CHEMICAL ADDITIVES FOR MONOMER

A preferred solution to the wet aggregate problem would be an additive which, when mixed with the monomer, would insure good bond to the aggregate by negating the effect of water. Many sources of information were utilized to identify potential additives for this purpose: technical literature, chemical manufacturers and suppliers, and other researchers. The suggestions included acrylic acid (AA), methacrylic acid (MA), hydroxy propyl methacrylate (HPMA), TTEGDA, water-compatible epoxies and silane coupling agents. Compressive strength tests were performed on 3-in. x 6-in. (76-mm x 150-mm) PC cylinders formulated from these materials and wet aggregate. Figure 2 indicates typical results when HPMA, AA, and MA were used in various combinations with the 95 percent MMA/5 percent TTEGDA monomer system and aggregate with 4 percent moisture. The basic MMA/TTEGDA monomer system provided the highest strength. Some of the additives produced significant decreases in strength.

The addition of silane coupling agent (SCA) can be used in several ways to improve bond between aggregate and polymer, but the direct addition of SCA to the MMA monomer system in this investigation produced no increase in strength when wet aggregate was used. Limited tests using Celanese Epi-Rez water-compatible epoxies did not produce satisfactory PC.

AGGREGATE TREATMENT

Two types of aggregate treatment were studied: moisture absorptive additives and aggregate coatings.

Moisture Absorptive Additives

Four moisture absorptive additives were investigated: type III portland cement, lime, gypsum and type J cement. These materials were mixed with the wet aggregate prior to adding the MMA monomer system. The 3-in. x 6-in. (76-mm x 150-mm) cylinders were tested to obtain compressive strength and splitting tensile strength 3 hours and 3 days after casting. Figure 3 indicates the splitting tensile strength results obtained when lime and type III portland cement were added to the wet aggregate. For a moisture content of 5.9 percent, 6 percent cement produced a 113 percent increase in compressive strength and a 95 percent increase in splitting tensile strength after a 3-day cure compared to specimens in which no cement was used. Nine percent cement produced a 115 percent increase in compressive strength and a 120 percent increase in splitting tensile strength. For a 3-hour cure, only slight increases in strength were found for cement, and strength reductions were found for lime. The test results indicate that most of the strength gain, if any, was due to hydration.

Type J cement, designed for curing at high temperature in oil well applications, has a high dicalcium silicate content. For a moisture content of 4.5 percent, the addition of type J cement caused a slight variation is strengths, which ranged from 400 to 500 psi (2760 to 3450 kN/m^2). For a moisture content of 7.7 percent, the addition of 6 percent type J cement resulted in strengths of 350 to 400 psi (2410 to 2760 kN/m^2) for both 3-hour and 3-day cures.

Gypsum was used as an additive because of its fast setting characteristics. However, the use of two kinds of gypsum produced no strength gain at the 3 or 6 percent gypsum levels.

Coated Aggregate

It was theorized that coated aggregate would provide a better surface for bonding to the polymer in addition to preventing moisture from being absorbed by the aggregate. The first coating investigated was poly(methyl methacrylate) (PMMA). The formulation used was 70 percent MMA, 30 percent MMA syrup (a partially polymerized MMA monomer which has a viscosity of ∿500 centipoise), 2 percent BzP, and 1 percent DMPT. The 3/8-in. (10-mm) silicious and limestone coarse aggregate was first dried to remove moisture. After cooling, it was immersed in the monomer for about one minute, removed with a strainer, and drained. The aggregate was then placed in the oven at 220°F (104°C) to accelerate polymerization. The aggregate was frequently stirred to prevent adhesion. Polymerization required 40 to 60 minutes.

The coated aggregate was soaked in water for 24 hours before monomer was added to make polymer concrete cylinders. Coated and uncoated coarse aggregates were used to provide a comparison. The polymer coating provided no increase in strength; in fact, lower strengths were obtained.

The second coating investigated was a silane coupling agent (Union Carbide A-174). Diluted acetic acid was added to distilled water to give a pH of 4.5 to 5. Five volume percent silane coupling agent (SCA) was added to the water. The dry aggregate (equal weights of sand and 3/8-in. (10-mm) coarse aggregate) was soaked in the solution for either 10 minutes or one hour. The treated aggregate was drained and cured at 210°F (100°C) over night. After cooling, the aggregate was soaked in water for at least 24 hours before making 3-in. x 6-in. (76-mm x 150-mm) PC cylinders.

The compressive and splitting tensile strengths are shown in Figures 4 and 5. While some reduction in compressive strength occurred for PC made with coated aggregate with increasing moisture content, the compressive strength was 5290 psi (36485 kN/m^2) at 4.3 percent moisture. Tensile strength was 870 psi (600 kN/m^2) for the same condition, but there was little reduction in strength from the specimens with 1.1 percent moisture content. It is apparent that the longer soaking time in SCA is important since the strengths for one-hour soaking were considerably greater than for 10 minutes. Flexural strengths for 4.1 percent moisture were 1110 psi (7655 kN/m^2) for SCA-coated aggregate and 300 psi (2070 kN/m^2) for non-coated. The use of SCA-coated aggregates appears very promising if the process for coating the aggregate on a large scale can be made economically feasible.

ADDITION OF FIBERS

The use of fibers in the PC mix was investigated to improve the strength when moisture is present. A screening study was first conducted to determine the optimum fiber type and quantity in PC. The PC was made using a monomer formulation of 95 percent MMA and 5 percent TTEGDA. The dry aggregate consisted of 50 percent sand and 50 percent 3/8-in. (10-mm) crushed limestone aggregate. Both 3-in. x 6-in. (76-mm x 150-mm) and 6-in. x 12-in. (150-mm x 300-mm) cylinders were made. The fibers used were made of steel (hooked), alkaline-resistant (AR) glass, polyethylene, and polypropylene. The strengths varied with the percentages of fibers by weight of aggregate (Table 1). Fibers were measured by percent weight instead of the more usual percent volume used in portland cement concrete since polymer concrete components are based upon weight. One weight percent of steel fibers is approximately equal to 0.23 volume percent in this study.

Based on the initial tests, the 0.5 mmϕ x 30-mm fibers, which produced the highest strength of 1838 psi (12680 kN/m^2) were selected for further use in PC made with wet aggregate. The aggregate, which consisted of 50 percent all-purpose sand and 50 percent 3/8-in. crushed limestone, was first dried at 250°F (120°C) cooled to room temperature, wetted to provide the desired moisture content, and permitted to soak for at least 24 hours. The steel fibers were added as a percentage of the dry aggregate weight and thoroughly mixed. The monomer (95 percent MMA and 5 percent TTEGDA) was added and mixed into the aggregate. The PC specimens were then cast into molds.

Compressive strength is shown in Fig. 6 for PC (3-in. x 6-in. cylinders) made with a moisture content of 3.7 percent. For 5 and 7 percent fibers, significant strength increases resulted. For the best combination of workability and strength, 5 percent fibers were selected for further testing.

Figure 7 compares the results for splitting tensile strength, compressive strength, and modulus of rupture for PC made with and without fibers, and for two different moisture contents, 2.5 and 5 percent. The fibers contributed considerable increase in strength, especially for the higher moisture contents. Even at 5 percent moisture, the PC with fibers developed 4230 psi (29170 kN/m^2) compressive strength and 810 psi (5585 kN/m^2) flexural strength, which represent excellent strengths for repairing concrete.

During the casting of modulus of rupture beams using fibers, it was observed that many beams broke upon removal from the form. The PC appeared to be weak and of poor quality. It was theorized that the water was acting as a heat sink, preventing complete polymerization. Beams were cast using 95 percent MMA and 5 percent trimethylolpropane trimethacrylate (TMPTMA) with higher percentage of BzP and DMPT, which corresponded to lower ambient temperatures. Quality of the PC improved with increasing levels of BzP and DMPT. Figure 8 indicates the flexural strength for PC beams for various levels of BzP and DMPT. Tests are in progress to determine if increasing the promoter-initiator levels alone would be an effective measure to increase the strength of PC.

The use of type III cement with fibers was investigated. Seven percent cement resulted in an 18 percent increase in splitting tensile strength 4 hours after casting. Five percent fibers and 5 percent moisture content were used in making the PC.

A series of tests was performed using silane coupling agent (SCA) on PC made with 5 percent fibers and 5 percent moisture content. Compared to strength without the use of SCA, the following increases in splitting tensile strength were obtained: SCA-treated aggregate, 12.5 percent; SCA-treated fibers, 14.25 percent; and SCA-treated fibers and aggregate, 27.0 percent. Using SCA-treated fibers and aggregate, an increase of 48.1 percent in modulus of rupture was obtained for 3-in. x 3-in. x 12-in. (76-mm x 75-mm x 300-mm) beams with a 9-in. (225-mm) span with a 5 percent moisture content and 5 percent fibers compared to a beam with no SCA and with no fibers. An increase of 18.1 percent was obtained for non-treated aggregates and fibers.

The use of steel fibers also provides considerable flexural ductility compared to PC made without them. Figure 9 indicates the load-deflection response for a PC beam made with dry aggregate and 5 percent of 0.5-mm x 30-mm fibers. The increased ductility alone may be sufficient reason for using steel fibers in many repair applications in which minimizing cracking may be important.

CONCLUSIONS

Several techniques, including chemical additives, aggregate treatment, and addition of fibers, have been investigated for improving the strength of MMA-PC made with wet aggregate. The following conclusions can be made.

1. No chemical additive was identified which appreciably increased strength.

2. Cement, lime, and gypsum were used as moisture absorptive additives for aggregate with limited success. PC made with type III cement and tested after 3 hours of curing had strengths only slightly greater than PC made without cement;

after 3 days of curing, the compressive and tensile strengths were approximately twice as large, which indicates that hydration played a major role in the strength increase.

3. Aggregate coated with silane coupling agent produced PC with excellent strength compared to PC producted without aggregate coated with SCA.

4. Steel fibers proved to be effective in reducing the strength loss of PC made with wet aggregate. Compressive strengths in excess of 4000 psi (27590 kN/m^2) were obtained using 5 percent steel fibers to make PC with aggregate having a moisture content of 5 percent.

5. The use of increased levels of promoter and initiator was found to yield significant increases in strength.

Fiber Type	Percent, Weight	Splitting Tensile Strength, psi	Cylinder Size, in.	Percent, Increase[e]
None	0	1260	3x6	--
None	0	1040	6x12	--
AR GLASS 1 in.	0.96	1302	3x6	3.3
AR GLASS 1 in.	1.60	1315	3x6	4.4
AR GLASS 1 in.	2.24	1375	3x6	9.1
POLYETHYLENE (short)	0.58	490	3x6	--
POLYPROPYLENE	0.60	614	3x6	--
STEEL ZL 30/40[b]	2.0	1355	3x6	7.5
STEEL ZL 30/40[b]	2.5	1385	3x6	9.9
STEEL ZL 30/40[b]	5.0	1735	3x6	37.7
STEEL ZL 30/40[b]	7.0	1690	3x6	34.1
STEEL ZC 50/50[c]	5.0	1750	3x6	38.9
STEEL ZC 50/50[c]	5.0	1425	6x12	37.0
STEEL (Galvanized) ZC 50/50[c]	5.0	1195	6x12	14.9
STEEL ZL 30/50[d]	3.0 5.0 7.0	1680 1838 1893	3x6 3x6 3x6	33.3 45.9 50.2

[a]95% MMA/5% TTEGDA
Moisture Content = 0%

[e]3x6 control cylinder strengths were used as reference for 3x6 PC specimens; 6x12 control strengths used as reference for 612 PC specimens.

[b]0.4mmϕ x 30mm

[c]0.5mmϕ x 50mm

[d]0.5mmϕ x 30mm

Table 1--Splitting tensile strength of polymer concrete (PC) made with different types of fibers[a]

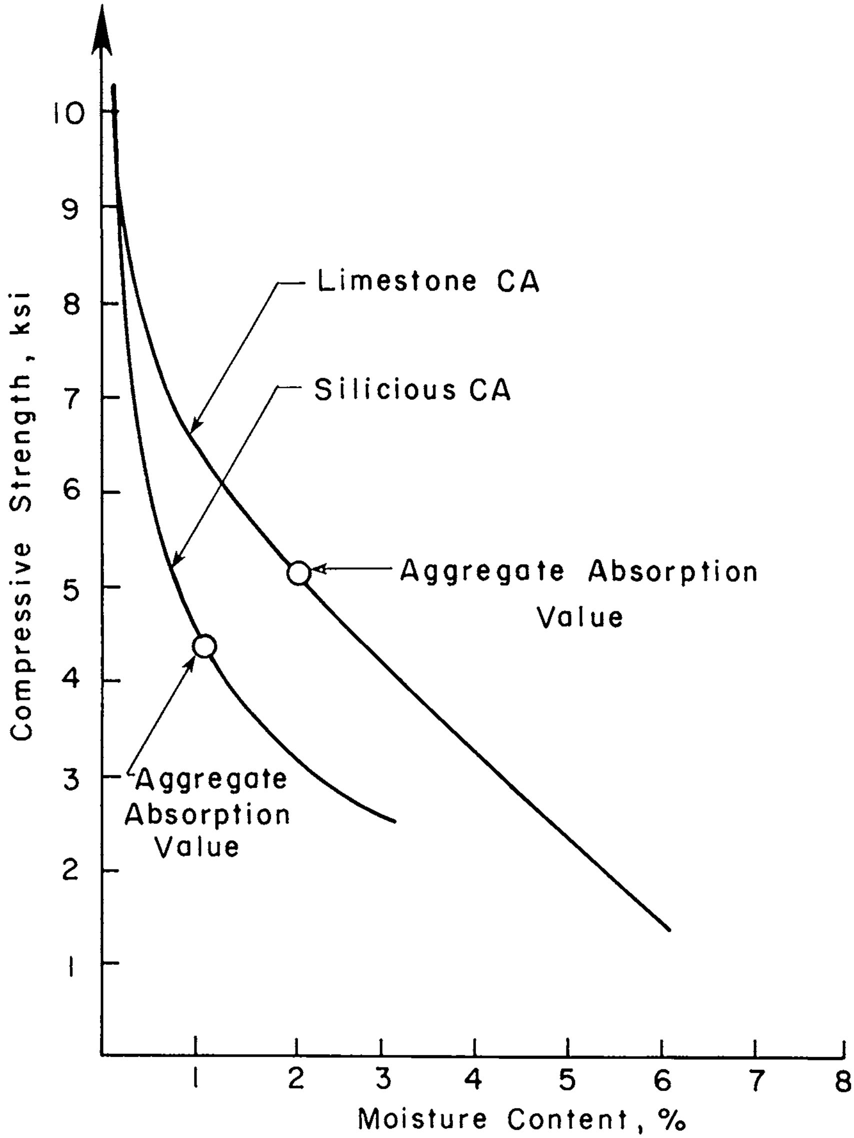

Fig. 1--Effect of moisture on compressive strength of polymer concrete made with silicious and limestone aggregates

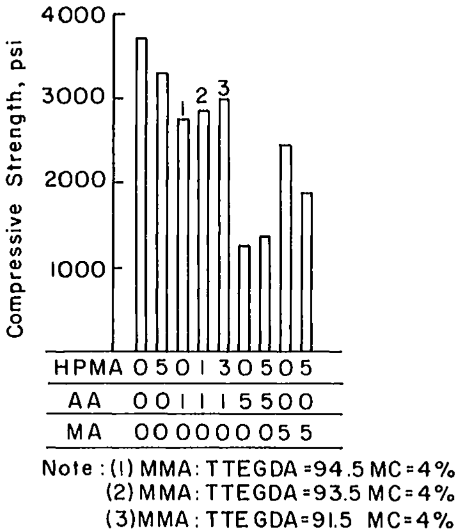

Fig. 2--Effect of additives on compressive strength of polymer cement made with wet aggregate. Moisture content 4.4 percent except as noted

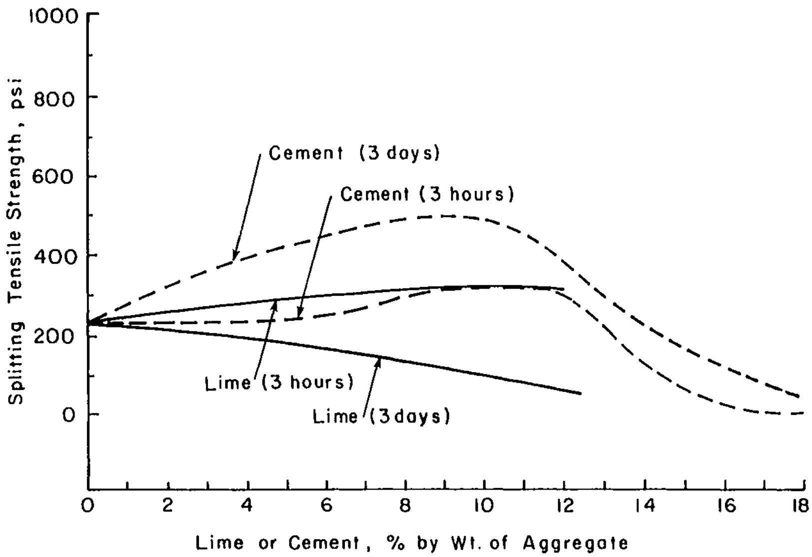

Fig. 3--Effect of lime and type 3 cement on splitting tensile strength of polymer concrete made with wet aggregate (MC = 5.9 percent)

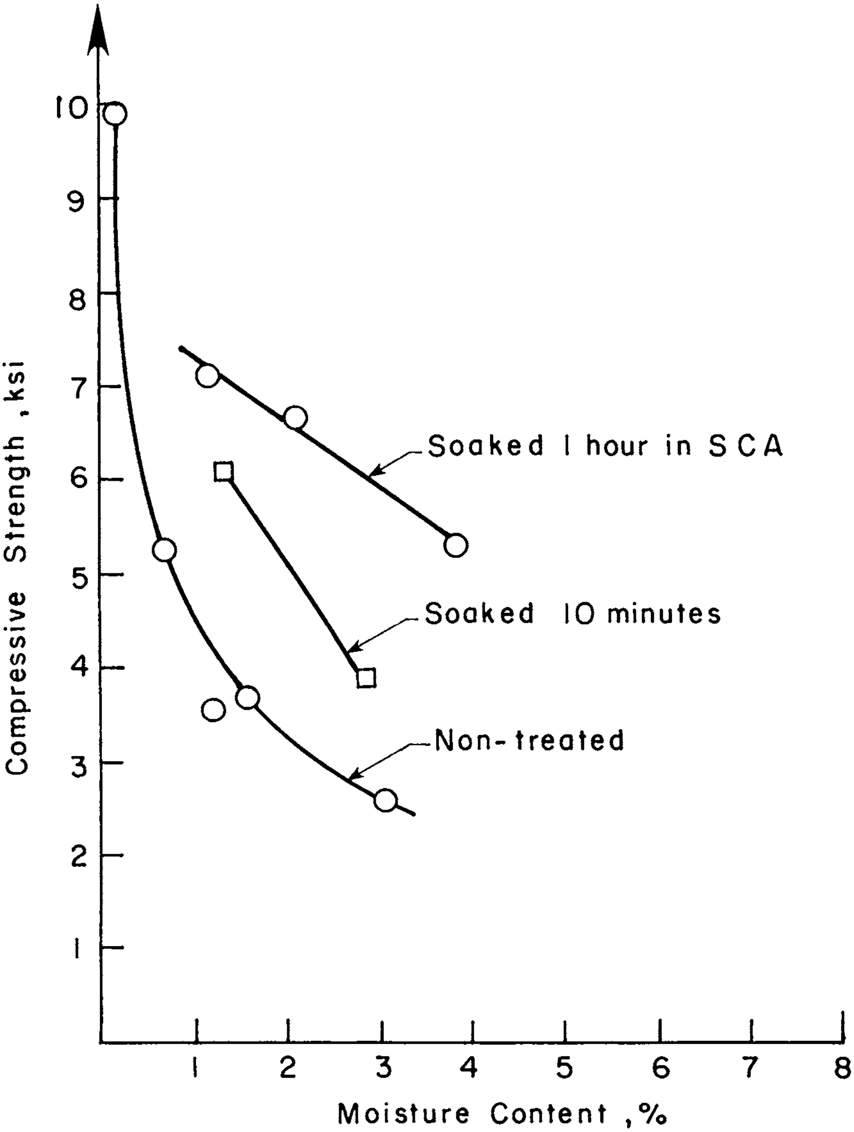

Fig. 4--Effect of silane coupling agent coated aggregate on compressive strength of polymer concrete made with wet aggregate

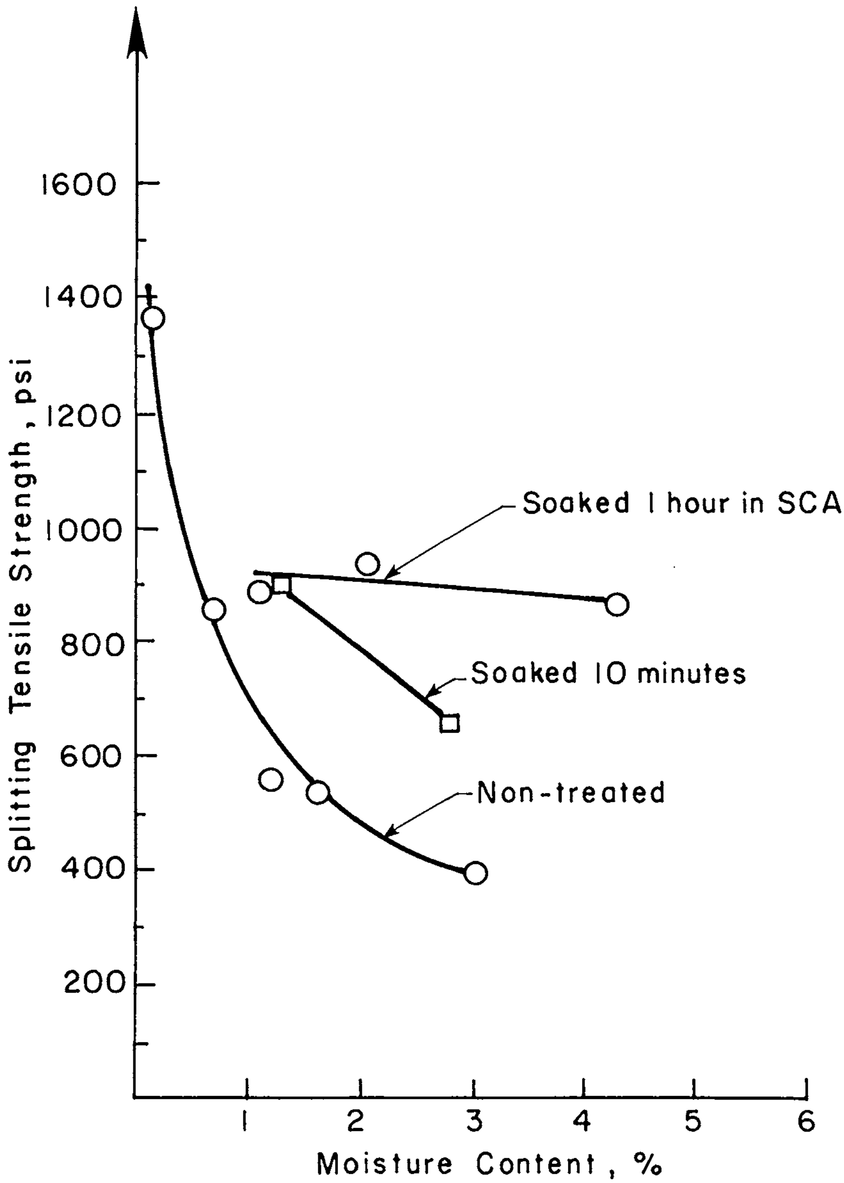

Fig. 5--Effect of silane coupling agent coated aggregate on splitting tensile strength of polymer concrete made with wet aggregate