

Polymers in Concrete*

Reported by ACI Committee 548

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ACI Committee 548 has prepared a state-of-the-art report on polymers in concrete, a comprehensive compilation of information on the current state of knowledge relating to polymers used in concrete, process technology, properties of the various composites of concrete and polymers, structural design information, and applications under study or in use. The following is an abstract of the information in the report. For detailed information and in-depth discussions, the full report should be consulted.

INTRODUCTION

The following three types of concrete materials utilize polymers to form composites: (1) polymer-impregnated concrete (PIC), which is a hydrated portland cement concrete that has been impregnated with a monomer and subsequently polymerized in situ, (2) polymer-portland cement-concrete (PPCC), which is produced by adding either a monomer or polymer to a fresh concrete mixture, and subsequently curing and polymerizing the material in place, and (3) polymer concrete (PC), which is a composite material formed by polymerizing a monomer and aggregate mixture.

For this review, the incorporation of monomers and polymers is made for the purpose of substantially altering some property of the final hardened concrete. Small quantities of polymer added to modify the properties of fresh concrete are considered to be admixtures and are not discussed here.

CHAPTER 1—MONOMERS AND POLYMERS

A monomer is an organic molecular species which is capable of combining chemically with molecules of the same or other species to form a high molecular weight material known as a polymer. A polymer consists of repeating units derived from the monomers which are linked together in a chain-like structure. The chemical processes through which these linkages occur is known as polymerization.

Linear polymers are composed of long chains and are termed thermoplastics because their properties change reversibly with temperature. Condensation polymer

*The full report was published as a separate publication in 1977. It has 92 pp. and is available in cover format. Discussion of the report will be published in the ACI JOURNAL, Proceedings, Vol. 5, No. 8, Aug. 1978.

chains which are crosslinked or interconnected in a random three-dimensional network are called thermosets since they do not show reversible changes with temperature. It is possible to link the polymeric chains of thermoplastics with strong chemical bonds through the use of crosslinking agents. Increasing amounts of crosslinking will raise the glass transition temperature T_g , and eventually a thermoset results.

Polymer-impregnated concrete

Monomers—The selection of suitable monomers for polymer-impregnated concrete (PIC) is based upon the impregnation and polymerization characteristics, availability and cost, and the properties of the resultant polymer and PIC. Liquid vinyl monomer systems have generally been used. The viscosity of the monomer must be low to permit it to impregnate the concrete. Monomer viscosities can be altered by blending with higher or lower viscosity monomers or polymers. Monomers are normally supplied containing an inhibitor to prevent premature polymerization of the monomer.

Polymers—Most glassy, vinyl polymers have tensile strengths in the range of 5000 to 10,000 psi (34.5 to 68.9 MPa), compressive strengths range from about 11,000 to 19,000 psi (75.8 to 131.0 MPa), and moduli of elasticity of about 100 ksi (690 MPa). Above T_g , the materials exhibit plastic behavior. Generally, polymers are inert materials. They may, however, be attacked by certain oxidizing agents or organic solvents. Absorption of ultraviolet radiation may lead to eventual degradation, and stress cracking can be a problem. The thermal decomposition temperature of typical vinyl polymers ranges from about 110 C for polyvinyl chloride (PVC) to 260 C for polymethyl methacrylate (PMMA), but is generally about 200 C.

Polymerization—There are three commonly used methods for free radical initiated polymerization. In one method, small amounts of a compound which will generate free radicals on heating are added to the monomer. This method is generally called thermalcatalytic, although the compounds are not strictly catalysts since they are consumed during the reaction. Decomposition of catalysts can also be initiated by promoters or accelerators. Since polymerization begins immediately on adding a promoter, its use in PIC would be restricted to shallow impregnations. Production of free radicals can also be achieved by the use of ionizing radiation such as gamma rays emitted by cobalt-60.

Polymer-portland cement-concrete

Polymer-portland cement-concrete (PPCC) has been prepared with both pre-mix and post-mix polymerized materials. The pre-mix polymerized materials include latexes and polymer solutions or dispersions. The post-mix polymerized PPCC has been made with a number of resins and monomers.

Polymer latexes—At present, latex-modified concretes represent the large majority of commercial applications of polymer-modified concretes in the United States. Suitable latex formulations greatly improve the shear bond, tensile, and flexural strength of cements and mortars. Thermoplastic latexes include polyvinyl esters, polyacrylics, and polyvinyl chlorides. Elastomeric latexes include acrylonitrile-butadiene and styrene-butadiene.

Polymer solutions—Thermosetting water-soluble polymers which have been added to fresh concrete include epoxies, amino-resins, polyesters, and formaldehyde derivatives. Thermoplastic materials include polyvinyl alcohol and polyacrylamides.

Monomers—Preparation of PPCC by adding vinyl monomers directly to the wet mix, followed by polymerization, has not been very successful. Furfuryl alcohol PPCC has been successfully used in the Soviet Union, but it requires up to 45 days of curing to develop full strength.

Thermosetting resins—A polyester formulation has been used in England to produce "Estercrete." When the system is mixed with water the catalyst is activated, polymerization occurs, and cement hydrates. Water-soluble epoxy resins for use in concrete have been developed in the USSR, while water-dispersible epoxy resins have been patented in Japan and have recently been developed in the United States.

Polymer concrete

Monomers and resins—Most of the work on polymer concrete (PC) has been with polyester-styrene resin systems, and to a lesser extent with furan, epoxy, and vinyl ester resins systems. The polyester resins are attractive because of moderate cost, availability of a great variety of formulations, and moderately good PC properties. The furan resins are low cost, and highly resistant to chemical attack. The epoxy resins are generally higher in cost, but may offer advantages such as adhesion to wet surfaces. Polyurethane concretes have been developed and used in England. PC has also been made with an MMA-TMPTMA monomer system. The composite has structural and durability properties comparable to PIC.

Additives and modifiers—Silane coupling agents added to the monomer system increase the interfacial bond between polymer and aggregate, and hence increase the strength of the composite.

Polymerization—Most of the monomer and resin systems for PC are polymerized at ambient temperatures. Vinyl monomer systems can be polymerized with catalysts such as benzoyl peroxide with an amine promoter. The polyester-styrene systems are polymerized with promoter-catalyst systems such as methylethyl ketone peroxide with cobalt naphthanate promoter. Other systems include amine curing agents for epoxy resins.

CHAPTER 2—PROCESS TECHNOLOGY

Polymer-impregnated concrete

The basic method of producing polymer-impregnated concrete (PIC) consists of the fabrication of precast concrete specimens, oven drying, saturation with monomer, and in situ polymerization.

Concrete fabrication—No special procedures are necessary for the preparation of concrete for impregnation. A dense concrete will, of course, require a lower polymer loading for full impregnation than will a more porous concrete.

Drying requirements—To achieve maximum improvement in strength of PIC, the concrete must be dried to constant weight, evacuated, and saturated with monomer under pressure prior to polymerization. A drying temperature of 302 F (150 C) appears to be near optimum.

For large specimens, special control of heating and cooling temperatures and rates may be required to minimize cracking of the concrete.

Monomer saturation techniques—For full impregnation, good quality concrete having a cross section of up to 12 in. (305 mm) will require soaking in monomer for about 60 min under a pressure of 10 psig (68.9 kPa). Concrete may be only partially impregnated when improved strength is not needed but greater durability is desired. Concrete is not normally evacuated prior to partial impregnation. The use of pressure is dependent on the viscosity of the monomer. Higher viscosity monomers result in more uniform depth of penetrations but require positive pressures.

Polymerization techniques—Care must be taken to minimize monomer evaporation and drainage losses from the concrete during the polymerization process. Polymerization of monomer-saturated specimens while immersed underwater appears to be the most practical for large scale application. As described in Chapter 1, three methods for polymerization of monomers are the thermal-catalytic, promoter-catalyst, and radiation techniques. The thermal-catalytic process has been used extensively for PIC and is the most practical for present day use. The primary advantage of the method is that the polymerization rates are rapid, resulting in short processing times. A disadvantage is that the process involves storing and handling of monomer containing a chemical initiator, which will require suitable safety precautions.

Monomer handling and safety—Manufacturers recommend proper storage temperatures, toxicity limits, and other precautions for safe handling of monomers. Manufacturers place sufficient inhibitor in the monomers to maintain safety during shipping and storage, but inhibitor concentrations must be tested periodically to assure that no change has occurred. The greatest potential hazards exist after catalyst has been added to the monomer. Monomers should not be exposed to flames, sparks, or other sources. When handling monomers, adequate ventilation, protective goggles, and gloves should be provided.

Polymer-portland cement-concrete

PPCC process technology is based upon overcoming the incompatibilities of most organic polymers and their monomers with mixtures of portland cement, water, and aggregate.

Latex modified concretes—The mix proportioning of latex PPCC will vary in much the same way as do normal concretes and mortars. However, air-entraining agents should not be used. In fact, antifoaming agents are generally added to control excessive air entrainment. Latexes are normally more effective in richer mixes. The water content of the mix is generally reduced on a volume basis by the volume of the polymer latex added. Care should be taken not to overvibrate the PPCC to prevent bringing excess water to the surface. Optimum properties are obtained by moist curing from 1 to 3 days followed by dry curing. The use of heat during dry curing increases early strength.

Toxicological considerations—Latexes are safe materials to handle, and their use requires only normal precautions. Repeated exposure can cause mild skin irritation in much the same manner as conventional

portland cement systems. In post-mix polymerization PPCC, the precautions discussed for PIC monomer handling techniques should be observed.

Water-soluble polymers—These polymers are added to the mixture in the form of a water solution during the mixing operation. Normal mixture proportioning and batching procedures are used. Most of these water-soluble electrolytes and liquid resins are thermosetting. Curing usually involves some period of standard moist curing followed by curing at elevated temperatures.

Polymer concrete

Mixing and placing techniques for PC are based on adaptation of existing equipment and methods for producing portland cement concrete. A knowledge of polymer chemistry is helpful, but not essential, as directions for curing mixes are available from the resin manufacturers and the published literature.

Materials and mix proportioning—PC has been made with epoxy, polyester, and furan resins, and more recently with MMA and styrene monomer systems. It is conceivable that many other resins could be used. In the proportioning of PC mixes, the primary objective is to obtain an aggregate gradation which will give good workability with minimum amounts of monomer or resin. Aggregates should be dried to less than 2 percent moisture. The use of finely divided materials such as portland cement and silica flour will improve workability. Mixes have been made with between 5 and 30 percent by weight of monomer. Mixes containing between 7 to 9 percent MMA have developed compressive strengths approaching those of PIC. The lowest polymer loadings have been obtained in pipe, where pressure, vibration, and centrifugal force were used.

Fabrication and curing methods—PC mixes are placed and vibrated in a manner similar to conventional concrete. With some harsh mixes, external vibration is required. Solvents may be needed to clean equipment when using polyesters and epoxies. Volatile systems such as MMA evaporate quickly and present no cleaning problems. However, such systems are potentially explosive and require nonsparking and explosion-proof equipment. Curing of PC may be performed by thermal-catalytic, promoter-catalyst, or radiation techniques. Promoter-catalyst systems are frequently best suited for PC, with curing times varied, as needed, between a few minutes and several hours. Full strength is attained when polymerization is completed.

CHAPTER 3—PROPERTIES

Polymer-impregnated concrete

PIC looks very much like conventional concrete. Apart from some surface coating of polymers which may be present, PIC is indistinguishable from plain concrete on casual observation.

Strengths—High strengths in compression, tension, and flexure can be achieved in PIC, with increases being as much as four times that of control specimens. When a nonporous aggregate is used, the improvement in strength depends mainly on the degree to which the cement paste is impregnated. PIC produced from a low-quality concrete with a high water-cement ratio will require more polymer, but may approach or be equal in quality to PIC produced from a high-quality, low water-cement ratio concrete. Impregnation of light-