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RESEARCH ARTICLE

Effect of nonionic side chain length of polycarboxylate-ether-based high-range water-reducing admixture on properties of cementitious systems

Süleyman ÖZEN[a], Muhammet Gökhan ALTUN[b], Ali MARDANI-AGHABAGLOU[b*], Kambiz RAMYAR[c]

[a] *Department of Civil Engineering, Faculty of Engineering and Natural Sciences, Bursa Technical University, Yildirim-Bursa 16330, Turkey*

[b] *Department of Civil Engineering, Faculty of Engineering, Bursa Uludag University, Nilufer-Bursa 16059, Turkey*

[c] *Department of Civil Engineering, Faculty of Engineering, Ege University, Bornova-Izmir 35040, Turkey*

**Corresponding author. E-mail: ali.mardani16@gmail.com*

ABSTRACT Despite the large variations in the behaviors of water-reducing admixtures upon changes in their structures, most previous reports on the cement-admixture compatibility did not provide sufficient information on the structure of the admixture. Hence, the evaluation and generalization of the reports on the cement-admixture compatibility are challenging. In this study, three different polycarboxylate-ether-based water-reducing admixtures with the same free nonionic content, anionic/nonionic molar ratio, and main chain length and different side chain lengths were produced. The compatibility of these admixtures with a CEM I 42.5R-type cement was investigated. In addition, an analysis of variance was performed on the experiment results to evaluate the contributions of the admixture type, admixture/cement ratio, and elapsing time to the Marsh funnel flow time, mini-slump, slump flow, and compressive strength. The water-reducing admixtures having long or short side chains reduced the initial flow characteristics of the cementitious systems. However, the admixture having the shortest side chain was better with regard to flow retention. The side chain length of the admixture did not have significant effects on the compressive strength and water absorption capacity of the mortar mixtures and mini-slump performances of the cement paste mixtures. Regarding the behaviors of the admixtures in the cementitious systems, an optimal admixture side chain molecular weight is proposed.

KEYWORDS water-reducing admixture, side chain length, cement paste, fluidity, compressive strength

1 Introduction

The variety and rate of consumption of concrete chemical admixtures largely increased in the past 40 years. Nowadays, almost all concrete mixtures contain one or more chemical admixtures, some of which affect the cement hydration kinetics. Different types of chemical admixtures are used to modify one or more properties of concrete, particularly its durability [1]. In addition, chemical admixtures are used in special concrete mixtures such as self-compacting concrete, high-performance concrete, underwater concrete, and shotcrete [2].

High-range water-reducing (HRWR) admixtures are the most commonly used chemical admixtures in concrete. For given consistency, these admixtures considerably reduce the water requirement of concrete and disperse cement particles in the mixture without a significant effect on the setting time of concrete [1,3,4]. In this manner, the water tied up in the flocculated cement particles becomes free and the workability of concrete increases [5,6]. Moreover, the local non-uniformity of the water/cement ratio in concrete originated from the agglomeration of cement particles is removed [7].

In addition to their plasticizing effect, water-reducing admixtures may contain components that affect the rate of cement hydration. Such admixtures generally contain both accelerator and retarder components to reduce the admixture production cost and meet the requirements of

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specification and construction site [1,8].

The invention of polycarboxylate-based polymers as a new class of plasticizing admixtures in 1981 was a milestone in concrete technology [9]. The production of some special concretes such as ultrahigh-strength concrete and self-compacting concrete was enabled by the use of these admixtures. In addition, specific polycarboxylate-based admixtures have been designed to provide consistency retention without reduction in concrete early strength [10].

In general, the chemical structures of polycarboxylate-based HRWR admixtures are composed of two parts, a carboxylic main chain and polyethylene oxide side chains [11]. Numerous studies suggest that the dispersion mechanisms of these admixtures in the cementitious systems are similar, despite the differences in composition. The carboxylic groups adsorb primarily at the solid-water interface and thus all surfaces carry uniform charges of same sign. The polyethylene oxide side chains exhibit a steric effect. Both mechanisms prevent the flocculation of cement particles. In this manner, the water tied up in the flocculated particles or adsorbed on the solid surfaces becomes free and reduces the viscosity of the cementitious system. Accordingly, the combined effects of the carboxylic groups and polyethylene oxide side chains determine the dispersing capability of the water-reducing admixture in the cementitious system [6,12]. Therefore, it is of significance to investigate the effect of the side chain length on the dispersing ability of the admixture. Studies on this subject are summarized below.

Janowska-Renkas [13] studied the effects of four types of superplasticizers produced by acrylic acid and maleic acid on the properties of cement paste. The maleic-based superplasticizers had hydrophilicity originated from their larger molecular mass, as well as long main chains, long side chains, and carboxylic groups. The pastes containing these admixtures exhibit superior workabilities, whereas acrylic-acid-based plasticizers with short main and side chains without carboxylic groups had minimal effects on the paste behavior. In addition, the maleic-based superplasticizers reduced the rate of cement hydration considerably more than the acrylic-acid-based superplasticizers.

Peng et al. [14] analyzed the effects of three polycarboxylate-based superplasticizers having short, long, and short and long side chains on the dispersion properties of a cement paste. The rate of admixture adsorption on the surface of cement particles increased with the amount of short side chains of the admixture. Furthermore, compared to that of the admixture containing short side chains, the admixture containing both short and long side chains exhibited a superior electrostatic effect.

Zhao et al. [15] investigated the effects of four types of plasticizer admixtures having star-shaped polymers on the microstructure, hydration, fluidity, and setting time of cement pastes. For given admixture content, the fluidity of the paste decreased with the increase in the side chain density and molecular weight of the admixture. However, with the reductions in the side chain density and molecular weight, the rate of admixture adsorption on the cement particles increased, which shows that the star-shaped chemical structure of the admixture affected its adsorption behavior.

Feng et al. [16] studied the effects of five polycarboxylate-based superplasticizers having different side chain lengths and densities on the behaviors of cement pastes containing two types of stone dust (5 and 20 wt.% of cement). Three of the admixtures had side chains with the same length and carboxylate groups with different densities. The fourth admixture had short side chains, while the fifth admixture had both long and short side chains. The plasticizer admixtures having long side chains and low densities of carboxylate groups exhibited higher dispersion performances in the cement pastes than those of the other admixtures. However, at the admixture saturation point, the flowability of the stone-dust-bearing paste containing the short-side-chain admixture was higher than those of the mixtures containing the other admixtures. The admixture was more easily absorbed to the stone dust having a layered structure. This led to the encapsulation and consequent low flow performance of the admixture with long side chains in the pastes containing the layered-structure stone dust.

The mechanisms of action of cement-based factors affecting the water-reducing admixture-cement compatibility have been analyzed in numerous studies [4,17–26]. However, owing to the unknown nature of the admixtures and complexity of the cementitious systems, no definite conclusion on the mechanism of action of water-reducing admixture has been presented. The major problem in the cement-admixture compatibility studies is the use of commercial admixtures prepared using ready-made polymers. To improve the properties of the admixture, mainly some targeted agents are externally added to the commercial polymers. As the structures of the raw materials of various polymers are quite different (in general, detailed information about their physical and chemical characteristics is lacking), the comparison of results of different studies and provision of general conclusions are challenging.

Contradictory reports on the effects of the admixture main and side chain lengths on the performances of cementitious systems exist. Thus, further studies are required on this subject. In this study, three types of polycarboxylate-based HRWR admixtures having different side chain lengths and fixed main chain length, anionic/non-ionic molar ratio, and free nonionic content were synthesized. In this regard, all properties of the admixtures, except for the side chain length and molecular weight, were constant. The effects of the water-reducing admixtures with different side chain lengths on the fresh and hardened properties of cement paste and mortar mixtures were investigated. In addition to the experimental analyses, an analysis of variance (ANOVA) was carried out on the Marsh funnel flow times and mini-slumps of cement paste mixtures and slump flows and compressive strengths of mortar mixtures to statistically evaluate the effects of different variables. Regarding the behaviors of admixtures in the cementitious systems, an optimal admixture side chain molecular weight is proposed.

2 Experimental study

2.1 Materials

In this study, a CEM I 42.5 R-type Portland cement conforming to the TS EN 197-1 standard and standard sand conforming to the TS EN 196-1 standard were used. The chemical composition and mechanical and physical properties of the cement are shown in Tables 1–3. The specific gravity and water-absorption capacity of the CEN standard sand were determined to be 2.72 and 0.7% (mass), respectively.

Table 1 Chemical composition of the cement

item	content (%)
SiO_2	18.86
Al_2O_3	5.71
Fe_2O_3	3.09
CaO	62.70
MgO	1.16
SO_3	2.39
$Na_2O + 0.658K_2O$	0.92
Cl^-	0.01
insoluble residue	0.32
loss of ignition	3.20
free CaO	1.26

Table 2 Mechanical properties of the cement

time	compressive strength (MPa)
1-d	14.7
2-d	26.8
7-d	49.8
28-d	58.5

Table 3 Physical properties of the cement

physical properties	value
specific gravity	3.15
blaine specific surface (cm^2/g)	3530
residual on 0.045 mm sieve (%)	7.6

In this study, HRWR admixtures were synthesized according to the method applied by Altun et al. [27]. Three types of polycarboxylate-based HRWR admixtures with different lengths of the side chains (consequently, different molecular weights) were synthesized. The anionic functional group of the admixtures was carboxylate. The anionic/nonionic ratio, main chain length, and free nonionic content of the admixtures were fixed. The molecular weights of the HRWR admixtures were in the range of 23 to 60 kg/mol. The optimized side chain molecular weights (lengths) of the HRWR admixtures were 1000, 2400, and 3000 g/mol. The chemical admixtures are denoted according to their side chain lengths. For example, the admixture with the longest side chain (3000 g/mol) is denoted as PCE-SC3000. The characteristics of the HRWR admixtures were determined by gel permeation chromatography. The results are shown in Table 4.

2.2 Mix proportions

The production of high-performance concretes has become possible using the new-generation HRWR admixtures. Thus, a concrete with a high workability can be produced with a water/cement ratio between 0.30 and 0.40 and, in some cases, between 0.25 and 0.30. In addition, more workable and more cohesive concretes can be produced with compatible and robust cement-admixture combinations. In addition, segregation cannot occur when the water/cement ratio is in the range of 0.30 to 0.40. Considering the previous studies, the water/binder ratio of the paste mixtures in the mini-slump and Marsh funnel flow tests was set to 0.35 [28]. The admixture amounts of the paste mixtures were varied in the range of 0.75% to 2.25% with respect to the weight of the cement.

The mortar mixtures were produced according to the American Society for Testing and Materials (ASTM) C109 standard. The water/binder ratio, sand/binder ratio, admixture content (with respect to the weight of the cement), and flow values were fixed to 0.485, 2.75, 0.6%, and 270±20 mm for all mixtures, respectively. The same notation as for the pastes is used for the mortar mixtures. The fresh unit weights of the PCE-SC1000, PCE-SC2400, and PCE-SC3000 mortar mixtures were determined to be 2068, 2001, and 2155 kg/m^3, respectively.

2.3 Test methods

Marsh funnel flow and mini-slump tests were carried out according to the methods recommended by Aïtcin [28], Wedding and Kantro [29], respectively. The flow retentions of the mortar mixtures were determined according to ASTM C1437 at time intervals of 15 min for 60 min. The mini-V-funnel flow time test on the mortar mixtures was carried out in conformity with the EFNARC [30] criteria.

The 1-, 3-, 7-, and 28-d compressive strengths of the

Table 4 Characteristics of HRWR admixtures

type	anionic monomer type	anionic/non-ionic group ratio (mol/mol)[a)]	free non-ionic group (mol)[a)]	molecular weight (kg/mol)	main chain length[a)]	side chain molecular weight (g/mol)[b)]
PCE-SC1000	carboxylate	3.47	2.78	23	21k	1000
PCE-SC2400	carboxylate	3.47	2.78	48	21k	2400
PCE-SC3000	carboxylate	3.47	2.78	60	21k	3000

Note: a) Calculated from GPC analysis and given as coefficient; b) side chain molecular weight of admixtures is directly proportional to its length.

mortar mixtures were measured using 50-mm cubic specimens according to the ASTM C109 standard. In addition, the water absorption ratios were determined using the 28-d mortar specimens according to ASTM C642.

The contribution ratios of parameters influencing test results were calculated using a two-way ANOVA.

3 Results and discussion

3.1 Fresh state properties

3.1.1 Marsh funnel flow time and mini-slump

The Marsh funnel flow times of the paste mixtures are shown in Fig. 1. None of the mixtures with admixture contents below 0.75% flowed from the Marsh funnel. As expected, the Marsh funnel flow times of the mixtures decreased with the increase in the admixture dosage, regardless of the HRWR admixture side chain length. At an admixture dosage of 1%, PCE-SC1000 containing the shortest side chain exhibited the lowest performance with respect to the Marsh funnel flow time. This mixture exhibited an approximately 10% slower flow than those of PCE-SC2400 and PCE-SC3000.

Irrespective of the HRWR admixture side chain length, the saturation points of the admixtures were determined to be 1.5% (Fig. 1). At the admixture saturation point, PCE-SC2400 and PCE-SC1000 exhibited higher and lower flow performances than that of PCE-SC3000, respectively. At the saturation point, the Marsh funnel flow time of PCE-SC1000 was 24% higher than that of the PCE-SC2400 mixture. The increase in the side chain molecular weight from 1000 to 2400 g/mol improved the flow performance of the paste mixture. However, the further increase in the side chain molecular weight decreased the Marsh funnel flow performance of the paste. The flow performance of the paste depends on the adsorption of the admixture on the cement surface and admixture side chain length [21,31]. Similar results were obtained in this study. The higher flow performance of PCE-SC2400 could be attributed to the optimal side chain length of PCE-SC2400.

The adsorption capability of the admixture increases with the reduction in the side chain length of the admixture [32,33]. Although the adsorption amount of PCE-SC1000 with the shortest side chain was higher than those of the other admixtures, it exhibited a lower flow performance than that of PCE-SC2400. This contradictory behavior could be attributed to the insufficient steric hindrance of the admixture because of its short side chain [34]. On the contrary, when the length of the side chain exceeds a certain value, the polymers may intertwine, which reduces

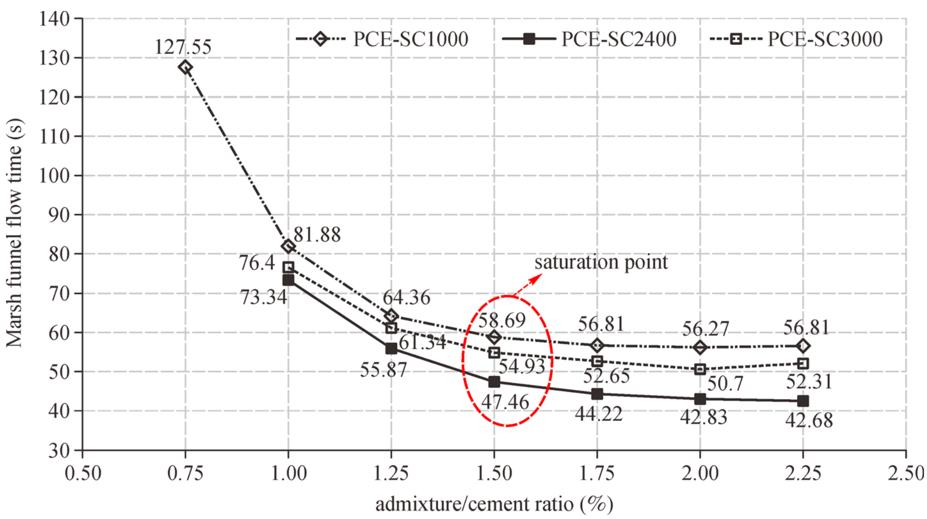

Fig. 1 Marsh funnel flow times of cement pastes.

the adsorption of the admixture and its steric effect [26,33,35]. In addition, the destruction of the polymer film formed on the cement particles and reduction in the steric hindrance originated from very long side chains further reduce the adsorption of the admixture [36,37]. Thus, irrespective of the admixture dosage, owing to its longer side chain, PCE-SC3000 exhibited a larger Marsh flow time than that of PCE-SC2400. Among the admixtures used in this study, PCE-SC2400 having a medium side chain molecular weight (length) exhibited the highest performance in the Marsh funnel flow test.

The mini-slump test results for the cement paste mixtures are shown in Table 5. Irrespective of the side chain length of the admixture, the mini-slump of the paste increased with the admixture dosage up to a certain limit. Beyond certain admixture dosage, the segregation tendency of the paste increased, which led to even slight reduction in its mini-slump.

PCE-SC2400 exhibited a higher slump flow performance than those of PCE-SC1000 and PCE-SC3000. However, at the admixture saturation point and above it, the mixtures exhibited very similar slump flow values. As the mini-slump of the mix is a measure of its yield stress, the length of the admixture side chain (within the range of this study) does not have a significant effect on the yield stress of the paste.

As shown in Table 5, a slight gradual reduction in the temperature of the mixture was observed with the increase in the admixture dosage. This could be attributed to the retarding effect of the admixture.

3.1.2 Time-dependent behaviors of the mortar mixtures

The variations in the flow and V-funnel flow time of the mortar mixtures over time are presented in Table 6 and Fig. 2. Regardless of the HRWR admixture side chain length, an admixture dosage of 0.6% was sufficient to provide the desired initial flow (27±2 cm) in the mixtures. The flows were determined at time intervals of 15 min for 60 min. In terms of the initial flow, PCE-SC1000 exhibited a slightly lower performance than those of the other mixtures. PCE-SC2400 and PCE-SC3000 exhibited almost equal initial and late flow performances. The smallest and largest V-funnel flow times were observed for PCE-SC2400 and PCE-SC3000, respectively. After 15 min, all mixtures blocked the V-funnel.

The 60-min flow losses of PCE-SC1000, PCE-SC2400, and PCE-SC3000 were measured to be 26%, 30%, and 32%, respectively (Fig. 2). In terms of flow retention, PCE-SC1000 was best, while PCE-SC2400 with the medium side chain was worst.

A too long side chain of the admixture may reduce the accessibility of the admixture anionic groups to the cement grains, intertwine to establish a polymer bridge among the cement particles preventing their free movement, and thus reduce both adsorption capability and steric hindrance of the admixture [33,35,38,39]. However, some reports indicate that long side chains of the polymer improve the steric hindrance of the admixture [38,40,41]. Therefore, a specific relationship between the side chains and anionic groups of the admixture exists in terms of its adsorption and dispersion capability. The part of the admixture adsorbed on the cement grain improves the fluidity of the mixture, while the part remained in the solution provides flow retention in the cementitious system [36,42,43]. The flow and flow retention characteristics of the HRWR admixture-bearing cementitious systems are inversely interrelated. Therefore, to provide the intended flow as

Table 5 Time-dependent flow value and V-funnel flow time of mortar mixtures

admixture/cement ratio (by weight %)	mini slump (cm)			temperature (°C)		
	PCE-SC1000	PCE-SC2400	PCE-SC3000	PCE-SC1000	PCE-SC2400	PCE-SC3000
0.75	8.0	10.0	8.5	27.2	29.6	29.2
1.00	12.5	16.3	13.8	29.4	29	28.3
1.25	15.8	16.5	16.5	27.6	28.8	27.8
1.50	17.5	17.5	17.8	27.5	28.4	27.4
1.75	17.5	17.0	17.5	26.5	28.1	26.6
2.00	18.0	17.5	16.5	26.1	27.8	26.3
2.25	18.2	17.5	16.6	26.3	27.7	26.3

Table 6 Time-dependent flow value and V-funnel flow time of mortar mixtures

mixture	admixture dosage (%)	time dependent flow value (cm)					V-funnel flow time (s)	
		0 min	15 min	30 min	45 min	60 min	0 min	15 min
PCE-SC1000	0.60	25.8	22.0	21.0	20.0	19.0	9.25	blocked
PCE-SC2400	0.60	27.0	22.5	20.5	19.5	18.3	6.37	blocked
PCE-SC3000	0.60	26.8	22.0	20.5	19.8	19.0	11.04	blocked

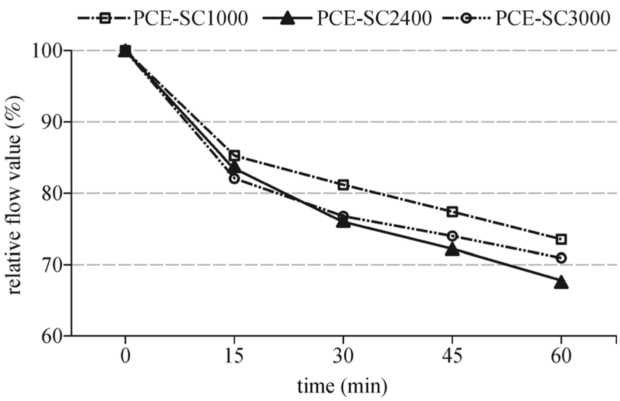

Fig. 2 Flow retention of mortar mixtures.

well as an acceptable flow retention in the cementitious systems, the admixture should have the optimal side chain length.

The PCE-SC2400 admixture exhibited the best Marsh funnel flow time (Fig. 1) but the lowest flow retention performance (Fig. 2). This indicates that the PCE-SC2400 admixture had a high adsorption capability. Thus, majority of the admixture was adsorbed on the cement grains. Consequently, a small part of the admixture remained free in the solution. The flow retention performance of PCE-SC3000 was higher than that of PCE-SC2400. This could be attributed to the high intertwining of the PCE-SC3000 polymer, which reduces the polymer adsorption and thus increases the amount of free polymer in the solution, which contributes to flow retention. Similar conclusions have been presented [33,35,36,42].

The adsorption of the admixture on the cement grains is facilitated and strengthened with the reduction in its side chain length [32,33]. In addition, the decrease in the admixture side chain length delays the setting and hardening of cementitious systems [33]. The set retardation can be attributed to the adsorption of the admixture on the hydrated/anhydrous grains [44–46]. This occurs by the interaction between admixture anionic groups and calcium ions on the surfaces of cement particles, which leads to chelating of the calcium ions through a complex formation [47]. Ouyang et al. [48] explained that this chelating process has an important role in the admixture adsorption and thus is responsible for the retardation of the cement hydration. In this regard, PCE-SC1000 exhibited the highest flow retention performance, which could be attributed to the high adsorption capability of the PCE-SC1000 admixture, which retards the cement hydration. In addition, the short side chain of the admixture favors its adsorption on the cement grains and thus the thickness of the water film on the grains is reduced. In this manner, the free water content of the mixture increases, which contributes to its flow retention [49]. It seems that the retardation of the cement hydration and high free content of the mixture provided by the admixture are the main factors responsible for the high flow retention of the PCE-SC1000 mixture.

As shown in Table 6, all mixtures passed through the mini-V-funnel immediately after casting. However, irrespective of the admixture side chain length, all mixtures clogged the V-funnel, without flow 15 min later. The fastest-flowing mixture from the V-funnel was PCE-SC2400. PCE-SC3000 and PCE-SC1000 exhibited 76% and 48% lower V-funnel flow performances than that of PCE-SC2400.

The mini-V-funnel flow performances of the mixtures containing the admixture with variable side chains exhibited a similar trend to that of the Marsh funnel flow performances. In general, up to a certain level, the increase in the side chain length of the admixture increased its steric hindrance and flow performance of the cementitious system. However, entangling of the side chains prevented their movement in the mixture when the side chains were too long. Therefore, the steric hindrance required for fluidity could not be achieved, which was also previously reported [35,38]. Short side chains may slightly decrease the flow performance owing to weakening of the steric hindrance [14,34,36].

The entangling of long side chains, one of the parameters adversely affecting the fluidity, has a more pronounced negative effect than that of shorter side chains. In this regard, as shown in Table 6, PCE-SC3000 containing the longest-side-chain admixture exhibited the most negative behavior in terms of mini-V-funnel flow. PCE-SC1000 exhibited a slightly lower flow performance than that of PCE-SC2400. The comparison of the admixtures showed that the side chain length of the PCE-SC2400 admixture was optimal.

The flow and mini-V-funnel flow time are indicators of the yield stress and viscosity of a mortar mixture, respectively [25]. In this study, compared to that of the PCE-SC2400 admixture, the increase or decrease in the side chain length of the admixture increased the yield stress and thus decreased the flow performance of the mortar. In addition, the mini-V-funnel flow behavior of the mortar was adversely affected when the admixture side chain was longer or shorter than a certain value. Therefore, the reduction in the fluidity of mortars containing such admixtures could be attributed to the high viscosity of the mixture.

3.2 Hardened-state properties

3.2.1 Compressive strength

The water/cement ratio and effectiveness of the water-reducing admixture are one of the most important parameters affecting the compressive strength development of concrete. The compressive strengths of the mixtures are shown in Fig. 3. The results are averages of

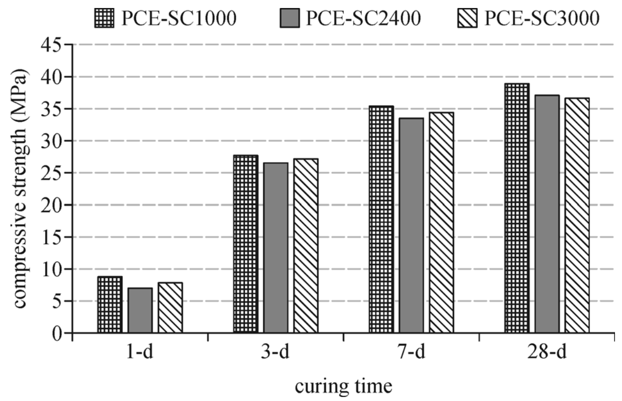

Fig. 3 Compression strength of mortar mixtures containing HRWR admixtures.

three specimens. Figure 3 reveals that the length of the admixture side chains did not have considerable influences on the 1- to 28-d compressive strengths of the mortar mixture. The effect of the HRWR admixture on the strength of a cementitious mixture is directly related to the amount of polymer in the structure of cement hydration products. As the side chain length of the admixture does not participate in the structure of hydration products, it does not have a significant effect on the strength of the concrete [11].

3.2.2 Water absorption

The water adsorption rates of the mortar mixtures are shown in Fig. 4. Each value is the average of three measurements. Regardless of the length of the admixture side chain, the 28-d water absorptions of the mortar mixtures were approximately 8%. The 28-d water absorption ratios of the mortar mixtures were not considerably affected by the side chain length of the HRWR admixture.

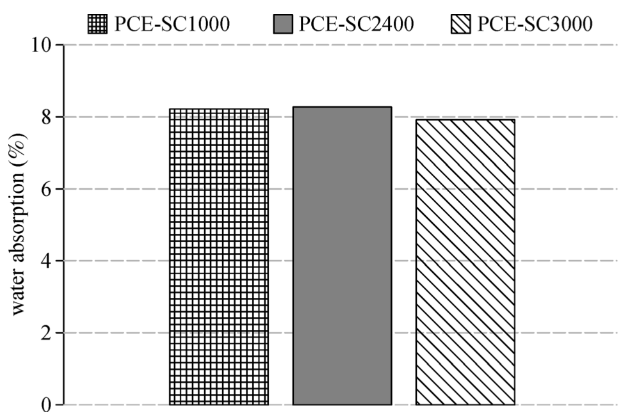

Fig. 4 Water absorption of 28-d mortars containing HRWR admixtures

3.3 Analysis of variance

The ANOVA of the fresh properties and compressive strengths of the cementitious systems was performed to statistically investigate the effects of different parameters.

The results of the ANOVA of the Marsh funnel flow times of the cement paste mixtures are presented in Table 7. The *P* values are approximately zero for the admixture type and admixture/cement ratio. Thus, a statistically significant difference between these values exists. Their contribution to the Marsh funnel flow time is essential. The admixture/cement ratio exhibited the highest importance (79.97%), compared to the admixture type (19.03%).

According to the two-way ANOVA mini-slump results in Table 8, we statistically determined that the admixture type did not influence the mini-slump (contribution ratio: 1.19%). In addition, the admixture type was not statistically significant because its *P* value was 0.293, larger than 0.05. However, a statistically significant difference was observed for the admixture/cement ratio. For the dependent variable mini-slump values, the independent variable admixture/cement ratio was statistically significant. The admixture/cement ratio had the highest importance (93.60%) with an error contribution of 5.22%.

The ANOVA results in Table 9 indicate that the test elapsing time had the largest effect on the slump flow of the mortar mixture (98.56%), while the admixture type had no influence (contribution: 0.01%). In addition, a statistically significant difference was observed for the test elapsing time as its *P* value was smaller than 0.05. However, the *P* value of the admixture type was larger than 0.05%. Thus, it was statistically nonsignificant.

According to the ANOVA results for the compressive strengths of the mortar mixtures, shown in Table 10, the *P* values were calculated to be almost zero for the admixture type and age. Therefore, a statistically significant difference existed between these parameters. The contribution of the age to the compressive strength was 99.61%, while the contribution of the admixture type was too low (0.33%).

According to the results of the ANOVA, regardless of the type of admixture, the change in the amount of admixture used in the mixture and elapsing time of the experiment had significant effects on the fresh-state properties of the mixtures. However, the change in the admixture type did not statistically affect the fresh properties and compressive strength of the mixture owing to the small number and similar properties of the admixtures.

4 Conclusions

Based on the experiments carried out in this study, the following conclusions can be summarized.

1) The flow properties of the cementitious systems were

Table 7 Results of ANOVA for Marsh funnel flow time in cement paste mixtures

parameters	sum of squares (SS)	degrees of freedom (d_f)	variance (V)	F	P value	contribution (%)
admixture type	396.730	2	198.365	95.328	3.07E−7	19.03
admixture/ cement ratio	1666.959	5	333.392	160.218	3.29E−9	79.97
error	20.809	10	2.081			1.00
total	2084.498	17				100

Table 8 Results of ANOVA for mini-slump in cement paste mixtures

parameters	sum of squares (SS)	degrees of freedom (d_f)	variance (V)	F	P value	contribution (%)
admixture type	2.340	2	1.170	1.364	0.293	1.19
admixture/ cement ratio	184.670	6	30.778	35.881	5.53E−7	93.60
error	10.293	12	0.858			5.22
total	197.303	20				100

Table 9 Results of ANOVA for slump-flow in mortar mixtures

parameters	sum of squares (SS)	degrees of freedom (d_f)	variance (V)	F	P value	contribution (%)
admixture type	0.012	2	0.006	0.030	0.971	0.01
elapsing time	110.751	4	27.688	138.323	2.04E−7	98.56
error	1.601	8	0.200			1.42
total	112.364	14				100

Table 10 Results of ANOVA of compressive strength of mortar mixtures

parameters	sum of squares (SS)	degrees of freedom (d_f)	variance (V)	F	P value	contribution (%)
admixture type	5.308	2	2.654	17.955	0.003	0.33
day	1597.409	3	532.470	3602.569	3.74E−10	99.61
error	0.887	6	0.148			0.06
total	1603.604	11				100

adversely affected when the side chain of the HRWR admixture was shorter or longer than a certain value.

2) Long side chains promoted entanglement and thus reduced the probability of adsorption of the polymer molecules on the cement grains. Moreover, the steric hindrance effect of the admixture with the long side chains was decreased, which further adversely affected the flow properties. On the contrary, when the side chains of the admixture were too short or too long, the flow properties of the cementitious system were negatively affected owing to the weak steric effect despite the good adsorption of the admixture. Therefore, the admixture having a side chain molecular weight of 2400 g/mol exhibited the best behaviors in terms of the Marsh funnel and V-funnel flow times.

3) The admixtures having either short or long side chains improved the flow retention of the mortar. This was attributed to the free polymer content of the pore solution in the mixture containing the long-side-chain admixture and low cement hydration rate in the short-side-chain admixture-bearing mortar. The admixture with a side chain molecular weight of 1000 g/mol (shortest side chain) had the highest performance in terms of mortar flow retention.

4) The mini-slump values of the paste mixtures were not significantly affected by the variation in the HRWR admixture side chain length.

5) The compressive strength and water absorption capacity of the mortar mixtures were not affected by the side chain length variation of the HRWR admixture.

6) Based on the ANOVA of the Marsh funnel flow time and mini-slump test results, the admixture type did not have a statistically significant influence, while the admixture/cement ratio exhibited the largest contribution in the cement paste mixtures. In addition, a statistically significant difference was observed for the admixture/ cement ratio. The admixture type did not exhibit a statistically significant difference in the mini-slump test, while a significant difference was observed in the Marsh

funnel flow test.

7) According to the ANOVA of the mortar mixture, the admixture type exhibited the smallest contribution (almost 0%). However, the contribution level of the elapsing time was very high (approximately 99%) for the slump-flow and compressive test results. A statistically significant difference was observed for the elapsing time/day in these tests. A nonsignificant difference was observed for the admixture type in the slump-flow test, while a statistically significant difference was observed for this parameter in the compressive strength test.

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