-B (%)	τ (Pa)	μ (Pa.s)
10%	0.3	0.307
	0.25	0.314
	0.28	0.296
30%	0.2	0.316
	0.21	0.324
	0.215	0.309
40%	0.2	0.287
	0.18	0.306
	0.225	0.292
50%	0.18	0.288
	0.19	0.29
	0.101	0.306
60%	0.17	0.288
	0.14	0.3
	0.18	0.305
80%	0.13	0.289
	0.15	0.298
	0.16	0.305

Table B.2: Rheometer results of Cement 2

Cement 2		
SP-A fraction in SP-B (%)	τ (Pa)	μ (Pa.s)
10%	0.1	0.188
	0.11	0.187
	0.1	0.183
30%	0.09	0.18
	0.1	0.174
	0.075	0.195
40%	0.07	0.175
	0.09	0.176
	0.08	0.163
50%	0.08	0.129
	0.06	0.178
	0.07	0.186
60%	0.08	0.15
	0.04	0.151
	0.06	0.166
80%	0.06	0.141
	0.07	0.166
	0.04	0.159

Table B.3: Rheometer results of Cement 3

Cement 3		
SP-A fraction in SP-B (%)	τ (Pa)	μ (Pa.s)
10%	0.28	0.216
	0.29	0.202
	0.3	0.234
30%	0.3	0.231
	0.27	0.238
	0.26	0.249
40%	0.304	0.241
	0.28	0.231
	0.27	0.237
50%	0.26	0.223
	0.3	0.267
	0.29	0.265
60%	0.25	0.239
	0.28	0.272
	0.24	0.276
80%	0.26	0.287
	0.27	0.307
	0.23	0.312

9 Appendix C: Adsorption

Table C.1: SP-C adsorption results of Cement 1

SP-C	CEMENT 1					
SP-A fraction in SP-B (%)	TOC in solution (mg/L C)	TOC in cement (mg/L C)	TOC in SP (mg/L C)	SP remaining in solution (%)	SP adsorbed on to cement (%)	SP adsorbed on to cement (mg/g cement)
10%	141	83	151	38.41	61.59	153.97
30%	126	83	155	27.74	72.26	180.65
40%	116	83	172	19.19	80.81	202.03
50%	121	83	164	23.17	76.83	192.07
60%	110	83	163	16.56	83.44	208.59
80%	111	83	153	18.30	81.70	204.25

Table C.2: SP-C adsorption results of Cement 2

SP-C	CEMENT 2					
SP-A fraction in SP-B (%)	TOC in solution (mg/L C)	TOC in cement (mg/L C)	TOC in SP (mg/L C)	SP remaining in solution (%)	SP adsorbed on to cement (%)	SP adsorbed on to cement (mg/g cement)
10%	149	58	151	60.26	39.74	99.34
30%	148	58	155	58.06	41.94	104.84
40%	138	58	172	46.51	53.49	133.72
50%	110	58	164	31.71	68.29	170.73
60%	102	58	163	26.99	73.01	182.52
80%	93	58	153	22.88	77.12	192.81

Table C.3: SP-C adsorption results of Cement 3

SP-C	CEMENT 3					
SP-A fraction in SP-B (%)	TOC in solution (mg/L C)	TOC in cement (mg/L C)	TOC in SP (mg/L C)	SP remaining in solution (%)	SP adsorbed on to cement (%)	SP adsorbed on to cement (mg/g cement)
10%	128	82	151	30.46	69.54	173.8411
30%	111	82	155	18.71	81.29	203.2258
40%	131	82	172	28.49	71.51	178.7791
50%	116	82	164	20.73	79.27	198.1707
60%	103	82	163	12.88	87.12	217.7914
80%	89	82	153	4.58	95.42	238.5621

10 Appendix D: Mini-slump

Table D.1: Mini-slump results of Cement 1

Cement 1				
SP-A fraction in SP-B (%)	Time of spread (sec)	Mean spread (mm)	Yield stress (Pa)	Mean Yield stress (Pa)
10/90	4.66	126	0.271	0.280
	4.71	125	0.282	
	4.53	124.5	0.287	
30/70	5.56	131	0.223	0.203
	5.3	136	0.185	
	5.05	133.5	0.203	
40/60	5.18	134.5	0.195	0.199
	5.31	133.5	0.203	
	6.29	134	0.199	
50/50	6.56	137.5	0.175	0.164
	6.08	142.5	0.146	
	6.28	138	0.172	
60/40	6.42	142.5	0.146	0.150
	6.59	140.5	0.157	
	6.82	142.5	0.146	
80/20	6.54	146	0.130	0.135
	6.2	142.5	0.146	
	6.6	146	0.130	

Table D.2: Mini-slump results of Cement 2

Cement 2				
SP-A fraction in SP-B (%)	Time of spread (sec)	Mean spread (mm)	Yield stress (Pa)	Mean Yield stress (Pa)
10%	7.13	146.5	0.128	0.116
	7.42	152.5	0.104	
	7.01	149.5	0.115	
30%	7.08	154.5	0.098	0.098
	7.48	153	0.103	
	8.53	155.5	0.095	
40%	8.84	157.5	0.089	0.087
	7.35	158.5	0.086	
	7.41	158	0.087	
50%	7.99	165.5	0.069	0.073
	9.48	162	0.077	
	7.83	164	0.073	
60%	8.35	165.5	0.069	0.067
	8.17	166.5	0.067	
	7.4	167.5	0.065	
80%	8.66	175	0.052	0.060
	9.77	167	0.066	
	8.2	169	0.062	

Table D.3: Mini-slump results of Cement 3

Cement 3				
SP-A fraction in SP-B (%)	Time of spread (sec)	Mean spread (mm)	Yield stress (Pa)	Mean Yield stress (Pa)
10%	5.12	125.5	0.275	0.285
	6.76	124	0.292	
	5.71	124.5	0.287	
30%	5.83	125.5	0.275	0.272
	5.72	126.5	0.265	
	5.5	125.5	0.275	
40%	5.25	124	0.292	0.274
	5.96	126.5	0.265	
	5.7	126.5	0.265	
50%	5.32	126	0.270	0.274
	6.23	125.5	0.275	
	5.09	125.5	0.275	
60%	5.45	127.5	0.254	0.248
	6.03	129.5	0.235	
	5.55	127.5	0.254	
80%	5.3	127	0.259	0.243
	6.1	129.5	0.235	
	5.37	129.5	0.235	