Polymeric superplasticizers based on polycarboxylates for ready-mixed concrete: current state of the art

Daniel Wiliński[1), *)], Paweł Łukowski[1)], Gabriel Rokicki[2)]

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Abstract: Chemical admixtures are one of the basic components of the contemporary concrete. The most important admixtures are superplasticizers, *i.e.* the modifiers which allow for high-range reducing of the water content in the concrete mix. The most effective superplasticizers are based on polycarboxylates and their derivatives. The state of the art in the range of polycarboxylate admixtures for concrete is presented in the paper. The methods of synthesis and modification of carboxylic polymers are characterized and the mechanism of action of polycarboxylate superplasticizers is described. The influence of the chemical structure of polycarboxylates on the consistence of the concrete mix, as well as the prognosis of the superplasticizers development is also presented.

Keywords: superplasticizers, polycarboxylate, chemical admixtures, cement, concrete.

Polikarboksylanowe domieszki upłynniające mieszankę betonową: aktualny stan wiedzy

Streszczenie: Podstawowym składnikiem betonu są obecnie domieszki chemiczne. Za najważniejsze uznaje się superplastyfikatory, czyli domieszki silnie redukujące zawartość wody w mieszance betonowej. Do najefektywniejszych znanych superplastyfikatorów zaliczają się polikarboksylany i ich pochodne. Artykuł stanowi przegląd aktualnej literatury dotyczącej polikarboksylanowych domieszek chemicznych. Scharakteryzowano metody syntezy i sposoby modyfikacji polimerów z grupami karboksylowymi i omówiono mechanizm działania takich superplastyfikatorów. Przedstawiono zależność między strukturą chemiczną polikarboksylanów a stopniem upłynnienia mieszanki betonowej oraz prognozę rozwoju superplastyfikatorów.

Słowa kluczowe: superplastyfikatory, polikarboksylany, domieszki, cement, beton.

In the current concrete technology, the chemical admixtures are important components of the concrete mix. The main progress in the concrete technology is associated with the admixtures development. The admixture for concrete is defined as the material added to the concrete mix in a quantity not more than 5 wt % of the cement mass. Therefore, the concentration of the polymer is too low to form the film inside the hardening cement paste; this can take place when the content of polymer is higher (in such case the polymer modifier is called an addition) [1]. Most chemical admixtures applied in concrete present anionic polyelectrolytes which physically adsorb on the cement grain surface for effective acting. Such admixtures aimed at modification of the concrete mix properties were first introduced in thirties of the last century. Their function was to improve the consistence of the cement paste [2]. Figure 1 clearly indicates that the introduction of superplasticizers, which made possible a decrease of water to cement ratio (*w*/*c*), afforded a significant increase in the concrete strength [3]. Nowadays, the use of admixtures varies greatly from one country to another. For example, in Japan almost 100 % of concrete contains admixtures. But, for example, in the United States more than 50 % of concrete contains chemical agents, although this percentage is increasing constantly as the beneficial role of admixtures is understood [4]. Apart from concrete, polycarboxylate (PCE) superplasticizers are also used in the manufacture of gypsum materials [5].

The admixtures affecting the consistence of the concrete mix can be categorized as water reducing admixtures (plasticizers) and high-range water reducing admixtures (superplasticizers, also called the liquefying admixtures), the latter being much more effective. The efficiency of the admixtures is evaluated by the possible

[1)] Warsaw University of Technology, Faculty of Civil Engineering, Department of Building Materials Engineering, Al. Armii Ludowej 16, 00-637 Warsaw, Poland.

[2)] Warsaw University of Technology, Faculty of Chemistry, Noakowskiego 3, 00-664 Warsaw, Poland.

[*)] Author for correspondence; e-mail: d.wilinski@il.pw.edu.pl

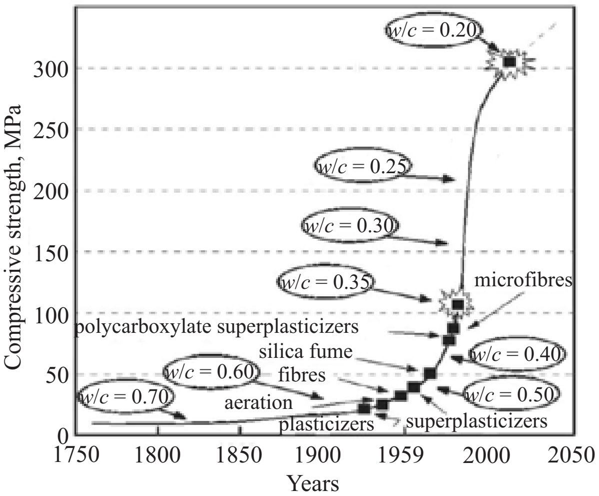


Fig. 1. Generalized curve of concrete development [3]

reduction of the water content in the concrete mix, with keeping the same consistence. This reduction (as compared to the control mix) should be ≥ 5 wt % for the plasticizers and ≥ 12 wt % for the superplasticizers [6]. The main goals in the use of the superplasticizers are:

– improvement of the concrete strength (due to the reduction of the water content),

– improvement of the concrete mix consistence without change of the concrete composition (*w*/*c* = const),

– decrease in the cement consumption without affecting the strength of the concrete and consistence of the concrete mix.

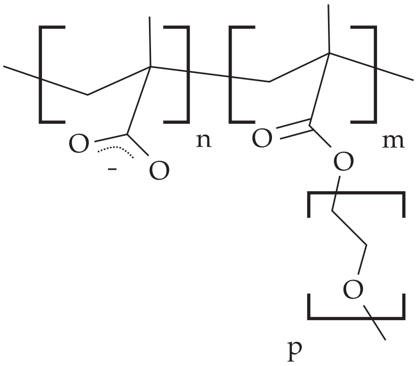
The effectiveness of superplasticizers depends on various technological factors. These factors could be divided into three groups:

– concrete constituent characteristics (mainly cement, superplasticizers and mineral additives characteristics),

– mixture proportions (water to binder mass ratio, superplasticizer, cement and mineral additives content, presence of other chemical admixtures in mixture),

– the methods and conditions of concrete production (order of addition, temperature of the mixture) [7].

The polycarboxylate admixtures, based mainly on the polymers with carboxylate and oligo(ethylene oxide) side groups, are one of the most effective superplasticizers from among all known modifiers; they are usually referred to as the liquefying admixtures of a new generation. The



(I)

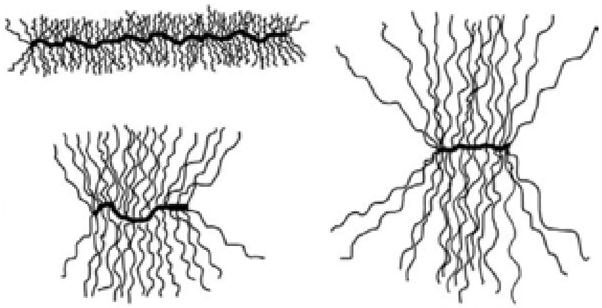


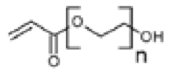
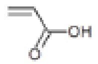
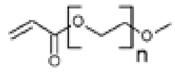
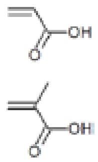
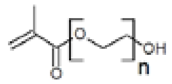
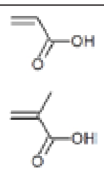
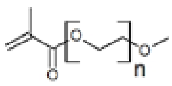
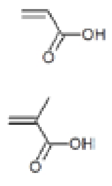
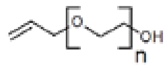
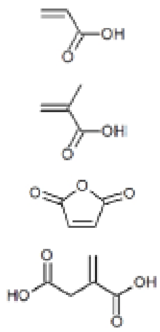
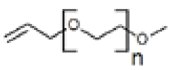
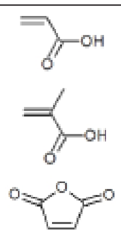
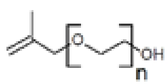
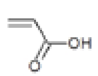
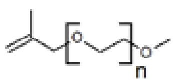
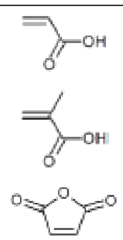
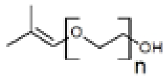
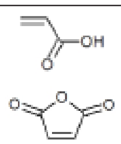
Fig. 2. Schematic examples of molecular architecture of PCE superplasticizers [8]

methacrylate copolymers of methacrylic acid and methacrylic ester with the oligo(ethylene oxide) group is an example of such admixture [Formula (I)], commonly called the polycarboxylate (PCE) superplasticizer. It is a comb-like polymer built up with ionic hydrophilic carboxylate groups (COO^-) and long, elastic side nonionic hydrophilic oligo(ethylene oxide) chains Fig. 2 [8].

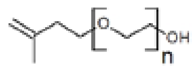
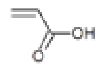
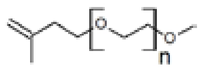
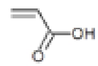
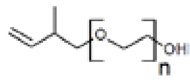
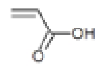
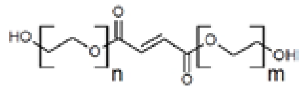
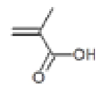
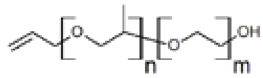
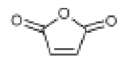
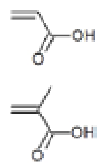
Superplasticizers are useful in obtaining a dispersion of the cement grains in water. The carboxylate groups (COO^-) interact with the surface of the cement grain, which leads to polymer adsorption and electrostatic repulsion between grains (COO^- groups create a negative charge around the grain). In many publications, also a steric repulsion is considered as a potential mechanism of cement grains dispersion. Detailed information about interaction mechanism of cement and superplasticizers can be found in [5, 9, 10]. Also, the wettability of grains is improved, fostering the full cement hydration (setting). The viscosity of the concrete mix decreases leading to the consistence improvement. The research by Borget *et al.* [11] showed behavior of PCE superplasticizers (PCEs) in different salt solutions. In classical cement-based media at room temperature, PCEs behave generally as polymers in good solvent, except in case of very high sulfate concentration. Duan *et al.* [12] studied the molecular polarization of polycarboxylate by measurement of electrical conductivity in deionized water solution. It was found that the PCE significantly increased the conductivity of the solution with maximum values reached at PCE concentrations between 20 and 25 wt %. These results indicate that the degree of polarization was in connection with the molar mass of the polymers.

Numerous studies, for instance Winnefeld *et al.* [13], Peng et al. [14], Kjeldsen *et al.* [15], Ran *et al.* [16], Zingg *et al.* [17, 18], Rai and Gajbhiye [19], Üzer and Plank [20], have proved that the superplasticizers in the cement pastes directly influence their rheological properties. It is commonly accepted that the influence of superplasticizers on rheology of cement binder mixture depends primarily on the superplasticizer and cement characteristics and their interaction. Effects of PCEs on increasing workability [13, 21, 22] and fluidity [14, 23–33] of fresh concrete have already attracted many attentions so far. The authors reported that PCEs have a good performance on

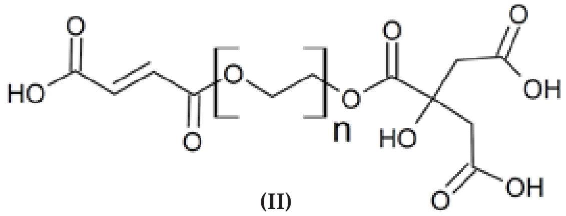
T a b l e 1. Monomers for synthesis of polycarboxylate-type superplasticizers with oligo(ethylene oxide) chains

Macromonomer introducing oligo(ethylene oxide) side chains into polymer	Monomer introducing carboxyl groups into polymer	Reference
		[26, 29, 47, 53]
		[12, 16, 21, 37, 39, 54] [21, 38]
		[27] [19, 48, 55]
		[21, 33, 42, 56] [9, 11, 13–15, 17, 18, 20–23, 36, 40, 45, 48, 49, 53, 57–66]
		[12, 28] [67] [24, 25, 30, 68] [30]
		[21, 39] [21] [8, 21, 35, 46, 59, 64, 65]
		[27, 31]
		[21, 44] [21, 44] [21, 60]
		[32, 69] [32]

T a b l e 1. *(Continued)*

Macromonomer introducing oligo(ethylene oxide) side chains into polymer	Monomer introducing carboxyl groups into polymer	Reference
		[31]
		[43]
		[12]
		[23]
		[57]
		[41] [41]

improving workability of concrete and fluidize the mixture more effectively than other superplasticizers. Some types of superplasticizers cause the rise of excessive air content [34] and exhibit foaming action [35]. Morin *et al.* [36] and Chen [37] analyzed the influence of PCEs on the shrinkage of the concrete. The shrinkage partly compensates the volume augmentation during mixing caused by the air entrapment induced by the superplasticizer. There are many works [9, 33, 38–44] devoted to effects of polycarboxylate superplasticizers on the hydration behavior of cement paste, however, influence of molecular structure of PCEs on the hydration behavior of cement remain poorly understood. In addition to influence of PCEs on hydration of cement, effects of PCEs on microstructure of cement paste and durability of concrete were reported as well [17, 30, 45, 46]. The research by Huang *et al.* [46] showed that the mortars with PCEs have lower porosity than that with conventional superplasticizers based on naphthalene (PNS). The fraction of pores with diameters larger than 100 nm in the mortars with PCEs is lower than in the mortar with PNS. It can be concluded that PCEs leads to denser microstructure in concrete than PNS and, therefore, better durability performances of concrete. The compressive strength of concrete, influenced by PCEs was investigated by Li *et al.* [32] and Wu *et al.* [47]. They have found that compressibility of the concrete mixture increased after adding PCEs (after 28 days reached even 30 % more compressive strength than concrete without PCEs). According to Winnefeld *et al.* [13], Zingg *et al.* [18] and Plank *et al.* [48] the presence of PCEs not only shift the main peak of heat of hydration of cement pastes but also changes the peak shape.



(II)

METHODS OF POLYCARBOXYLATE SYNTHESIS

The most commonly used side chain for PCE superplasticizers is oligo(ethylene oxide). The polymers with carboxylate and oligo(ethylene oxide) groups can be obtain by radical copolymerization of monomer introducing the carboxylic group into polymer (*e.g.* acrylic acid) with macromonomer introducing the oligo(ethylene oxide) chain into polymer [*e.g.* oligo(ethylene oxide) acrylate].

The optimal esterification condition of macromonomer has been studied by Jiang *et al.* [49]. The monomers used for manufacturing of the polycarboxylate superplasticizers are collected in the Table 1.

It should be mentioned that there are other ways of PCE synthesis. Lu *et al.* [26] obtained polycarboxylate superplasticizers by terpolymerization of macromonomer – monoester of maleic acid [Formula (II)], oligo(ethylene oxide) acrylate and acrylic acid.

Liu *et al.* [50] used poly(acrylic acid) and poly(ethylene oxide) terminated with amino and methoxy groups as reactants for synthesis of amide-PCE (Scheme A).

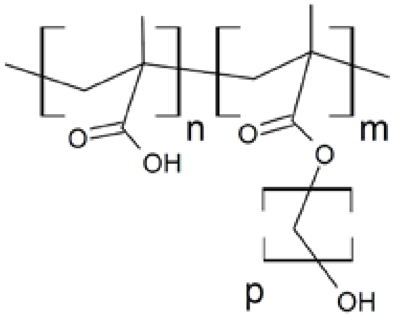
Lei and Plank [51] reported on a structurally modified PCE superplasticizer which was synthesized from methacrylic acid and 2-hydroxyethyl methacrylate, 3-hydroxypropyl methacrylate or 4-hydroxybutyl methacrylate esters. These PCEs possess hydroxyalkyl side chains [Formula (III)].

In other papers Lei and Plank presented synthesis of terpolymers from maleic anhydride, monoalkyl maleate esters, and 4-hydroxybutyl vinyl ether [52]. Taking into account the above considerations, we propose to classify the PCEs as the following five categories:

– **EsMa** – type PCEs, when **Es**ters and **M**onoprotic **a**cids are used as substrates,

– **EsPa** – type PCEs, when **Es**ters and **P**olyprotic **a**cids or anhydrides are used as substrates,

– **AlMa** – type PCEs, when **Al**lyl or ether compounds and **M**onoprotic **a**cids are used as substrates,



(III)

– **AlPa** – type PCEs, when **Al**lyl or ether compounds and **P**olyprotic **a**cids or anhydrides are used as substrates,

– **Amide** – type PCEs, when **amide** bonds are formed.

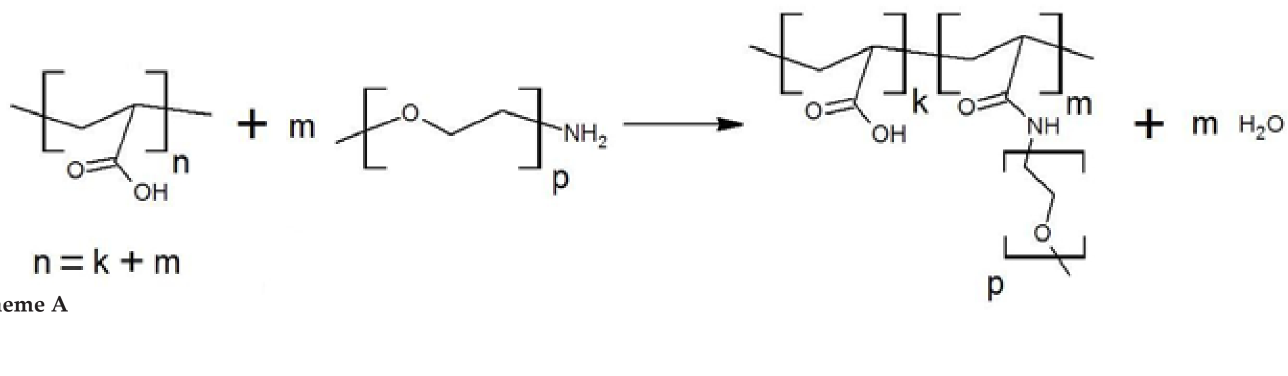
Table 2 presents examples of each type of polycarboxylates. The most commonly used PCE superplasticizers are classified as EsMa-type.

MODIFICATION OF POLYCARBOXYLATES

At present, polycarboxylate superplasticizers are modified by insertion of other monomers to afford terpolymers (Table 3). The particular attention is also paid to versatility of the liquefying admixtures, *i.e.* their high effectiveness with various types of cements. For instance, the polycarboxylates modified with methoxysilanes [Formula (IV)], contrary to the traditional superplasticizers, are very effective when the cements with high sulphates content are used [22]. In the field of water-reducing admixtures, the research and development of newer polymers is being undertaken utilizing tailored superplasticizers [70].

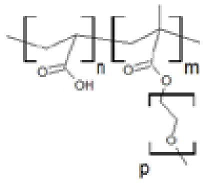
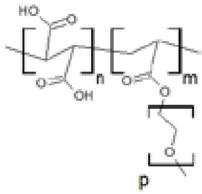
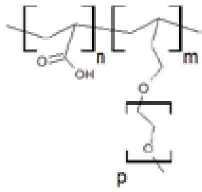
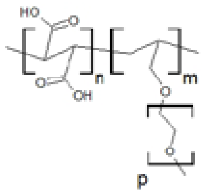
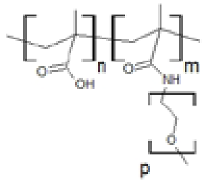
INFLUENCE OF THE CHEMICAL STRUCTURE OF POLYCARBOXYLATES ON THE LIQUEFYING PROPERTIES OF CONCRETE MIX

The molecular structure of PCE have a close relationship with their performance in cement system. Peng *et al.* [61] showed that the effectiveness of the polycarboxylate superplasticizers grafted with poly(ethylene oxide) depends strictly on the molar mass of the polymer used. In other research, Peng *et al.* [14] synthesized six polycarboxylates with similar molar mass and dispersion

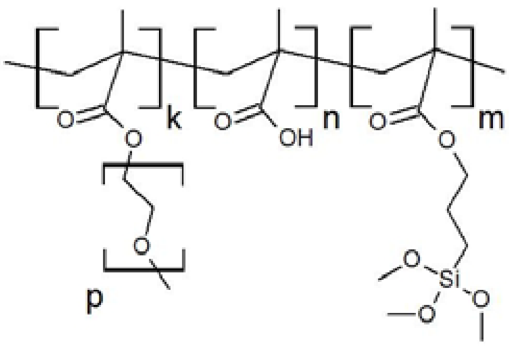


Scheme A

T a b l e 2. Examples of EsMa, EsPa, AlMa, AlPa and amide-type polycarboxylate superplasticizers

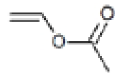
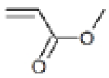
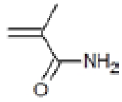
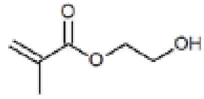
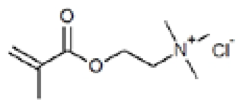
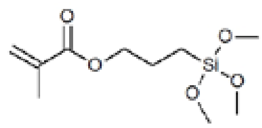
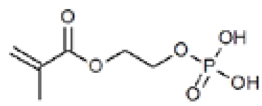
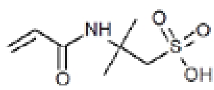
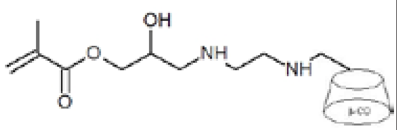
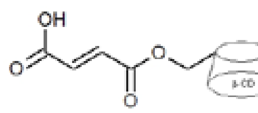
Type of PCEs	Example
EsMa	
EsPa	
AlMa	
AlPa	
Amide	

and constant length of side chains of poly(ethylene oxide) [p = 45, Formula (I)], varying in the content of the carboxylate groups (*i.e.*, molar ratio of the monomers used) (Table 4). The consistence of the cement mortar *vs.* amount of the admixtures as well as ability of the particular superplasticizers to reduction of the water content in the mix are presented in Fig. 3. The optimum molar ratio of the monomers n/m in PCE was 3.6.



(IV)

T a b l e 3. Monomers used as modifiers for polycarboxylate superplasticizers

Monomer		Reference
Compound name	Chemical structure	
Vinyl acetate		[12]
Methyl acrylate		[26]
Methacrylamide		[12]
2-Hydroxyethyl methacrylate		[60]
Sodium 2-methyl-2-propene-1-sulfonate*)		[9, 23–25, 28, 32, 40, 44, 47, 48, 55, 57, 59, 67]
Sodium allylsulfonate*)		[26]
[2-(Methacryloyloxy)ethyl]trimethyl ammonium chloride		[41, 68]
3-(Trimethoxysilyl)propyl methacrylate		[22]
2-(Methacryloyloxy)ethyl phosphate		[64, 65]
2-Acrylamido-2-methyl-1-propanesulfonic acid		[20, 33, 37]
β-Cyclodextrin with methacrylic ester group		[69]
β-Cyclodextrin with maleic ester group		[28]

*) As chain transfer agents in the polymerization.

T a b l e 4. Molecular characteristics of PCE [14]

Sample	Molar ratio		M_n	M_w	$[M_w/M_n]$	*DP*
	Poly(ethylene glycol) methyl ether methacrylate (*m*)	Methacrylic acid (*n*)				
PCE-1	1	1.2	23600	40100	1.7	10.8
PCE-2	1	2.4	24150	42760	1.8	10.6
PCE-3	1	3.6	25470	40900	1.6	10.7
PCE-4	1	4.8	25880	41410	1.6	10.4
PCE-5	1	6.0	26460	44980	1.7	10.2
PCE-6	1	7.2	27240	49030	1.8	10.1

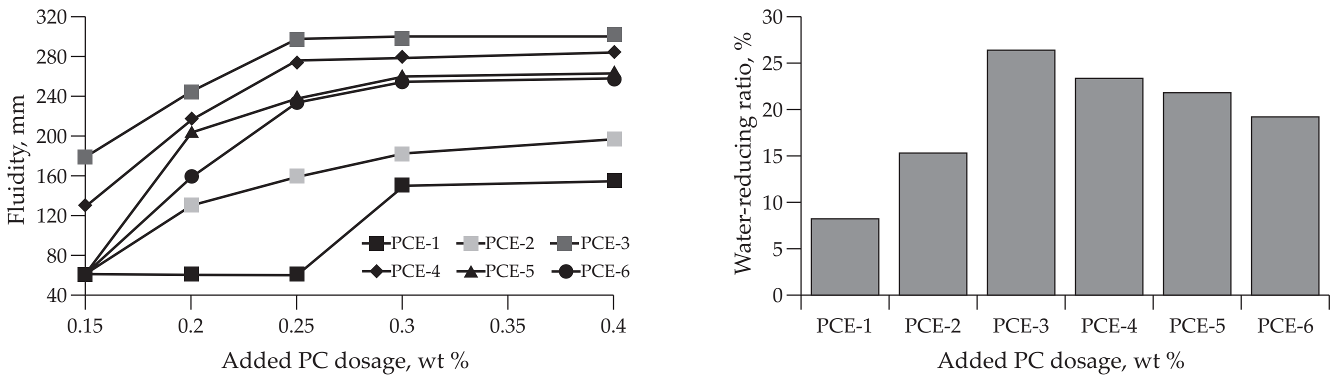


Fig. 3. Effect of carboxylic groups content in PCE on the fluidity at the *w/c* ratio of 0.24 (left) and the water-reducing ratios, dosage: 0.2 wt % by cement weight (right) [14]

T a b l e 5. PCE concentration to reach a paste flow of 26 ± 0.5 cm in the "mini slump" test [48]

	PCE 17 $-OCH_3$	PCE 17 -OH	PCE 24 $-OCH_3$	PCE 24 -OH	PCE 45 $-OCH_3$	PCE 45 -OH
Concentration, wt %	0.16	0.15	0.15	0.19	0.12	0.11

Plank *et al.* [48] modified the poly(ethylene oxide), the side chain of the polycarboxylates, changing its length and kind of terminal group. The authors studied the polycarboxylate superplasticizers with the side chains composed of 17, 24 or 45 repeating units of ethylene oxide, terminated with the hydroxyl (–OH) or methoxy ($–OCH_3$) group [Formula (I)]. The effectiveness of the admixtures was evaluated by measuring the content of superplasticizer necessary for achieving a slump (measure of consistence) 26 ± 0.5 cm (Table 5). The admixture with the longest side chains ($n = 45$), terminated with hydroxyl group appeared to be most effective.

PERSPECTIVES OF SUPERPLASTICIZERS DEVELOPMENT

The currently used superplasticizers have some specific advantages as well as weaknesses. There is a growing demand for polymers improving the consistence of the concrete mix with extended time of effective action, and simultaneously inducing no excessive bleeding of water from the mix, air-entraining and set-retardation. Besides the basic criterion of superplasticizer's action, the other requirements are considered, like versatility of using, easy production and application, stable efficiency at various temperatures [71], no negative impact on environment (with a favor for the superplasticizers "consuming" the wastes and allowing for saving the water, cement and energy).

When designing new superplasticizers, the introduction of the acidic group other than carboxylic one into the polymer's structure can be considered. Also, the chain of poly(ethylene oxide) can be modified by introduction of other hydrophilic units, especially those characterized by branched structure, providing reduced viscosity of the polymer solution.

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