Guide for the Use of Polymers in Concrete

Reported by ACI Committee 548

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This Guide presents information on how to use polymers in concrete to improve some characteristics of the hardened concrete. Recommendations are included for polymer-impregnated concrete (PIC), polymer concrete (PC), polymer-modified concrete (PMC), and safety considerations for the use of polymers in concrete. Information is provided on types of materials and their storage, handling, and use, as well as concrete formulations, equipment to be used, construction procedures, and applications. Glossaries of terms and abbreviations are appended.

Keywords: bridge decks; chemical resistance; concrete durability; impregnating; latex, monomers; patching; permeability; plastics, polymers; polymer concrete; polymer-modified concrete; polymerization; physical properties; repairs; resurfacing; safety.

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CHAPTER 1—INTRODUCTION
1.1—Purpose of the guide

The improvement of properties of hardened concrete by the addition of polymers is well into its fifth decade. The purpose of this Guide is to provide the user with the fundamental background needed to apply the technology of polymers in concrete to a variety of engineering problems and applications.

The Guide's format provides ease of modification and updating as polymer technology continues to develop. The Guide is written in four basic sections to address polymer-impregnated concrete (PIC), polymer concrete (PC), polymer-portland-cement concrete (PPCC) now called polymer-modified concrete (PMC), and safety. Each of the three categories of concrete containing polymers is usually applied to particular types of concrete elements or specific concrete property improvements, although there are significant overlapping areas. Safety, however, is a prerequisite for all polymer usage and thus is discussed collectively. The Guide does not contain extensive tabulated data from specific studies. This type of information is available in other documents and does not contribute significantly to an understanding of how the polymers are to actually be used in or applied to concrete.

1.2—Background

The mission of ACI Committee 548, Polymers in Concrete, was to gather, correlate, and evaluate information on the effects of polymers used in concrete on the properties of concrete, and to prepare a guide for their use. This mission has now been changed to simply "Report information on the use of polymers in concrete." Since its organization in 1971, the committee has sponsored symposium or technical sessions at convention meetings in 1972, 1973, 1976, 1980, 1983, 1985, 1986, 1988, 1989, 1990, 1993, 1994 and 1996 on a variety of topics relating to the use of polymers in concrete. Eight symposium volumes containing the papers presented at these sessions have been published. Most of the other papers presented at sessions not covered by symposium volumes have been published either in the *ACI Materials Journal* or in *Concrete International*.

Benefits derived from the use of polymers in concrete have world-wide appeal, as demonstrated by the extensive international attendance at the many symposia and congresses that address this subject (ACI SP-40; ACI SP-58; ACI SP-69; ACI SP-89; ACI SP-99; ACI SP-116; ACISP-137; First [1975], Second [1978], Third [1981], Fourth [1984], Fifth [1987], Sixth [1990], and Seventh [1992] International Congress on Polymers in Concrete). The contributions made at these meetings, along with the practical experience gained within the growing industry that applies polymer technology to concrete, form the base of applied concrete technology that is limited only by the ingenuity of the concrete user.

A State-of-the-Art report entitled "Polymers in Concrete," was published in 1977 as ACI 548R-77 and reaffirmed, with modifications, in 1981. Another document, ACI 548.2R-88, "Guide for Mixing and Placing Sulfur Concrete in Construction," was published in 1988 and reaffirmed with editorial changes, in 1993. A third document, ACI 548.3R-91, "State-of-the-Art Report on Polymer-Modified Concrete," was published in 1992 and revised in 1995. This was followed by the first specification developed by the committee, ACI548.4, "Standard Specification for Latex-Modified Concrete (LMC)," that was published in the *ACI Materials Journal* in 1992, presented to the Institute at a standards presentation at the annual convention in March 1993, and balloted by the institute in *Concrete International* in August 1993. A subsequent document, ACI 548.5R, "Guide for Polymer Concrete Overlays," was published in 1993. Anoth-
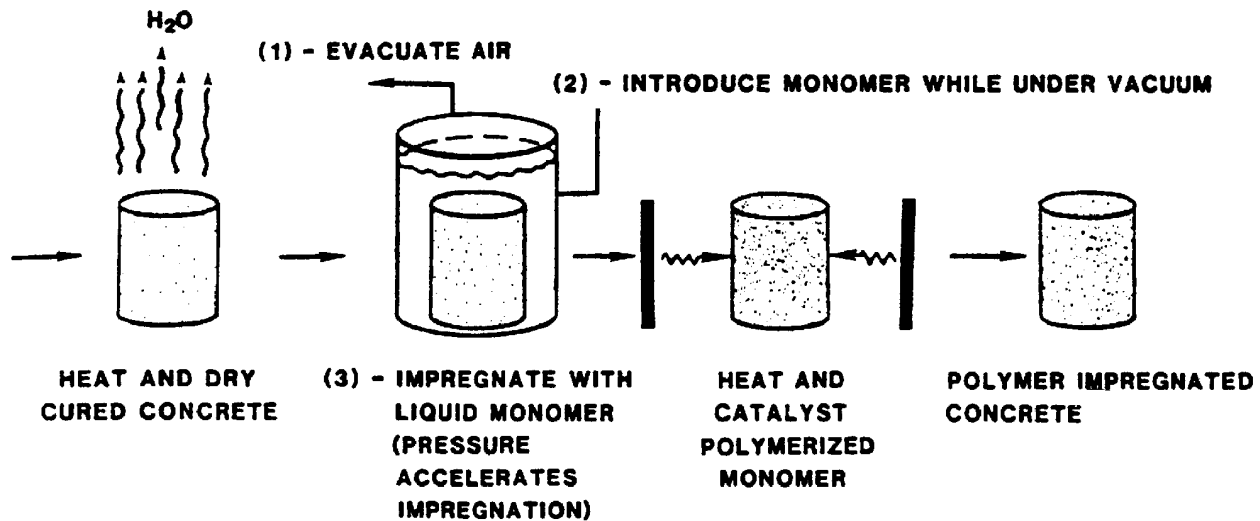
Fig. 2.1—Schematic for the method of producing PIC

er report, published in 1996, is "State-of-the-Art Report on Polymer Concrete Structural Applications."

CHAPTER 2—POLYMER-IMPREGNATED CONCRETE

2.1—Introduction

Polymer impregnated concrete (PIC) is a hydrated portland cement concrete that has been impregnated with a monomer that is subsequently polymerized in situ. In general, almost any shape, size, configuration, orientation, and quality of hardened portland cement concrete can be impregnated to some degree with monomer provided the monomer has access to the void space within the concrete. A substantial portion of this space is usually obtained by removing free water from the pores in the concrete by drying the concrete in some manner.

The monomer is introduced into the concrete by soaking at atmospheric pressure or above. The degree to which the available space in the concrete is filled with monomer during soaking determines whether the concrete is partially impregnated or fully impregnated. Full impregnation implies that about 85 percent of the available void space after drying is filled, whereas partial impregnation implies some degree less than full. The usual process for partial impregnation consists of a process in which the concrete is impregnated to only a limited depth beneath the surface. The different production methods used for full and partial impregnation produce concrete of differing physical characteristics. Therefore, full and partial impregnation are treated separately in this chapter.

After impregnation, the concrete containing the desired amount of monomer then undergoes a treatment to convert the monomer into a polymer. This polymerization reaction causes the molecules of the monomer to chemically link into a long repeated chain-like structure with higher molecular weight, known as a polymer. The two most common methods used for polymerization are called thermal-catalytic and promoted-catalytic. A third method, involving ionizing radiation, is less commonly used.

After polymerization has occurred, the resulting composite material consists essentially of two interpenetrating networks: one is the original network of hydrated portland-cement concrete and the other is an essentially continuous network of polymer that fills most of the voids in the concrete.

A simplified process description for PIC using pressure or vacuum soaking and thermal catalytic polymerization is shown in Fig. 2.1.

2.2—Concrete requirement for impregnation

Almost all existing types of concrete, whether they were made with impregnation in mind or not, can become PIC using the steps described in this Guide. No special procedures are necessary for the preparation of concrete to be impregnated. All types of aggregates, cements, and admixtures used in preparation of modern concrete can be used for PIC. Similarly, curing procedures and curing duration plus age requirements needed for strength development prior to impregnation are not critical. Of course, the final properties of the PIC may vary somewhat, depending on the nature of the materials or curing conditions used. The highest strengths have been obtained with high-pressure steam-cured concrete (Fukuchi and Ohama 1978). Use of a good quality dense concrete requires less polymer for full impregnation than a more porous, poorer-quality concrete. Some badly fractured concrete has also been repaired using impregnation techniques (ACI 224.1R).

2.3—Monomer systems

The selection of a suitable monomer for PIC is usually based on the impregnation and polymerization characteristics, the availability and cost, and the resultant properties of the polymer and the PIC. In principle, any monomer capable of undergoing polymerization in the void system of a hardened concrete can be used. At ambient temperature and pressure, the monomers can be either gases or liquids, although liquid-type monomers are more easily adaptable to impregnating hardened concrete. In practice, impregnation is usually done using vinyl monomers that contain a poly-

Table 2.3.1—Physical properties of common monomers used in PIC and PC

	Viscosity, cp[A]	Density, gm/cm^3 [B]	Vapor pressure, mmHg[C]	Boiling point, deg C	Solubility in 25 deg C water, percent
Methyl methacrylate	0.34[D]	0.81	85.0[E]	77	7.4000
Styrene	0.76[E]	0.91	2.9[E]	135	0.0700
Tert-butylstyrene	1.46[F]	0.88	1.0[F]	218	0.0005

A. cp = μPa • s = centistroke × density
B. gm/cm^3 = 1000 kg/m^3
C. mmHg at 0 deg C = 133 Pa
D. 25 deg C
E. 20 deg C
F. 46 deg C
Note: Trimethylolpropane-trimethacrylate is used as a crosslinking agent for MMA, styrene, or tert-butylstyrene

merization initiator that can be activated by heat. These include acrylonitrile, methyl methacrylate, and other acrylic monomers, styrene, and vinyl acetate. In general, best results in terms of process and performance are achieved with methyl methacrylate, often in combination with an acrylic cross-linking agent, such as trimethylolpropane trimethacrylate. In general, systems based on methyl methacrylate are the most widely used. They offer superior rates of both impregnation and polymerization and lead to an optimum combination of pore-sealing and mechanical properties, including durability. While combinations of styrene with acrylonitrile may produce properties comparable to those obtained with the acrylic systems, most users prefer to avoid the problem of toxicity associated with acrylonitrile.

2.3.1 *Viscosity*—The rate and degree of monomer penetration into hardened concrete depends on the density and pore structure of the concrete, the viscosity of the monomer (Steinberg et al. 1968; Dikeou et al. 1969), and the type of impregnation process used. Table 2.3.1 lists some common liquid monomers of low viscosity at ambient temperature, that are suitable for impregnation.

With greater effort, precast concrete can be impregnated with higher viscosity monomers (greater than 20 centipoise or 20 millipascal seconds) (Kukacka et al. 1973; Kukacka and Romano 1973), although it is usually more economical to reduce viscosity by suitable blends with low-viscosity co-monomers, for example, methacrylate monomers (Kukacka et al. 1975).

2.3.2 *Vapor pressure*—When selecting a monomer for impregnating precast concrete, considerations must be given to its vapor pressure (see Table 2.3.1) for safety and processability.

The high vapor pressure of vinyl chloride, for example, requires special precautions in handling. Considerations must also be given to the effect of curing temperature on vapor pressures, since monomer depletion on the surface of the specimen may occur due to evaporation (Steinberg et al. 1968; Steinberg et al. 1969; ACI SP-40). See Section 2.8 for encapsulation techniques to prevent monomer depletion. Low-viscosity monomers tend to have low boiling points, while high-boiling monomers are more viscous (Dikeou etal. 1971).

2.3.3 *Chemical stability*—See Sections 5.2 and 5.3.2 for descriptions of the chemical stability of monomers and how they should be stored and handled.

2.3.4 *Toxicological considerations*—Most monomers have annoying odors and varying degrees of toxicity. Precautions recommended for handling monomers include adequate ventilation to keep concentrations in air below the maximum limits recommended by the manufacturers. Emergency washes and drains should be available, and environmentally acceptable provisions should be established for handling an accidentally spilled monomer. See Sections 5.3 and 5.4 for detailed descriptions of the potential problems.

2.4—Additives and modifiers

Various co-monomers and other additives to the monomer system are frequently used to modify or produce desired changes in the properties of the resulting polymer and hence in the properties and characteristics of PIC. Safety aspects of these additions are discussed in Chapter 5.

2.4.1 *Plasticizers and extenders*—Plasticizers such as dibutyl phthalate may be added to monomers to improve the flexibility of inherently brittle polymers such as poly(methyl methacrylate) and polystyrene (PS). Specific examples are the addition of "internal plasticizers" like vinyl stearate or butyl acrylate (BA), that copolymerize with monomer (Dikeou et al. 1972).

2.4.2 *Cross-linking agents*—Cross-linking by means of the addition of an appropriate bi-functional or poly-functional monomer increases the rigidity of the polymer, its resistance to the action of solvents, and its softening-point temperature. The amount of change depends on cross-linking density of the polymer. The cross-linking agent most commonly used in PIC is trimethylolpropane trimethacrylate (TMPTMA) (Steinberg et al. 1968), that is a tri-functional acrylic monomer that can copolymerize with other vinyl monomers such as methyl methacrylate (MMA) or styrene.

2.4.3 *Initiators*—Initiators are often called catalysts in the context of PIC. In reality they are not catalysts in the pure chemical sense since they are consumed during the polymerization reaction. Only small amounts of initiators are generally used. The following commercially available compounds have been used in forming PIC (Steinberg et al. 1968; Steinberg et al. 1969; Dikeou et al. 1971; Dikeou et al. 1972; Dikeou et al. 1969): dibenzoyl peroxide (BPO), 2,2'-azobis (isobutyronitrile), a-tert-butyl-azoisobutyronitrile, tert-butylperbenzoate, and methyl ethyl ketone peroxide (MEKP). These compounds decompose at different rates over a range of temperatures to generate free radicals. The selection of type and concentration of initiator and the optimum poly-

merization temperature are important in the production of a uniformly good-quality PIC. BPO is well suited for most vinyl monomers, such as methyl methacrylate and styrene, because it decomposes well below their boiling points.

BPO is susceptible, however, to induced chemical decomposition, that increases the risk of an accidental bulk polymerization. These problems have not been encountered with such azonitrile compounds as 2,2'-azobis (isobutyronitrile), that has proven to be useful and convenient for PIC. A higher temperature initiator such as tert-butyl-perbenzoate is more effective with higher boiling point monomers like diallyl phthalate. See Section 5.2.2 for safety considerations necessary for some initiators.

2.4.4 *Promoters*—Promoters, often called accelerators, are reducing agent compounds added to the monomer system to cause the decomposition of the peroxide initiators in the system. This decomposition produces the necessary free radicals needed for polymerization at ambient temperatures. Several promoters that have been successfully used are N,N-dimethyl-p-toluidine, N,N-dimethyl aniline, cobalt napthenate and mercaptans.

2.4.5 *Silane coupling agents*—Silane coupling agents are silicon compounds used to chemically bond organic polymers to such inorganic materials as sand, rock, glass and metals (Sterman and Maisden 1963; Plueddlemann 1970; Marsden 1970). They have the general formula (HO)3SiR, where R is an organic group compatible with thermoplastic or thermosetting resins. Coupling agents are used frequently in PIC for improvements in strength (Dikeou et al. 1972) and to improve aggregate bond in long-term exposure to moisture.

2.5—Polymerization techniques

Two general methods for the polymerization of monomers are commonly used in PIC. These are the thermal-catalytic and promoted-catalytic. Both methods result in free radical initiated polymerization of properly formulated monomer systems.

The selection of a particular polymerization process depends on its particular advantages for a specific application and evaluation of the effects of: a) drainage and evaporation losses from the concrete during the polymerization, b) safety problems associated with the storage and reuse of large quantities of monomer and initiator, and c) the economics of the entire process.

As a third method of polymerization, radiation techniques have been used in the past; they are discussed in Section 2.5.3 as a topic of general interest. This technique is not commonly used now.

2.5.1 *Thermal-catalytic method*—The polymerization method involving the use of chemical initiators and heat, commonly referred to as the thermal-catalytic process, has been used extensively for preparing PIC. The process can be performed in air or under water. Several initiators that have been used in this method are described in Section 2.4.3.

The primary advantage of the thermal-catalytic polymerization method is that the polymerization rates are very rapid and, therefore, processing times are short. Relatively simple electric ovens, water, or raw steam can be used as a

heat source (DePuy and Kukacka 1973; Sopler et al. 1973; Fowler et al. 1973; Kukacka et al. 1972; DePuy and Dikeou 1973). A disadvantage is that the chemical initiator must be dissolved in the monomer prior to introducing the mixture into the concrete. In a commercial operation of almost any size, this involves storing and handling large batches of monomer containing a chemical initiator. Although potentially dangerous, using relatively stable azo-type initiators in conjunction with established safety practices can reduce the hazards to manageable levels (Kukacka and DePuy 1972; DePuy and Kukacka 1973).

2.5.2 *Promoted-catalytic method*—Decomposition of organic peroxide initiators can be accomplished by the use of promoters or accelerators (see Section 2.4.4) instead of temperature or heat, as in the case of the thermal-catalytic method. The decomposition produces the free radicals, which then allows the polymerization to take place at ambient temperature without the need for an external source of energy. Promoted-catalyst systems can induce polymerization at an ambient temperature of 40 F (5 C) or lower. Disadvantages of this method are the difficulties in obtaining predictable polymerization times and in being able to match the monomer saturation time with that of the onset of polymerization. As the induction period for polymerization begins immediately on adding the promoter to the monomer-initiator system, its use in PIC is limited.

2.5.3 *Radiation method*—Radiation-induced polymerization of monomers in concrete has been successfully performed in both air and water (Steinberg et al. 1968 and 1969; Dikeou et al. 1971; DePuy and Kukacka 1973; Levitt et al. 1972).

The production of free radicals during initiated polymerization can also be achieved by using such ionizing radiation as gamma rays emitted by cobalt-60. Absorption of the radiation energy by the monomer results in secondary processes including the production of free radicals. The rate of polymerization varies with the different monomers under constant radiation and temperature conditions. The polymerization rate is dependent upon the square root of the intensity, but at very high radiation intensities it reaches a limiting value.

An important advantage of radiation is that chain reactions can be initiated at room temperature or lower. Lower-temperature polymerization increases the chain length of the polymer and tends to reduce the amount of monomer lost by evaporation before complete polymerization takes place, particularly when monomers of high vapor pressures are used.

Since initiators and promoters are not required for this process, the inhibited monomer can be used directly as it comes from the manufacturer, has essentially unlimited storage, and can readily be reused once opened. Relatively thick sections of impregnated concrete can be polymerized uniformly using radiation.

Disadvantages of radiation include the high cost of radiation sources, the necessity of massive biological shielding, and the low polymerization rates. The latter, when combined with the radiation attenuation due to the thick sections and high density, results in large radiation requirements and long

processing times. Some monomers also require high radiation doses and polymerize slowly.

2.6—Partially impregnated concrete

Partially impregnated concrete (sometimes called surface impregnated concrete) is usually accomplished by impregnating conventional portland cement concrete to a less-than-full depth using a simple soaking technique, in contrast to fully impregnated concrete (Section 2.7), which has been impregnated to the full depth of the section using the vacuum-pressure technique (see Fig. 2.1). The partial impregnation is intended to provide the concrete with a relatively impermeable, in-depth protective zone to increase its durability. While there would be some increase in strength in the impregnated zone, the primary purpose of partial impregnation is to increase durability by reducing the permeability. The chief function of the partial impregnation is to reduce the permeability of the concrete to moisture and aggressive solutions. The concrete pores in the impregnated zone contain less polymer than could be achieved with the full impregnation techniques.

2.6.1 *Applications of partial impregnation*—The potential applications include treatment of precast concrete elements and existing concrete structures to improve durability, reduce maintenance requirements, and restore deteriorated structures (Kaeding 1978). Most of the work on partially impregnated concrete has been in developing a technique to protect concrete bridge decks and spillways from damage caused by deicing salts and freeze-thaw deterioration (Fowler et al. 1973; Smoke 1975; Schrader et al. 1978; Bartholomew et al. 1978; Schrader 1978). The process has also been applied to concrete stilling basins, curbstones, concrete pipes and mortar linings, and deteriorated buildings (Kaeding 1978).

In some cases, the use of partial impregnation may be advantageously combined with the use of other systems such as PC or PMC. In a rehabilitation project, PC or PMC thus may be used to repair cracks and holes, with impregnation used to treat the entire surface.

2.6.2 *Characteristics of partially impregnated concrete*—The impregnation of concrete surfaces with a suitable monomer that is subsequently cured in-situ has been shown to improve several important properties, including tensile, flexural, and compressive strengths; Young's modulus; abrasion resistance; resistance to penetration by, and damage from, water, acids, salts, and other deleterious media; and resistance to freezing and thawing.

Resistance to typical freezing and thawing has been found to be good, when the polymer depth is more than 1in. (25mm) and abrasion resistance is increased significantly. In addition, some laboratory evidence indicates that impregnating a chloride-contaminated concrete can effectively immobilize the chloride, at least to the depth of the impregnation, if the cracks induced by drying are effectively sealed by the polymer (Manson et al. 1978). However, such sealing with respect to salt intrusion has not been demonstrated under field conditions, and chloride intrusion after impregnation has been observed in most cases. See Tables 2.6.2(a), 2.6.2(b), and 2.6.2(c) for typical data on mechanical properties on fully impregnated concrete. Resistance to chloride intrusion and resultant corrosion is improved by partially impregnating concrete before it is open to service and before chlorides are present (Texas SDHPT 1977).

Although increases in strength may be observed as a result of the partial impregnation, such increases in strength are usually not as great as the increases produced by full impregnation. The increases in strength are a function of the depth of impregnation and the polymer loading in the impregnated zone, that is generally only a small proportion of the cross section of the member. It should generally be assumed that partial impregnation does not significantly increase the strength of a member unless the partial impregnation is specifically designed to increase the strength and the increases in strength are verified by tests.

2.6.3 *Limitations of partial impregnation*—Polymer impregnation reduces the permeability of concrete and thereby increases its durability in exposure to aggressive agents. Note that the impregnation does not render the concrete completely impermeable, and that in exposure to very aggressive agents, such as sulfuric acid, concrete is attacked slowly. In such cases, it is recommended that the impregnated concrete be given an additional protective coating treatment of a suitable resistant protective coating material. The polymer used for the impregnation may be a suitable protective coating system. The protective coating should be applied in two or three layers to ensure that pinholes or defects are sufficiently covered.

Although partial depth (surface) impregnation is a technically feasible process for the treatment of concrete surfaces to reduce permeability and increase resistance to abrasion, freezing and thawing, and corrosion, the status of surface impregnation for the protection of concrete bridge decks is currently in doubt. The principal reason for using the technique on concrete bridge decks is to prevent deicing salts from penetrating the concrete and corroding the reinforcing steel. Investigations by the Bureau of Reclamation and Federal Highway Administration have indicated that a number of bridge decks treated by the process have been observed to contain cracks, and there is no assurance that any of the cracks are sealed by the process. It appears that concrete invariably cracks over a period of time. The surface impregnation technique requires the application of heat to dry the concrete surface. This may itself induce cracking. If the cracks are not sealed, they could serve as channels for salt solutions and possibly cause local concentrations of salt in the concrete, thereby defeating the purpose of the impregnation treatment.

2.6.4 *Monomers and polymers for partial impregnation*—The various monomers that can be used for partial impregnation are described in Section 2.3. As noted, impregnation is normally achieved using vinyl monomers containing a polymerization initiator that can be activated by raising the temperature. At present such systems offer the best available combination of cost, convenience, and performance.

While raising the temperature in order to initiate polymerization does add a process step, it is generally desirable to do so, for it is difficult, using ambient-temperature polymeriza-

Table 2.6.2(a)—Mechanical properties of PIC using methacrylate (MA) esters (Brookhaven National Laboratory, 1968, 1969, 1971, 1973)

Polymer	Viscosity of monomer, centistrokes[A]	Loading weight, percent	Compressive strength, psi[B]	Modulus of elasticity, 10^6 psi
Control	—	0.00	6600	3.5-4.5
MMA	0.60	5.27	16,350[C]	6.12
Isobutyl-MA	0.98	4.99	16,290[C]	5.42
Stearyl-MA	10.50	2.52	6920	3.48
Isobornyl-MA	6.00	2.80	9060	4.70
Isodecyl-MA	3.30	3.51	7000	3.38
+ 20 percent MMA	—	3.63	8510	3.78
+ 40 percent MMA	—	4.97	14,060	4.85
+ 80 percent MMA	—	5.19	16,593[C]	5.90

A. Centistroke = 1.0 mm^2 / s = cp / density
B. 1 psi = 7 kPa
C. Exceeded capacity of the testing machine

Table 2.6.2(b)—Physical properties of PIC (thermal-catalytically cured; dried at 105 C prior to impregnation) (Brookhaven National Laboratory, 1968, 1969, 1971, 1973)

Property	Control		MMA	Styrene	MMA + 10 percent TMPTMA
	Undried	Dried			
Hardness (impact hammer)	32.000	27.000	52.000	50.000	—
Water absorption, percent	6.400	6.200	0.340	0.700	0.21
Water permeability, 10^4 ft / yr[A]	5.300	29.000	1.400	1.500	1.2
Thermal conductivity, btu / ft / hr deg F[B]	1.332	1.105	1.265	1.305	—
Thermal diffusivity, ft^2 / hr[C]	0.039	0.039	0.039	0.041	—
Specific heat, btu / lb / deg F[D]	0.241	—	0.220	0.221	—
Thermal coefficient of expansion, 10^{-6} in. / in. deg F[E]	4.020	4.280	5.250	5.000	5.06

A. 1 ft = 0.305 m
B. 1 btu / ft / hr deg F = 12.0 mW / in. deg K
C. 1 ft^2 / hr = 25.8 mm^2 / s
D. 1 btu / lb / in. deg F = 4.19 kJ / kg / deg K
E. 1 in. / in. deg F = 1.8 mm / mm deg C

tion initiators, to coordinate the time of polymerization initiation with the time required to achieve the desired depth of impregnation.

2.6.5 *Partial impregnation process*—The principal steps in partial impregnation are a) surface preparation, b) concrete drying, c) concrete cooling, d) monomer soaking, e) polymerization, and f) cleanup.

2.6.5.1 *Surface preparation*—The surface of the concrete to receive the monomer should be cleaned of such contaminants as oil, grease, or dirt. Conventional cleaning methods and materials are adequate to do this. Any undesirable irregularities in the surface (popouts, spalls, bugholes, large cracks, etc.) should be repaired at this time.

2.6.5.2 *Concrete drying*—The concrete surface should be dried for 6 to 8 hr at a surface temperature of 250 to 275F (121 to 135 C). The rate of temperature development to reach the drying temperature should not exceed 100 F (38 C) per hour. Prior to drying, surfaces that can retain a sand layer should be covered with clean sand to a depth of $^3/_8$ to $^1/_2$ in.

(9 to 13 mm); this helps to minimize the temperature gradient in the concrete. The sand should be composed of hard, dense, low-absorption particles that passes a No. 16 sieve (1.18 mm), but with not more than 5 percent passing a No. 100 sieve (0.15 mm). Infrared heaters have been used successfully in many projects for drying concrete.

2.6.5.3 *Concrete cooling*—After drying, the concrete surface temperature should be allowed to cool to 100 F (38 C) or less before adding any monomer. On cold days, the rate of cooling should be retarded by placing a covering over the heated surface. This helps to minimize temperature-gradient induced cracking of the surface.

2.6.5.4 *Monomer soaking*—Monomers can be introduced into the concrete by either atmospheric soaking or pressure soaking. The simplest approach is to immerse the concrete in a low-viscosity monomer and soak under atmospheric pressure. This technique is applicable to precast concrete elements and is based upon the ease of penetration to a limited depth by a low-viscosity monomer and the economics

Table 2.6.2(c)—Durability of PIC (thermal-catalytically cured; dried at 105 C prior to impregnation) (Brookhaven National Laboratory, 1968, 1969, 1971, 1973)

Property	Control		MMA	Styrene	MMA + 10 percent TMPTMA
	Undried	Dried			
Freeze-thaw: Number of cycles	740	440	3650	5440	4660
Freeze-thaw: Weight loss, percent	25	28	2	21	0
Sulfate attack: Number of days	480	605	720	690	630
Sulfate attack: Expansion, percent	0.466	0.522	0.006	0.030	0.003
Acid resistance, 15 percent HCl: Number of days	105	106	805	805	709
Acid resistance, 15 percent HCl: Weight loss, percent	27	26	9	12	7
Acid resistance, 15 percent H_2SO_4: Number of days	49	77	119	77	—
Acid resistance, 15 percent H_2SO_4: Weight loss, percent	35	30	26	29	—
Abrasion loss, in. [A]	0.050	0.036	0.015	0.037	0.019
Abrasion loss: Percent weight loss, g [B]	14.0	7.0	4.0	6.0	5.0
Cavitation (2-hr exposure), in.	0.032	0.262	0.020	0.009	—

A. 1 in. = 25.4 mm
B. 1 g = 0.0022 lb

of a simple process that does not require an elaborate vacuum or pressure soaking facility, or both. For horizontal surfaces, the monomer should be applied to the sand layer (see Section2.6.5.2) on the concrete surface at a rate of approximately 0.8 lb/ft^3 (3.9 kg/m^3) and allowed to soak for 6 hr. The sand helps to retain even distribution of the monomer over the surface. The monomer-saturated sand should be covered with plastic film to reduce evaporation. A commonly used monomer system for this type of soaking consists of 95 percent (by weight) MMA and 5 percent (by weight) TMPTMA with 0.5 percent (by weight) 2,2-azobis-(2,4-dimethylvaleronitrile) or 2,2'-azobis (isobutyronitrile) initiator.

For soaking surfaces that cannot have monomers ponded on them (for example, walls), a shallow [$^1/_4$ to $^3/_8$ in. (6 to 10mm)], leak-tight enclosure must be constructed and attached to the surface. The enclosure is then completely filled and maintained filled with a monomer. Soaking times from 4 to 6 hr are usually satisfactory, at which time the excess monomer is drained from the enclosure.

Another approach is to use a higher viscosity monomer and pressure soaking. This approach is based upon the assumption that the higher viscosity monomer gives a dense polymer loading in the impregnated zone, and that the pressure soaking can be controlled to produce a consistent penetration to a predetermined depth; therefore, it should be possible to realize economies in production by impregnating the concrete to a controlled depth, thereby minimizing the amount of monomer used for impregnation. Lower viscosity monomers can also be used with pressure soaking. The manner in which the pressure is applied depends, to a degree, on the orientation of the surface being impregnated. Horizontal surfaces can be enclosed to prevent lateral movement of the monomer while a uniform weight distribution (for example, water) is applied to the top surface of the liquid monomer with perhaps an interface barrier of polyethylene sheeting to prevent intermingling. Any significantly inclined or vertical surface would probably need a pressure-tight enclosure to

hold the monomer to the concrete surface while external pressure (for example, air pressure) was applied to the free surface of the monomer.

A number of investigations have been made to develop processes for partial impregnation of existing concrete structures in the field. These approaches have involved treatment of sections of such concrete structures as concrete bridge decks and spillways, and have employed both the atmospheric pressure soaking and pressure soaking processes. These processes have been used for both horizontal and vertical surfaces.

2.6.5.5 *Polymerization*—Any of the methods described in Section 2.5 can be used. A common method used on horizontal surfaces is the thermal-catalytic method. This method, described in Section 2.5.1, includes application of heat to the surface of the impregnated concrete so that a temperature, at the surface, of 165 to 195 F (74 to 90 C) is maintained for 5 hr. Infrared heat units within shallow enclosures over the areas to be polymerized have been successful in accomplishing this.

Concrete surfaces that used monomer-tight enclosures for soaking can be filled with hot water and the required temperature maintained by strip heaters mounted on the back of the enclosure (Schrader et al. 1978). In all cases, open flame heat sources that could cause combustion of monomer vapor should not be used.

2.6.5.6 *Cleanup*—Spillage of monomers should be avoided as much as possible for safety reasons. An absorbent compound may be used to contain spills until they can be removed for disposal. After the polymerization step is complete, the absorbent compound used to contain the monomer can usually be shoveled or swept from the impregnated surface. Hardened polymer sand composites are often very difficult to remove from the concrete.

2.6.6 *Depth of impregnation*—Depth of impregnation can usually be determined by visual inspection of small cores or samples taken from the polymerized concrete. Other methods

that have been successful in determining polymer depths include (Heller 1977; Locke and Hsu 1978; Patty 1978) a) acid etching, b) color enhancement by use of phenolphthalein in conjunction with microscopic examination, c) petrographic examination of polished sections using polarized light, d) nondestructive sensitivity measurements, e) thermal analysis, and f) pyrolysis coupled with infrared spectroscopy.

2.7—Fully impregnated concrete

Full impregnation is obtained by first thoroughly removing free moisture from the concrete in order to provide the maximum amount of previously water-filled pore space for monomer filling.

This is followed by complete monomer saturation, usually under pressure, and subsequently polymerization of the monomer system. The principal reason for full impregnation of the concrete is to improve the strength characteristics of the concrete. This improvement is accompanied by improved resistance to water penetration and improved durability. In many instances, the modulus of elasticity is also significantly increased. The improved strength and increased modulus can be used effectively to establish economies in both design and construction.

2.7.1 *Applications for fully impregnated concrete*—The physical requirements for moisture removal and monomer saturation needed for fully impregnated concrete usually dictate the size and configuration of concrete elements that can undergo this treatment. Therefore, fully impregnated concrete is restricted to concrete that can be made and handled in precast plant operations. Examples of fully impregnated concrete elements include precast tunnel lining and support systems, beams, pipes, curbstones, plumbing and electrical fixtures, prestressed piling, fender piling, wall panels, trench covers, and other smaller elements (Dikeou 1976, Dikeou 1980; Fowler 1983).

2.7.2 *Characteristics of fully impregnated concrete*—Polymer impregnated concrete looks very much like conventional concrete, but may have a surface coating of polymer if it was not cleaned after polymerization. Increases in strength in compression, tension, and flexure can be achieved with increases as much as four to five times those of unimpregnated concrete strengths. PIC can be made from both high-quality and low-quality concrete; however, the strength of PIC made from high-quality concrete is generally higher than the strength of PIC made from lower-quality concrete. Strength is directly related to the degree of impregnation achieved. Concretes subjected to either high- or low-pressure steam curing prior to impregnation generally result in higher strengths than comparable concretes that were moist cured at room temperatures (Steinberg et al 1968; Kukacka and DePuy 1972; Auskern 1971). Tables 2.6.2(a) and 2.6.2(b) give some typical mechanical properties for PIC.

The strength increase attributed to polymer impregnation depends on the temperature of the exposure conditions. The strength of PIC shows a gradual decrease with an increase in the temperature at which it is tested. Exposure to elevated temperatures for short periods of time followed by a return to normal temperatures usually shows no noticeable effect. Prolonged exposure at elevated temperatures may result in a permanent decrease in strength. Exposure to temperatures at or above the glass transition temperature of the polymer produces a more rapid strength loss.

For fully impregnated concrete, increases in modulus of elasticity (compressive and flexural) accompany the strength increases of PIC over unimpregnated concrete. For partially impregnated concrete, the increases (or decreases) are not significantly different from the control specimens.

Durability of PIC to most forms of environmental attack is significantly improved over that of untreated concrete. This is attributed primarily to filling of the pore system in the concrete with a polymer. Typical durability information for PIC is shown in Table 2.6.2(c).

2.7.3 *Limitations of full impregnation*—Full impregnation is limited almost exclusively to precast plant operations. Capital expenditures to begin production may be large. The monomer storage and transfer system should be designed to be completely enclosed, to reduce hazards and offensive odors of monomer vapors escaping to the atmosphere. Disposal of curing water containing polymers requires additional filtration systems. Safety is a primary consideration.

Another limitation of polymer-impregnated concretes is the loss of stiffness and strength at temperatures greater than the softening point of the polymer. The designer should consider the softening point of the particular polymer used in relation to the expected service temperature. However, for a typical acrylic-concrete system, the improved mechanical properties should be retained because of the excellent insulating properties of concrete. Therefore, for most purposes, this is not a limitation, though the possibility of such a loss should be considered in designing structural elements that may be subjected to these high temperatures and that are not reinforced with steel. Fire resistance has been studied, and the evidence suggests that typical PICs are self-extinguishing (Carpenter et al. 1973).

2.7.4 *Monomers and polymers for full impregnation*—The various monomers that can be used for full impregnation are described in Section 2.3.

2.7.5 *Full impregnation process*—The principal steps in full impregnation are the same as in partial impregnation (see Section 2.6.5). The procedures for some of the steps are different, however, and these are described in the following sections.

2.7.5.1 *Surface preparation*—See Section 2.6.5.1.

2.7.5.2 *Concrete drying*—For full impregnation, the concrete must be as dry as practicable while maintaining a cost-effective balance between energy expended for drying and the time constraints associated with a precasting operation. In general, both the drying temperature and the time period over which this temperature operates are increased over that used for a partial impregnation process. Drying temperatures of 300 F (150 C) are recommended with a rate of temperature development to reach the drying temperature not to exceed 100 F (38 C) per hr. If the concrete section being dried has steel reinforcement held in place with plastic chairs, then the maximum drying temperature should not exceed the melting point of the plastic chairs. The concrete should be dried to a constant weight. The duration of drying

depends on the size and thickness of the element being dried. Large, thick sections take much longer than small, thin sections. For sections up to 12 in. (305 mm) thick, dryness should be achieved in 24 hr (DePuy and Kukacka 1973).

Vacuum drying, either by itself or as part of a two-step process of initial vacuum drying followed by elevated temperature drying, can also be used, but has been neither particularly effective nor economical. This is usually adaptable to smaller-sized concrete elements, although with large vacuum chambers larger sizes can be handled.

2.7.5.3 *Concrete cooling*—After drying, the concrete temperature should be allowed to reach 100 F (38 C) or less before beginning the monomer impregnation.

2.7.5.4 *Monomer soaking*—For the purposes of this Guide, it is assumed that full monomer impregnation through soaking takes place in an impregnation vessel. In vessels of this type, the extent to which the concrete can be fully impregnated depends on the degree of dryness of the concrete, vacuum and soak pressures, and soak time, that is also dependent on the viscosity of the monomer used for a given soaking pressure. As a practical matter, the properties or quality of the PIC produced is the result of a trade-off with processing costs and time. A moderately good-quality PIC may be made at a lower cost by simple atmospheric soaking (without the vacuum and pressure soaking); however, the depth of impregnation and polymer loading is limited. A better-quality PIC at a higher cost can be made by applying a vacuum to remove air from the concrete after drying, followed by soaking in monomer under pressure. The vacuum- and pressure-soaking steps reduce the time required for saturation. Increased pressures in the pressure soaking step result in slightly higher polymer loadings and a better-quality product.

Studies have shown that good-quality dense concrete specimens having a cross-section of up to 12 in. (305 mm) that have been thoroughly dried can be adequately impregnated using the following steps (DePuy and Kukacka 1973):

a) Place the dried concrete specimen in the impregnation vessel.
b) Evacuate the vessel down to a pressure of 0.5 in. Hg absolute (0.35 kPa) or less and maintain this vacuum for 30min.
c) Introduce the monomer under vacuum until the concrete is inundated and subsequently pressurize the entire system to 10 psi (68.9 KPa).
d) Pressure-soak for 60 min.
e) Release pressure and remove the monomer from the vessel.
f) Remove and place the concrete section underwater or, for larger sections, backfill the impregnator with water. See Section 2.8 for guidance on encapsulation techniques to reduce monomer losses during this step.

2.7.5.5 *Polymerization*—Of the polymerization methods described in Section 2.5, only the thermal-catalytic and radiation methods are suitable for full impregnation. The promoter catalytic method begins polymerization too quickly and without suitable controls for a full impregnation process. Determination of which process to use should be based on an evaluation of the safety problems associated with storage and handling of monomers, initiators, and radiation sources as well as the economics of the entire process.

For the thermal-catalytic process, the heat necessary to accomplish the polymerization of the fully impregnated specimens has usually been provided by heated water. If the impregnated specimens remain in a water-filled vessel, the temperature of that water can be raised by various techniques to appropriate levels [165 to 195 F (74 to 90 C)] and maintained until polymerization is complete. Open-flame heat sources or high-temperature elements that could cause combustion of monomer vapor should not be used.

2.7.5.6 *Cleanup*—Specimens can be cleaned as needed using conventional methods. If underwater polymerization is used, some polymer escapes to the water and may adhere to the wall of the impregnator and collect in the valves and piping. Using the thermal-catalytic process, less polymer is formed in the water, probably due to the decreased solubility of monomers in water at the elevated temperature. The problem can be minimized by designing the vessel to drain all the excess monomer and installing filters in the water system.

2.7.6 *Depth of impregnation*—Because the requirement is for full impregnation, only through-thickness cores or slices provide a surface by which this can be validated. Methods described in Section 2.6.6 are applicable. Theoretical calculations based on saturated-surface-dry weight, dried weight, and weight after saturation and polymerization of the concrete plus the specific gravity of the polymer can be used to give an approximate indication of whether the full impregnation process was successful.

2.8—Encapsulation techniques to reduce monomer losses

Care must be taken to minimize monomer evaporation and drainage losses from the concrete during the polymerization process. Evaporation is a problem when such high-vapor pressure monomers as MMA are used. Monomer drainage losses become appreciable when low-density concretes are impregnated.

Several techniques have been used to minimize monomer evaporation and drainage losses from concrete during the polymerization reaction. (Kukacka and DePuy 1972; Kukacka and Romano 1973; Sopler et al. 1973; Fowler et al. 1973; Kukacka et al. 1972; Steinberg et al. 1970; DePuy and Dikeou 1973).

The following methods for reducing monomer losses are:
a) Wrapping monomer-saturated specimens in polyethylene sheet or aluminum foil.
b) Encapsulating the specimen in a tight form during impregnation and polymerization.
c) Impregnating with monomer, followed by dipping the impregnated concrete in high viscosity-monomer prior to polymerization.
d) Polymerizing monomer-saturated specimens underwater.

Of the methods studied, underwater polymerization appears to be the most feasible for large-scale applications. Pipe, beams, and panels have been treated in this manner. The method has been used successfully in conjunction with radiation and thermal-catalytic use with very little surface depletion observed (DePuy and Kukacka 1973). Underwater

polymerization does not have any detrimental effects on the PIC properties and can produce specimens with highly reproducible polymer loadings (Sopler et al. 1973; Kukacka et al. 1972; Steinberg et al. 1970).

NOTE: Although full scale impregnation facilities were designed for precast concrete elements and operated at both Brookhaven National Laboratory and the Bureau of Reclamation, the process has never achieved commercial success.

CHAPTER 3—POLYMER CONCRETE
3.1—Introduction

Polymer concrete (PC) is a composite material in which the aggregate is bound together in a matrix with a polymer binder. The composites do not contain a hydrated cement phase, although portland cement can be used as an aggregate or filler. PC composites possess a unique combination of properties dependent upon the formulation (Fontana and Bartholomew 1981). These include:

a) Rapid curing at ambient temperatures from –18 to +40 C (0 to 104 F).
b) High tensile, flexural, and compressive strengths.
c) Good adhesion to most surfaces.
d) Good long-term durability with respect to cycles of freezing and thawing.
e) Low permeability to water and aggressive solutions.
f) Good chemical resistance.
g) Light weight.

Polymer concretes have been used for (Fowler and Paul 1978; Fontana et al. 1978; Kukacka and Fontana 1977; Fowler et al. 1983):

a) Patching material for portland cement concrete (Dimmick 1985).
b) Skid-resistant protective overlays and wearing surfaces on concrete (Fontana and Bartholomew 1981, Dimmick 1994, Dimmick 1996).
c) Structural and decorative construction panels (Prusinski 1976).
d) Sewer pipes, equipment vaults, drainage channels, etc.
e) Linings in carbon-steel pipes for geothermal applications (Kukacka 1978).
f) Swimming pool and patio decking.

These widely divergent uses clearly indicate that no single commercially available product could be compounded to perform all of these tasks well; therefore, the term PC should never suggest only one product, but rather a family of products. Application and performance of PC is dependent upon the specific polymeric binder as well as the type of aggregate and its gradation. Copolymerization techniques allow the production of a variety of binders with a wide range of physical properties. The user of PC should insist on field and engineering performance data to support laboratory data whenever possible.

3.2—Polymer concrete patching materials

PC can provide a fast-curing, high-strength patching material suitable for use in the repair of portland cement concrete structures (Fontana and Bartholomew 1981; Fowler and Paul 1978; Fontana et al. 1978; Kukacka and Fontana 1977; Fowler et al. 1983, Dimmick 1985). Many PC patching materials are primarily designed for the repair of highway structures where traffic conditions allow closing of a repair area for only a few hours (Fontana and Bartholomew 1981; Fowler et al. 1981; Fowler et al., 1978 Fontana et al. 1978). PCs are not limited to that usage; however, and can be formulated for a wide variety of application needs. For any patching, the following aspects of the repair should be given consideration by the user: a) evaluating the surface to be repaired, b) preparing the surface, c) materials selection, d) PC formulations, e) placement techniques, f) cleanup of tools and equipment, and g) safety.

3.2.1 *Surface evaluation*—Before attempting repairs on concrete surfaces, it is necessary to determine the condition of the surface to be treated and to determine what surface preparation is required. To obtain good performance over a weak surface would be futile, since failure at the surface (bond line) is likely to occur. Poor bond also can occur with sound surfaces if those surfaces have not been properly prepared.

Two surface conditions must be met if repairs are to be successful: a) the concrete surface must be strong and sound and b) the concrete surface must be dry and clean (free from laitance, dirt, oil, grease, paint, and curing compounds).

In areas where PC is to be used as a patching material, experienced personnel may test concrete for delamination by sounding with a hammer. A good solid ring usually indicates that the concrete is sound and there are no delaminations below the exposed surface. The use of a chain drag is also an acceptable surface evaluation method. A simple visual examination of the concrete surface to be repaired is not acceptable.

Some PC patching materials require dry surfaces, some can be applied to moist surfaces (no free-standing water), and some are not sensitive to moisture. The application determines the type of patching material to use.

3.2.2 *Surface preparation*—In general, PC patching materials should be used only in the repair of asphalt-free, air-dried areas in concrete structures. While the presence of small pieces of asphalt [for example, 1 in^3 per 10 ft^3 (60 cm^3 per m^3)] may not be detrimental, optimum results are obtained with the cleanest surface possible. All loose deteriorated and unsound material should be removed. Patching over delaminated areas is not recommended unless the delaminations are made sound by epoxy injection or other techniques. In spalled areas concrete removal may require the use of chipping hammers, pavement breakers, scarifiers, sand blasters, high pressure water blasters or combinations of these. Chipping hammers rated at 30 lb or less (< 14 Kg) should be used for bridge decks and suspended slabs.

Moisture on the concrete surface should be removed unless it is known that the adhesion of the PC material to be used is not affected by moisture. If it is necessary to dry the concrete surface, such methods as gas-fired torches or clean, dry compressed air may be used. Whenever external heating methods are used, care must be exercised to avoid causing spalling or crazing the concrete substrate and adjacent good concrete.

Dust and debris may be removed by blowing with clean, dry compressed air. Mechanical abrasion or acid etching or both are means to clean the contaminated concrete surfaces that is necessary to achieve the desired bond between PC and the concrete. Any exposed reinforcing steel in the repair area should also be cleaned by a mechanical abrasion method prior to the application of the PC patching material. Mechanical abrasion methods that result in damage to reinforcement should not be used.

A sawed edge approximately $^1/_2$ in. (13 mm) deep at the perimeter of the repair area may be required for some PC patching materials. If a slight keying action is desired, the saw blade can be tilted to undercut the edge at a slight angle. Some producers of PC patching materials have indicated that their product can be feather-edged; hence, sawing would not be required. However, saw cutting or undercutting the perimeter of the repair area is good practice and is recommended.

Special care should be taken to prevent damage to surrounding areas during the removal of unsound concrete. The bond of remaining sound concrete with reinforcing steel should not be impaired.

3.2.3 *Formwork*—Formwork may be required for bulkheads or when it is necessary to establish or maintain line or grade with an existing surface. Forms are also required when patches are made at expansion or construction joints. Care should be exercised to prevent PC patching materials from bonding concrete sections, and from filling joints that are intended to remain open to accommodate differential expansion of adjacent elements.

Conventional wooden or steel forms treated with such release agents as plastic sheeting (such as polyethylene), vegetable oils, paraffin wax, or silicone greases can be used. The forms must be tight enough to hold the PC-type material that is being used. All surfaces where bond is not desired, but which is exposed to the monomer or resin, should be treated with a release agent. If this is not done the monomer or resin thoroughly wets and becomes attached to all materials with which it comes in contact. Once attached, it is very difficult to remove.

Some silicone or latex caulking compounds, epoxy-bonding agents, and cementitious fast-setting compounds can be used as joint sealers. Whenever possible, it is desirable to have the joint sealer form a part of the permanent repair.

3.2.4 *Polymer concrete formulations*—As previously mentioned in this report, many PC formulations have been used for patching materials. Each one was designed for specific applications; thus, care must be exercised in selecting the right material for the job it is to perform.

Some of the most widely used monomers for PC patching materials include MMA, styrene, unsaturated polyester resins, and vinyl esters. Other materials that have been used for PC patches are furfuryl alcohol and furan resins (Suguma et al 1981, 1983, 1984). Epoxy resins with their curing agents are the most commonly known PC compounds. Epoxy mortars are, in fact, true PC materials; thus, the recommendations outlined in this report are applicable. Epoxy mortars are composed of two components for the epoxy and aggregate blend. The aggregate/resin ratio varies with the

epoxy formulation and has been used in ratios from 1:1 to 15:1 by weight, depending on the aggregate gradation. Users of epoxy PC materials should also refer to publications issued by ACI Committee 503.

In most cases, cross-linking agents or plasticizing agents, or both are added to the binder formulations described above to improve some of the physical properties of the finished products.

Curing of the formulations for PC patching materials is generally referred to as exothermic reaction curing. The working and curing time for PC is affected by the amount of the promoter and initiator concentrations; the ambient, substrate, and component temperatures; thickness (or mass volume); and the time required to mix, transport, and place the materials.

3.2.5 *Polymer concrete components*

3.2.5.1 *Initiators for monomers and resins*—The types of initiators are dibenzoyl, lauroyl, and methyl ethyl ketone peroxides. Dibenzoyl peroxide (BPO) may be obtained in the following forms: a) powders or granules, b) pastes, and c) liquid dispersions. The free-flowing powders and granules have BPO concentrations of 35 to 50 percent. Higher concentrations are avoided for safety reasons. BPO powders or granules may contain dicalcium phosphate, phthalate plasticizers, water, or combinations of these diluents to make them safer and easier to handle, store, and transport. Pastes are generally made with phthalate or phosphate plasticizers. Liquid dispersions generally contain a phthalate plasticizer as the dispersing agent.

Lauroyl peroxide (LP) generally comes as a free-flowing white powder and methyl ethyl ketone peroxide (MEKP) comes in liquid form with a phthalate plasticizer.

3.2.5.2 *Promoters for monomers and resins*—Promoters used are dependent upon the monomer or resin system and initiators selected. In general, they are tertiary amino compounds, such as N, N-dimethylaniline and dimethyl-p-toluidine, and cobalt salts, such as naphthenate and octoate. BPO-amine systems are commonly used with MMA, while ketone peroxide-cobalt systems are used with polyester resins.

3.2.5.3 *Epoxy compounds*—Epoxy compounds are generally formulated in two or more parts. Part A is most often the portion containing the epoxy resin and Part B is the hardener system. Almost without exception, epoxy systems must be formulated to make them suitable for specific end uses.

3.2.5.4 *Epoxy compounds' curing characteristics*—The ratio of resin to hardeners varies considerably with the formulation of the epoxies. The range of curing temperatures also varies depending on the formulations. Curing can take place at temperatures varying from 140 to 5 F (60 to –15C) or below. Some epoxies bond to moist surfaces; however, ice prevents adequate bonding.

3.2.5.5 *Aggregates*—All of the aggregates used in conjunction with the monomer systems should be of the highest-quality available. Aggregates composed primarily of silica, quartz, granite, good limestone, and other high-quality material have been used successfully in the production of PC. The aggregate must usually be dry and always be free of dirt, asphalt, and other organic materials. Moisture on the aggregates reduces the bond strength between most monomers

and epoxies and the aggregate (Fowler et al. 1981). Unless otherwise specified, surface moisture should not be allowed for aggregates used in the production of PC. Moisture contents of less than 1 percent are acceptable but some systems can tolerate up to 3 percent.

The required aggregate size distribution is generally dependent upon the depth of the patch to be made. The maximum-sized aggregate should not be greater than one-third the depth of the patch area. The distribution should be such as to allow for a minimum void volume for dry-packed aggregate. This minimizes the amount of monomer required to assure proper bonding of all the aggregate particles and results in a more economical PC.

3.2.6 *Polymer concrete placement*—Several methods have been used for placing PC patching materials; these are described individually.

3.2.6.1 *Dry pack placement*—In this method, the graded aggregate is placed in the area to be repaired and compacted by tamping. Then the compacted aggregate is saturated with the monomer mixture, using sprinkling cans or other monomer dispensing system. This method eliminates the necessity of using a mechanical mixer, but it is difficult to determine the amount of monomer required for the patch area. Care must be taken to assure that the aggregate is completely wetted with monomer; therefore, several monomer applications are necessary. This method generally uses a higher concentration of monomer than the premixing methods, and is generally limited to monomer systems with viscosities less than 100 cp.

3.2.6.2 *Premix placement*—The placement of PC by this method is identical to that used for the placement of portland cement concrete. The polymer binder is added directly to the mixer, then fine aggregates are added, and the coarse aggregates are added last. Mixing is continued until all particles are completely wetted. Once the composite material has been mixed as required, it is transported and placed. This method can be used for polymer binders with low and high viscosities and uses a predetermined quantity of polymer binder. Depending on the product, the PC is consolidated after placement by tamping, vibratory screeding, or with finger vibrators. Continuous mixing machines are very useful in this method. Generally the surfaces to be coated with the PC should first be primed with the polymer binder.

3.2.6.3 *Prepackaged PC*—Prepackaged PC systems can be mixed by hand or in mechanical mixers. If a rotating drum mixer is to be used, all of the monomer or resin system should be added to the mixer and blended first. The powders and fine aggregates, followed by the coarse aggregates, are then added and the entire blend is mixed for the specified time. In all cases manufacturers' recommendations should be strictly followed. The entire composite is then placed and can be consolidated utilizing the proper methods as outlined by the manufacturer.

Once the PC has been placed by any of the methods described, it can be finished by using manual or vibrating screeds, or manual or power trowels. Power trowels are not recommended with MMA systems.

3.2.7 *Cleaning of tools*—Cleaning tools after placement of a PC patch is easily accomplished. Tools such as shovels, tampers, and trowels can be wiped clean with a rag saturated with an organic solvent such as 1,1,1-trichloroethane, methylene chloride, xylene or methyl ethyl ketone (MEK). Clean-up of a mechanical mixer can be accomplished by immediately rinsing the drum with one of these chemicals, followed by operating the mixer with a load of coarse aggregate. This method removes all traces of monomers or resins from the drum surfaces. For disposal of these solvents, the user should consult the Material Safety Data Sheet (MSDS). Additionally, more environmentally safe cleaners are becoming available that act as emulsifiers instead of solvents.

3.3—Polymer concrete overlays

Overlays of PC can provide a durable and wear-resistant surface for portland cement concrete. In addition, the overlays may be formulated to provide low permeability to water and chloride ions, and thus also helps to prevent deterioration and spalling of the concrete due to freezing and thawing cycles and corrosion of the reinforcing steel.

PC has good bonding characteristics to clean and sound portland cement concrete. The bond in tension and in shear for the product selected should be at least equal to the tensile and shear strength of sound concrete.

Surface texture of a PC overlay for highway applications can be made to provide an acceptable skid-resistant surface and hydroplaning characteristics that are within acceptable limits.

3.3.1 *Surface evaluation*—Prior to the application of a PC overlay, a surface evaluation should be conducted. This evaluation should determine the condition of the concrete surface and what surface preparation is required to assure that the pavement is in such condition to receive the overlay materials selected.

Two surface conditions must be met if the PC overlay is to be successful: a) the concrete surface must be strong and sound and b) the concrete surface must be dry (free only of standing water for some epoxies) and clean (free from laitance, dirt, oil, grease, paint, curing compounds and asphaltic compounds).

When overlays are being considered, the entire concrete surface should be tested for delaminations. This identifies any delaminated or unsound concrete that should be removed and replaced with a patching material prior to the application of an overlay, or included as part of the overlay.

A visual examination of the concrete surface without further evaluation is unacceptable. In the case of overlays, it is critical that surface laitance and curing compounds are not present since they adversely affect the adhesion of the overlay to the concrete surface. Prior treatments of the concrete surface with materials such as linseed oil can also affect the bonding of the overlay; such material should therefore be removed.

3.3.2 *Surface preparation*—The surface preparation of concrete prior to placement of a PC overlay is critical to assure good adhesion of the overlay to the concrete substrate. All loose and unsound material should be removed by chipping hammers or bush hammers, scarifiers, or other similar equipment. Dry or wet sandblasting, airless blasting using steel shot, and high-pressure water blasting [8000 to

23,000psi (55 to 160 MPa)] are considered acceptable methods of removing laitance, curing compounds, and other surface contaminants. Care should be used in combining hydroblasting with thin polymer overlays. Surface preparation should not result in high moisture content in the concrete. If some other mechanical means of removing the surface, such as scarification, is used, final preparation by dry sandblasting is recommended. Mechanical cleaning of the concrete surface should not leave it polished and it is not necessary to completely expose the coarse aggregate.

Delaminations should either be repaired by epoxy or monomer injection or removed.

3.3.3 *Polymer concrete formulations*—As with PC patching materials, numerous monomer formulations can be used for PC overlays. Care should be exercised in selecting the right material for the intended purpose.

The monomer and aggregate systems used for PC overlays are similar to those described for PC patching materials. They are described in Section 3.2.5.

3.3.4 *Types of polymer-concrete overlays*

3.3.4.1 *Thin sand-filled resin overlays*—This thin PC overlay is placed by multiple applications of resin and aggregate. A thin layer of initiated and promoted resin is applied to a cleaned concrete surface. Immediately thereafter a slight excess of aggregate is broadcast onto the resin before the resin has gelled or cured. When the resin has cured completely, the excess aggregate is broomed off and the operation is repeated until a total of three or four layers has been applied. This gives a nonpermeable overlay with a highly skid-resistant surface. This type of overlay has been placed using polyesters, vinyl esters, or epoxies.

3.3.4.2 *Polymer seal coat overlay*—For the application of a polymer-seal-coat overlay, a 0.25 in. (6 mm) layer of dry concrete sand is placed upon the clean, sound, dry concrete surface. A skid-resistant, hard, durable aggregate is broadcast over the sand and hand rolled to set the aggregate.

The monomer mixture requires two applications. The first application uses a low-viscosity system to penetrate the aggregate mixture on the concrete surface. A second application of monomer, whose viscosity has been increased by the addition of a polymer, is then spread over the aggregate surface. Light frames covered with polyethylene film are often used to cover the fresh surface to reduce the monomer evaporation.

3.3.4.3 *Premixed polymer-concrete overlay*—In this type of PC overlay the graded aggregate and monomer or resin system are mixed together in a portable concrete mixer, or a continuous PC mixing machine, placed on the concrete surface, and then spread and compacted. Continuous pavement-finishing machines may be used for highway overlays. Some overlays require a final broadcasting of aggregate onto the finished surface to provide a skid-resistant surface.

In most cases, a tack coat of initiated and promoted resin is spread over the concrete surface to which the overlay is to be applied. The polymer concrete is then mixed and placed onto the wet or dry tack coat depending on the system being used. A finishing machine, if used, riding on preset rails, can then spread, compact, and screed finish the overlay.

3.3.4.4 *Prepackaged polymer-mortar overlays*—Prepackaged PC mortar overlay materials are generally applied in thicknesses of $^1/_4$ to $^1/_2$ in. (6 to 13 mm). Guide-rails or forms consisting of mild steel plates measuring $^1/_4$ in. × 6 in. × 15 ft (6 mm × 150 mm × 4.6 m) placed on both sides of the lane to be overlaid have been used with success.

The mixed mortar is placed within the forms and screeded to level off the overlay. The forms are moved along as required. With practice it is possible to apply a broom finish to the PC surface. In all cases, the manufacturer's recommendations should be followed.

3.3.5 *Cleaning of tools*—All tools should be cleaned immediately after use with an organic solvent such as 1,1,1-trichloroethane, xylene, methyl ethyl ketone, methylene chloride, or with an emulsifying cleanser.

3.3.6 *Safety*—See Section 3.2.8 and Chapter 5.

3.4—Precast polymer concrete

Many PC products can be plant precast more efficiently and economically than site-cast (Koblichek 1978; Prusinski 1978; Perry 1981; Imamura et al. 1978; Kukacka 1978; Barnaby and Dikeou 1984). Precast PC has been used, for example, in the following applications:

a) Structural and building panels.
b) Sewer pipes, equipment vaults, and drainage channels.
c) Corrosion resistant tiles, brick, and linings.
d) Small water-flow control structures.
e) Stair treads and nosings.
f) Nonconductive, nonmagnetic support structures for electrical equipment.
g) Manhole structures and shims.
h) Components for the animal feeding industry.
i) Large-scale preinsulated wall panels for segmental building construction.
j) Electrical insulators.

Most of the procedures used for precast portland cement concrete can be applied to making PC. An obvious advantage of PC for precasting is its extremely short hardening time. Depending on the selection of monomeric system, form removal can take place in as little as 40 sec after form filling. Such rapid removal allows for the efficient use of forms and production facilities.

3.4.1 *Precast polymer-concrete formulations*—Formulations used to produce polymeric binders for precast PC are available with a wide range of properties. When selecting a material for a particular product, these properties must be examined to determine whether a particular mix formulation is suitable. By making the proper material choice, one can obtain concrete resistant to acid, alkali, ultraviolet radiation, solvents, or combinations of these.

Temperature development in the PC formulations is important in precast production. As noted previously, the polymerization reaction is exothermic, with the amount of heat produced at the different stages of the polymerization process dependent on the types and amounts of materials in a given formulation. This heat development affects the time at which formwork can be removed from the PC. The polymerization process may be examined by plotting the mix temper-

ature versus time for each formulation being considered and noting on these graphs the time at which gelation occurs and when the casting has hardened sufficiently to permit form removal. Forms may be removed after gelation at a time when the PC has developed sufficient strength so as not to damage the part that is being cast.

3.4.2 *Formwork*—Formwork for production casting PC must be extremely durable, solvent resistant, have a low coefficient of thermal expansion, have smooth, cleanable surfaces, and preferably should be a good heat conductor. The very low-viscosity monomers, such as methyl methacrylate, require sealed forms. In addition, some materials adhere strongly to the most conventional forming materials. Selection of form-release agents is therefore important.

Forms should be designed so that very little, if any, post-casting processing or finishing is required. Very intricate castings are possible from PC. Formwork design must, however, account for the effects of polymerization shrinkage; exothermic heat; accessibility for removing entrapped air; and for cleaning, coating, and reinforcing. Also, since monomers solidify rather than evaporate, provisions must be made to handle surplus monomer that, due to vibration, rises to the unformed top surface. If possible, for greater uniformity of appearances, the forms should be designed so that the unformed surface is not exposed in the finished product. Either matte or highly glossed surfaces may be used. Forms should be stiff enough so that no distortion occurs during vibration. All form joints should seal tightly to prevent monomer leakage. Leaking forms after casting may result in defective parts and can cause form removal difficulties.

Forming materials should be able to withstand peak exothermic temperatures. Negative draft angles should be avoided. Positive draft angles greatly improve the ease of form removal. Efforts should be made to improve accessibility for cleaning. Release agent coating greatly improve production rates. Stainless steel, mild steel, silicone rubber, polyethylene, polypropylene, melamine, cast aluminum, and wood have all been used successfully as forming materials for various monomers.

3.4.3 *Vibration*—Conventional concrete vibrators may be used for mix consolidation and entrapped air removal. Form vibration provides better results than internal vibration. Amplitude and frequency are more critical with PC than with conventional concrete. Low-viscosity monomers require low-frequency, high-amplitude vibration to break up and remove entrapped air, while the higher viscosity monomers are better consolidated by high-frequency, low-amplitude vibrators. For high-viscosity resins, 6000 to 9000 cycles/sec (Hz) with an amplitude of about 1 mm provides the best results. Generally, higher vibration energies than those used for conventional concrete are preferred. Physical strength of the cast parts is affected by the total vibration energy supplied and extended vibration times are preferred where polymerization time permits and segregation of the mix can be controlled. PC should be compacted by stable vibration, without any system resonance. To eliminate spark hazard, air-powered vibrators are preferred over those that are electric powered. If electric-powered vibrators are used, the motors should be explosion-proof.

3.4.4 *Mixers*—Mixer selection is again dependent on the monomer system being used. Conventional concrete mixers perform well with low-viscosity formulations, but high-viscosity formulations tend to adhere to the mixing paddles. Mixers should be selected that do not generate sparks and should be powered by hydraulic motors, air motors, or explosion-proof electric motors.

For production casting, a continuous flow, high-speed mixer is far superior to batch mixers. Such mixers are self-cleaning while running and, therefore, require much less manpower than batch mixers, that should be thoroughly cleaned after each batch. Refined continuous mixers with various degrees of sophistication are available, including automatic and variable metering of aggregate-monomer ratios. Automatic and variable metering of initiators and promoters, resin preheaters, and automatic solvent-flushing accessories are also available. Such mixers have relatively high output rates and, with continuous delivery, can provide very high daily production with much lower maintenance requirements than batch mixers.

3.4.5 *Finishing*—Smooth, high-quality finishes are best achieved against formed surfaces. As with conventional concrete, different forming materials produce varying surface textures. Texture variations from glassy smoothness to a lightly sandblasted appearance have been achieved. Polymer concrete architectural panels filled with coarse, decorative, exposed aggregates in the unformed surface have been in commercial production for many years.

3.4.6 *Plant design and safety*—Information published to date on polymer concrete has dealt primarily with its use as a construction material or with basic monomer and PC properties. Fixed plant operations using monomers for precasting polymer concrete are governed by municipal building and fire codes, in addition to the general industrial standards considered in construction activities. Local zoning and building code ordinances frequently have special classifications for plants handling and polymerizing monomers. Criteria established by these ordinances must be complied with when selecting a plant site and during the plant design procedure. Typically, such codes govern a) loading and unloading bulk monomer shipments, b) monomer storage limitations, c) fire protection and detection, d) employee safety, e) in-plant monomer handling restrictions, f) plant ventilation requirements, and g) site use restrictions.

PC is generally not discussed as such in these standards. Until sufficient background and research results are made available to and considered by code administrators and organizations, control of its safe use is best accomplished by considering the characteristics of its component parts. In lieu of definitive PC safety guidance, the material safety data sheets that are available from the manufacturers of the component chemicals should be referred to and carefully followed to assure safe use of the required chemicals. See Chapter 5 for additional safety information.

CHAPTER 4—POLYMER-MODIFIED CONCRETE
4.1—Introduction

Polymer-modified concrete (PMC) has at times been called polymer-portland cement concrete (PPCC) and latex-

modified concrete (LMC). It is defined in ACI 548.3R as portland cement and aggregate combined at the time of mixing with organic polymers that are dispersed or redispersed in water. As the cement hydrates, coalescence of the polymer occurs, resulting in a comatrix of hydrated cement and polymer film throughout the concrete. The use of concrete in this chapter also includes mortar.

The addition of polymers to portland cement results primarily in improvements in adhesion, resistance to permeation of water, durability, and some strength properties.

A wide variety of polymer types have been investigated for use in PMC (Ohama 1984), but the major types in use today are as follows:

- styrene-butadiene copolymers (S-B).
- acrylic ester homopolymers (PAE) and copolymers, particularly with styrene (S-A).
- vinyl acetate copolymers (VAC).
- vinyl acetate homopolymers (PVAC).

Selection of the type of polymer depends on the service life requirements and cost. It should be noted that PVACs should not be used where the PMC will be exposed to moist conditions.

Essentially, mixing and handling of PMC is similar to conventional portland cement concrete (PCC). Short mixing times are recommended to ensure acceptable air contents and, because of the good adhesion exhibited by PMC, prompt clean up of mixing equipment is suggested. Curing of the PMC is different from PCC in that extended moist curing is not required. In fact, moist curing beyond 24 to 48 hr is not recommended because it slows the coalescence or formation of the polymer film. The formation of the polymer film retards the loss of water from the concrete thus making it available for hydration of the cement. Moist curing of PMC is required during the early stages of cure to prevent the occurrence of plastic-shrinkage cracks. Except for polymers that are subject to hydrolysis, subsequent wetting of cured PMC results in loss of strength while wet, but a gain in strength upon redrying (Lavelle 1988). It is accepted that the application temperature should be above the minimum film-forming temperature (MFFT) of the polymer, although recent work (Kuhlmann 1996) indicates that with some PMCs the concrete can be placed below the MFFT. Also, PMC should be placed when temperatures are between 45 and 85 F (7 and 30 C) because of the rate of hydration of the cement.

4.2—PMC polymers

4.2.1 *Latexes*—The majority of PMC placed today uses a polymer in latex form. Latex has been defined as a dispersion of organic polymer particles in water (Walters 1987). The average particle size varies from 100 to 2000 nanometers. Most latexes are made by a process known as emulsion polymerization, where the polymer is formed directly in water. Typical characteristics of the latexes commonly used with portland cement are given in Table 4.2.1. The surfactants used to stabilize these latexes are usually nonionic, such as polyvinyl alcohol or alkyl phenols reacted with ethylene oxide.

4.2.1.1 *Polyvinyl acetate (PVAC)*—The use of this type of latex is declining because of the poor water resistance of PVAC-modified mortars. When wet the PVAC hydrolyses, in the high alkalinity of portland cement mixtures, and the reaction products are water soluble. This type of latex is still used extensively for plaster bonding applications.

4.2.1.2 *Vinyl acetate copolymers (VAC)*—Typical comonomers are ethylene, BA, and the vinyl ester of versatic acid (VEOVA). The incorporation of these comonomers reduces the tendency of the vinyl acetate to hydrolyze, and the reaction products are less water soluble. These materials are used as plaster bonding agents and also as polymer modifiers for portland cement mortars in less severe environments.

4.2.1.3 *Acrylic esters and copolymers (PAE and S-A)*—These latexes have been used for many years, primarily in tile adhesives, floor overlayments, stuccos, exterior insulation finish systems (EIFS), and repair of concretes. It has been claimed that acrylic esters are the latex of choice where color and color fastness are important (Lavelle 1988).

4.2.1.4 *Styrene-butadiene copolymers (S-B)*—It has been reported that this type of latex has been used in concrete for over thirty years (Walters 1991). In North America, one of its major applications has been the overlayment of bridge and parking-garage decks to reduce the penetration of water-soluble salt (sodium chloride). These salts contribute to the corrosion and deterioration of embedded reinforcing steel, that in turn cause deterioration of the concrete deck. This type of latex is widely used where either adhesion or water resistance is required, providing color fastness is not a requirement.

4.2.2 *Redispersible powders*—There is a fast developing market using polymers in powder form that redisperse when mixed with water or aqueous mixtures. Typically the polymer powder is premixed with the cement and aggregates, and water is added at the jobsite. This operation allows for more accurate mixture proportioning and is more convenient than using a two-component latex system. Currently vinyl acetate copolymers dominate this market, but recently acrylic powders have been introduced (Tsai et al 1993). The use of polyvinyl acetate powders is declining because of their tendency to hydrolyze.

4.2.3 *Epoxy resins*—Epoxy resins have been used as polymer modifiers for portland cement mixtures and some large applications have been placed with varying success, see ACI548.3R-94. Today little epoxy modification of portland cement occurs, possibly because of cost, mixing difficulties, and placement problems.

4.3—PMC applications

The primary reasons for using PMC are to improve adhesion or watertightness. Consequently, major applications include providing corrosion protection to reinforcing steel, providing resistance to attack by dilute aqueous solutions of acids and salts, providing water-resistant coatings and linings, repairing of spalled or broken concrete, leveling of floors, and as a bonding agent between fresh and hardened concrete, and between tiles and various surfaces.

4.3.1 *Bridge and parking-garage decks*—It has been reported that over eight-thousand bridge decks in the United States have been overlaid with PMC either as original construction or as repair of a deteriorated deck (Walters 1991).

Table 4.2.1—Typical properties of latex polymer modifiers

Latex type	PVAC	VAC	PAE (S-A)	S-B
Nonvolatile or solids content, percent	52	55	47	47
pH value	5	5	9	10
Average particle size, nm	2000	800	220	180
Density, g /mL	1.09	1.07	1.06	1.01
Glass transition temperature by differential scanning calorimetry, deg C (inflection)	+ 30	− 3	+ 12	+ 5
Viscosity, Brookfield RV, 20 rpm, Pa	500	500	50	30

Also, a large number of decks in parking garages have been similarly treated. S-B latexes are the most widely used polymer modifiers for this application.

Normal concrete permits moisture, oxygen and chlorides from deicing salts to migrate through the concrete and reach the reinforcing steel, causing corrosion and subsequent spalling. This permeability of the concrete is caused by micro-cracks and micro-pores generated during the hydration of the cement. The S-B polymer film bridges these cracks and pores, reducing the passage of water. Additionally, the polymer films and hardened cement paste form a comatrix that has better adhesion than the paste alone. Consequently, the PMC is more durable and weather resistant, and the reinforcing steel is protected from corrosive elements that continually plagued such decks. Typically the minimum thickness of a PMC overlay is 1 in. (25 mm).

In addition to the improved chemical resistance and adhesion, the S-B latexes are water-reducing agents. This characteristic contributes to improved properties while giving adequate workability for placement techniques.

4.3.2 *Floors—*Industrial floors are subjected to a wide variety of exposures that can cause deterioration of conventional concrete. Floors in wineries, citrus juice plants, dairies, slaughter houses, and chemical plants have been placed or repaired with PMC because of its resistance to dilute aqueous solutions of salts and acids.

Also, floors and ship decks are overlaid with thin $^1/_4$ to $^1/_2$ in. (6 to 12 mm) layers of PMC to level the floor or deck prior to application of the final floor treatment.

4.3.3 *Walls—*Exterior and interior walls are often treated with a polymer-modified, and sometimes a fiber-reinforced, mortar. The latter is used in exterior insulation and finish systems (EIFS) for many buildings. This system is the subject of an ASTM special publication (ASTM STP 1187). Also walls are often finished with spray-applied polymer-modified cementitious mixtures, called stuccos.

4.3.4 *Water-resistant renderings—*Renderings of PMC, often with low levels of fine aggregates, are used to provide water-resistant coatings for basement walls and swimming pools. Similar mixtures, often with no fine aggregate, are used for corrosion-resistant coatings of metallic pipes and beams.

4.3.5 *Tile mortars and grouts—*PMC is used extensively in the application of ceramic tiles, both in the thin-set bedding mortar and in the grout between the tiles.

4.3.6 *Patching—*The excellent adhesion of PMC is utilized in the repair of spalled areas, potholes, and non-working cracks in concrete. As with all good concrete repairs, deteriorated and unsound concrete should be removed so that the PMC is not placed on a surface that will subsequently fail.

4.4—Mixture proportioning

Specific mixture proportioning depends on the particular application and the type of polymer being used. In general, polymer levels of 10 to 25 percent by mass of the hydraulic cement are required for optimum performance. Except for a few unusual applications, an antifoam is required to control the air content of the PMC. Where the polymer is not supplied already formulated with a suitable antifoam, one should be added.

Types I, II and III portland, calcium aluminate, and blended cements have been successfully used in PMC. The use of air-entraining cements is not recommended.

Sound fine and coarse aggregates should be used. However, because most PMC restricts the movement of water, alkali-reactive aggregates do not pose significant problems.

Water-cementitious material ratios of polymer-modified concrete are typically 0.30 to 0.40 by mass. These low ratios result from the lubricating qualities attributable to the polymers. When latexes are used, the water content of the latex should be included when calculating the water-cementitious material ratio.

Water-cementitious material ratios of polymer-modified mortars and coatings range from 0.25 to 0.60. The higher ratios are required for applications that use very fine aggregates, have highly porous surfaces, or have high evaporation rates.

4.4.1 *Polymer-modified concrete—*As with all hydraulic cementitious mixtures, proper mixture proportioning requires the correct balance of several factors; aggregate size and gradation, aggregate void volume, excess paste and required workability. Maximum aggregate size should be no greater than one third the thickness of the thinnest portion of the structure.

A typical proportioning for a concrete deck overlay is as follows:

portland cement, lb/yd^3 (kg/m^3)	658 (415)
fine-coarse aggregate ratio	55:45 to 65:35
latex, (usually styrene-butadiene)	
about 47 percent nonvolatile	
content, gal/yd^3 (L/m^3)	24.5 (100)

water-cementitious material ratio	0.25 to 0.40
air content, maximum, percent	6.5

4.4.2 *Polymer-modified mortar*—Polymer-modified mortars are used for a wide range of applications. Because of this diversity, mixture proportioning varies widely. The following gives typical ranges for ingredients:

	parts by mass
hydraulic cement	100
fine aggregate	150 to 450
polymer (polymer powder or latex nonvolatile content)	10 to 20
antifoam (such as poly[dimethyl siloxane])	0.02 to 0.10
total water	25 to 40

4.4.3 *Polymer-modified cementitious coatings*—These PMC coatings have low levels (less than one part to one part of cement by mass) of fine aggregate and may contain none at all. Also the gradation of such aggregates is fine, typically having 100 percent passing a No. 30 (600 μm) sieve. The following gives typical ranges for ingredients:

	parts by mass
hydraulic cement	100
fine aggregate	0 to 100
polymer (polymer powder or latex nonvolatile content)	10 to 20
antifoam (such as dimethyl polysiloxane)	0.02 to 0.10
total water	25 to 65

4.5—Construction procedures

The construction procedures listed in Sections 4.5.1 to 4.5.4 are for latex-based PMCs because these are the most commonly used. Procedures for placing PMC should be agreed upon by the purchaser and contractor and should consider the recommendations of the polymer manufacturer. Because much of PMC use is for repairs, the reader should also refer to ACI 546.1R.

4.5.1 *Bridge decks*—ACI has a standard specification for LMC overlays (ACI 548.4-93). That specification should be used for placement of LMC overlays for both construction of new bridge decks and rehabilitation of existing decks.

That specification covers materials, equipment, and construction procedures.

4.5.2 *Parking garages*—The procedures described in ACI548.4 are also used for repairing parking garages, except for differences caused by some garages having considerably less working room and overhead clearance than bridge decks.

4.5.3 *Floors*—The equipment, surface preparation for both new and old concrete, mixing and placement, finishing, and curing described in ACI 548.4 for bridge decks is also applicable to floors. If the volume of PMC concrete to be used on the floor is small, mixing procedures following the requirements of ASTM C 192 may be used. Caution should be exercised that excessive mixing (over 5 minutes) not be done on polymer-modified mixes, as there could be a tendency to entrap excessive air. Small clearances between the mixer blades and body are also desirable to minimize loss of the fines. Batch sizes should be selected so that a placement can be completed and finished before initial set occurs. Spud vibrators, as well as vibrating screeds, assure good consolidation of the mix. PMC should be covered with plastic sheeting (or other similar covering) as soon as possible after placement to avoid formation of plastic-shrinkage cracks. After the initial curing (24 to 48 hours), the PMC should be uncovered and allowed to dry.

4.5.4 *Patching*—Since the quantities used for this application are normally small, a small mixer [for example, 1 ft^3 (0.03 m^3)] can be used. Most types of mixers are suitable; however, good cleanup and maintenance is essential with these high-bond PMC materials to assure long life of the equipment. Surface preparation equipment includes hand chippers, scabblers, concrete saws and sandblasters similar to those described in ACI 548.4. Finishing is done with screeds and trowels. Metal tools are preferred to wooden ones. Procedures for removing deteriorated concrete are similar to those described in ACI 548.4. In addition, the edges of the hole to be patched should be saw-cut to provide a square edge at least $^1/_4$ in. (6.5 mm) deep. Five minutes is usually sufficient to provide proper mixing in drum-type mixers. Procedures for brooming in the paste and vibrating to achieve consolidation are similar to those described in ACI548.4. Proper finishing of patches can be achieved with screed and hand trowels. Curing of patches should be done as described in Section 4.5.3.

4.6—Quality control

Most of the common test procedures for freshly mixed concrete are applicable to PMCs. Slump and compressive strength are easily measured using standard procedures. Measuring air content is determined with the same methods as used for conventional concrete.

CHAPTER 5—SAFETY ASPECTS CONCERNING THE USE OF POLYMERS IN CONCRETE
5.1—Introduction

The use of polymers in concrete construction requires that careful consideration be given to safety. The chemical systems used create the most obvious hazards, but the use of high-temperature drying and curing equipment and their energy sources also pose potential dangers. When properly planned and supervised, construction projects using these techniques can be safe and successful. However, the unique nature of these materials and processes in construction requires careful attention by engineers, contractors, and inspectors. Actual applications of these materials by contractors are in many cases just beginning and field experience is limited.

Local zoning and building code ordinances frequently have special classifications for plants handling and polymerizing monomers. Criteria established by these ordinances must be complied with when selecting a plant site and during the plant design procedure. Typically, such codes govern a)loading and unloading bulk monomer shipments, b) monomer storage limitations, c) fire protection and detection, d) employee safety, e) plant ventilation requirements, and f) site use restrictions.

The chemicals used in the production of some PCs may be flammable, volatile, toxic, or a combination of these. The de-

Table 5.2.1—Monomer properties

Monomer	Viscosity, cp	Boiling point, deg C	Frezzing point, deg C	Flash point, deg C	Explosive limits, volume percent in air
Styrene	0.71	145	−30.6	34.4 [A]	1.5 - 7.0
Methyl methacrylate	0.85	101	−48.0	21.1 [A]	2.1 - 12.5
Trimethylolpropane trimrthacrylate (TMPTMA)	50.0	—	−14.0	< 300 [A]	—
Polyester-styrene	400 - 2000 [C]	—[C]	—[C]	34.4 [A]	1.5 - 7.0
Butyl acrylate	0.80	147	—	49.0[B]	1.9 - 8.0

A. Open cup
B. Closed cup
C. Values are dependent upon the relative amount and type of polyester base

gree of hazard is greater for the high-vapor pressure materials. With proper precautionary measures, these materials can be handled safely. This chapter is intended only as a general discussion of the safety aspects of concrete polymer materials to inform the user of the nature of potential safety hazards and safe handling practices (Fowler et al. 1978). It is not intended as a substitute for the various applicable ordinances, regulations and codes, and safety literature provided by manufacturers, suppliers, and associations. The user should consult the literature provided by federal, state, and local governments and manufacturers and associations for guidance before using any of the specific materials involved. A working knowledge of the potential hazards would be most helpful to all working crews prior to applying chemical products.

5.2—Chemicals

The chemicals required to produce concrete with polymers are relatively new to the construction industry, but are well known in the chemical industry. It is important that contractors using them have a good understanding of their properties, hazards, and the safety precautions required. Experience has shown that safety can be achieved if sound practices are followed. The manufacturer's instructions and safety procedures should be carefully followed whenever chemicals for producing concrete with polymers are used. The safety aspects of these chemicals are discussed individually. They include monomers, initiators, promoters, latexes, and epoxies. In general, greater safety considerations are required for monomer systems used in PC and PIC, followed by epoxies and then latex systems for PMC.

5.2.1 *Monomers*—Some of the most widely used monomers for producing concrete with polymers include MMA, BA, styrene, and TMPTMA. These monomers may be used alone or in combinations. The properties of these monomers are given in Table 5.2.1.

Generally, monomers are volatile, combustible, and toxic liquids. However, practice has shown that prolonged stability and safety can be achieved by following recommended practices in storage and handling (see Dow, Rohm and Haas, and DuPont bulletins). Manufacturers usually provide safety and handling guidelines that should be carefully observed.

The principal factors that influence the stability of monomers and determine the methods to be used for safe handling are a) level and effectiveness of inhibitors, b) storage temperature, c) flammability and combustibility, d) toxicity, and e) effect on construction materials with which they are used.

Secondary safety considerations include sensitivity to light, moisture, and oxygen. Odor may be an indirect problem because it causes discomfort, but in itself is not a physical hazard.

To prevent premature polymerization, most monomers, including all of those shown in Table 5.2.1, contain an inhibitor when they are shipped by manufacturers.

Inhibitors are free-radical scavengers. More specifically, they serve two functions. First, they can react with and deactivate the free radicals in growing polymer chains. Second, they can act as antioxidants and prevent polymerization by reacting with oxidation products that may be formed in the storage vessel through contamination or through the formation of peroxides from oxygen in the air.

MMA is usually inhibited with hydroquinone (HQ) or the methyl ether of hydroquinone (MEHQ) at levels ranging from 10 to 100 ppm. When MMA is to be stored for a short time in a cool environment, a minimum of 10 ppm has been found to be adequate. Styrene and unsaturated polyester-styrene may be inhibited with t-butyl pyrocatechol at levels of 45 to 55 and 10 to 20 ppm, respectively. HQ at concentrations of 60 to 100 ppm is used for TMPTMA. The inhibitor level should be maintained above a minimum concentration at all times. If the inhibitor is used up over a period of time and its concentration is allowed to drop below this danger level, the amount remaining may not be adequate to prevent a premature or runaway polymerization; for example, the danger level for styrene is 4 to 5 ppm. Excessive inhibitor concentrations, however, can prevent or unduly delay desired polymerization.

The time required for initial inhibitor concentrations to fall to a critical level varies greatly with storage and handling conditions. Factors affecting the depletion of inhibitor are heat and air, with heat being the most important. In hot climates [temperatures in excess of 90 F (30 C)] some monomers may need to be cooled. Some air must be present for the inhibitors to be effective in methyl methacrylate or styrene.

There are various chemical methods for monitoring inhibitor concentration. Methods for monitoring inhibitors in specific monomers are available from the suppliers and in other published technical literature (Kukacka et al. 1975). Since the required inhibitor may need to be specific for a given

monomer, care must be taken to assure that the proper inhibitor is added to the monomer.

Drums containing monomers should not be stored in the sun. As soon as possible after they are received, these monomers should be placed in a cool, shaded area. In hot weather, drums can be cooled by water spray. It is also advisable to keep inventories to a minimum during hot weather and use them in the order received so that the monomer is not stored any longer than necessary.

Drums of MMA can be stored at ambient temperatures. The cooler the monomer is kept, the longer the inhibitor is effective in preventing polymerization. Storage of drums of methyl methacrylate in the sun can be allowed provided the inhibitor concentration remains at a safe level and excessive pressure in the drum due to expansion/vaporization of the monomer is avoided. Data on the effect of temperature and inhibitor level on the storage stability of methyl methacrylate is available from the manufacturers.

The flash points and explosive limits of the well-established monomers in air are given in Table 5.2.1.

The flash point is the temperature at which a liquid gives off a sufficient amount of vapor to form an ignitable mixture with air near the surface of the liquid or within a container. The explosive limits indicate the range of vapor concentrations in air, at room temperature, and normal atmospheric pressure that supports combustion.

MMA, styrene, and BA are classed as flammable liquids by the U.S. Department of Transportation (DOT) because their closed-cup flash points are less than the 100 F (38 C) limit. The other monomers listed in Table 5.2.1 are not classified as flammable by the DOT, but are nevertheless combustible materials and should be treated accordingly.

Like most organic chemicals, most common monomers have varying toxic properties; thus some precautions are necessary. The Department of Labor Occupational Safety and Health Administration (OSHA) has established a limit of 100 ppm of MMA and styrene as the 8-hr time-weighted average concentration to which employees may be exposed. Some individuals can smell less than 1 ppm of MMA, and most workers would probably find concentrations significantly less than 100 ppm objectionable because of the odor. Normally, irritation to the eyes or respiratory membranes becomes noticeable long before explosive or flammable concentrations are reached. A few people may be allergic to MMA and develop dermatitis, but no case of ill health caused by MMA has been reported.

5.2.2 *Initiators*—Initiators, often loosely referred to as catalysts, are agents that initiate growth of polymer chains by decomposing into free radicals that actually start the chain's growth. The rate of the reaction, and hence the rate of polymerization, depends upon the temperature and initiator concentration.

The polymerization initiators generally used are either organic peroxides or azo-compounds. They should be kept in a cool place, away from heat or any source of sparks and light. They should be stored separately, away from monomer, flammables, combustibles, and, in particular, away from promoters or other oxidizing materials. Inventories should be kept to a minimum. Initiators have a limited shelf life and

therefore lose efficiency with time. Any initiator accidentally spilled should be cleaned up and disposed of immediately.

The initiators most commonly used in producing concrete with polymers are 2,2'-azobis (isobutyronitrile), commonly abbreviated as AIBN; 2,2-azobis-(2,4-dimethylvaleronitrile) (AMVN); BPO; LP; cumene hydroperoxide, and various ketones such as MEKP. The amount of initiator used as a percentage of monomer weight is low (0.5 to 4 percent). Only quantities sufficient for one day's operation should be present in operating areas.

A widely used initiator for polymer impregnation of cast-in-place concrete is AIBN. It is a white crystalline solid that is stable and can be stored almost indefinitely at room temperature [75 F (24 C)]. At this temperature, it decomposes at a rate of about 0.6 percent of its weight in a month. Since this rate doubles for each 9 F (5 C) rise in temperature, at 104 F (40 C) it decomposes 2.5 percent in one week. In addition, at this temperature it tends to cake in closed containers (DuPont Bulletin A-67782).

AIBN is sensitive to ultraviolet light from solar radiation. After mixing with monomer, the resulting solution should not be exposed to sunlight. AIBN is not shock sensitive. In bulk form it does not deteriorate or explode on impact nor can it be ignited by an electrical spark. The decomposition of AIBN is an exothermic reaction, and as a result it can accelerate itself at elevated temperatures. Momentary ignition and minor explosion may occur when the temperature reaches 140 F (60 C). In such instances, the pressure opens the container and discharges the contents as dust; therefore, AIBN should not be stored in tightly sealed containers (DuPont Bulletin A-67782).

Dry, solid AIBN burns when exposed to open flame or electrical arc. It burns mildly and completely when air is supplied. Precautions should be taken to avoid exposure to smoke and fumes from burning AIBN since toxic vapors may be present. Air masks should be worn when fumes from burning AIBN cannot be avoided (DuPont Bulletin A-67782).

Dusty conditions with AIBN present a hazard since the dust is extremely easy to ignite. The lower explosion limit is 0.02 gm/L. A spark-proof environment and good ventilation should be provided where AIBN is handled.

AIBN has a low acute-inhalation toxicity and has moderate oral toxicity, based on tests on animals. It may produce some eye and respiratory irritation, but does not appear to irritate the skin (DuPont Bulletin A-67782).

The more reactive azo-type initiator AMVN has also been used to polymerize PIC in the field. Storage and handling precautions for this material are more stringent than for AIBN in that the recommended storage temperature is 32 to 50 F (0 to 10 C). In this temperature range, the rate of decomposition of this material is less than 0.03 percent per day. During this decomposition, however, nitrogen gas is generated, a phenomenon common to most azo-type catalysts, and tightly closed storage containers should be avoided. This catalyst is sensitive to solar radiation, but is not shock sensitive. AMVN dust in air has a lower explosive limit (LEL) of 0.02 gm/L and concentrations above the LEL are easily ignited. Spark-proof storage facilities are thus required. The catalyst is flammable and can be ignited to open flames, sparks, or continuous

electrical arc. Foam and CO2 fire extinguishers are suitable for use on AMVN fires. AMVN fires may result in toxic fumes; thus air respirators should be used by personnel fighting AMVN fires.

Studies on animals show that AMVN and its decomposition products have relatively low toxicity. Good personal hygiene practices dictate, however, that skin contact with this material be avoided by using rubber gloves, glasses or goggles, and impervious aprons.

BPO is one of the most commonly used organic peroxide initiators used for PC. It is supplied in a variety of forms ranging from liquid dispersions (40 percent BPO) to pastes (50 to 55 percent BPO) and granular-powder forms (35 to 50percent BPO). For ease of handling and safety purposes, the balance of these formulations is generally a plasticizer or inert filler. Purer forms of BPO (for example, 98 percent dry granules) are not recommended for PC because of their higher sensitivity to shock, friction, and sparks.

BPO is an oxidizing material that presents both fire and explosion hazards if improperly stored or handled. It is sensitive to explosive decomposition from heat, flame, friction, shock, or reaction with other chemicals.

BPO formulations are stable at room temperature. As with any organic peroxide, the most important safety parameter to consider is the self-accelerating decomposition temperature (SADT). SADT is the lowest temperature at which self-accelerating decomposition may occur with a substance in the packaging used for transport. The SADT varies widely depending upon the specific BPO formulation, with values as low as 50 C (122 F). Other parameters such as control temperature (for transport) and maximum storage temperature (for quality purposes) are derived from the SADT.

If an accelerating decomposition is in progress, large quantities of vapors, smoke and heat may be released. Sometimes a decomposition is of such force that it is confused with a fire or explosion. If a decomposition has occurred, after the air has cleared there may not be any evidence of a fire. The vapors generated during decomposition can be very flammable, so that if an ignition source is present, vigorous burning and possible explosion may occur. The best safeguard against decomposition is to carefully follow the manufacturer's safety and handling instructions, including recommended storage conditions for each product. For peroxides, such conditions include storing them away from all sources of heat including sunlight.

BPO can also be decomposed by heat that is indirectly created by reaction with other chemicals. Special care should be taken to avoid contamination with easily oxidizable compounds (Malkemus 1963).

Some suggested rules for handling BPO include the following (Manufacturing Chemists Association 1960):

a) Handle in as small quantities as possible, preferably 1 lb (0.45 kg) or less.
b) Avoid confinement.
c) Prevent overheating.
d) Prevent friction or shock.
e) Avoid any source of ignition.
f) Prevent contamination with other reactive chemicals.

g) Clean up spilled BPO immediately.

MEKP is generally used as a 50-percent solution in a plasticizer. It is relatively safe, but is still considered hazardous by the ICC and must be packaged and shipped according to ICC regulations. MEKP solutions are not as easily ignited as BPO. Since the flash point ranges from 126 to 180 F (51 to 81C), MEPK solutions as such are not considered flammable by the ICC. However, once ignited, MEKP solutions burn vigorously, even more so than gasoline.

Larger amounts of MEKP solutions are reasonably stable and may be kept for long periods of time, although they should never be stored in sealed glass bottles. MEKP solution can be decomposed by heat, sunlight, and many chemicals. It is not completely stable in the presence of metals, including iron. For this reason, the solution should never be shipped or stored in a metal container.

The relatively easy decomposition of MEKP by many contaminants makes its handling critical when used in pressure equipment. Ordinary steel or galvanized pressure vessels are not safe. Some accidents involving pressure pots and MEKP have occurred, and extreme caution should be exercised in using pressure equipment.

Solutions of MEKP severely irritate the eyes and skin; BPO is not nearly as bad in this regard. If contact with skin or eyes occurs, the affected portion should be immediately and thoroughly washed with water and medical attention should be obtained (Malkemus 1963). Immediate medical attention is essential when the eyes are involved.

Many of the rules for handling BPO also apply to MEK peroxide solution. When handling MEKP a) store in a cool area away from sunlight in the original container; b) keep away from heat, open flame, or sparks; c) prevent contamination with oxidizable materials; d) do not add to hot materials; and e) avoid contact with body or clothing.

LP, frequently used in some concrete repair formulations, is one of the safest solid organic peroxides. It is not shock sensitive, can only be ignited with difficulty, and then does not burn as vigorously as most organic peroxides.

Disposal of waste or contaminated peroxide may be necessary in some instances. These materials are considered hazardous waste under Section 261.33(F) of the Title 40 of the Code of Federal Regulations. Disposal of these materials and their containers requires compliance with applicable labeling, packaging and record-keeping standards. For further information, the local or state waste agency, or the United States Environmental Protection Agency (US EPA) should be contacted. The US EPA hotlines are 1-800-424-9346 or 202-382-3000.

5.2.3 *Promoters*—Promoters (also referred to as activators or accelerators) are generally used in PC formulations when it is desired to conduct polymerization at ambient temperatures. A promoter is a chemical compound that greatly increases the decomposition rate of the initiators. The promoter-initiator system can be designed to cause polymerization over a wide range of times and temperatures.

Some of the most commonly used promoters are N,N-dimethyl-p-toluidine, N,N-dimethyl aniline, cobalt octoate, and cobalt naphthenate.

Promoters are used in small quantities compared to the monomer. However, procedures for handling promoters should be similar to those used for monomers. They should be stored in a cool place, not in the same area as the peroxide initiators, and should be treated as toxic and combustible materials.

Particular care must be taken to avoid mixing promoters directly with peroxide initiators because the mixture can react explosively. Promoters should first be added to the monomer and dispersed thoroughly. Then and only then should the peroxide be added.

One alternate procedure for making PC composites follows: Divide the monomer system into two equal parts, A and B. Add the total promoter quantity to Part A and the total initiator quantity to Part B. Take equal quantities of Part A (monomer with promoter) and Part B (monomer with initiator). Add Part B to Part A and mix thoroughly. A second alternate procedure involves adding a promoter to a liquid component and an initiator to a powder component. The liquid and powder are mixed at the jobsite.

5.2.4 *Latex*—Latex or redispersible polymer powder are added to conventional concrete or mortar to make PMC. From the standpoint of safety, latexes and powders can be thought of as monomers that have been polymerized, and the resulting polymer is dispersed in water. The formation of hardened polymer in the concrete occurs by removing the water through evaporation, absorption, and hydration of the cement.

Latexes for use in concrete are generally 50 percent water, and are considered nonflammable. Their boiling point is 212F (100 C). Vapors from the emulsion can be detected by smell, but are generally inoffensive and are nontoxic.

If latexes come in contact with the skin or eyes, flushing with water is generally sufficient. If not washed off of the skin, the emulsion becomes sticky and acts like an adhesive. Prolonged contact with the skin may cause minor irritation. Gloves are advised for continued exposure conditions.

5.2.5 *Epoxy*—Precautions should be taken when handling epoxy resins, curing agents, and solvents with which they are used. Part 1910 of Title 29 of the CFR regulates handling of hazardous substances including epoxy compounds. A number of different basic epoxy resins can be combined with an even greater number of curing agents, flexibilizers, fillers, and other chemicals to produce several hundred different end products with various combinations of their unique properties. This versatility, that makes the epoxies so useful, also contributes to handling problems for the user and the manufacturers of epoxy products. In general, most epoxy formulations are skin sensitizers and should be handled carefully.

Two typical health problems that may be encountered when epoxy materials are carelessly handled are such skin irritations as burns, rashes, itches, and skin sensitization, that is an allergic reaction similar to that which certain people get from contact with wool, strawberries, poison ivy, or other allergens. Sensitization reactions may occur immediately, but in other cases they occur only after long periods of continual exposure. Workers should guard against the possibility of delayed sensitization or thinking that they are immune to sensitization.

The variety of the epoxy compounds marketed today makes it essential that the labels be read and understood by those people working with the products. Part 1500 of Title 16 of CFR regulates the labeling of hazardous substances including epoxy compounds. ANSI K 68.1 and ANSI Z 129.1 provide further guidance regarding classification and precautions.

Safe handling of epoxy materials can generally be accomplished by working in a well-ventilated area and using disposable equipment wherever possible. Disposable suits and gloves available from many suppliers of work garments are suitable for this use. Disposable rubber or plastic gloves are generally used but should be checked to see if they are impermeable to the epoxy and the solvents used. They should be discarded after each use. Cotton gloves are only helpful in keeping resin from contacting the skin, since liquids pass through them. They should never be reused if they have become soiled with epoxy compounds. Safety eyeglasses or goggles are strongly recommended when handling epoxy compounds.

Such involuntary habits as face scratching or adjusting eyeglasses should be avoided. For similar reasons, handling tools, eating, or smoking should be avoided until the individual has washed up. When wearing soiled gloves, the workers should avoid touching door handles and other equipment that may subsequently be touched by a person not wearing gloves.

In case of direct contact with clothing, the worker should remove the soiled items at once and change to clean garments. If the soiled garment cannot be thoroughly cleaned, it should not be reused. In case of direct contact with skin, the individual should wash or shower immediately with soap and water to remove spilled epoxy compounds from the body, avoiding contact with the genital areas until after the hands are carefully cleaned of all epoxy. If epoxy comes in contact with the eyes, flush with large amounts of water, followed by immediate medical attention. Solvents other than soap and water, or water soluble proprietary cleaners are not suitable for personal cleanup. Most solvents merely dilute the epoxy compounds, aiding them in penetrating the skin. At the same time, solvents tend to dry out the skin and any subsequent exposure is more likely to cause problems. Further details on handling epoxies are contained in "Use of Epoxy Compounds With Concrete" (ACI 503R).

5.3—Construction practices

5.3.1 *General*—An excellent practice around any hazardous material, including monomers, is to limit personnel exposure and use only trained workers for operations involving these materials. Workers who are not essential to the chemical phase of work should not be in the area when monomer, initiator, or promoter are handled. The few workers who must deal with these chemicals can be given sufficient on-the-job training so that they understand their responsibility. These workers should be carefully selected and interviewed. On construction projects, unions have been helpful and cooperative in this aspect. Weekly safety meetings lasting from 5 to 15 minutes for all other job personnel are a good way to keep them advised of what work is being done and of their particular roles in the work.

All job personnel should be aware of basic first-aid requirements and the potential hazards of the chemicals. First aid equipment must be on hand and telephone numbers for emergency facilities made available. It is a good idea for at least one local hospital and doctor in the area to be notified of the chemicals in use prior to construction so that they are prepared in case of an emergency.

Respirators, that are suited for the particular chemicals at the jobsite and fit-tested, should be available for workmen to use for their own comfort even if concentrations stay below acceptable safe levels from a health standpoint. The workmen should be trained in the use of such respirators. Eyes are particularly sensitive to most monomers, and goggles are mandatory where any splash, spill, or ruptured monomer hose is possible. In some instances, face shields may be justified. Rubber gloves, aprons or coveralls, and boots protect personnel from monomer exposure under most conditions experienced in the laboratory or in practical applications of monomer with concrete. In any event, skin exposed to monomer should be washed with soap and water.

Smoking should be absolutely forbidden in and around facilities where monomers, initiators, and promoters are stored or used. On one large project, workers were required to leave all matches, lighters, and cigarettes in a storage tray before entering the specific work area where monomer was being used. This reduced the possibility of inadvertent flames or sparks igniting the material.

Workmen should not walk directly on monomer-saturated sand as used in the polymer impregnation process or in the monomer-saturated aggregate in polymer concrete applications because of the fire hazard. Should the monomer be ignited, the fire can spread faster than the workmen can escape. Workmen should either stand outside the monomer application area or use a noncombustible mat over the monomer-soaked aggregate to provide an escape route.

Open-flame heat or heaters with exposed elements are not recommended for applying heat for polymerization. If they are used, extreme caution should be exercised to prevent excessive vapor concentrations at the level of the flame or elements. Under no circumstances should open-flame heat sources or heaters with surface temperatures exceeding the lowest ignition temperature of any monomer present be placed inside an enclosure over the monomer-saturated aggregate. Adequate circulation must be provided, and the monomer concentration should be monitored. Membranes placed over the sand should not melt at the temperatures occurring at the sand surface.

Fire extinguishers should be strategically placed around the working areas. The extinguishers should use foam, dry powder, or carbon dioxide. Halon 1302 has been used effectively to fight MMA fires. Water is ineffective and, in fact, may spread and prolong the fire since the monomers are generally lighter than water and rise to the surface.

5.3.2 *Storage and handling*—Storage of all chemicals should be in accordance with previously stated guidelines and should meet all of the manufacturer's recommendations. It cannot be overemphasized that all materials should be stored in cool areas. The initiator should not be stored in the same area as the monomer and promoters. It is advisable to refrigerate initiators; however, all internal sparking devices should be removed from the refrigerator. All chemicals should be well-labeled to avoid using the wrong material. Empty drums or containers should not be reused on the site to avoid mislabeling, and caution should be exercised in reusing any container in which combustibles have been stored. Metallic containers in which monomers are mixed or from which they are poured should be grounded to prevent sparking from static electricity that could otherwise build up as is done with gasoline.

When separate chemical components are used, they should be thoroughly mixed just prior to using. Mixing can be accomplished by introducing bubbling air in the solutions or by using a stirring paddle made of wood or other nonsparking material. Particular care should be exercised when mixing to thoroughly dissolve solid initiators such as AIBN, AMVN, or BPO in the monomer.

With respect to electrical appliances, lighting, and power sources, compliance with National Electric Code explosion-proof requirements (National Fire Protection Association) should be sufficient, although the definition of "explosion-proof" may be difficult to establish. One construction project, that required storage and reservoirs of monomer within an enclosed area where a spill could have occurred and explosive concentrations of monomer were possible, solved this problem by requiring all electrical power to the area to be shut off by a main control switch panel during monomer applications. Any light necessary for the two workmen required in the area during this phase of work was provided by self-contained (explosion-proof) battery light packs. Portable lights used in underwater work are suitable. For monomer work that is done in the open environment, daylight can be used and atmospheric concentrations probably will never approach explosive levels. If, however, drying and polymerization enclosures are used for bridge decks, slabs, and walls, monomer vapor concentrations within the enclosure can reach explosive or flame-producing levels.

Accidental polymerization of bulk quantities of monomer must be prevented. The most probable cause of such an accident is attempted storage of catalyzed monomer (monomer to which initiator has been added). In some instances, impurities may cause accidental polymerization during storage in mixing equipment. The possibility of monomer becoming unstable can be determined by regularly scheduled monitoring of the inhibitor concentration. For example, one approach used at the Brookhaven National Laboratory records measurements after each use, or once per week, whichever occurs first. Since most polymerization reactions are exothermic, temperature sensors provide a warning when polymerization occurs in storage or mixing equipment. Once started, however, such reactions are difficult to stop. Proper venting of the storage drums, and a spark-free, isolated, and well-ventilated storage area limit the effects of an uncontrolled polymerization.

To avoid bulk polymerization, job regulations should provide that any monomer that has been catalyzed should be disposed of after a specified time. This time would vary somewhere between minutes and hours, depending on type of initiator used, job conditions, monomer exposure to sunlight,

the initiator concentration, the bulk quantity involved, and the temperature. Accidental polymerization of bulk monomer creates two hazards. First, the polymerization reaction is exothermic. This heat may cause bulk polymerization in adjacent monomer containers, damage other equipment, or cause personnel burns. Second, as the temperature of the polymerizing monomer reaches its boiling point, the monomer begins to vaporize, and in closed containers the pressure increase may cause a violent rupture of the container. This sudden release of large quantities of monomer vapor and hot polymerizing mass creates critical hazards. Because of these bulk polymerization hazards, storage of monomer containing catalyst (initiator) is not recommended except for short periods at low temperatures.

5.3.3 *Disposal*—Latexes are normally disposed of by diverting the liquid into a pond and letting it dry to a stable, hardened material. The dried latex can be burned or buried. Burning produces nontoxic black smoke and fumes. Spills into streams and waterways should be avoided. Although there is no substantial biological oxygen demand, the waters would be colored milky white.

Every reasonable effort should be made to prevent monomer spills. If monomer has been spilled, it can be rendered safe for disposal by covering it with a suitable absorbing agent, such as sand. Some absorbing agents such as untreated clays and micas cause an exothermic reaction that might ignite the monomer.

Disposal of waste or excess nonpolymerized epoxy and monomer, particularly if catalyzed, can be troublesome. Addition of catalyst to more epoxy or monomer than is required for a particular project should be avoided if possible. In the event that monomer disposal is necessary, two general procedures are available: incineration and bulk polymerization. Incineration of excess monomer or monomer-saturated material may be possible; however, compliance with local, state, and federal regulations applicable to the incineration process is mandatory. Used drums should be left open to permit vapors to escape, to prevent buildup of flammable air-vapor concentrations in the drum, and to allow expansion if any remaining monomer should polymerize. Flame arrestors should be used on all container vents where monomers are being withdrawn over a period of time.

Bulk polymerization of monomer is accomplished by adding a polymerization initiator and a promoter or heat to the monomer in open-top containers and allowing the monomer to polymerize. Epoxies can also be bulk-polymerized by adding curing agent. Irritating fumes may be given off during bulk polymerization of epoxies, so it should be done only in a ventilated or outside environment. If the container is partially filled with aggregate, the vigor of the polymerization reaction is moderated. The resulting stable polymer or hardened epoxy may then be disposed of in accordance with local, state, or federal regulations.

Disposal of catalyzed monomer may be accomplished safely by transferring it to a large metal pan containing aggregate about 6 in. (150 mm) deep, located in an isolated and secure area where no flames are permitted. About 5 percent more initiator is added to the mixture, that is then exposed to ambient temperatures [between 60 and 100 F (16 and 38 C)]

and to sunlight. Bulk polymerization takes place within a few hours to a few days. The polymerized material can be removed and the pan reused.

5.4—Other hazards

Many hazards are present when working with polymers in concrete that should not be overshadowed by concern with the chemicals. In the polymer-impregnation process, relatively high temperatures are required to dry the concrete in preparation for soaking and later polymerization. Procedures used for drying the concrete include forced hot air, infrared lamps, and open gas flames. Each of these procedures can be hazardous. In each case, some type of enclosure is needed to contain the heat in the area to be dried. Temperatures within the enclosure may exceed 400 F (200 C) and are much higher at the heat source. Severe burns can result. The enclosures are normally insulated to contain the heat for drying, but they should also be insulated for safety reasons. If wood or other flammable materials (including some types of insulation) are used in the enclosure, they must not be allowed to heat above their ignition temperature. Some insulation and possibly plywood glues can give off toxic fumes at the temperatures involved. Care must be taken with gas flames to avoid leaks and loss of the flame. In an enclosed area or room, carbon monoxide poisoning and oxygen depletion can be a problem where flames are used. Handling of fuel, either liquid or gas, must be done properly to avoid explosions and fires.

Forced-air heaters, when used, may have a capacity in the range of 500,000 to 750,000 BTU/hr (35,000 to 41,500 gram-cal/sec) and several units may be required. If electricity is used for forced-air heaters or infrared heat lamps, a high amperage system (probably at 480 volts) is needed. Wiring insulation and grounding are temporary, but must be safe and according to applicable codes. Insulation for wiring must not deteriorate at the temperatures involved. Prior to the soak cycle, all electrical equipment in the area should be de-energized. Electrical arcing must be avoided around the monomer.

During polymerization of polymer-impregnated concrete, temperatures are again high. A maximum of 160 to 212 F (70 to 100 C) may be specified, but actual procedures could produce higher temperatures. It is desirable to cover the monomer-saturated concrete with a plastic membrane to minimize the monomer vapor concentration in the enclosure used to contain the heat. Care must be taken to select a membrane that does not melt at exposure temperatures. Direct heat from infrared lamps or from open-flame burners should only be used with great care because of the danger of fire. One acceptable method uses forced hot air. In this instance, the fan blowers should be turned on to evacuate concentrated monomer fumes from the heater area before the heaters themselves are activated. The heater units should be located away from the monomer soak area. If high concentrations of monomer are present when the heaters are started, an explosion may result. Another procedure used for polymerization is ponding of hot water. The boiler used for the hot water should be located in an area free of monomer vapor, and personnel should be protected from hot piping.

A fast and effective method of polymerization uses steam or inert gas. Safe operation of steam or inert-gas generators is mandatory and personnel must be kept from scalding water, live steam, and hot gas. The enclosure unit may become extremely hot and require a cool-down period or the use of heat resistant gloves before it can be handled. The steam or inert-gas generator should use a closed flame or be located away from any monomer concentration that is created during a soak cycle. When steam vapor or inert-gas generators are used, care should be taken not to exhaust the unit into an enclosure until it is certain that steam or inert-gas is being produced. The raw gas that is produced initially can cause an explosion if vented into the enclosure. A bypass valve should be installed to eliminate this possibility.

5.5—Summary

Most of the chemicals mentioned here are sold by major companies who have technical representatives eager to educate and help users in safe handling and storage practices. Most of these companies have excellent literature on the chemicals they supply that includes safety information. Each user is encouraged to get to know these suppliers to take advantage of the help they can offer. When properly used and applied by well-informed workers under technically competent supervision, the chemicals should present no undue safety hazards.

This chapter summarizes the experience and concerns for safety that have been identified during the development of materials, procedures, and applications for concrete composites containing polymers. As concepts become more widely developed, it is expected that better-defined safety considerations will evolve. Hazards have been identified that do exist, but rarely materialize when a well-informed and common sense approach to their possibilities is taken.

Safety is a wide-ranging subject that includes aspects of normal construction practices, special construction practices arising from the use of concrete polymer materials, the intrinsic properties of the chemicals, and the codes and regulations of governmental regulatory agencies, and various groups and associations. This chapter is intended to alert the reader to the hazards from handling and using materials that are not familiar to most construction workers, but should not be considered as a substitute for the authoritative literature.

CHAPTER 6—REFERENCES
6.1—Referenced standards and committee documents

The documents of the standards-producing organization referred to in this document are listed below with their serial designation. Since some of these documents are revised frequently, generally in minor detail only, the user of this document should check directly with the sponsoring group if it is desired to refer to the latest revision.

American Concrete Institute (ACI)

224.1R   Causes, Evaluation, and Repair of Cracks in Concrete Structures
302.1R   Guide for Concrete Floor and Slab Construction
306R   Cold Weather Concreting
503R   Use of Epoxy Compounds with Concrete

503.1   Standard Specification for Bonding Hardened Concrete, Steel, Wood, Brick, and Other Materials to Hardened Concrete with a Multi-Component Epoxy Adhesive
503.2   Standard Specification for Bonding Plastic Concrete to Hardened Concrete with a Multi-Component Epoxy Adhesive
503.3   Standard Specification for Producing a Skid-Resistant Surface on Concrete by the Use of a Multi-Component Epoxy System
503.4   Standard Specification for Repairing Concrete with Epoxy Mortars
546.1R   Guide for Repair of Concrete Bridge Superstructures
548.3R   State-of-the-Art Report on Polymer-Modified Concrete
548.4   Standard Specification for Latex-Modified Concrete (LMC) Overlay
548.5R   Guide for Polymer Concrete Overlays
5488.6R   State-of-the-Art Report of Polymer Concrete Structural Applications

These publications may be obtained from:

American Concrete Institute
P. O. Box 9094
Farmington Hills, MI 48333-9094

American National Standards Institute (ANSI)

ANSI K 68.1   American National Standard Institute's Guide for Classifying and Labeling Epoxy Products According to their Hazardous Potentialities
ANSI Z 129.1   American National Standard for the Precautionary Labeling of Hazardous Industrial Chemicals

These publications may be obtained from:
ANSI
11, West 42nd Street
13th Floor
New York, NY 10036

America Society for Testing and Materials (ASTM)

C 192   Test Method of Making and Curing Concrete Test Specimens in the Laboratory

This publication may be obtained from:
ASTM
100 Barr Harbor Drive
West Conshohocken, PA 19428-2959

Code of Federal Regulations

Title 16   Commercial Practices
Title 40   Protection of the Environment

These publications are available from:
US Government Printing Office

Superintendent of Documents
Mail Stop SSOP
Washington, DC 20402-9328

National Fire Protection Association

National Electrical Code Handbook

This publication is available from:
National Fire Protection Association
One Batterymarch Park
PO Box 9101
Quincy, MA 02269-9101

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APPENDIX I—GLOSSARY OF TERMS FOR USE WITH POLYMERS IN CONCRETE

Accelerator—See *Initiator*

Additive—A substance added to another in relatively small amounts to impart or improve desirable properties or suppress undesirable properties.

Auto-ignition temperature—The temperature to which a monomer can be raised before it ignites itself.

Bulk polymerization—A technique used to produce stable polymer or hardened epoxy for disposal purposes. It is accomplished by adding a polymerization initiator and a promoter or heat to a monomer in open-top containers and allowing the monomer to polymerize. Curing agents are added to epoxies to accomplish this.

Catalyst—See *Initiator.*

Cross linking agent—Bifunctional or poly-functional monomer whose addition to a polymer system increases the rigidity, resistance to solvents, and softening point of the polymer.

Curing agent—See *Initiator* and *Hardener.*

Dry pack placement—Method of producing polymer concrete (PC) by placing and tamping graded aggregate into a prescribed location and then repeatedly sprinkling the exposed surface with a liquid monomer until all aggregate is completely wetted. This is followed by polymerization of the composite. Generally limited to monomer systems with viscosities less than 100 cp.

Emulsifier—A substance that modifies the surface tension of colloidal droplets, keeping them from coalescing and keeping them suspended.

Emulsion—A system consisting of a liquid dispersed with or without an emulsifier in an immiscible liquid, usually in droplets of larger than colloidal size.

Encapsulation techniques—Various techniques used in the production of fully impregnated concrete to minimize monomer evaporation and drainage losses during the polymerization process.

Endothermic—Pertaining to a reaction that occurs with the absorption of heat.

Epoxy resin—A resin that contains or did contain epoxy groups principally responsible for its polymerization.

Exothermic—Pertaining to a reaction that occurs with the evolution of heat.

Explosive limit—The range of vapor concentrations in air at room temperature and normal atmospheric pressure that supports combustion.

Flash point—The lowest temperature at which the vapor of a combustible liquid can be made to ignite momentarily in air.

Full impregnation—The process by which all moisture is thoroughly removed from hardened concrete and the resulting pore space in the concrete is completely saturated with a monomer that is subsequently polymerized.

Glass transition temperature (T_g)—The temperature at which an amorphous material (such as glass or a high polymer) changes from a brittle, vitreous state to a plastic state.

Hardener—The chemical component added to epoxy resins that causes the resin to harden or cure.

Impregnation—The process to cause the void and pore space in hardened concrete to be filled, permeated, or saturated with monomer. See Full impregnation and Partial impregnation.

Inhibitor—Free-radical scavengers added to monomers to react with and deactivate the free radicals in growing polymer chains, and to act as antioxidants to prevent polymerization by oxidation product reaction during monomer storage.

Initiator—Agent that initiates growth of polymer chains by decomposing into free radicals that actually start the chain's growth. Often incorrectly called a Catalyst.

Ionizing radiation—Used in the production of free radicals during initiated polymerization by the absorption of radiation energy by the monomer.

Latex—a dispersion of organic polymer particles in water, usually made by the emulsion polymerization process and often (incorrectly) referred to as an emulsion.

Microcracks—Small, numerous, noncritical cracks that can develop in hardened concrete in the matrix and at matrix-aggregate interfaces both prior to the concrete receiving external loads or during loading.

Modifier—See *Additive*.

Monomer—A small molecule from which much larger polymer molecules can be made. Usually in liquid form for concrete applications.

Monomer depletion—The loss of monomer due to evaporation from the surface of hardened concrete prior to the polymerization process associated with the production of polymer-impregnated concrete.

Partial impregnation—Accomplished by impregnating conventional portland cement concrete to a limited depth using simple soaking techniques. It is intended to provide a relatively impermeable, in-depth protective zone on the concrete surface in order to improve durability.

Plasticizer—Chemical additions to monomers to improve the flexibility of inherently brittle polymers.

Polymer—The product of polymerization, more commonly a rubber or resin consisting of large molecules formed by polymerization.

Polymerization—The reaction in which two or more molecules of the same substance combine to form a compound containing the same elements, and in the same proportions, but of high molecular weight, from which the original substance can be regenerated, in some cases

only with extreme difficulty.

Polymer concrete (PC)—A composite material in which the aggregate is bound together in a matrix with a polymer binder.

Polymer impregnated concrete (PIC)—A hydrated portland cement concrete that has been impregnated with a monomer that is subsequently polymerized.

Polymer portland cement concrete (PPCC)—see Polymer-modified concrete.

Polymer-modified concrete (PMC)—portland cement and aggregate combined at the time of mixing with organic polymers that are dispersed or redispersed in water.

Porosity—The ratio, usually expressed as a percentage, of the volume of voids in a material to the total volume of the material, including the voids.

Premix placement—The method of initially blending a polymer binder, with fine and coarse aggregate and fillers, if used, and then mixing until all particles are completely wetted. Once the composite has been mixed as required, it is transported and placed. Term applies to polymer concrete.

Prepackaged polymer concrete—Polymer concretes whose individual components (that is, monomer or resin, fillers, and aggregates) are premeasured and packaged by the manufacturer for a prescribed sequence of introduction into the mixing process.

Promoted-catalytic method—A polymerization method that uses promoters or accelerators to cause the decomposition of organic peroxide initiators, and subsequent release of free radicals that allow polymerization to take place at ambient temperature without the need for an external source of energy.

Promoter—See *Initiator.*

Resin—A natural or synthetic, solid, or semisolid organic material of indefinite and often high molecular weight, with a tendency to flow under stress. It usually has a softening or melting range and usually fractures conchoidally.

Shelf life—Maximum interval during which a material may be stored and remain in a usable and safe condition.

Silane coupling agent—Silicon compounds having the general formula (HO)$_3$SiR were R is an organic group compatible with thermoplastic or thermosetting resins. They are used to enhance the chemical bond of organic polymers to inorganic materials such as sand, rock, glass, and metals.

Solvent—A liquid capable of dissolving another substance.

Thermal-catalytic method—A polymerization method that uses chemical initiators that are dissolved in the monomer prior to introducing the mixture into the concrete. The subsequent application of external heat then causes the polymerization to occur at a very rapid rate.

Thermoplastic—Term applied to synthetic resins that may be softened by heat and then regain their original properties upon cooling.

Thermosetting—Term applied to synthetic resins that solidify or set on heating or curing and cannot be remelted.

Vapor pressure—The pressure (usually expressed in millimeters of mercury) characteristic at any given temperature of a vapor in equilibrium with its liquid or solid form.

Viscosity—Friction within a liquid due to mutual adherence of its particles. Low-viscosity liquid monomers flow more easily into the pores of concrete at ambient temperatures and pressures than do high-viscosity monomers.

APPENDIX II—GLOSSARY OF ABBREVIATIONS USED IN THIS GUIDE

AIBN	2,2'-azobis (isobutyronitrile)
AMVN	2,2'-azobis-(2,4-dimethylvaleronitrile)
BA	Butyl acrylate
BPO	Dibenzoyl peroxide
CFR	Code of Federal Regulations
DOT	U.S. Department of Transportation
EIFS	Exterior insulation finish systems
HQ	Hydroquinone
LEL	Lower explosive limit
LP	Lauroyl peroxide
MEHQ	Methyl ether of hydroquinone
MEKP	Methylethylketone peroxide
MFFT	Minimum film-forming temperature
MMA	Methyl methacrylate
MSDS	Material Safety Data Sheet
OSHA	Occupational Safety and Health Administration
PAE	Polyacrylic ester
PC	Polymer concrete
PCC	Portland cement concrete
PIC	Polymer-impregnated concrete
PMC	Polymer-modified concrete
PPCC	Polymer portland cement concrete
PS	Polystyrene
PVAC	Polyvinyl acetate
SADT	Self-accelerating decomposition temperature
S-B	Styrene-butadiene copolymer
TMPTMA	Trimethylolpropane trimethacrylate
US EPA	United States Environmental Protection Agency
VAC	Vinyl acetate copolymer

This report was submitted to letter ballot of the committee and was approved in accordance with ACI balloting procedures.