Effects of replacing of anionic monomer of water reducing admixture with sulfonate and phosphate groups on some properties of cement paste and mortar mixtures

Ali Mardani-Aghabaglou, Süleyman Özen, Muhammet Gökhan Altun, Sultan Husein Bayqra

Abstract—In this study, the effect of anionic functional group change of polycarboxylate-ether based water reducing admixture on some fresh state properties and compressive strength of the cement paste and mortar mixtures was investigated. For this purpose, in addition to the control admixture having 100% of carboxylate as anionic functional group, four different types of admixture were synthesized by replacing 10 and 30 mol% of anionic functional group with sulfonate and phosphate functional groups. In all admixtures anionic/non-ionic group ratios, free non-ionic group contents, molecular weights, main chain and side chain lengths were kept constant. In all mixtures CEMI 42.5R type cement were used as binder. In mortar mixtures water/cement ratio, sand/binder ratio and slump-flow values were kept constant as 0.485, 2.75 and 270±20 mm, respectively. According to the test results, flow time of the paste and mortar mixtures did not significantly change by substitution of carboxylate anion functional group with sulfonate one by 10 mol%. However, the flow performance of the mixtures was adversely affected upon the increase of mentioned substitution rate to 30%. The flow performances of the paste and mortar mixtures improved by replacing of carboxylate anion functional group with the phosphate one. The substitution of anionic monomer with sulfonate or phosphate functional groups had no significant effect on the mini-slump values of the paste mixtures. The substitution of the anionic monomer of the admixtures with sulfonate positively affected the time-dependent slump-flow performance of the mortar mixtures, while the substitution with phosphate monomer showed a negative effect.

The presence of sulfonate and phosphate functional groups as anionic monomer of the water reducing admixtures did not cause a significant change in the early and ultimate strength and water absorption capacity of the mortar mixtures.

Keywords—water reducing admixture, sulfonate functional group, phosphate functional group, cement paste, mortar

1. Introduction

Water reducing admixtures provide to manufacture high strength concrete, to increase the speed of construction and to produce more workable and longer lasting concrete. In addition to the positive effects it provides, these admixtures can also lead to negative effects in concrete mixtures. Some of the parameters that affect the properties of cementitious systems are due to the cement used, some of are due to water reducing admixture, the other part is due to factors such as mixing ratio, temperature and maintenance conditions [1-3]. Effects of cement properties might be related to the chemical composition of the cement (amount of C3A and C2AF and the crystal structure of C3A), the fineness and alkali content of the cement, and the amount and type of calcium sulfate (gypsum) [4-7]. The factors related to the water reducing admixture are main chain length, side chain number and length, molecular weight, intermolecular bond structure, chemical composition, form and order of incorporation into the mixture [8-12].

Yamada et al. [13] determined that water reducing admixtures with long side chains positively affect flowability and adversely affect time dependent fluidity. Qingjun et al. [14] set that water reducing admixtures increase the degree of hydration by increasing the length of the main chain or decreasing the length of the side chain. Lv et al. [15] found that water reducing admixtures having ester bond had higher viscosity and higher water reduction rates than water reducing admixtures having ether bond. Dalas et al. [16] investigated the effect of water-reducing admixture side chain length and anionic monomer type on the fluidity property of cementitious systems. As a result, it stated that short side chains increase adsorption but anionic monomer groups do not have a significant effect on adsorption and flowability. In another study, He et al. [17] investigated the effects of polycarboxylate-based water reducing admixtures with different carboxylic densities and anionic monomer content on adsorption and dispersion behavior. As a result, they found that substitution of carboxylic groups with sulfonic groups improves the adsorption and dispersion property of the admixture.
In this study, the effect of anionic functional group change of polycarboxylate-ether based water reducing admixture on some fresh state properties and compressive strength of the cement paste and mortar mixtures was investigated. For this purpose, in addition to the control admixture having 100% of carboxylate as anionic functional group, four different types of admixture were synthesized by replacing 10 and 30 mol% of anionic functional group with sulfonate and phosphate functional groups.

II. Experimental Program

A. Materials

In this study, a CEM I 42.5 R type portland cement conforming to TS EN 197-1 standard and a standard CEN sand conforming to TS EN 196-1 standard were used. Chemical composition, physical and mechanical properties of the cement are given in Table 1. The specific gravity and water absorption capacity of the standard sand was determined as 2.72 and 0.7% by mass, respectively.

5 different polycarboxylate-ether based water-reducing admixtures having same main chain but different anionic monomers bonded to the main chain were synthesized to investigate the effect of anionic monomers of water reducing admixture on some properties of cementitious systems. As the anionic side group, carboxylate, carboxylate with sulfonate groups in proportions of 10 and 30% and carboxylate with phosphate (carboxylate functional group was replaced with sulfonate and phosphate functional groups.

The designation of the admixtures produced for this study was identified according to the type of water reducing admixture. For instance, the mixture containing anionic monomer which consist 100% carboxylate functional group was defined by (C), the mixture containing anionic monomer which consist 10% phosphate and 90% carboxylate functional groups was defined by (P10), the mixture containing anionic monomer which consist 30% sulfonate and 70% carboxylate functional groups was defined by (S30). Some properties of all water reducing admixtures provided from its manufacturer are given in Table 2.

Table 2. Properties of water reducing admixtures

<table>
<thead>
<tr>
<th>Type</th>
<th>Solid content (%)</th>
<th>pH</th>
<th>Viscosity (cps)</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>48.0</td>
<td>4.10</td>
<td>300</td>
<td>1.15</td>
</tr>
<tr>
<td>S10</td>
<td>47.8</td>
<td>4.05</td>
<td>295</td>
<td>1.16</td>
</tr>
<tr>
<td>S30</td>
<td>48.1</td>
<td>4.12</td>
<td>295</td>
<td>1.14</td>
</tr>
<tr>
<td>P10</td>
<td>48.0</td>
<td>4.07</td>
<td>305</td>
<td>1.13</td>
</tr>
<tr>
<td>P30</td>
<td>47.9</td>
<td>4.10</td>
<td>310</td>
<td>1.16</td>
</tr>
</tbody>
</table>

B. Mix Proportions

In order to investigate cement admixture compatibility, cement paste mixtures containing admixtures with different chemical structures were prepared. Considering the studies in the literature, the water/binder ratio of the paste mixtures in the Marsh-funnel and mini-slump tests was chosen as 0.35 [18]. The admixture content of the paste mixtures varied in between 0.75 and 2.25% by weight of the cement.

In this investigation, mortar mixtures were prepared in accordance with ASTM C109 standard. Mortar mixtures were produced in Hobart mixer homogeneously. Water/binder, sand/binder ratios and flow values in all mixtures were fixed as 0.485, 2.75 and 270 ± 20 mm. Mixing method was applied to ASTM C309 standard in mortar mixtures. Cement paste and mortar mixtures were named in the same way as the names of admixtures.

C. Test Methods

The Marsh funnel test is based on the principle of determining the transition time of the paste mixes. In this test method, the saturation point of the admixture is determined by examining the relationship between admixture dosage and flow time. Immediately after preparing a homogenous paste with a volume of about 1.2 liters, the time flowed from the funnel to 700 mL of paste was measured. The time obtained was defined as the Marsh funnel flow time of that mixture [18]. The paste mixtures prepared for the marsh-funnel experiment were also used in the mini-slump experiment. The paste mixture prepared in this experiment is filled into a truncated cone-shaped mold with a lower inner diameter of 38.1 mm, an upper inner diameter of 19 mm and a height of 57.2 mm which is placed at the center of a smooth surface. The settling mold is slowly lifted vertically and a period of time (10-20s) is waited to complete spreading. Then, the average diameter is measured by measuring the spreading diameter in two directions perpendicular to each other with the help of a meter [19].

The flow retention of mortar mixtures was determined in accordance with ASTM C1437 at time intervals of 15
minutes for 60 minutes. The mini V funnel flow time of the mortar mixtures was carried out in accordance with the EFNARC [29] criteria. The 1, 3, 7, 28-day compressive strengths of mortar mixtures were determined on 50 mm cube specimens according to ASTM C109 standard. In addition, water absorption ratios were determined on the 28-day mortar specimens according to ASTM C642.

All specimens were removed from the molds after 24 hours and cured in lime saturated water cure pool with a temperature of 23±2°C until the day of the experiment.

III. Results and Discussion

A. Marsh-funnel flow time and Mini-slump

Marsh funnel flow times of cement paste mixtures containing admixtures with carboxylate anionic monomer, 10% and 30% molar sulphonate and phosphate anionic monomer are given in Table 3 and Fig. 1. Since the cement paste mixtures containing water reducing admixture less than 1 wt.% of cement did not flow through the Marsh funnel, the flow times of these mixtures could not be measured. As it can be seen from the results, the flow time of the cement paste mixtures decreased with the increase in the use of water reducing admixture regardless of the type of water reducing admixture. As it can be seen from Fig. 1, when the water reducing admixture/cement ratio is 1%, P30 mixture showed the highest performance and S30 mixture had the most negative behavior. P30 mixture showed about 10% higher flow performance than the control mixture.

In Fig. 1, the flow performance of cement paste increased with increasing amount of admixture in the mixture and tended to remain constant as the admixture amount exceeded a certain value. The increase in the dosage of the water reducing admixture in the mixture enhanced probability of the adsorbing of the admixture on the cement surface. Thus, the consistency and workability of the mixture were improved. When the amount of admixture in the mixture reaches a certain level, the adsorption behavior of the admixture reaches the saturation state and the admixture is released in the solution. In this way, the chemical admixture released in the solution cannot be adsorbed on the cement surface in a timely manner since the admixture adsorbing on the cement surface inhibit them. Therefore, the steric hindrance effects of admixture remain constant and the effect on fluidity of admixture is not significant [20].

The saturation point of all the paste mixtures was determined to be admixture/cement ratio of 1.25% regardless of the anionic monomer type of the water reducing admixtures used in the study. P30 mixture showed the best flow performance among admixtures containing phosphate at admixture saturation point in terms of Marsh funnel flow performance. At this saturation point, the P30 mixture showed about 15% higher flow performance compared to the control mixture. The Marsh funnel flow times of the paste mixtures improved by partially replacement of phosphate functional group as the anionic monomer with carboxylate group. This positive effect showed an increase with increasing phosphate functional group substitution ratio. This positive effect is thought to be the stronger anionic property of the phosphate functional group in comparison with the carboxylate group [21].

Among the sulphonate monomer substituted admixtures, the S10 mixture exhibited a similar behavior to the control mixture, while the S30 mixture showed more negative behavior than the control mixture. This adverse effect is thought to be the insufficient electrostatic effects due to poor adsorption ability of sulphonate substituted admixtures compared to admixtures containing carboxylate.

The mini-slump test results of the paste mixtures containing admixtures containing 10% and 30% molar sulphonate and phosphate anionic monomer are shown in Table 3. The utilization of water reducing admixtures enhanced the mini-slump values of the paste mixtures irrespective of the anionic monomer type of the admixture. However, it was observed that the mini-slump values did not change or even decreased in a small amount when the amount of admixture in the mixture exceeds a certain value. This is thought to be due to the fact that mixtures containing water reducing admixtures have a very flowing consistency and tend to segregation. P30 mixture showed higher mini-slump performance at the admixture saturation point and up to the saturation point while the mini-slump behavior of the mixtures was similar at admixture ratios higher than the saturation point. In this context, the change of admixture anionic functional group did not significantly affect the shear stress of the paste mixtures. In addition, the temperature values of the paste mixtures measured during the experiment are given in Table 3. It was observed that the temperature decreased between 2-3°C with the increase in the amount of water reducing admixture in the mixtures. It is thought that the reduction results from the set retarding effect of the water reducing admixture.
TABLE 3. Marsh-funnel flow time, mini-slump and temperature values of cement paste mixtures

<table>
<thead>
<tr>
<th>Admixture/ cement ratio (weight, %)</th>
<th>1.00</th>
<th>1.25</th>
<th>1.50</th>
<th>1.75</th>
<th>2.00</th>
<th>2.25</th>
</tr>
</thead>
<tbody>
<tr>
<td>Marsh funnel flow time (s)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>52.04</td>
<td>46.51</td>
<td>44.45</td>
<td>42.22</td>
<td>40.91</td>
<td>39.84</td>
</tr>
<tr>
<td>S10</td>
<td>50.2</td>
<td>45.51</td>
<td>43.53</td>
<td>41.36</td>
<td>40.19</td>
<td>38.90</td>
</tr>
<tr>
<td>S30</td>
<td>53.73</td>
<td>49.12</td>
<td>47.25</td>
<td>45.2</td>
<td>43.89</td>
<td>43.80</td>
</tr>
<tr>
<td>P10</td>
<td>49.08</td>
<td>42.31</td>
<td>39.06</td>
<td>36.73</td>
<td>35.11</td>
<td>33.88</td>
</tr>
<tr>
<td>P30</td>
<td>46.71</td>
<td>39.31</td>
<td>36.17</td>
<td>34.17</td>
<td>32.76</td>
<td>31.88</td>
</tr>
<tr>
<td>Mini slump (cm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>13.4</td>
<td>14.3</td>
<td>15.5</td>
<td>15.7</td>
<td>15.5</td>
<td>15.3</td>
</tr>
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<td>S10</td>
<td>13.5</td>
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<td>15.7</td>
<td>16.2</td>
<td>16.5</td>
<td>16.3</td>
</tr>
<tr>
<td>S30</td>
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<td>15.8</td>
<td>16.2</td>
<td>16.8</td>
<td>16.3</td>
</tr>
<tr>
<td>P10</td>
<td>16.1</td>
<td>16.2</td>
<td>16.9</td>
<td>16.2</td>
<td>16.6</td>
<td>16.2</td>
</tr>
<tr>
<td>P30</td>
<td>16.2</td>
<td>16.4</td>
<td>16.6</td>
<td>16.8</td>
<td>16.9</td>
<td>16.3</td>
</tr>
<tr>
<td>Temperature (°C)</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>27.8</td>
<td>28.2</td>
<td>29.2</td>
<td>28.5</td>
<td>28.8</td>
<td>27.3</td>
</tr>
<tr>
<td>S10</td>
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<td>28.7</td>
<td>28.4</td>
<td>27.9</td>
<td>27.5</td>
</tr>
<tr>
<td>S30</td>
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<td>28.9</td>
<td>28.8</td>
<td>28.3</td>
<td>28.4</td>
<td>28.3</td>
</tr>
<tr>
<td>P10</td>
<td>28.6</td>
<td>28.5</td>
<td>27.5</td>
<td>27.3</td>
<td>27.2</td>
<td>27.1</td>
</tr>
<tr>
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<td>29.3</td>
<td>28.6</td>
<td>27.2</td>
<td>27.7</td>
<td>27.4</td>
</tr>
</tbody>
</table>

b. Time-dependent Behavior of Mortar Mixtures

The time-dependent slump-flow and mini V funnel flow tests were carried out on the mortar mixtures containing 10% and 30% sulphonate and phosphate substituted admixtures. The slump flow value the mortar mixtures containing admixtures was determined every 15 minutes for 1 hour. For this purpose, the initial slump-flow values of all mixtures were kept constant at 27±2 cm. The time-dependent slump-flow and relative slump-flow changes of the mortars are shown in Table 4 and Fig. 2. It was indicated in Table 4 that water-reducing admixture of 0.6wt.% of cement weight was used to provide the initial target slump-flow value range in all mixtures. In Table 4 and Fig. 2 stated that the slump-flow and mini V funnel flow performances of the mixtures were adversely affected by elapsing time regardless of the admixture type.

The negative effect of phosphate group substituted admixture using is thought because of the faster adsorption of the admixtures on the cement surface and losing effect in a short time in comparison with the carboxylate group [22].

The time dependent mini-V-funnel flow time changing of the mortar mixtures is shown in Table 4. Since all mixtures did not flow through the mini V-funnel due to loss of consistency 15 minutes after casting, only the initial flow time was determined. The mini V funnel flow behavior of the mortar mixtures showed a similar trend to the Marsh funnel flow performances. Considering the flow times of the mortar mixtures, the fastest flowing mixture from the mini V funnel was the P30 mixture, while the slowest flowing mixture was the S10 mixture.

c. Compressive Strength

The 1, 2, 3 and 28-day compressive strength values of mortar mixtures containing admixture with sulphonate and phosphate functional groups are given in Fig. 3. The compressive strength of all mixtures increased by elapsing time. As it can be seen from Fig. 3, the use of sulphonate and phosphate functional groups of 10% and 30% moles as anionic monomer in water-reducing admixture did not cause a significant change in strengths of the mortar mixtures.
When water-reducing admixtures contain phosphate-group as the anionic functional group, the flow performance of cement paste and mortar mixtures improved. The positive effect on the flowability became more pronounced with the increase of phosphate functional group substitution ratio in admixture. Admixtures containing 30 mol% phosphate functional group in paste and mortar mixtures were the most successful mixture in terms of flow performance. It is thought that this favourable effect is because of the stronger anionic properties depending on the type of phosphate monomer according to carboxylate.

Replacement 10% and 30 mol% of carboxylate monomer with sulphonate or phosphate monomer did not significantly affect the mini-slump values of the paste mixtures.

Regardless of the type of anionic monomer, the mini V funnel flow could be performed only at the beginning of the experiment in all mortar mixtures. At 15th minutes post-casting, the mixtures did not flow through the mini V funnel due to loss of workability and consistency by elapsing time.

Mixtures containing sulfonate monomer substituted admixture were more successful in terms of time-dependent slump-flow performance compare to the mortar mixture containing the admixture with 100% carboxylate anionic monomer. The adsorption property of sulfonate substituted admixtures is weaker. Therefore, the amount of admixture which is not adsorbed on the cement and released in the mixtures increases. This has a positive effect on the consistency retention of the mixtures.

The replacement of the admixture anionic monomer with the phosphate functional group adversely affected the time-dependent slump-flow performance of the mortar mixtures. This negative impact was even more striking with the increase in substitution ratio.

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