Influence of polycarboxylate side chains length on cement hydration and strengths development

Moratti F.*, Magarotto R., Mantellato S.,
BASF Construction Chemicals Italia Spa, Development Admixture Systems Europe, Italy, Treviso

Roncer J.
BASF Construction Chemicals Espana S.L., Development Admixture Systems Europe, Spain Palau

Abstract
In this paper the influence of the side chains length of polycarboxylates on the kinetics of cement hydration is investigated by means of thermogravimetric analysis, nuclear magnetic resonance, scanning electron microscopy and other techniques. The correlation with the strength development in concrete is then reported. Short side chains bring retardation in the strength development at 24 hours, but the ultimate strengths at 28 days result as unmodified. The analysis of the microstructure of cement paste at 28 days revealed that the side chain length has no impact on the structure of the ettringite crystals and the other products of hydration thus assuring durability. Furthermore, the retardation given by short side chains can be modulated and compensated by playing with the number of charges and side chains per backbone, thus preventing the calcium ions chelation and speeding up the hydration. Short side chains can therefore be used in all those applications were superior robustness and rheology are requested without the drawback of the retardation if a careful design of the molecule is carried out.

Originality
In this paper it was demonstrated that the side chain length has a specific impact on the strength at all curing ages. This paper gives some guidelines to the design of polycarboxylates that can be engineered to achieve the desired performances in terms of strength development. Some evaluations were also carried out considering different types of cements, showing that the use of short side chains leads to higher retardation when used in combination with limestone blended cements. A specific design of the molecule can anyway be adopted in order to counterbalance this effect.

Chief contributions
A very detailed study on the cement hydration was carried out by means of several analytical techniques and different polymeric structures, giving a comprehensive picture of how the polycarboxylate design can be moduled in order to achieve the desired performances in terms of strength development.

Keywords: Cement hydration, side chain length, strength development, microstructure.

* Corresponding author: Email francesca.moratti@basf.com  Tel +39 0422 429 315, Fax +39 0422 307 894
1. INTRODUCTION

Many different chemical compounds are introduced in concrete with the purpose of altering one or more of its properties in the fresh or hardened state and, more and more, superplasticizers are recognized as essential components in concrete technology. Within this range polycarboxylates are considered to remarkably contribute to the key drivers of the construction industry as energy efficiency, construction process speed, durability, sustainability and robustness of performances.

While in the case of the more traditional superplasticizers such as NS (naphthalene-formaldehyde sulphonated) and MS (melamine-formaldehyde sulphonate) the possibility to tailor make the molecular structure is limited, many more are the possibilities to modify it in the case of the polycarboxylates.

The ratio between the negative electrical charges and the hydrophilic side chains is the first parameter to be optimized according to the desired performances, but it is possible to play with many other parameters (backbone length, side chains length, electrical charges, side chains density, additional functional groups), each of whom will impart different properties to the concrete mixture.

The technical requirements drive the molecular design, and the state-of-the-art polycarboxylates reflect their application in the market. For example, admixtures for the Ready Mix industry are generally characterized by short side chains (up to 3000 Da) and a low charge density, that provide a medium-high water reduction capability and assure proper workability retention. Short side chains give in fact several advantages in terms of robustness towards chemistry of cement and longer workability retention (Sakai et al., 2003, Yamada et al., 2003, Yamada et al., 2001), while also the rheology of the concrete mixture is generally much easier to manage. Short side chains are therefore perfectly fitting most of the requirements of Ready Mix users. On the other hand, the use of polycarboxylates containing short side chains can give problems in terms of retardation, since it is well known that the strength development is boosted by long side chains (Corradi et al., 2002, Khurana et al., 2002, Zeminian et al., 2010).

It is therefore of paramount importance to carefully balance the chemical structure of the polycarboxylates in order to better optimize the performances of fresh and hardened concrete.

In this paper the correlation between chemical structure of PCE, and in particular side chains length, and strength development will be analyzed with a special attention to the microstructure of the hydration products. Results will show that side short side chains cause a retardation in the early strength (18-24 hours) but the ultimate strengths at 28 day are unmodified. A careful design of the molecule will therefore promote a proper hydration without modifying the cement paste microstructure.

2. EXPERIMENTAL DETAILS

2.1 Materials

One cement type I 42.5R and one cement type II/A-LL 42.5R were employed, which will be named CEM A and CEM B respectively. Their chemical analysis was carried out according to the methods reported in EN 196/2. The chemistry of the pore solution extracted from the cements was also evaluated: soluble sulphates (after 5 minutes of hydration at w/c=0.5) were measured through ionic chromatography, while soluble alkalis and calcium were evaluated by means of Inductive Coupled Plasma (ICP). Three different polycarboxylate-based superplasticizers (PCE-1, PCE-2 and PCE-3) were used in this work. All of them are polymeric water solutions. The chemical structures of the polymers are summarized in the following table:

<table>
<thead>
<tr>
<th>Polymeric solutions</th>
<th>Active content (%)</th>
<th>Density (g/cm³)</th>
<th>Molecular weight (Da)</th>
<th>Side chains length</th>
<th>Charges/Side chains ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCE-1</td>
<td>30</td>
<td>1,082-1,102</td>
<td>35.000</td>
<td>500</td>
<td></td>
</tr>
<tr>
<td>PCE-2</td>
<td>46</td>
<td>0,95-1,16</td>
<td>50.000</td>
<td>3000</td>
<td></td>
</tr>
<tr>
<td>PCE-3</td>
<td>45</td>
<td>1,06-1,13</td>
<td>40.000</td>
<td>6000</td>
<td></td>
</tr>
</tbody>
</table>

The charge density (charge number/side chains number ratio) of the three polymers was selected in order to obtain similar water reduction capability.

Cement pastes were prepared according to EN 196-3 with a w/c ratio of 0.35. All the PCEs were dosed at 0.15% active on CEM A and 0.18% active on CEM B in order to obtain similar initial fluidity. The pastes...
were prepared at room temperature and cured at 20°C and 90% relative humidity in 4x4x16 cm specimens. At the desired curing age the hydration was stopped by several rinses with ethanol and the samples were dried at 40°C for 30 minutes, then analysis were carried out.

2.2 Thermogravimetric analysis (TGA)
The analysis was performed at early ages, 18 and 24 hours, as well as after 7 and 28 days. Samples were obtained by grinding the hardened paste in an agate mortar, the resulting powders were analyzed by increasing the temperature from 25 to 900 °C at the rate of 10°C/min in nitrogen flow at 50 mL/min.

2.3 Calorimetric tests
The rate of the cement hydration was monitored by means of heat development of the cement paste at a temperature of 20°C. The instrument contains eight separate channels constructed in twin configuration with one side for the sample and the other for the inert reference (sand). After mixing, the cement paste was poured in a plastic ampoule with the sample mass recorded. After capping the ampoule, the sample and the reference ampoules were inserted in the calorimeter.

2.4 29Si- NMR Measurement
A 300 MHz solid-state high-resolution spectrometer with thick-walled zirconia rotors, rotating at 3800 Hz, was used to perform the 29Si MAS (magic angle spinning) Nuclear Magnetic Resonance analyses of the pastes.

2.5 Scanning Electron Microscopy (SEM)
The samples were coated with gold and introduced in the vacuum chamber for their observation. The accelerating voltage used ranges from 10 to 20 kV, according to the age of the samples. All the observations were made on fractured surfaces.

2.6 Concrete tests
Some concrete tests were carried out in the lab, preparing 30 litres batches of in a vertical axis mixer. The mix proportion was the following: CEM = 330 kg/m³, sand 0-4 = 1075 kg/m³, crushed gravel 8-12 = 390 kg/m³, natural gravel 19-25 = 490 kg/m³, W/C = 0.48 for CEM A and 0.46 for CEM B. All the tests were performed at 20°C, with all the materials cooled down to 10°C for 24 hours before mixing. The mixtures were prepared according to the following procedure: cement and aggregates were placed in the mixer, two thirds of the mix water were added and mixed for 1 minute, the mixing was stopped for 1 minute to allow false set, if present, to take place. The mixing was continued for another minute introducing the superplasticizer, and then the remaining water was added. Initial slump was measured according to EN 12350-2; the air content was measured by air meter (EN 12350-7). 150 mm cubes were cast in steel moulds and cured at 10 and 20°C and 95% relative humidity and tested for compressive strengths after different curing times.

3. RESULTS AND DISCUSSION

3.1 Chemical composition
Table 2 reports the chemical composition of CEM A and CEM B according to EN 196/2:

<table>
<thead>
<tr>
<th></th>
<th>Loss on ignition (%)</th>
<th>SiO₂</th>
<th>CaO</th>
<th>MgO</th>
<th>Fe₂O₃</th>
<th>Al₂O₃</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>SO₃</th>
<th>Free CaO</th>
<th>Chloride</th>
</tr>
</thead>
<tbody>
<tr>
<td>CEM A</td>
<td>1,89</td>
<td>20,43</td>
<td>63,74</td>
<td>1,46</td>
<td>2,6</td>
<td>4,4</td>
<td>0,47</td>
<td>0,78</td>
<td>2,7</td>
<td>0,84</td>
<td>&lt;0,05</td>
</tr>
<tr>
<td>CEM B</td>
<td>4,5</td>
<td>20,41</td>
<td>61,6</td>
<td>1,53</td>
<td>2,1</td>
<td>4,6</td>
<td>0,48</td>
<td>0,8</td>
<td>2,89</td>
<td>1,26</td>
<td>&lt;0,05</td>
</tr>
</tbody>
</table>

* At 5 minutes and W/C = 0.5

3.2 TGA analysis
As reported in literature (Gabrovsek et al., 2006, Tsivilis et al., 1998), in the thermogravimetric plot of hydrated cement pastes, CSH gel and the Portlandite are identified at the following range of temperature:
- 25–150 °C: water present in the pores, dehydration of ettringite, calcium sulfates, monosulphate and water loss from C-S-H gel layers;
- 150 – 400 °C: complex mixture of hydrated silicate- and aluminate-type compounds;
- 400-450 °C calcium hydroxide;
- Calcium carbonate

CSH gel is characterized by different hydrated structures and its dehydration doesn’t come at a narrow range of temperatures as in the case of the Portlandite, making the investigation difficult. In this work the mass loss due to the dehydration of CSH gel has been detected between 150°C and 400°C.

![Figure 1](image1.png)  
**Figure 1** – Formation of CSH at different ages – CEM A (a) and CEM B (b)

![Figure 2](image2.png)  
**Figure 2** – Formation of Portlandite at different ages – CEM A (a) and CEM B (b)

Figures 1 and Figure 2 show the results of TGA analysis in the complete range, from 18 hours to 28 days. Results confirm the retardation at early ages (18 hours and 24 hours) when PCE-1 is added in the cement paste, due to the minor weight loss in the range 150°C-400°C and 400°C-450°C in comparison to PCE-2. At longer ages (28 days) PCE-1 and PCE-2 show similar behavior in terms of development of CSH gel and Portlandite.

It can be also noticed that the retardation induced by PCE-1 is much higher when CEM B is used, meaning that also the type of cement play a key role in determining the interaction with polycarboxylates. This behavior was validated with other limestone blended cements, which always resulted in a higher retardation of CEM II with respect to CEM I type cements.

### 3.3 Calorimetric results

Results shown in Figure 3 and 4 represent the conduction calorimetric curve of CEM A and CEM B in presence of PCE-1 and PCE-2. In each of these figures the reference curve without polymer is also reported. The addition of PCEs causes a significant delay effect on both cements: as reported in literature (Plank et al., 2009) the retardation on the cement hydration is due to the formation of complex salt between functional group of PCE and Ca²⁺ ions, decreasing the concentration of Ca²⁺ in the liquid phase and then delaying the starting of the hydration. Due to its structure, PCE-1 shows an induction time doubled in comparison to PCE-2 at the same dosage, when added on CEM B. In fact, PCE-1 has the highest number of charges and the lowest number of side chains, both promoting Ca²⁺ chelation and thus retarding the cement hydration. The initial retardation doesn’t compromise the proceeding of hydration and after 36 hours the difference in terms of heat development between the PCEs is similar on both cements.
3.4 $^{29}$Si- NMR measurement results

This technique provides useful information about the state of the tetrahedral SiO$_4^{4-}$ in the paste (Zanni et al., 1996, Masse et al., 1993), which is indicative of the formation of C-S-H due to hydration. In the process of silicate polymerization, the individual tetrahedrons (called monomers, whose state is designated as Q0) of the anhydrous silicate phases (C$_3$S, C$_2$S) of the cement are transformed through hydration in dimers (Q1) and polymeric chains (Q2) of tetrahedrons by means of connections through oxygen atoms. Each of these states, which reflect the degree of polymerization of the silicates in the paste due to the C-S-H formation, is represented by a peak in the NMR spectrum (given as a function of the chemical displacement). Figure 5 shows the $^{29}$Si NMR spectrum of the reference paste along with that of the pastes incorporating PCE-1 and PCE-2, at different ages. Two peaks can be identified in the plots: that of Q0 in the chemical displacement range of -66 to -74 ppm, and that due to the formation of C-S-H corresponding to Q1 and Q2 signals, in the range of -75 to -82 ppm and -85 to -89 ppm, respectively.

Since the peaks in the NMR spectra overlap, a semi-quantitative method is used to compare the curves obtained at different ages. The areas of the anhydrous silicates (Q0) and those of the C-S-H (Q1 and Q2), denoted respectively as $A_0$ and $A_{C-S-H}$, are obtained for each spectrum as in Figure 6 and Figure 7.

It can be observed that the PCE-1 leads to a delay on the hydration processes at early ages without affecting the formation of C-S-H at 28 days.
3.5 Scanning Electron Microscopy results

SEM can be used to observe the morphology of the different phases of the hardened cement paste and its evolution during hydration. Literature (Scrivener, 1989) shows that, during the first stages of the hydration, the cement particles are covered with an aluminate-rich gel and short ettringite rods. Later on, the reaction of the C₃S leads to the formation of the ‘outer’ C-S-H, which is followed by secondary hydration of C₂A producing ettringite in the form of long rods and the beginning of the formation of the ‘inner’ C-S-H. The formation of C-S-H is accompanied by the crystallization of portlandite, which is, however, not easily observed through SEM.

Figure 8 and 9 show the evolution of the hydration for CEM B in presence of PCE-1, PCE-2 and without any admixture. Results for CEM A are almost identical. It can be observed a higher formation of ettringite crystals at 18h in presence of PCE-2 with respect to PCE-1, but at after 28 days of hydration the microstructure of cement paste is the same for all the samples.

3.6 Concrete tests results

Results of concrete test are shown in Table 3. It can be seen that all the data relating to the strength development are in line with all the previous analysis. PCE-1 show a retardation in the early strength
development (18 and 24 hours, both at 10 and 20°C), as expected, while the difference between PCE-2 and PCE-3 can hardly be observed, even if their molecular structure is different. This can be explained considering that the higher number of side chains of PCE-2 allows a recovery of the retardation given by the shorter side chains length and the higher number of charges.

<table>
<thead>
<tr>
<th>Table 3 - Concrete tests</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>3</td>
</tr>
<tr>
<td>4</td>
</tr>
<tr>
<td>5</td>
</tr>
<tr>
<td>6</td>
</tr>
</tbody>
</table>

3.7 Conclusions
Molecular structure of polycarboxylates can be easily modified in order to drive the performances in fresh and hardened concrete. The side chains length is a key parameter that controls the development of the mechanical strengths that are boosted at early ages by long side chains. The use of shorter side chains is nevertheless preferred in Ready Mix application, where the workability retention is of paramount importance. Furthermore, the use of short side chains improves the robustness of the admixture and the rheology of the resulting concrete. In this paper it was demonstrated that the use of short side chains, thus having an expected impact on the initial strength development, does not chain the final microstructure of cement paste, thus guaranteeing a proper growth of the hydration product and assuring durability. Furthermore, the retardation given by short side chains can be modulated and compensated by optimizing the number of charges and side chains per backbone, thus preventing the calcium ions chelation and speeding up the hydration.

References