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Effect of Molecular Weight and Carboxylic Density of Polycarboxylates Ether Superplasticizer on Its performance in Cement Pastes

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ABSTRACT

The main difficulty encountered in the formulation of high performance concrete (HPC) consists in choosing the most efficient cement-superplasticizer pair allowing to obtain maximum water reduction, good workability of the concrete in the fresh state and very good mechanical resistance in the hardened state. The aim of this work is to test the efficient of three polycarboxylate ether based superplasticizers (PCE) marketed in Algeria with CEMI 52.5 R cement and to study the effect of chemical structure of PCE on zeta potential, rheological and mechanical properties of cement pastes. The property of the polymers in cement was tested by a Malvern Zetasizer 2000 apparatus and VT 550 viscometer. Results showed that the zeta potential and its rheological properties are related with the molecular weight and the carboxylic density of PCE. The PCE with a moderate molecular weight and highest carboxylic groups had the best dispersion (high value of zeta potential) and lowest viscosity. The effect of chemical structure of PCEs on mechanical properties are evaluated by formulation of cement mortar with this PCEs, the result shows that there are a correlation between zeta potential of polymer and compressive strength of cement paste.

1 Introduction

Polycarboxylate-type superplasticizers (PCEs) are necessary for the production of high performance concrete [1, 2]. They improve the workability of fresh mixes, the compactness and the strength of hardened concrete [3-6]. The positive effects are based on the unique comb structure of PCEs [7], which are constructed with polycarboxylate main chains and pendant polyether grafted groups [8-10], their main chain carries a negatively charged carboxylic group (COO-) for facilitates the adsorption of the molecule on the surface of the cement particles by electrostatic interaction, the side chains contain

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polyethylene glycol (PEG) structures which promote the dispersion of the cement particles due to the steric hindrance they produce [10-16].

The adsorption and dispersing capacity of PCEs in cement-based materials depends on their chemical structure, including molecular weight, carboxylic groups, density and length of the side chain [17, 18].

The molecular weight of PCEs has a significant impact on the properties of concrete. There have been many studies on the effect of molecular weights on the performance of PCEs [11, 19-23].

The results studies of Peng [23] suggested that PC with medium molecular weight has the best dispersion performance, while PC with high molecular weight performs the worst in dispersion. In addition, the loss rate of flowability increased with the increase of molecular weight. Similar observations were obtained by Liu and al [22].

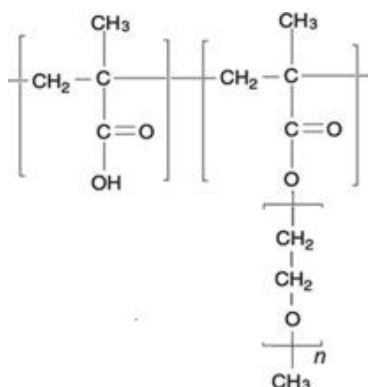


Fig. 1 – Chemical structure of PCE

The increase in the number of COO^- groups will increase the adsorption capacity of PC [24], which means that the flowability of cement paste increased with the content of COO^- .

The aim of this study was to investigate the performance of three commercial PCEs with different molecular weight and different carboxyl group content in fresh and hardened cement-based materials. The impact of PCEs on the fresh cement was investigated by studying the flowability, rheological properties and the zeta potential of cement particles with PCE.

In this study the mechanical properties were evaluated by measurement of compressive and flexural strength of cement mortar prepared with these PCEs.

2 Experimental

2.1 Materials

2.1.1 Superplasticizer

Three types of superplasticizers marketed in Algeria are used, the first, marketed under the name Polyflow SR 5400 is designated by PCE_1 , the second, Medaflow 30 is designated by PCE_2 , the third, Asa Super HG 25 is designated by PCE_3 .

The three polymers are new-generation non-chlorinated, based on modified polycarboxylic ether. The structure of this superplasticizers is given in figure 1.

The characteristics of these superplasticizers are shown in Table 1.

Note: PDI = polydispersity index.

Mn: Number average molecular weight of superplasticizer

Mw: The weight average molecular weight of superplasticizer

2.1.2 Cement and silica fume

Portland cement CEM I/52.5 R (Lafarge Msila, Algeria) was used throughout all the experiments. The compositions of the cement was shown in table 2.

Table 1 – Properties of PCEs sample.

Samples	PCE ₁	PCE ₂	PCE ₃
Dry extract	30%	30%	30%
Ph	4.46	3.35	6.1
Density (g/cm ³)	1.07	1.07	1.06
Mn (Da)	13 621	4 771	4 067
Mw (Da)	15 959	5 157	4 629
PDI	1.172	1.081	1.138
Carboxyl content (mmol/g)	1.87	1.95	1.65

Table 2 – Composition of the cement sample CEM I/ 52.5 R used in this study.

Phases	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	K ₂ O	Na ₂ O	Na ₂ O Equivalent
Cement Mass %	22.18	3.72	0.17	66.55	1.75	2.53	0.52	0.07	0.41

2.2 Experimental measurements

2.2.1 Multi-Detector Steric Exclusion Chromatography

The molecular weight (Mn, Mw) and the polydispersity indices (PDI) of the superplasticizers were measured using a SEC (C2P2, France). The analytical conditions are tabulated in table 3.

Table 3 – The analytical conditions of SEC

System	Column	Col Temp (C)	Solvent	Flow Rate (ml/min)	InjVol (μl)
SEC THF	SDV	35.00	THF	1.0000	100.0

The acid-base titration method is used to measure the carboxyl group content. The carboxyl group content can be calculated as follows:

$$C(\text{COO}^-) = [C_{\text{NaOH}} V_{\text{NaOH}}] \times m / 100 \quad (1)$$

where:

$C(\text{COO}^-)$ = carboxyl group content (mmol/100 g);

C_{NaOH} = molar concentration of NaOH (mmol/L);

V_{NaOH} = volume of NaOH solution used (L); and m = weight of sample.

2.2.2 Fluidity

To evaluate the fluidity of cement pastes, we used the Marsh cone as proposed by Halal et al [25]. The test consists of measuring the time it takes to empty a cone containing 1 liter of grout through a 5 mm diameter discharge port (Figure 2).

An initial fluidity was measured at 5 min after the first contact of the cement with water. The grout is then placed in a container which will be covered with a plastic film to prevent any water evaporation; a second flow measurement at 1 hour, the grout was mixed one minute before taking the measurement. For preparation of this grouts, the cement CEMI/52.5 R was mixed with water ($w/c = 0.35$) and PCEs (at saturation dosage).



Fig. 2 – Marsh cone

2.2.3 Rheology

The experimental steps are as follows: In a cement-PCE system, the water to cement ratio (w/c) is 0.35: (that is, the water quantity is 35 g, and the cement quantity is 100 g), and the PCE content from 0.0 to 2.0 wt % of cement.

In the cement-PCE-SF system, 10% of total cement binder was partly replaced by silica fume. The water to binder ratio (w/b) is 0.35: (that is, the water quantity is 35 g, the cement quantity is 90 g and silica fume 10g, PCE: 0.0-2.25 wt% of total cement-based binder).

The rheology of the cement paste was appraised by a VT 550 viscometer.

2.2.4 Zeta potential

The zeta potentials of cement pastes with w/c = 0.5 containing PCEs at saturation dosages were determined on a Malvern ZETASIZER 2000. In a typical experiment, one centimeter cube of the cementitious suspension was diluted in 30 cm³ of distilled water, after which 5 ml of this suspension was injected into the analyzer.

2.2.5 Compressive strength

The compressive strength was measured according to the EN 196-1 protocol. A batch of three mortar specimens was prepared with cement, water, standard sand (c:w:s = 1: 0.5: 3), and superplasticizers PCE/C= 1.25 %). After casting for 1 day, samples were demolded and cured in a saturated calcium hydroxide solution for durations of 1, 7, and 28 days. The compressive strengths of the samples were determined.

3 Results and discussion

3.1 Molecular weight analysis

The molecular properties are shown in Table 1, from this table, the PDI values for these polymers are slightly above 1.00, indicating a fairly narrow molecular weight distribution. Furthermore, the PDI value of PCE2 is closest to 1 compared to the other two polymers.

3.2 Fluidity

The results of initial fluidity and fluidity at 1hour measurement are shown in Fig. 3. The PCE2 with higher charge density and moderate molecular weight exhibits higher initial fluidity, and 1h fluidity. COO⁻ on the backbone of PC adsorbs on the surface of cement particles through complexation with Ca²⁺ or electrostatic attraction. Increase in the number of COO⁻ groups

will increase the adsorption capacity of PCE [26], which means that the flowability of cement paste increased with the content of COO^- .

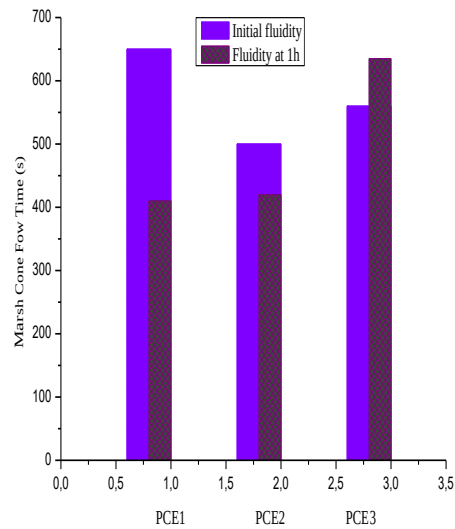


Fig. 3 – Variation of the flow time for various PCEs ($w/c = 0.35$).

The PCE3 with lower density carboxylic and lower molecular weight exhibits a bad flowability and bad fluidity retention.

The PCE1 with highest molecular weight presents bad initial fluidity and the highest fluidity retention. The adsorption amounts of PC on the surface of cement paste increases with the decrease of molecular weight, but the PC with high molecular weight delays cement hydration strongly. This is because that main chain of PCs adsorbing on different cement particles simultaneously, making cement particles agglomeration and hindering the hydration of cement [27].

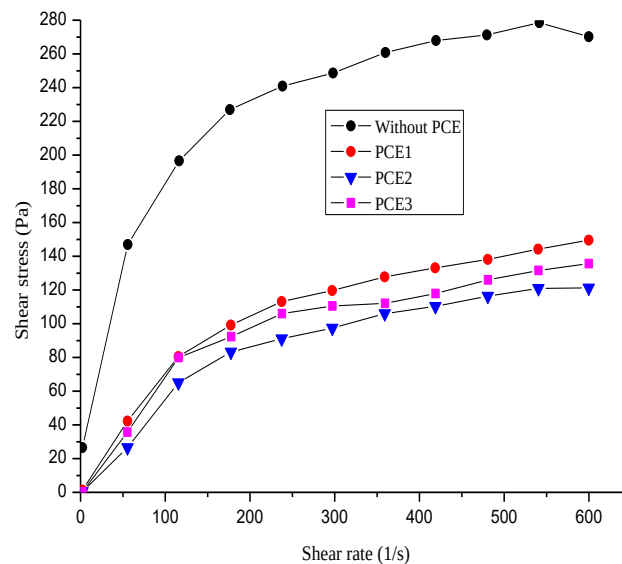


Fig. 4 – Shear stress as a function of shear rate of cement pastes with $w/c = 0.35$.

3.3 Rheology

The saturation point is the dosage beyond which the superplasticizer has no effect on the rheological properties of the cement paste. It is determined, using the viscometer VT 550. The saturation points of PCEs with a w/c ratio of 0.35 are 1.5; 1.25 and 1.5 respectively for PCE1, PCE2 and PCE3.

From this results (figures 4 and 5), at Saturation dosage, the shear stress and viscosity depend on the applied shear rate. The shear stress increases with increasing shear rate, the viscosity decreases with increasing shear rate, when the PCEs were added the yield stress was reduced [25, 26]. Paste incorporating PCE of moderate molecular weight and high carboxylic group exhibits the lowest shear stress and lowest plastic viscosity. The carboxylic density and molecular weight of PCE make great effects on the dispersing performance of PCE superplasticizers. As carboxylic density increases, the dispersing capability of PCE improves [27, 28]. PCE2 has highest carboxylic density in the backbone and moderate molecular weight possesses stronger adsorption behavior onto cement particles; therefore, the lowest viscosity and shear stress.

PCE3 has the lower carboxyl content and lower molecular weight signifies its side chains are length; it exhibits less viscosity and shear stress compared to PCE1 in cement paste.

The rheological results demonstrate that the dispersion ability of PCEs depends not only on the carboxylic content but also on the long side chain steric hindrance. The longer the side chain of PCEs, the greater the steric hindrance effect is, and the more easily cement particles is dispersed in the slurry signifies an increasing the flowability of cement paste. In the paste with PCE3 it can be understood that the main mechanism for the dispersion is the steric hindrance between the cement particles that carry the adsorbed polymer molecules [24].

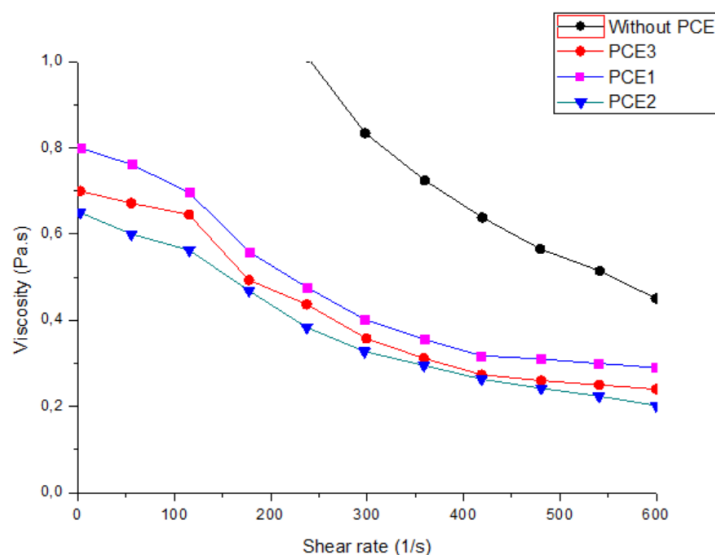


Fig. 5 – Viscosity as a function of shear rate of cement pastes with $w/c = 0.35$

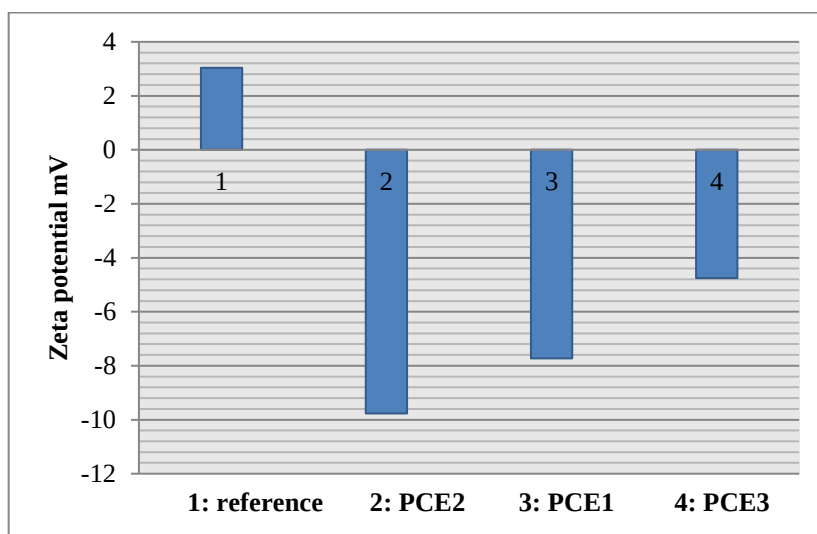


Fig. 6 – Zeta potential of cement paste as a function of PCE type

3.4 Zeta potential

The Zeta potentials of cement paste mixed with PCEs having different Carboxylic densities and molecular weight are shown in Figure 6, the order of zeta potentials is:

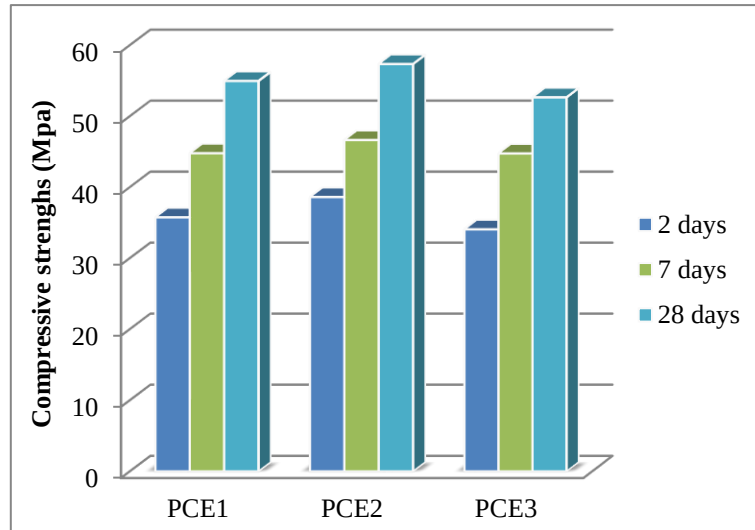


Fig. 7 – Compressive strengths of cement mortar containing various superplasticizers after hydration for various durations.

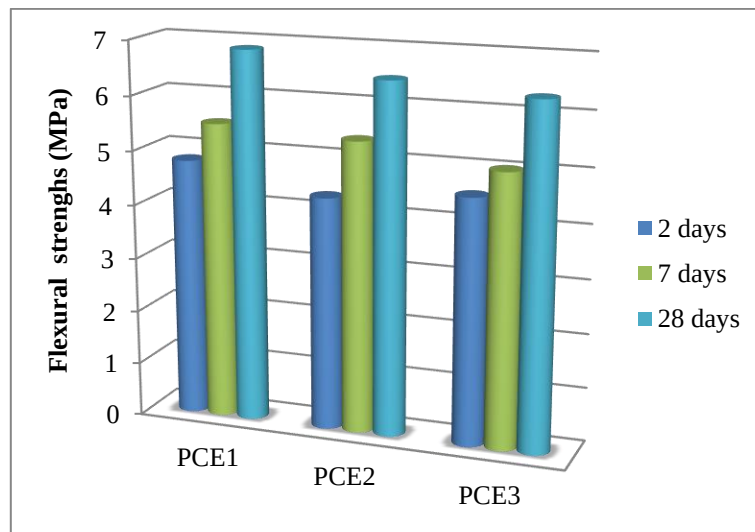


Fig. 8 – Flexural strengths of cement mortar containing various superplasticizers after hydration for various durations.

Reference $\text{PCE3} < \text{PCE1} < \text{PCE2}$ respectively, this implies a good correlation between zeta potential and carboxylic density. The results show that the zeta potential of cement paste initially exhibits positive value (3.035 mV) but then changes to negative value when adding the PCE due to the adsorption of the anionic groups (COO^-) in the backbone of PCE onto the surface of hydration products of cementitious via electrostatic adsorption by complexation with Ca^{2+} .

PCE2 has high Carboxyl content (1.95 mmol/g) and moderate molecular weight and polydispersity index (5 157Da, 1.081) presents high absolute value of zeta potential in cement paste (9.7735 mV), this are correlated with best adsorption capacity onto cement particles.

3.5 Compressive strength

The compressive and flexural strength of cement mortars with PCEs is shown in figures 7 and 8 respectively.

The compressive strengths of cement mortars in the presence of PCE2 measured at 2, 7 and 28 days are: 38.6, 46.64 and 57.35 MPa respectively are the highest strength values for various durations.

The PCE with high zeta potential exhibited better compressive strength value which is correlated with better adsorption [29-32].

The flexural strengths of cement mortars in the presence of PCE1 measured at 2, 7 and 28 days are: 4.79, 5.5 and 6.86 MPa respectively are the highest strength value. The PCE1 with highest molecular weight presents the highest flexural strength for various durations.

4 Conclusion

The molecular weight and the anionic charge density of polycarboxylate superplasticizer have a great impact on the properties of cement paste. The PCEs with a moderate molecular weight and highest carboxylic group had the best dispersion (high value of zeta potential) and lowest viscosity. The zeta potential and rheological properties of cement paste strongly depend to the anionic charge density and molecular weight of PCEs.

The PCEs with different architectures exhibit different impacts on the mechanical strength of cement mortar. The PCEs with moderate molecular weight and higher carboxylic groups lead to higher compressive strength of cement mortar. The PCEs with higher molecular weight present the higher flexural strength.

It was found that zeta potential, carboxylic density and compressive strength are well correlated.

The results from the time-dependent fluidity tests show that, the PCEs with a high molecular weight can be applied to precast concrete where a fluid consistency has to be retained over a longer period of time until delivery at the construction site has been achieved.

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