Can Soy Methyl Esters Reduce Fluid Transport and Improve Durability of Concrete?

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Nearly all problems that lead to the deterioration of concrete can be related to the presence of moisture or transport of fluid in the pore structure of the concrete (*1*). Common forms of this type of deterioration would include chloride ion ingress and freeze–thaw damage. Many methods have been used in the past to reduce the ingress of fluid to preserve the durability of concrete. These methods include improved mixture proportioning (*2*), special curing techniques (*3*), and the use of membrane coatings, penetrating sealers, and crack sealants (*4*). For example, the use of linseed oil in certain forms has shown that hydrophobic solutions can be used as penetrating sealers on pavements to reduce the absorption of moisture (*5*). The research program discussed here evaluated the potential for using soy methyl esters (SMEs) for similar purposes.

This research program is similar conceptually to classic studies dealing with substances such as linseed oil (*6*); however, SMEs are a derivative of soybean oil (as opposed to flax oil), which has a different chemical composition and structure after esterification, consequently properties that differ from those of the original oil. These properties include high solvent capacity, altered surface tensions, and enhanced viscosities. All of these properties lead to a substance with a unique potential for application in the field of concrete construction.

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RESEARCH PROGRAM OVERVIEW

Results are described from a pilot investigation aimed at evaluating the potential for using soy methyl ester–polystyrene (SME–PS) blends as both an additive and a topical application for concrete. The program examines the influence of SME–PS on the fresh properties, fluid transport properties, and the mechanical properties of concrete. Table 1 is a matrix of the testing program that was used in this investigation for examining SME–PS blends in both topical and admixed applications.

BACKGROUND ON SME–PS BLENDS

Oil crops, such as soybeans, are used mainly for livestock feed (*8*). The extracted oils from this feed have many potential uses (soaps, lubricants, crayons, candles, etc.) including the production of SMEs through transesterification. SMEs are biodegradable, nontoxic, renewable materials with potential application in the construction industry. Specifically SMEs are hydrophobic and have the potential to repel water or reduce fluid transport if used in concrete (*9*). The addition of SMEs leads to the modification of concrete properties while also creating a "green" concrete due to their biodegradable and nontoxic form.

SMEs consist of plant oils that are composed of long-chain fatty acids (14 to 20 carbons), which are esterified to a methyl group. Methyl esters are produced from plant triacylglycerides (oil) by alkaline-catalyzed transesterification with methanol. Each molecule of triacylglyceride reacted requires three molecules of methanol, resulting in the production of three molecules of methyl esters and one molecule of glycerin.

While remaining biodegradable and nontoxic, methyl esters have physical properties that are distinctly different from those of the triacylglyceride (soybean oil) since SMEs are excellent solvents for many synthetic polymers, unlike the original oil, which is a poor solvent for these materials. Since the SME is an excellent solvent, polystyrene (PS) and polyvinyl chloride (PVC) can be dissolved in the SME to make an SME–polymer combination that creates blends with significantly different fluid properties; this procedure enables the selection of blends best suited for certain applications. Furthermore, the addition of PS can lead to its deposition in the pores of the concrete. An effort was made in this pilot study to quantify the effect

TABLE 1 Overview of Pilot Testing Program

Property	Test Method	Description	SME–PS Blends Tested
SME–PS Blend Properties			
Viscosity	Anton Paar, MCR-301 rheometer	SME–PS blends only	SME–0% PS SME–1% PS SME–5% PS
Surface and interfacial tension	Du Nouy (tensiometer) ASTM C971		SME–10% PS SME–20% PS SME–40% PS
Fresh Properties			
Set time	Vicat Needle, ASTM C191	Admixed	SME–1% PS SME–5% PS SME–10% PS
Evaporation	Environmental chamber at 23°C, 50% RH	Admixed, topical	SME–5% PS
Cement paste viscosity (*7*)	Anton Paar, MCR-301 rheometer	Admixed	SME–40% PS
Transport Properties			
Water absorption	Ponding test	Topical, admixed	SME–1% PS SME–5% PS SME–10% PS
SME absorption	X-ray measurements	Topical	SME–5% PS
Water absorption	X-ray measurements	Topical	SME–5% PS
Mechanical Properties			
Compressive strength	4-in. × 8-in. cylinders ASTM C39	Admixed	SME–1% PS SME–5% PS SME–10% PS SME–20% PS
Shrinkage	ASTM C157	Admixed	SME–1% PS SME–5% PS SME–10% PS SME–20% PS

NOTE: All tests compared with plain references.

of the PS content on the SME blend properties, as well as its impact on the properties of fresh and cured concrete.

PHYSICAL PROPERTIES OF SME–PS

The high solvency of SME allows polymers to be easily dissolved into SME solution, which can significantly change the fluid's molecular shape and size distribution, and in turn modify the viscosity of the fluid. The SME–PS blends used in this study are created by heating SME and adding PS until the desired PS content is achieved. Although any form of PS can be used, it is particularly advantageous to use waste or recycled PS because of potential environmental benefits, reduced cost, and the abundance of recyclable materials (*10*).

The viscosity of admixtures and topical additives has direct implications on fluid absorption, fresh paste properties, and ionic transport (*11*, *12*). To evaluate how the viscosity of SME–PS blends changes as a function of mixture composition (i.e., PS content), an Anton Paar MCR-301 rheometer utilizing a vane geometry was used (*7*). A flow curve was created for each SME–PS blend, and a Bingham fluid model was fit to the curves resulting in the corresponding viscosities of the blends.

Figure 1 shows the change in viscosity of SME–PS with 1%, 5%, 10%, 20%, and 40% PS added by mass of SME at 25°C. It can be seen that the viscosity increases as the PS content increases. The change in viscosity is likely due to the long chainlike shape of the PS molecule. During fluid movement, the long PS molecules would become entangled and hinder the flow of the liquid, which results in a viscous response. There appears to be a critical PS content that, when reached, causes the most significant changes in the viscosity of the blends. This critical PS content appears to be between 5% and 10%. The ability to alter the viscosity of SME enables it to be tailored for specific uses, applications, or application temperatures (*7*). It should be noted that the viscosity of the SME–PS blends is temperature sensitive. This sensitivity is due to both the basic effect temperature has on molecular kinetic energy and the polymer content (resulting from the presence of PS). The higher the polymer content, the more sensitive the viscosity will be to temperature variations.

Surface tension of the SME–PS blends was measured against air (at the free surface) by using a Du Nouy tensiometer (ASTM C 971-99a). The SME has a surface tension of 27.9 dynes/cm at 25°C, and this value increases slightly with the addition of PS. Although the blends of SME–PS are immiscible in water, they can still have an effect when in contact with water since the interfacial tension may affect the response of the fluid system. Figure 2 shows the measured surface tension for SME–PS blends. The SME obviously drives the surface tension values since PS content had little effect on the values.

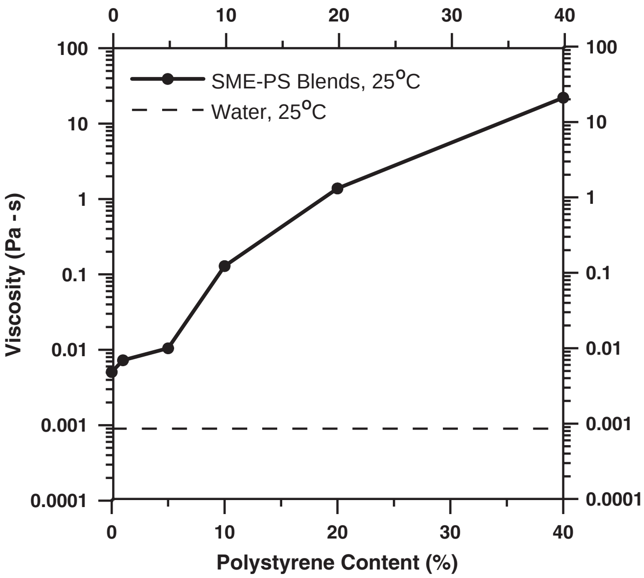


FIGURE 1 Viscosity of SME–PS blends.

SME–PS EFFECT ON FLUID TRANSPORT

Admixed Solutions

Several methods were used to explore the effects of SME–PS on fluid transport in cementitious systems. Tests included the use of SME as both an admixture and a topical application. The application of SME as an admixture is discussed here, and in the next section, similar testing done with SME–PS applied topically is reviewed.

Absorption

It was found that SME–PS blends can have a large impact on the rate of water absorption in cementitious specimens. Use of SME–PS as an admixture dramatically decreased the sorptivity of the specimens. This decrease in rate of water absorption is thought to be due to the presence of the SME inside the pores of the concrete and the presence of the PS molecules, which are large enough to congest pores and reduce fluid transport.

Figure 3 shows an example of the absorption of cementitious materials and the associated reduction in sorption due to the admixing of SME–PS. The testing was performed by using 4-in. by 8-in. (102- by 203-mm) cylindrical specimens created with several different SME–PS blends added at 1.25% and 2.5% by weight of cement. The cylinders were cut into 2-in. (50-mm) thick discs after curing and allowed to dry at 23°C and 50% relative humidity for 90 days. The samples were then subjected to water absorption. The average reduction in total absorption of samples containing SME–PS at 192 h (8 days) is 91% for samples dosed at 1.25% and 94% for samples dosed at 2.5% (*13*). Figure 3 shows this reduction in absorption, which indicates that this application may be particularly effective in reducing moisture ingress in cementitious materials. This reduction may be attributed to the presence of SME in the pore structure of the concrete. Having a fluid coating on the wall of pores reduces the capillary pressure that draws the water into the pores.

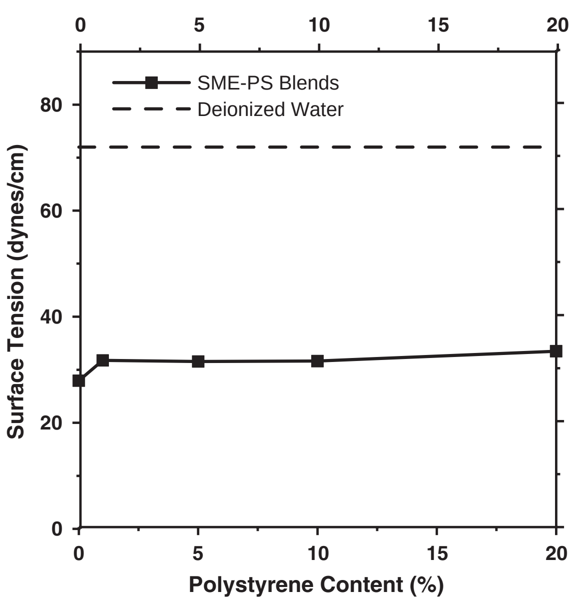


FIGURE 2 Surface tension of SME–PS blends.

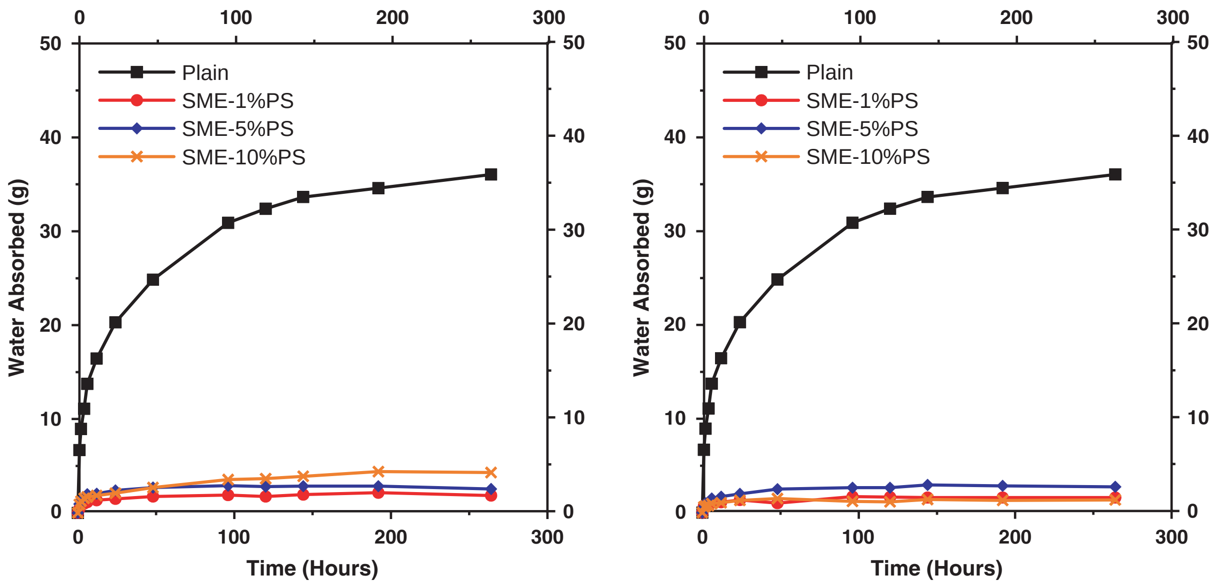
Ion Diffusion

To determine the effects of SME–PS blends on ion mobility in cementitious systems, samples similar to those utilized for the sorption tests just described were created. The samples were created with SME–PS blends admixed to the system at 2.5% by weight of cement and were completely saturated in deionized water. The samples were sealed around their circumference by using aluminum tape. Then the samples were subjected to ponding of a 10% chloride solution for 9 days. After 9 days, the samples were split open, and silver nitrate was applied to the interior surface. With this method, the chloride penetration depth could be measured, as seen in Figure 4.

Figure 4*a* shows that the chloride diffusion depth of the mortar sample created without SME–PS blends had significantly greater penetration than the mortar sample created with SME–PS (Figure 4*b*). For all samples examined, the ion diffusion depth was reduced by up to 77% with an average reduction of 68%, which would aid in creating a concrete that could reduce corrosion and increase service life by slowing chloride ingress.

Topical Applications

To determine the potential topical applications of SME–PS to hardened concrete, two tests were performed: conventional water absorption like that described in the section on admixed solutions and the use of X-ray absorption to track the penetration and ingress of both SME–PS blends and water. As mentioned previously, such a sealant may be practical for protecting concrete pavement joints from freeze–thaw deterioration; accordingly, the geometry chosen for the X-ray absorption experiment is representative of a cross section in a typical concrete pavement saw-cut joint. The samples were placed in the X-ray absorption device (*14*) and a series of measurements were taken with an X-ray camera to track ingress of both the SME–PS as it penetrates the samples upon application and the moisture of water ponded on samples that have either been treated



(a) (b)

FIGURE 3 Effect of admixed SME–PS on sorption: (*a*) 1.25% dose by weight of cement and (*b*) 2.50% dose by weight of cement.

with SME–PS or left plain. This information can be used to look at how water is typically drawn into concrete and how SME–PS blends affect this process.

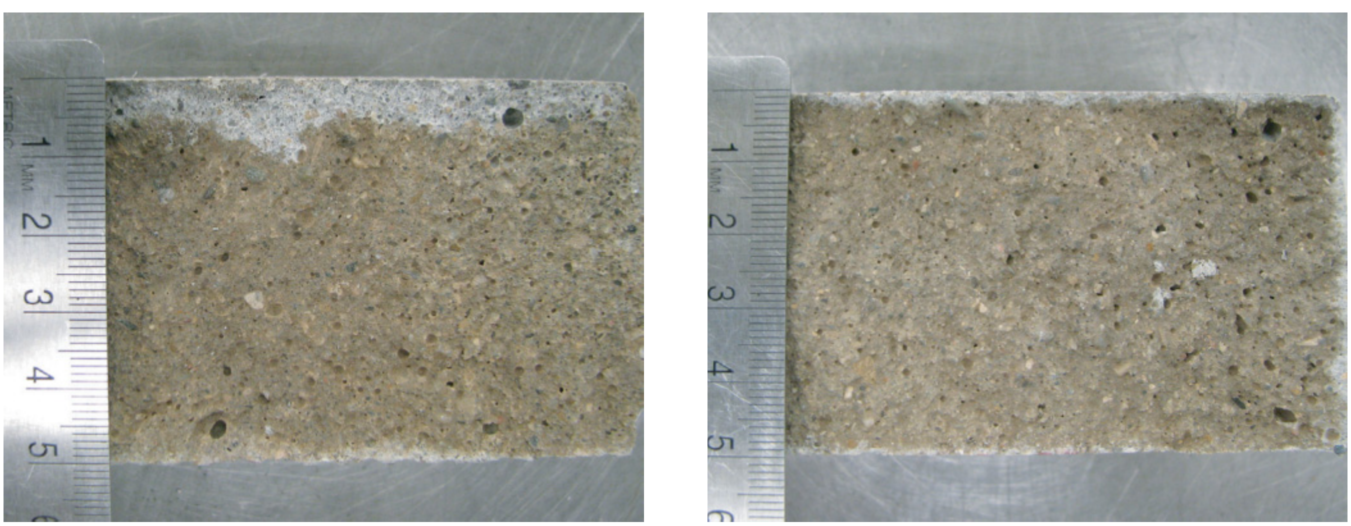
Penetration of SME–PS

The rate of penetration of SME–PS blends was measured in order to determine whether the blends could adequately penetrate cementitious materials in a practical time frame. Figure 5 shows the depths of penetration for an SME–5%PS blend placed in the saw cut of a dry cement paste specimen with a water-to-cement ratio of 0.30. It can be seen that the SME–PS can quickly penetrate the material several millimeters in a relatively short period of time (4 mm in 5 h).

Evaluation of SME–PS Topically Applied in Saw Cuts

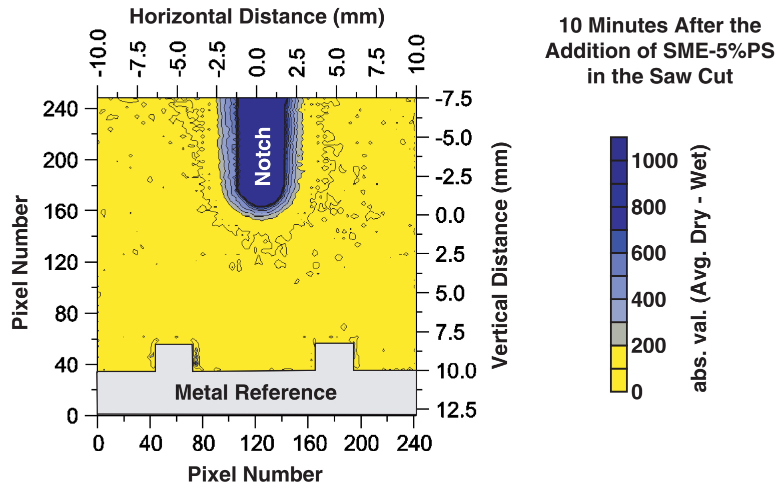
Water absorption tests were performed on plain mortars like those described earlier, where one surface was coated with SME–PS. Total water absorption was reduced by 85% to 93% after 12 days for application rates of different blends between 0.020 g/cm^2 and 0.036 g/cm^2. These application rates are for flat surfaces where, because of the method of application (atomization), only small amounts may be applied at a given time. In the case of saw cuts, however, it is possible to pond the SME–PS blends, where even more SME–PS can be allowed to penetrate over time.

Saw cuts are made in a concrete pavement shortly after it is placed to control stresses induced by shrinkage and thermal contraction. Several states (including Indiana) have noted premature damage

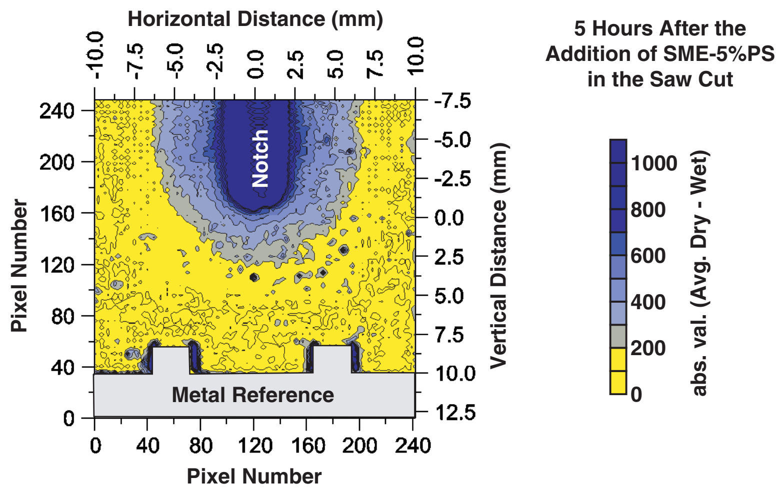


(a) (b)

FIGURE 4 Chloride penetration of mortar samples: (*a*) mortar without SME–PS admixed and (*b*) mortar with SME–PS.



(a)



(b)

FIGURE 5 Elapsed-time X-ray measurements of SME–PS penetration in cement paste: (*a*) 10 min and (*b*) 5 h.

development at the joints in pavements. Preliminary analysis suggested that this deterioration may be due in part to freeze–thaw damage that occurs when water enters the pore system in the concrete. One potential method that may be used to increase the freeze–thaw resistance of concrete is to provide a sealer that prevents water and aggressive fluids from entering the pore structure of the concrete. Previous research has shown that SME–PS has the potential to act as a penetrating sealer that would limit the fluid's ability to penetrate the concrete.

The rate at which concrete absorbs water is dependent on the condition of the concrete, most notably its relative humidity, as well as the porosity of the cement paste. In this experiment, mortar samples were created and then dried in an oven. The first measurements performed were of the typical rate of absorption of water into these oven-dried samples.

Figure 6 shows the penetration of water 20 min and 2 h after its addition. The penetration of the water can be easily seen since there is a clear moisture front boundary. At 20 min the moisture front has penetrated 4.4 mm into the sample, and at 2 h the penetration has reached 8.1 mm.

Another oven-dried sample was then pretreated with the SME–5% PS blend by ponding the blend in the saw cut of the sample and allowing it to be absorbed freely in to the sample over 48 h. The sample was then subjected to the same wetting process as the plain oven-dried sample shown in Figure 6. The resulting images indicated that there was no detectable penetration of water over the course of the measurements (4.5 h). Further testing is needed and is currently under way; however, it is recommended for field applications that long-term penetration and freeze–thaw behavior be determined beforehand.

EFFECT OF SME–PS ON FRESH CONCRETE

Several methods were used to explore the effects of SME–PS on the fresh properties of cementitious systems. Tests included the use of SME as an evaporation retarder and as an admixed water repellant and sealer. The SME–PS was investigated for potential use as both an admixed material and a topical application for fresh properties.

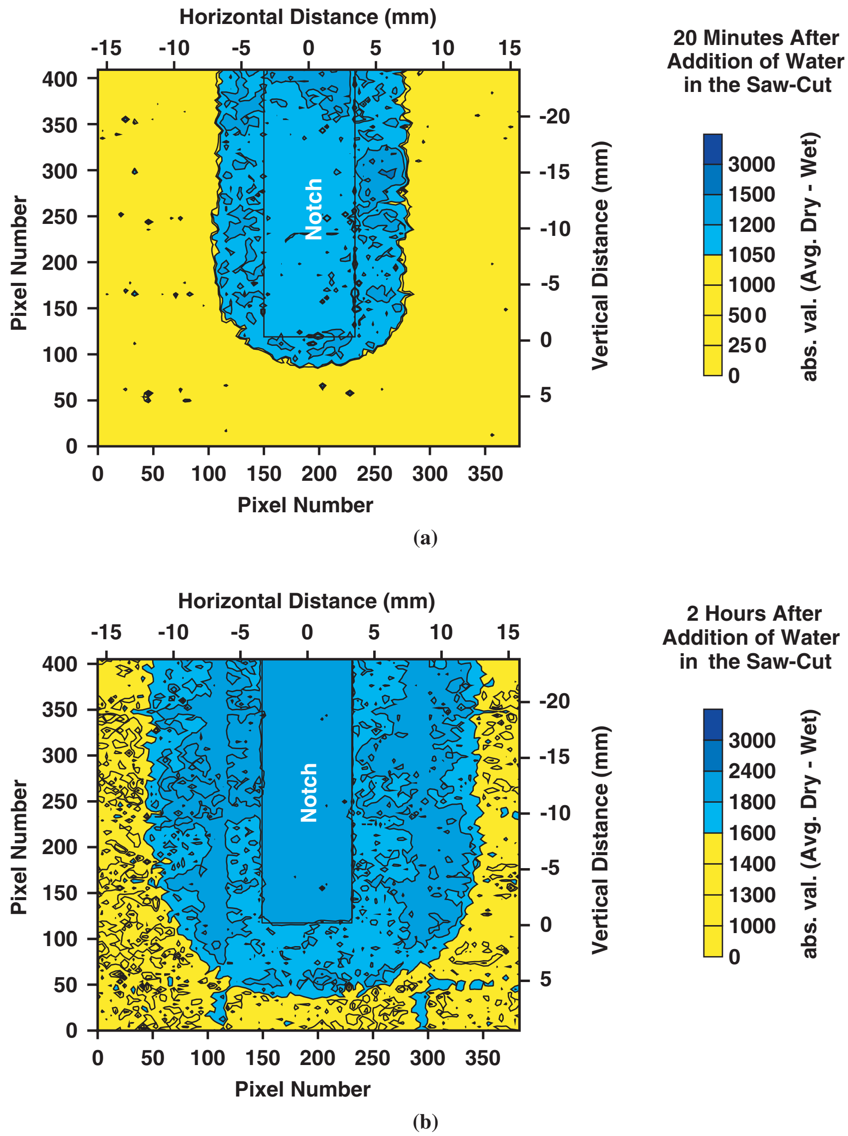


FIGURE 6 Elapsed-time X-ray measurements of water penetration in oven-dried mortar after addition of water in saw cut: (*a*) 20 min and (*b*) 2 h.

One problem in concrete construction occurs when water evaporates from a freshly placed concrete slab. This loss of water is problematic for two reasons. First, the loss of water results in a reduction in the amount of cement that reacts (hydrates), making a more porous, weaker, and more open surface layer and a less durable concrete. Second, the loss of water results in the generation of stresses, which, if high enough, can cause cracking. In the first phase of this project research was conducted to determine the benefits of spraying SME–PS on the surface of fresh concrete so that it can act as an evaporation retarder or curing compound.

Evaporation Retarder

Topical Application

SME–PS blends have the potential to be used as evaporation retarders. By application of a layer of SME–PS to the surface of fresh concrete, the amount of water that evaporates during the curing process can be reduced significantly because of the presence of a thin film of SME–PS on the surface of the sample. This retarder can reduce the potential for plastic shrinkage cracking.

To quantify the effectiveness of SME–PS in retarding evaporation of water in fresh concrete, specimens were cast and immediately treated accordingly (with or without SME–PS) and then placed in an environmental chamber where the conditions were 50% relative humidity and a temperature of 23°C. The samples were placed on scales that continuously monitor the mass of the samples. Figure 7 shows the typical mass loss due to evaporation for a plain mortar sample (no SME–PS on surface) and a mortar sample surface treated with 0.018 g/cm^2 of SME with 5% PS by mass. The graph clearly shows a reduction in evaporation for the sample surface treated with SME–PS.

An additional benefit of using SME–PS blends is that since SME has an extremely low evaporation rate (compared with water), the SME that remains on the surface when setting occurs for concrete

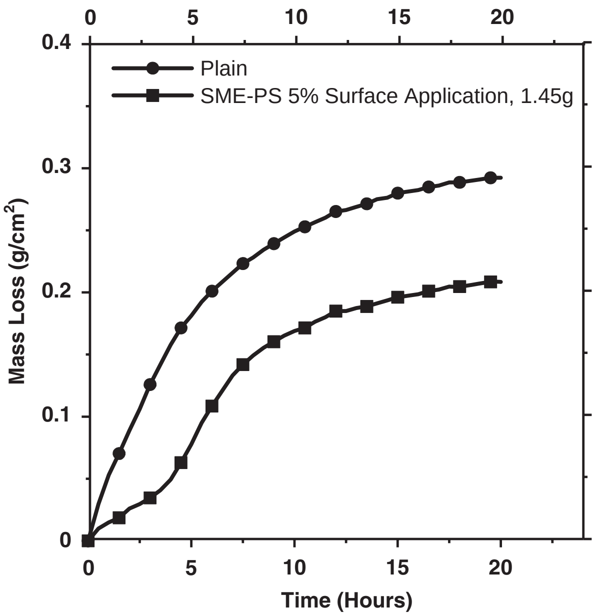


FIGURE 7 Topical evaporation results.

will be absorbed into the concrete. The benefits associated with the absorption of SME–PS were discussed earlier.

Admixed Solution

There is also the potential to use SME–PS in several applications as an admixture in cementitious materials. Evaporation retardation is most commonly achieved through topical application of substances on the surface of freshly placed concrete. However, it is of interest to examine the effects of SME–PS blends used as an admixture on evaporation of fresh concrete. Figure 8 shows the results from the same evaporation experiment conducted for the topical appli-

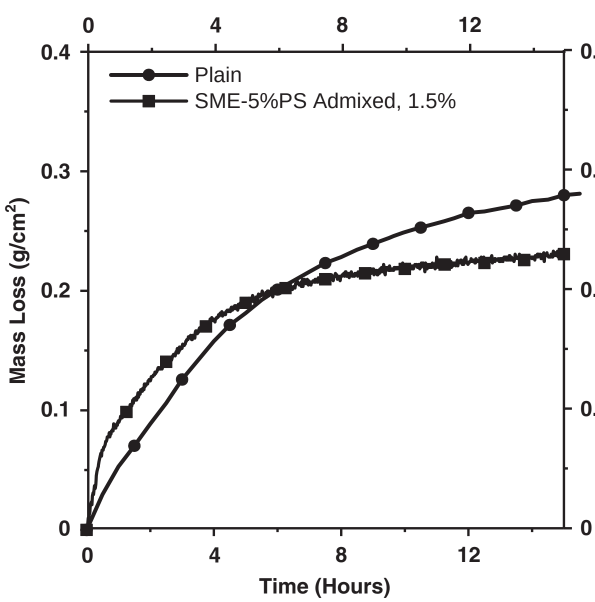


FIGURE 8 Admixed evaporation results.

TABLE 2 Set Time Results from Vicat Needle Test

SME Blend	Dosage[a] (%)	Initial Set (min)	Final Set (min)	% Delay of Final Set Time
Control	0.00	81	375	0.0
10% PS	1.25	77	340	–9.3
	2.50	N/A	330	–12.0
5% PS	1.25	83	390	4.0
	2.50	70	380	1.3
1% PS	1.25	N/A	400	6.7
	2.50	N/A	385	2.7

[a]Dosage is mass of SME–PS blend by weight of cement.

cation except that the SME–5%PS blend was added during the mixing process at 1.5% by weight of cement. Results consistently showed an initial evaporation rate greater than that of plain samples. This evaporation led to higher mass loss during the first 5 h (approximately until set), and then the evaporation rate decreased significantly. This reduction in evaporation agrees with the results of mass loss measured during drying shrinkage measurements, discussed in the next section, which indicate a decrease in mass loss after 28 days of drying.

Setting and Early Hydration of Admixture

To determine if the use of SME had any effect on the hydration process of cement, a Vicat needle test was performed on cement paste with SME–PS blends. The samples made used several different blends, as well as dosages, of SME–PS (Table 1). The results, shown in Table 2, indicate that since the set times were not changed significantly, there was no notable retarding effect on the hydration of the cement. This finding suggests that SME–PS could be used as an admixture in concrete without any additional curing time or special requirements for placement and finishing.

EFFECT OF SME–PS ON MECHANICAL PROPERTIES OF CONCRETE

In addition to assessing the influence of SME–PS on the fresh and transport properties of concrete, it is important to determine if these properties have any influence on the hardened properties of the concrete. As such, compressive strength and free shrinkage were assessed in this study.

Compressive Strength

Compressive strength tests were performed following ASTM C 39-05. Three mortars were prepared using the SME–PS blends from Table 1. Compressive strength was determined at each age from the average of three 4-in. by 8-in. (102- by 203-mm) cylinders. Figure 9 shows the results of the compressive strength tests for the SME–PS blends at 1, 7, and 28 days. The samples containing SME–PS were dosed at 1.25% SME–PS by weight of cement. The admixed samples showed slightly lower average strength than the plain samples. The most dramatic reduction in strength was 18%, which was seen for the SME–5%PS blend at 28 days. The error bars represent one standard deviation of the data for that day of testing. These results show that

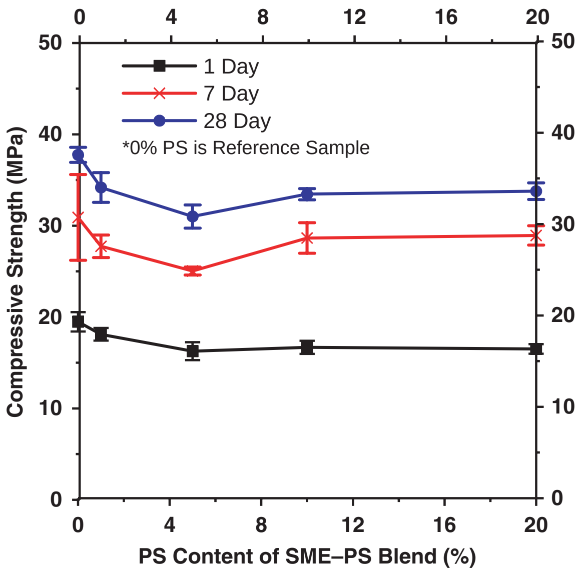


FIGURE 9 Compressive strength.

the addition of SME–PS blends to concrete does not significantly affect the strength achieved.

Shrinkage

Drying shrinkage measurements were conducted according to ASTM C 157-93. Four 1-in. by 1-in. by 111/4-in. (25- by 25- by 286-mm) mortar samples were made with each of several blends of the SME–PS (Table 1), which were then placed into an environmental chamber at 23°C and 50% relative humidity. The shrinkage strains and mass loss over 28 days were measured. The shrinkage samples made with the SME–PS blends exhibited less mass loss than the plain samples (Figure 10*a*). At 28 days, the mass loss due to drying for the blends containing SME–1%PS was approximately 10% less than the plain samples. Also, the results of these tests indicated that there was no significant effect on the shrinkage of cementitious materials. Figure 10*b* shows a small difference in shrinkage strain values throughout the 28-day test.

SUMMARY OF PILOT STUDY TESTS

The following observations can be made from this pilot study, which investigated the potential use of SME–PS blends as concrete additives:

- SME–PS blends reduced water absorption by 74% to 94% when the SME–PS was admixed. When the SME–PS blends were applied topically, water absorption results showed a reduction in water absorption of 85% to 93% and X-ray results showed no visible water penetration after 4.5 h. The magnitude of these reductions is significant and creates the potential for the use of SME–PS blends as a penetrating or admixed sealant.
- SME–PS blends reduce ion diffusion by an average of 68% and up to 77% after 9 days of ponding with a 10% chloride solution.
- SME–PS blends do not have significant impacts on the basic mechanical properties investigated in the pilot program. The maximum reduction in strength was 18%. In addition, these blends do not have any adverse effects on the rate of hydration as determined from the Vicat test.

This pilot test program showed that there is great potential for this nontoxic, based on biodegradable materials, substance for use in the concrete industry. The results discussed indicate that SME–PS blends can successfully reduce water absorption and fluid transport properties of cementitious systems. This finding in turn has direct implications for the durability of concrete. Additional research will continue to characterize the behavior of SME–PS blends as well as their long-term durability. This research will play a large role in the effectiveness of SME–PS blends in protecting cementitious materials from moisture-related damage and degradation. Further research is also needed to examine the possibility of leaching.

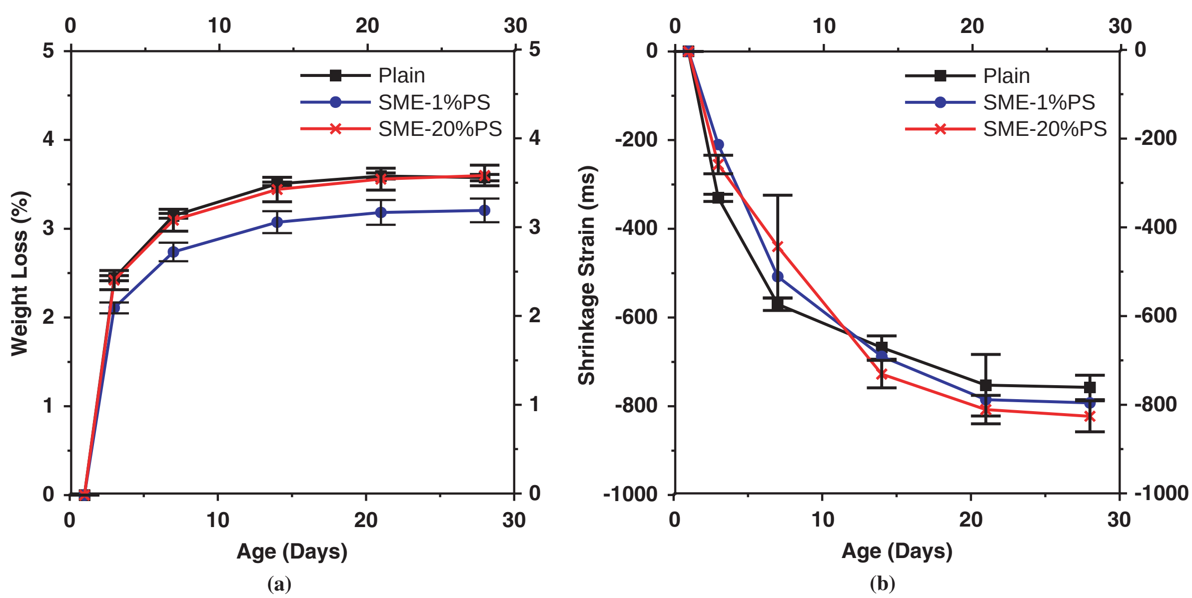


FIGURE 10 Drying shrinkage: (*a*) mass loss due to drying and (*b*) measured shrinkage strains.

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