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THE EFFICIENCY OF MIXED SURFACTANTS AS AIR ENTRAINING AGENTS IN CEMENT PASTES

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ABSTRACT: *The interaction that occurs when combining surfactants is more than the sum of the properties of each surfactants. These interactions can either enhance or detract from the action of these surfactants as air entraining agents. In an attempt to understand these interactions of some surfactants used as air entraining agents, the effect of several air-entraining agents was compared, in addition to two mixtures of them. The results show that CABP surfactants can be used lonely and in conjunction with other surfactant groups, taking into consideration that the compatibility of betaines with anionic surfactants is better than that with cationic surfactants. Higher compressive strength and less pore size appeared when using LM solo and in mixes which demonstrates the positive impact of using LM in these mixes.*

KEYWORDS: *air-entraining agent, density, compressive strength, SEM, HYPR, LM, SDBS, CABP, mixed surfactant.*

INTRODUCTION

Surface-active agents, commonly called surfactants, can be divided into four groups depending upon the charge on the organic portion of the molecule; these groups are anionic, cationic, non-ionic and amphoteric**.** These materials are used in a variety of formulations and rarely are used alone. These formulations may interact with each other; these interactions make formulations work or fail. Surfactants are widely used in construction field as air entraining agents. Air entrainment is the process whereby many small air bubbles are incorporated into cement paste and become part of the matrix that binds. Air-entraining admixtures cause small stable bubbles of air to form uniformly through a cement paste. The bubbles are mostly below 1 mm diameter with a high proportion below 0.3 mm. The lightweight aerated concrete, mortar and paste is acceptable for the use in civil construction purposes as a result of their peculiar features such as heat-insulating, sound absorption, low self-weight and self-compacting features, hence their high workability.

The volume of entrained air depends on the application and the mix design. After mixing, air can be lost during transport and pumping, this air can be stabilize by using surfactants as effective air entraining agents. Air entrainment reduces the compressive strength and the density of the mix and increases yield, this needs to be taken into account when batching and mixing. For every 1% of additional air entrained, hardened pastes strength will fall by around 1-3%. ***Rosen (2004)*** reported that formed air bubbles in cement paste are unstable and have a limited lifetime. Air entrainment may be accomplished by the use of an air-entraining agent (AEA). Nearly all modern day air-entraining agents are part of a chemical group called surfactants ***(Algurnon, 2013)***. Surfactants are used to entrain air bubbles and stabilized them in the fresh cement pastes. ***Lea***

(1971) suggested that air-entraining surfactants operate at the air-water and the solid-water interface, as shown in Figure (1). At the air-water interface, the agent helps by reducing surface tension, which promotes dispersion and bubble formation. ***Dodson (1990)*** demonstrated that absorbed surfactants molecules at the surface of the bubble form a film, with their polar heads in the water phase. If the molecule is charged, the bubble acquires this charge. The electrostatic repulsion keeps bubbles separated and prevents coalescence.

Qaraman et al. (2016) suggested that the efficiency of a surfactant as an air-entraining agent in cement media depends on three main factors: (1) the sensitivity of the surfactant to water hardness or pH changes. The metal ions (e.g., Ca^{+2} and Mg^{+2}) present in the medium may compete with other metal ions present in the structure of the surfactant this may affect the amount of the free surfactant available for the desired purpose and hence its efficiency. (2) The mechanism of interaction between the surfactant and the cement grains surface (the ionic attraction which is stronger than hydrogen bonding), this determines the ability of the surfactant to stabilize the formed air.(3) The electrostatic repulsion between similar charges which keeps bubbles and cement grains separated, this leads to media expansion (dispersion action).

It is well known that the pore structure of the hardened cement pastes strongly influence its physical properties. The presence of the air-entraining agent not only improves workability, but also enhances its freeze-thaw resistance ***(Hewlett, 2004)***. ***Du and Folliard (2005)*** noted that there is a minimum dosage of air entraining agent required to entrain air in the cement paste. ***Leslie and Qingye (2004)*** concluded that the addition of air-entraining agent increased the air content up to a saturation level, above which no further increase in air content was observed.

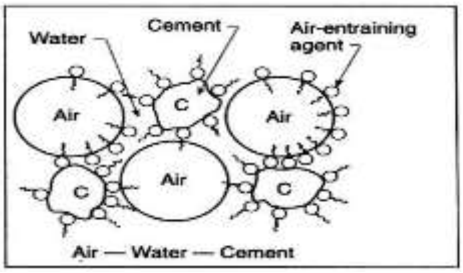

Figure (1): Interaction between air bubbles and cement particles.

The objective of this work is to study the efficiency of mixed surfactants as air entraining agents in cement pastes and accordingly the bulk density and the compressive strength of cement specimens. In addition, the microstructure of the hardened cement paste samples is examined SEM analyses.

Experimental:

2. a. Materials

- Portland cement of mark CEM I 52.5N obtained from El-Arish cement factory. Its chemical composition is given in Table (1).
- Alkyl dimethyl hydroxyl ethyl ammonium chloride **(HYPR)** supplied from Clariant.
- Luramide 11 **(LM)**, Sodium lauryl benzene sulfonate **(SDBS) and** cocamido propyl betaine **(CAPB)**, are supplied from Zohar Dalia and used as such.

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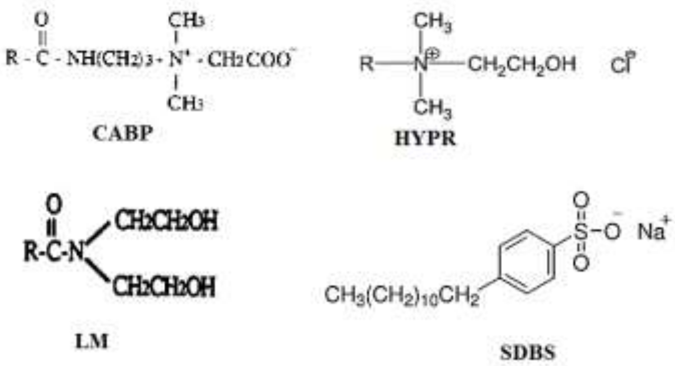

Figure (2): The chemical structure of the used surfactant.

Table (1): Chemical composition of the used ordinary Portland cement (OPC).

Oxide (%)	OPC
SiO_2	22.12
Al_2O_3	5.56
Fe_2O_3	3.69
CaO	62.87
Na_2O	0.26
K_2O	0.11
Cl^-	0.02
MgO	2.36
SO_3	0.91
Free CaO	0.92
Ignition Loss	1.22

2. b. Techniques and Instrumentation:
2. b.1 Paste preparation:

The cement specimens are prepared by dissolving different concentrations of each surfactants mentioned above in 650 g H_2O then adding to 1500 g cement. The water to cement ratio (W/C) is 0.43 as recommended (***Carmel et al., 2003)***. The percentages of the surfactants used range from 0.005 to 0.20 % by weight of cement.

Two Mixtures of optimum concentrations are prepared:

1. The first mixture (M1) consist of 0.20 CABP, 0.06 HYPR and 0.08 LM.
2. The second mixture (M2) consist of 0.20 CABP, 0.08 SDBS and 0.08 LM.

The mixing are carried out under continuous and vigorous stirring for about three minutes (***Carmel et al., 2003)***. After complete mixing the resulted pastes is poured into (12 ×4 ×4 cm^3) moulds. The moulds are kept at about 100% relative humidity at room temperature for one day.

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The hardened cement pastes are then removed from the moulds after they attained the final setting and cured under water for the rest of the hydration ages (up to 90 days).

2. b. 2 Compressive Strength:

Three specimens of each mix at different hydration times (3, 7, 28 and 90 days) are used for examination the compressive strength of the pastes. The mean value of the three specimens at each hydration age is considered as the determined compressive strength. The strength test machine used is of point load taster (20063 cemasco S/N-Controls) type, Milano-Italy.

2.b. 3 Stopping of hydration:

This is performed after doing the compressive strength test by taking about 10 g of the crushed hardened pastes and putting into a beaker containing 100 ml of acetone/ethyl alcohol (1:1 by volume) to stop the hydration process. The mixture is stirred for 0.5 hr. The residue is filtered off, washed with ethanol and dried at 50º C for about 24 hrs. The dried samples are then stored in a desiccator for the following physico-chemical analysis.

2. b. 4 Determination of the bulk density of the cement pastes:

The bulk density is determined by measuring the weight of the sample in air and under water. The density is then calculated as mentioned in (ASTM Standard C 138-08 – 2008).

2. b. 5 Determination of the air entrained in the cement pastes:

The percent of air entrained in pastes was determined by the difference in weight of a hardened cement paste in absence and in presence of surfactants by the equation:

$$\text{Percent of air entrained} = \frac{A - B}{A} \times 100\ \%$$

Where: A: The weight of hardened cement paste in absence of surfactant.
B: The weight of hardened cement paste in presence of surfactant.

2. b. 6 Scanning Electron Microscopic (SEM) measurements:

The morphology and microstructure of the dried hydrated samples are studied using JEOL JXA 840 an electron Probe micro analyzer SEM. The specimens are coated with a thin film of gold, under vacuum evaporator with cathode rays then analyzed.

3. RESULTS AND DISCUSSION

3. a. Effect of the presence of surfactants on the air content of the cement paste:

Air content is an important factor, which affects other aspects of the cement paste (i.e. density, compressive strength and workability). On adding an air entraining surfactant to cement pastes, its molecules are inserted between adjacent molecules at the water surface; the mutual attraction between the separated water molecules is reduced. Lowering the surface tension stabilizes the bubbles against mechanical deformation and rupture, making it easier for bubbles to be formed.

The values of the air content entrained in Portland cement pastes hydrated for 90 days in presence of different percentages of surfactants are determined. It should be mentioned that the content of air entrained in cement pastes show a slight change at the different hydration ages (from 3 up to 90 days). However, the air content exhibits the best value at 90 days of hydration.

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The values of the air content in Portland cement pastes in presence of different percentages of HYPR, CAPB, LM and SDBS are given in Table (2). The results show a gradual increase in the air content with increasing surfactant concentration and reaches its maximum value at the concentration of 0.06 %, 0.20%, 0.08%, and 0.08% for HYPR, CAPB, LM and SDBS respectively.

Two Mixtures of previous surfactants optimum concentrations are prepared, the values of the air content in Portland cement pastes in presence of the two mixtures (M1) and (M2) are given in Table (3) the air entrained by the two mixtures are 48.92 and 52.78 respectively.

Table (2): the air entrained by HYPR, CAPB, LM and SDBS at 90 days.

Surfactant conc. (wt %) / Surfactant	0.005	0.020	0.060	0.080	0.200
	% of air entrained				
HYPR	3.04	9.60	17.87	14.08	14.50
CABP	7.90	22.10	35.80	38.70	58.09
LM	6.05	6.44	8.36	8.55	8.40
SDBS	5.60	5.77	6.64	7.80	7.40

Table (3): The air entrained by M1 and M2 at 90 days

Surfactant mixture	% of air entrained
M1	48.92
M2	52.78

The results show that (CAPB) is the most docile of the used surfactants. It is the most effective surfactant as air entraining agent. Lonely it is able to provide high percent of entrained air in the cement paste. On other hand, when (CAPB) is coupled with other surfactants the air entrained is decrease slightly, which may explained by side reactions with other surfactants. Generally, amphoteric surfactants can be used solo and in conjunction with any other surfactant groups. There adaptability is just one of the reasons why they are so widely used.

Cocamidopropyle betaine ,CAPB, contrary to true amphoterics, does not exhibit anionic behavior under alkaline conditions (**Milton, 2012**). It behaves as a zwitterionic surfactant in neutral and alkaline media and cationic below its isoelectric point, i.e. in acidic medium. Accordingly, in the cement pastes, which is highly alkaline (pH is ~ 11), CAPB is expected to be isoelectric having two opposite charges. ***Danov et al. (2004)*** stated that the addition of Betaines to anionic surfactants significantly increases its surface elasticity**.** On other hand **O'Lenick et al., (2008)** study the interaction of cationic surfactant with other surfactants, he concluded that the positive charge of cationic surfactant attract to a negative charge of a surfactant and form a salt complex,

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the formation of this complex is slightly decrease the air entrain activity of M2. From the above and our results, it can be concluded that the compatibility of betaines with anionic surfactants is better than that with cationic surfactants this may explain why M1 is slightly entrained air more than M2.

3. b. Effect of the presence of surfactants on the bulk density of the cement paste:

The density of cement pastes is directly affected by the air content; they are inversely proportional to each other. The determined density of the hardened control specimen (zero surfactant concentration) and those of the specimens containing HYPR, CAPB, LM and SDBS and mixed surfactants after 90 days of hydration are shown in Table (4) and table (5) respectively. The results showed that density decrease with increasing concentration which refer to the increase of air content. It is found that, the density decreases by about 0.3g/ cm^3 when the air content is increased by about 14%***. (Qaraman et al., 2016)***

Table (4): The density (g/ cm^3) of hardened cement paste in presence of HYPR and CAPB surfactant at 90 days

Surfactant Conc. (wt %) / Surfactant	0.00	0.005	0.02	0.06	0.08	0.20
	ρ (g/ cm^3)					
HYPR	2.00	1.92	1.73	1.57	1.65	1.63
CAPB	2.00	1.87	1.57	1.37	1.35	0.84
LM	2.00	1.93	1.88	1.85	1.83	1.84
SDBS	2.00	1.91	1.89	1.87	1.85	1.86

Table (5): The air entrained by M1 and M2 at 90 days

Surfactant mixture	ρ (g/ cm^3)
M1	0.98
M2	0.90

3. c. Microstructure and Morphology Investigations (SEM Analysis):

The scanning electron microscope (SEM) is a powerful tool for imaging and chemical analysis in cement research. With a high resolution and a large depth of focus, it enables a detailed study of surface topography of the rough surfaces of e.g. the formed calcium silicate hydrate (CSH) and calcium hydroxide (CH).

Scanning electron microscope (SEM) is used to examine the surface structure of hardened cement pastes, in absence and in presence of 0.20 % CAPB, 0.06% HYPR, 0.08% LM and 0.08 % SDBS

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surfactants in addition to M1 and M2 mixtures, at the two hydration ages 7 and 90 days to examine the early and late ages of hydration.

Microscopic photos for the early hydration age are illustrated in Figure (3) (a, b, c, d, e, f & g). The figure shows that main hydration products formed at 7 days are Calcium hydroxide appears as hexagonal plates beside the calcium silicate hydrates (CSH) phase. Figure (4) (a, b, c, d, e, f & g) shows the micrographs of the hardened Portland cement pastes in absence of surfactants (blank) and in presence of 0.20 % CAPB , 0.06% HYPR , 0.08% LM and 0.08 % SDBS surfactants in addition to M1 and M2 mixtures after 90 days hydration. It can be noticed that the hydration products have more compact structure composed of CSH, which explains the improvement in the strength for all mixes.

On other hand, the structure of hardened cement paste with addition of LM produces consistent bubble structure with a uniform small air voids system (70.92 µm) it seems to be more compact, which resulted in much better strength compared to the other type of mixes. Micrograph of other mixes indicates some empty spaces, CAPB produces a homogenous bubble structure with a uniform air voids system (85.7 µm), SDBS moulds has a large air voids system (103.3 µm), while HYPR has the largest air voids (124.2 µm). M1and M2 have a uniform air voids with (75.83 µm) and (79.76 µm) respectively. This indicates that the addition of LM help to homogenize the air bubbles system, this result is confirmed by **Concrete Construction Staff ,1988**, they stated that LM have many advantages: increased compressive strength for mixes , better distribution of air voids ,more uniform bubble size and shape, less bubble coalescence during mixing and placing and fewer bubble clusters at aggregate particle surfaces.

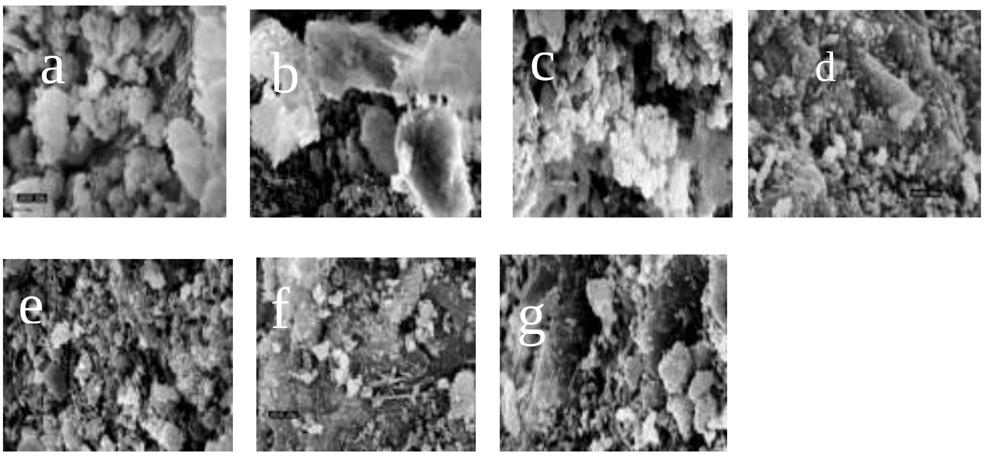

Figure (3): SEM of hardened cement pastes after 7 days hydration (X = 5000).
a) Without surfactant b) With 0.20 % CAPB c) With 0.06% HYPR d) With 0.08 %LM
e) With 0.08% SDBS. f) With M1 g) with M2

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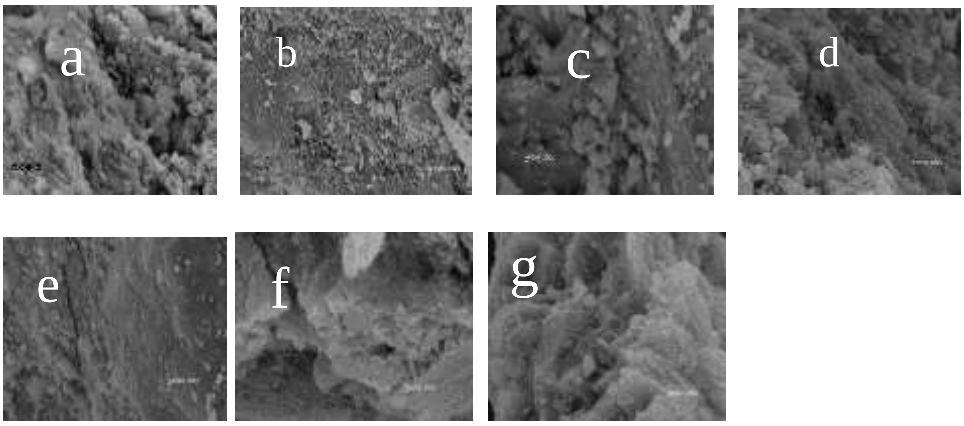

Figure (4): SEM of hardened cement pastes after 360 days hydration (X = 5000).
a) Without surfactant b) With 0.20% CAPB c) With 0.06% HYPR d) With 0.08% LM
e) With 0.08% SDBS. f) With M1 g) with M2

3. d. Effect of Surfactant Type on the Compressive Strength of the Hardened Cement Pastes:

Compressive strength is an important criterion specified in the design of light weight cement pastes and should be considered equally important as density. The properties of hardened cement pastes are time dependent, therefore, any test method performed on the cement pastes should be done at a certain hydration age.The values of the compressive strength of hardened Portland cement pastes without surfactants and in presence of the investigated surfactants CAPB, HYPR, LM and SDBS in addition to M1 and M2 mixtures at optimum concentrations and different hydration ages (3, 7, 28 and 90 days) have been determined .Three specimens of each mix at each hydration time are used for examining the compressive strength of the pastes. The mean value of the compressive strength of the three specimens at each hydration age is considered.

The results are given in Figure (5). All mixes show an increase in the values of the compressive strength with increasing hydration time. This is believed to be due to progress of the cement hydration. As mentioned above, the compressive strength of the cement pastes increases with the hydration time both in absence and presence of surfactants regardless of their concentrations.The above results of the compressive strength values of the specimens of the investigated surfactants after hydration for 90 days indicate that they decrease in the following order

LM > SDBS > HYPR >M1 > M2 > CAPB.

It is noticed that compressive strength decreases by increasing the entrained air where lower strength is caused if more voids exist in the cement paste. The strength loss is 1.32 to 2.72 % for each percent of entrained air. Although a high air content in M1 and M2 mixtures 48.92% and 52.78% respectively but they has maintained acceptable level of compressive strength (table (6)) which may refer to two reasons:

1. A well distributed small air bubbles.
2. The probability of forming hydrogen bonds with CSH which refer to a hydroxyl group (OH) in both LM and HYBR.

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Table (6) illustrate the relationship between the entrained air by different surfactants and the pore size with the compressive strength.
The results show that (1) for each 1% increasing in the air content the compressive strength decreases by 1.32-2.72%. (2) The pore size have a great effect on the percent of decrease in compressive strength, whereas this percent decrease as the pore size decrease.
(3) Higher compressive strength and less pore size appeared when using LM lonely and in mixes which demonstrates the positive impact of using LM in these mixes.

Table (6): The relationship between of the entrained air by different surfactants and the pore size with the compressive strength.

Surfactant (S)	% of entrained air	C.S at 90 days	% of decreasing in C.S $\frac{C.S\,(B) - C.S\,(S)}{C.S\,(B)} \times 100\%$	% of decreasing in C.S per 1% of entrained air.	Pore size (µm)
Blank (B)	0	72.7	0	0	0
M1	48.92	24.24	66.66	1.36	75.83
M2	52.78	18.44	74.91	1.42	79.76
HYPR	17.87	37.42	48.53	2.72	124.2
CABP	58.09	10.24	85.91	1.48	85.7
LM	8.55	64.48	11.31	1.32	70.92
SDBS	7.80	61.04	16.03	2.06	103.3

C.S (B): Compressive strength of hardened cement paste in absence of surfactant (Blank).
C.S (S): Compressive strength of hardened cement paste in presence of surfactant.

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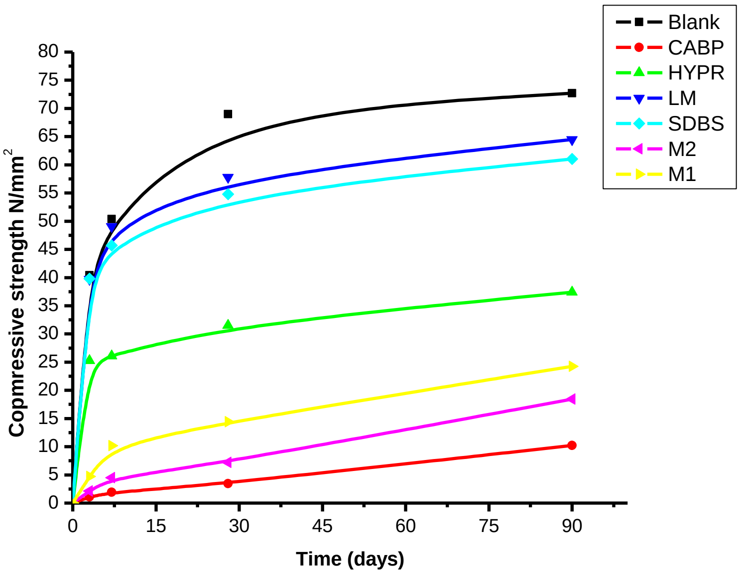

Figure (5): The compressive strength of hardened Portland cement pastes without surfactants and in presence of CAPB, HYPR, LM and SDBS in addition to M1 and M2 mixtures at different hydration ages.

CONCLUSION

1. CABP surfactants can be used solo and in conjunction with any other of the surfactant groups.
2. The addition of LM surfactant improve the properties of the air system by produce a well distributed small air bubbles.
3. The pore size have a great effect on the percent of decrease in Compressive strength, whereas this percent decrease as the pore size decrease.
4. The compatibility of betaines with anionic surfactants is better than that with cationic surfactants.
5. Using CABP in mixtures with LM and SDBS surfactants improve its efficiency as air entraining agents by improving the entrained air system and hardened paste compressive strength.

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