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## The influence of the chemical structure of polycarboxylic superplasticizers on their effectiveness in cement pastes

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### Abstract

The efficiency of polycarboxylic superplasticizers (derivatives of acrylic (SP-A and SP-B) or maleic (SP-C and SP-D) acids) after esterification with polyoxyethylene glycols (PEG) in cement pastes was analysed.

The chemical structure of the superplasticizers was defined by gel permeation chromatography (GPC) and Fourier transformed infrared spectroscopy (FTIR). According to the experimental results the superplasticizers - derivatives of maleic acid - display greater molar mass and are built from backbone polymaleic chains and very long side polyoxyethylene chains.

It is shown that acrylic superplasticizers display lower molar mass and are built from polyacrylic backbone chains and a higher number of shorter polyoxyethylene side chains. The efficiency of superplasticizers has been measured through their hydrophilicity, defined as the absorbance ratio of the ether band  $A_{ET}^{1110}$  ( $STRCH_2-O-CH_{2ET}$ ) (referred to as the hydrophilic oxyethylene groups) to the ester band  $A_{ES}^{1730-40}$  ( $STRC=O_{ES}$ ) (referred to as the hydrophobic ester groups  $O=C-O-C$ ) (with constant contents of aliphatic groups). A higher hydrophilicity of maleic superplasticizers, in comparison to acrylic, results from greater participation by the hydrophilic than the hydrophobic groups. It is shown that superplasticizers based on maleic anhydride derivatives (SP-C and SP-D) are more efficient than superplasticizers - acrylic acid derivatives (SP-A and SP-B).

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**Keywords:** Cement, rheology, heat of hydration, superplasticizers, chemical structure SP

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## 1. Introduction

The development of high-performance concrete technology, with the growing demands for increased durability, was possible due to the introduction of new-generation superplasticizers by Japanese industry in the 1990s [1-3]. These superplasticizers are suitable polycarboxylic derivatives (PC), particularly polyacrylic (PA) and polymaleic (PM) derivatives, polyethers (PE), co-polymers of acrylic acid and acrylic ester (CAE) and polyacrylic ether (PAE) [4-7].

The functional mechanism of such superplasticizers is connected with the effect of spatial steric blockade, formed due to long, polyoxyethylene side chains existing in their structure. The side chains of the polymer molecule adsorbed at the cement grains can block them against other cement particles thus enabling flocculation into large agglomerates leading to the fluidization of cement pastes [8, 9].

Numerous authors have proved that the different efficiencies of polycarboxylic superplasticizers are connected to their chemical structures and particularly with the type, length and arrangement of the backbone and side chains as well as with the presence of functional groups [10-12].

It seems generally accepted that efficiency of the polycarboxylic superplasticizer increases with the number and length of the side chains while short side chains have a minor impact on cement paste fluidization [13, 14].

The presence of hydrophilic groups in the superplasticizer structure plays an important role in their effectiveness. A change of structure through the introduction of the hydrophilic hydroxyl ( $-OH$ ) or oxyethylene ( $-O-CH_2CH_2-$ ) groups instead of the hydrophobic methoxyl groups ( $-O-CH_3$ ) within the side chain can result in an increase of the superplasticizer's steric effect due to simultaneous adsorption of the backbone chain at the cement particle surface [15] (Plank et al. 2008). Hydrophilic polyoxyethylene chains undergo hydration in the cement paste, thus forming hydrogen bridges between oxygen atoms (in the ether group) and hydrogen atoms (in the water molecule); this influences the length, volume and morphology of the chains [16, 17].

The superplasticizers may react with the cement components [18-20] or with products in the cement hydration [21, 22] thus affecting the cement hydration and cement setting [23, 24]. Superplasticizers in the cement pastes directly influence their rheological properties [25-28].

The article presents the results of research into polycarboxylic superplasticizer structure. The superplasticizers studied were ester derivatives of acrylic acid and maleic anhydride (after esterification with polyoxyethylene glycols PEG). The effect of the superplasticizer polymer chemical structure on the rheological properties of the cement paste was determined, and thus the superplasticizer efficiency.

## 2. Materials used

The superplasticizer efficiency was studied in pastes made of cement (C) prepared in the laboratory by the co-grinding of industrial Portland clinker (K) with dihydrate gypsum (5wt%). Chemical and mineral composition of the clinker and the Blaine surface are shown in Table 1.

Table 1. Chemical and mineral composition of clinker (K) and its Blaine specific surface.

Component	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>	K <sub>2</sub> O	CaO <sub>free</sub>	C <sub>3</sub> S	C <sub>2</sub> S	C <sub>4</sub> AF	C <sub>3</sub> A	Blaine surface [m <sup>2</sup> /kg]
<b>Clinkier K</b> [wt%]	21.6	2.5	4.7	65.1	0.8	0.4	0.2	0.6	62.0	15.0	8.0	8.0	320

Four solid phase superplasticizers were tested. The following symbols were ascribed to the superplasticizers: SP-A and SP-B (for polyoxyethylene derivatives of acrylic acid), and SP-C and SP-D (for polyoxyethylene derivatives of maleic anhydride). Superplasticizers used in rheological studies contained 40 wt % of solid matter in the aqueous solution; 1 wt % of the solution was added with respect to the cement weight.

### 3. Experimental techniques

The structures of superplasticizers were investigated using gel permeation chromatography (GPC) and absorption infrared spectroscopy (FTIR). Rheological tests were performed to investigate the relationship between the structures of the superplasticizers and their performance in cement pastes.

#### 3.1. Gel Permeation Chromatography (GPC)

Phase compositions of the superplasticizer samples were studied using chromatographic fractionation into polymer cuts via the low temperature gel permeation chromatography (GPC) method. The tests were performed using the chromatograph (Watt Technology) equipped with a refractive index (RI) detector and Down EOS multi-angle light scattering detector. THF (tetrahydrofuran) was used as the eluent, and the samples of commercial superplasticizers were injected as 1-2% solutions in THF. The analytical temperature was 35°C, and the THF flow rate was adjusted to 1 ml/min. The set of GPC columns PSS SDV 1·10-6A+2·100A (300 × 8 mm, from Polymer Standard Service) was employed.

#### 3.2. Fourier Transform infrared Spectroscopy (FTIR)

The IR absorption spectra of the samples were recorded using FTIR spectrometer (model PU9804, Philips Analytical) with a constant spectral resolution  $R = 2\text{cm}^{-1}$ ; each sample was scanned twenty times. The samples were prepared for tests as potassium bromide (KBr) disks. In order to find the contents of the hydrophobic aliphatic groups CH, CH<sub>2</sub> and ester groups O=C–O–CH<sub>2</sub>, as well as the hydrophilic polyoxyethylene groups O–CH<sub>2</sub>CH<sub>2</sub>, FTIR spectra for superplasticizers were taken over the whole spectral range (4000 – 400 cm<sup>-1</sup>). The spectra were subjected to standardisation by referring them to the same sample content in the beam path, with the use of the band for stretching the vibrations of aliphatic groups 2887cm<sup>-1</sup> STRCH<sub>2</sub>CH<sub>2</sub> – adopted as the internal standard.

#### 3.3. Rheological studies

The rheological measurements were carried out using the Viscotester VT550 rotary viscometer, equipped with two coaxial cylinders. Yield stress and plastic viscosity values were established according to the Bingham model. The experiments were performed for the cement pastes with 1 wt % addition of a superplasticizer, and constant water cement ratio (w/s) amounting to 0.38, at a temperature of 21°C.

### 4. Experimental results: chemical structure of superplasticizers

Quantitative chromatographic analysis of the polymer fractions contained in the superplasticizers was performed to establish the superplasticizer's chemical structure. Applying the GPC method, the quantity of the polymer fractions and the weight-averaged molecular mass ( $M_w$ ) were derived. The results of the GPC analysis are presented in Figure 1 for the SP-A through SP-D superplasticizers.

The GPC results of the SP-A, SP-C and SP-D samples show two different polymer fractions; for SP-B, a third fraction was additionally found (cf. Fig. 1). Polymer fractions denoted as 1 derive from superplasticizers and fractions 2 and 3 from unreacted polyoxyethylene glycols (PEG). The highest content of the poor superplasticizer polymer was found in the SP-C technical sample (about 85%), and the lowest was in the SP-B

sample (about 52%). Samples SP-A and SP-B were mostly contaminated with unreacted polyoxyethylene glycols, 31% and 48.3%, respectively, compared with the SP-C and SP-D samples (14-18%). The presence of unreacted polyoxyethylene glycols can decrease superplasticizer efficiency.

According to the data presented in Figure 1, the average molecular mass,  $M_w$ , of the superplasticizers was 6050 g/mol (SP-A), 11700 g/mol (SP-B), which is lower compared to the SP-C and SP-D samples (14850 and 14800, respectively; cf. Fig. 1).

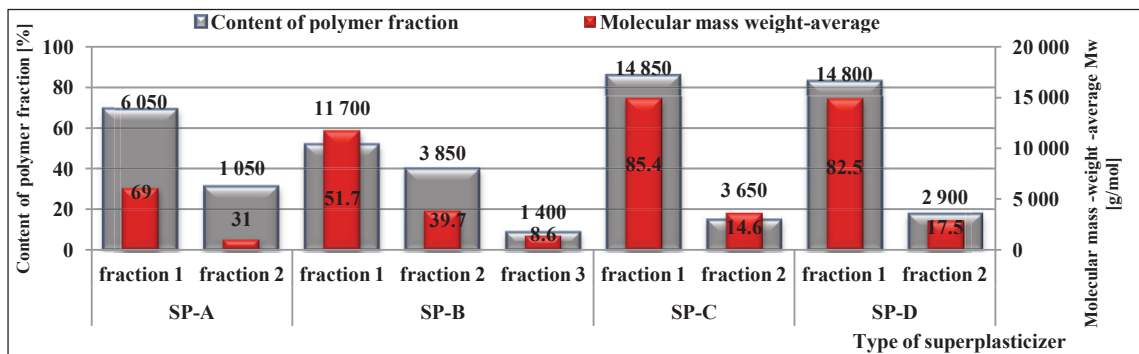
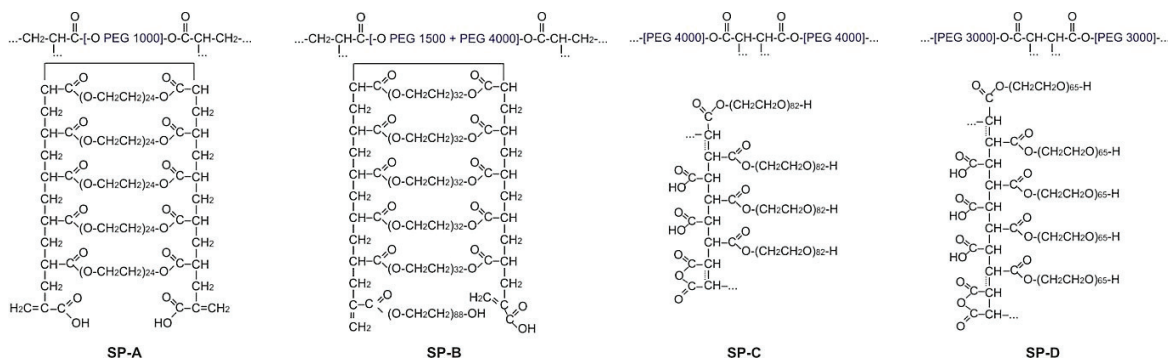


Fig. 1. Results of the GPC chromatographic analysis of superplasticizer polymer fractions.

Infrared spectral analysis (FTIR) was performed for the superplasticizers, to identify the functional groups. When also considering the molecular mass of the polymer fractions (based on the GPC analysis), it was shown that the superplasticizers studied are ester derivatives of acrylic acid and maleic anhydride (after their esterification with diverse polyoxyethylene glycols PEG). The SP-A sample was derived from acrylic acid esterification with the polyoxyethylene glycols PEG 1000 while the SP-B from acrylic acid esterification with the mixture of glycols PEG 1500 and PEG 4000. Samples SP-C and SP-D originated from maleic anhydride esterification with PEG 4000 and PEG 3000, respectively. Approximated structures of the superplasticizers polymers SP-A, SP-B, SP-C and SP-D, derived using mathematical calculation of molecular mass, are presented in Figure 2.



where: PEG to  $\text{HO}-(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$  1000 -  $n=22$ ,  $n=22$ , experimentally derived value  $n=24$   
 1500 -  $n=34$ , experimentally derived value  $n=32$   
 3000 -  $n=68$ , experimentally derived value  $n=65$   
 4000 -  $n=90$ , experimentally derived value  $n=82$  for SP-C and  $n=88$  for SP-B

Fig. 2. Approximated chemical structures, ladder-shaped (SP-A, SP-B) and comb-shaped (SP-C, SP-D), of the superplasticizers derived using mathematical calculation of molecular mass [29].

The SP-A and SP-B superplasticizers display a stiff ladder structure, in which two ester groups ( $\text{CH}_2\text{CHCOO}$ ) of the polyacrylic backbone chain are connected with a single polyoxyethylene side chain; the mer numbers in the chain amount to  $n=24$  and  $n=32$ , respectively. The SP-B superplasticizer comprises, apart from the shorter side chains ( $n=32$ ), a single, very long polyether side chain ( $n=88$ ). On the other hand, the SP-C and SP-D superplasticizers have an elastic comb-shaped structure that results from a single ester bond between the polymaleic backbone chain and the very long polyoxyethylene side chains (comprising number of mers  $n=82$  and  $n=65$ , respectively); note the number of side chains is higher in SP-D.

The occurrence of characteristic functional groups in the superplasticizers was proven, based on the FTIR spectra within selected spectral ranges characteristic of the C-H aliphatic groups ( $3200\text{-}2500\text{ cm}^{-1}$ ), carbonyl groups ( $1900\text{-}1500\text{ cm}^{-1}$ ) and ether groups ( $1250\text{-}950\text{ cm}^{-1}$ ), cf. Figure 3.

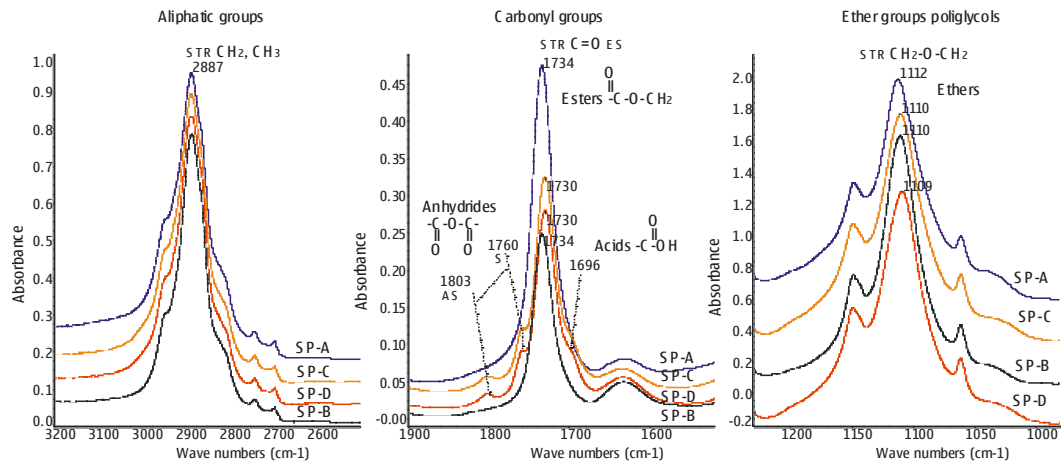


Fig. 3. Standardised FTIR spectra for superplasticizers within the ranges specific for aliphatic, carbonyl and ether groups [30].

Based on the FTIR spectra characteristic for the carbonyl groups ( $1900\text{-}1500\text{ cm}^{-1}$ ), the SP-C and SP-D superplasticizers contain a certain amount of carboxylic acids ( $1696\text{-cm}^{-1}$ ), maleic anhydride (doublet  $1803$  and  $1760\text{ cm}^{-1}$ ) and from esters ( $1730\text{ cm}^{-1}$ ). For the acrylic superplasticizers SP-A and SP-B, in addition to the ester band ( $1734\text{ cm}^{-1}$ ), a distinct carbonyl group band originated from acids ( $1696\text{ cm}^{-1}$ ) was not found, thus content of  $\text{COOH}$  groups is very small.

Based on the spectra presented in Figure 3, absorbances were derived of the bands that were characteristic of hydrophobic aliphatic groups (at wavenumber  $2887\text{ cm}^{-1}$   $\text{STRCH}$ ,  $\text{CH}_2$ ) and ester groups within the backbone chain (at wavenumber  $1734\text{-}1730\text{ cm}^{-1}$   $\text{STRC=OES}$ ), as well as hydrophilic oxyethylene groups ( $1112\text{-}1109\text{ cm}^{-1}$   $\text{STRCH}_2\text{-O-CH}_2\text{ET}$ ).

The FTIR spectra was standardized to reach identical absorbance of the aliphatic groups band ( $\text{CH}$ ,  $\text{CH}_2$ ,  $2887\text{ cm}^{-1}$ ) for comparative quantitative analysis of the absorbances of hydrophilic ether groups (within oxyethylene mers of side chains,  $1112\text{-}1109\text{ cm}^{-1}$ ) and of hydrophobic ester groups (within backbone chain,  $1734\text{-}1730\text{ cm}^{-1}$ ). The absorbance results for the aliphatic (C-H), ester ( $-\text{C=O-O-}$ ) and ether ( $\text{CH}_2\text{-O-CH}_2$ ) bands are shown in Figure 4.

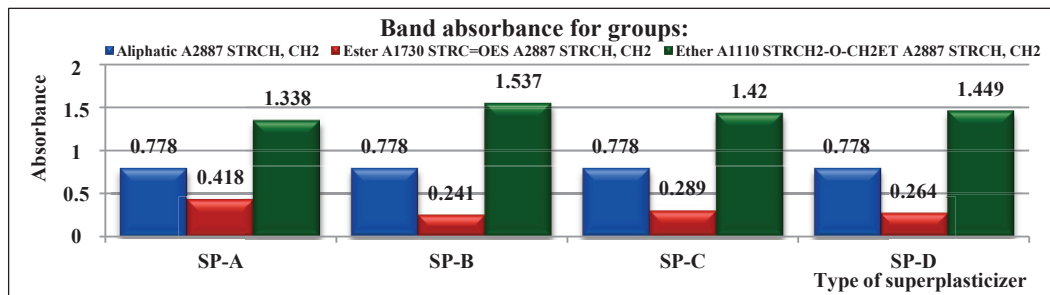


Fig. 4. Results of FTIR spectral analysis of superplasticizer samples.

Based on the GPC originated weight contents of the superplasticizer polymer SP fraction (Fraction 1) and unreacted PEG glycols (Fractions 2 and 3), the absorbances of the ether groups were derived and gathered in Table 2.

Table 2. Distribution of ether groups between the superplasticizer polymer and free polyglycols.

Sample of SP	Mass fraction of polymer		Absorbance of ether band	
	in SP (fraction 1)	in PEG (fractions 2 and 3)	in SP (fraction 1)	in PEG (fractions 2 and 3)
SP-A	0.690	0.310	0.923	0.415
SP-B	0.517	0.483	0.793	0.742
SP-C	0.854	0.146	1.213	0.207
SP-D	0.825	0.175	1.195	0.254

To assess the superplasticizer's hydrophilicity, the hydrophilicity coefficient was defined ( $A_{ET}^{1110}/A_{ES}^{1730}$ ), as a ratio of the ether band absorbance  $A_{ET}^{1110}$  ( $STRCH_2-O-CH_2ET$ ) (hydrophilic oxyethylene groups  $O-CH_2CH_2$ ) to the ester band absorbance  $A_{ES}^{1730-40}$  ( $STRC=O_{ES}$ ) (hydrophobic ester groups  $O=C-O-C$ , at constant content of aliphatic groups  $A^{2887}=\text{const.}$ ). Hydrophilicity coefficients are shown in Figure 5.

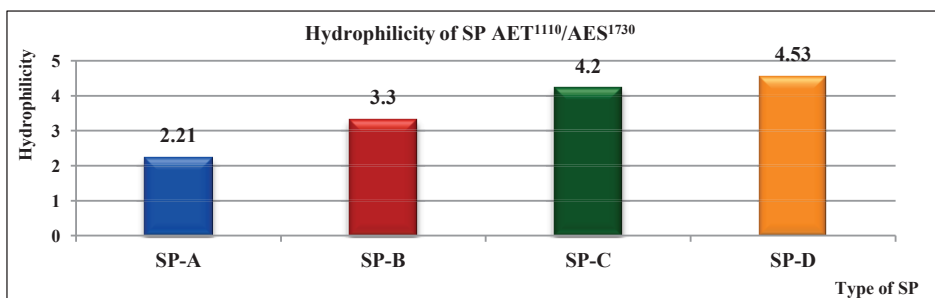


Fig. 5. Hydrophilicity of the superplasticizers.

Based on the data in Figure 5, maleic superplasticizers display higher hydrophilicity, and the hydrophilicity of the acrylic superplasticizers is lower. Superplasticizer SP-B shows higher hydrophilicity (3.30) within the acrylic superplasticizers (SP-A and SP-B). Within the maleic group (SP-C and -D), superplasticizer SP-D displays the highest coefficient (4.53). The hydrophilicities derived were applied to assess the superplasticizer efficiencies in the cement pastes.

## 5. Effect of superplasticizer's chemical structure on the cement paste rheological properties

To assess the superplasticizer's chemical structure effect on the cement paste rheological properties, rheological experiments were performed. The pastes were made of the cement C containing % wt% of gypsum (setting time

regulator) and 1wt% of superplasticizer (SP-A through -D). The rheological research was done after 10 and 60 minutes. The results are shown in Figure 6.

Analysis of the plastic viscosity  $\eta_{pl}$  (Fig. 6) demonstrated that the SP-C and SP-D superplasticizers (maleic derivatives) lead to better fluidization of the paste (lower plastic viscosity) compared to acrylic superplasticizers SP-A and SP-B. Plastic viscosity for SP-A was the highest, then SP-B, SP-C, and finally SP-D.

The plastic viscosity of cement paste with the SP-D admixture, after 10 and 60 minutes, was less than half that of the paste with SP-A. Superplasticizer efficiency decreased in the order: SP-D > SP-C > SP-B > SP-A. The higher the superplasticizer hydrophilicity coefficient (Fig. 5), the better its efficiency (Fig. 6).

For the maleic superplasticizers, a higher share of the hydrophilic groups (compared to the hydrophobic ones) brought about higher superplasticizer hydrophilicity, and thus better efficiency. Hydrophilicity of the SP-D was highest ( $A_{ET}^{1110}/A_{ES}^{1730}_{SP-D} = 4.53$ ), and slightly lower is that of SP-C ( $A_{ET}^{1110}/A_{ES}^{1730}_{SP-C} = 4.20$ ). Hydrophilicity of the maleic superplasticizers increased due to the hydrolysis of carboxylic acids and anhydrides, present in their structure, accompanied by the formation of carboxyl groups  $-COO^-$ .

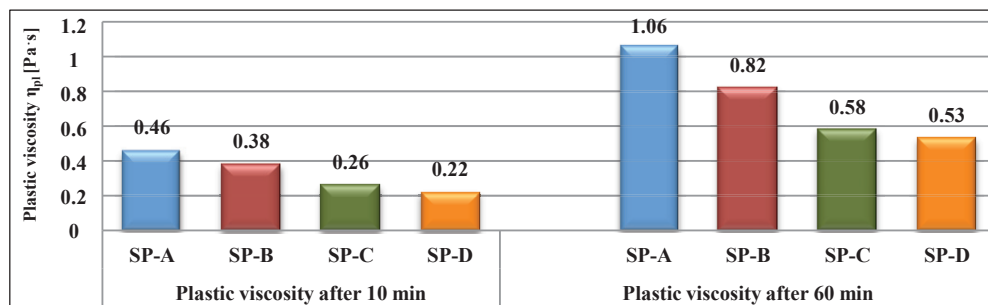


Fig. 6. Plastic viscosity  $\eta_{pl}$  of pastes in cement C containing 1% mas. superplasticizer SP-A, SP-B, SP-C i SP-D, after 10 and 60 minutes of hydration.

Acrylic superplasticizers containing very low amounts of carboxyl groups displayed significantly lower hydrophilicity compared with the maleic ones (i.e. lower ratio of hydrophilic to hydrophobic groups). This results in much lower efficiency in cement pastes. The SP-B superplasticizer had higher hydrophilicity ( $A_{ET}^{1110}/A_{ES}^{1730}_{SP-B} = 3.30$ ) than the SP-A one ( $A_{ET}^{1110}/A_{ES}^{1730}_{SP-A} = 2.21$ ).

The higher efficiency of the maleic superplasticizers (SP-C and SP-D) results from the very long hydrophilic side chains (built from more than 320 oxyethylene mers) and carboxylic groups (more than 4) present in their structure. Carboxylic groups undergo hydrolysis in the paste, additionally increasing superplasticizer hydrophilicity.

The lower efficiency of acrylic superplasticizers SP-A and SP-B, compared with SP-C and SP-D, results from a lower number of hydrophilic groups (120 and 248 oxyethylene mers, respectively, in the shorter side chains), as well as a lower number of carboxylic groups (less than two, cf. Fig. 2).

The superplasticizer efficiency can also be connected to their molecular mass. The SP-D superplasticizer displays the highest molecular mass and it has the highest efficiency; then the superplasticizers SP-C, SP-A and SP-B, according to their molecular mass. These problems are discussed in details in [30].

Other factors affecting superplasticizer efficiency are:

- presence of carboxylic acids and anhydrides in the superplasticizers (due to possible formation of the  $-COO^-$



groups in the cement paste, as a result of carboxylic group hydrolysis),

- content of the superplasticizer polymer in the sample.

Superplasticizer efficiency decreases, however, with the content of the unreacted PEG glycols.

## Conclusions

- Acrylic superplasticizers have lower molecular mass; they are built from polyacrylic backbone chains and more shorter polyoxyethylene side chains.
- The higher efficiency of maleic superplasticizers results from, among other things, the presence of carboxylic acids ( $\text{IR } 1696 \text{ cm}^{-1}$ ) and of maleic anhydride ( $\text{IR } 1803 \text{ cm}^{-1}$  i  $1760 \text{ cm}^{-1}$ ). In the alkaline environment these form carboxylic anions  $-\text{COO}^-$  that can anchor the suspension grains due to electrostatic forces. Such a property doesn't appear for acrylic superplasticizers.
- The efficiency of the superplasticizer's polymer fraction increases with its hydrophilicity, defined as the ratio of absorbance of the hydrophilic oxyethylene groups  $\text{CH}_2-\text{O}-\text{CH}_2 - \text{A}_{\text{ET}}^{1110}$  to absorbance of the hydrophobic ester groups  $\text{O}=\text{C}-\text{O}-\text{CH}_2 - \text{A}_{\text{ES}}^{1734}$ .

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