

POLYMER-MODIFIED CONCRETE: REVIEW

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ABSTRACT: Composites of concrete and polymers of various kinds are used in many applications. This paper briefly reviews the history of polymers in combination with cement as a building material, where the polymer is not in the form of fiber or mesh reinforcing, but in the form of a polymerized matrix comingled with the hydrated cement paste. The microstructure and properties of the composite polymer-modified concrete are described, and some current and possible future applications are mentioned. Several recently published articles and technical papers dealing with polymer-modified concrete are critically reviewed.

INTRODUCTION

Concrete has high compressive strength but is relatively weak in tension and adhesion, and its porosity can lead to physical and chemical deterioration. Polymers, on the other hand, are weaker in compression but can have higher tensile capacities, and provide good adhesion to other materials as well as resistance to physical (i.e., abrasion, erosion, impact) and chemical attack. Combinations of these two materials can exploit the useful properties of both and yield composites with excellent strength and durability properties.

In addition to polymer fibers and meshes, polymers are used in combination with concrete in several ways. Polymer-impregnated concrete (PIC) is produced by infusing a monomer into the cracks and voids of already hardened concrete. The monomers are polymerized after they enter the voids by the action of a chemical hardener or the application of heat. Since the polymer ideally fills the voids and binds with the cement matrix and the aggregates, there is no need to have high-quality concrete for PIC. Impregnation depth is limited by the porosity of the concrete, the viscosity and volatility of the monomer and hardener, the setup time of the polymer, and the pressure applied. PIC strength is dependant on the type and amount of polymer used, and the degree of polymerization achieved. Applications of PIC are typically limited to precast thin panels and to the repair of highway surfaces due to the limit on impregnation depth and the difficulties in applying the material on anything but the top of a horizontal surface.

Polymer concrete (PC) is a material made of aggregate and a polymer binder. There is no portland cement in polymer concrete. The polymer matrix binds very well to the aggregate particles with no transition zone, unlike portland cement concrete. Since polymer materials are more expensive than portland cement, and can generate heat and undergo shrinkage during curing, PC is made with evenly graded aggregates to achieve close packing, minimizing the space between the aggregates to be filled with polymer. Uses for PC include cast-in-place PC connections for precast concrete construction, precast PC elements, and overlays for concrete repairs. A possible problem with some PC is its sensitivity to high temperature and to cyclical temperature changes (O'Connor and Saiidi 1993). An interesting type of PC (Rebeiz et al. 1994) involves the use of recycled polyethylene terephthalate (PET). Plastics represent a large portion of the garbage stream, and significant environmental benefits can be realized if good-quality construction materials can be made from some plastics.

Polymer-modified concrete (PMC), or polymer portland ce-

ment concrete (PPCC or PCC), is normal portland cement concrete with a polymer admixture. The polymer and the cement hydration products comingled and create two interpenetrating matrices, which work together, resulting in an improvement in the material properties of PCC alone. PMC is the term for such concrete with lower dosages of polymers, typically 5% or less, and PPCC or PCC generally is the term for composites with more than 5% polymer by weight of concrete (Chandra and Ohama 1994). The subject of this paper is PMC and PPCC. I will use the term PMC for all polymer-portland cement composites.

HISTORY OF POLYMERS IN CONCRETE

Polymers have been used in construction as long ago as the fourth millennium B.C., when the clay brick walls of Babylon were built using the natural polymer asphalt in the mortar. The temple of Ur-Nina (King of Lagash), in the city of Kish, had masonry foundations built with mortar made from 25 to 35% bitumen (a natural polymer), loam, and chopped straw or reeds. The walls of Jericho were built using bituminous earth in about 2500–2100 B.C. Other historic applications of bituminous mortars in construction have been identified in the ancient Indus Valley cities of Mohenjo-Daro and Harappa around 3000 B.C., and near the Tigris River in 1300 B.C. Many natural polymers have been used in ancient mortar, including albumen, blood, rice paste, and others (Chandra and Ohama 1994).

The earliest indication of the use of polymers in PCC was apparently in 1909, in the United States, when a patent for such use was granted to L. H. Backland; and in 1922, in France, when a patent was granted to M. E. Varegyas. In Britain, polymers in concrete advanced in 1923 with L. Cresson's patent for rubber-modified road surfacing material; in 1924 with V. Lefebure's development of natural rubber latex cement; and in 1925 by S. H. Kirkpatrick's innovation on that product (Ohama 1978; Chandra and Ohama 1994).

Synthetic polymers were invented in the 1940s in response to the wartime decline in the availability of natural rubber and the increased demand of the war effort. Incorporation of synthetic polymers in portland cement mortars and concrete started in the 1950s (Dikeou 1978; Chandra and Ohama 1994).

POLYMER-MODIFIED CONCRETE

Polymers are materials with long chain molecules made up of many individual monomers connected end to end. Polymers made up of one type of monomer are called homopolymers, and those made up of more than one monomer type are called copolymers. Polymers are classified as elastomers, thermosetting, or thermoplastics, each characterized by the type and relative amount of crosslinking of the polymer chains. Polymers most often used in PMC are the thermosetting and thermoplastic type (Su 1995). The effectiveness and density of the crosslinking influences the physical characteristics of the polymer. Elastomers have weaker crosslinking of the molec-

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ular chains, thermosetting polymers have strong crosslinking, and thermoplastics have crosslinking that is less effective than thermosets and more effective than elastomers. The physical characteristics of the polymers used in PMC affect the properties of the hardened PMC (Popovics 1993; Manling et al. 1994).

A characteristic physical property of the polymers used in PMC is their glass transition temperature range (T_g). At temperatures above T_g , the material acts more rubbery, undergoing plastic deformation when loaded. Below T_g , the material behaves more in a glassy manner, deforming elastically and being susceptible to brittle failure (Su 1995). Thermosetting polymers have relatively high T_g values, elastomers have low T_g values, and thermoplastics have intermediate T_g values. The significance of the polymer's T_g in PMC is the influence of the polymer's plastic or elastic behavior on the properties of the composite.

Another characteristic of a polymer is its minimum film temperature (MFT). This is the temperature below which polymerization will not form a continuous film, but instead forms discrete particles. It is desirable for polymers used in PMC to have MFT values lower than the temperatures to which the material is exposed during curing (Su 1995).

The atomic composition of the monomers, and of the polymer side chains, affect the amount and type of crosslinking and the chemical properties of the polymer, and influence the properties of the fresh PMC. Polymerization can occur with little energy input or only in the presence of a chemical catalyst, depending on the chemical nature of the monomers. Polymers can be ionic or nonionic, depending on the atomic charge of the side chains. Ionic polymers tend to orient themselves around other particles, such as cement grains, in the same manner as water-reducing admixtures. They act as surfactants and tend to disperse the clinker grains, reducing water demand and facilitating hydration.

Polymers are incorporated into PMC in several forms: as a latex, or suspension of monomers or polymers in water; as a redispersible powder; or as a resin, which is a monomer or polymer in liquid form. Polymerization of the monomers can take place prior to combination with portland cement mortar or concrete, or can be initiated after mixing (Popovics 1985). Polymerization can take place by combination with a hardener or activator, by thermal catalysis, or by drying.

When polymers are incorporated in PMC as latex, the composite is referred to as latex-modified concrete (LMC). LMC is the most common type of PMC because latex is relatively simple to incorporate in mortar or concrete. It is added with the other ingredients during the mixing of fresh concrete. The water portion of the latex must be considered in the overall mix design of the concrete.

Elastomeric polymers used in LMC include bitumen, natural rubber, and styrene-butadiene (SB). Thermoplastics used in LMC include vinyl acetate-ethylene (VAE), polyacrylic ester (PAE), styrene-acrylic (SA), and others. Polyvinylidene chloride (PVDC) was used during the popularization of LMC in the early 1970s, but the chlorine resulted in corrosion of reinforcing steel and the use of PVDC was discontinued. Polyvinyl acetates (PVAC) hydrolyze in moist environments, so their use in LMC is limited (Ramakrishnan 1994).

Polymers can be incorporated in LMC as a powder. They are referred to as redispersible powders since they are manufactured by spray-drying polymer latexes, and must be returned to the latex form in order to disperse within the cement paste and to coalesce into a film (Ohama 1985). An advantage of redispersible powders is that they are easier to store and handle than latexes, and can be supplied in cheaper packaging. Most importantly, they can be prepackaged with cement and sold as a one-part product that needs only water (Walters 1992).

Monomers and polymers that are in a liquid state under normal temperature and pressure conditions are called resins. (Latexes are suspensions in the water of solid monomers or polymers.) Polymerization of resins can require chemical hardeners or catalysts. Resins used in PMC are combined with their catalysts either prior to mixing with fresh concrete or added to the mix along with their catalysts in order to combine in the fresh concrete (Popovics 1993).

Resins that are used in PMC include epoxies, polyester-styrene copolymer, methyl methacrylate (MMA), urethane, furan, phenolics, and others (Fowler 1994).

The thermosetting polymers called epoxies are widely used in PMC. The word "epoxy" is derived from "epi," the Greek word for "on the outside of," and "oxygen," which describes part of the molecular structure of the polymers (Popovics 1993). Epoxy-modified concrete or mortar (EMC) is typically made by adding an epoxy resin and a hardener separately into the concrete mix (Walters et al. 1994). EMCs often incorporate additives with the hardener or catalyst that control the rate at which crosslinking of the polymerizing chains proceeds, and hence control the rate of hardening (Su 1995). EMC has some advantage over LMC because of its relative insensitivity to water (McClain 1978).

Several researchers have noticed that epoxies will polymerize in freshly mixed portland cement paste and harden without the addition of a separate catalyst (Jo et al. 1994). Alkali solutions of hydration products such as $\text{Ca}(\text{OH})_2$ (CH) catalyze the polymerization of the resin. This process can result in a high-quality cement-epoxy composite and can simplify the manufacture of EMC.

MICROSTRUCTURE

Polymers differ in their microstructure and interaction with cement microstructure depending on the type of polymer, method of polymerization, delivery system, and curing conditions. A general description of the microstructure development of latex-modified concrete is instructive and can be a basis for understanding the microstructure of other types of PMC as well (Ohama 1987, 1995; Chandra and Ohama 1994; Su 1995).

When first mixed with fresh concrete, the polymer particles suspended in the latex are (ideally) dispersed throughout the cement paste. Cement hydration starts, saturating the solution with CH, and generating ettringite and large CH crystals in the zone adjacent to aggregates and probably a calcium silicate layer on the aggregates. Polymer particles deposit on the gel products and on the unhydrated clinker particles.

With the consumption of water by the hydration process, and the growth of hydration products, the polymer particles gradually concentrate in the capillary pores, forming a close-packed layer on the gel product surfaces, on the unhydrated cement grains, and on the developing silicate layer over the aggregates. The accumulating polymer particles eventually fill many of the capillary pores and coat the inner surfaces of those they don't completely fill.

When water is further withdrawn by hydration or drying, the close-packed polymer particles on the gel products and in the voids coalesce into continuous films or membranes, forming a comatrix intermingled with the hydrated cement paste, and binding the hydrates to each other and to the aggregates.

Some polymers participate in chemical reactions with the cement hydration products to the detriment of the composite (Shanyuan and Gongshan 1994). Coupling agents can be added to the polymer products to prevent chemical deterioration of the cement gel products.

PROPERTIES

Polymer modification affects the workability of fresh PMC. The dispersed polymer particles act as "ball bearings" to ease

the relative movement of cement and hydration particles. Also, the polymers themselves, or the surfactants added in the latexes to reduce segregation of the suspension, act like water-reducing admixtures and significantly increase slump and reduce water demand (Chandra and Ohama 1994; Ramakrishnan 1994; Su 1995).

The surfactants, emulsifiers, and stabilizers added to polymer latexes act to entrain a lot of air in fresh LMC. Some amount of air entrainment improves the consistency of the fresh mix and the freeze-thaw resistance of the hardened concrete. Too much air entrainment can excessively weaken the concrete, though. Therefore, antifoaming or air-reducing compounds are often added to PMC in order to limit air entrainment to a maximum of 6.5% (Chandra and Ohama 1994; Ramakrishnan 1994; Su 1995).

Due to the improved particle packing, air entrainment, and enhanced cement particle dispersion of PMC, there is less bleeding and segregation, and a more homogeneous microstructure. This contributes to higher strength and lower permeability of the concrete (Chandra and Ohama 1994; Ramakrishnan 1994; Su 1995).

Hydration is somewhat slowed by polymer modification because of the dispersing effect of the polymers and because of the absorption of surfactants on the developing cement matrix (Ramakrishnan 1994). The water-retention properties of fresh LMC, due to the hydrophobic and colloidal properties of the latexes, reduce the need for long wet-curing of LMC (Chandra and Ohama 1994; Ramakrishnan 1994; Su 1995).

The transition zone in PMC is refined due to the coating of the developing hydration products with the polymer, which affects ettringite and large CH crystal growth, and also due to the coalescing of the polymer film in the transition zone voids (Chandra and Ohama 1994; Su 1995).

Compression, tension, and flexural strength are improved by polymer modification. Much of the increase in compressive strength can be attributed to the lower water requirements of PMC. In fact, PMC has been shown to have lower compressive strength than unmodified concrete when both are prepared with the same water-cementitious material ratio (w/c) (Ramakrishnan 1994; Su 1995).

Tensile and flexural strength increase because of the refinement of the transition zone, improving the bond between the aggregate and the matrix and reducing the presence of microcracks. The polymer matrix, comingled with the hydrated cement paste (HCP), bridges microcracks as they initiate under stress and inhibits their propagation. The homogeneity of HCP, enhanced by the improvements in workability and dispersion, is also a cause of improved tensile and flexural capacity (Su 1995).

Properties of hardened PMC are dependant on temperature and humidity. The polymers soften and weaken in elevated temperatures and moisture contents to varying degrees depending on their type and makeup (Popovics 1987; Chandra and Ohama 1994; Ramakrishnan 1994).

Fire resistance of PMCs can also be problematic. Apart from the decreasing strength with increasing temperature, PMC with high polymer content is slightly combustible (Chandra and Ohama 1994).

The resistance of PMC to the effects of freeze-thaw, temperature and humidity cycling, and chemical penetration are all generally better than concrete without polymer modification, apparently due to the presence of the polymer film, and the lower w/c achievable using polymer modification (Ohama 1987). An exception to this general observation was seen in experiments with EMC, where samples produced with w/c of 26% exhibited more susceptibility to chloride penetration than unmodified samples of the same w/c (Marusin 1987). Marusin observed that the pores of her EMC samples were misshapen,

but did not offer an explanation of the lower performance of EMC.

Adhesion of PMC to substrates is much better than that of normal concrete, because of the bonding of the polymers with the base material (Ramakrishnan 1994; Su 1995).

The modulus of elasticity (E) of PMC is typically lower than unmodified concrete since polymers have lower E values than HCP. Properly cured PMC undergoes less drying shrinkage than unmodified concrete probably because of its higher water-retention ability. In combination with the increase in tensile strength of PMC, this characteristic results in improved extensibility, which reduces drying shrinkage cracking.

Different polymers and percentages of polymer by weight, curing and setting differences, exposure conditions, and other variables significantly influence the mechanical properties of PMC (Walters 1990; Gierloff and Schimmelwitz 1987; Popovics 1987).

APPLICATIONS

Current applications of PMC are primarily as overlays on roadways and bridges, both as new construction and as repairs of existing deteriorated structures (Darwin 1984b). PMC is also being used in flooring, water tanks, swimming pools, septic tanks, silos, drains, pipes, and ship decks (Ohama 1978; Su 1995).

Two very promising, relatively new applications of PMC are its use in combination with fiber reinforcing (Gerwick 1978; Soroushian et al. 1993; Chen and Chung 1996; Zayat and Bayasi 1996), and its use as a pneumatically applied material or shotcrete (Schorn 1985).

Possible future applications of PMC mentioned in the literature include: in roller-compacted concrete (RCC) for air-strips, roadways, and parking lots; and in ductile concrete foundation and shear wall construction, as well as marine and offshore structures (Gerwick 1978; Ohama 1978; Ramakrishnan 1994). PMC use has also been predicted in concrete structures wherever there is a need for its tensile strength, resistance to cracking, and impermeability (Darwin 1984a).

EXAMPLES FROM THE LITERATURE

Review Paper 1

Kuhlmann (1991): In 1990, after 20 years in service, the purported largest garage building, a six-level structure at O'Hare Airport in Chicago, received a new PMC overlay on its roof deck. The original construction was of lightweight, cast-in-place, posttensioned concrete with no protective overlay. Since it opened in 1970, many areas of the deck surface were damaged by deicing salts and the action of snow removal equipment. Over the years, portions of the roof deck had been patched with overlays of various types, and monitored. The subject article describes the complete resurfacing of the 50,000 m² roof deck with a styrene-butadiene (S-B) LMC. The requirement to interfere as little as possible with the operation of the parking garage resulted in the overlay work being done in stages and only during the midweek periods of lower parking demand. It also required that portions of deck surface, where work took place, be returned to service quickly.

The paper by Kuhlmann states the LMC overlay was allowed to wet-cure under wet burlap and polyethylene film (another application of the use of polymers with concrete!) for 24 hours, then allowed to air-cure for 72 hours. The design intent of the overlay was to require no extensive repairs for another 20 years.

In a sidebar, Kuhlmann (1991) describes the benefits of LMC in combination with air entrainment. He states, "Because normal air-entrained concrete is relatively porous, mois-

ture, oxygen, and chlorides from deicing salts can migrate through the surface and reach the reinforcing steel, causing corrosion and subsequent spalling." This statement may not be correct. The porosity of concrete due to air-entraining agents (AEA) does not lead to penetration of corrosive elements because AEA pores are extremely small and are not well interconnected.

Kuhlman goes on, "This porosity is caused by the micro-cracks and micropores generated during the hardening of the cement matrix." This is correct, and it is the reason to maintain low w/c, low cement content, and to allow for proper curing. Neither the paper nor the sidebar states that the LMC included an air-entraining agent, although the paper mentions the intent of the mix design was to "provide precise control of . . . air content . . . and other parameters required for LMC." This assumedly refers to the propensity of PMC to entrain large amounts of air, which generally results in manufacturers including an antifoaming compound in their polymer admixtures. The effort with PMC is to reduce air entrainment, not enhance it. The earlier statement may be thought to imply the LMC was added to counteract porosity problems arising from air entrainment.

The sidebar concludes: "In addition to improved chemical resistance, LMC's have improved workability at low water-cement ratios. This reduction in water, while maintaining adequate workability for placement requirement, also contributes to improved strength and durability characteristics. This is an important feature for the contractor and owner and can affect the final installed cost in an advantageous way."

The context of the statement might imply that decreased water demand is the reason to employ PMC, when, in fact, other water-reducing measures may be less expensive.

Review Paper 2

The Soroushian et al. (1993) technical paper is a report of research into the use of a polymer latex in glass-fiber-reinforced concrete (GFRC). The effect of the varying amounts of polymer on flexural strength, crack size and spacing, elastic limit, and modulus of rupture was examined under different aging conditions. The impetus for the research is the observed deterioration of glass fibers in GFRC. Chemical deterioration is due to the alkali-silica reaction, which occurs even in alkali-resistant glass in moist cement environments given enough time. The reaction results in loss of fiber cross-sectional area and tensile strength. Physical deterioration is apparently caused by the moisture-induced growth of the cement hydration product CH in the spaces around glass-fiber filaments. The CH binds well with the fibers and locally increases the bond strength, creating stress risers resulting in embrittlement of GFRC.

Increasing proportions of polymer in the concrete were shown to correspondingly improve the toughness and strength of GFRC under all tested conditions. When exposed to hot-water aging, GFRC both without and with polymer (at all proportions) underwent significant loss of strength and toughness, although the polymer-modified GFRC (PM-GFRC) performed better than the unmodified GFRC. The authors attribute the improved performance to the accumulation of polymer particles on the filaments, preventing alkali attack and bonding of CH. The losses in properties under hot-water aging were concluded to have been caused by the growth of CH in between the filaments.

In his discussion of the Soroushian et al. (1993) paper, Bijen (1993) criticized the hot-water aging as being nonrepresentative of the actual conditions to which PM-GFRC is exposed in service. He suggests that the lower water content of PM-GFRC in equilibrium with its environment, due to the hydrophobic nature of the polymer and the decreased permeability

of PM-GFRC, will result in less moisture take-up by PM-GFRC from rain, spraywater, and the like. PM-GFRC will therefore be more resistant than GFRC to alkali reactivity and CH production in the same ambient environment because of its lower water content.

In his discussion of the Soroushian et al. (1993) paper, Walters (1993) points out that the authors' description of the polymer used in the tests, "acrylic polymer emulsion supplied at 47% solid content by weight of polymer latex compound," is extremely vague. He says that identifying the product this way is similar to "describing some research work on 'animals' without further description. Both mice and elephants are animals; similarly the term 'acrylic' covers polymers that differ much." Walters notes that the effects observed in hot-water aging may or may not have been caused by the acrylic esters hydrolyzing in the high-alkali environment of wet cement. Different acrylic esters used to make the polymers behave differently in such conditions. For researchers and practitioners to benefit from and expand on the Soroushian (1993) paper, a complete description of the polymer is essential.

The paper (Soroushian et al. 1993) and the discussions point out one of the challenges of working with PMC. There are so many polymers available, and there are so many variables in employing them, that it is difficult to isolate a particular material property of PMC and attribute it to a particular characteristic of the materials and their combinations. Obviously, there is a significant need for more high-quality research.

Review Paper 3

Lewis and Lewis (1990) clearly and thoroughly present the technology, microstructure, and properties of PMC made with styrene-butadiene rubber (SBR) and acrylic polymer modifiers.

The most important contribution of this paper is the recognition that much of the published literature presenting comparisons between PMC and unmodified concrete, and between concretes modified with different types and amounts of polymers and under varying conditions, mistakenly substitute "consistency" for w/c. In most other papers, sample mixes are adjusted to yield similar workability, flow, or consistency characteristics. Polymers in fresh cement mortar or concrete (especially latexes and resins, but also redispersible powders as they combine with the process water), generally improve workability and reduce water demand because of their natural lubricating and dispersing effects. The unmodified samples are usually prepared at very high w/c in order to get equal consistency. This unfairly penalizes the unmodified samples, which are weaker, less durable, and more porous than they would be with less water. Lewis and Lewis performed their investigation using constant w/c and constant aggregate volume. They reduced the volume of both water and cementitious material, holding w/c constant, by an amount equal to the volume of polymer added.

Another important contribution of their paper is the development of a technique for measuring the amount of polymer in a prepared sample of hardened PMC. Energy dispersive analysis of X-rays (EDAX) cannot be used to examine the latex polymer in PMC since the polymer is made up of carbon and hydrogen atoms, which EDAX cannot detect. Previously, a costly and highly toxic reagent, osmium tetroxide, had been used to "tag" the carbon-carbon double bonds of the monomers, allowing them to be detected. The authors developed a lower-cost and safer method of tagging these polymer bonds using bromine, allowing the analysis of the prepared samples. Lewis and Lewis suggest this method could be used to determine, by examination of the hardened concrete, whether a contractor used the correct amount of latex in a concrete mix. This is very important for quality assurance, and it should encourage design engineers to specify PMC in their projects.

Review Paper 4

Chen and Chung (1996) describe research done to compare concrete reinforced with 5-mm-long microfibers of polymer, carbon, and steel, with each other, and with PMC reinforced with the microfibers. The research methodology used is a good example of the problems raised in the Lewis and Lewis (1990) paper. Water-cement ratios were adjusted to achieve the same 170-mm slump in all samples. The measured strength values of the hardened samples probably were significantly influenced by the higher water content of the fresh paste prepared without polymer modification. Therefore, the effect of polymer modification alone could not be reliably identified.

Additionally, the fibers were selected to have equal lengths, regardless of their differing diameters and material composition. It is reasonable to expect the length and the diameter of fibers to influence their effects on the concrete they reinforce, whether it is modified by polymers or not. Holding the fiber lengths equal may have imposed an arbitrary and unfair bias on all the experimental results. Also, sand grain size distribution, which may have an influence on the mechanical properties of small-diameter carbon fiber reinforcing, was not considered.

A more accurate understanding of the influence of polymer modification on fiber-reinforced concrete may be gained by better control of experimental variables.

Review Paper 5

Zayat and Bayasi (1996), in their technical paper titled "Effect of Latex on the Mechanical Properties of Carbon Fiber Reinforced Cement," prepared samples of carbon fiber reinforced (CFR) PMC using varying percentages of polymers while holding fiber amounts and w/c constant. One of the characteristics of the samples that was compared, along with strength and toughness, was workability.

Test results indicate low polymer content might actually result in a decrease in the compressive strength of CFR-PMC. A higher polymer content appears to result in increased flexural and compressive strength, better impact resistance, and better workability, but a decrease in tensile toughness. The authors surmise the loss in tensile toughness at higher polymer levels is a consequence of higher bond strength between the carbon fibers and the cement and polymer comatrix, which promotes fiber rupture rather than pullout.

No consistent relationship was seen between polymer content and workability; the authors did not comment on the possible explanation for that observation.

Zayat and Bayasi present research methods and findings of high value to other investigators. The experiments were well controlled, so the data generated can be relied upon and used as a springboard for further research. Areas in need of further research were made apparent by the authors.

Review Paper 6

"Latex-Modified Concrete and Mortar for Repair" (1984) describes the materials and methodology used in the construction of PMC overlays on existing concrete roadway surfaces. Latex-modified mortar (LMM) and concrete (LMC) are described for use in thin (1/4–3/4 in.) and thick (greater than 3/4 in.) applications respectively. In the paper, LMM and LMC are presented for use in repair materials, but they can be just as appropriately used in new construction.

The latex materials discussed are styrene-butadiene rubbers (SBR) and polyvinyl acetates (PVA). PVAs are not recommended due to the propensity of some PVAs to hydrolyze in wet environments.

For the most part, the paper presents a clear and accurate

description of latex-modified mortar and concrete overlays. There is one point that I believe needs correcting. The need for using low w/c, in the range of 30–40%, and for including the water of the latex in the total water content of the mix are appropriately described. However, in describing the mixed procedure, the paper states, "(after most of the ingredients are introduced into the mixer, add) the remainder of the mixing water needed to achieve the desired consistency." This reversion to consistency of the mix, as opposed to the actual ratio of the weights of water versus cementitious materials, may result in improper application and poor performance.

Review Paper 7

The paper by Sprinkel (1988a) describes the failure, due to plastic shrinkage cracking, of a 1-in.-thick LMC overlay on a highway bridge deck in Virginia. Plastic shrinkage can occur when the evaporation from the surface of the concrete is faster than the rate of bleeding. The surface of the concrete dries, increasing surface tension in the remaining capillary pore water, which pulls the unhydrated solid particles closer together.

Based on his observations, the author recommends that special measures be employed to prevent plastic shrinkage cracking of LMC overlays when the weather conditions (temperature, relative humidity, and/or wind) result in evaporation rates greater than 0.10 lb/sq ft/h. This is lower than the 0.20 evaporation rate value of the American Concrete Institute (ACI) Standard Practice for Curing Concrete (ACI 308-81).

Sprinkel's explanation is certainly plausible and is most probably correct. Another condition that can result in plastic shrinkage, however, is sedimentation (Mehta and Monteiro 1993). It is possible that latex modification could result in increased sedimentation if the water content is high, since the polymer emulsion can act as a dispersing agent, allowing better mobility of solid particles. Other possible causes of plastic shrinkage include the placement of the overlay on a substrate that is too hot or too dry, or variations in the amount of polymer. No description of the LMC mix design was included in the Sprinkel's paper, nor was there any indication as to the time of day the material was placed, or the temperature or degree of saturation of the substrate. The contribution of these unknown conditions could not be evaluated.

Turton (1989), in an objection to Sprinkel's analysis and recommendations, said that reliance on a "'magic' evaporation rate" based on the bleed rate can be a mistake, since the bleed rate can depend on various conditions, and can vary widely independent of the evaporation rate. He recommends incorporating air entrainment to reduce surface tension, which lowers the driving force of the plastic shrinkage. This may not be an appropriate solution since the polymers in LMC may already result in air entrainment, and excess air can reduce the strength of the overlay. In fact, many polymer modifiers include a defoaming agent to reduce the amount of air entrainment caused by the polymer. However, Turton's comment about the magic evaporation rate is correct.

Review Paper 8

In another paper, Sprinkel (1988b) describes the construction and evaluation of LMC made with Type III, high early strength cement (LMC-HE). The requirement to return repaired roadways to service as quickly as possible is the impetus for the use of LMC-HE. Sprinkel points out that one problem with Type III cement, the high heat of hydration, is mitigated in LMC-HE overlays because of the thin section that does not allow the heat to build up. He presents test data that show the favorable strength and permeability characteristics of LMC-HE. Long-term inspection of LMC-HE applications in service indicate excellent durability.

LMC overlays are usually wet-cured 24 hours to promote hydration of the cement, and are then dry-cured several days to allow the polymer to coalesce. The LMC-HE application Sprinkel describes included the same 24-hour wet-cure as the normal LMC application made with cement other than Type III cement. Since polymer coalescence occurs only during the drying stage, it is apparent that there was no contribution to fast turnaround time attributable to the latex modification. Apparently, the coalescence of the polymer from the latex, and the formation of the polymer film, occurred in the uncontrolled conditions present during the first few days the roadway was returned to service.

Type III cement produces faster hardening concrete with higher early strength. The typical problem of thermal shrinkage cracks is obviated in this application by the thin section. Higher cement content can result in increased drying shrinkage, but that tendency is diminished by using lower w/c, as implied by Sprinkel. Lower thermal and drying shrinkage lead to better impermeability and more durable concrete regardless of latex modification. It is not conclusive from this paper that incorporating latex modification in a well made high early strength concrete overlay provided any benefit other than reducing the water demand.

Review Paper 9

The major point of the Cusson and Mailvaganam (1996) paper is the need to match the properties of repair materials in general with those of the materials they are applied to for repair purposes. The authors correctly assert the need of the repair design engineer to take into account support and restraint conditions, load transfer, and the need for temporary shoring, in addition to differential shrinkage, thermal expansion coefficients, and other properties of the materials.

A most significant potential problem with the use of PMC as a repair material is described in the paper. One of the characteristics of PMC that makes it valued as a repair material is its impermeability. Since a root cause of deterioration in the base material is typically excessive permeability, it seems reasonable to make the repair with an impermeable product to prevent recurrence of the original problem. Unfortunately, the distinct difference in permeability between the repair material and the remaining undamaged material, could lead to the formation of concentration cells that give rise to corrosion of embedded steel in the repair.

Moderating the potentially damaging effect of the permeability differential is, of course, the impermeability of the PMC itself. Low permeability prevents charge transfer in the pore solution electrolyte. Perfect impermeability is impossible, however, so there seems to be a possibility of corrosion of embedded steel starting just inside the PMC interface.

One solution of this problem is to exclude embedded steel from PMC repairs. Where reinforcing steel must be continuous in the base material and the repair, the use of PMC is perhaps not advisable due to the difference in the permeability of the materials. Another possible solution might be to prevent water intrusion in the remaining undamaged base material by the application of a separate impermeable membrane. This approach adds another layer of complexity and possible source of future maintenance or repair problems. The obvious answer is to take the time and spend the money to install durable, life-cycle cost-effective materials from the start.

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One of the impediments to the use of PMC is its cost. Gerwick (1978) very simply but effectively presents the "benefit" side of the economic equation used in the decision to incorporate polymers in concrete for marine structures. Although

the paper mentions only PIC and PC, in my judgement, the same analysis can hold for PMC.

The conditions for which marine structures must be designed include: cyclic loading due to wave action; severe environmental conditions of salt water, spray, freeze-thaw cycling, ice impact, and ice accumulation; and exposure to aggressive chemicals such as sour crude oils that release H_2S gas, the lighter fractions of petroleum, urea, and sewage. The tensile strength and impermeability of PMC makes it well-suited for such applications.

Gerwick identifies another benefit of PMC in marine construction arising from its impermeability. Since concrete with polymers will not absorb water as much as concrete without polymers, floating concrete structures made with polymers will have higher net buoyancy. He says: "Consider an underwater oil storage vessel which is being emplaced. Its air weight of 200,000 tons has been carefully balanced with its displacement of 195,000 tons to permit it to be emplaced by a buoyant control force of 5,000 tons. However, absorption during submergence can raise the net negative buoyancy by 200 percent, to 15,000 tons. Use of polymer-impregnation effectively eliminates absorption."

Estimating the break-even cost for incorporating polymers in marine structures, Gerwick considers limiting its use to locations in structures where it is most beneficial such as at the splash zone, where corrosion, ice adhesion, abrasion, and freeze-thaw cycling are most severe. Also, the high tensile strength of concrete with polymers could reduce cover and prestress requirements for concrete ships, reduce their displacement, and thus increase their deadweight-displacement ratio. Lower propulsion or towing power would be required. Reduced draft would decrease construction costs by lowering required dry-dock sill gate depths, and enable mooring in shallower waters.

Gerwick estimated that an incremental cost of \$200/m³ could be justified by taking the foregoing benefits into account. He also suggested that the combination of polymer fiber reinforcing with a concrete-polymer composite could provide impact resistance that could justify a \$10/sq ft cost premium. Similar cost analyses must be made with current prices and incorporating improvements made in polymer modification technology since 1978 in order to evaluate the true costs and benefits of PMC.

This paper is an example of the contributions that can be made both by advances in materials technology, and by the involvement of engineers experienced in the practical aspects of construction.

CONCLUSIONS

The combination of portland cement concrete or mortar with polymers can result in extremely durable, tough, and strong building-material composites that are economical and kind to the environment. Such materials can respond to the many needs of current and future construction. Structures in extreme environments, or inaccessible for repairs, or subject to impact, cyclic, or dynamic loading may all benefit from the use of PMC. The aging infrastructure can be repaired using PMC.

There are challenges to be met, however, if PMC is to be effectively used. One is the seemingly vast number of different polymers with different properties and characteristics, and the various modes of their incorporation in concrete and mortar. Compounding that problem is the fact that many manufacturers of proprietary polymer modifiers do not fully disclose or explain their products' makeup or characteristics. In October 1995, I was approached by a client who asked me to consult with him concerning the use of a precast modular housing system for underdeveloped countries. The wall and roof panels were to be prefabricated of polymer-modified concrete. I could

not help this client evaluate the structural system partially because the fabricator did not provide complete information of its ingredients, manufacture, or testing history. I was given strength and modulus of elasticity values, and was told the polymer additive was a "secret sauce."

Another challenge is the departmentalization of research and knowledge. Chandra and Ohama (1994) describe this problem as follows:

Polymers are used both in repairs and in making new concretes and mortars. Polymers are often used to make repairs without taking into consideration the cause of damage and without proper preparation of the repair object. Polymers are also used to make new concretes and mortars without considering the demands on the job that the polymer-modified material has to do. Without this information, the material fails and the polymer is blamed. Any material used inappropriately can give bad results, but the material itself is not responsible. The problem is that people knowledgeable about polymers lack background in building materials and that people versed in building materials do not well understand polymer technology. In fact, both disciplines must be taken into account.

Review of the published record suggests that a third challenge is the effective and efficient use of PMC in light of an apparent lack of understanding among some researchers and practitioners of the basics of concrete material science, such as the influence of w/c on the durability of concrete.

When evaluating test samples, it is important to have control and knowledge of all contributing conditions in order to gain an understanding of the capabilities of PMC. In the 1960s Haynes (personal communication, April 11, 1996), a knowledgeable concrete investigator and engineer, performed experiments on 2 by 6 by 20 in. prisms of portland cement mortar and PMC, wet-cured for 14 days. He recalls his (unpublished) results were very disappointing. The PMC samples had about half the flexural capacity of the unmodified samples. As a result of that experience, he has never considered PMC as a practical material. In fact, when I mentioned to Haynes that I was writing this paper on PMC, he denigrated the material and suggested I write about "something more interesting, like super-plasticizers." I am not aware of the particulars of his experiments, but if the polymers used were water soluble, or introduced into the mix in latex form, the 14-day wet cure would certainly have prevented the full development of PMC's beneficial properties. I can only imagine the advances in the state of knowledge and practice that would have accrued in the past decades had Haynes been interested.

In 1975, after the First International Congress on Polymers in Concrete, the promise of PMC contribution to the future of concrete construction prompted Nutt, Chair of the Congress, to say: "No one who previously had an impression in his mind that he knew exactly what concrete was can in the future think of concrete as being the same material again" (Dikeou 1978). In the 21 years since Nutt's statement, it seems, from the reading of some of the published articles, that his prediction is proving to be correct. Polymer modification can impart new worthwhile properties to concrete, but only if the details of its function and mechanism and, just as importantly, the basics of concrete science, are understood. If "the impression of what concrete is in one's mind" is incorrect, one certainly is not going to be capable of understanding what concrete becomes in combination with polymers.

On the other hand, many papers demonstrate that clear thinking and a thorough grasp of concrete material science can only improve one's understanding of PMC; these ingredients will make PMC a useful construction composite.

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