POLYMER CONCRETE PREPARED FROM AN MMA-STYRENE COPOLYMER SYSTEM

T. Y. Chang, Department of Civil Engineering; and
H. L. Stephens and R. C. Yen, Institute of Polymer Science,
University of Akron

Polymer concrete is a premixed material that is prepared from portland cement, aggregate, and polymer such as methyl methacrylate (MMA) or styrene or a combination of the two. A polymer is used as the main binder in the material matrix. Experiments were conducted to investigate the effect of using different copolymer ratios of MMA and styrene and the effect of polymer loading on the strength of the material. Mortar specimens with thermal curing process at 158 F (70 C) were prepared for the test program. Test results indicated that a 50:50 copolymer system of MMA and styrene gave much higher strength than the system containing MMA or styrene alone. Results also showed that the strength of the composite increased as polymer loading up to 12 percent (wt) increased; the strength decreased for higher polymer loading. Less polymer loading was required for polymer concrete containing coarse aggregate. A series of polymer concrete with 9 percent (wt) copolymer of 50:50 MMA and styrene was prepared. Tests including compression, tension, bending, double shear, water absorption, and chemical resistance (18 percent hydrochloric acid) were conducted, and results compared favorably with those for conventional concrete. Moreover, the polymer concrete appeared to have the same type of physical properties as the polymer-impregnated concrete.

•THE USE of polymers in concrete has been of considerable interest recently because concrete based on cement has limited strength, insufficient durability, and poor resistance to cracking and corrosion, especially under severe weather conditions. Polymers added to concrete or used as the binder in place of cement can substantially improve not only the strength of concrete by three to four times but also its durability and resistance to cracking and chemical attack. The continuing availability of new polymers with more desirable physical properties will offer even better prospects for making high-quality polymer concrete (PC).

Polymers can be used in concrete in several forms. One is polymer-impregnated concrete(PIC), for which a precast portland cement concrete is cured, impregnated in a monomer, and subsequently polymerized to form a new composite. Most research efforts in the development of PC have been in this area. Results show that the material has remarkable strength, durability, and resistance to chemical attack (1-7). However, in view of its preparation techniques, PIC appears to be more suitable for precast structural components. The second form is the polymer-modified (or polymer cement) concrete, for which a polymer or polymer latex is added to portland cement mortar or concrete to improve the physical properties of the material composite. Epoxy resin (8), polyvinyl acetate, styrene-butadiene, and other types of polymer latices (9-13) have been used only to a limited degree of success. The third form is PC, which is formed by polymers and aggregates with or without portland cement. In the composite, polymer is the main binder, and cement and aggregate are the fillers; water was not used at all. PC has previously been researched and there have been varying degrees of success (5, 14, 15, 16). Although most research in the United States has been on PIC, Russian scientists have been working primarily on PC (17).

Polymer is a natural binder material for making concrete because, before its polymerization, the polymer is in a liquid monomer state that can be easily mixed with the aggregate and then polymerized to form a solid. Further, polymer has a high strength in compression, tension, and bending; provides excellent bonding strength when formed in place; and is waterproof, i.e., resistant to corrosion and chemical attacks. Because of all these desirable properties, PC could be a potential material for surfacing and patching deteriorated bridge decks and highway pavements.

A research program was started at the University of Akron to develop an effective PC for highway patching. Different polymer systems, cross-linking agents, and catalysts and the effects of the curing process (thermal or room-temperature curing) and polymer loadings with respect to the strength and durability of the composites were investigated. Results are discussed for the polymer mortar and PC prepared from the copolymer system of methyl methacrylate (MMA) and styrene. A sequence of mortar mixes was used to investigate the effect of copolymers with various MMA-styrene ratios and the effect of polymer loadings on the strengths of the composites. A mortar mix containing 50 percent MMA and 50 percent styrene and 11.7 percent (wt) polymer loading gives more favorable strength. One series of PC prepared from 50 percent MMA and 50 percent styrene, portland cement, sand, and coarse aggregate was tested. The test results on compressive, tensile, bending, and bonding strengths; water absorption; and resistance to chemical attack [18 percent hydrochloric acid (HCl)] are compared with those of the ordinary concrete (control). The results indicate that PC is much superior to ordinary concrete.

MATERIAL COMPOSITION

Polymer mortar or PC may be produced by mixing monomer and aggregate with or without portland cement. However, recent test results (18) clearly indicate that the material containing portland cement is several times stronger than the one without it. Therefore, for the materials that have been tested, portland cement was always included.

Both MMA and styrene were considered in this investigation. Two parameters were varied to study their effect on the strength of polymer concrete: the effect of using MMA, styrene, or different combinations of the two in the mixes, and the effect of polymer loading. A sequence of mortar mixes with 1:3 cement-sand ratio was prepared. The material composition of the polymer mortar was as follows:

1. MMA, styrene, and a combination of the two;
2. 8 to 15 percent (wt) polymer loading;
3. 3 percent (wt) benzoyl peroxide as the initiator;
4. 10 percent (wt) butylene dimethacrylate as the cross-linking agent;
5. 1 part by weight type 1 portland cement; and
6. 3 parts by weight silica sand.

The percentages of the benzoyl peroxide and butylene dimethacrylate are based on the amount of polymer loading.

Eleven percent (wt) polymer and 89 percent (wt) cement, sand, and coarse aggregate were mixed in proportions of 1:2.14:2.72 to determine the strengths, water absorption, and chemical resistance of PC. The composition of the PC was as follows:

1. 50 percent (wt) MMA and 50 percent (wt) styrene;
2. 9 percent (wt) polymer loading;
3. 2 percent (wt) benzoyl peroxide as the initiator;
4. 10 percent (wt) butylene dimethacrylate as the cross-linking agent;
5. 1 part by weight type 1 portland cement;
6. 2.14 parts by weight river sand; and
7. 2.74 parts by weight silica gravel $\leq ^{33}/_{64}$ in. ($\leq$13 mm).

The percentages of the benzoyl peroxide and butylene dimethacrylate are based on the amount of polymer loading. Originally, limestone was used as the coarse aggregate, and excessive expansion was found in the specimens because the limestone reacted with the monomers, released large amounts of carbon dioxide, and thus produced air bubbles in the specimens. Later, ≤33/64-in. (≤13-mm) silica gravels in accordance with ASTM C 33-67 were used, and no more expansion problem was experienced.

For thermal curing, 2 percent (wt) benzoyl peroxide based on the weight of monomer was used to initiate the polymerization of monomer, and 10 percent (wt) butylene dimethacrylate based on the monomer was used as a cross-linking agent.

MIXING AND CURING

The mixing of polymer mortar and PC follows the same procedure. Since the monomer has very low viscosity, during preparation of the monomer solution most of the liquid settled in the lower part of the specimen when pure monomer was used. Since monomer has a high evaporation rate, a significant amount of monomer may evaporate during mixing and preparation of specimens. To eliminate these problems, a solution prepared from dissolving 20 percent (wt) polymer solids into 80 percent (wt) monomer was used. One hour was required for the polymer to be completely dissolved in the monomer when the solution was stirred at 200 rpm. Then the initiator and cross-linking agent were added to the solution and stirred for an additional 3 min; thus, the solution was ready for use.

The aggregate was surface dried and mixed with cement in a small mechanical mixer. Then, the required monomer solution was added to the cement-aggregate mixture, and the system was mixed for about 3 min. The wet system was poured into specimen molds and thoroughly rodded. Finally the specimens were placed in a 158 F (70 C) oven for curing. Several different curing times have been tried, and the results indicated that 6 hours of curing time are sufficient for the monomer to be completely polymerized.

TEST PROGRAM AND RESULTS

To determine the effect of the copolymer ratio of MMA and styrene and the effect of polymer loading on the strength of polymer concrete, compression, tension, and bending tests were conducted on the mortar system. The compressive specimens were 2.5- × 5-in. (6.35- × 12.7-cm) cylinders that had a diameter-height ratio of 1:2. The tensile strengths were obtained from the testing of briquet specimens in accordance with ASTM C 190. To reduce the material consumption, small 2- × 1.5- × 8-in. (5.1- × 3.8- × 20.3-cm) rectangular beams were tested to determine the flexural strength. The beams were subjected to two point loads as shown in Figure 1. With this setup, the maximum stress in the beam corresponds to the load reading. In most cases, failure occurred at the midspan of the beam.

Copolymer System

The objective of the test sequence for the copolymer system was to determine the effect of using various copolymer ratios of MMA and styrene on the strength of the material. Polymer loadings of 11.7 and 7.7 percent (wt) were used, and the copolymer ratios of MMA to styrene were varied at 100, 75, 50, 25, and 0 percent for the tests. MMA or styrene alone gave lower strength than the copolymer system. The compressive, tensile, and bending strengths were plotted against the styrene-MMA ratios as shown in Figures 2, 3, and 4. For the 11.7 percent (wt) polymer loading, an increase in styrene content improved the overall strengths of the material; however, no great advantage was obtained above a 50:50 mixture of MMA and styrene. The mixtures containing 7.7 percent (wt) polymer loading indicated a similar trend, but the results were somewhat less consistent. This was probably because the polymer loading was too low, and the material matrix did not have sufficient binding strength.

Figure 1. Bending test.

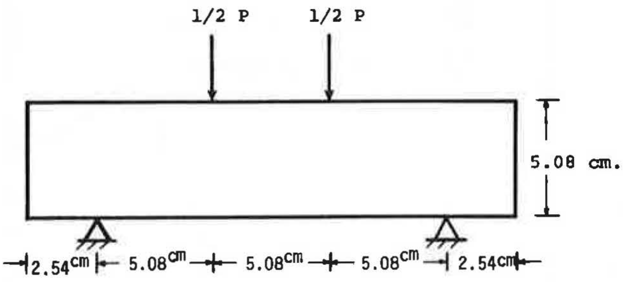


Figure 2. Effect on compression strength of styrene in copolymer mortar.

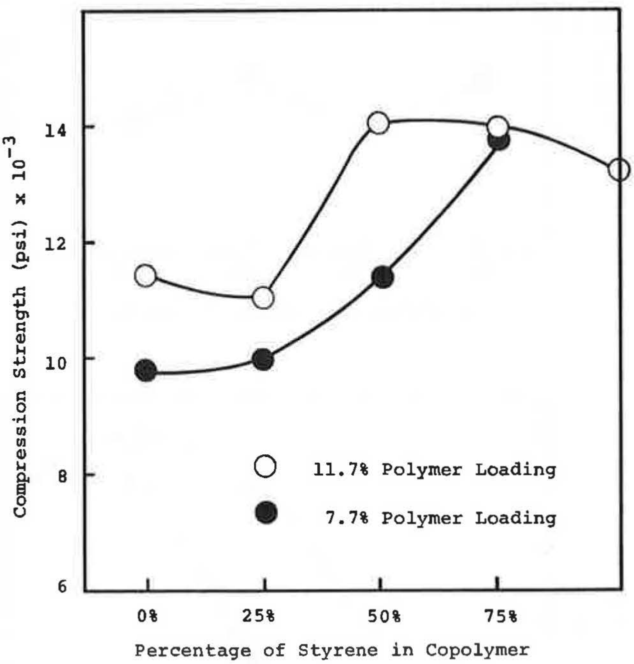


Figure 3. Effect on tensile strength of styrene in copolymer mortar.

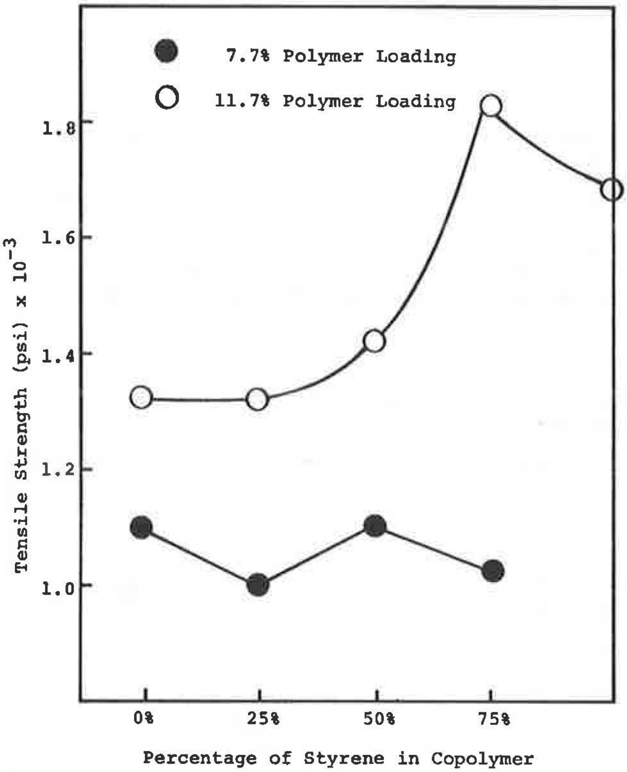
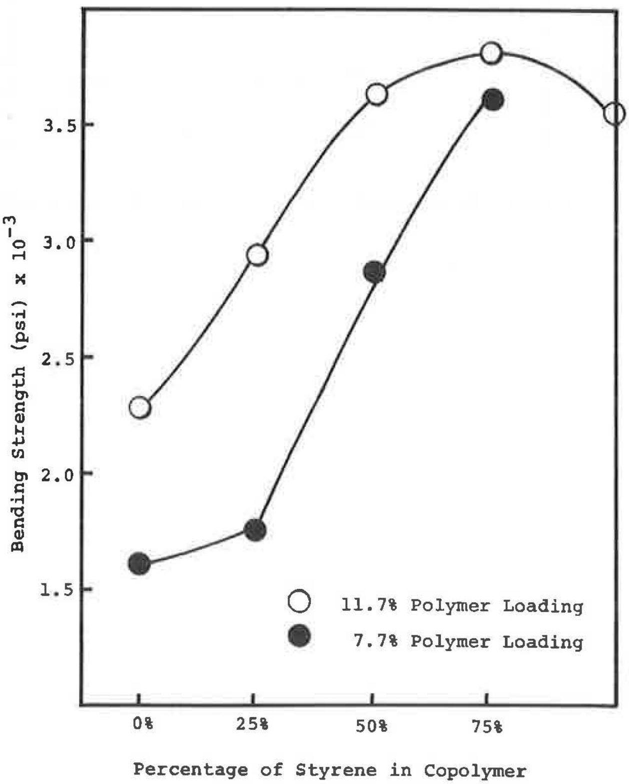


Figure 4. Effect on bending strength of styrene in copolymer mortar.



Polymer Loading

One important question for the preparation of PC is whether the strength of the material increases in proportion to increases in polymer loading. To answer this question, a series of mortar systems containing 50:50 MMA and styrene was tested. The polymer loading was varied between 7.7 and 15 percent (wt), and the test results are shown in Figure 5. Both compressive and bending strengths increase as polymer loading increases up to a peak level then decrease with more polymer loading. However, the tensile strength remains almost unchanged. The material containing 12 percent (wt) polymer loading gives the best strength: 14,000 psi (96 530 kPa) in compression, 1,350 psi (7140 kPa) in tension, and 3,700 psi (25 511 kPa) in bending. These values are about four times those of the control mortar with 1:3 cement-sand ratio as given in Table 1.

Properties of Polymer Concrete

A series of specimens was prepared from 50:50 MMA-styrene copolymer system with 9 percent (wt) polymer loading. Higher polymer loadings, i.e., 10 and 12 percent (wt), have been tried, and the mixtures appeared to be too wet during mixing. The mixture containing 9 percent (wt) polymer yielded better consistency.

Both compressive and bending tests were conducted in the same manner as the mortar system. The compressive strength has an average value of 11,700 psi (80 670 kPa), and the control 6,195 psi (42 700 kPa). The modulus of rupture averaged 3,780 psi (26 063 kPa), which is more than four times that of the control. Since the PC contains coarse aggregate of $\leq ^{33}/_{64}$ in. ($\leq$13 mm), the tensile strength was thus determined from the standard splitting tensile test (ASTM C 496-66) on 2.95- × 5.9-in. (7.5- × 15-cm) cylinders. The tensile strength averaged 1,520 psi (10 480 kPa), and the corresponding value for the control was 515 psi (3551 kPa). In addition, double shear tests were conducted to determine the bonding strength of the PC when it was bonded onto the old concrete blocks. As seen in Figure 6, the patch material in between the two endpieces can be either PC or ordinary concrete. The shear stress τ at the interfaces was calculated from the equation

$$\tau = \frac{P}{2A}$$

where

P = applied load and
A = cross-sectional area of the specimen.

In this way, the shear (or bonding) strength of the PC (50:50 MMA and styrene) was 417 psi (2875 kPa), which is more than five times that of the control. More detailed strength values are given in Table 2.

Water absorption and acid (18 percent HCl) resistance were also tested, and the results are given in Figures 7 and 8 respectively. For the water absorption test, 2.5- × 5-in. (6.35- × 12.7-cm) cylinders were used. The specimens were oven dried for 24 hours and then submerged in the tap water. After 72 hours of soaking, the PC gained only 0.1 percent of the specimen's weight, and the weight of control was increased by 3.5 percent. The same specimens were then used for acid resistance test. The specimens were soaked in 18 percent HCl solution, and the weight loss was measured at various time intervals. The test was conducted for 48 hours. As shown in Figure 8, the weight percentage loss of the control material was much greater than that of the PC.

Figure 5. Effect of polymer loading on strengths of copolymer mortar.

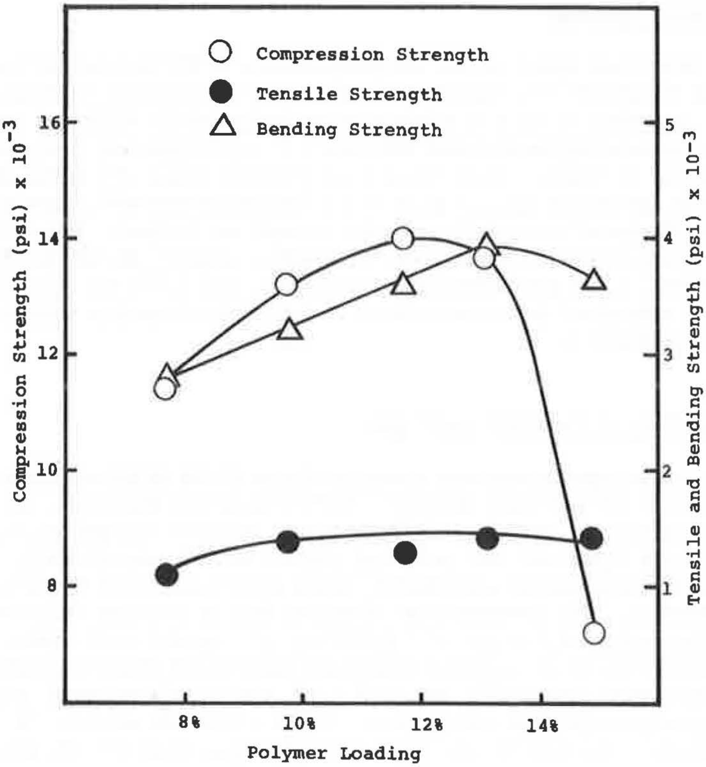


Table 1. Effect of polymer loading on strengths of copolymer mortar system.

Item	Polymer Loading, Percent (wt)	Compressive Strength[a] (psi)	Tensile Strength[a] (psi)	Modulus of Rupture[a] (psi)
Control[b]	–	3,575	332	715
Other specimens	7.65	11,400	1,100	2,860
	9.68	13,200	1,400	3,210
	11.7	14,000	1,320	3,620
	13.1	13,700	1,430	3,890
	14.9	7,200	1,430	3,650

Note: 1 psi = 6.895 kPa.

[a]Obtained from average of three specimens. [b]28-day strength.

Figure 6. Double shear test.

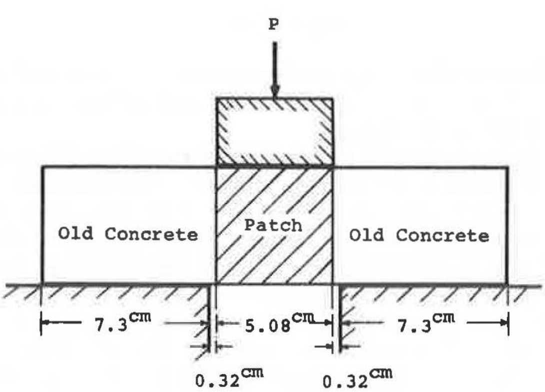


Table 2. Strengths of polymer concrete.

Batch[a]	Compressive Strength (psi)	Tensile Strength (psi)	Modulus of Rupture (psi)	Bonding Strength (psi)
Control[b]	6,195	515	850	74
1	11,300	1,500	3,650	367
2	12,100	1,400	4,220	467
3	11,700	1,660	3,480	—
Average	11,700	1,520	3,780	417

Note: 1 psi = 6.895 kPa.

[a]PC specimens contain 9 percent (wt) polymer loading.

[b]Strength values were obtained from average of three specimens.

Figure 7. Water absorption of control and polymer concrete.

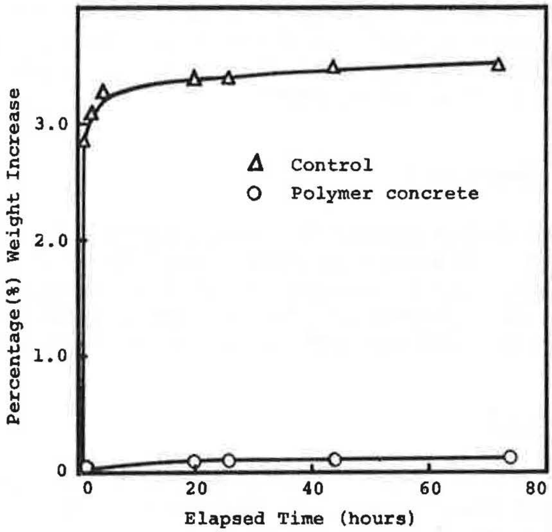
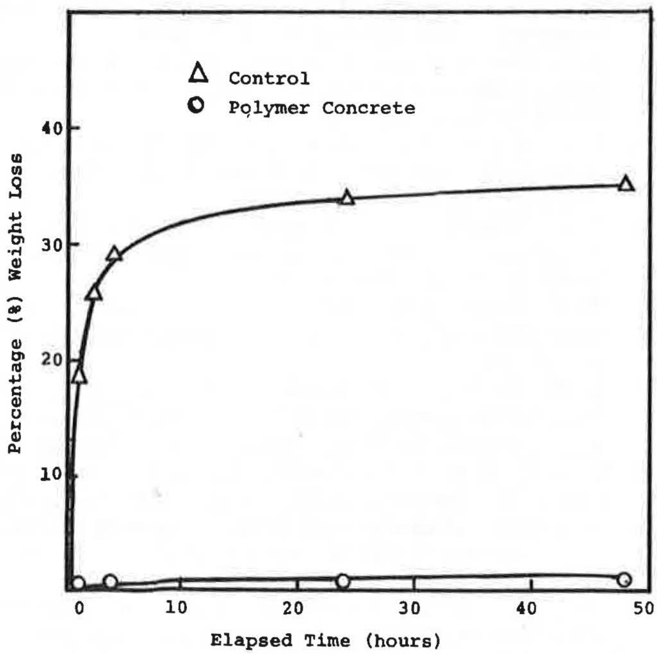


Figure 8. Acid resistance of control and polymer concrete.



CONCLUSION

Test results of polymer mortar and PC indicate that PC has the same order of strength and other physical properties as the PIC. By use of the thermal curing process, the copolymer system of 50:50 MMA and styrene gave much higher strength than the system containing each polymer alone. Based on the testing of mortar specimens, the strength of the material increases as polymer loading increases, and the 12 percent (wt) polymer loading gave, overall, the highest strength. Beyond this point, the material's strength decreases sharply. This result is indicative but cannot be directly applied to the PC. In fact, for PC containing coarse aggregate, less polymer loading is needed to achieve the same strength.

PC requires higher polymer loading [7 to 10 percent (wt)] than the PIC [5 to 6 percent (wt)]. This implies that the PC is somewhat more expensive; however, its major advantage is that it can be readily formed in place. Especially for field work, preparation and application of this material does not require additional equipment other than that needed for ordinary concrete.

ACKNOWLEDGMENT

The support of this work by the Ohio Department of Transportation is deeply appreciated. The contents of this report reflect the views of the authors, who are responsible for the findings and the accuracy of the data presented. The contents do not necessarily reflect the official views or policies of the Ohio Department of Transportation. This paper does not constitute a standard, specification, or regulation.

REFERENCES

1. M. Steinberg et al. Concrete-Polymer Materials, First Topical Report. Brookhaven National Laboratory, BNL 50134 (T-509), 1968; U.S. Bureau of Reclamation, USBR General Rept. 41, 1968.
2. M. Steinberg et al. Concrete-Polymer Materials, Second Topical Report. Brookhaven National Laboratory, BNL 50218 (T-560), 1969; U.S. Bureau of Reclamation, USBR REC-OCE-70-1, 1970.
3. J.T. Dikeou et al. Concrete-Polymer Materials, Third Topical Report. Brookhaven National Laboratory, BNL (T-602), 1971; U.S. Bureau of Reclamation, USBR REC-ERC-71-6, 1971.
4. J.T. Dikeou et al. Concrete-Polymer Materials, Fourth Topical Report. Brookhaven National Laboratory, BNL 50328, 1972; U.S. Bureau of Reclamation, USBR REC-ERC-72-10, 1972.
5. L.E. Kukacka et al. Concrete-Polymer Materials, Fifth Topical Report. Brookhaven National Laboratory, BNL 50390, 1973; U.S. Bureau of Reclamation, USBR REC-ERC-73-12, 1973.
6. W.F. Chen and E. Dahl-Jorgensen. Polymer-Impregnated Concrete as a Structural Material. Magazine of Concrete Research, Vol. 26, No. 86, March 1974, pp. 16-20.
7. D.W. Fowler, J.T. Houston, and D.R. Paul. Polymer-Impregnated Concrete Surface Treatments for Highway Bridge Decks. In Polymers in Concrete, American Concrete Institute, Publ. SP-40, 1973, pp. 93-117.
8. R.A.Y. Raff and H. Austin. Epoxy Polymer Modified Concrete. In Polymers in Concrete, American Concrete Institute, Publ. SP-40, 1973, pp. 339-345.
9. J. Hosek. Properties of Cement Mortars Modified by Polymer Emulsion. American Concrete Institute Journal, Proc., Vol. 63, No. 12, Dec. 1966, pp. 1411-1423.
10. Durable Concrete Roadway Surfaces With Dow Paving Systems. Dow Chemical Co., Midland, Mich., Technical Sales Bulletin.
11. S.A. Frondistou-Yannas and S.P. Shah. Polymer Latex Modified Mortar. American Concrete Institute Journal, Jan. 1972, pp. 61-65.

12. S. Akihama et al. Improvement of Mechanical Properties of Concrete Through the Addition of Polymer Latex. In Polymers in Concrete, American Concrete Institute, Publ. SP-40, 1973, pp. 319-338.
13. R. G. Pike and R. E. Hay. Polymer Resins as Admixtures in Portland Cement Mortar and Concrete. Federal Highway Administration, Rept. FHWA-RD-72-50, Oct. 1972.
14. L. I. Knab. Polyester Concrete: Load Rate Variance. Highway Research Record 287, 1969, pp. 19-31.
15. Y. Ohama. Mix Proportions and Properties of Polyester Resin Concretes. In Polymers in Concrete, American Concrete Institute, Publ. SP-40, 1973, pp. 283-294.
16. D. R. Bloss, S. J. Hubbard, and B. H. Gray. Development and Evaluation of a High-Strength Polyester Synthetic Concrete. U. S. Army Construction Engineering Research Laboratory, Champaign, Ill., Technical Rept. M-2, 1970.
17. A. M. Ivanov. Furfurol-Acetone Polymer Concrete—A Structural Building Material. In Structural Chemically Stable Polymer Concretes (N. A. Moshchanskii and V. V. Paturoev, eds.), U. S. Department of the Interior and National Science Foundation, Washington, D. C., TT-71-5007, 1971, pp. 25-38.
18. T. Y. Chang and H. L. Stephens. Development of Polymer Concrete as a Highway Patching and Material. College of Engineering, Univ. of Akron, Quarterly Progress Rept., March 28, 1974.