SP 69-1

Overview of Current Research on Polymer Concrete: Materials and Future Needs

By John A. Manson

Synopsis: 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—the subject of this paper—is to combine the two technologies of concrete and high polymers, using not only familiar kinds of concrete but also less familiar ones. It should be noted that combinations of siliceous materials with polymers require in many cases lower energy inputs per unit of performance than either component alone.

The purpose of this paper is to provide an overview of current research and unsolved problems with the various classes of polymer-concrete materials. While a comprehensive review of the literature is not within the scope of the paper, the general state-of-the-art is described, principal areas of research are illustrated with typical examples, and areas needing further research are suggested.

Indeed, significant progress has been made recently in both fundamental and applied research on all kinds of polymer/concrete systems. It is suggested that further progress to achieve sophisticated understanding, design, and materials selection will still require much work in combining the science, technology, and economics involved.

Keywords: concrete durability; concrete technology; impregnating; plastics, polymers and resins; polymer concrete; polymer-portland cement-concrete; polymerization; research; reviews; strength.

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Classes of Polymer-Concrete Materials

As shown in Fig. 1, three principal classes of polymer-concrete materials exist: (1) polymer-portland-cement concrete (PPCC); polymer-impregnated concrete (PIC); and polymer concrete (PC). The distinctions between these classes are important to the selection of materials and to design. With PPCC, a monomer, prepolymer, or dispersed polymer is incorporated into a portland cement mix, and a polymer network formed in situ during curing of the concrete. With PIC, previously formed concrete is impregnated with a monomer which is subsequently polymerized in situ; here the polymer adds properties to those characteristic of the original concrete. With PC (or resin concrete), a polymer is used to bind an aggregate together. For typical properties of these systems, see Table 1. Polymeric materials used in small proportions for such purposes as water reduction are not usually considered within these classes, but rather are treated as simple additives.

Historical Development of Polymer-Concrete Materials

While several kinds of what are now called PCs and PPCCs (the latter being latex-modified mortars) were in use during the 1950s, major interest in such materials, and in PIC, developed in the middle 1960s (1-3). A major thrust was the desire to obtain improved materials for rigorous applications such as desalination process equipment, water and waste-water pipes, and bridge decks. Both research and development activities accelerated as the 1970s approached.

In 1971, the American Concrete Society formed Committee 548, "Polymers in Concrete", and by the late 1970s the Society had sponsored two symposia on the general topic (4,5) and a state-of-the art report (1); a manual of recommended practice is also in preparation. Interest has by no means been confined to the U.S.A. Thus, for example, the Concrete Society (London) formed a working group on this topic, and numerous other symposia, workshops, and seminars have been sponsored and articles written throughout the world (6-7). In particular, it is noteworthy that two major international congresses have been held - the first in London in 1975 (13), and the second in Austin, Texas, in 1978 (14). The papers presented by delegates from over 20 countries covered an extraordinarily wide range of research and applications.

Some polymer-concrete materials have already been in use for many years, some are undergoing their first applications, and some are awaiting acceptance by a justifiably conservative technological world. After about 15 years of research and development, enthusiasm for fascinating new combinations of properties has been tempered with a healthy skepticism about whether or not polymer-concrete materials really have a place in engineering applications. Fortunately, even under the cold and impartial eye of cost-effectiveness, there are indeed applications which appear suitable for the unique properties of such materials.

Thus the field appears to have reached a first level of maturity. Older applications are being consolidated into practice and newer ones are being sought. Indeed a major development has been that several major classes of applications have been, or are being, commercialized generally throughout Europe and the Americas. In fact, a reading of Chemical Abstracts reveals that about 150-200 publications on polymer-concrete materials are currently being abstracted each year. Most of them come from a dozen-odd countries, and an increasing number (about one third) are based on patents, thus reflecting a high incidence of tailor-making products for particular applications.

DISCUSSION

Polymer-Impregnated Concrete (PIC)

General State-of-the-Art--The general principles required for impregnation and polymerization of monomers in situ are now reasonably well established (18-21). Provided that most of the water ($\sim$ 90%) is removed by drying, impregnation to levels of, e.g., $\sim$ 15% by volume of a wide variety of liquids (monomers, solutions, and even liquid sulfur) has been shown to be feasible. While there is still some disagreement about whether impregnation proceeds by a capillary-rise mechanism or a simple diffusion process (18), the impregnation follows a square-root-of-time rate law over most of its course. Consistent with a capillary-rise phenomenon, the rate of impregnation varies with the square-root of the ratio of surface tension to viscosity times the average pore radius, and with the applied pressure. The kinetics of polymerization may differ somewhat from that in bulk, but it is not difficult to achieve an adequate polymerization of many monomers by use of irridation or thermocatalytic methods. In this way, one obtains an interpenetrating network system comprising cement gel and a polymer that can confer useful properties.

Much emphasis has been given to acrylic monomer systems such as methyl methacrylate (MMA) or acrylonitrile mixtures because the use of these monomers has generally led to superior properties in the composite. Since such liquids have high surface tensions, low viscosities, good wetting properties, relatively low costs, and high reactivities, the empirical discovery of their virtues has a sound physico-chemical basis (18). Epoxies and other viscous monomers have also been used though the rate of impregnation is necessarily reduced.

With impregnation by an appropriate monomer, the principal effect of technological interest is the sealing of the continuous capillary pore system, resulting in exceptional decreases (to ∿ 99%) in the permeability to water and to salts such as sulfates and chlorides. Other effects include increases in the coefficient of thermal expansion (to 30%) and thermal diffusivity (to 13%) and a decrease in specific heat (to 17%). The pore-sealing also minimizes changes in properties, e.g., dielectric constant and loss, that are sensitive to moisture content.

Dramatic improvements in abrasion resistance, Young's modulus and in compressive, tensile, and impact strengths (by factors up to about 5) have been noted by many investigators for impregnation with PMMA and other glassy polymers (Table 2), and related to the polymer loading. In general, impregnation with a glassy polymer yields a solid whose strength-strain behavior is linearly elastic almost to the point of failure. However, the stress-strain behavior can be modified from elastic and brittle to ductile by introducing plasticizing comonomers (15). Indeed, the state of the polymer in the pore is important; relaxation studies have shown that reinforcement requires that the polymer be in its glassy state (15).

A fracture-mechanics approach to strength has been used in a few cases to explain the improvement in strength. Using Griffith's equation it has been suggested that reinforcement improves strength by increasing both E and fracture energy, γ, but especially the latter (22).

In any case, the beneficial effects of impregnation may be due to the ability of the polymer: (i) to act as a continuous, randomly-oriented reinforcing network; (ii) to increase the bond between the aggregate and cement paste; (iii) to absorb energy during deformation; (iv) to penetrate and reinforce the micropores; and (v) to bond with the hydrated or unhydrated cement (23).

As a result of the improvements in properties described above, PIC has long been considered as a potential material where properties such as high strength and stiffness, or resistance to corrosion of concrete or reinforcing steel are important. Thus, from the beginning, end-uses such as in bridge decks, pipes, and structural elements have been examined, and a few large-scale applications have been made, especially with bridge decks (1, 4, 5,13,14). The principal limitation is that of cost, for the process is complex, and monomer costs high if more than a surface impregnation is effected.

Recent Research and Development--While the results of impregnations using various vinyl monomers and epoxies continue to appear, some attention has been given to other impregnants such as oligomeric isocyanates (24), ester acrylates (25), silicates

(26) and sulfur (26a). In general, it seems likely that impregnation yields products having levels of properties not exceeding those of earlier MMA-based PICs. On the other hand, over the past few years, impressive improvement in mechanical properties have been attained by combining the use of autoclaved high-strength concrete with impregnation (27-29) (see Table 1). The use of impregnated aggregates has also been studied recently (30). Earlier, work on the impregnation of other porous inorganic substrates such as gypsum (19) had been reported. More recently, good results have been reported with pozzolan, lime, and slag-based concretes (31). The impregnation of fiber-reinforced concrete has also continued to receive some attention (32,33).

An interesting spin-off from PIC research has been the adaptation of impregnation techniques to the case of non-polymeric sealants such as linseed oil (34) and silane-type materials (35). By eliminating the polymerization step, this approach can offer economies in process costs, and is currently being evaluated further for bridge-deck sealing (36).

Little research seems to be directed towards either the fundamental aspects of impregnation of process improvement, though the possibility of simplifying the impregnation process is being considered at least on paper (36). The occurence of shrinkage during impregnation has been studied, and shown to be only slightly greater than that noted during the curing of concrete (37). An interesting approach to characterizing the polymerization process in situ has been reported, based on dielectric measurements (38). This technique should be useful in process control.

The modeling of PIC as a composite material has recently been studied (39,40) using a lower bound model proposed by others several years proviously. Though the model has been questioned (41), it does seem to give reasonable predictions, after allowance is made for uncertainties in the values for modulus of the polymer actually in the pores. At the London Congress (13), several investigators had discussed the question of the properties of the polymer (e.g., molecular weight, physical state, and polymer-matrix interaction). Recent results (42) suggest that acid-base interactions proposed earlier (43) — interactions between, e.g., Ca^{++}ions and ester groups — may well explain the anomalously high softening point of PMMA in the pores of concrete.

The routine characterization of the depth of partial impregnation, has often posed problems. Promising results using petrographic observations (44) and resistivity measurements (45) have been described. New techniques for predicting corrosion rates in reinforcing steel (35) will also be useful in comparing PIC with other protective systems.

As mentioned above, the attainment of exceptionally high strengths by the impregnation of autoclaved high-strength concrete has now been demonstrated in several laboratories in the

U. S., Italy and most recently, in Japan (29). In fact the compressive-strength-to-density ratio of this material is nearly three times that of steel. Although Young's modulus is not much greater than with ordinary PIC, the maximum strain at break is significantly increased.

Sulfur-impregnated concrete continues to be of interest, and earlier findings about this were confirmed by several groups (see, for example, ref. 26). However, the deleterious effect of water (45a) is troublesome; attempts to inhibit the interaction between sulfur and $Ca(OH)_2$ have shown promise (45b).

Surprisingly little has been done on design criteria with PIC. Two exceptions are the development of design criteria for post-tensioned PIC beams (46) and analytical studies of ultimate strength and plastic ductility in PIC beams and columns compared with conventionally reinforced concrete beams and columns (47).

While carefully made PIC offers an unusual combination of excellent mechanical behavior and relative impermeability to deleterious salts, most applications involve "hard cases", in which the gain in service life is believed to offset the high cost, or in which no other material or process appears to be more suitable. Thus, in spite of predictions of many different end-uses (see references cited in ref. 1), relatively few applications appear to have reached commercial practice.

Perhaps the most extensive programs continue to be concentrated on highway bridge decks, and an increasing number of impregnations are being conducted by contractors, in collaboration with the Federal Highway Administration (48). Although most of these have involved the shallow impregnation of new decks to hinder the penetration of deicing salts, one project, sponsored by the National Cooperation Highway Research Program (49), demonstrated the feasibility of deep impregnation of salt-contaminated decks in order to delay the onset of corrosion. This project has continued (36), though it is no longer restricted to the polymer-impregnation approach.

Another major area of current interest is in hydraulic structures in which PIC's strength and abrasion resistance makes it an ideal candidate as a material for such applications as spillways and stilling basins (50). PIC is also being used, at least from time to time, in the restoration of structural elements and floors in deteriorated buildings (51). A program of research into PIC for such applications as pipes and storage tanks is being supported in India through the United Nations Development Program. Another example of application is in the use of PIC to contain radiation wastes (52). PIC also shows considerable promise for marine applications (35); in a recent study, PIC pilings showed much less corrosion after prolonged exposure to sealants than controls (53).

Polymer Concrete (PC)

General State-of-the-Art--With PC, a thermoplastic, or more commonly a crosslinked polymer, is used to replace Portland cement as binder in a concrete mix. Since the polymer constitutes the continuous phase, behavior of the composite will clearly be determined by the polymer, whose properties are, of course, very dependent on time and temperature.

A wide variety of monomers, prepolymers and aggregates has been used. While epoxy resins are commonly used in PC, much attention has been focussed on the use of cheaper vinyl monomers such as polyester-styrene, MMA, furane derivative and styrene, usually in conjunction with a crosslinking agent (55,56). Setting times and times for development of a high proportion of maximum strength can be readily varied from a few minutes to hours. Bond strengths to substrates are also usually high. In spite of high cost, PC is particularly useful for maintenance and repairs, especially when delay and inconvenience are important factors (56). Thus the cost/benefit ratio is favorable (Table 1).

By carefully grading the aggregate it is possible to wet the aggregate and fill the interstices by the use of as little as 7-8 wt. % ($\sim$ 14 - 16 vol. %) polymer (55). With high packing densities, high compressive strengths can be obtained (Table 1). Flexural strengths, though much higher than for concrete, are limited by the aggregate-matrix bond strength and by asperities in the aggregate, which can introduce stress concentrations. The use of silane coupling agents has been shown to improve compressive strength, presumably by improving bond strength. In general, as with glass-reinforced composites, strengths tend to be reduced by exposure to water, presumably because of deterioration of the aggregate-matrix bond. With proper selection of materials, the dielectric properties characteristic of good insulation can be achieved.

The deformation response of PC is highly variable with elastic moduli ranging up to about 35 GPa for a rigid matrix with a tensile failure strain of $<1\%$; of course, moduli are much lower, and failure strains much higher, for rubbery matrices. It should be noted that shrinkage strains vary from polymer to polymer (high for polyesters, lower for epoxies), and must be considered in any application; such strains may, if not relieved by creep, result in premature failure in a rigid PC. Since a polymer constitutes the continuous phase, it is not surprising that creep is generally higher than for concrete, and enhanced at high temperatures.

The versatility in formulation and in processing has led to many applications in the past, including flooring, cast articles of various kinds, patching, and overlays for highway bridge decks (3,4,13).

Recent Research and Development--Of the 3 classes of polymer-concrete systems, PC is currently attracting the most attention, at least in the U.S. A major reason for this is the realization that economies of scale can be achieved by continuous rather than batch processing (57). This fact has long been known in Europe, but is only now being fully appreciated in the U.S. Thus while continuous processing of cultured-marble units has been practiced for some time, most other applications have involved batch operations, typically on-site. A second major development in the U. S. has been the rapid development of tailor-made PCs for various uses; indeed an increasing number of companies now offer a range of formulations, many in prepackaged form (57). As these trends continue, and as the need for sophisticated product design and development increases, we may expect to see more intensive basic research as well.

While new formulations continue to appear (for reviews, see ref. 58a), and mix design has been studied systematically (58b), both scientific and engineering research on PCs has been limited in scope. A notable exception has been research associated with the development of PCs for geothermal applications, where the extreme service conditions place exceptionally severe demands on the maintenance of properties at high temperature in an aggressive medium (58-61). Dental and bone cement materials constitute another example of an application posing severe materials problems (62,63). Still another example is the need for patching systems that can cure rapidly and bond to a wet substrate (64).

Thus, much of the recent published research on new monomer systems and on properties and behavior has been stimulated by the applications mentioned. (Presumably much proprietary research has gone on as well.) In the BNL research on geothermal materials, many copolymer systems, both thermoplastic and thermosetting, have been, or are being, studied. Monomer systems include various combinations of divinylbenzene, trially cyanurate, siloxanes, various methacrylates, and acrylamides (58-61a). While aggregates such as quartz, silica, fly-ash and portland cement give composites serviceable up to $\sim$ 220°C, a combination of silica sand with portland cement is required for use at higher temperatures. The benefits obtained by including portland cement have been noted in other research as well (63). The basic chemistry of the interfacial interactions is under study; the formation of ionic bonds between Ca^{++} ions and carboxylate groups appears to be involved (65-68). Such ionic bonds also provide the basis for the so-called ionomer cements recently developed in the UK as dental cements (61b), and have been suggested to occur in PIC as well (69). With respect to dental cements, at a recent symposium on dental materials sponsored by The American Chemical Society, current research on a wide variety of acrylic and other monomers many containing specialized functional groups was reviewed (62). Research on monomers that can bond effectively to wet substrates is under way at BNL and the University of Texas as part of a program for the development of methods for the rapid repair of aircraft runways.

In all these cases, fundamental knowledge of the chemistry of the binder and aggregate and the surface chemistry involved in binder-aggregate interaction is required. While such knowledge is not necessary for PCs used in many structural applications it is clearly important in more demanding cases. In addition to the examples mentioned, the use of PCs in load-bearing applications subject to a combination of high stress (static, cylic or impact) and an aggressive environment (water, high temperature, chemicals) will require a sound base of research. Surface chemistry is also important to demolding. Research into both the physical and chemical factors that can cause failure in PCs has been very helpful in the case of polyester composites (69a).

In spite of the knowledge that creep can be high in PCs, there have been few recent studies. However, at least for an epoxy-based PC (63) it has been recently shown that the viscoelastic behavior was linear at low loads [up to 3ksi](21MPa). The effects of higher loads are under study. Another important point to note is that in contrast to portland cement concrete, creep in PC is not reduced when the specimen size is increased. This reflects the difference in creep mechanism, that of the polymer involving molecular (segmental) motions. Interestingly, the creep of the PC at given load was only slightly higher (∿30%) than that of a typical PCC.

Some research on static and fatigue fracture in bone cement has been reported (70-72). A beneficial effect of carbon fibers has been observed (70), and some environmental studies have been made (72).

Research is also in progress on the ability of PC overlays to minimize the corrosion of reinforcing steel (35), and on bonding to the substrate. The new technique developed by the FHWA (35) for prediction of corrosion rates will be helpful in comparing PCs with each other as well as with other protective systems. Dielectric behavior continues to be of interest, as PC is a candidate for the replacement of porcelain in high-voltage insulators (73-74). The combination of facile processing, good insulating qualities, and high fracture toughness is indeed attractive.

As with PIC, highway applications have received much attention (75). Thus the FHWA Implementation Division has encouraged a large number of trials with PC overlays on bridge decks (35,48), and published a user's guide. Indeed, so far the overlays have performed well. The NCHRP has also included PC within the scope of a current program (36). Patching has been of interest for quite a few years (76); as mentioned above, one of the most recent applications is in the rapid repair of aircraft runways (64). PC has been successfully applied to the renovation of structures, both buildings and dams (50,51), and is being evaluated in pilings (35). PC is also to be used in rehabilatating roadbeds of railway lines in the Northeastern corridor. Much successful experience in highway applications in Germany has been reviewed (77).

Miscellaneous applications include: various kinds of panels and tiles, cultured marble, pipes and liners, flooring, pilings and sanitary ware (54, 57). Current potential applications in electric utilities include: tunnel segments, conduits, support structures, and as mentioned above, high-voltage insulators (78). Examples of other extremely demanding applications such as materials for dental and bone cements and geothermal applications have already been given.

Polymer-Portland Cement Concrete (PPCC)

General State-of-the-Art--From the standpoint of process technology, this most obvious approach is attractive.

Unfortunately typical vinyl monomers such as MMA or styrene either interfere with the hydration of the cement or one degraded by the high alkalinity present (21). Prepolymers such as polyester-styrene and epoxies can be effective, though fairly high proportions are usually required if mechanical properties are to be improved. However, most attention has been given to the incorporation of a polymeric latex. In this case, the physical process of film formation is required rather than the chemical process of polymerization. Also, since the emulsion lubricates the mix, less water is usually needed for workability, so that the optimum water content from the standpoint of final properties can be approached. In fact, polymer latexes —usually of acrylics, styrene-butadiene copolymers, poly(vinylidene chloride), epoxies, and poly(vinyl esters) — have been used in mortars and concrete for about 45 years.

In general, latex-type PPPCs exhibit excellent bonding to steel reinforcement and to old concrete, good ductility, resistance to penetration by water and salt, and excellent durability to freezing and thawing. Not surprisingly, the precise balance of properties depends on the nature of the polymer and its concentration. While flexural strength and toughness are usually increased, the modulus may or may not be increased; the more rubbery the polymer, the lower the modulus.

Several factors are apparently involved in improving properties the reduction in water-cement ratio and, hence, in the volume of capillary porosity; the entrainment of air as a fine dispersion; specific interactions with the cement gel; and specific properties of the polymer, for example, toughness. More specifically, the following requirements for the polymer are believed to exist:

(1) The latex must be able to form a film under ambient conditions, to coat cement grains and aggregate particles, and to form a strong bond between the cement matrix and the aggregate.

(2) The polymer network must possess the capacity to intercept a growing microcrack and, by dissipating energy through microfibril formation (across a crack without separation from the