



LES POLYMERES DANS LE BETON

S.E BOUDRAA; M.BENHOUNA
BP 1523 Oran Mnaouar Oran Algérie

Synopsis

L'intérêt croissant pour l'amélioration de la résistance, dureté, ductilité et durabilité du béton à base de ciment Portland ou carrément son remplacement par un matériau présentant de meilleures caractéristiques à un coût moindre a initié plusieurs approches, l'une d'elle est l'amélioration du béton lui même, une autre, qui constitue le sujet de notre article est la combinaison du béton avec des polymères.

Abstract

As we have become more and more concerned with the conservation of energy and materials, interest has grown in improving the strength, toughness, ductility, and durability of Portland cement concrete or in finding replacements that exhibit a superior cost property balance. Thus one approach has been to improve the properties of concrete itself; another, which is our subject, is to combine the two technologies of concrete and high polymers.

Some polymers concrete materials have already been in use for many years, some are undergoing their first application, and some are awaiting acceptance by a justifiably conservative technological world. After about fifteen years of research and development, enthusiasm for fascinating new combinations of properties has been tempered with a healthy scepticism about whether polymers-concrete materials really have a place in engineering applications. Fortunately, even under the cold and impartial eyes of cost-effectiveness, there are indeed applications, which appear suitable for the unique properties of such materials.

There are three basic types of concrete polymers materials (1,2,3).

1-POLYMER IMPREGNATED CONCRETE or P.I.C.

This is a hydrated Portland cement, which has been impregnated with a monomer and is subsequently polymerised in situ ⁽⁴⁾. It is produced by drying the precast Portland cement concrete to remove moisture, full or partial saturation with monomers, and in-situ polymerisation. The precast Portland cement concrete used to produce P.I.C. can be made from practically all types of aggregate, cement and admixture that are used in current concrete practice. Any method of

curing the concrete may be used although high pressure steam cured concrete usually produces highest strength P.I.C. Dense concrete requires less monomers than lower quality, more porous concretes or concrete made with lightweight aggregate.

1-1 Monomers

Many monomers have been used to produce P.I.C., although vinyl monomers, eg methyl methacrylate, styrene and acrylonitrile, have been the most widely investigated. Methyl methacrylate (MMA) has been the most widely used monomer because of its low viscosity (less than 1 CP), relatively low cost, and good mechanical properties.

1-2 Impregnation processes

There are two impregnated processes:

Full impregnation of concrete specimen: it is usually feasible only in laboratory or plant facilities since the entire specimen must be dried and fully saturated with monomers. Drying temperatures must be in excess of 100°C, and 150°C are near optimum. Temperatures in excess of 150°C may result in decreased strengths. Drying should be uniform and the drying time will be dependent on the thickness of the concrete. Large specimen may require careful heating and cooling techniques to prevent cracking. Monomer saturation may begin when the concrete is cooled to a temperature that will not cause premature polymerisation, usually about 38°C or less for MMA. Evacuation of air in the concrete by use of a vacuum chamber, immersion in monomer, and application of a modest overpressure (70 kPa) reduce the time required for complete saturation. Without evacuation, overpressures approximately ten times higher must be applied to achieve saturation in about one hour.

Partial depth impregnation: Extensive research has been conducted to develop

processes for impregnating conventional Portland cement concrete to depths of 10-40 mm^(5 to 14). Partial depth impregnation (sometimes called surface impregnation) is desirable when durability rather than strength is of primary concern. It can be performed under many field conditions whereas full depth impregnation may not be feasible because of the difficulty of obtaining full depth drying, evacuation, and applying pressure. It should be noted that partial depth impregnation will not result in polymer loading within the pores as high as obtained when the full impregnation process is used, and the mechanical properties of the impregnated zone will not be as high.

1-3 Properties

The strength and durability properties of P.I.C., particularly PIC produced by the full impregnation process, are generally much greater than for the unimpregnated concrete. It should be noted that the values shown in the table are primarily for fully impregnated P.I.C. made with MMA. The strength stress relationship for P.I.C. produced with MMA has been shown to be very linear, with practically no ductility. The additions of monomer with lower glass transition temperatures (T_g) result in much more ductile behaviour.

1-4 Applications

Bridges throughout the United States have been surface impregnated, and on several the contractors were selected by competitive bidding for a price of 31\$/m² or less. Costs have widely varied as a result of differences in bridge size, working conditions, location and process. References^(10,12,15) describe the impregnation of several bridges.

Impregnated techniques were developed for the walls of a dam outlet, which were repaired after being seriously damaged by cavitation and erosion^(19,20).

The use of polymer impregnation to restore the structural integrity of a building has also been demonstrated⁽¹⁷⁾.

Current applications of fully impregnated P.I.C. are very limited, Although many applications have been proposed. Precast

P.I.C. bridge decking have been investigated in the USA⁽¹⁸⁾.

P.I.C. reinforced beams have been tested to determine their potential as a replacement for wood supports in mines⁽¹⁹⁾.

The use of P.I.C. for concrete sea structures has been studied. Concrete ships, off shore structures, underwater oil storage vessels, and ocean thermal-energy plants were included in the study⁽²⁰⁾. Spherical model hulls have been tested, and a cost comparison indicated that P.I.C. was competitive with regular concrete and steel⁽²¹⁾.

1-5 Conclusion

When polymer impregnated concrete was introduced, it was believed that the very high compressive strengths that could readily be achieved (100-120 N/mm²)⁽²²⁾ would be of a value to the designer. However, the costs of both the polymers and of the impregnation and polymerisation have precluded their use, except in a few special cases. Moreover, the effectiveness of the method in raising the strength depended on the initial quality of the concrete. If it was a high strength concrete, the porosity is already low, and a prospect for a significant increase in strength resulting from impregnation are poor. With low strength concrete, the porosity will be high so that large quantities of the polymer will be required to fill the pores and thus impart the high strength. This will be uneconomic, a better concrete mix using Portland cement with, perhaps, a water reducer giving better value for money. Occasionally for repairs, or for use in chemically aggressive environment, polymer impregnated concrete can provide the best solution.

Partial impregnation of concrete members might prove to be an economical solution, only using polymers in areas in which they can be of particular use. Dikeou⁽²³⁾ reports that polymer impregnation increases the shear capacity of concrete beams without shear reinforcement by about 60% and anchorage stresses are increased. Hence impregnation at the ends of precast floor units, for example, could improve their load capacity.

2-POLYMER PORTLAND CEMENT CONCRETE or PPCC

PPCC has been of considerable interest to researchers and users because of the similarity to current concrete technology. However PPCC has not received as much attention as PIC or PC since most of the successful polymer that have been identified for PPCC have been proprietary.

2.1 monomers and polymers

Most monomers used successfully with PIC and PC have not worked well when added to the fresh concrete. Most of these organic monomers, including MMA are practically insoluble in water, generally interfere with the hydration of cement, and are subject to slow alkaline degradation. Strength is often found to be reduced in the hardened concrete. Acrylonitrile and styrene are exceptions in that they appear to be alkaline resistant and provide improvement in properties compared to unmodified controls. ⁽²⁴⁾

Polymer latexes which are very small (0,05-1 μm diameter) spherical particles held in suspension, have been used very successfully in PPCC, usually referred to as latex modified concrete. Polymer latexes are usually copolymer systems of two or more monomers including vinyl acetate, styrene, vinyl chloride and butadiene. Reference ⁽²⁴⁾ summarises the properties of some of the polymer latexes. LMC is the most widely used PPCC in the United States.

Thermosetting resins have been used to produce PPCC. A polyester formulation has been used in the United Kingdom to produce 'Estercrete'. ⁽²⁵⁾

Epoxies have been developed which can be added to fresh concrete and will produce improvements in the properties of the hardened concrete. ^(26,27,28,29)

2-2 Process technology

The process by which LMC is used is very similar to that of portland cement concrete. The latex is added to the cement portland concrete. Normally, LMC uses a cement rich design. ⁽²⁶⁾ Air entraining agents are not used because polymer latexes entrain large amount of air. Since the latexes act as water

reducing agents. The water content of the mix is reduced by an amount equal to the polymer volume or water in the polymer. LMC is prepared and placed in the way that conventional concrete is placed. Excessive vibrations should be avoided to prevent excess water from collecting on the surface. Curing for LMC is much shorter than for portland cement concrete. LMC is usually moist cured for no more than three days after which it is air cured. Steam heat is not recommended.

2-3 Properties

There are several reference in the literature which review the properties of PPCC ^(24 to 32). Polymer latexes alter the properties of the fresh and hardened concrete. In fresh concrete, the latexes will usually increase workability and allow reductions in water cement. They will often delay the setting time. Anti-foaming agents are often added to control the excessive amounts of air that are entrained by the latexes. LMC generally has improved durability due to reduced porosity because of the lower water cement ratio and the partial filling of pores with polymer. The polymer also tends to seal existing pores and micro-cracks, resulting in reduced water permeability. The frost resistance of LMC is generally excellent. The chemical resistance depends upon the types and amount of polymer used. Abrasion and impact resistance are increased. LMC exhibits excellent adhesive properties which makes it attractive for repairing and overlaying concrete. ⁽²²⁾ Properties of LMC are described in ^(31 and 32). Several investigations have reported on the properties of epoxy modified concrete EMC ^(28,33,34,35).

LMC has been developed and used for many years for patching and overlaying deteriorated bridge decks ⁽³⁴⁾. The excellent bond strength, freeze thaw resistance to penetration of chlorides, and its ease of application have made it a widely used material ⁽³²⁾. Latex modified mortar has also been used to producing prefabricated bricks panels, which have sufficient strength for handling. Panels as large as 3x4,6 m have been prefabricated. ⁽³²⁾

Epoxy modified concrete has been developed for the deep patching and

resurfacing of bridge decks and the resurfacing of food packing plant floor. It is also recommended for industrial floors, sewer pipes and piling. A repair, which required 35 m² of epoxy modified concrete, of an 8,5 × 85 m bridge deck is described in reference ⁽²⁸⁾.

2-4 Conclusion

Development of polymer cement concrete has extended to commercial markets for a number of years, it has also been widely studied around the world. Among the countries who have commercially produced PCC are the USA, JAPAN and the USSR. The ease of adapting the existing concrete production equipment to the manufacture of PCC, and the relatively low cost of simply adding one more ingredient to an otherwise conventional concrete mix, enhances the potential attractiveness of PCC. However, properties of PCC are generally only moderately improved. The main benefits derived from these materials are good bonding properties with portland cement concretes, good durability, and a high degree of abrasion resistance. Where strength improvement has been obtained, the magnitude of improvement has been relatively minor.

3-POLYMER CONCRETE or PC

Polymer concrete or PC is an aggregate bound with a polymer binder. These materials can be cast and formed in the field. It is called a concrete because of the general definition concrete consists of any aggregate bound with a binder. ⁽³⁷⁾

A wide range of aggregates and monomers may be used, although the cost and properties of the PC may be strongly influenced by the gradation and monomers. A well graded aggregate may require as little as 5 to 8% monomer by weight, while more than 15% may be required for gap graded aggregate.

3-1 Monomer systems

PC, a thermoplastic, or more commonly a cross linked polymer, is used to replace Portland cement as a binder in a concrete mix. Since the polymer constitutes the continuous phase, the polymer, whose

properties are, of course, very dependent on time and temperature ⁽³⁸⁾ will clearly determine behaviour of the composite.

A wide variety of monomers, prepolymers and aggregate have been used. While epoxy resins are commonly used in PC, much attention has been focused on the use of cheaper vinyl monomers such as polyester-styrene, MMA, furane derivatives and styrene. Usually in conjunction with a cross-linking agent ⁽³⁹⁾.

MMA has received the attention of most of the work in PC development in the USA in the last several years, especially for the repair of concrete. Benzoyl peroxide (BzP) is perhaps the most commonly used initiator, and dimethylparato-luidine (DMTP) and dimethyl aniline (DMA) are widely used promoters with user formulated MMA systems. THPTHA, a multifunctional monomer, is used in some user-formulated systems to increase the rate of polymerisation ^(40,41). Polyester styrene and vinyl ester systems generally use cobalt naphthenate and/or DMA as the promoters and methyl ethyl ketone (MEK) peroxide as the initiator. ^(24,41,42)

There are several commercially available polymer concrete systems that use MMA as the basic monomer. One system consists of two components, a liquid monomer and a package of premixed fine aggregate, polymers, initiator and pigment ⁽⁴³⁾ – and was originally developed in Europe; other similar systems are now available in many countries.

Other commercially available systems include polyester and furan resins. One furan system requires that the initiator first be mixed with the aggregate and then the resin be added.

Most of the monomer systems are formulated to provide a work time of 15-60 minutes. The peak exotherm, which is typically 20-50°C greater than ambient temperature, is usually reached 45-90 minutes after the PC is placed. For highway repairs, traffic can usually be restored in one hour and a half to two hours after the PC is placed.

Aggregate should be sound and free of dirt, asphalt and other organic materials. The aggregate should be dry, preferably with a

moisture content of 0,5% or less to insure adequate bond to the polymer. The aggregate gradation varies according to the application, but generally the gradation should provide a relatively low void volume and have sufficient fines to provide workability^(40,44)

3-2 Properties

The mechanical properties of PC are strongly influenced by the viscoelastic behaviour of the polymer and, to some extent, the properties of the aggregate. The response of most polymers used in PC is a function of time, temperature, and the molecular structure. Creep is much more pronounced in PC than in PIC, especially at elevated temperatures. Shrinkage can vary widely depending upon the polymer type and polymer bonding. PC is usually more ductile than Portland cement concrete, except when it is cast at low temperature. The properties can be expected to have a greater range than those for PIC or PPCC since PC, even when made with the same monomer, can be produced from many types and gradation of aggregate under a wide range of environmental and working conditions. It should be noted that shrinkage strain varies from polymer to polymer (higher for polyester, lower for epoxies), and must be considered in any applications; such strains may if not relieved by creep, result in premature failure in a rigid PC.

3-3 Applications

PC has been used very successfully as a repair material for Portland cement concrete, especially for bridge decks.^(40,44,45) The rapid curing, excellent mechanical and durability properties, and excellent bond to Portland cement have made PC, a very desirable patching material for bridges, pavements and other concrete structures^(46,47,48,49)

PC has also been used as overlays to provide:

A highly impermeable membrane to prevent intrusion of water and chlorides.

A surface material to repair spalled and deteriorated concrete surfaces.

Skid resistance

The advantages of PC overlays are their good bond to Portland cement concrete, their relatively shallow depth, and their fast cure time.

PC for use in high temperatures geothermal environments has been developed. One monomer system containing styrene, acrylonitrile, acrylamide and divinyl benzene used with an aggregate consisting of a silica sand and Portland cement produces a compressive stress of 159 to 207 MPa at 20 °C and is thermally stable to about 240 °C. Field tests have been successful.⁽⁵⁰⁾ The use of siloxanes in conjunction with silica flour and Portland cement to produce PC for the completion of geothermal wells has been shown. Tests indicate that compressive strength (72 MPa) over a temperature range of 25-350 °C with little weight loss of polymer.⁽⁵¹⁾

Manholes of polyester PC have been mass produced in Japan. Over 40 000 of the large manholes have been produced.⁽⁵²⁾

A plant in West Germany has been manufacturing wall panels, cable channels, facades, drains and curbstones. The PC is made with MMA.⁽⁵³⁾

3-4 Safety considerations

The chemicals and techniques used in production of concrete polymer materials require careful considerations to handling. The chemicals create the most obvious safety hazards. And a thorough discussion of safety has been published with addresses, chemicals and construction practice.⁽⁵⁴⁾ Manufacturers of chemicals are good sources of safety and handling literature.

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