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Polymer Concrete

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CONTENTS

FOREWORD

This RECORD contains seven papers from a symposium on the application of polymers to portland cement concrete. They should be of interest to researchers, practicing engineers, and maintenance engineers.

Eash and Shafer describe the results of a 14-year project on the various mechanisms and reactions of styrene-butadiene and Saran (polyvinylidene chloride) latexes with portland cement. The chemical reactions and the curing mechanism are described, and the fundamental behavior of latex concrete is discussed in relation to structural and weathering properties.

Fowler describes laboratory tests and a small-scale field polymer treatment of a bridge deck, in which a monomer system is used that consists of methyl methacrylate, 10 percent (wt) trimethylpropane trimethacrylate, and 1 percent (wt) benzoyl peroxide. The monomer was polymerized with steam heat. Surface-treated slabs indicated increased freeze-thaw durability and permeability. Surface wear and abrasion were the same for treated and untreated slabs, and skid resistance was not affected by impregnation.

Kukacka, Fontana, and Steinberg describe the four types of polymer materials that have been investigated at the Brookhaven National Laboratory: polymer concrete, polymer portland cement concrete, polymer-impregnated concrete, and surface-impregnated portland cement concrete. This research describes studies on polymer concrete and its use in bridge deck and pavement repair. Monomer selection, mix design, fabrication, and polymerization techniques are described, and the corresponding laboratory results are presented.

Mehta, Chen, Manson, and Vanderhoff discuss preliminary experiments with two new approaches: the use of a pressure-mat technique for impregnation of concrete with organic and other materials and the use of sulfur as an impregnant. They suggest that sulfur may have a potential in bridge decks, provided that no steel corrosion problems arise because of side reactions with water and oxygen.

Weyers, Cady, Blankenhorn, and Kline report on the effects of polymer impregnation on concrete cores taken from bridge decks. They found that the depth of impregnation did not depend on deicer salt concentration but that the rate of penetration was a linear function of the square root of time.

Chang, Stephens, and Yen conducted studies on the effect of using different copolyme ratios of methyl methacrylate and styrene and the effect of polymer loading on the strength of the material. Results indicate a 50:50 copolymer system gave a higher strength than the system containing methyl methacrylate or styrene alone. The strengt of composite increased as polymer loading increased up to 12 percent (wt).

DePuy describes a prestressed, polymer-impregnated bridge deck system. Mechanical and physical properties and durability are given for polymer-impregnated concrete and polymer concrete.

REACTIONS OF POLYMER LATEXES WITH PORTLAND CEMENT CONCRETE

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This paper explains the physical and chemical actions and reactions of polyvinylidene chloride and styrene-butadiene polymer latexes on the aggregate and portland cement in concrete. It also describes how the polymer particles irreversibly bond to the aggregate and cement, form a monolayer of plastic particles over their surfaces, and subsequently coalesce to form a continuous polymer phase throughout the concrete. The need for curing procedures with latex concrete different from those required for the optimum cure of conventional concrete is also discussed. These basic data are expanded to explain how polymer latexes reinforce concrete, improve its structural properties, control its elastic behavior, and greatly enhance its durability. Data are presented to describe polymer latex concrete with compressive strengths from 5,000 to 15,000 psi (34 500 to 103 000 kPa), flexural strengths from 800 to 2,000 psi (5520 to 13 800 kPa), elastic moduli from 2 to 5 × 10^6 psi (13.8 to 34.5 × 10^6 kPa), bond strength to steel >2,500 psi (17 200 kPa), and bond strength to concrete >600 psi (4140 kPa) at which the concrete substrate fails. Practical applications of latex concrete over the past 20 years are described, and why the materials are ideally suited for each application is explained.

• POLYMER latexes have been used in portland cement mortars and concrete for about 40 years; their major application has been in thin section overlays and in the repair of damaged concrete. They have been used in these areas because of the improved bond strength and durability properties they impart to portland cement concrete (PCC). Little was known about the reactions and interaction between latexes and portland cement. This report describes the research findings developed over the past 14 years by the Dow Chemical Company on the various mechanisms and reactions of styrene-butadiene and polyvinylidene chloride (Saran) latexes with portland cement and relates these findings to the improved properties in the resulting mortars and concrete.

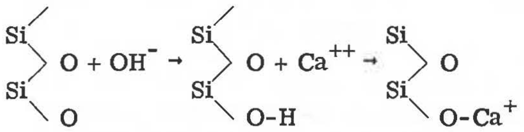
The hydration of portland cement is important to the interactions of latex, cement, and aggregate and to external surfaces in contact with the wet concrete. The hydration of portland cement is not discussed in this paper, although the effects of some of the reaction products of hydration, as they affect the polymer latexes, will be discussed. An excellent explanation of the hydration of portland cement is described by Lea (1).

Polymer latexes are a colloidal dispersion of plastic particles in water. The particles are stabilized in the water by coating the surfaces with anionic and nonionic surfactants that stabilize the plastic particles against agglomeration in the presence of polyvalent ions always in portland cement systems and that prevent coagulation of the particles under the high shear forces developed when concrete is mixed. These surfactants are usually good "soaps" that produce excessive amounts of foam when agitated. Therefore, an effective antifoaming agent must be incorporated in the polymer latex to prevent excessive air entrapment in the PCC containing the latex.

The ingredients and handling characteristics of polymer latex PCC are similar to those of conventional concrete. Polymer latex PCC is made of portland cement, coarse and fine aggregates, water, and from 1 to 4 percent polymer based on the weight of the concrete.

CHEMICAL REACTION

The initial reactions that take place in both polymer-modified and conventional concrete are the same. Water reacts with the portland cement, produces sodium, potassium and calcium hydroxide, and dissolves some of the calcium sulfate. The hydroxide ions in turn react with silica and form a basic surface on the aggregate. Calcium ions available from the hydration of the portland cement under alkaline conditions react with the basic silica surface and deposit calcium ions on the aggregate surface to form a calcium silicate. Our observations on these reactions are consistent with those reported by Iler (2) and Kolthoff and Stenger (3). This total reaction is complex but can be shown in a simple form as follows:



At this point in the reaction, the polymer latex particles associate in a monolayer on the aggregate surface through the Ca^+ ion linkage. If the calcium ion on the silica surface is replaced with a sodium ion, no polymer association will take place. The association of the polymer particle with the calcium silicate surface of the aggregate is irreversible in that it cannot be removed by washing with distilled water or with hydrochloric acid. A portion of the calcium ion cannot be removed by acid washing at this point; this indicates that it is chemically bound to the latex particle. We do not know the chemical reaction that takes place between the polymer and the calcium ion on the silica surface; however, we are pursuing two hypotheses at the present time: (a) that the calcium ion reacts with double bonds either present or formed in the polymer and (b) that the calcium ion reacts with the surfactants on the surface of the polymer. We do know that the polymer particle, either styrene-butadiene or Saran, is irreversibly and strongly affixed to the surface of the silica aggregates in the concrete. This eliminates one of the weak points in concrete: the bond of the cement paste to the aggregate.

The latex particles also bond to the surface of all the portland cement particles in the concrete. We believe this reaction is the same as that to the calcium silicate surface of the aggregate and takes place early in the reaction process of portland cement. Fifteen percent styrene-butadiene or 20 percent Saran, based on the weight of portland cement, have almost equal numbers of polymer particles introduced into the concrete and are enough to deposit about two layers of latex particles over the total surface of the unhydrated cement grains and aggregate particles. The latex particles are coated with surfactants that are also highly effective dispersants for portland cement when associated with latex. The result of this is that the latexes act as effective water-reducing agents in concrete. The hydration process continues as water passes around the latex particles into the surface of the cement and reacts to form the portland cement hydrate or gel. As the reaction proceeds, the gel increases in size, and the surface area is increased. Additional latex particles deposit in a monolayer on this new surface area. The latex particles do not penetrate the gel area, and the gel does not form around the particles. This has been determined by X-ray analysis of fractured cement particles on a scanning electron microscope. The hydration process continues until the surface comes in contact with another cement particle or an aggregate surface. At this point in time, because of the greatly increased surface area produced by the hydration of the portland cement, there are enough latex particles present to coat all surfaces with a monolayer. When these surfaces come in contact, the latex particles on the surfaces are forced together, and free water is removed from the immediate area around the particles. The latex particles then coalesce and start to form a continuous film about two particles thick throughout the concrete matrix. A new continuous polymer phase has now been introduced into the concrete.

CURING MECHANISM

There are major differences in the curing of polymer latex concrete and that of regular concrete. In conventional PCC, long exposure to a moist or wet environment allows the portland cement to continue to hydrate and gain strength properties. This is also true with latex-modified PCC, but the method of obtaining the optimum cure is different. Latex concrete must undergo a second curing mechanism in addition to the hydration of the cement. The latex particles must coalesce to form a film, and this film must cure to gain its maximum strength. The curing of the latex film is best achieved under a dry environment. It would appear that it would be impossible to obtain a good cure for both reactions. Fortunately, this is not true. Portland cement continues to hydrate as long as a relative humidity ≥78 percent is maintained. Latex films will cure at relative humidities below about 98 percent; the lower the humidity is, the faster the cure will be. Therefore, in latex PCC, the relative humidity in the concrete should be maintained between 78 and 98 percent to obtain optimum results.

Another phenomenon in latex concrete is that some of the latex particles migrate to any surface exposed to the air and form a latex film on this surface. Subsequently, this film will prevent any rapid loss of water from the concrete. This results in an optimum wet curing condition within the concrete even though the surface of the concrete is exposed to a dry cure. It is desirable to cover or to wet the surface of latex concrete for up to 24 hours to prevent excessive drying out of the surface of the concrete. When the plastic film in latex concrete has attained its initial cure, the latex will be unaffected by repetitive wetting with water and, in fact, will continue to gain strength under these conditions (4).

Latex concrete will develop about 75 to 85 percent of its ultimate strength in 28 days when cured under ambient conditions of 73 F (22.8 C) and 50 percent relative humidity.

FUNDAMENTAL BEHAVIOR OF LATEX CONCRETE

The understanding of how latexes react in PCC is of great interest to the chemist, but in itself is of little practical value to the material or structural engineer. However, by studying how the latexes reinforce PCC, we can develop some interesting insights into why they improve the performance properties of concrete, and this is of great interest to the engineer.

When PCC drys out, the cement hydrate or gel shrinks because of the loss of water, which creates structural stresses within the gel. When these stresses exceed the tensile strength of the gel, the material yields producing microcracks as shown in the micrograph in Figure 1. This is the typical condition of all PCC. As structural and thermal stresses are applied to concrete, these microcracks propagate, join with other microcracks, and lower the tensile capacity of the concrete. If the stresses are high enough or repeated often enough, the concrete can fail in tension or through fatigue.

An analysis of the microstructure has revealed some remarkable differences between latex concrete and regular concrete. Figure 2 shows the microstructure of concrete containing Saran latex. It is the first example of a concrete without any microcracks that we have ever observed. It is a seven-bag concrete with a water-to-cement ratio of about 0.30 to 1 and a 1-in. (25.4-mm) slump. It was cured under optimum conditions. Although we have achieved this optimum microstructure, it is not typical of most latex concrete. Figure 3 shows the typical microcrack structure of latex concrete. Polymer microfibers bridge across the microcracks and restrain the propagation of the microcrack (5). Often these microcracks will terminate in polymer-rich areas. Because of the relatively low elastic modulus of the polymer in comparison to the portland cement, the polymer will undergo strain, thereby relieving the stresses in the cement hydrate. At this point we can see why it is so important that the latex particles bond well to the aggregate and to the cement hydrate. It is this high bond strength that allows the polymer to sustain high tensile loadings and that increases the tensile capability of the PCC.

The structural properties of the plastic film are all important to the resulting con-

Figure 1. Unmodified concrete paste phase.

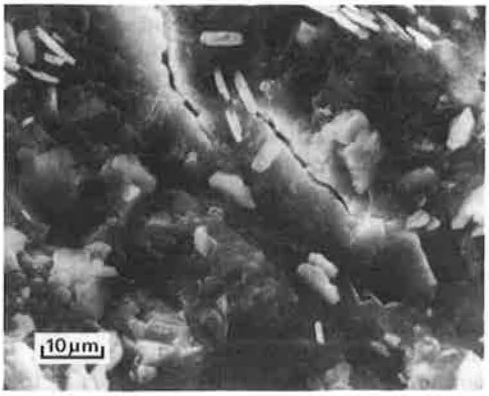


Figure 2. Saran latex concrete.

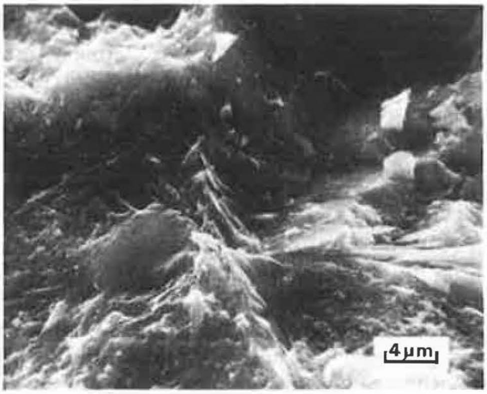


Figure 3. Polymer microfibers in latex concrete.

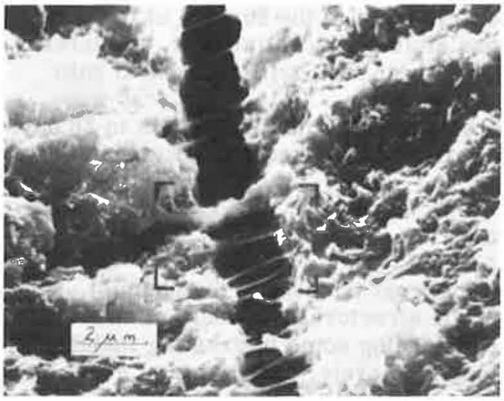


Table 1. Mechanical properties of mortars.

	Strength (psi)				Flexural Elastic Modulus
Mortars	Compressive	Tensile	Shear	Flexural	(psi)
Control[a]	4,480	350	50 to 200	820	3.4×10^6
Styrene-Butadiene[b]	5,500	740	>650	1,620	1.92×10^6
Saran[c]	8,430	870	>650	1,820	2.52×10^6

Note: 1 psi = 6.8948 kPa.

[a] Water-to-cement ratio = 0.57/1.

[b] Water-to-cement ratio = 0.40/1; latex-to-cement ratio = 0.15/1.

[c] Water-to-cement ratio = 0.40/1; latex-to-cement ratio = 0.20/1.

crete properties. A latex that produces a film with a low elastic modulus will actually lower the elastic modulus of the concrete, make it quite ductile, yet impart high tensile properties to the concrete. A high-modulus, high-strength polymer will increase the elastic modulus of the concrete, improve its structural properties, and still impart improved ductility. Improved ductility usually improves the abrasion resistance properties of the concrete, and the low porosity due to the continuous polymer network improves the weathering, freeze-thaw resistance, and chemical resistance properties of the concrete. All these factors lead to greater durability.

STRUCTURAL PROPERTIES

The structural properties of polymer latex mortar and concrete can vary considerably depending on the type and amount of latex, the type of aggregate, the cement factor, and the water-to-cement ratio. In general, increasing amounts of latex produce higher strengths. Styrene-butadiene latexes produce high tensile or flexural strengths, average compressive strengths, and a low elastic modulus. Saran latexes produce high compressive, tensile, and flexural strengths and a high elastic modulus. Small-sized aggregate produces higher strengths than larger aggregate. Table 1 gives typical mechanical properties of latex mortars versus a control mortar (sand-to-cement ratio = 3/1). All test specimens were cured 28 days unless otherwise noted. Table 2 gives the strength properties of small-aggregate concrete (water-to-cement ratio = 0.30/1) containing Saran latex, and Table 3 gives the compressive and flexural strength of latex concrete containing $^5/_8$-in. (15.9-mm) aggregate. Figure 4 shows the compressive strength stress-strain curve for a standard concrete with no latex, 15 percent Saran latex, and 15 percent styrene-butadiene latex. These curves are for the same concrete as described in Table 3. The Saran latex increases the elastic modulus of the concrete, and the styrene-butadiene latex decreases the elastic modulus.

The use of steel- and alkali-resistant glass fibers is of current interest. Table 4 gives the effect of Saran latex on the mechanical properties of small-aggregate concrete containing fibers.

Another important benefit of latexes in concrete is their ability to increase concrete's bond strength to reinforcing steel. Conventional concrete will develop bond pull-out strengths to No. 5 reinforcing bars of 300 to 800 psi (2068 to 5516 kPa). Styrene-butadiene latex will increase this strength from 1,700 to 2,200 psi (11 720 to 15 170 kPa), and the Saran latex bonds so well to the steel that the steel bar yields at a bond strength >2,700 psi (18 620 kPa), depending on the strength of the steel.

APPLICATIONS OF LATEX CONCRETE

Polymer latex concrete was first used for restoring and resurfacing deteriorated concrete floors. The excellent bond strength to existing concrete allowed these materials to be used in thin sections, ≤0.5 in. (12.7 mm). This did not appreciably increase the dead weight loading on the floor. A natural extension of this application with the styrene-butadiene and Saran latexes was the resurfacing of exterior, deteriorated concrete and especially concrete bridge decks. The first resurfacing of bridge decks with latex concrete was in 1957 in Michigan (6). Figure 5 shows this bridge in 1970. Since that time, hundreds of bridge decks have been restored with latex concrete. The main advantages of latex concrete for this use are excellent bond strength to the base concrete, excellent freeze-thaw resistance, excellent resistance to the penetration of chloride ions from deicing salts, good ductility, good abrasion resistance, and greatly improved tensile and flexural properties.

Saran polymer latex mortars have been used in brick masonry construction since 1961. Although these mortars have excellent weathering and freeze-thaw durability, they are primarily used in this area because of their excellent flexural bond strength to brick. Saran latices increase the flexural bond strength by a factor of 4 or more, and allow a nominal 4-in. (101.6-mm) single-wythe wall to perform the same function

Table 2. Strength properties of small-aggregate concrete containing Saran latex.

Aggregate-to-Cement Ratio	Latex (percent)	7-Day Strength (psi)		28-Day Strength (psi)		
		Compressive	Tensile	Compressive	Tensile	Oven-Dry Tensile
3:1	0	8,640	580	8,760	520	550
	8	13,220	—	15,260	—	—
	14	11,650	700	14,370	860	1,290
	20	9,440	610	13,110	890	1,170
4:1	0	4,400	—	5,320	—	—
	8	12,010	—	13,260	—	—
	14	10,850	640	13,370	880	1,210
	20	10,430	650	13,570	890	1,450

Note: 1 psi = 6.8948 kPa.

Table 3. Strength properties of concrete made with 5/8-in. (15.9-mm) aggregate.

Latex (percent)	W/C	Strength (psi)	
		Compressive	Flexural
0	0.44/1	6,400	690
5 S	0.38/1	8,420	800
10 S	0.38/1	8,230	810
15 S	0.37/1	9,080	950
5 S/B	0.37/1	6,500	850
10 S/B	0.37/1	6,210	940
15 S/B	0.30/1	6,090	1,050

Note: S = saran latex; S/B = styrene-butadiene latex. Aggregate void volume = 28.5 percent; cement content = 7 bags/yd^3; and wet density = 152 to 156 pcf. 1 psi = 6.8948 kPa. 1 in. = 25.4 mm. 1 yd^3 = 0.07646 m^3. 1 pcf = 1,602 kg/m^3.

Table 4. Mechanical properties of small-aggregate concrete containing fiber.

Item	Property (psi)		
	Compressive Strength	Flexural Strength	Flexural Elastic Modulus
Control			
No fiber	7,070	1,550	2.6×10^6
Steel fiber	7,800	1,920	2.4×10^6
Glass fiber	8,920	1,150	2.3×10^6
Saran latex			
No fiber	11,900	2,680	3.2×10^6
Steel fiber	12,700	2,700	3.1×10^6
Glass fiber	13,300	2,710	3.3×10^6

Note: Sand/cement = 2.5/1; water/cement for control = 0.44/1, for latex = 0.34/1; latex solids/cement = 0.20/1; fiber content = 1.75 percent by volume; 7-day curing at 100 percent relative humidity; 21-day curing at 73 F (22.8 C) and 50 percent relative humidity; and 7-day curing at 200 F (93.3 C), tested cool. The compressive strength was obtained on 2-in. cubes; flexural properties were obtained on bars 2 in. wide, 0.5 in. deep and 10 in. long, center point load. 1 psi = 6.8948 kPa, 1 in. = 25.4 mm.

Figure 4. Concrete compressive strength stress-strain curves.

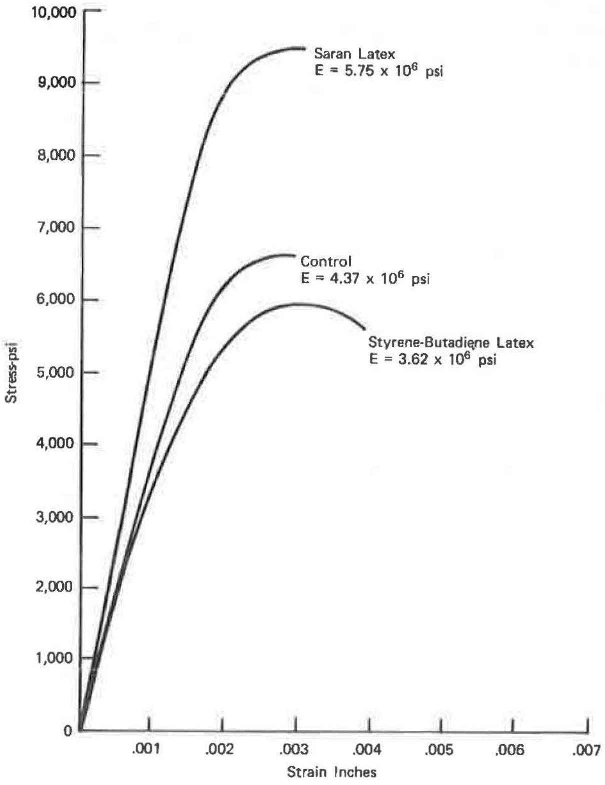


Figure 5. Mortar bridge surface after 13 years of service.

Figure 6. Single-wythe architectural panel for high-rise building.

Figure 7. Architectural panels in place.

as a conventional double-wythe masonry wall. Saran latex also allows the prefabrication of single-wythe architectural brick panels. Figure 6 shows a typical panel being lifted into place on a high-rise building in Austin, Texas. The almost completed building is shown in Figure 7.

CONCLUSIONS

Currently, research is under way to investigate the structural properties of reinforced and prestressed flexural concrete containing polymer latexes. Of particular interest is the use of these materials in prestressed concrete railroad ties. The excellent durability of latex concrete and its structural properties and excellent bond strength to steel should produce another ideal use of polymer latex concrete, a new and remarkable material based on the established technology of the portland cement and plastics industries.

ACKNOWLEDGMENTS

We wish to acknowledge the research work of Herman B. Wagner of Drexel Institute of Technology, and Jerry E. Isenburg formerly of the Dow Chemical Company and currently with John Hoag and Associates, Cincinnati, who have greatly contributed to this basic concept of the interaction between polymer latexes and portland cement concrete.

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PARTIAL POLYMER IMPREGNATION OF HIGHWAY BRIDGE DECKS

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Polymer-impregnated concrete is being considered as a means of increasing the durability of bridge decks. For application to existing bridges, the process includes drying the bridge deck to remove the free moisture in the pores, soaking a low viscosity monomer solution into the concrete, and applying heat to polymerize the monomer. Drying, soaking, and curing requirements are discussed. A limited area of a bridge deck has been successfully polymerized to a depth of approximately 1 in. (2.5 cm). Evaluation studies were conducted to determine the freeze-thaw resistance, skid and wear resistance, and protection against corrosion of the reinforcement in relation to polymer-impregnated concrete. Freeze-thaw resistance was significantly increased, and skid resistance improved significantly for the partially impregnated slabs when the tests were performed when the surfaces were dry. Skid resistance was slightly higher when the surfaces were covered with abrasive grit and kept wet. Wear measurements generally indicated little difference between treated and untreated specimens. Corrosion resistance for slabs with a low-quality polymer impregnation is about 25 times greater than that for unimpregnated slabs.

•POLYMER-impregnated concrete (PIC) development has given rise to many potential applications in the construction industry. The significant increases in strength, stiffness, water permeability, resistance to corrosion, and abrasion resistance (1, 2, 3) suggest many possible applications in highway construction. Although the possibilities of using the material structurally to take advantage of the strength and stiffness are appealing, the most logical uses at first appeared to be in the area of materials improvement for durability. As PIC is proved as a practical, durable material, the structural uses will naturally evolve.

The maintenance of deteriorating bridge decks is a major problem throughout the United States that results in the annual expenditure of many millions of dollars. The primary cause of bridge deck deterioration appears to be the presence of moisture in the concrete, which causes corrosion of the reinforcing and freeze-thaw deterioration. Researchers at the Center for Highway Research at the University of Texas have pursued the idea of developing methods to partially impregnate bridge decks in situ. They theorized that, if such a polymer surface treatment were practical, the increased resistance to water penetration and the strength of the impregnated concrete should result in significant increases in durability.

There were many questions to be answered, but generally they fell into two basic categories:

1. How can the concrete be impregnated with polymer?
2. What are the advantages of the partially impregnated concrete for use on bridge decks?

Research was initiated in 1970 in an attempt to develop and to evaluate polymer surface treatments for bridge decks (3, 4).

FIELD IMPREGNATION OF BRIDGE DECKS

Prior to this research, practically all of the research had been directed toward full impregnation in which the concrete is fully dried, evacuated, and soaked in a monomer solution until it is fully saturated. The liquid monomer is then converted to a polymer by addition of heat or by irradiation. Under laboratory or plant conditions the full-impregnation process is relatively simple and reproducible.

Surface impregnation in the field is a more complicated process even though only partial impregnation is required. There are three basic interrelated steps in the process: (a) drying the concrete, (b) impregnating the surface zone of concrete with the liquid monomer solution, and (c) polymerizing the monomer. The depth of monomer impregnation is affected by the depth to which the concrete is dried. The type of monomer system affects the requirements for polymerization.

Drying

Normal weight concrete has 11 to 13 percent voids that are partially filled with moisture under usual environmental conditions. This moisture must be removed to the depth at which monomer penetration is desired. The amount of moisture removed is primarily a function of surface temperature and drying time, although other variables such as air humidity and velocity can also be important.

Initially, concrete was to be dried at less than 200 F (95 C) to avoid any danger of cracking or of excessive thermal expansion. Slabs 40 × 43 in. (102 × 109 cm) were cast and treated under field conditions. Drying was accomplished by air drying in the sun for several months and by using a curing blanket for a minimum of 3 days; these methods developed maximum concrete surface temperatures of 140 to 150 F (60 to 65 C). PIC depths from $\frac{1}{4}$ to $\frac{3}{4}$ in. (0.6 to 1.9 cm) were obtained, although there was considerable variation in depth and some of the polymer was faint. However, the durability properties of this material were good as will be discussed subsequently.

Based on later research at the University of Texas, Lehigh University, and the U.S. Bureau of Reclamation, there seems to be little question that higher temperatures are both preferable and safe. The temperature at the depth to which penetration is desired should be at least 212 F (100 C).

Figure 1 shows the temperature gradients in a 6-in. (15-cm) slab for a surface temperature that increases to 320 F (160 C). Thermocouples were inserted into holes drilled from the bottom surface and were located at various depths from the heated surface. Temperatures are shown for times varying from 30 to 180 min after the heat source was applied. Although the temperature varied with depth, the change in temperature with time was approximately constant. After 1 hour, only the upper $\frac{1}{2}$ in. (12.7 mm) of concrete is heated to 212 F (100 C) or higher. The concrete is heated to 212 F (100 C) at a depth of 1.7 in. (4.3 cm) after 2 hours, and at nearly 2.5 in. (6.3 cm) after 3 hours. These temperature gradients and rates depend on the rate of temperature buildup on the surface. Temperature gradients can be predicted analytically with good accuracy.

The drying time required to achieve a particular depth of polymer impregnation has been found to be considerably longer than the time required to achieve a temperature of 212 F (100 C) at the same depth. Figure 2 shows the depth of polymer impregnation achieved for a surface temperature-time relationship similar to the one shown in Figure 1. From Figure 1 it was observed that a temperature of 212 F (100 C) was reached nearly 2.5 in. (6.3 cm) from the surface after 3 hours. However, the depth of polymer impregnation after 4 hours of drying was only about 0.6 in. (1.5 cm). Slightly over 8 hours of drying produced a polymer depth of 1.25 in. (3.1 cm).

At this time, drying is the most difficult step in the process from a practical standpoint. The maximum or optimum temperature for drying is still not well defined. It is reported that other researchers have used temperatures of 500 to 700 F (260 to 370 C) and even higher without serious effects. We think the maximum temperatures should not exceed 300 F (149 C) until more experience is gained in large-scale field treatments.

Figure 1. Temperature gradients in 6-in. (15-cm) concrete slab heated from upper surface.

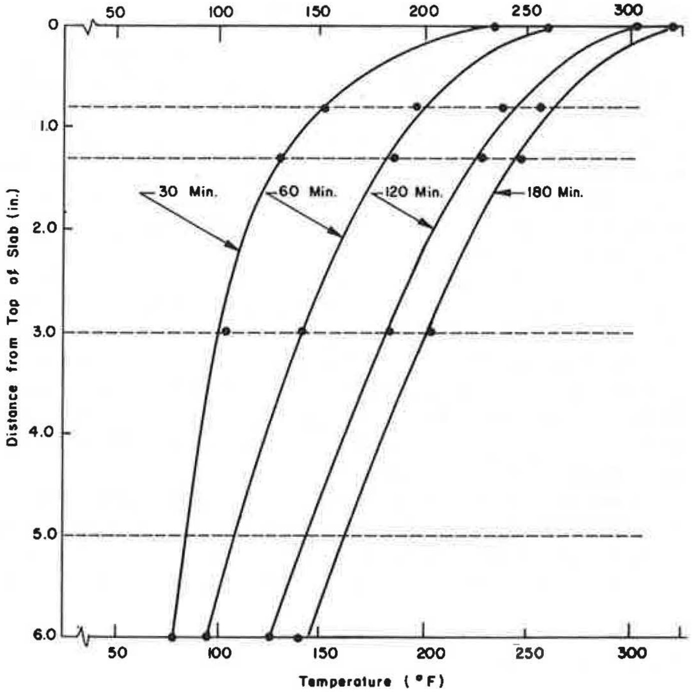
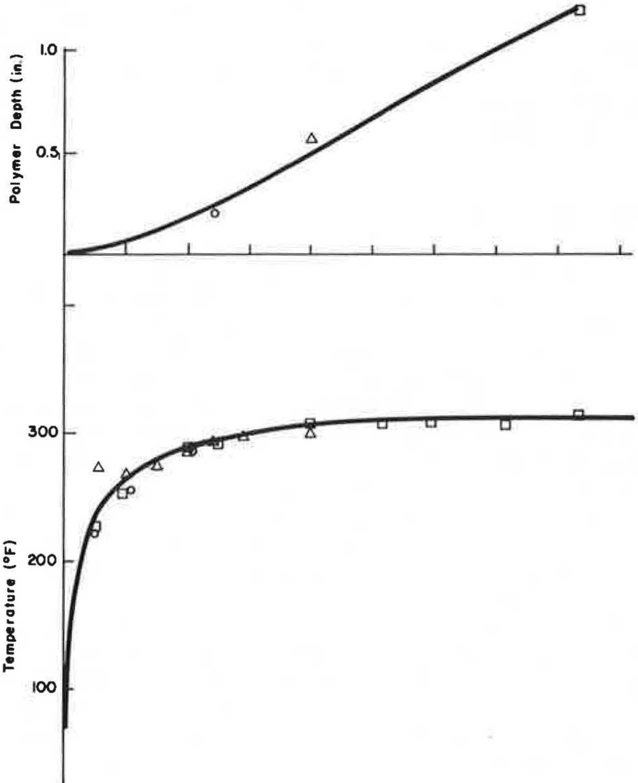


Figure 2. Effect of drying on polymer depth.



Monomer Systems and Application

The monomer system that was used initially consisted of methyl methacrylate (MMA), 10 percent (wt) trimethylpropane trimethacrylate (TMPTMA) and 1 percent (wt) benzoyl peroxide (BP). More recently, other catalysts have been used because of their improved mixing characteristics and their longer storage life when in solution. This monomer system has a low viscosity, which is essential to achieving good penetration without overpressure. In addition, polymerization occurs relatively fast at temperatures of 150 F (66 C) or higher. Other monomers that have been used are isobutyl methacrylate (IBMA) and isodecyl methacrylate (IDMA).

A $\frac{1}{4}$-in. (0.6-cm) sand layer is used on the surface to hold the monomer in place during soaking and to prevent monomer evaporation from the concrete surface. The monomer solution is sprinkled or sprayed onto the sand in the usual amount of ≥3,000 to 4,000 ml/m^2 (0.073 to 0.089 gal/ft^2). The primary requirements are to initially moisten the sand thoroughly and to keep it moist during the soaking period. A plastic sheet or aluminum foil is applied during the soaking period to retard evaporation. It is also necessary to keep the temperature of the slab to <100 F (38 C) to prevent polymerization from occurring.

Figure 3 shows the polymer impregnation achieved for soaking times ranging from 5 to 8 hours in 6-in. (15-cm) slabs that had been thoroughly dried. A soaking time of 4 hours produced an impregnated depth of 1 in. (2.54 cm). Longer soaking times of 7 or 8 hours resulted in about 1.5 in. (3.8 cm) of polymer depth.

Polymerization

The two most common methods for polymerizing a monomer in concrete are radiation and thermal-catalytic processes. Because of the weight of shielding and the potential safety hazards for a mobile irradiator, this research has relied on thermal-catalytic methods. Several sources of heat have been investigated: solar energy, microwave ovens, reactive monomer systems, heating blankets, steam, and ponded hot water. Currently, steam and ponded hot water appear to be the most practical means of achieving polymerization.

Ponded Hot Water

Hot water can be ponded by erecting a simple framework on the slab and lining it with a waterproof membrane such as polyethylene film. The sand cover is usually left in place because the time required for removal would permit evaporation of the monomer from the slab. Water heated to about 195 F (90 C) is ponded to a depth of approximately 3 in. (7.5 cm). This produces a maximum temperature on the slab surface of about 140 F (60 C). The slab surface was initially at room temperature. The water was removed after 2 hours after which the slab temperature dropped rapidly.

Figure 4 shows the polymer depth for different application times of the water. Both lightweight aggregate fines and regular sand were investigated. For 2 hours of hot water application over regular sand, a 1.25-in. (3.2-cm) polymer depth was achieved. The use of lightweight aggregate fines resulted in only about 60 percent as much impregnated depth, apparently because of the greater insulating effect.

The advantages of hot water are (a) uniform heat, (b) creation of an airtight barrier over the concrete that eliminates monomer evaporation, and (c) progression of polymerization without additional application of heat or energy after the hot water is initially applied. This last advantage minimizes the problems encountered in mechanical or electrical failures during polymerization. The curing time could be accelerated by use of submersible heaters or a hot water circulating system. Insulation for the sides and top would be required for large-scale treatments to reduce the energy requirements. An enclosed water bag may have some merit.

The disadvantages of ponded hot water are that it is difficult to use on superelevated

Figure 3. Effect of soaking time on polymer depth.

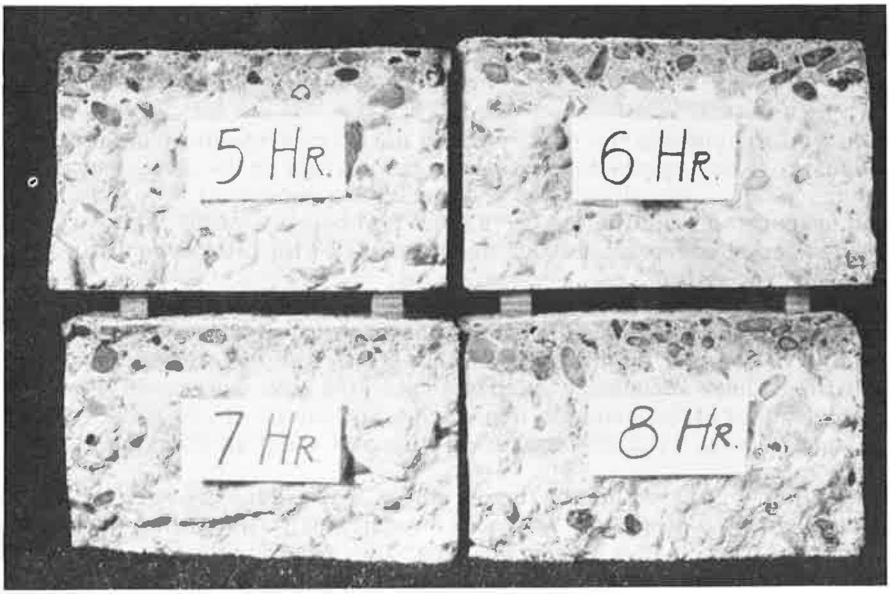
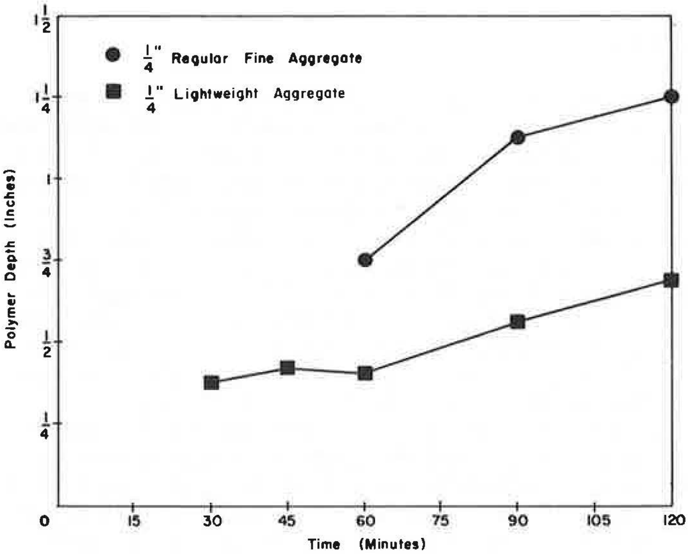


Figure 4. Polymer depth as a function of curing time with hot water.



bridge decks and to move from one location to another and that relatively large amounts of water are required.

Steam

Steam has worked well to generate the heat required for polymerization. In the first attempts to use steam, it was sprayed directly onto the surface of the slabs that had been soaked with monomer. The slabs were polymerized to a depth of $^3/_4$ in. (2 cm), but the monomer had evaporated from the top $^3/_{16}$ in. (0.5 cm) because of the high surface temperature. A number of evaporation barriers were tried with little success in an attempt to reduce the evaporation.

Steam injected into an enclosure over the slab heats the slab more slowly and to a lower maximum temperature. However, slab temperatures can be increased to 203 F (95 C) in a short time. Polymer depths of 1 to 2 in. (2.5 to 5 cm) are regularly obtained in slabs that have been adequately dried and saturated with monomer. Figure 5 shows the polymer depth of slabs heated to a surface temperature of 170 F (77 C) and cured for 30, 60, and 90 min. The 30-min curing time was about as effective as the longer times.

The advantages of steam are (a) higher temperatures that reduce the curing time, (b) usability on superelevated decks, (c) less water requirement, and (d) simpler movement without the ponded water. The disadvantages are the need for steam-generating equipment and for a continuous supply of steam for the curing period. The continuous supply may require a backup capability in case of a malfunction. It will be necessary to have an easily portable, well-insulated enclosure to minimize labor and energy requirements.

SMALL-SCALE FIELD TREATMENT

In addition to laboratory treatments and simulated field treatments, a limited small area on a new bridge deck in Austin, Texas, was successfully treated. The bridge had already been sprayed with linseed oil but had not been opened to traffic. An area 12 × 12 ft (3.7 × 3.7 m) was selected to be treated, and one-half of the area was lightly sandblasted to remove the linseed oil. One-half of each sandblasted strip and each nonsandblasted area was dried for 72 hours, with a kerosene construction heater with a blower, and undried. A maximum surface temperature of 270 F (132 C) was measured. The monomer system (MMA, 1 percent BP, and 10 percent TMPTMA) was applied to a $^1/_4$-in. (6.35-mm) sand cover and soaked overnight for approximately 13 hours. Just before the monomer was applied, a cloudburst passed over the bridge and rainwater broke the dike that had been erected around the test area and wet most of the sand on the undried area. Only the nonwet area was treated with the monomer that was polymerized with steam heat. Cores taken from the sandblasted area indicated a polymer depth of about 1 in. (2.54 cm). The nonsandblasted, dried area was not successfully impregnated. This indicates the need to remove the linseed oil film. For this test, a light steel frame 24 in. (61 cm) high was used to support a tarpaulin enclosure for drying. Figure 6 shows the uncovered frame while sand is being spread over the slab. The same enclosure was used to contain the steam heat during curing.

A 4-in. (10-cm) core taken from the sandblasted, dried area has undergone 155 cycles of freeze-thaw testing. A steel ring was attached to the treated surface, and a $^1/_4$-in. (0.6-cm) depth of water is maintained on the specimen. No deterioration has been observed except minor surface scaling typical for all treated slabs during freeze-thaw tests.

One other field treatment has been attempted on an older bridge deck. The drying and monomer application steps apparently were quite successful, but polymerization was not achieved when continued malfunctions of the steam generator occurred and prevented the necessary slab temperatures from being attained.

EVALUATION OF SURFACE-TREATED SLABS

The performance of surface-impregnated concretes has been evaluated for freeze-thaw durability, resistance to water penetration, surface wear and abrasion, and skid resistance (3, 4). Long-term tests have been under way to evaluate the protection afforded reinforcement in polymer-impregnated slabs subjected to frequent applications of saltwater spray. Following is a summary of some of these evaluations.

Freeze-Thaw Behavior

A large number of specimens have been subjected to freeze-thaw tests to determine their durability. These specimens were tested with a ¼-in. (0.6-cm) depth of water ponded within a 7.8-in.-diameter (20-cm) steel ring bonded to the surface.

One series of specimens, treated under simulated field conditions, provided a good indication of the durability of surface-impregnated slabs that would be representative of less-than-ideal quality. These 1.0- × 1.0-ft (30- × 30-cm) specimens were sawed from 40- × 43- × 5.5-in.-thick (102- × 109- × 14-cm) slabs that had been cast, dried, and cured outdoors. The slabs were air dried for several months and then further dried with a heating blanket for a minimum of 3 days. The usual monomer system was applied to the slabs, which were covered with lightweight fine aggregate. Some were cured with heating blankets, and others were cured with ponded hot water. The low temperatures used for drying, which were typical for the earlier treatment processes in the study, produced polymer depths of ¼ to ¾ in. (0.6 to 1.9 cm). The color of the polymer was relatively light indicating a low polymer loading. This was due to the low drying and the high quality of the unimpregnated concrete that developed 6,400 psi (44 126 kPa).

The treatments are given in Table 1. Slabs 8 and 9 were treated with a second reactive monomer system consisting of MMA, 4 percent (wt) lauryol peroxide (LP), and 4 percent (wt) n, n-dimethyl-p-toluidine (DMPT), which polymerized in a short time and bonded the aggregate cover to the slabs. It was theorized that the lightweight aggregate topping would provide a skid-resistant topping that would also provide additional protection to the impregnated concrete. Figure 7 shows the control specimen after 40 cycles and a treated specimen after 120 cycles, which was the arbitrary limit of freeze-thaw cycles.

Horizontal strain measurements were made on the side of each of the freeze-thaw specimens by means of four stainless steel tabs bounded 8 in. (20 cm) apart, 1.25 cm (4.9 in.) above the bottom surface and 1.25 cm (4.9 in.) below the top surface. Measurements were made with an 8-in. (20-cm) Berri gauge when the slabs were frozen. The strain measurements indicated that eight of the field-treated specimens developed a contraction, 45 μin./in. (45 μm/m) greater in the top than in the bottom, and the control specimens averaged zero strain differential. The other two treated slabs (8 and 9) exhibited a contraction 120 μin./in. (120 μm/m) greater in the top. The greater contraction in the top is apparently due to the 30 percent higher coefficient of thermal expansion for polymer-impregnated concrete compared to that for unimpregnated concrete (1). For slabs 8 and 9, the even greater differential was probably caused by the high concentration of polymer in the 0.6-cm layer of intentionally bonded lightweight fine aggregate.

The strains in the top of the slab for the specimens impregnated with MMA are shown in Figure 8 as a function of the number of freeze-thaw cycles. Figure 8 shows that the strain measurements provide a good indication of the impending failure of a slab. The control specimens had an average strain of about 1,500 μin./in. (1500 μm/m) after only 20 cycles, although failure occurred at an average of 35 cycles. Although slabs 8 and 9 continued for 120 cycles, the volume instability as evidenced by the increasing strains and by cracking observed visually indicated that failure was imminent. Slab 10 developed a strain of about 1,000 μin./in. (1000 μm/m) at 55 cycles but then stabilized for the remainder of the testing. Moderate cracking and moderate water loss were noted during this period. A relatively large amount of monomer and a long soak time were used in the treatment of this specimen, and this indicates that durability is

Figure 5. Effect of steam curing time on polymer depth.

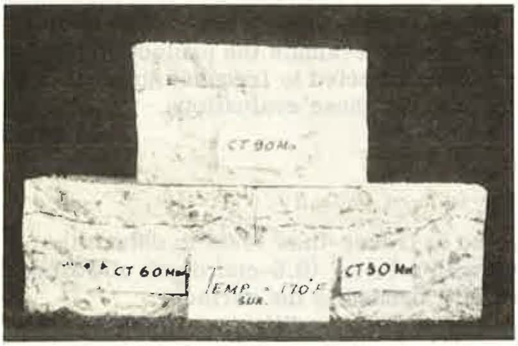


Figure 6. Application of sand cover to bridge deck.

Table 1. Freeze-thaw test treatments.

Slab Number	Monomer System	Quantity of Monomer (ml/m^2)	Soak Time (hours)	Soak Time Temperature (C)	Cure Method	Average Polymer Depth (in.)	Polymer Color	Maximum Freeze-Thaw Cycles
1	Control	—	—	—	—	—	—	30
2	MMA[a]	4280	10	23 to 34	HW[b]	0.25 to 0.75	Faint, uniform	120
3	IBMA[a]	3600	10	25 to 34	HW	0.75	Faint, uniform	91
4	IBMA[a]	4500	24	24 to 32	HW	0.5 to 1.5	Faint, uniform	117
5	IDMA[a]	2700	10	25 to 34	HW	0.25 to 0.5	Very faint, uniform	120
6	Control	—	—	—	—	—	—	40
7	IDMA[a]	3600	24	24 to 32	HW	0.25 to 0.5	Dark to faint	117
8	MMA[a] MMA[c]	6750 900	24	24 to 34	HW	0.5 to 0.75	Faint, uniform	120
9	MMA[a] MMA[c]	4500 1350	18	21 to 27	HB[d]	0.25 to 0.5	Faint, nonuniform	120
10	MMA	6750	24	24 to 32	HW	0.5 to 0.75	Faint, uniform	120
11	MMA	9900	18	21 to 27	HB	0.25 to 0.50	Faint, uniform	120
12	MMA	9900	24	20 to 28	HB	0.5	Very faint, uniform	120

Note: 1 in. = 2.54 cm.

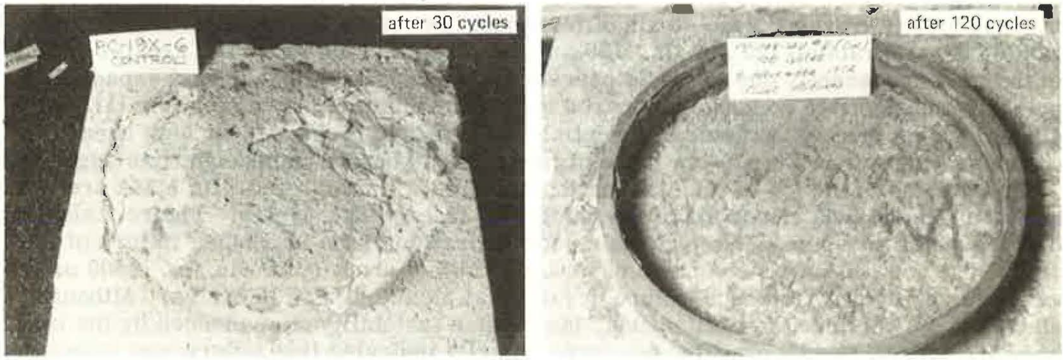
[a] Included MMA, 1 percent (wt) BP, and 10 percent (wt) TMPTMA.

[b] HW = hot water.

[c] Included MMA, 4 percent (wt) LP, 4 percent (wt) DMPT.

[d] HB = heating blanket.

Figure 7. Surface of freeze-thaw specimens.



not a simple function of monomer quantity or soaking time used. The other treated specimens indicated good volume stability.

The strain measurements have provided a more reliable measure of strain stability and freeze-thaw durability than visual observation alone, especially since surface scaling is not the primary mode of deterioration for treated specimens. Visual cracks were usually observed whenever the top strain exceeded about 1,000 μin./in. (1000 μm/m). It may be reasonable to define the durability range of the concrete as the number of cycles below which the top strain does not exceed a certain value, say 750 μin./in. (750 μm/m).

Other freeze-thaw tests on specimens in which good polymer impregnation was achieved also indicate good durability. Reinforced specimens with reinforcement in the bottom and in the top and bottom are still in progress after 150 cycles. But the tests on the marginal-quality field-treated specimens are significant because good improvements were obtained over the unimpregnated controls.

Corrosion Protection

Reinforced companion slabs were treated at the same time and with the same treatments as given in Table 1. These slabs [also 40- × 43-in.-thick (102- × 109-cm) slabs] were sprayed with salt water twice daily, 5 days a week, for 20 months to determine the protection against corrosion provided by the surface polymer impregnation. The No. 8 bars had a nominal 1-in. (2.54-cm) cover. After the tests were terminated, the bars were removed and measured to determine the corroded area.

The treated slabs had the same quality of polymer impregnation as given in Table 1. The reinforcing near the edges of the slab, which were not sealed against water intrusion, indicated some corrosion. But considering only interior bars and not the outer 3 in. (7.62 cm) of each interior bar, the bars from the treated slabs had an average of only 1.1 percent of corroded surface area compared to 27.0 percent for the corresponding bars from the unimpregnated controls. The fact that the treated slabs do not represent the quality of polymer impregnation that can now be achieved makes the results even more significant. Studies are in progress to determine the chloride content in the concrete.

Skid Resistance

The skid resistance of PIC was of considerable interest since it was not initially known if the polymer impregnation would result in a surface with a lower frictional resistance. A series of 2-in.-thick (5.08-cm) trapezoid-shaped slabs, including controls, was placed in the Texas Highway Department wear track facility. The facility has a 10-ft-diameter (3-m) test track over which a nongrooved tire mounted at each end of a weighted beam was driven at 10 mph (16 km/h). Periodically the tire loading was stopped while surface friction measurements were made with the British portable tester (BPT) in accordance with ASTM E 303-69.

Typical skid numbers as a function of wear track loading revolutions are shown in Figure 9. Skid resistance increases with the skid number. For the first 70,000 revolutions (140,000 wheel passes), the slabs were kept dry. An additional 140,000 revolutions were made under wet conditions, and No. 46 silicone carbide grit was used as a wearing agent. Immediately after the grit was applied, the surface was abraded and resulted in a higher short-term skid resistance for all slabs.

Throughout the testing, all treated slabs developed skid numbers, as high as or higher than the controls, that indicate no loss in skid resistance due to polymer impregnation. In fact, before the grit was applied, the skid numbers were significantly higher for the treated slabs. The highest skid resistance was achieved by treating the specimen with the lightweight aggregate topping intentionally bonded to the surface as was previously described for specimens 8 and 9 in the freeze-thaw tests.

During the wear track tests, depth-of-wear measurements were made across the

Figure 8. Top strains of freeze-thaw specimens in frozen state for MMA-treated specimens.

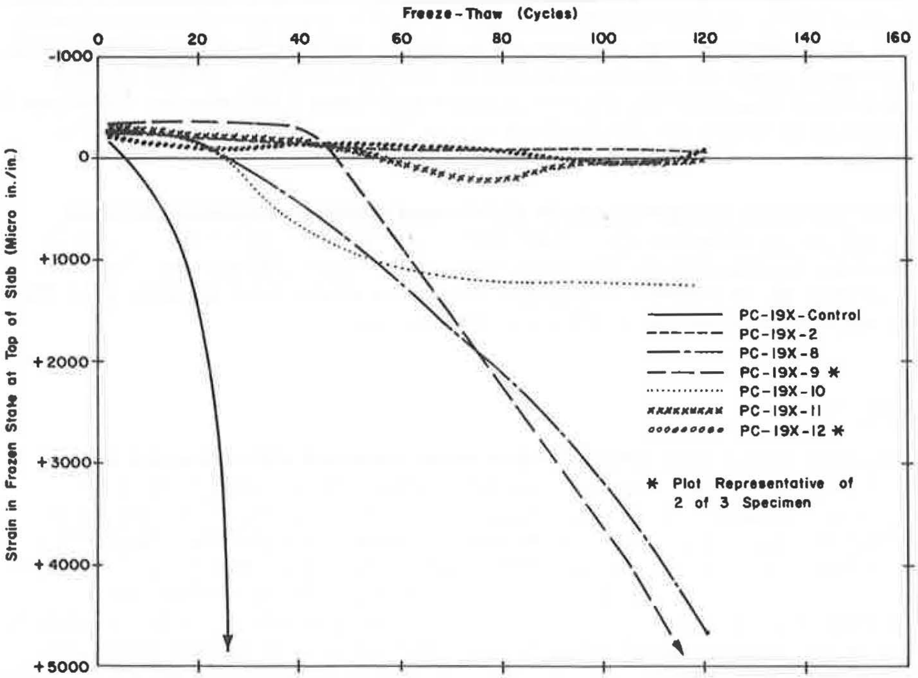
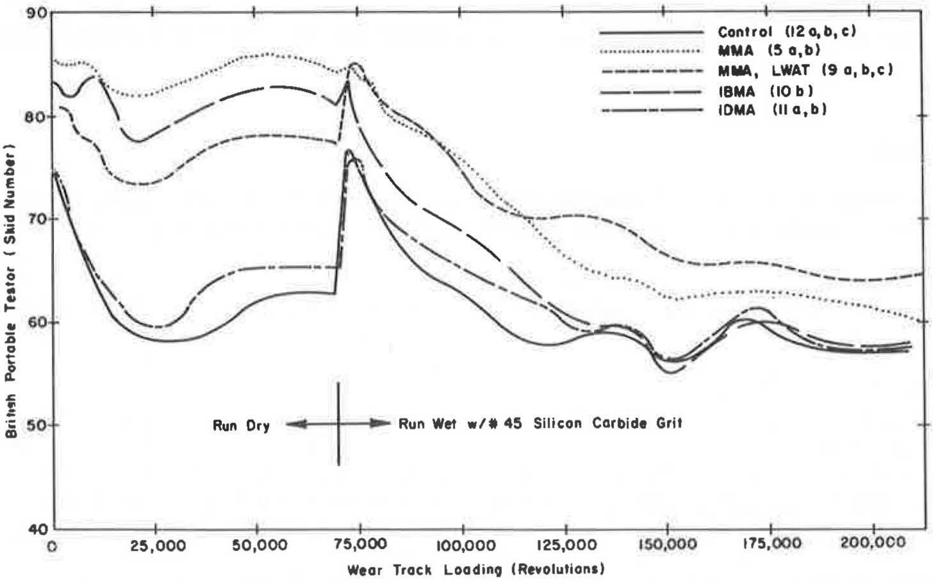


Figure 9. Skid numbers from wear track tests.



wheel path on each test slab. These measurements provided a measure of the cross section worn away during the tire loading. There was no appreciable difference in wear between the controls and treated slabs except for the specimens with the lightweight aggregate topping. After the grit was applied, the wear in these slabs was more than twice as great as that in the other specimens.

CONCLUSIONS

Partial polymer impregnation of concrete can be accomplished by properly drying the concrete, impregnating it with an appropriate low-viscosity monomer solution, and curing it with external heat. A limited test treatment on a bridge deck has confirmed the validity of the process.

Extensive evaluations of partially impregnated slabs have shown that

1. The freeze-thaw resistance is significantly increased,
2. Corrosion of reinforcing in PIC slabs is about 5 percent of that found in unimpregnated slabs,
3. Skid resistance is lower and in some cases higher than for control slabs, and
4. Wear is generally about the same for both control and impregnated concrete.

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The contents of this paper reflect the views of the authors, who are responsible for the facts and the accuracy of the data presented. The contents do not necessarily reflect the official views or policies of the Federal Highway Administration. This paper does not constitute a standard, specification, or regulation.

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POLYMER CONCRETE FOR REPAIRING DETERIORATED BRIDGE DECKS

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One of the most severe problems facing the highway industry is the rapid deterioration of highway structures. As part of a concerted effort to solve this problem, research is being performed to determine if polymer-concrete materials can be used for the repair of deteriorated and delaminated bridge decks. Polymer concrete consists of an aggregate mixed with a monomer, which is subsequently polymerized in place. It is mixed and placed by using techniques similar to those used for portland cement concrete and, after curing, produces a high-strength, durable material. Process variables studied include monomer type, aggregate size distribution, and polymerization method. Field testing of polymer concrete has been in progress for almost 3 years, and to date deterioration has not been observed. One test on a major arterial highway in New York City has been in progress for 7 months. Based on the success obtained in this experiment and in concurrent laboratory evaluations, further work on the same highway was scheduled for September 1974. These data are summarized.

•FOUR distinct types of material for repairing deteriorated bridge decks are being investigated as a joint effort between Brookhaven National Laboratory (BNL) and the U.S. Bureau of Reclamation (USBR). They are

1. Polymer concrete (PC), which consists of an aggregate mixed with a monomer and which is subsequently polymerized in place;
2. Polymer portland cement concrete (PPCC), a premixed material in which monomer is added during the mixing of water, portland cement, and aggregate and which is subsequently polymerized in place;
3. Polymer-impregnated concrete (PIC), which consists of cured portland cement concrete (PCC) impregnated by a monomer system and which is subsequently polymerized in situ; and
4. Surface-impregnated, cured portland cement concrete.

For each of these main types of material, process variations can be exercised, and variations in properties and characteristics will result.

The main, and most successful, effort in improving the structural and durability properties of PCC has been with PIC. Several reports describing the preparation and testing of these materials have been published (1, 2, 3, 4, 5, 6, 7); these have generated worldwide interest, and research is currently in progress at many laboratories (8). The work has advanced from the determination of basic material characteristics and methods for producing the composite to the design and testing of prototypes and full-sized sections for specific applications.

During the past 3 years, considerable success has been achieved at BNL and USBR in the development of PC. Methods to produce specimens with polymer contents and properties that approach those of PIC have been developed (5). As a result of the premixed nature of the material, the ability to rapidly cure it over a wide range of temperature, and its excellent properties, PC appears to have many potential applications. In Japan, PC pilings, 3 ft wide × 45 ft long (1 × 15 m), and precast manholes are marketed commercially (9). One Japanese firm is reported to produce 4,000 pilings/month. It has also been reported that PC pipe is being produced in Australia (10, 16).

Current work at BNL is to evaluate PC as a patching material for use in the rapid repair of holes in bridge decks and pavements. It may also be possible to use the high-strength PC to enhance the structural characteristics of the decks. The methods for producing these materials, their properties, and the results of field tests are described in this paper.

PRODUCING POLYMER CONCRETE

Monomer Selection

The important considerations in the selection of a monomer system for use in PC include cost, durability under anticipated exposure conditions, adhesion to aggregate, and the ability to be polymerized predictably at ambient temperature by promoter-catalyst techniques. Low vapor pressure is also an important characteristic since it results in reduced evaporation losses and minimizes safety problems.

Two monomer systems that have been studied extensively at BNL are methyl methacrylate (MMA) and polyester-styrene. It is expensive to polymerize MMA alone in a predictable manner by using promoter-catalyst techniques, but, with this exception, both materials meet the selection criteria given above. The polymerization problem can be overcome by the addition of a polyfunctional monomer such as trimethylpropane trimethacrylate (TMPTMA) to the MMA. This results in a greatly enhanced polymerization rate and produces a cross-linked polymer with increased temperature and solvent resistance. Based on this finding, two monomer systems, 95 percent (wt) MMA-5 percent (wt) TMPTMA and 54 percent (wt) polyester-46 percent (wt) styrene are currently being used in laboratory and field tests. Polymerization conditions for these systems and several other monomer mixtures are given in Table 1.

Mix Design

The design of a mix to optimize the properties of PC is largely accomplished by aggregate gradation to give a void volume that will require minimal amounts of monomer to fill the voids and to give good workability to the mix. This work has been described by many authors (4, 5, 11, 12, 13, 14, 15). Generally, the aggregate should be dried before it is used. Some epoxy resins are less affected by moisture, and, therefore, the drying conditions are less stringent. The major mix variables are maximum particle size, gradation, and composition. Crushed stone and natural sand and gravel are generally used. Finely divided materials such as portland cement, powdered chalk, clay, fly ash, and silica have also been used. Test results indicate that aggregate type and composition do not significantly influence the strength properties of the mix (15) but do affect the durability (16). Aggregate gradation and maximum particle size influence the amount of resin required to coat the filler particles and to fill the voids. Tests have indicated that for a well-graded filler larger maximum particle sizes require less resin. Gap grading also tends to reduce the amount of resin required. Conversely, smaller maximum particle sizes produce higher strength mixes. At USBR (5), an aggregate size distribution has been developed that when mixed with 7 to 8 percent (wt) MMA produces specimens with compressive strengths of ~19,000 psi (131 000 kPa). BNL work has indicated that dense-graded aggregate mixes of the type used in asphalt concrete (Table 2) will produce composites with a strength of 13,000 psi (89 630 kPa) when mixed with 9 percent (wt) of an MMA-TMPTMA monomer system (7).

The monomer content of the mix, a dependent variable, is the minimum necessary to coat the aggregate and to fill the voids. Excess monomer will bleed to the surface because of the low density relative to the density of the aggregate. Monomer concentrations ranging from 5 to 30 percent (wt) have been reported. The former was obtained in a pipe when a compaction method that involved pressure, vibration, and centrifugal force was used on a graded aggregate and filler (16).

Fabrication

The batching, mixing, and placing techniques for producing PC are, to a great extent, based on the adaptation of existing equipment and methods for producing PCC. However, volatile and potentially explosive monomers, such as MMA, require nonsparking and explosion-proof equipment. Mixing should be done in a closed system or outdoors in a well-ventilated area. Some of the chemicals may be irritants or toxic and should be handled safely.

The PC mix is cast into forms or molds in a manner similar to that used for conventional concrete. Wood, steel, glass, and paper molds have all been used successfully. A great variety of mold-releasing agents such as silicone gels, vegetable oils, automobile wax, and paraffins, have also been used.

After the mix is placed, it should be consolidated by external vibration, rodding, mechanical pressure, or application of vacuum to remove entrapped air.

Polymerization

Curing of PC may be performed by radiation, thermal-catalytic, or catalyst-promoter methods (7). Curing times may be varied between a few minutes and several hours, and full strength is attained when polymerization is completed.

If the PC is to be cured at ambient temperature by promoter-catalyst techniques, these materials in concentrations generally ranging between 0.5 and 2 percent (wt) of the monomer are added to the monomer prior to mixing with the aggregate. Materials used are given in Table 1.

Laboratory Testing

When compared to the extensive testing program (at BNL and USBR) that was performed to determine the properties of PIC, the PC evaluation effort has been small. To date, only a few of the mechanical and durability properties have been measured.

One detailed evaluation was performed at USBR (5). Initially, a graded, sand-aggregate mix closely approximating that of PC (1) was integrally mixed by hand with catalyzed MMA and was polymerized at 158 F (70 C). The heat generated during polymerization of these specimens was quite high, and as a result the samples developed relatively low compressive strengths from 8,000 to 12,000 psi (55 160 to 82 740 kPa). Subsequent work on the method and incremental temperature control during polymerization resulted in more consistent specimens with compressive strengths of 11,000 to 12,000 psi (75 840 to 82 740 kPa). The addition of cross-linking and coupling agents, glass-fiber reinforcement, and a change to α tert-butylazoisobutyronitrile catalyst improved the strength to 14,800 psi (102 000 kPa).

Development of the method continued until in its present form oven-dried, Clear Creek aggregate was machine-mixed with the monomer system, placed in molds, and polymerized at room temperature by the promoter-catalyst technique. The specimens are prepared with 7 to 8 percent monomer by total weight of the wet mix. Based on the maximum size of the aggregate and the amount of cross-linking agent in the monomer system, the specimens develop average compressive strengths varying from 18,400 to 20,000 psi (126 860 to 137 900 kPa). These mixes have produced consistent specimens with individual strengths that vary <2 percent from the mix average.

USBR specimens prepared by using conventional concrete-mixing procedures and room-temperature polymerization have been tested for compressive stress-strain, tensile splitting, unit weight, specific gravity, and water absorption (Table 3). Other specimens were exposed to a 5 percent H_2SO_4 solution for two months without any

Table 1. Promoter and catalyst systems for monomer mixtures.

Monomer Mixture (percent)	Viscosity at 77 F	Catalyst	Catalyst Concentration, Percent (wt)	Promoter	Promoter Concentration, Percent (wt)	Ambient Temperature (F)	Gel Time (min)	Cure Time (min)
MMA	0.5	Bzp + AIBN	0.5/0.5	DMA + DMT	0.5/0.5	77	20	60
95 MMA-5 TMPTMA	~1.0	Bzp + AIBN	1.0/1.0	DMA + DMT	1.0/1.0	77	15	36
95 MMA-5 TMPTMA	~1.0	Bzp	2.0	DMA	2.0	82	20	38
70 MMA-30 TMPTMA	1.9	Bzp	1.0	DMT	1.0	77	8	14
90 styrene-10 TMPTMA	~1.0	Bzp	1.0	DMA	1.0	106	—	—
90 styrene-10 TMPTMA	~1.0	Bzp	2.0	DMA	2.0	106	50	1,050
85 styrene-15 TMPTMA	~1.2	Bzp	2.0	DMA	1.0	106	30	220
60 styrene-40 TMPTMA	1.7	Bzp	1.0	DMA + DMT	0.5/0.5	77	15	45
75 styrene-25 polyester	2.4	MEKP	1.0	CoN	0.4	60	53	<120
54 polyester-46 styrene	~100	MEKP	1.0	CoN	0.75	70	20	35

Note: 1 F = 1.8 (C) + 32. Bzp = benzoyl peroxide, AIBN = azobisisobutyronitrile, CoN = cobalt naphthenate, DMA = dimethyl aniline, DMT = dimethyl toluidine, and MEKP = methylethyl ketone peroxide.

Table 2. Sieve analysis for aggregate used in Brookhaven National Laboratory polymer concrete.

Sieve Size	Percent Passing Sieve Size	Sieve Size	Percent Passing Sieve Size
¾ in.	94.8	No. 16	37.1
½ in.	83.1	No. 30	30.5
⅜ in.	78.1	No. 50	11.0
¼ in.	61.6	No. 100	2.6
No. 4	51.8	No. 200	1.2
No. 8	40.9		

Table 3. Property tests on 6- x 12-in. (15- by 30-cm) polymer concrete cylinders.

Test	Temperature (F)	Result
Tensile splitting strength[a], psi	-15	1,510
	70	1,430
	190	1,370
Compressive strength[a], psi	-15	24,800
	70	19,600
	120	15,800[b]
	190	14,100
Modulus of elasticity[a], psi	-15	6.11×10^6
	70	5.28×10^6
	190	4.44×10^6
Poisson's ratio[a]	-15	0.24
	70	0.23
	190	0.22
Elastic limit stress[a], psi	-15	14,000
	70	7,500
	190	4,800
Ultimate compressive strain, μin./in.	-15	5,360
	70	7,080[c]
	190	>8,000
Unit weight[a], pcf	—	149.1
Specific gravity[a]	—	2.40
Water absorption[c], percent	—	0.6

Note: 1 F = 1.8 (C) + 32. 1 psi = 6.895 kPa. 1 μin./in. = 1 μm/m. 1 pcf = 1.602 kg/m³.

[a] Average values for three specimens.

[b] Value for single specimen.

[c] Average value for two specimens.

apparent effect on their properties.

Creep tests have also been performed on PC specimens containing MMA. The tests were conducted on 6- × 12-in. (15- × 30-cm) cylinders that were subjected to compressive stresses of 800, 1,301, and 3,938 psi (5515, 8970, 27 150 kPa) for 63 days. The stresses were ~5, 8, and 24 percent respectively of the ultimate compressive strength. After 63 days, the specimens exhibited less creep than normal weight concrete. The unit creep deformation [(μin./in./psi)(μm/m/Pa)] of PC specimens under the 3,938-psi (269 160-kPa) compressive load was close to that of unimpregnated PC under a compressive load of 2,313 psi (15 948 kPa).

PC development work at BNL has focused primarily on highway applications: for repairing holes or as an impervious overlay on bridge decks. Criteria considered essential for these applications are the ability of PC to be mixed and placed conventionally, its rapid predictable polymerization rates over a wide range of temperatures, high strength, and good bonding.

Several studies were performed to select aggregate size distributions that would produce high-strength, low-porosity materials. To date, the best results have been obtained by using a dried, dense-graded aggregate mix such as that used on Long Island in asphalt concrete. A sieve analysis for this material is given in Table 2.

Experiments were performed by using the MMA-TMPTMA and polyester-styrene monomer mixtures. The results indicate that high-strength materials [compressive strengths >10,000 psi (68 900 kPa)] with low water absorptions (<0.5 percent) can be produced with polymer concentrations of 9.1 percent (wt). The water absorptions are similar to those of PIC.

Shear tests have been performed to determine the bonding characteristics of PC when applied to steel or sound concrete surfaces. Two monomer systems, 60 percent (wt) styrene-40 percent (wt) TMPTMA and 53 percent (wt) polyester-28 percent (wt) styrene-19 percent (wt) TMPTMA, were used to produce PC that was applied as ¾-in.-thick (1.9-cm) liners on 6- and 8-in.-wide (15- and 20-cm) steel pipe. A shear strength of 1,100 psi (7584 kPa) was measured for PC applied to sandblasted steel surfaces, and 400 psi (2758 kPa) was obtained for samples that had not been sandblasted.

Cores taken from concrete specimens that contained 6-in.-thick (15.2-cm) PC overlays were subjected to shear strength measurements. Bond strengths at the PC-concrete interface of >1,000 psi (6895 kPa) are normally obtained.

Preliminary tests to determine the coefficient of thermal expansion for PC have been performed. PC specimens containing a 15 percent concentration of 75 percent (wt) styrene-25 percent (wt) polyester exhibited an average value of 8.2 μin./in./F (8.2 μm/m/-17.2 C). It is expected that the coefficient will decrease as polymer concentration decreases. Measurements made at USBR (1) on unimpregnated normal weight concrete and PIC containing 5 percent (wt) styrene indicated values of 4 and 5 μin./in./F (4 μm/m and 5 μm/m/-17.2 C) respectively.

The largest laboratory tests performed at BNL consisted of pouring a series of 4- × 4- × 1-ft (1.2- × 1.2- × 0.3-m) slabs. This work was performed to support the field experiments described later. PC containing 13 percent (wt) of a 95 percent (wt) MMA-5 percent (wt) TMPTMA monomer mix and 10 percent (wt) of 54 percent (wt) polyester-46 percent (wt) styrene was used. The materials were mixed and placed conventionally. Both systems cured in <60 min, and essentially no shrinkage was observed. Cores taken from the MMA-TMPTMA PC indicated compressive and shear strengths of 9,600 psi (66 190 kPa) and 2,175 psi (14 996 kPa) respectively. A similar compressive strength, 9,730 psi (67 085 kPa), was obtained for the polyester-styrene PC. Water absorption measurements on both materials indicated values <1 percent. After 150 cycles of freeze-thaw testing, no deterioration was apparent.

FIELD EVALUATION OF POLYMER CONCRETE

Preliminary field testing of BNL-prepared PC has been in progress for almost 3 years. Initially several potholes in a road leading to a receiving depot at BNL were filled with polyester-styrene PC. Since that time, several patches have been made on bridges located at Sag Harbor and Greenport, New York (7).

Based on the results obtained in the preliminary field experiments, PC was used in New York City to repair a badly deteriorated section of a bridge. The work, which was conducted as a joint venture of the New York State Department of Transportation, the New York City Arterial Highway Maintenance Department, and BNL, involved filling a 3- × 10- × 1.25-ft (1- × 3- × 0.4-m) hole through the bridge on the Major Deegan Expressway at Third and Lincoln Avenues in the lower Bronx (Figure 1). The high traffic densities in this area (~85,000 vehicles/day) prevent closing of a lane for more than 5 hours. Because conventional repair methods could not be used, the hole had been covered with a steel plate.

On December 4, 1973, one lane was closed while the form work was prepared. The hole was filled on December 6 with a PC consisting of 13 percent monomer [95 percent (wt) MMA-5 percent (wt) TMPTMA] and 87 percent of the dense-graded aggregate (Table 2). Because of an ambient temperature of ~50 F (10 C), 2 percent (wt) benzoyl peroxide was used as the catalyst and a mixture of 2 percent (wt) dimethyl aniline and 1 to 2 percent (wt) dimethyl toluidine as the promoter. A silane coupling agent was added at a concentration of 1.5 percent to enhance bonding to the adjacent concrete. Mixing and pouring were completed in 1 hour by using conventional equipment. Polymerization was complete within 1 hour, at which time the side forms were removed. The completed patch is shown in Figure 2. After 1 hour, estimates of the compressive strength made by using a Windsor probe indicated values between 5,400 and 8,000 psi (37 230 and 55 160 kPa). The measured compressive strength of a cylinder cast from the same mix was 12,200 psi (84 116 kPa), and the water absorption was 0.4 percent. At 3:00 p.m., 5 hours after work was started and 2 hours after the pour was completed, the lane was reopened to traffic. The top and underside of the section have been inspected on a routine basis. After 7 months in service, essentially no changes have been noted. Based on the results from this test, work to repair five larger holes in the bridge was scheduled for September 1974.

COST ESTIMATES FOR POLYMER CONCRETE

As a result of the limited number of small-scale field tests that have been performed to date, only the material costs associated with the use of PC have been determined. Attempts to determine placement and traffic control costs will be made in conjunction with repair work scheduled on the Major Deegan Expressway in September 1974.

Since the required formwork and the placement techniques for PC are essentially the same as those used for PCC, installation costs should be similar. Traffic control costs will be significantly lower because of the shorter cure time. Future maintenance costs should also be reduced.

The cost for the materials used in the first test on the Major Deegan Expressway was \$302/yd^3 (\$392.60/m^3). Of this total, \$77 was directly attributable to the low ambient temperature [50 F (10 C)] during placement, which necessitated the use of 1.25 percent (wt) dimethyl toluidine [\$9.50/lb (\$20.90/kg)] in conjunction with 2 percent (wt) dimethyl aniline [\$1.50/lb (\$3.30/kg)] as the promoter and 2 percent (wt) benzoyl peroxide [(\$1.26/lb (\$2.77/kg)] as the catalyst. For temperatures >70 F (21 C), 1 percent (wt) benzoyl peroxide and 1 percent (wt) dimethyl aniline would be sufficient to produce complete polymerization in <60 min.

Further reductions in cost can be obtained by use of polyester-styrene. As indicated above, PC containing 10 percent (wt) of a 54 percent (wt) polyester-46 percent (wt) styrene mixture produced compressive strengths of 9,730 psi (67 090 kPa) in <60 min. Polymerization conditions for the mixture were given in Table 1. Based on a current price of \$0.37/lb (\$0.81/kg) for the polyester-styrene, the materials for this mix can be obtained for \$170/yd^3 (\$221/m^3).

Compared to the cost of PCC, PC is expensive, and as a result it will probably not be used as a general substitute for concrete. There are, however, many specific applications for which the properties of concrete are inadequate. One such application would appear to be as a specialized bridge deck or pavement patching material. For

Figure 1. Hole in Major Deegan Expressway before filling with polymer concrete.

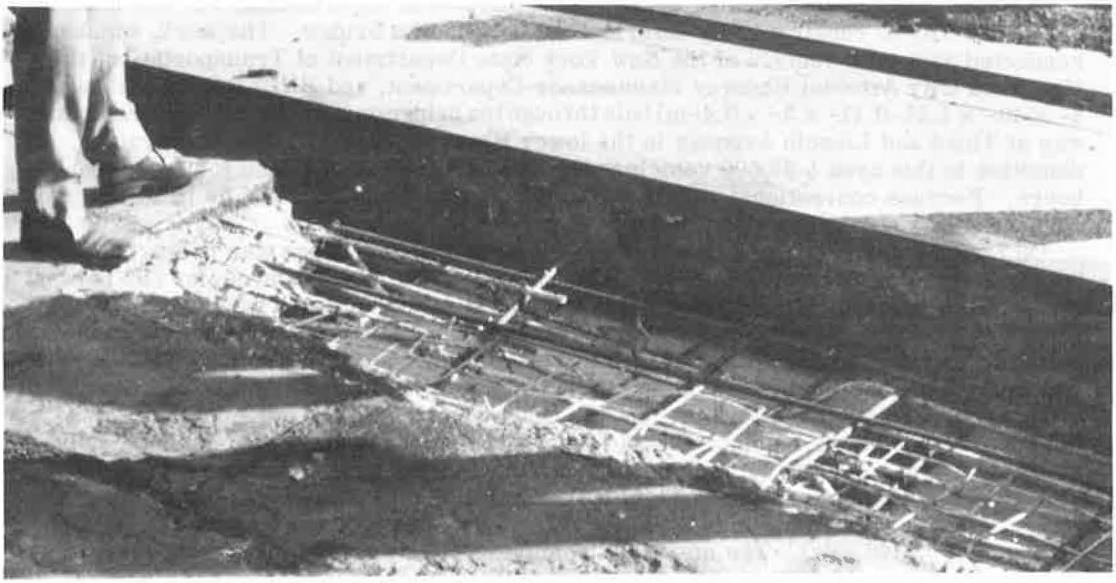
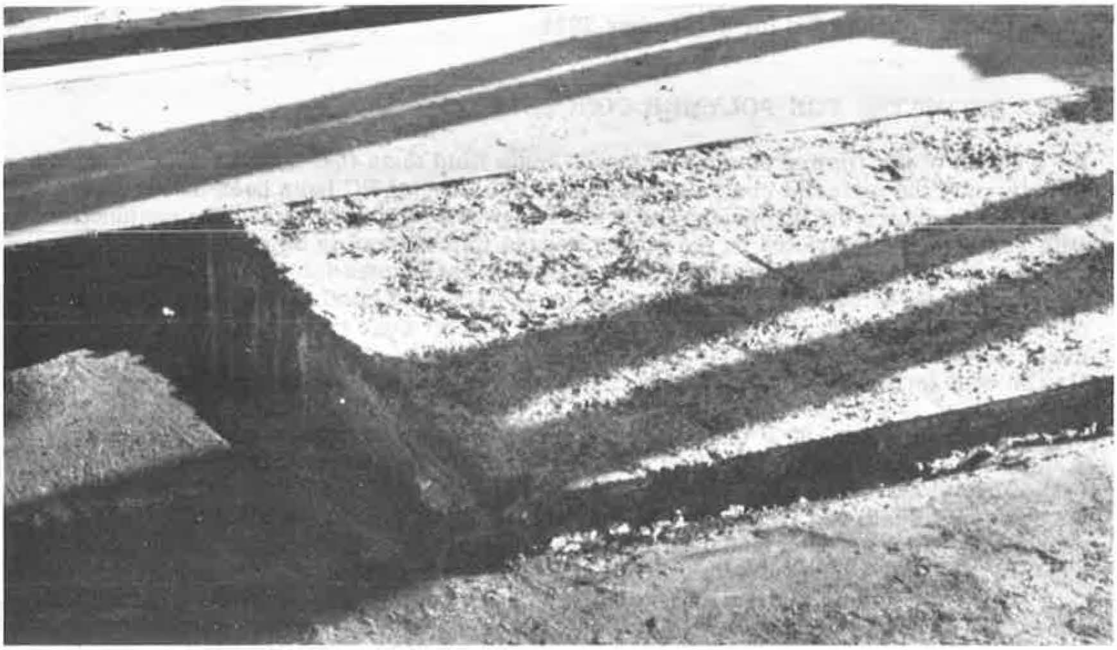


Figure 2. Completed polymer concrete patch on Major Deegan Expressway.



these applications, the high-strength, rapid-curing characteristics and good durability will result in minimum traffic delays and improved safety and in some cases may eliminate the necessity of constructing expensive detours. In these cases, the material cost becomes insignificant.

CONCLUSION

Polymer-concrete has the potential of combining the premix characteristic of PCC with strength and durability properties approaching those of PIC. As a result of the premixed nature of the material, its quick cure time at ambient temperature, and high strength, PC appears suited for use in the repair of highway structures where traffic conditions allow closing of the area for only a few hours.

Field testing of materials containing MMA-TMPTMA and polyester-styrene has been in progress for almost 3 years, and to date no detrimental effects have been noted. The most severe test was performed on the Major Deegan Expressway in New York City where a 3- × 10- × 1.25-ft (1- × 3- × 0.4-m) hole through a bridge deck was filled with a PC containing 13 percent (wt) of a 95 percent (wt) MMA-5 percent (wt) TMPTMA mixture. Polymerization was completed within 1 hour, and traffic was restored 2 hours after completion of the pour. After 7 months in service, no deterioration was apparent. Hopefully, the use of PC has resulted in a permanent repair to the bridge deck. All of the work was confined to the non-rush-hour period and therefore minimized the inconvenience to the traveling public to a few hours rather than for several days. With further PC experience, the repair time could undoubtedly be reduced.

When compared to the material cost for PCC, PC is expensive: \$170 to and \$302/yd^3 (\$221 to \$392.60/m^3). Installation costs should be essentially the same as for conventional concrete. Since the material cost represents only a small part of the total repair cost on major highways, where traffic conditions impose severe limitations on the type of repairs that can be made or require the construction of expensive detours, the use of a more expensive PC to make a permanent repair may be cost effective.

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INNOVATIONS IN IMPREGNATION TECHNIQUES FOR HIGHWAY CONCRETE

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Corrosion of reinforcing steel due to the penetration of deicing salts poses a considerable problem in bridge decks. One approach that has received much attention has been impregnation of the bridge deck with a liquid monomer followed by polymerization to effectively seal the capillary pores against salt intrusion. This approach is technically feasible in the field. The present impregnation techniques, however, are costly in terms of energy, materials, and time, and simplifications and improvement would be desirable. In this paper, results are described of preliminary experiments with sulfur, tar, and mixtures of the two as surface impregnants and with a pressure-mat technique for mechanically assisting monomer or sealant penetration. It is shown that the impregnation of portland cement concrete and mortar by molten sulfur, tar, and an 80:20 mixture of the two yields significant reductions in moisture absorption and increases in strength and that, in the case of concrete slabs, predrying may not be necessary. It is also shown that pressure mechanically applied to patterned rubber mats can effect uniform impregnation with a monomer such as methyl methacrylate or with a sealant such as tar or linseed oil. Such an impregnation could conceivably be effected by using rollers. Thus, initial feasibility of two potential improvements in concrete impregnation processes has been demonstrated.

•EVERY highway department is confronted with the problem of deterioration of concrete bridge slabs. The extensive use of deicing salts induces corrosion of the reinforcing rods and consequent spalling; alternate freezing and thawing compound the problem. Because polymer-impregnated concrete (PIC) (1-20) effectively resists water and salt penetration, and hence freezing and thawing, several research programs have been initiated to apply it to bridge decks in the hope of forestalling or arresting corrosion of the steel by salts and improving strength and abrasion resistance. Other approaches are also under investigation (21). Brookhaven National Laboratory and the U.S. Bureau of Reclamation (1, 2, 3, 5) and the University of Texas (7, 8) showed that surface penetrations [up to 2 in. (5 cm)] of decks could be achieved within a reasonable time by surface-drying and monomer-ponding techniques. The goal of the research at Lehigh and Pennsylvania State Universities (6), however, has been to achieve a 4-in. (10-cm) penetration in sound, salt-contaminated decks that will envelop the steel, seal the pores, and immobilize the salt already present. Such deep penetration has now been demonstrated recently, at least on a small scale (13, 17, 18).

There is considerable room for simplification and improvement of the overall process so that time and cost can be reduced. The purpose of this paper is to describe successful preliminary experiments with two new approaches: (a) a pressure-mat technique for impregnation with organic and other materials and (b) sulfur as an impregnant. This paper also discusses other nonmonomeric materials for hot impregnation.

PRESSURE-MAT TECHNIQUE

Laboratory Experiments

Preliminary impregnation experiments were conducted by using a patterned, flexible rubber pressure mat with methyl methacrylate (MMA), tar (AASHO M-214-65), undiluted boiled linseed oil, and water as impregnants. The technique involves entrapment of the liquid in the cells of the mat and mechanically pressured impregnation of the concrete with the trapped liquid.

Concrete Slab Fabrication

Three 2.0- × 2.0- × 0.5-ft (61- × 61- × 15-cm) concrete slabs were cast from a conventional non-air-entrained mix [water, type 1 portland cement, coarse ≥1-in. (2.5-cm) sand, and limestone aggregate in proportions of 1.00:1.92:6.10:6.75] that had a cement factor of 485 lb/yd^3 (286 kg/m^3) and a 28-day average compressive strength of 4,750 psi (33 MPa). The measured air content was 3 percent, and the slump was 2.5 to 3.0 in. (6.4 to 7.6 cm). The slabs were troweled and cured in a fog room (90 to 100 percent relative humidity) for at least 28 days before they were used. All slabs contained a nominal steel reinforcement at a 4-in. (10-cm) depth. Slabs 1, 2, and 3 were oven dried at 250 to 260 F (121 to 127 C) for 45 hours and cooled overnight before use. Slabs 4, 5, and 6 were dried more rigorously: (a) by a propane torch (17) for 15 hours [maximum surface temperature = 750 F (399 C)] and (b) for 10 hours in an oven at 650 F (343 C).

Impregnation

For the initial experiment, a used, 16- × 20-in. (41- × 51-cm) patterned doormat was used (Figure 1). In subsequent experiments, specially molded neoprene rubber mats (durometer hardness = 70) with similar patterns were used. As shown in Figure 2, a hydraulic tester was used to apply the pressure to a steel loading plate slightly smaller than the mat. A steel frame sealed and clamped to the slab was used as a diked reservoir.

During each load cycle, the load was increased from 0 to 30 kips (133 kN) over a 15.5- × 15.5-in. (39.4-cm × 39.4-cm) area [or from 0 to 125 psi (0 to 0.86 MPa)] within 22 sec and then released within 8 sec. A 30-sec break-in period before reloading was provided to simulate the passage of a roller over a particular cross section of a mat. At peak pressure, liquid squirted out through a small side crack in the slab. This indicated that there was efficient pressure in the diamond-patterned cells. During the pressurization cycle, the liquid level in the framed area rose slowly as the rubber mat was squeezed by the loading head. When the load was released, the liquid level in the dike immediately dropped as the liquid rushed under the mat and filled the cells in readiness for the next load cycle. Figure 3 shows the load cycles used for slabs 1 and 2 (impregnated with MMA and water), and Figure 4 shows the cycle used for slabs 3, 4, 5, and 6 (impregnated with MMA, tar, and linseed oil). Impregnation data are summarized. The rubber mat in slab 1 (MMA) was attacked by the MMA after several hours. In subsequent experiments, however, neoprene mats proved to be quite resistant to MMA.

Polymerization

After impregnation, slabs 1 and 3 were mounted on a pedestal, an insulated steam chamber was placed on top (18), and steam was applied for 6 hours. Before the chamber was mounted, some excess monomer [about 1 lb (2 kg)] was sprinkled over several pounds

Figure 1. Rubber pressure mat.

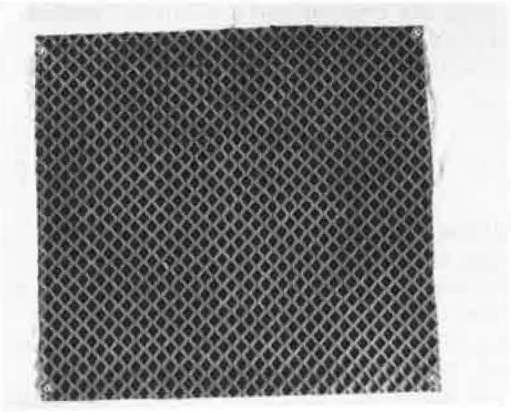


Figure 2. Experimental setup for pressure-mat impregnation.

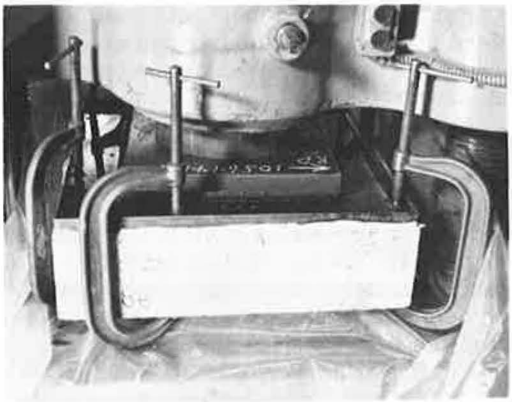


Figure 3. Loading and unloading cycles for slabs 1 and 2.

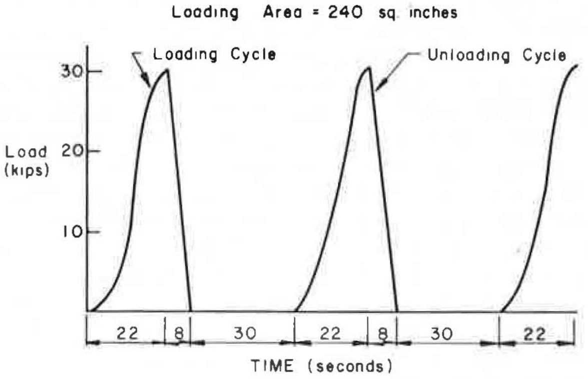


Figure 4. Loading and unloading cycles for slabs 3 and 4.

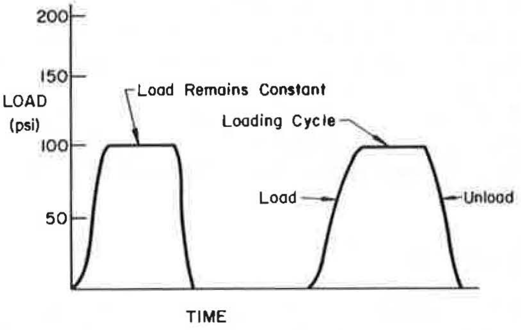


Table 1. Pressure-mat impregnation data.

Slab	Impregnant	Uptake (lb)	Maximum Penetration[a] (in.)	Cycles	Effective Time (hour)	Maximum Pressure (psi)
1	MMA	6	3.5 to 4.0	425	3.2	120
2	Water	7	4.0 to 4.5	710	5.0	100
3	MMA	6	3.5 to 4.0	62[b]	4.0	100
4	Tar	4	2.5 to 3.0	80	5.3	100
5	Tar	3	2.5 to 2.8	160	5.3	100
6	Linseed oil	2	1.0 to 1.5	90	6.0	100

Note: 1 lb = 2.2 kg. 1 in. ≈ 2.5 cm. 1 psi = 6895 Pa.

[a] Corresponds to dense impregnation as observed.

[b] Slabs 3 and 4: 30-sec loading and unloading times, 4-min dwell time. Slabs 5 and 6: 15-sec loading and unloading times, 2-min dwell time.

of cement leveled evenly on the slab area so that loss of monomer by evaporation could be minimized. Aluminum foil was then placed over the cement and a neoprene gasket placed between the chamber and slab. The steam pressure was 6 to 10 psi (41 to 69 kPa) at the propane-fired pressure cooker source; the surface temperature of the slab was 220 F (104 C).

Discussion of Results

As given in Table 1, a 6-in. (15-cm) band of full impregnation was observed in the central 6 in. (15 cm) of slab 1 (MMA). This depth was greater than that predicted by using an equation developed previously (18). Around the central region, an impregnation depth of about 2 in. (5 cm) was obtained (Figure 5), and outside the pressure-mat area, the impregnation depth was ≤1 in. (2.5 m). (The crosshatched area indicates the limit of dense impregnation.) For slab 2 (water), the predicted depth of penetration [4.5 in. (11 cm)] was confirmed. A uniform gray color was observed for the top 4.5 in. (11 cm) of the slab; the bottom 1.5 in. (3.8 cm) of the slab was white. Without the pressure, only about 1.5 in. (3.8 cm) of penetration would have been expected (18).

For slab 3 (MMA), examination of 3-in.-wide (8-cm) cores revealed dense and uniform impregnation to depths of up to 4 in. (10 cm) and evidence of fracture through the aggregate in the impregnated region (Figure 6). Excellent acid resistance and a major decrease in water absorption were noted in the impregnated region. Thus, in contrast to the original slab, which absorbed 7.2 percent of the water by weight (in 24 hours), the cores absorbed an average of only 0.3 percent of the water: a relative reduction of 96 percent, close to the reductions achieved by using simple hydrostatic pressurization (17, 18). Only 62 cycles were required to effect this improvement.

For slabs 4 and 5 (tar), deeper penetrations (Figure 7) were achieved than predicted, even though the viscosity of 16 cp (0.016 Pa·s) is much higher than the viscosity of MMA or water, 0.7 cp (0.0007 Pa·s) and 1 cp (0.001 Pa·s) respectively. The treated depth may be due to the more rigorous drying used. Essentially similar results were obtained regardless of the differences in load cycling (Table 1). Thus, use of a slow-moving roller could reduce the number of passes required. For slab 6 (boiled linseed oil), less penetration was achieved because of the higher viscosity of the oil, 36 cp (0.036 Pa·s), but the depth was still greater than the few millimeters typically achieved in the treatment of decks with diluted oil.

Thus, these experiments confirm our hypothesis that deep and efficient impregnation with a variety of typical liquids (both monomers and sealants) can be obtained with a pressure-mat technique. In principle, this technique may eliminate some of the limitations associated with the elaborate pressure impregnation (17, 18) and the slow ponding technique (6, 13). More experiments are obviously required to refine and quantify this technique by using different pressure cycles and monomers.

Pressure-Mat Impregnation in the Field

The pressure-mat technique may be expected to be more efficient in the field than in the simulated laboratory setup. In the field, the loading cycle could be as shown in Figure 4, in which the pressure is applied for a long period of time per cycle (as with a slow-moving roller). In practice, it should be possible to impregnate a bridge deck (presumably one land width) by using a large mat to cover the required area and a 15- to 20-ton (14 000- to 10 000-kg) roller to apply the pressure. Conceivably, the new technique could be used to impregnate large sections or even a whole deck at one time, assuming that drying would not be a limitation.

Several concepts of possible field pressure-mat impregnation systems are shown in Figures 8, 9, and 10. In Figure 8, a closed system with an exterior roller is proposed to minimize evaporation and toxicity or flammability problems. In Figure 9, the mat is incorporated in the roller itself. In Figure 10, the area under the roller is sealed ef-

Figure 5. Concrete slabs fractured after pressure-mat impregnation with MMA.

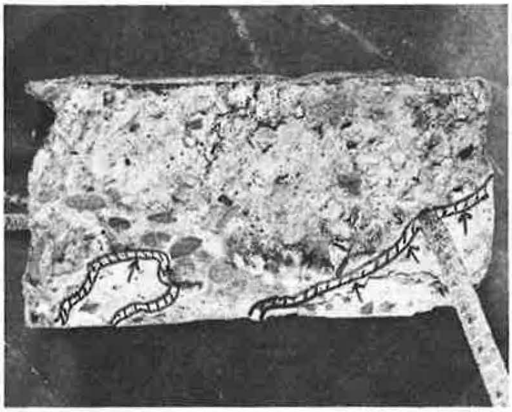


Figure 6. Acid-etched (left) and non-acid-etched (right) sections of core from slab 3.

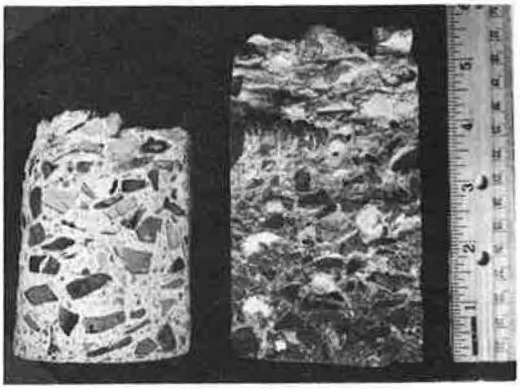
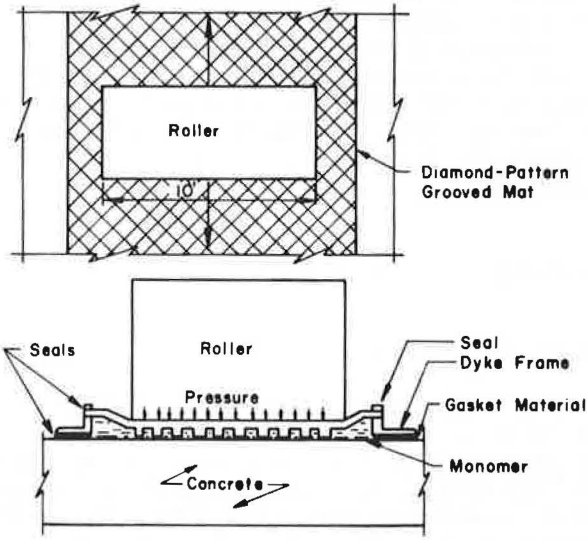


Figure 7. Concrete slabs fractured after pressure-mat impregnation with tar.

Figure 8. Roller pressure-mat impregnation in field.



fectively under pressure, and the monomer is fed under pressure through the roller until the interior pressure counterbalances the weight of the roller; ponding could thus be eliminated.

SULFUR IMPREGNATION OF CONCRETE

Sulfur-impregnated portland cement concrete (SIC) (22) yields compressive strengths as high as 25,000 psi (172 MPa), a value higher than for typical PIC, and a loading of only 8 percent of sulfur by weight (9 percent by volume). Because sulfur is about 30 times cheaper than MMA, SIC is of interest as an alternate to PIC. In view of the good freeze-thaw resistance and low water permeability of sulfur concrete (23) and the excellent resistance of sulfur to acids and salts (24), sulfur may have potential applications in bridge decks, provided that no steel corrosion problems arise because of side reactions with water and oxygen. Furthermore, currently available methods for bridge deck impregnation require drying and cooling the deck, impregnating the concrete, and polymerizing the monomer in the pores of concrete. All of the four steps are expensive and time-consuming. For example, drying at a low temperature, say, 250 F (120 C), requires an inordinately long time and, consequently, high costs; drying at a high temperature, say, 600 F (315 C), reduces the time drastically but may, on a large scale, be limited by expansion or cracking of the deck. The use of sulfur may permit use of a simpler process.

Two inherent advantages of using sulfur are that it melts between 235 and 248 F (113 and 120 C), and the viscosity of the molten sulfur remains relatively low, from 12.5 cp (0.0125 Pa·s) at 248 F (120 C) to 6.6 cp (0.0066 Pa·s) at 320 F (160 C). Above this temperature, the sulfur becomes highly viscous because of polymerization (probably undesirable in this case). Also, in the impregnation of a bridge deck with a monomer such as MMA, the high vapor pressure and flammability of the monomer require that the deck be allowed to cool down before impregnation. Thus, an enormous amount of energy is lost: energy that could be used to reduce the viscosity of materials such as sulfur (after drying of the concrete) for easy penetration into the concrete. Moveover, such energy could be conserved if drying could be effected concurrently.

We propose to combine the three steps of drying, cooling, and impregnation into one and to eliminate the polymerization step required for a monomer. The basic idea is to use sulfur to simultaneously dry and impregnate concrete by covering the deck with molten sulfur. The underlying hypothesis is that sulfur will act as an effective heat transfer medium and dry the deck in advance of the penetration front. Of course the portion to be impregnated must be kept at a temperature high enough to avoid solidification in the pores.

When a slab is heated from the surface, the moisture migrates from the hot surface down to the cool underside and condenses in the cooler region (17, 18). As the water migrates downward from a surface heated with molten sulfur, the molten sulfur may follow the water migration because of the suction created in the pores by the moisture migration. If so, the time required for the process should be equivalent only to the drying time.

Laboratory Experiments

Cylinder Fabrication

Experiments were conducted by using 3-in. × 6-in. (8-cm × 15-cm) cylindrical specimens prepared from a conventional non-air-entrained mix [water, type 1 portland cement, coarse ≤1-in. (2.5-cm) sand, and limestone aggregate in proportions of 1:2.0:3.42:4.16] that had a 28-day average compressive strength of 4,000 psi (28 MPa). The measured air content was 3 percent, and the slump was 4.5 in. (11 cm). All cylinders were cured in a fog room (90 to 100 percent relative humidity).

Figure 9. Rubber mat fitted on roller for pressure impregnation.

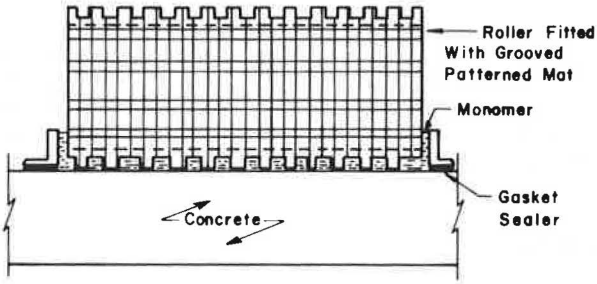


Figure 10. Pressure impregnation by rubber mat fitted on roller.

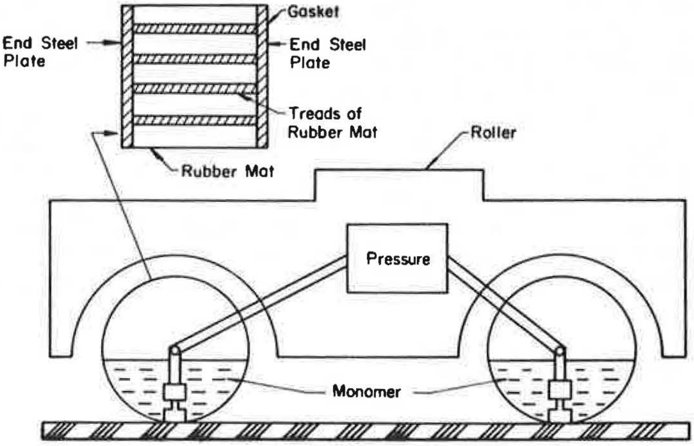


Figure 11. Experimental setup for sulfur impregnation.

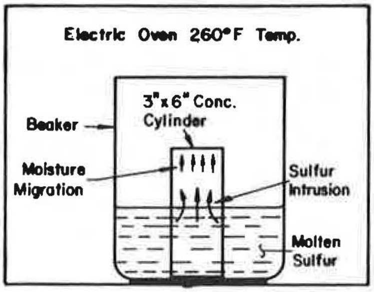


Figure 12. Sulfur-impregnated cylinder after compressive failure.

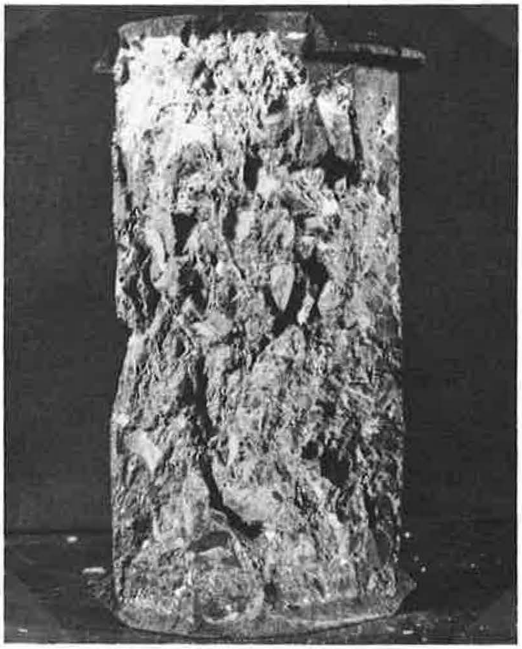
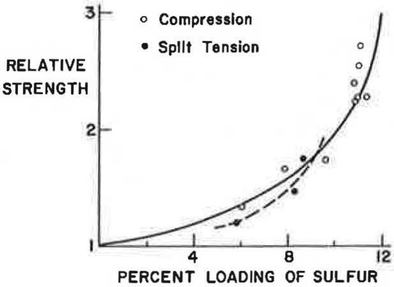


Figure 13. Relative strength of sulfur-impregnated specimens versus sulfur loading.



In the first experiment, a cylinder was half-immersed in a molten sulfur bath (Figure 11) and held in an oven for 45 hours at 240 to 260 F (116 to 127 C). Impregnation times for the additional specimens were either 45 or 60 hours. Except for two specimens that were dried beforehand, all specimens were immersed moist in a propane-fired sulfur bath held in the range 250 to 281 F (121 to 138 C).

Slab Impregnation

To simulate the case of an actual bridge deck, the impregnation of two 2.0- × 2.0- × 0.5-ft (61- × 61- × 15-cm) concrete slabs with sulfur was carried out. The experiment with slab 1 was to determine the effect of an applied vacuum on the rate of penetration; the experiment with slab 2 was to determine the effect of a higher porosity. Slab 1 was prepared as it was for monomer impregnation. Impregnation was effected in the moist slab by partial immersion for 45 hours in a propane-fired molten sulfur bath described above. During impregnation, slab 1 was evacuated [25 in. (64 cm) of mercury] from the top surface [effective area, 16 in. (41 cm) wide] with the vacuum chamber described previously (18). After 45 hours, the vacuum was released and the slab was removed and allowed to cool. Slab 2 was prepared similarly except that, to increase porosity, the slab was steam-cured at a low pressure for 24 hours and the air content was increased to 8 percent. Impregnation was effected as with slab 1, except that the vacuum chamber was not used; the top surface was covered with an asbestos sheet.

Discussion of Results

Cylinders

When the cylinders were removed from the bath and cooled in water, a hard, scratch-resistant surface coating of sulfur was observed. When the cylinder from the first experiment was broken open, the sulfur had penetrated completely through the cylinder and had followed the moisture migration path to within 1 in. (2.5 cm) of the upper surface. This is indicated by a change in color of the matrix from white to deep gray (Figure 12). However, examination of a fracture surface indicated that full loading had not been obtained throughout. Although fracture path passed through the aggregate particles in the outer 0.5-in. (12.7-mm) shell, some aggregate pullout, indicating a lower loading of sulfur, was observed in the central region. This was also seen when the cylinder was acid etched; the outer 0.5-in. (12.7-mm) shell was not affected by 15 percent hydrochloric acid, but the core was somewhat affected. It was concluded that full impregnation would require still longer times (but short compared to the usual drying, cooling, and pressurizing times) or applied pressure.

Sulfur loadings for the additional specimens ranged between 6 to 10 percent by weight (at 45 hours) and 11 percent by weight (at 60 hours). Water absorption was reduced by an average of 60 percent for the six 45-hour specimens and by an average of 97 percent for the six 60-hour specimens. As shown in Figure 13, both compressive and tensile strengths increased as sulfur loading increased.

The maximum strength obtained was nearly three times that of the control: an improvement typical of the MMA type of PIC (1-19). The predried specimens exhibited strengths and water absorptions in the same range as the nondried specimens.

A high level of loading and reinforcement was conferred by the sulfur (60-hour impregnation) and was evident in observations of fracture behavior. During compression testing, all such specimens failed explosively. The strong but brittle MMA-impregnated concrete (3, 10, 14, 15) also failed explosively. With the exception of a few regions that exhibited aggregate pullout (such as the cores of less fully impregnated specimens), fracture tended to proceed through, rather than around, the aggregate. The degree of impregnation was also reflected in the improved acid-etched behavior in 15 percent hydrochloric acid (Figures 14 and 15).

Thus, the impregnation of concrete with sulfur yields improvements in strength, water permeability, and acid resistance that are comparable to those obtained with MMA. The strength improvement has been noted previously (20); the lower water permeability and acid resistance have not.

Slabs

For slab 1, examination of cores revealed uniform sulfur penetration to a depth of 0.75 in. (1.9 cm), a depth about one-half the value predicted (18, equation 1 and Figure 7). One reason for the deviation may be ineffective wetting of concrete with sulfur; the use of vacuum in this case did not appear to be beneficial. Better results were obtained with the more porous slab 2, for which cores show a uniform penetration of about 1 in. (2.5 cm) and a 0.5-in. (10-cm) band of partial impregnation (Figure 15). As noted with cylinders, the fracture occurs through the aggregates in the more fully impregnated regions.

Thus, in practice, surface ponding with sulfur may be useful for the shallow impregnations being considered for new bridge decks (or, perhaps, older decks in which salt has not penetrated far). If deeper penetration is required, pressure may be used to facilitate impregnation (18). Tests of freeze-thaw stability and rebar-corrosion resistance remain to be performed.

OTHER NONMONOMERIC MATERIALS FOR HOT IMPREGNATION

Principles developed in this and previous papers should be able to be used for impregnating concrete bridge decks with a wide variety of nonpolymer impregnants (22), such as low-viscosity tar, linseed oil, and inorganic penetrants. Deep-drying temperatures or those high enough to effect concurrent drying, as well as low material costs, could be significant advantages, especially if a suitable pressure mat can be developed. Further, the environmental and fire hazards should be much less important for these materials than for volatile monomers such as MMA. Preliminary experiments with the impregnation of portland cement mortar with tar, tar-sulfur combinations, and barium hydroxide are described in the following.

Laboratory Experiments

Mortar specimens [1.0 × 2.0 in. (2.5 × 5.0 cm)] were prepared by using a mix [water, portland cement (type 1), and Ottawa sand in proportions of 0.5:1.0:2.7] that was cured for 28 days. These specimens were immersed in the impregnant for 24 hours at atmospheric pressure and at a temperature between 230 and 240 F (110 and 115 C). The barium hydroxide impregnant was held at 194 F (90 C).

Discussion of Results

As given in Table 2, all impregnants reduced the water absorption significantly, from 47 percent for the barium hydroxide (22) to 97 percent for tar and to 99 percent for sulfur or an 80:20 sulfur-tar mixture. The most impermeable specimens were about as effective as PIC specimens (18). Compressive strengths were, as expected, significantly increased (Table 3) by the impregnation with sulfur and with a tar mixture with a high sulfur content; they were not increased with the less viscous tar by itself (7). A number of specimens of each category are being tested for salt pickup and corrosion of the embedded steel reinforcement.

In addition to having the advantages of low cost and convenience, such systems would eliminate the need for heating or catalysis to polymerize the materials, as required for a monomer. Further research is needed in the laboratory and the field to evaluate per-

Figure 14. Acid-etched (left) and non-acid-etched (right) sections from specimen partially impregnated with sulfur.

Figure 15. Acid-etched (left) and sulfur-impregnated (right) specimens.

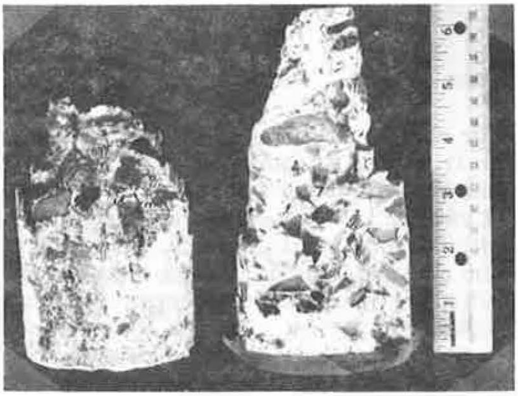


Table 2. Water absorption of impregnated mortar specimens.

Impregnant	Specimen Number	Average Loading[a] (percent)	Average Water Absorption (g)	Average Reduction in Water Absorption[b] (percent)
Barium hydroxide[c]	1 to 7	2.3	2.02	47
Molten sulfur[d]	8 to 14	12.5	0.03	99
	29 to 33	10.5	0.06	98
Tar[e]	15 to 21	6.8	0.10	97
Sulfur-tar (80:20)	22 to 28	11.2	0.05	99
Water (control)	34 to 38	7.8	3.84	—

[a] Percent loading = $\left(\frac{\text{impregnated weight - dry weight}}{\text{dry weight}} \times 100\right)$; immersion time = 24 hours.

[b] Percent reduction in water absorption = $\left(\frac{\text{water required for saturation - water absorbed}}{\text{water required for saturation}} \times 100\right)$.

[c] Barium hydroxide dissolved in its own water of crystallization; surface of concrete specimens severely attacked by solution.

[d] Specimens 8 to 21 and 34 to 38 were immersed in water for 24 hours; the remaining specimens were immersed in water for 72 hours.

[e] Tar used complied with AASHO M-214-65; specific gravity = 1.08.

Figure 16. Acid-etched (left) and non-acid-etched (right) sections of core from sulfur-impregnated slab.

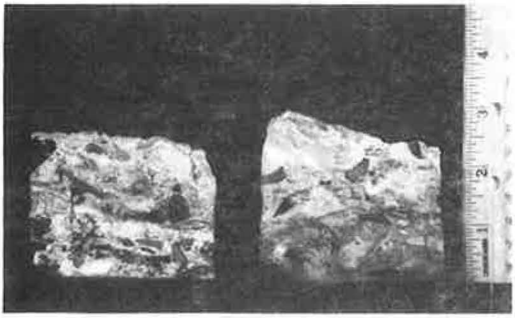


Table 3. Strength of impregnated mortar specimens.

Impregnant	Specimen Number	Loading (percent)	Compressive Strength (psi)
Sulfur	29	10.2	1,500
	30	10.1	1,480
	31	11.5	1,530
Sulfur-tar (80:20)	39	11.6	1,140
	40	11.9	1,050
	41	10.7	1,180
Tar	43	7.3	640
	44	6.7	640
	45	6.9	640
Control specimens	48	—	650
	49	—	770
	50	—	700

Note: 1 psi = 6895 Pa.

formance with respect to freeze-thaw and rebar-corrosion resistance relative to MMA-based PIC.

CONCLUSIONS

Preliminary experiments with two new approaches to the impregnation of bridge decks, neoprene-pressure-mat impregnation (with MMA, tar, and linseed oil) and sulfur impregnation of moist concrete, show excellent promise for economizing, simplifying, and rationalizing the laboratory field techniques developed so far. Further work is being continued in this area because these techniques show promise of adaptation for the large-scale impregnation of bridge decks, highways, and airport runways.

ACKNOWLEDGMENTS

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EFFECTS OF DEICER SALTS AND ROADWAY CONTAMINANTS ON POLYMER IMPREGNATION OF BRIDGE DECK CONCRETE

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Cores, 4 in. (10 cm) wide, extracted from three 7-year-old concrete bridge decks were impregnated with methyl methacrylate to evaluate the effects of deicer salts and roadway contamination on polymer impregnation. All specimens were impregnated by soaking from the top (traffic) surface at atmospheric pressure for a sufficient period of time to achieve approximately 5 in. (12.7 cm) of penetration. Deicer salts, in the quantities measured in the three bridge decks, did not reduce the depth of polymer penetration or the volume of voids filled with polymer. However, the rate of penetration decreased as salt concentration increased. The rate of penetration was a linear function of the square root of time. Removal of roadway contaminants by lye, detergent, or sandblasting had no apparent effect on the rate or extent of polymer impregnation.

•DEVELOPMENT of polymer-impregnated concrete (PIC) in this country was largely the result of the work of Steinberg et al. (1) of Brookhaven National Laboratory. Several organic thermoplastic monomers were investigated in that work for use as impregnants. Of these monomers, methyl methacrylate (MMA) showed the greatest ability to significantly improve the physical properties of concrete, i.e., compressive and tensile strengths, modulus of elasticity, and water permeability and absorption. In addition, Whiting, Blankenhorn, and Kline (2) investigated epoxy (thermosetting polymer) impregnated concretes and showed that the compressive modulus and strength are functions of porosity, age, and other parameters.

Because of the significant physical improvements offered by PIC, it was suggested (3) that MMA could solve the problem of rapid deterioration of concrete bridge decks caused by deicer salts. Fowler, Houston, and Paul (4) demonstrated the feasibility of the use of PIC surface treatments for field use on bridge decks. In their work, the soak time (impregnation period) was an important variable in relation to depth of penetration, and an evaporation barrier was necessary to prevent excessive loss of monomer. Other work in this area is being conducted at Brookhaven National Laboratory, the U.S. Bureau of Reclamation, the California Department of Transportation, Lehigh University, and Pennsylvania State University.

Few, if any, data have been reported concerning the feasibility of impregnating sound concrete in bridge decks, which may contain road contaminants such as motor oil, linseed oil, grease, asphalt cement, dirt, and deicer salts. The purpose of this paper is to evaluate the effects of deicer salts and three cleaning methods on the impregnation of bridge deck concrete with MMA that has been impregnated from the wearing surface.

EXPERIMENTS

Materials

Concrete cores were taken from three 7-year-old bridge decks with an average daily traffic (ADT) of 5,160 in 1969. The three decks were in excellent condition and did not display large cracks, spalled areas, or potholes. The concrete used in the construction of the three decks was required to meet the Pennsylvania Department of Transportation specifications for class AA reinforced vibrated concrete. Type 1 portland cement was used, and glacial sand and crushed limestone were the aggregates. The average slump, air content, and flexural strength for the concrete used in these decks are given in Table 1 (5).

The impregnation system consisted of methyl methacrylate (MMA), trimethylpropane trimethacrylate (TMPTMA), and 2, 2′-azobisisobutyronitrile (AZO) mixed in the ratio of 100:10:0.5 parts by weight respectively.

Coring of Bridge Decks

Twenty-six cores were taken from the three bridge decks. The coring positions represented the lateral range of the different use areas on a bridge deck: water tables and truck and passing lanes. Duplicate cores were taken from these areas so that chloride determinations could be made. Figure 1 shows the positions from which the cores were taken.

Sample Preparation

The bottoms of the cores were trimmed with a diamond saw to provide specimens that were 4 in. (10 cm) wide by approximately 5 in. (12.7 cm) long. The cores were then dried in a forced draft oven at 115 C for 72 hours and then for 24 hours at 115 C in a vacuum oven at 29-in. (98-kPa) Hg vacuum. After cooling under the vacuum, the sides of the cores were painted with a coat of epoxy. A metal ring, 1 in. (2.5 cm) high and 4 in. (10 cm) wide, was bonded to the top of each core with epoxy to provide a reservoir for ponding the monomer during the impregnation of the cores.

Deicer Salt Content

The chloride titration procedure (6) was used to determine the quantity of deicer salts in the cores. Chloride analyses were performed on cores 1-2, 1-4, 1-6, 2-2, 2-4, 2-6, 3-5, 3-6, and 3-8. To provide the cement paste sample used in the titrations, the cores were first split by using the tensile splitting method. The cement paste was then extracted as a fine powder by drilling on the split face with a $^3/_{16}$-in. (4.8-mm) carbide drill bit. The positions drilled were in the cement paste areas, and care was taken to avoid any large aggregate particles. Cement paste samples were obtained from four areas on each core [0 to $^1/_4$ in. (0 to 6 mm), $^1/_4$ to $^3/_4$ in. (6 to 19 mm), $^3/_4$ to $1^3/_4$ in. (19 to 44 mm), and $1^3/_4$ to $3^3/_4$ in. (44 to 95 mm) in depth from the wearing surface].

Impregnation of Cores

The impregnation of the dried cores with the MMA system was accomplished by allowing the monomer to soak through the cores from the wearing surface; only an evaporation barrier was provided above the free monomer surface. The rate of impregnation was determined by periodic weighing of the specimens during impregnation. Completion of impregnation was assumed to occur when the monomer exuded uniformly from the bottoms of the specimens.

Table 1. Average concrete control parameters.

Bridge Structure Number	Slump (in.)	Air Content (percent)	Flexural Strength (psi at 7 days)
6254 NB	2.2	6.5	769
6254 SB	2.2	6.5	641
6258 NB	2.2	6.2	956

Note: 1 in. = 2.54 cm. 1 psi = 6.895 kPa.

Figure 1. Coring positions of bridge decks 6254 NB (1-1 to 1-9), 6254 SB (2-1 to 2-9), and 6258 NB (3-1 to 3-8).

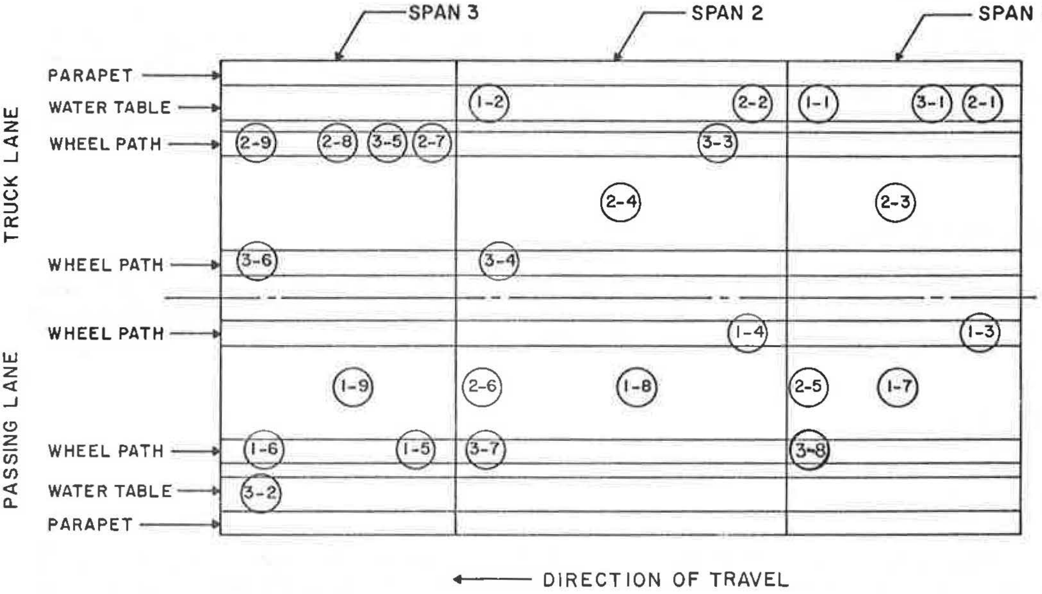
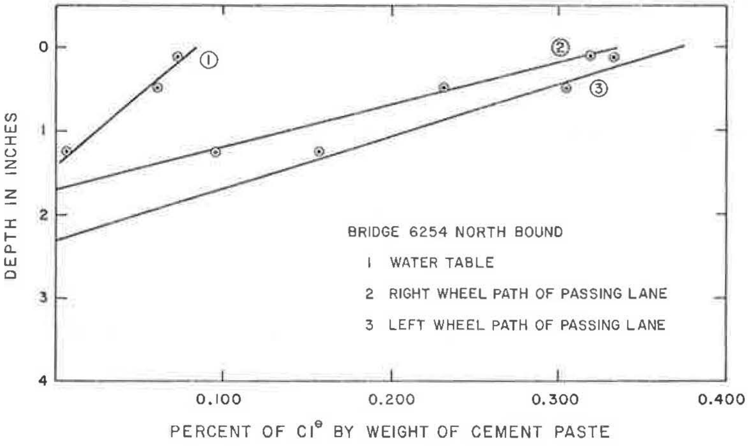


Figure 2. Chloride content of bridge 6254 NB.



Cleaning of Cores

It was assumed that the heaviest traveled areas would have the greatest amount of surface contamination. Therefore, six cores were taken from the truck lane: three from the right wheel path and three from between the wheel paths. The surfaces of these cores were cleaned by three methods (detergent, lye, and sandblasting). Cores 1-7 and 2-7 were scrubbed for 5 min with a 20 percent by weight detergent solution, cores 2-7 and 2-8 were scrubbed for 5 min with a 20 percent by weight lye (NaOH) solution, and cores 1-9 and 2-9 were cleaned by sandblasting at 75 psi (517 kPa) for 10 min.

Water Absorption

After the cores were impregnated and the MMA system was polymerized in a constant temperature water bath at 167 F (75 C), they were dried at room temperature for 15 days. The cores were then vacuum saturated with water and allowed to soak for 24 hours. Water absorption was measured by the weight gained because of the penetration of the water during vacuum saturation.

Estimate of Core Porosity

A section was cut from each core, dried as previously cited, vacuum saturated with water, and placed under water at 75 psi (517 kPa) for 24 hours. The porosity was determined by the weight gained during saturation.

RESULTS

Deicer Salt Content

Typical results of the nine bridge deck cores analyzed for chlorides are shown in Figure 2. The concentrations of the chlorides appear to decrease linearly as a function of depth. This agrees with other results concerning the durability of concrete bridge decks (7) for sound decks. The degree of contamination by chlorides was approximately the same for the areas investigated. For the areas not used by traffic, the concentrations were lower.

Impregnation

The percentage of monomer gained in 96 hours was calculated as follows:

$$\text{Percentage at 96 hours} = \frac{\text{monomer gained in 96 hours}}{\text{total monomer gained}} \times 100$$

The percentage of the volume of the core filled by the monomer system was calculated as

$$\text{Percentage of volume filled} = \frac{\text{weight of MMA system gained/density of MMA}}{\text{bulk volume of core}} \times 100$$

The impregnation data are given in Table 2. Figure 3 shows results of the impregnation

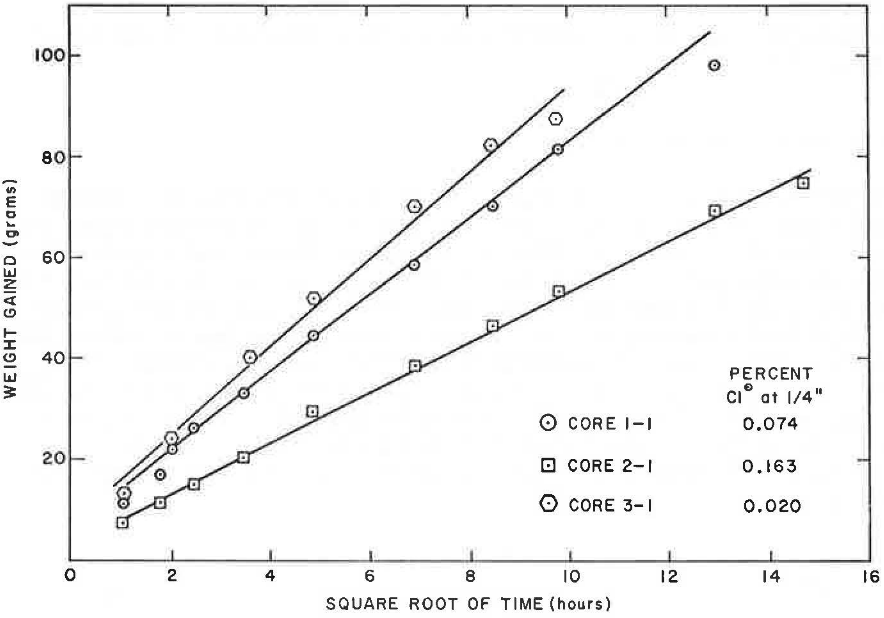
Table 2. Impregnation data for bridge deck core.

		Monomer Gained at 96 Hours					
Core Number	Slope $(g/\sqrt{h})$	Amount (g)	Percent[a]	Total Monomer Gained (g)	Volume Filled (percent)	Chloride at 1/4 In.	Soak Time (days)
1-1	7.4	81.5	82.7	98.5	9.8	0.074	7
1-3	6.7	71.1	81.2	87.6	8.8	0.333	7
1-5	5.6	54.8	62.3	87.9	8.7	0.319	11
1-7	5.0	54.0	66.1	81.7	8.5	0.319	11
1-8	4.7	50.4	73.1	68.9	8.0	0.319	9
1-9	5.9	58.8	70.0	84.0	8.5	0.319	9
2-1	5.0	53.0	71.0	74.6	7.4	0.163	9
2-3	5.0	52.7	64.4	81.8	8.2	0.355	11
2-5	5.1	56.1	66.6	84.2	8.5	0.377	11
2-7	5.9	65.2	75.1	86.8	8.8	0.355	9
2-8	5.1	50.0	61.6	81.2	8.1	0.355	11
2-9	5.8	68.1	67.2	93.9	9.4	0.355	11
3-1	8.7	87.5	100.0	87.5	8.8	0.020	4
3-2	7.7	78.2	83.5	93.7	9.4	0.020	6
3-3	7.6	76.0	91.9	82.7	8.3	0.298	5
3-4	5.6	60.9	79.6	76.5	7.7	0.192	7
3-7	5.4	58.8	81.1	72.5	7.3	0.020	7

Note: 1 in. = 2.54 cm.

[a] Percentage of 5-in. (12.7-cm) core depth impregnated.

Figure 3. Weight gained as function of the square root of time.



of the concrete with MMA plotted as weight gained in grams as a linear function of the square root of time in hours (8, 9). The slope of the curve (the rate of impregnation) varied both with position on the bridge decks and from deck to deck for the three decks. Cores 1-1 to 1-9 and 2-1 to 2-9 of bridge decks 6254 northbound (NB) and 6254 southbound (SB) were in close agreement, and cores 3-1 to 3-8 of deck 6258 NB displayed a higher rate. The percentage of monomer gained at 96 hours (Table 2) varied considerably.

The lateral position of the cores on the decks was matched with the closest lateral position of the cores used for chloride analyses. The values of chlorides in the top ¼ in. (6 mm) were then assigned to the respective impregnated cores. These chloride values are also given in Table 2.

Correlation coefficients were calculated for the chlorides in the top ¼ in. (6 mm) versus the percentage of MMA at 96 hours and the percentage of volume filled with MMA. The correlation coefficients were compared for significance at the 95 percent confidence level. No significant correlation was established for percentage of chloride at ¼ in. (6 mm) versus total percentage of volume filled with MMA. However, significance at the 95 percent confidence level was established for the percentage of chlorides at ¼ in. (6 mm) and percentage of volume filled with MMA at 96 hours.

Figure 4 shows a cross section of an impregnated core. The almost uniform tone of the photograph indicates a high degree of uniformity in penetration by the monomer. However, the voids in the upper part of the core appear to be filled to a greater degree than do those near the bottom, as indicated by close visual examination.

Because of the small sample sizes of the cores subjected to the various cleaning processes, no statistical analyses were performed. However, a comparison of the percentage of MMA gained in 96 hours for the six cores that were cleaned (1-7, 1-8, 1-9, 2-7, 2-8, and 2-9) with the remaining cores from the same two bridge decks (Table 2) shows that contamination from materials considered here has no significant effect on polymer loading.

Water Absorption After Impregnation

The estimated porosity, the core volume filled with water and the estimated porosity filled by absorbed water after impregnation and polymerization, the estimated porosity filled with polymer, and the decrease in water absorption due to the soak impregnation are given in Table 3. After polymer impregnation, the majority of the cores showed between 2 and 4 percent volume filled with water. However, no significant correlation existed between the chloride content at ¼ in. (6 mm) and the percentage of volume filled with water by vacuum saturation. No significant correlation was established for the estimated porosity versus the rate of impregnation and the total monomer gained. The polymer filled approximately 50 percent of the estimated porosity. The water, after impregnation and polymerization, filled about 15 percent of the estimated porosity. The water absorption was decreased by about 85 percent after the soak impregnation technique was used.

DISCUSSION OF FINDINGS

When the soak method with MMA was used (4), the penetration depths were ¼ to 1½ in. (6 to 38 mm) in laboratory-prepared concrete. This paper has shown that a depth of at least 5 in. (12.7 cm) can be achieved in sound concrete from in-service bridge decks provided the concrete is thoroughly dried. The rate of impregnation was a linear function of weight gained in grams versus the square root of time in hours. This agrees with Washburn's equation (10) for a porous body that behaves as an assemblage of small cylindrical capillaries. In this equation, the volume of flow V that penetrates the given medium in time t behaves in accordance with

$$V = k\left(\frac{r}{\eta}t\right)^{1/2}$$

where r is the radius of the capillary, and η the viscosity of the liquid.

When the soak method is used, deicer salts appear to decrease the rate of impregnation of bridge deck concrete. However, bridge decks may be impregnated to a depth of 5 in. (12.7 cm) regardless of the presence of deicer salts.

The rate of impregnation and the percentage of monomer gained in 96 hours varied within each deck and from deck to deck. The monomer gained at 96 hours varied from 61.6 to 100 percent. This implies that, in 96 hours, the cores were impregnated from 60 to 100 percent of their 5-in. (12.7-cm) depth. Therefore, for a 96-hour impregnation period, penetration will be nonuniform at a depth of 5 in. (12.7 cm).

Because of the small number of cores that were cleaned, it is not possible to provide quantitative conclusions about the effect of roadway contaminants on the impregnation rate. However, the data indicate that bridge decks may be impregnated when heavy accumulations of contaminants are removed.

The percentage of volume filled by polymer and the percentage of the volume filled with water absorbed after impregnation are probably related to the two parameters that govern permeability: the porosity and pore size distribution. Because of this, it is probable that deicer salts in concrete at the concentrations found in this research do not appreciably change the permeability of the PIC.

Since there was no correlation established for porosity versus rate of impregnation and total monomer gained, the rate of impregnation and the percentage of the void volume filled with polymer may depend to a large extent on the pore size distribution rather than on the overall total porosity.

Water absorption was decreased to 15 percent of the original porosity when 50 percent of the porosity was filled with polymer, indicating that voids were made inaccessible by the MMA polymer in the concrete.

SUMMARY AND CONCLUSIONS

Cores were obtained from in-service bridge decks. Chloride contents of selected cores were determined by a titration technique. The remaining cores were dried by using forced air and vacuum ovens. They were impregnated by using the soak method with an MMA system, and the monomer was thermally polymerized.

Chlorides present at the concentrations reported do not affect the percentage of volume of voids filled or the impregnation depth achieved [5 in. (12.7 cm)] with the monomer system used. Chlorides do appear to decrease the rate of monomer impregnation when the soak method is used. Removal of roadway surface contaminants by three different procedures did not appear to affect the rate or extent of polymer impregnation.

ACKNOWLEDGMENTS

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The opinions and conclusions expressed or implied in this paper are those of the authors. They are not necessarily those of the sponsoring and administering agencies.

Figure 4. Cross section of core of polymer-impregnated bridge deck.

Table 3. Void volume with MMA and water.

Core Number	Estimated Porosity (percent)	Volume Filled With Water (percent)	Porosity Filled With Water (percent)	Porosity Filled With Polymer (percent)	Decrease in Water Absorption (percent)
1-1	17.7	3.9	22	55	88
1-3	18.4	2.9	16	48	84
1-5	16.7	3.1	19	52	81
1-7	19.0	2.2	18	45	82
1-8	17.6	5.0	29	45	71
1-9	15.1	1.3	09	56	91
2-1	14.1	2.2	16	52	84
2-3	20.7	5.8	23	40	77
2-5	19.7	3.6	13	43	87
2-7	16.0	1.5	09	55	91
2-8	15.4	0.8	05	53	95
2-9	19.0	1.3	07	50	93
3-1	17.2	3.3	13	45	87
3-2	16.6	2.8	16	57	84
3-3	16.4	2.5	15	51	85
3-4	18.5	3.6	20	41	80
3-7	15.5	2.2	14	47	86

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POLYMER CONCRETE PREPARED FROM AN MMA-STYRENE COPOLYMER SYSTEM

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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, $\leq {}^{33}\!/_{64}$-in. ($\leq$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.

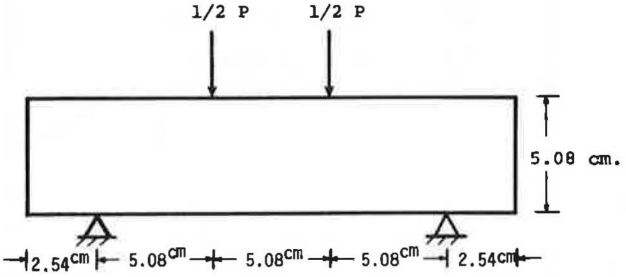


Figure 2. Effect on compression strength of styrene in copolymer mortar.

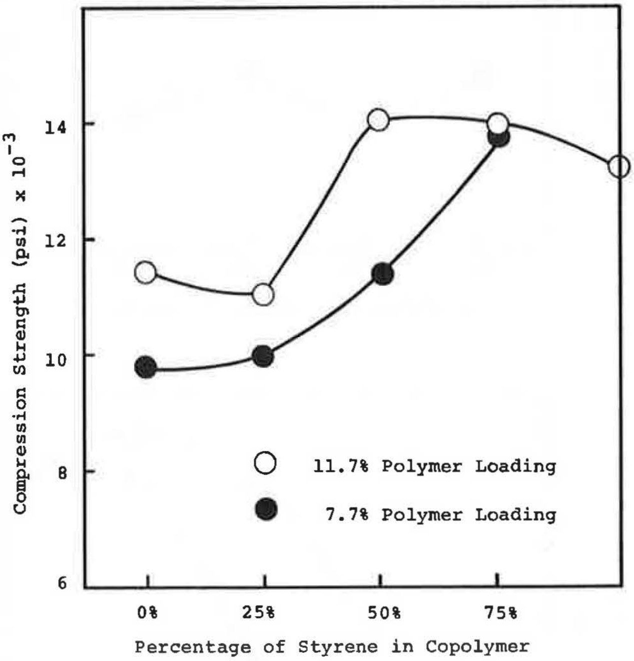


Figure 3. Effect on tensile strength of styrene in copolymer mortar.

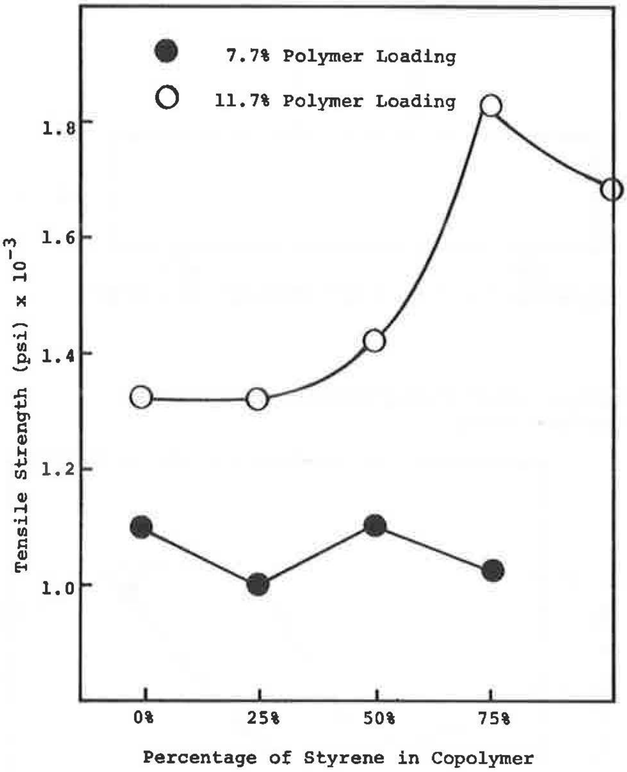
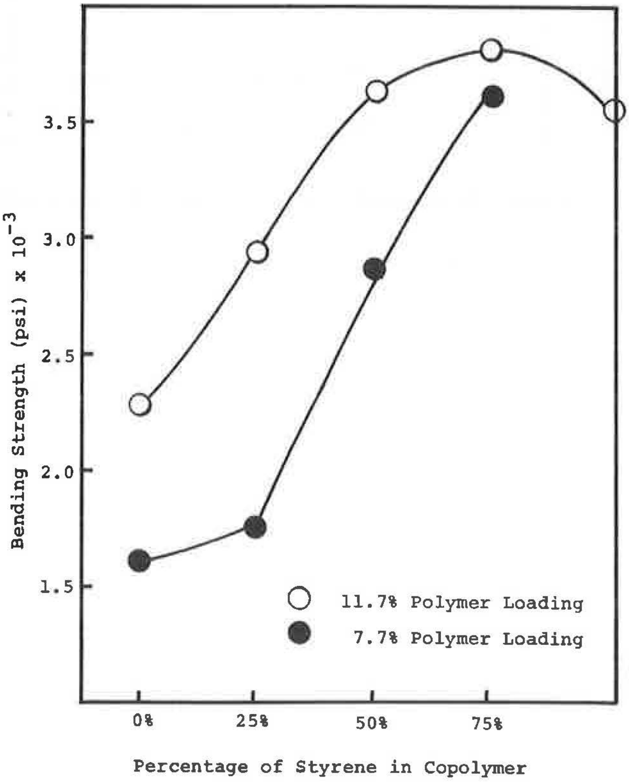


Figure 4. Effect on bending strength of styrene in copolymer mortar.



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.

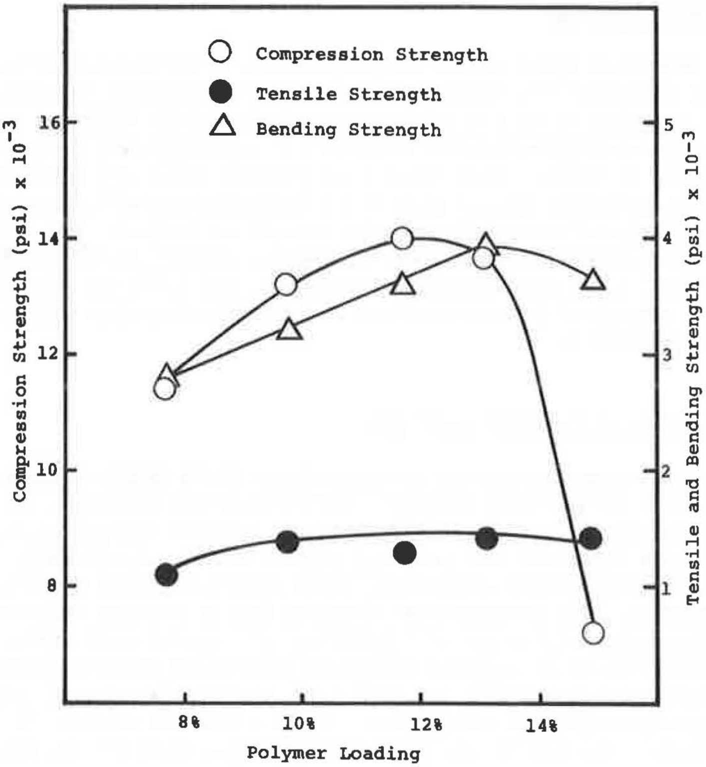


Table 1. Effect of polymer loading on strengths of copolymer mortar system.

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.

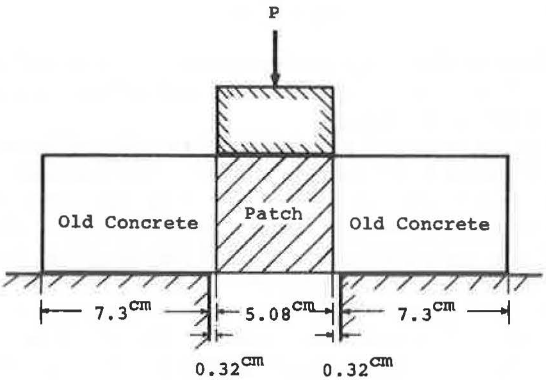


Table 2. Strengths of polymer concrete.

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.

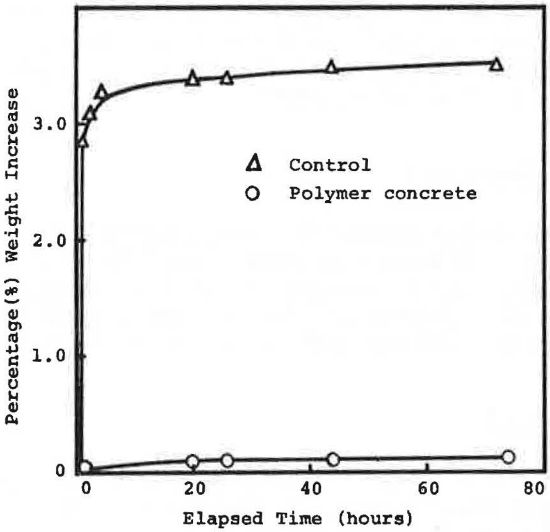
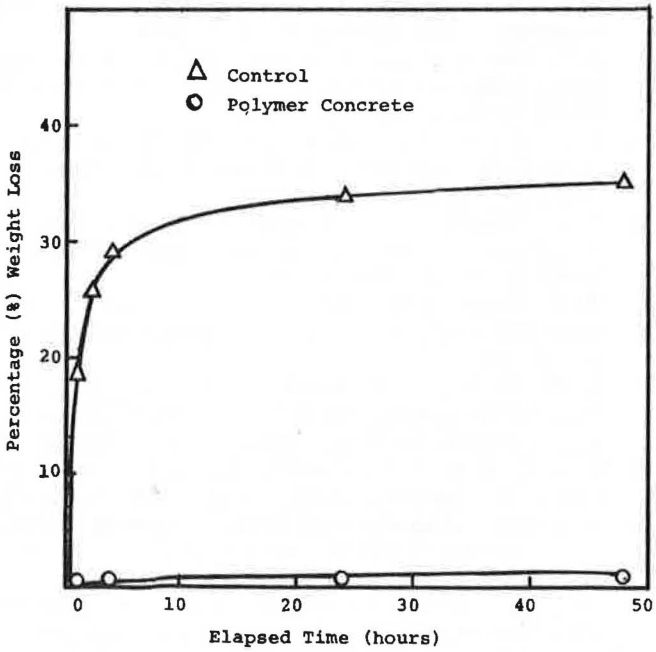


Figure 8. Acid resistance of control and polymer concrete.



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

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HIGHWAY APPLICATIONS OF CONCRETE POLYMER MATERIALS

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The deterioration of concrete bridge decks and pavements presents many highway organizations with major problems of providing safe and satisfactory riding surfaces. Concrete polymer materials, with their excellent durability and strength properties, have potential application to highway construction and maintenance and offer potential benefits of an increase in service life and a reduction in the costs, safety hazards, and inconveniences in performing maintenance and repair work. Polymer-impregnated concrete is highly resistant to freeze-thaw damage and water penetration and provides protection from deicing salt penetration and corrosion of reinforcing steel. A precast, prestressed polymer-impregnated concrete bridge deck system is being developed that incorporates the advantages of a precast, prestressed system for rapid construction and strength, and a surface-impregnation technique is being developed for field treatment of newly constructed concrete bridge decks to provide protection of reinforcing steel from deicing salts. Polymer concrete is a versatile, new material with properties comparable to polymer-impregnated concrete and appears to be suitable for both precast and field applications, such as for curbstones, pavement overlays, shotcrete, and rapid-curing patching and repair materials.

•DETERIORATION and premature failure of concrete bridge decks are caused by deicing salts, corrosion of reinforcing steel, freeze-thaw deterioration, spalling, and heavy traffic loads. Maintenance work is costly and difficult to perform under hazardous traffic conditions and presents delays and safety hazards to the traveling public because of lane closures, detours, traffic jams, and the increased risk of accidents. One approach to the problem is the use of concrete polymer materials in new highway construction and for maintenance and repair work. The materials of prime interest are polymer-impregnated concrete (PIC) and polymer concrete (PC), both of which have excellent durability and strength properties.

The Federal Highway Administration (FHWA) has sponsored research at the U.S. Bureau of Reclamation (USBR) to develop both a bridge deck system of precast, prestressed PIC and a field process of surface impregnation for protecting newly constructed concrete bridge decks from deicing salts. The prestressed PIC bridge deck panel program is cosponsored by the Prestressed Concrete Institute, which performed a parallel design of the system with USBR. Other organizations in the United States are engaged in development of field treatments for protection and repair of existing concrete bridges. The University of Texas at Austin, under the sponsorship of the Texas State Department of Highways and Public Transportation and FHWA, is investigating surface impregnation of new, old, and badly deteriorated bridge decks; Pennsylvania State and Lehigh Universities, under National Cooperative Highway Research Program sponsorship, are jointly developing techniques for deep impregnation of chloride-contaminated bridge decks; and Brookhaven National Laboratory is developing techniques for repair of deteriorated bridge decks under the sponsorship of FHWA. Much of this basic work has common application, and there has been a large exchange of information.

POLYMER-IMPREGNATED CONCRETE

PIC is prepared by impregnating hardened conventional portland cement concrete with a liquid monomer (starting material for making plastics) that is subsequently polymerized. The polymerization reaction converts the liquid monomer into a solid plastic or polymer. The polymer fills voids and microfractures in the concrete, greatly increases strength and durability, and significantly reduces permeability.

Typical mechanical and physical properties of PIC are given in Table 1; the durability properties of PIC are given in Table 2. The concrete specimens were impregnated with methyl methacrylate thermal-catalytic polymerization. The strength of PIC is four to five times greater than that of unimpregnated concrete; water absorption and permeability are greatly reduced, and resistance to freeze-thaw and acid attack is greatly improved.

Fully impregnated PIC requires prior oven-drying of the concrete to remove moisture and an appropriate vessel for impregnation and polymerization. The impregnated concrete is thermal-catalytically polymerized in the impregnation vessel. Methyl methacrylate is the most widely used monomer because of its low viscosity, low cost, and excellent properties in PIC. Various other monomers and combinations of monomers and resins such as styrene, polyesters, acrylonitrile, and trimethylpropane trimethacrylate have been used to make a satisfactory PIC or to improve certain properties. Azonitrile catalysts are used because these compounds are chemically stable and, under appropriate safety conditions, permit storage and reuse of catalyzed monomer.

The steps for producing fully impregnated PIC are as follows:

1. Dry concrete at 300 F (148.9 C) for 24 hours to remove free moisture (or at a lower temperature for a longer time).
2. Allow concrete to cool to room temperature.
3. Place concrete in the impregnation vessel and apply a vacuum for ½ hour.
4. Introduce catalyzed monomer under a vacuum to completely submerge the specimen, then soak under a compressed air pressure at 25 to 50 psi (170 to 340 kPa) for 2 hours.
5. Drain excess monomer and immediately backfill the vessel with warm water. Submersion in water minimizes monomer evaporation losses.
6. Apply heat (steam is commonly used) and polymerize to completion. Polymerization temperature and length of time depend on the monomer system, the catalyst, and the size of specimens. Polymerization is generally conducted at about 160 F (71.1 C) for about 4 hours.

Partially impregnated or surface-impregnated concrete may be produced by a simpler and less costly process that does not require vacuum and pressure soaking and that consequently eliminates the need for a pressure vessel as required for fully impregnated concrete. The process consists of drying the concrete to remove moisture, soaking it with a monomer at atmospheric pressure, and polymerizing the soaked concrete. Thermal-catalytic polymerization is accomplished by immersing the concrete in warm water or by other appropriate applications of heat. Partially impregnated and surface-impregnated concrete is reported to have good structural properties and excellent resistance to freeze-thaw deteriorations, water penetration, abrasion, and wear and to have a skid resistance at least equal to that of unimpregnated concrete (2, 3).

POLYMER CONCRETE

PC uses a polymer as the cementing material and is made by mixing a monomer or resin system with aggregate and casting and polymerizing the mixture. PC contains no portland cement binder and is sometimes referred to as resin-bound concrete. The material has excellent durability characteristics and good structural properties and is basically suitable for precast and cast-in-place applications. The material has been widely investigated throughout the world, and several PC products and potential applications have been introduced to the market: pipe, piles, curbs, tunnel liners, railroad sleepers, panels, overlays for highway bridge decks and approaches, various surface coatings and linings, patching and repair materials, and specialty products such as window sills, tiles, and sanitary fixtures. When fillers and reinforcement are added, the material grades into the family of composite materials such as is represented by reinforced plastic mortar pipe. In this paper, PC refers to a concrete material with a polymer content of ≤10 percent (wt).

Developmental work on PC has been with epoxy, polyester, and furan resins and more recently with methyl methacrylate and styrene monomers. Epoxy resins are commercially available for use in PC applications that so far appear to be mostly for mortars and patching compounds. The chief obstacle to wider use of epoxies is their relatively high cost. Polyester PC has been widely investigated. The polyesters are usually blended with a styrene monomer, which serves as a solvent and cross-linking agent. A notable demonstration of polyester PC was a highway overlay system applied with a commercial asphalt paving machine.

A feasible method for fabricating PC has been developed at USBR (1, pp. 20-21). Using modified conventional concrete mixing equipment and conventionally graded, oven-dried concrete aggregate plus suitable nonporous fines, which serve as a filler and to improve the workability of the mix. The aggregate is mixed with a methyl methacrylate monomer system, cast, and polymerized at room temperature. The monomer system is composed of methyl methacrylate monomer, trimethylolpropane trimethacrylate, cross-linking monomer, benzoyl peroxide catalyst, dimethyl aniline promoter, and a silane coupling agent. This system polymerizes in about 2 to 4 hours after mixing. In the present procedure, the casting step requires vibrating to fully consolidate the mix and sealing to reduce evaporation of the monomer.

In tests performed on the mechanical and physical properties of PC (Tables 3 and 4), the specimens produced by the method described above are comparable in properties with PIC specimens. The PC specimens contain from 6 to 8 percent (wt) polymer as compared to 5 to 7 percent (wt) polymer for PIC. Compressive strengths of the PC specimens range from 12,000 to 24,000 psi (83 000 to 165 000 kPa). Current creep tests show creep deformation is comparable to that of conventional concrete. After 63 days under a compressive load of 3,938 psi (27 150 kPa), creep deformation for PC was 0.232 μin./in. per psi (0.0059 μm/m/6.9 kPa) as compared with about 0.240 μin./in. per psi (0.006 μm/m/6.9 kPa) for conventional concrete under a compressive load of 2,313 psi (15 948 kPa).

In other tests, specimens have been exposed to 5 percent sulfuric acid for 9 months, and no signs of deterioration or loss in weight have been visible. Specimens tested after the 9 months' exposure had an average compressive strength of 18,200 psi (124 000 kPa).

The use of methyl methacrylate requires certain safety precautions because it is flammable and explosive within certain vapor concentration limits. The mixer used must be equipped with an explosion-proof electric motor and nonsparking mixing blades. Mixing should be conducted in a well-ventilated area. Mixing and casting can be accomplished conveniently and safely by following recognized safety procedures for the handling of methyl methacrylate.

PC is versatile and may be conveniently adapted to patching, crack repair, and various applications through modifications of the mix. These would include dissolving polymers in the monomer to control viscosity or to impart certain qualities to the mix, using internal plasticizers such as butyl acrylate to increase ductility or flexibility, and using more rapid promoters such as dimethyl-p-toluidine to accelerate polymerization.

PC was also investigated by several federal agencies for use as shotcrete, a material mixed in and shot from a gun with a nozzle (4). The nozzle of a conventional field type of shotcrete gun was modified for polymer shotcrete application of a three-part shotcrete mix: the aggregate and a two-part monomer system. The monomer system was composed of 72 percent methyl methacrylate, 13 percent trimethylolpropane trimethacrylate, and 15 percent polymethyl methacrylate molding powder and was divided into two parts in which the additions of the catalysts were based on total weight of the monomer system: (a) benzoyl peroxide catalyst in a concentration of 2 percent (wt), and (b) n, n dimethyl-p-toluidine promoter in a concentration of 2 percent (wt). When the two parts of the monomer system are mixed, the mixture has about a 2-min polymerization pot life in 100-g (3.5-oz) bulk samples at room temperature. The application of polymer shotcrete is potentially hazardous and should be used only in well-ventilated areas or outside. Safety precautions to be followed include using protective

Table 1. Mechanical and physical properties of polymer-impregnated concrete.

Property	Unimpregnated Concrete	Polymer-Impregnated Concrete
Compressive strength, psi	5,300	18,200
Modulus of elasticity, 10^6 psi	3.5	6.2
Tensile strength, psi	420	1,500
Modulus of rupture, psi	740	2,300
Abrasion loss, in.	0.050	0.015
Cavitation, in.	0.320	0.020
Water absorption, percent	6.40	0.34
Water permeability, 10^{-4} ft/year	5.3	1.4
Thermal conductivity, Btu/ft-hr-deg F	1.332	1.265
Thermal diffusivity, ft^2/hour (73 F)	0.0387	0.0385
Coefficient of expansion, μin./in./deg F	4.02	5.25
Specific heat, Btu/lb/deg F (73 F)	0.241	0.220
Specific gravity	2.317	2.386

Note: 1 psi = 6.895 kPa. 1 in. = 2.54 cm. 1 ft = 0.305 m. 1 Btu · in./h · ft^2 · deg F = 0.144 W/m · K. 1 ft^2 = 0.09 m^2. 1 Btu/lb · deg F = 4187J/kg · K. 1 μin./in. = 0.025 μm/m. 1 F = 1.8 (C) + 32.

Table 2. Durability properties of polymer-impregnated concrete.

Test	Unimpregnated Concrete	Polymer-Impregnated Concrete
Freeze-thaw		
Number of cycles	740[a]	10,340
Loss, percent (wt)	25	12.5
Sulfate attack		
Test cycle, days	480[a]	1,814
Expansion, percent	0.467	0.042
15 percent hydrochloric acid		
Exposure, days	105[a]	1,395
Loss, percent (wt)	27	10
15 percent sulfuric acid		
Exposure, days	49[a]	119[a]
Loss, percent (wt)	35	26
5 percent sulfuric acid		
Exposure, days	210[a]	423[a]
Loss, percent (wt)	33	26

[a] Test completed; failure criteria are 25 percent weight loss for acid immersion and freeze-thaw test and 0.5 percent expansion for sulfate attack test.

Table 3. Mechanical properties of polymer concrete.

Property	Test Temperature (F)	Result
Unit weight, pcf	70	149.1
Specific gravity	70	2.40
Water absorption, percent	70	0.6
Coefficient of expansion, μin./in.	-4 to 70	5.30
	70 to 140	7.53

Note: 1 pcf = 1.602 kg/m^3. 1 μin./in. = 0.025 μm/m. 1 F = 1.8 (C) + 32.

Table 4. Physical properties of polymer concrete.

Property (psi)	Test Temperature (F)	Result
Compressive strength	-15	24,800
	70	19,600
	120	15,800
	190	14,100
Tensile strength	70	1,610
Modulus of rupture	-10	2,960
	70	3,050
	140	2,940
Shear strength	70	4,100

Note: 1 psi = 6.895 kPa. 1 F = 1.8 (C) + 32.

clothing and respirators, if necessary, eliminating sparks and sources of ignition, and electrically grounding the equipment.

The polymer shotcrete that was applied to a near-vertical surface (Figure 1) cured and achieved full strength in 10 to 15 min after application. Aggregate rebound was estimated at 15 to 30 percent. Cube-shaped specimens taken from the applied shotcrete had a compressive strength of 10,000 psi (69 000 kPa).

PRESTRESSED POLYMER-IMPREGNATED CONCRETE BRIDGE DECKS

The prestressed PIC bridge deck system makes use of prestressed panels for rapid construction, and the polymer protects the steel from deicing salts (3). The concept envisions use of precast panels as long as a deck width, rapid erection and placement of panels at the site, and connection of panels by posttensioning. In the program for development of this system, prestressed panels 16 ft long, 4 ft wide, and 6 in. thick (4.88 × 1.22 × 0.15 m) were cast, impregnated and polymerized, and tested.

The concrete mix was designed for a compressive strength of 5,500 psi (38 000 kPa) and 4,000 psi (28 000 kPa) at 24 hours for prestress release. Concrete control test specimens [6 × 12-in. (0.15 × 0.30-m) cylinders] averaged about 5,500 psi (38 000 kPa) at 24 hours and 6,800 psi (47 000 kPa) at 28 days.

The panels were treated at the USBR impregnation and polymerization facility (Figure 2). They were first dried at a temperature of 200 F (93 C). Higher drying temperatures were not used to prevent excessive prestress strand relaxation. The panels were then placed in the specimen carrier (Figure 3), which was rolled into the vessel. Specimens were impregnated and polymerized within the vessel by the pressure-soaking, warm-water bath method. Four panels, about 5,000 lb (2270 kg) each, were treated simultaneously.

The test program for the panels included static- and cyclic-fatigue load tests on single panels and on sets of three connected panels to determine deflections, strain distributions, load at first crack, ultimate load, and load transfer across panel joints. The equipment and specimen arrangement for a three-panel test are shown in Figure 4. The panels are supported by concrete girders on 8-ft (2.44-m) centers. The load is applied to a 5 × 20-in. (12.7 × 50.8-cm) steel plate to simulate an HS20-44 truck wheel load. The panels withstood loads in excess of the 42,000-lb (19 000-kg) ultimate design load and showed good transfer of the load to adjacent panels. Failure occurred at 95,000 lb (43 100 kg) in the single-panel test and at 160,000 lb (73 000 kg) in the three-panel test.

SURFACE IMPREGNATION OF BRIDGE DECKS

The surface-impregnation technique is being developed at USBR as a method to protect newly constructed concrete bridge decks from damage resulting from the use of deicing salts. The objective of the program is to develop a practical method and equipment capable of impregnating the concrete bridge deck with polymer to a depth of at least 1 in. (2.54 cm).

This surface-impregnation technique is a modification of the basic full-impregnation technique and uses adaptations of the method being developed at the University of Texas at Austin (3). The present procedure involves drying the bridge deck, applying the catalyzed monomer, and polymerizing the impregnated concrete by application of heat. The procedure uses relatively simple equipment and does not require vacuum or pressure apparatus. Initial test results indicate this method is capable of producing a 2-in.-deep (5-cm) layer of polymer in the concrete.

The surface-impregnation technique was demonstrated on a newly constructed bridge in Denver during October 1974. The entire bridge deck, 28 ft wide × 61 ft long (8.5 × 18.6 m), was treated at one time. The concrete bridge deck was dried under a portable enclosure by blowing hot air over the surface. The framework for the enclosure is

Figure 1. Application of polymer shotcrete using a modified commercial shotcrete gun.

Figure 2. Impregnation and polymerization facility.

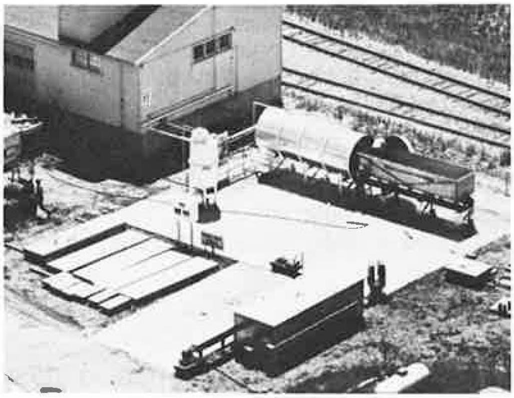

Figure 3. Loading bridge deck panel into carrier for impregnation and polymerization.

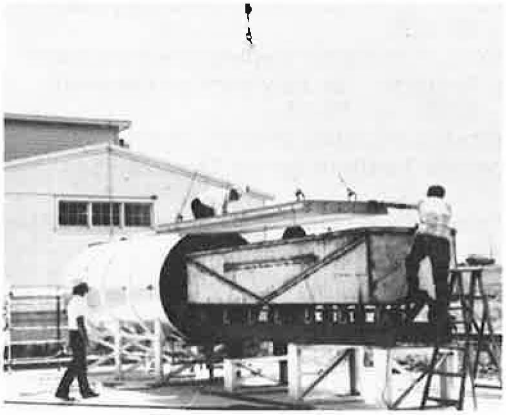

Figure 4. Load test set up for polymer-impregnated concrete bridge deck panel.

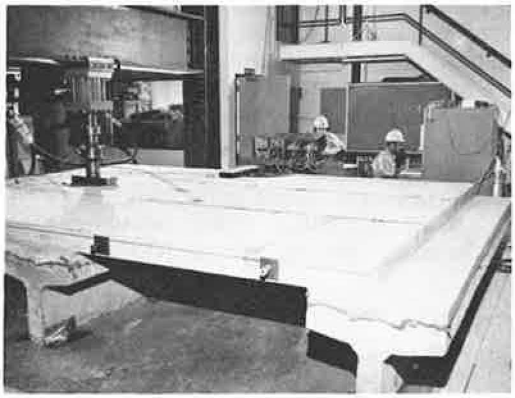

Figure 5. Drying one lane of small concrete bridge before surface impregnation.

Figure 6. Applying monomer to concrete bridge deck.

shown in Figure 5. Air temperature under the enclosure was maintained at 250 F (120 C) for about 3 days or until the concrete was sufficiently dried to a depth of 3 to 4 in. (8 to 9 cm). The enclosure was then removed, and the concrete deck allowed to cool overnight. Sand was spread over the bridge deck to a depth of about ¼ in. (6.35 mm) and then thoroughly saturated with monomer that was allowed to penetrate the concrete overnight (Figure 6). The sand serves as a reservoir for the monomer. A polyethylene sheet was placed over the monomer-saturated sand to prevent evaporation of the monomer. Monomer was reapplied several times to maintain a sufficient supply of monomer for penetration. The enclosure was then placed over the monomer-saturated sand and polyethylene evaporation barrier, and hot air was blown into the enclosure at a temperature of about 160 F (70 C) to initiate polymerization. Cores taken from the deck indicated a little more than 1-in. (2.5-cm) polymer penetration.

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