Performance of Concretes Produced with Superplasticizer

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ABSTRACT: Nowadays, additive chemical substances are used in the production of high-performance concrete composites. These additives increase the fresh workability of concrete by decreasing the water/cement (W/C) ratio. The aim of this study was to examine the effects of water-soluble polymers on concrete performance. For this purpose concretes with and without additives were produced with W/C values of 0.52, 0.56, and 0.60. Chemical admixtures such as naphthalene formaldehyde sulfonate (N), melamine formaldehyde sulfonate (S), and a hyperplasticizers admixture (a special type of melamine sulfonated polymer) (H) were used in concrete. The amounts of these admixtures were at a ratio of 0.3, 0.5, and 1.0 wt % of the cement's weight. Experiments assessing slump, VeBe, percentage of air, and unit

weight were done for comparison with the test results of the characteristics of fresh concrete with and without admixtures. The compressive strength of concretes was determined at 7, 28, and 56 days. The effects of chemical admixtures were studied by comparing the properties of fresh and hardened concrete samples with and without admixtures. When the W/C ratios were 0.56, 0.60, and H was 1 wt %, the biggest slump was obtained and found to be 22 cm. Concrete with a W/C ratio of 0.52 and H of 1% has the highest compressive strength. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 3214–3219, 2007

Key words: water-soluble polymers; additives; composites; density; hydrophilic polymers

INTRODUCTION

Concrete is the most-used building material. The requirements of preferred concrete is not only compressive strength but also workability and durability.^{1–3} Concrete that provides high strength, good workability, and durability is called high-performance concrete. The water/cement (W/C) ratio is an important parameter in concrete. Various chemical admixtures are used in concrete technology and admixtures have physicochemical effects on fresh concrete.

Self-compacting concretes (SCCs) have high workability and high segregation resistance at low W/C ratios. They are new and special types of concretes that can be compacted without any vibration. It is common knowledge that the pore structure of SCC differs from the pore structure of conventional concrete due to the presence of a high amount of fine material with a new-generation superplasticizer. In a this type of concrete produced using fine aggregate, silica fume, hyperplasticizers, and steel fibers, the W/C ratio was decreased up to 0.23.⁴ New generated superplasticizers decrease the W/C ratio to 0.30.³ But some admixtures are known that decrease the W/C ratio to 0.20 and increase compressive strength to 200 MPa.⁵

The air percentage and slump loss properties of concretes differ relative to the mixing of chemical

Journal of Applied Polymer Science, Vol. 103, 3214–3219 (2007) © 2006 Wiley Periodicals, Inc. admixtures and cement type. The superplasticizers are organic polyelectrolytes that are polymeric dispersants. They are classified according to their chemical compositions as sulfonated synthetic polymers, carboxylated synthetic polymers, and synthetic polymers with mixed functionality.⁶

There are four different chemical admixtures: modified ligno sulfonated polymers (LS), naphthalene formaldehyde sulfonated polymers (N), melamine formaldehyde sulfonated polymers (S), and polycarboxylate derivates (CE). In the relevant literature, the most attention has been paid to superplasticizers of LS, N, and S, while polycarboxylate-type superplasticizers have not been sufficiently emphasized.^{7,8} Water-soluble polymers such as sulfonated phenolic resin (SPF) and sulfonated acetone formaldehyde (SAF) have also been used successfully in this area.^{9–14} It is possible to see examples of high-performance self-compacting concrete in practical use up to 200 m in height.⁵

In this study the effects of different dosages of three different sulfonated superplasticizers on concrete at various W/C ratios were compared to control concrete.

EXPERIMENTAL

Materials

Composite Portland Cement (CPC) was used for the concrete mixtures. Aggregates such as sand and



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Properties of Aggregates											
Passing %							Specific gravity Unit mass				
Sieve (mm)	31.5	16	8	4	2	1	0.5	0.25	(kg /m^3)		Abs. % (H ₂ O)
Sand	100	100	100	100	93	76	38	21	2.57	1.37	0.90
Crushed stone 1	100	95	45	20	5	0	0	0	2.62	1.34	1.40
Crushed stone 2	100	9	3	0	0	0	0	0	2.57	1.31	1.40

TABLE I Properties of Aggregate

crushed stone 1 and 2 were used. The properties of the aggregates are given in Table I. The formula of superplasticizers (SPs) used in this study are presented in Figure 1. The specific gravities of admixtures naphthalene formaldehyde sulfonate (N) (ASTM C 494 Type G), melamine formaldehyde sulfonate (S) (ASTM C 494 Type F), and a special type of melamine sulfonated polymer with high sulfonation degree (H) were 1.19, 1.14, and 1.29 kg/dm³, respectively.

Concretes, sample size, and cure conditions

The aggregates mix design of concretes were between the A32-B32 reference curves. W/C ratios: 0.52, 0.56, and 0.60. The admixture portions in three different concrete admixtures were 0.3, 0.5, and 1.0%. Concrete samples were cured in water at room temperature around $20 \pm 2^{\circ}$ C. The produced concrete codes, W/C, and admixture portions are given in Table II. A calculated amount of the compounds given in Table III was first mixed with water containing superplasticizer for 2 min to produce the concrete.

Experiments

Fresh concrete tests of concretes were made based on unit mass, slump, VeBe, and air tests. Air percent was tested with an air test method according to the pressure method.⁴ Compactness was calculated from unit mass. Compressive strength experiments of hardened concretes were made at 7, 28, and 56 days.

RESULTS AND DISCUSSION

The test results of the fresh concrete properties of unit weight (fresh density), compactness, VeBe, slump, and air content are presented in Figures 2–6, respec- F2-F6 tively.

Unit weight (fresh density) and compactness

The change of unit weights of the concretes with different proportions of admixtures and W/C ratios are shown in Figure 2 and compactness in Figure 3. When the W/C ratios of these concretes were changed from 0.52 to 0.60, the unit masses of the concretes were decreased. The unit masses of the concretes were independent of the percentage and nature of admixture for W/C ratios of 0.52 and 0.56, whereas a minimum was observed for 0.3% at a W/C ratio of 0.60 for N and S. As seen in Figure 2, N and S show similar behavior on an admixture amount with a minimum admixture of 0.3%. The sodium sulfonated group of admixtures ionizes to an anionic surfactant component with a large molecule and an Na⁺ cation. The surface charge density of cement particles generated by the initial hydration can be effectively neutralized by adsorption of the surfactant anion. When a surfactant anion is adsorbed by hydrophilic head group on cement particles, hydrophobic tail groups are oriented toward the water phase.¹⁵ This behavior decreases hydration of cement particles and the amount of free water increases, resulting in particle-particle repulsion and separation of cement particles. As a result of



Figure 1 Chemical formula of superplasticizers.

			Code	s of Con	crete Sar	nples			
Admixture code N			de N	Adn	nixture co	de S	Admixture code H		
	А	dmixture	%	А	dmixture	%	А	dmixture	%
W/C	0.3	0.5	1.0	0.3	0.5	1.0	0.3	0.5	1.0
0.52 0.56 0.60	C1N1 C2N1 C3N1	C1N2 C2N2 C3N2	C1N3 C2N3 C3N3	C1S1 C2S1 C3S1	C1S2 C2S2 C3S2	C1S3 C2S3 C3S3	C1H1 C2H1 C3H1	C1H2 C2H2 C3H2	C1H3 C2H3 C3H3

TABLE II Codes of Concrete Samples

this behavior, a more porous structure might be formed. A gradual increase in the unit weight suggests that a critical micelle concentration of sulfonatebased H surfactant is lower than that of N and S. Therefore, adsorptive micelles are formed on cement particles and negative head groups of surfactant oriented to water phase are surrounded with water molecules. The amount of free water and the distance between hydrated cement particles are decreased.¹³

A comparison of Figures 2 and 3 shows that the unit weight and compactness of all samples with the same W/C ratio show similar trends. When the W/C ratios increase in the order 0.52, 0.56, and 0.60, their average unit weights are found to be 2300–2310, 2272–

TABLE III Concrete Mixtures (1 m³)

	Water	Cement	Sand	Crushed	Crushed
Codes	(kg)	(kg)	(kg)	stone 1 (kg)	stone 2 (kg)
C1	221.5	425.9	328.0	1081.9	242.8
C1N1	221.9	426.7	328.5	1083.7	243.2
C1N2	222.0	427.0	328.8	1084.7	243.4
C1N3	222.0	426.9	328.7	1084.2	243.3
C1S1	221.8	426.5	328.4	1083.3	243.1
C1S2	222.0	426.9	328.7	1084.2	243.3
C1S3	222.2	427.2	329.0	1085.1	243.5
C1H1	222.2	427.2	329.0	1085.1	243.5
C1H2	222.3	427.4	329.1	1085.6	243.6
C1H3	222.5	427.8	329.4	1086.6	243.8
C2	239.1	427.0	316.0	1054.7	239.1
C2N1	238.7	426.3	315.4	1052.9	238.7
C2N2	238.7	426.3	315.4	1052.9	238.7
C2N3	239.3	427.4	316.3	1055.0	239.3
C2S1	238.7	426.3	315.4	1052.0	238.7
C2S2	238.9	426.7	315.7	1053.8	238.9
C2S3	239.6	427.8	316.6	1056.0	239.6
C2H1	238.9	426.5	315.7	1053.6	238.9
C2H2	239.0	426.8	315.9	1054.3	239.0
C2H3	239.9	428.3	317.0	1058.0	239.9
C3	255.7	426.2	311.0	1027.0	230.1
C3N1	254.0	423.5	309.1	1020.6	228.7
C3N2	254.8	424.6	310.0	1023.3	229.3
C3N3	256.5	427.5	312.0	1030.2	230.8
C3S1	253.8	422.9	308.7	1019.2	228.4
C3S2	254.9	424.8	310.1	1023.3	229.4
C3S3	256.7	427.8	312.3	1031.1	231.0
C3H1	256.0	426.7	311.5	1028.4	230.4
C3H2	256.5	427.5	312.0	1030.2	230.8
C3H3	256.7	427.8	312.3	1031.1	231.0

2283, and 2233–2259 kg/m³, respectively. Respective compactness was calculated as 0.768-0.771, 0.750-0.754, and 0.730-0.738, respectively.

VeBe and slump

The VeBe values of the fresh concretes, which were produced with different amounts of admixture and W/C ratios, are shown in Figure 4. The Slump changes of the concretes are shown in Figure 5.

The VeBe values of three control groups (C1, C2, and C3 series) of the concretes were 10, 9, and 7 s, respectively. The values of VeBe for the C1 series with and without admixtures changed between the 10 and 5 s limits (open symbols in Fig. 4). However, the values for C2 and C3 were more affected by admixture species and amounts following the order 9-1 and 7-1 s, respectively. The slump values of the control groups changing in the opposite direction were 1.9, 2.7, and 4.8 cm, respectively. As shown in Figure 5, the smallest VeBe of 1 s and the highest slump values of 22 cm were the same for the C2H3 and C3H3 samples, respectively.



Figure 2 Unit weights of concrete with different dosages of superplasticizers at different W/C ratios.



Figure 3 Compactness of concrete with different dosage of superplasticizers at different W/C ratios.

The fluidifying effects of high range water reducers (HRWRs) are due to their high dispersive property occurring in solid cementitious materials. Dispersion results occur from the adsorption of the HRWR molecules by cementitious powder particles. The dispersibility of cement particles should also remain stable. Dispersion and stability can be explained based on different theories. As referred to in Ref. 6, the first is the DLVO theory (Derjaguin, Landau, Verwey, Overbeck) of the lyophobic colloids.^{12,13} An electrostatic repulsion among the solid cement particles is created



Figure 4 VeBe of concrete with different dosages of superplasticizers at different W/C ratios.



Figure 5 Slump of concrete with different dosages of superplasticizers at different W/C ratios.

by the adsorption of HRWR molecules that charges them negatively. This electrostatic repulsion is the main cause of the dispersion in the case of sulfonated synthetic polymers such as N and S. The second theory is the steric effect theory. The steric effect arises due to the geometric structures of the admixture. The formation of intermolecular hydrogen bonds create larger molecules. Stereochiometric structures of the adsorbed molecules create higher repulsive potential between the cement particles.⁶



Figure 6 Air content of concrete with different dosages of superplasticizers at different W/C ratios.

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Figure 7 Time-dependent compressive strengths of concrete with different dosages of superplasticizers and W/C ratios: (a) 0.3%, 0.52, (b) 0.5%, 0.52, (c) 1.0%, 0.52, (d) 0.3%, 0.56, (e) 0.5%, 0.56, (f) 1.0%, 0.56, (g) 0.3%, 0.60, (h) 0.5%, 0.60, (i) 1.0%, 0.60.

Air content

As shown in Figure 6, the air percentages of control concretes are independent of W/C ratios and were found to be around 2.4%. The air percentage depending on admixtures decreases in the order N > S > H. A decrease in the air percentage indicates that the workability of a concrete is better.

Compressive strengths

The compressive strengths of the hardened concretes at 7, 28, and 56 days and on three different W/C ratios are shown in Figure 7(a–i), respectively. It was

observed that the compressive strengths of all concretes in the C1 series are higher than those found for control concrete at 7 days [Fig. 7(a–c)]. The compressive strengths of C1N2, C1S2, and C1H2 decreased at 28 and 56 days compared to control concrete [Fig. 7(b)]. The smallest compressive strengths were obtained for an admixture content of 0.5%. This suggests that surfactant anions are oriented in the same direction at the lowest and highest loadings, whereas they are adsorbed in the opposite direction on cement particles. The highest value was obtained for the C1H1 series for all times at the lowest W/C ratio.

As seen in Figure 7(d–f), although some discrepancies are observed the compressive strengths generally increase compared to control concrete at medium W/C ratios. It is difficult to explain the effects of admixtures on compressive strengths because of the nonavailability of data for critical micelle concentration and orientation of the molecules in solution and in cement phases.

It can be deduced from Figure 7(g–i) that the lowest compressive strength values were obtained for the concrete with and without admixtures at the highest W/C ratio of 0.60.

CONCLUSIONS

The following conclusions were drawn from the results of this experimental investigation: The unit weights of the concretes are almost the same at W/C ratios of 0.52, 0.56, and 0.60. The compactness also did not significantly change with W/C ratio. The VeBe values of control concretes by increasing W/C ratios (C1, C2, and C3) decreased from 10 to 7 s, whereas they were reduced up to 1 in the presence of superplasticizers. The values of slump of control concretes increased from 1.9 to 4.8 from C1 to C3, while they increased from 2 to 22 for the same range of W/C ratios. The workablity increased according to the following sequence N < S < H. Similarly, the air content of additive concretes were not significantly affected by the type and amount of superplasticizers. The minimum value of air content of 1.2% was obtained for the C2H3 sample. An optimal condition both for

workability and compressive strength was provided for the C2H1 sample.

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