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Polymer-Concrete Composites

Béton de résine synthétique

Kunstharzgebundener Beton

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SUMMARY

This report reviews the principal characteristics of the polymer-concrete materials and summarizes the state-of-the-art of the development and application of concrete-polymer composites. The three main types of polymer-concrete composites available so far are described as well as the monomer systems and process technology used in their production. Possible civil engineering applications under study and the current use of polymer-concrete composites around the world are included.

RÉSUMÉ

Cet article donne un aperçu des principales caractéristiques des matériaux de béton de résine synthétique et résume le stade actuel du développement et de l'application du béton de résine synthétique. Les trois principaux types de béton de résine synthétique disponibles à ce jour de même que leur technologie de production y sont décrits. L'article mentionne les possibilités d'application au génie civil actuellement à l'étude et l'emploi du béton de résine synthétique dans le monde.

ZUSAMMENFASSUNG

Dieser Artikel gibt einen Überblick über die grundsätzlichen Eigenschaften von Kunstharz-beton und zeigt den heutigen Stand in der Entwicklung und Anwendung von kunstharz-gebundenem Beton. Die drei bis heute bekannten Haupttypen von kunstharzgebundenem Beton sowie deren technologische Herstellung werden hier aufgezeigt. Mögliche, in Erwägung gezogene Bauanwendungen und der Einsatz von kunstharzgebundenem Beton auf der ganzen Welt werden diskutiert.



1. INTRODUCTION

Cement concrete is an inherently porous material and as such, it has a low tensile strength, exhibits a tendency to cracks and can deteriorate under the influence of severe chemicals in the atmosphere or in solution. Concrete polymer materials have been developed during the last fifteen years in a number of laboratories around the world, for applications as a constructional material offering the potential advantages of a higher strength, water tightness, and improved durability and resistance to freeze-thaw cycles over normal portland cement concrete (1, 2, 3, 4). The production of polymer-concrete composites involves the introduction of chemicals within the pores of the concrete and their polymerization through thermo-catalytic or radiation methods to achieve improved physical and mechanical properties.

1.1. Definitions

Some of the terms used in this report are explained below: Monomer as used in this report is a low viscosity liquid organic material which is capable of combining chemically with molecules of like kind to form a polymer.

Polymers are hard glossy solids commonly called plastics.

Polymerization is a chemical process by which a monomer is converted to a polymer plastic. The polymerization process may take place either by an addition or a condensation reaction. Polymer chains can be cross-linked in a random three-dimensional network. Such structures form rigid materials which are called thermosets since they do not show the reversible changes with temperature typical of thermoplastic polymers.

Promoters are chemicals used to accelerate the polymerization reaction. Emulsion is essentially stable two-phase mixtures made up of very fine particles of a liquid dispersed in a non-solvent liquid.

A latex is a rubber emulsion in which water is the continuous phase. Thermoplastic polymers undergo an abrupt change in their physical state, passing from a hard glassy material at low temperatures to a "plastic" material of a much lower viscosity at higher temperatures. This change is reversible upon cooling and the temperature at which this transition occurs is known as the glass transition temperature (t_g) and marks a pronounced change in physical and mechanical properties.

For further information concerning definitions and polymer chemistry, in general, the reader is referred to text-books on polymer science (5).

1.2. Classification

Polymer-Impregnated Concrete (PIC) is based on the concept of diffusion of a monomer into portland cement concrete and its polymerization in-situ.

Polymer-Cement Concrete (PCC) consists of a monomer or a polymer that is added to a water-portland cement-aggregate mix followed by polymerization as the concrete hardens.

Polymer-concrete (PC) is a resin-bound aggregate, the polymer being the binder.

For each of these three main types of polymer-concrete composites, the process technology can be altered to tailor the desired properties and characteristics of the composites. Polymer impregnated concrete can be manufactured either as a partially impregnated or as a fully impregnated concrete, the latter being common only in thin sections or small elements. The partial impregnation finds application in the repair of roads, bridgedecks and precast concrete elements.

Another type of polymer-concrete is a combination of the PIC and PC types. This is manufactured as a sand filled resin overlay, composed of multiple layers of synthetic thermosetting resins and dry silica sand which are placed by spreading (or spraying) a selected resin over a clean, sound portland cement concrete bridge deck. Silica sand is broadcast immediately over the impregnating unpolymerized resin to excess and compacted by rolling. After curing of the resin, the procedure is repeated in general to four layers.

1.3. Characteristics

Polymer-Impregnated Concrete (PIC) is generally, a precast and hydrated portland cement concrete, which has been cleaned, dried (eventually evacuated) and impregnated with a low viscosity monomer (eventually soaked under pressure) before being polymerized. Polymer loadings of up to 8 wt.% of the dry concrete can be obtained. The most appreciable improvements in the structural and durability properties have been obtained with PIC (6). A hard glossy polymer formed throughout the cross section of the concrete transforms it from an elasto-plastic to an elastic material with an increase of at least two times in the modulus of elasticity, a four-fold increase in compressive strength and a reduction of water absorption by 95%. The tensile strength of PIC also increases proportionately as does the freeze-thaw resistance appreciably, with increasing polymer loadings. The unique feature of impregnating concrete is that a large part of the voids volume (formed by shrinkage of set concrete) in the capillary pores is filled with the polymer and forms a continuous internal reinforcing structure which is thus responsible for the remarkable improvement in strength and durability (Table I).



TABLE 1

Physical, mechanical and chemical properties of a PIC (7)		
Property	Unimpregnated Concrete	Polymer Impregnated Concrete
Compressive strength 10^6 N/m^2	37	125
Modulus of Elasticity 10^6 N/m^2	24000	43000
Tensile strength 10^6 N/m^2	2.9	10
Modulus of rupture 10^6 N/m^2	5.1	16
Water absorption %	6.4	0.34
Water permeability 10^{-4} /yr.	1.6	0.43
Coefficient of expansion $10^{-6} \text{ cu/cu/}^\circ\text{C}$	7.24	9.45
Freeze-Thaw cycles	740	10340
weight loss %	25	12.5
Sulphate attack test cycles		
days	0.467	0.042
Acid 15% HCl days exposed	105	1395
weight loss %	27	10
Acid 15% H_2SO_4 days exposed	49	119
weight loss %	36	26

The ability to vary the components and technology of the PIC composites presents some possibility of tailoring the desired properties for particular structural applications as illustrated in Fig. 1

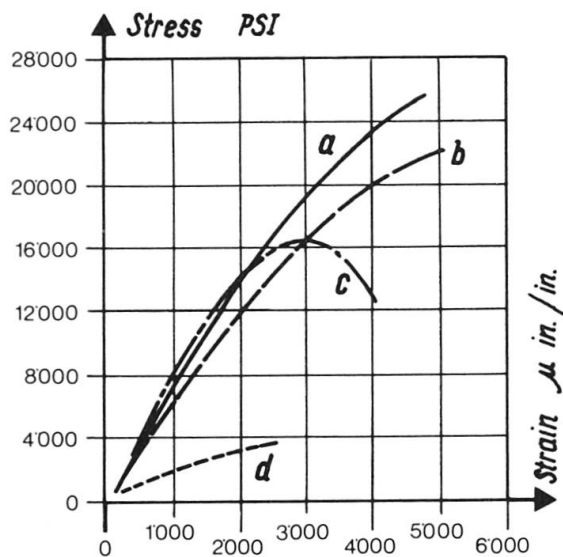


Figure 1. Compressive stress-strain curve for polymer-impregnated concrete. Curve a, MMA; curve b, 78wt% MMA - 28 wt% DP; curve c, 64 wt% MMA - 35 wt% BA; curve d, unimpregnated concrete.

The remarkable improvements of physical and mechanical properties of PIC are also being measured in polymer-impregnated structural lightweight concrete. Tests performed (8) include compressive strength, tensile-splitting strength, flexural strength, reinforcement pull-out strength, freeze-thaw resistance and fatigue durability. The resulting improvements reported for the first three tests are 325%, 244% and 282% respectively.

POLYMER CEMENT CONCRETE (PCC) is a mixture of cement paste and aggregate to which an emulsion of a polymer or a monomer is added prior to the setting and curing of cement. The addition of a monomer (or polymer) to the initial

slurry of concrete has identified a number of problems (9). The results obtained are relatively modest for strength and durability. Organic materials interfered in many cases with the alkaline cement hydration process. This explains the relatively less dramatic effect of polymer in PCC as compared to PIC. Organic materials are incompatible with aqueous systems. The action of water and its affinity of organic and inorganic components of PCC seems to be essential for the physical and mechanical properties of the material and its behaviour in the course of time (10). Another problem with monomer dispersion is to ensure that the polymerization of monomer chains are not inhibited. This can be done most promisingly by adding to the concrete mix an appropriate polymer emulsion based on poly-methyl methacrylate. Such an emulsion does not require polymerization (10). Heating after the hydration of cement helps to melt the polymer distributed in the concrete mass to produce additional bonds and hence an impermeable material.

POLYMER-CONCRETE (PC) consists of an aggregate system bound with a polymer binder. Different aggregates have been used to form composites with polymers. To produce a satisfactory filling of the void space of carefully graded aggregates, some 15 to 25 volume % of polymer are required. Mostly, polymers of two component systems are used. A silane coupling agent is sometimes added to the monomer to improve the bond strength between the polymer and the aggregate. Viscoelastic properties of the polymer give rise to low moduli of elasticity and high creep values. This is the reason for the restricted use of plastics in structural applications (Fig. 2). On the other hand, the use of plastic as a binder with mineral aggregates has helped develop a new class of structural material. Aggregates used for PC are classified into standard weight (granite, sandstone etc.), structural lightweight and insulating lightweight and insulating lightweight. The physical, mechanical and chemical resistance characteristics of PC are determined by the chemical nature of the binder and by the amount and type of fillers and aggregates. The end use and applications often dictate the selection of materials. In general, crushed stone, natural sand and gravel aggregates are used, but fine grained material such as portland cement, clay, fly ash and silica flour have also been incorporated as fillers to improve workability of the mix and to fill the voids.

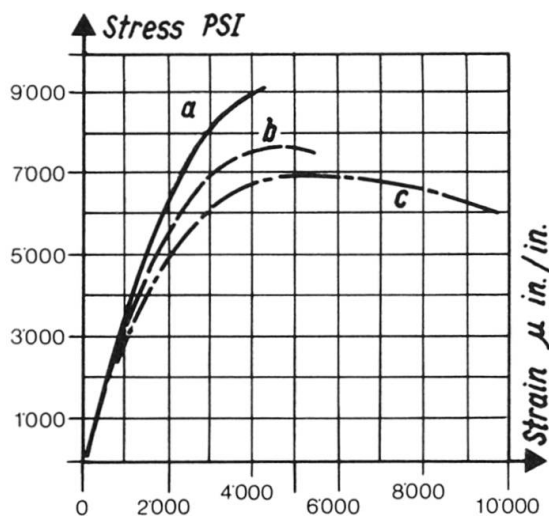


Fig. 2 Compressive stress strain curves for polymer-concrete. Curve a, MMA; curve b, 95 wt % MMA - 5 wt % BA, curve c, 80 wt % MMA - 20 wt % BA.

MMA = methyl methacrylate
BA = butyl acrylate



2. PROCESS TECHNOLOGY

2.1. Polymer Impregnated Concrete (PIC)

The basic method of producing polymer impregnated concrete composites consists of the following steps:

A. Concrete formation is the same as in modern concrete technology. All types of aggregates, cements and admixtures can be used. The final properties of PIC may vary somewhat, depending on the nature of the materials or curing conditions used. The amount of free water and the voids volume in the concrete determine the quantity of monomer that can be loaded into a concrete during impregnation.

B. Drying to remove moisture is the most important step in the process of impregnation of concrete. The polymer fills air voids, interstices and microfractures in the concrete. In order to maximize the porosity available for intrusion of monomer, it is necessary to remove as much water as possible from within the pores. The strength and durability properties of PIC are strongly influenced by the fraction of the porosity of the cement phase filled with the polymer. The amount of water removed from a given concrete specimen is a function of drying time and temperature. Surface drying temperatures up to 400°C have been successfully used for slabs and small bridge deck sections. It has been found (2) that drying temperatures from 150°C to 250°C appears to be near optimum, giving a reasonably fast drying rate (2 hours for medium sized elements 1.0 x 1.8 x 0.1 m), and a high quality product. For larger elements, however, special care and control of heating and cooling rates are necessary to prevent or minimize possible cracking of concrete (3). For drying the concrete surface for partial impregnation, a gas-fired hot air heater or open-flame burners are successfully used. Warm, forced-air, infra-red heaters or heat lamps may also be used. After oven-drying, the slabs had approximately three times greater polymer penetration and proportionately higher polymer loadings. For prefabricated elements, special autoclaves are constructed in which all impregnating processes, including drying, evacuating, soaking monomer eventually under pressure and polymerization are automatically controlled.

C. Saturation with monomer for a full or partial impregnation depend on such parameters as degree of dryness and vacuum, soak pressure and soak time. All of them have an effect on the strength of PIC. Good results can be obtained on good quality dense concrete specimen of 30 cm, cross-section by using the following process (3):

1. Oven-dry to constant weight at 150°C (for about 24 hrs).
2. Evacuate for 30 min. at about 100 KPa (30 in.Hg).
3. Introduce monomer under vacuum and subsequently pressurize to 70 KPa or pressure-soak for about 60 minutes.
4. Polymerize monomer in-situ with radiation or thermal-catalytic system (hot water steam).

Partial impregnation of concrete could also be obtained with soaking the unevacuated dry surface at atmospheric pressure by complete immersion in a low viscosity monomer. Soaking under pressure improves monomer penetration. Atmospheric soaking with low viscosity monomers has produced impregnation depths of up to several centimeters.

Care must be taken to minimize monomer evaporation and drainage losses from the concrete during the polymerization process. Under water polymerization appears to be the most practical method for large-scale applications.

D. Polymerization of monomers. There are three general methods for the polymerization of monomers used in PIC: radiation, thermo-catalytic, and promotor-catalyst techniques.

The selection of a particular method depends on drainage and evaporation losses, safety problems and the economics of the entire process for a specific application.

The thermo-catalytic method is generally used, and involves the use of chemical initiators and heat. The process can be performed in air or under water, or raw steam can be used as a heat source (3). In the thermal-analytic processing method the greatest potential hazards exist when a catalyst has been added to the monomer. The transport, storage and handling of monomers requires rigid safety controls.

Investigations to develop reliable methods for quality control of PIC products are being undertaken (2).

2.2. Polymer Cement Concrete (PCC).

The process technology associated with PCC is very similar to that of conventional concrete. The aim is to permit simultaneous formation of inorganic (crystalline) and organic (polymeric) structures. Most organic polymers and their monomers are incompatible with a mixture of portland cement, water and aggregate. It is not only the solution of the monomer itself that may inhibit hydration of cement but also various other admixtures such as emulsifiers, accelerators and protective colloids. Extensive field experience has been gained with pre-mix polymerisation (polymer-latex). Polymer latex generally act as water reducing agents and polymer latex entrain considerable amounts of air in the concrete. Standard concrete mix designs are normally employed when using polymeric latex systems. The water content of the mix is reduced on a volumetric basis by the inclusion of the polymer-latex. The optimum curing of latex PCC is different from ordinary concrete. The optimum properties are obtained by moist curing until after final set (from 1 to 3 days) followed by air curing of the concrete at ambient temperature. The curing of later PCC may be accelerated by the use of heat but steam heat has been found to be detrimental to the gain in strength properties of those system. Typical mix design for a latex concrete (PCC) is shown below:

Portland cement	263 kg
Sand	627 kg
Aggregate	1017
Water	113.5 - 90.8
Latex solids (5 - 15%)	13.6 - 40.9

The latex should be formulated with an antifoamer. Total water included in the mix is corrected for the water content of the latex and sand. Good results were obtained with polymer emulsions based on poly-methyl methacrylate which is relatively easy to make (10) and does not require polymerisation.



2.3. Polymer Concrete (PC)

Two techniques are used to mix monomer with aggregate. The first is the conventional method of adding monomer to dry aggregate and stirring until a uniform blend is achieved. This method has been successful in some cases, but usually results in the formation of excessive air bubbles and increased porosity. The second technique consists of placing the monomer in the specimen mould and then gradually adding aggregate to the monomer. The mixture is consolidated by mechanical vibration. Most of the work on PC has been with epoxy, polyester and furan resins and more recently with MMA and styrene monomer systems. The important considerations in the choice of a resin system are low cost, durability under anticipated exposure conditions, adhesion to aggregates, handling properties, and ease of curing. Aggregates composed of silica, quartz, limestone, and other high quality material have successfully been used in the production of PC. Aggregates must be dry, and free of dirt, asphalt, and other organic contaminants. The moisture content must be less than 1% and preferably at ambient conditions (less than 30°C) prior to contact with the monomer. The required aggregate size and grading is dependent upon the size of PC element. The mixing operation should be performed in a well-ventilated and shaded area that is free from sources of accidental ignition. Several precautions should be taken with the mixing equipment and during the mixing operation. The preparation and curing time for PC is a function of the promoter and initiator concentrations and the ambient and aggregate temperature. Curing may be performed by radiation, thermal-catalytic or catalyst-promoter methods. Catalyst and promoters are added to the monomer prior to mixing with the aggregate. Curing times may range from a few minutes to several hours. Care must be taken to reduce the evaporation losses from the surface before completion of the polymerization reaction. Typical mix design for a PC sample used at temperatures between 20°C and 35°C is given below:

Aggregate concentration	88 wt %
Monomer concentration	12 wt %
composition	90 wt % MMA, 5 wt % TMPTMA - 5 wt % PMMA
Initiator concentration	2 % benzol peroxide - 70 by weight of monomer.
Promoter concentration	1 % DMA by wt. of monomer

The work time for this formulation will be approximately 30 to 45 minutes and cure time will be between 45 and 90 minutes. Full strength is attained when polymerization is complete.

3. APPLICATIONS

A number of applications of polymer impregnated concrete and polymer concrete are being investigated all over the world. It is very important for the practical development of concrete-polymer materials that a good balance be achieved between cost and performance. Applications of PIC in building and industrial structures include: structural floors, swimming pools high performance structures, food processing buildings, main structures, pipes, storage tanks for hot brine spectic and distilled water, bridge decks breweries, anti-abrasive surface, marine structures, tunnel liners, wall panels, telephone cable ducts (11). In Japan, an industrial construction company toge-

ther with a chemical company is reported to have constructed a large pilot plant for production of PIC using thermal-catalytic initiation. The material is called powercrete and beams, panels, and pipes have been produced. Telecommunication facilities are mostly constructed under roads or side-walls in difficult conditions because of increasing traffic congestion. In Japan, over 20'000 manholes, in the form of precast PIC polymerconcrete segments which are assembled at site are installed annually. Four companies mass-produce such manholes in five different dimensions and weights of 2 to 6 tons each. Investigations and ongoing research over the last 15 years have recommended, for general use, polymer concrete manholes, because of their strength, manufacture, transportation and installation efficiency (12). Another design of an automatic plant by thermal polymerization for mass-production of polystyrene impregnated concrete products has been presented in 1975. The productivity of the plant is 23'000 tons/year. The unit cost of polystyrene impregnated concrete products has been presented in 1975. The productivity of the plant is 23'000 tons/year. The unit cost of polystyrene impregnated concrete products manufactured by the plant in 1958 was US \$ 200/ton or US \$ 500/cu.m.

3.1. Applications of PIC to sea structures

Polymer concrete offers tremendous potential for floating structures and ships. Initial applications were to critical zones of concrete sea structures which are subjected to the extremes of exposure, abrasion and strain. An economic evaluation indicates that relatively little cost constraint exists in applications of PIC to sea structures.

A number of research projects related to the use of polymer-concrete for marine applications have been undertaken in Norway, the United Kingdom, France, West Germany and the United States. The search is now leading to deep water and to extreme environments including the North Sea, the Arctic Ocean and Southern Hemisphere Ocean. Offshore terminals are essential for the shipping and receiving of bulk cargoes and hazardous cargoes such as oil, coal and liquified gas. Development of the oceans' resources remain the most promising endeavour for the next 25 years. Experience with concrete sea structures have emphasized the following special requirements related to service in the oceans: (a) the dominance of cyclic loading; (b) the need to provide durability under severe environmental conditions of salt water, spray and ice; (c) the need to reduce weight; and (d) the importance of the tensile strength.

Polymer-concrete alone and in combination with prestressing or fibre reinforcement techniques offer many of the desirable properties. Offshore power, offshore waste disposal, floating industrial plants and ocean terminal energy plants are under detailed feasibility studies (12).

3.2. PC Applications for high voltage electrical insulation

A recent research programme sponsored by the Electric Power Research Institute shows that specially formulated and vacuum processed polymer-concrete PC is a high quality dielectric material which possesses significant overall cost and design advantages over electrical porcelain. Its ability to be reinforced with glass or organic fibres and the possibility of encapsulating metal will facilitate the manufacture of vastly superior insulators specially for futuristic siliceous aggregate mix and organic materials mix (poly-



ester resin and styrene monomer). The energy consumed in the processing of Polysil is one half the energy consumed in processing porcelain for the high voltage electric insulation. Detailed industrial testing of the mechanical, physical and electrical properties of heavy cap and pin disc-type insulators have recently been concluded in the Fritz Engineering Laboratory at Lehigh University. Polysil has excellent dielectric and mechanical properties. Coupled with maximum design flexibility, low cost and simple technology, it promises to be an effective insulating material for the electric power industry. The feasibility of PC application as a material of construction in geothermal processes has been demonstrated, tested and the economics studied by the Brookhaven National Laboratory in the US (12). A high temperature PC system has also been formulated and field tests performed using styrene-acrylonitrile-amid mixture to produce a combination of high strength, thermal and chemical stability, resistance to brine, flashing brine and to steam at temperatures up to 240°C. Potential applications include the use of PC-lined composite as replacements for stainless steel and other expensive metals in brine supply and condensate piping system, re-injection lines, and steam separators. Uses in cooling towers, power transmission towers, to protect concrete surface is very promising. Economic impact of the use of PC in geothermal electric generating process determine the possibility of reducing the cost of power by ca. 10%. In this work, conceptual design for a 50 MWe power plants at Heber and Niland, California, were reviewed to determine the saving in capital and operating costs resulting from the use of PC in the applicable areas of the plants. Similar applications of PC have been reported for geothermal processes at the Geysers, Klamath Falls, Raft River and Baca Wells.

Polymer impregnation procedures have been applied to improve the durability of bridge decks and roads. Bridge decks impregnation has been successfully accomplished in many parts of the USA (Charleston, West Virginia, Washington, Big Spring, Lubbock, Texas). Essentially the same MMA monomer system was used for all bridges but the heat for drying and polymerization was supplied by several sources. The detailed recommendations for bridge deck impregnation were formulated. The low bids for the bridge deck impregnation ranged from U.S. \$ 12 to \$ 31/m² in 1979 (12). Protective PC overlays have been applied for the repair and maintenance of the concrete spillway floor (like Shadow Mountain Dam). Concrete structures such as dams, culverts and bridges that are subjected to high velocity water flows often experience severe damage due to cavitation and erosion. Polymer concrete PC & PIC have demonstrated an unusual resistance to such damage. PIC has been used at Libby and Dworshak dams to repair such damage under adverse conditions, with normal construction crews and in heavy construction environments (12).

3.3. PC Applications for Hydrotechnical Constructions

Polymer concrete has been successfully applied for Hydrotechnical Constructions in USSR, based mostly upon furan and advanced furan resins. Protective facings of water intakes in land reclamation systems are subject to considerable damage. Constructions of large irrigation systems, water intakes and spillways are exposed to damage. Overhaul work done using polymer concrete were conducted in the Ingulets and Kakhovka irrigation system (Ukrainian USSR) over a total area of 45'000 m², and in one of the dams near the town of Ogre (Latvian USSR). It has been found efficient compounds for carrying out under water repair, working at negative temperatures and injecting under a pressure exceeding 150 atm into the zones of cracks formed in bulky

concrete structures. Technical-economic analysis promises the bright prospects of utilization of polymer concrete and solutions in hydrotechnical construction. The cost of one m² of protective wear-resistance facing made of rufan polymer is 2 - 2,5 times cheaper than that of facings produced from steel, cast iron, or natural stone materials. Accomplished investigations in the Polymer Institute (NIIZB) show that ferro-polymer concrete is not only advisable but allows for obtaining a high economy with a complex use of strength characteristic, high chemical stability and electroinsulating properties. The most rational fields of ferropolymer concrete application are the bearing structures, chemically stable to the presence of different corrosive media, for industrial construction (12).

3.4. Other Applications

Investigators in Norway, Denmark, Germany, France, Poland, Spain, Belgium are known to be exploring PIC applications. In Italy a high pressure steam cured concrete using underwater polymer curing is being used. Construction of ship plate, sewer pipe and building facing are being explored. Rehabilitation of Highways with polymer concrete overlay in West Germany is regulated by official "Instructional Manual for the Maintenance and Rehabilitation of Concrete Roadways". Federal Highway Administrations in some countries recommended that International standard test methods and application procedures of polymer concretes should be adopted.

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