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16. Abstract

The report consists of three parts. In part I a review of literature is presented concerning the combinations of polymers and concrete. The most important findings were that (a) as of 1973, reported investigations concerning the incorporation of polymerizable product into fresh concrete have been confined to limited and small-scale feasibility studies; and (b) disappointing results have precluded further investigations.

Part II presents four series of our own exploratory experiments as follows:

(a) Experiments with four monomer systems;
(b) PCC experiments with monomer + catalyst systems;
(c) Experiments with a polyvinyl acetate emulsion; and
(d) Concrete experiments with coated aggregates.

None of these experiments provided results that were good enough technically or economically to justify the continuation of these investigations on a larger scale.

In Part III the addition of urea-formaldehyde prepolymers to standard Ottawa-sand mortars was investigated. Certain combinations produced considerable increases in strengths. Thus, further investigations are justified but no implementation at this time.

17. Key Words

coated aggregate; concrete; epoxy; furfuryl alcohol; polymers; PCC; prepolymer; strength; urea-formaldehyde system.

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FINAL REPORT

Polymer Pavement Concrete for Arizona - Study I

HPR 1-10(144)

PREFACE

This document is the report on Study I of a project entitled "Polymer Pavement Concrete for Arizona." The project identified as No. HPR 1-10(144) by the Arizona Highway Department, was sponsored by the Arizona Highway Department in cooperation with the Federal Highway Administration through contractual agreement with Northern Arizona University in Flagstaff, Arizona. The project started on November 16, 1972, and ended on January 27, 1974.

The project made use of staff and facilities of the College of Engineering and Technology, Northern Arizona University. The principal investigator was Dr. Sandor Popovics. Dr. Leslie L. Turai worked as consultant on the project for approximately six months, while Mr. Thomas L. Ryan worked approximately 11 months as a research assistant.

The following companies contributed materials for the project:

Adhesive Engineering Company, San Carlos, California
Celanese Coatings Company, Jefferson Town, Kentucky
E. I. Dupont de Neupurs & Company, Wilmington, Delaware
Phoenix Cement Company, Clarkdale, Arizona
Union Carbide, Silicons Division, New York, New York.

The contribution of these companies is certainly appreciated. The help of the Bureau of Reclamation, especially the cooperation of Mr. Carl Selander and Mr. W. C. Cowan is also acknowledged with thanks.

ABSTRACT

This study is the final report for the research project entitled "Polymer Pavement Concrete for Arizona" Study I. This project was a prelimary investigation of limited scope the objectives of which were:

(a) to try out a few methods through laboratory investigation that are suitable for producing polymer-cement concrete for pavements;

(b) to investigate the strength of such mortars and concretes.

The body of the report consists of three parts. In Part I, a review of literature is presented concerning the combinations of polymers and concrete. Only those papers were discussed in detail that had direct relationships with polymer-cement concrete suitable for pavements. The most important findings were that:

(a) as of 1973, reported investigations concerning the incorporation of polymerizable product into fresh concrete have been confined to limited and small-scale feasibility studies; and

(b) disappointing results have precluded further thorough investigations.

Part II presents four series of our own exploratory experiments as follows:

(1) Experiments with four monomer systems produced by Dupont;

(2) PCC experiments with the addition of monomer + catalyst systems;

(3) Experiments with a polyvinyl acetate emulsion; and

(4) Concrete experiments with coated aggregates.

None of these experiments provided results that were good enough technically or economically to justify the continuation of these investigations on a large scale. However, further limited investigations with some of these chemicals are still recommended. Particularly, new approaches with using polymer-coated aggregates in concrete should be tried out.

In Part III the addition of urea-formaldehyde prepolymers to standard Ottawa sand mortars was investigated in an exploratory manner. Certain combinations produced considerable increases in the compressive strengths. Thus, further investigations in this direction are justified but no implementation at this time.

KEY WORDS:
coated aggregate; compressive strength; concrete; concrete-polymer composites; epoxies; flexural strength; furfuryl alcohol; mortar; polymers; polymer-cement concrete; portland cement; post-mix polymerization; premix polymerization; pre-polymer; tensile strength; urea-formaldehyde prepolymer.

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PART I

Concrete - Polymer Composite Materials -- A Review of the Literature

Introduction

This portion of our report presents a review of literature on the various combinations of polymers and concrete with an emphasis on the so called polymer-cement concretes. There are several published and unpublished reviews of literature available on polymer-concrete compositities but these deal only superficially with the kind of polymer-cement concretes that is the subject of the investigation to be reported here. Therefore, it seems useful to present here a new, organized review of lieterature, or state-of-the-art report, that discusses in details the topic of polymer-cement concrete in addition to a brief summary of polymer-impregnated concrete and polymer concrete.

Concrete is used in nearly all types of construction throughout the world because of its capacity to be formed into a variety of sizes and shapes, the ready availability of the raw material from which it is made and its relatively low cost. Although concrete is an excellent building material, certain limitations to its use are recognized. These relate mainly to its relatively low tensile strength, its tendency to crack with changes in temperature and moisture, and its deterioration because of permeability, absorption, and chemical attack under various enviromental conditions. Improvements in these properties could significantly extend the usefulness of concrete.

A recent effort to achieve these improvements has been to produce concrete-polymer composites, that is, suitable combinations of a portland cement concrete and a polymer. Several different forms of such combinations have been tried out which are discussed below. Before that, however, a brief description of the background is provided. (1)

Background

Hydraulic binders, that is cements, have been used for several thousand years. Ancient concrete structures can still be found in various places of the Roman Empire in Europe, Middle East, etc. (2)(3). The modern development in cement and concrete began with the discovery of portland cement.

Portland cement is the far most significant class of the hydraulic cements beacuse of its price and properties and, consequently, because of the quantity consumed. The term "portland cement" was given in 1825 by Joseph Aspdin, a bricklayer of Leeds, England, to a powdery material that he patented because when set with water and sand, it resembled a natural limestone quarried on the island of Portland in England. His material, however, was probably only a hydraulic lime because of the apparently low burning temperature used. The production of portland cement in the modern sense started about 20 years later by Issac C. Johnson.

The first portland cement to be made in the United States was produced by David Saylor at Coplay, Pa., in 1871, in vertical kilns somewhat similar to those used for burning lime. The increasing demand for both quantity and quality led to the introduction in 1899 of the rotary kiln. From the turn of the century the production of portland cement in the United States has assumed giantic proportions rising from less than 10 million barrels, 376 lbs. each, to almost 400 million barrels by the end of the 1960's. (4) The world production of Portland cement at present is about six times as much as the production of the United States. Further details concerning the development of portland cement are comprehensively described in several places in the technical literature. (5-7)

Compared to concrete, synthetic polymers are a recent development.

Natural polymers have existed since the advent of organic and living matter on earth, but man-made polymers began with the discovery of celluloid in the late 19th century and the synthesis of Bakelite in 1909 by Baekeland. The present plastics industry started in the late 1930's and grew rapidly after World War II. During the war polyethylene gained prominence in England as an insulating material for high electronic equipment, especially the radar installations that were so vital for defense. (8)

Polymers are divided into two classes: thermoplastic polymers, which soften on heating and harden when cooled; and thermosetting polymers, which do not soften again after formation. The chemistry and technology of polymers have been highly developed by industrial organizations such as duPont in the U.S. and Imperial Chemical Industries in England, and by univeristy institutions such as the Polymer Institute at Brooklyn Polytechnic Institute and Brookhaven National Laboratory (BNL).

An organic polymer consists of a chain of organic molecules linked together through chemical bonds. The basic molecular unit is called a monomer. In order to form a polymer, the monomer must contain an unsaturated or double bond which can be broken and which can be made to link up with another molecule. Polymerization processes are of two types: addition and condensation. Polymerization is initiated via free radicals, ions, or excited species. The free radical, addition type of process is one of the most important industrially. Polymerization can be initiated by heat plus catalysts, by a catalyst plus a promoter, or by radiation.

The advantage of initiation by radiation is that a free radical can be formed at any temperature and no chemical catalyst is required; the disadvantage is mainly in the cost of the radiation facility and the radioactive sources. The advantage of catalyst plus heat is that no special facility is required and the processing costs are relatively low; the disadvantage is that runaway polymerizations leading to explosions can take place which poses a safety problem. Monomers are very sensitive and can polymerize spontaneously, especially if they become contaminated in storage. Inhibitors such as hydroquinone, which are free radical scavengers, are added to monomers to extend their periods of safe storage of shelf-life. The third method of initiation is carried out at ambient temperature by using a chemical catalyst plus a chemical accelerator or promoter which causes the catalyst to decompose and form a free radical. With this method it is difficult to control the rate of polymerization, and this presents problems when delay is desirable, as when the mix is to be impregnated into a material such as concrete and subsequently polymerized in situ.

The principal monomers of commerce are ethylene, styrene, acrylonitrile, vinyl chloride, and methyl methacrylate. Their raw materials are oil, coal, and natural gas plus water and air. Production in the U.S. is of the order of 20 billion pounds or 10 million tons annually. Monomers cost between 2 and 30¢/lb; the basic plastics industry produces on the order of 3 billion dollars' worth per year and is growing at a high incremental rate; it is becoming of the same order of magnitude as the cement and concrete industry. If the raw materials are readily available and remain relatively cheap, this assures widespread and continuing growth.

The basic properties of plastics are light weight (density usually 1 g/cm^3), reasonable strength (compressive strength 15,000 to 20,000 psi and tensile strength 3,000 to 10,000 psi), impermeability to water, and relative stability and resistance to chemical attack by acids and alkalis. The main drawback is lack of stiffness; plastics behave plastically and deform badly under load; and the high temperature stability is limited. (8)(9)

The impregnation of concrete with monomer followed by treatment of the monomer with radiation originated with a suggestion by the U.S. Bureau of Reclamation (USBR) of the Department of the Interior to the Division of Isotopes Development of the U.S. Atomic Energy Commission (US AEC) in 1965. The Commission at the time was supporting a program on the development of wood-plastic combinations. The idea was transmitted to the Radiation Division, Nuclear Engineering Department, Brookhaven National Laboratory (BNL) by the USBR and US AEC, and late in 1965 and early in 1966 exploratory experiments are carried out. Mortar bar specimens were impregnated with several gaseous and liquid-phase monomers and polymerized in situ with Co^{60} gamma radiation. Results of these initial exploratory experiments were completed early in 1967. (10)

General Types of Concrete - Polymer Composites

Polymer-Impregnated Concrete

Polymer impregnated concrete (PIC) is a precast and cured hydrated cement concrete which has been impregnated with a low vicosity monomer and polymerized in-situ. This material is the more developed of the composites. The largest improvement in structural and durability properties have been obtained with PIC. With conventional concrete (28 day water-cured), compressive strengths can be increased from 5000 psi (352 kg/cm^2) to as high as 20,000 psi (1410 kg/cm^2). Water absorption is reduced by 99% and the freeze-thaw resistance is enormously improved. With highsilica cement, strong basaltic aggregate, and high temperature steam curing strength increases from 12,000 psi (845 kg/cm^2) to 38,000 psi (2630 kg/cm^2) can be obtained. The tensile strength of PIC is essentially approximately 10 times less than the compressive strength similar to conventional concrete. A miximum of 3500 psi (238 kg/cm^2)

tensile strength has been obtained with the steam cured concrete. In steam cured concrete, polymer loadings (i.e. polymethyl methacrylate, (PMMA)) roughly around 8% by weight (wt. polymer/wt. of dry concrete) are obtained. (11)

In contrast to conventional concrete PIC exhibits essentially zero creep properties. Furthermore, by polymer impregnation concrete, conventional concrete is transformed from a plastic material to essentially a linearly elastic material with an increase of atleast 2 times in the modulus of elasticity. This is indicated by the linearity of the stress-strain curve for PIC in Figure 1. The ability to vary the shape of the stress-strain curve presents some interesting possibilities for tailoring desired properties of concrete for particular structural applications. (12)(13)

PIC is basically formed by drying cured conventional concrete in a convenient and economical way (hot air, oven, steam, dielectric heating, etc.), displacing the air in the open cell void volume (vacuum or monomer displacement and pressure), diffusing a low viscosity monomer (10cps) through the open cell structure, saturating the concrete with the monomer and in-situ polymerizing the monomer to a polymer by the most convenient and economical means (radiation, heat or chemical initiation). Mainly the free-radical vinyl type monomers, i.e. methyl methacrylate, styrene, acrylonitrile, t-butyl styrene, and other thermoplastic monomers are used. Good results are also obtained with cross-linked and thermosetting monomers such as styrene-trimethylol propane trimethacrylate (TMPTMA) and polyester-styrene. The more important criteria are that the monomer should be a relatively low cost readily available material and have a relatively low viscosity. Much information on the formation and structural and durability properties of PIC have been accumulated over the past four years in the U.S. (1)(10)(12-22) and elsewhere. (23-25) A U.S. patent has also been issued on the production of PIC. (26)

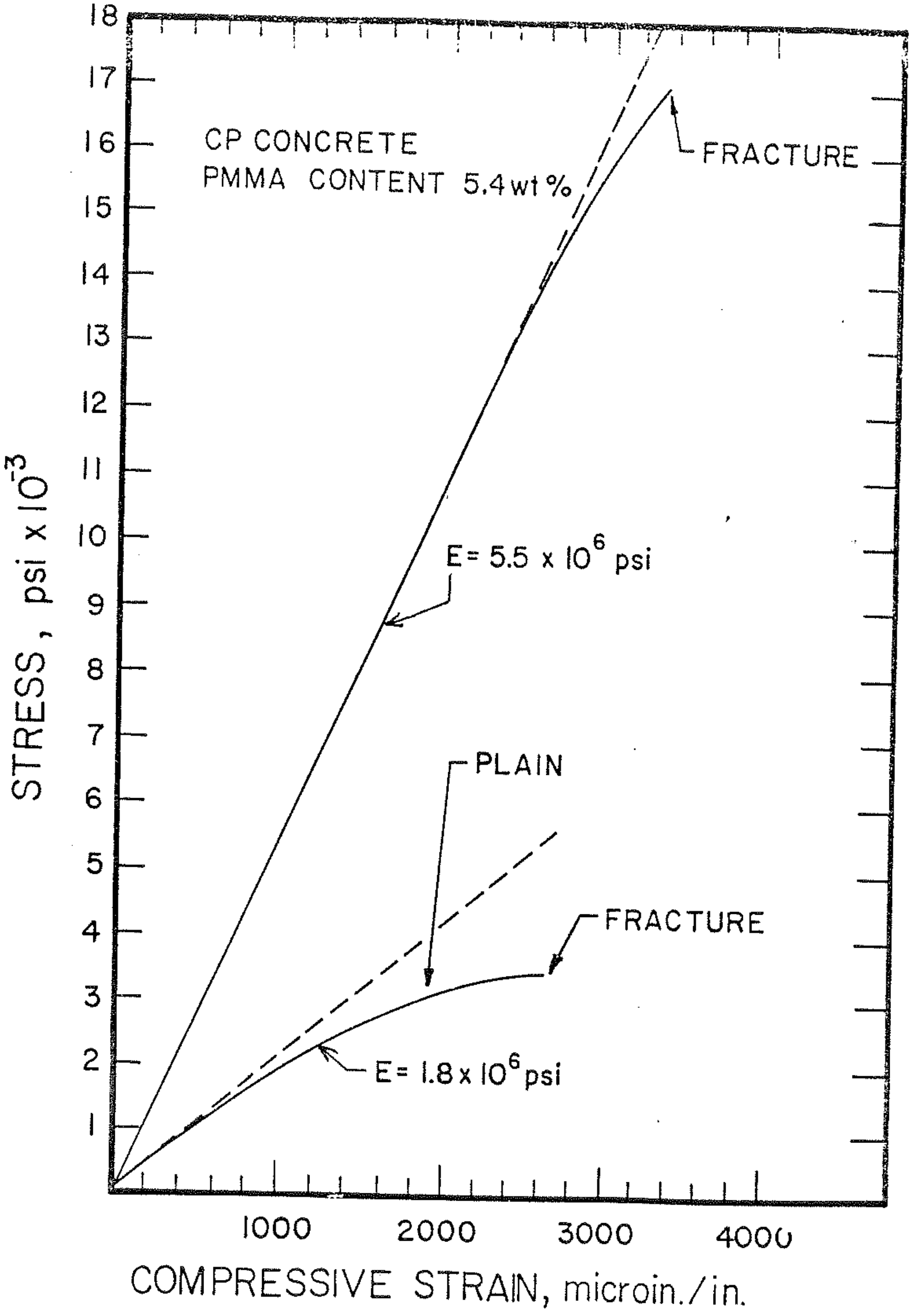

Figure 1. Stress-strain curve of concrete impregnated with polymethyl metacrylate (PMMA), and that of non-impregnated concrete. Specimens: 3 in.x6in. cylinders. (26)

A particular form of PIC is the partially impregnated hardened concrete which has an in-depth polymer coating. (12)(13)(15-17)(20)(27-29) Partially impregnated concretes do not show significant increases in strength but their durability, impermeability, absorption, and the resistance to chemical attacks can be markedly improved.

The obvious disadvantage of the PIC is that it requires a very complex technology and, consequently, it is quite expensive. Also, it is unsuitable for field application. Therefore, it is economical in its present form only in special cases. (30)(31)

Polymer Concrete

Polymer-concrete (PC), or resin concrete as it is called in the European literature, is an aggregate bound with a polymer binder. (32-34) This material can be cast and formed in the field. It is called a concrete because by the general definition, concrete consists of any aggregate bound with a binder. The cheapest binder is portland cement, which costs in the U.S. about 1¢/lb. Polymer can also be a binder, however, it is more costly than hydrated cement, varying from 5¢/lb. upwards to 30¢/lb. for the majority of the polymers of commerce. Polymer filled with aggregate, for example powdered walnut shells in plastics for table tops and furniture products, has been known for a long time. What is referred to with PC is an aggregate filled with a polymer.(8) The main technique in producing PC is to minimize void volume in the aggregate mass so as to reduce the quantity of the relatively expensive polymer needed for binding the aggregate. This is accomplished by grading and mixing the aggregates to minimize void volume. For example to obtain less than 20% by volume voids, a stone aggregate mix of 3/8"-1/2" stone (60.7% by wt.), 20-30 mesh sand (23.0%), 40-60 sand (10.2%) and 170-270 sand (6.1%) are mixed and vibrated together in a form. Monomer is then diffused up through the mixed aggregate and the polymerization is initiated by either radiation or chemical means. There is also another reason for looking forward with interest to the development of this new class of PC materials. The problem with conventional concrete is the alkaline portland cement which forms voids and cracks on hydration with stone aggregate. Water can intrude and crack the concrete. Also, the alkaline cement is deteriorated by acidic materials. With polymer as a binder, most of these difficulties are overcome: the polymer can be made compact with a minimum of open voids, and most polymers are hydrophobic and resistant to chemical attack. The most feasible areas for the use of PC are not those where the polymer concrete replaces other materials but rather where itself is irreplaceable, for instance, in constructions where the concrete is subject to corrosive actions of the enviroment.

As shown in summary Table 1, PC compressive strengths can be obtained as high as with PIC (20,000 psi (1410 kg/cm^2). (26) A silane coupling agent is added to the monomer to improve the bond strength between the polymer and the aggregate. (35-40) The main problems arise from the viscoelastic properties of the polymer. Polymer usually has a low modulus of elasticity which means that it is flexible and exhibits creep properties. This is mainly why plastics are not used alone in structural members. By using polymer as a binder with aggregates some of these difficulties are overcome and there is much hope for developing and important new class of high benefit-to-cost ratio materials. Much more investigation and experience are required with PC to make it a reliably acceptable material of construction.

Table 1 briefly summarizes the properties of concrete-polymer materials produced to date including surface coated (SC) and partially penetrated PIC referred to as coated in-depth concrete (CID). A rating of the strength and a

TABLE 1

Classification of Concrete-Polymer Materials (26)

Type	Polymer loading, wt % PMMA	Density lbs/ft^3	Compressive, strength, lbs/in.^{2}	Strength weight, ratio	Durability	Benefit cost index
Conventional Concrete Control	0.0	150	5,000	33	Poor	1.0
Surface Coating (SC) Paint or Overlay	0.0	150	5,000	33	Limited	1.1
Coating in Depth (CID)	1.0	150	6,000	40	Good	1.3
Polymer Cement Concrete (PCC) Premix	35.0	130	7,500	58	Fair	0.4
Polymer Impregnated Concrete (PIC)						
Standard Aggregate						
a. Undried-Dipped	2.0	153	10,000	49	Fair	1.4
b. Dried-Evac.-Filled	6.0	159	20,000	126	Very Good	2.0
c. Hi-Silica Steam Cured	8.0	159	38,000	240	Very Good	3.0
Lightweight Aggregate						
a. Struct. Lt. Wt. Concr.	15.0	130	25,000	193	Very Good	2.5
b. Insul. Lt. Wt. Concr.	65.0	60	5,000	84	Very Good	2.5
Polymer Concrete (PC) Cementless	6.0	150	20,000	133	Excellent	4.0

benefit-cost ratio are given for each of the materials.

Many details concerning research on and application of polymer concretes can be found in the technical literature published in the U.S. (13)(18)(22)(26)(41-44) and elsewhere. (24)(25)(45-67) It can be seen from this literature that investigators in the Soviet Union have advanced the development of PC to a greater extent than in the U.S., whereas PIC is much more advanced in the U.S. than in the USSR.

Fiber Reinforced Concrete

In the early 1970's, the use of fiber reinforced concrete (FRC) in North America began to emerge from its childhood. It has moved from the laboratory to field applications with the same growing pains that accompany adolescence. (68) The concept of fiber reinforcement is not new, however, Fibers have been used to reinforce brittle materials since ancient times. Long before the European settlement of North America the American aborigines used straw and animal hair to reinforce sunbaked mud. The application of fiber reinforcement to concrete or mortar is also not new. In 1910, Harry Porter from Connecticut, USA, reported that strength increases of nearly eight times resulted from the addition of cut nails and spikes to concrete. (69) In 1914, William Ficklin filed a patent in New York, USA, to cover his abrasive-resistant and spall-resistant concrete which he achieved by mixing an assortment of metal pieces of "tortuous shapes" into concrete. (70)

Until the early 1950's, little enthusiasm was shown for the fiber reinforcement of portland-cement products except for the use of asbestos fibers in precast products. Glass-fiber reinforcement began to emerge then and was followed by steel-and plastic-fiber reinforcement studies in the early 1960's. Most of the efforts involving FRC in the English-speaking world are collected and summarized in several excellent documents. (71-73)

Fiber reinforced concrete can utilize polymers either in that the concrete is a PIC, PC, or PCC and the reinforcement is non-polymer, or that the concrete is a traditional (non-polymerized) concrete and polymer fibers are applied. Of course, the combination of these two, that is, polymerized concrete with polymer fibers, is also possible.

Mortar bars reinforced by chopped steel wire and fiber glass were impregnated with methylmethacrylate which was then polymerized with benzoyl peroxide at 75^0C. Monomer loading was 10 wt%, fibrous reinforcement 2 vol%. Tensile, compressive, and flexural strengths were measured for control specimens (without reinforcement and impregnation), reinforced specimens, impregnated specimens, and impregnated and reinforced specimens. Flexual strength was increased significantly by polymer impregnation (510% of control) and by fiber reinforcement (450% of control); the greatest increase was obtained with both polymer and steel fibers (2820% of control). This increase is probably caused by enhanced fiber paste bonding with polymer impregnation. (74)

Plastic fibers, such as nylon, polypropylene, polyethylene, Saran, rayon acetate, Orlon, and Dacron were studied in the middle and late 1960's as a means to increase the spall and impact resistance of concrete. These fiber types varied considerably in diameter (3 to 630 denier) but generally were no longer than 3 inches. The types and amounts of these fibers used in concrete has been on an intuitive and empirical basis.

All of the plastic fibers tend to increase the viscosity of the concrete mixtures to a more or less degree. The increased viscosity is the factor which limits the amount of fibers that can be added to a given mixture. Some varieties of nylon, polypropylene, polyethylene, and Saran have a lesser effect and can be added in greater quantities. In general, the percent by volume of nylon, polyethylene, and Saran does not exceed 3 percent while the polypropylene does not exceed 7 percent.

There is a difference of opinions about the effects of the synthetic fibers on the strength of the concrete. Some studies have indicated that the flexural strength of mortar is increased by a factor of 3 with the addition of nylon fibers, while other studies indicate little or no change in flexural and compressive strengths due to the presence of the nylon. All the studies agree, however, that the concrete containing plastic fibers holds together much better after cracking and failure of the concrete begins with much more energy being absorbed to failure than is the case of the concrete containing no fibers. This is due to ability of the flexible plastic fibers to firmly anchor themselves in the hardened concrete and elongate considerably under load. This behavior is indicative of good impact resistance, and experimental data are available to substantiate this.

Some synthetic fibers, such as rayon acetate and Dacron, appear to be adversely affected by the alkalinity of the cement and may not be suitable on a long-term-use basis.

Some nylon fiber is being used as a filler in cement pastes applied in the grouting of deep well casings. Polypropylene fibrillated film fibers are presently being used as a concrete reinforcement in the United Kingdon. These 6,000 to 26,000 denier fibers range from 1/2 to 4 inches in length and are usually used at concentrations from 0.2 to 0.5 percent of the concrete weight. Panels, slabs, piles, flotation units, and swimming pool linings have been made with the polypropylene fibrillated fibers. (70)

The proper combination of polymerized concrete with a suitable polymer fiber will probably eliminate some of the problems of fiber reinforcement. At present, however, nothing more can be said about this due to the lack of pertinent experimental evidence.

Applications of Polymer Coatings

Polymer can be used to coat the surface of the hardened concrete, the surface of the reinforcement before it is embedded into the concrete, and the surface of the aggregate, especially that of the coarse aggregate, before batching concrete. Of course, any combination of these three is also possible.

The purpose of coating the surface of hardened concrete with a polymer is to achieve a sealing, either for increasing the wear resistance (75), or increasing the chemical resistance (76), or for the reduction of absorption (18), or for the reduction of permeability (77)(78), or for decorative purposes (79), or for repair (42)(80-83). The "paint-on" technique has been proved effective for coating, although other techniques, such as plastering, has also been used. A proper coating technique usually assures the adequate bond between the polymer and the concrete surface. (84) In one case, for instance, polyester-styrene mixture was diluted with styrene monomer to reduce the viscosity. Then the mixture was applied to the surface of the hardened concrete with a paint brush or a roller. The depth of penetration obtained by this method depends on the viscosity of the mixture and the number of coats applied but three-fourth inch is not unusual. The resin can be polymerized by introducing a catalyst-accelerator system to the resin prior to application, or by the thermal-catalytic or radiation method. Conventional concrete coated in this manner showed only 0.3 percent by weight water absorption. (18)

Coating the reinforcement with a suitable polymer has as its purpose either to increase the bond between the reinforcement and the hardened paste, or to protect the reinforcement from corrosion, or both. Experiments have demonstrated that resin-coated steel bars behave in concrete like deformed bars as far as bond is concerned. (85) The U.S. Bureau of Standards just recently completed a comprehensive series of experiments with concrete elements reinforced with epoxy-coated steel bars and their primary findings were quite favorable. (86) The coating of glass fibers appears also advantageous. (87)

Similar benefits are expected from using polymer-coated aggregate particles in concrete. The improvement in the bond between the cement paste and aggregate surface may improve the concrete strength, especially the flexural and tensile strengths. (88-95) Of course, the strength reducing effect of harmful coatings on the concrete aggregate, such as a clay film or grease layer, has been recognized long time ago. The other aspect, the protective capability of polymer coating may improve the durability of certain aggregates of doubtful frost resistance because it reduces the water absorption of the aggregate.

Further details concerning the polymer coating of concrete aggregates will be discussed later in another part of this report presenting our own experiments.

General Description of Polymer-Cement Concrete

Polymer-cement concrete (PCC), or polymer-modified concrete is prepared by integrally mixing water solutions or emulsions of polymers or prepolymers or polymerizable monomers with cement and aggregate. The water in the emulsion or solution hydrates the cement; the chemicals should form a polymer before or during the hydration of the cement and enter into the structure of the cement paste. The chemicals are used here in a way similar to the use of concrete admixtures but there are also differences. These differences are that (a) the amount of chemicals in PCC is much greater than the usual amount of any admixture; and (b) the polymer in the concrete may supplement the cement in binding the mineral aggregate through the adhesive and cohesive properties of the polymer.

The great advantage of PCC is that it requires a much simpler technology than PIC and is less expensive than PC; meanwhile it maintains some of the good properties of these materials. In most cases it does not require sizeable additional capital investment. It is far more suitable for field applications than the other types of polymerized concretes. For this reason the introduction of various organic materials to concrete mixtures has been tried numerous times in the past. The results obtained have been either disappointing or relatively modest in improvements of strength and durability. In many cases materials poorer than the plain concrete were obtained. Under the best conditions compressive strength improvements over comparable plain concrete of approximately 50% have been obtained with relatively high polymer concentrations of 30% or more. This was explained by the fact that the organic materials applied were incompatible with aqueous systems and in many cases, interfered with the hydration process of the cement. (12)(26)

A promising approach for eliminating these problems was found in our research which will be discussed later in this report. Before that, however, a brief review of literature is given concerning the state of the art of the two main types of PCC, namely polymer-cement concrete with premix polymerization, and polymer-cement concrete with post-mix polymerization. (96)

Polymer-Cement Concrete with Premix Polymerization (25)

This is a PCC where an emulsion or a solution containing water and a previously polymerized material or materials of high molecular weight, is mixed to the fresh concrete.

1. Use of Polymer Suspensions. The most widely used type of PCC is the one that contains aqueous suspensions of polymers, such as polyvinyl thermoplastics or latexes (that is, rubbers). It is likely that the first detailed description of this type of PCC was published in 1953. (97)

The first thermoplastic used in making PCC's was polyvinyl acetate, but work has also been done on adding other high-molecular-weight vinyl compounds--polyvinyl chloride, polystyrene, polyvinyl propionate, polyacrylates, and various copolymers--to cement. (96)(98)(99) In these compounds, the carbon chain usually contains the $-CH_2-CH-$ group, to which other atoms or radicals are attached.

Compositions of rubber and cement were originally made from natural latex which is not in very abundant supply. With the development of industrial synthesis of elastomers, the use of divinylstyrene, polychloroprene, and others was introduced. At ordinary temperatures rubbers have a small modulus of elasticity, 100 kg/cm^2 (9810 kPa) or lower, and/or a high index of relaxation and extensibility (up to 2000%)

Adhesion and cohesion are also important properties of polymers from the standpoint of their suitableness for making PCC's. One reason that polyvinyl acetate has been preferred in many investigations is that it is a polymer with a polar structure, possessing high adhesive strength.

Natural latexes are the modified juices of rubber plants stabilized with natural proteins, soaps, and lipids and containing solid particles averaging 1.5μ in size. These particles are negatively charged. Synthetic latexes and emulsions, made by emulsion polymerization of monomers, may have particles with dimensions from fractions of a micron (rubber latexes) up to more than 10μ (thermoplastic emulsions). The dimensions of the particles in the emulsions affect the rheological properties of the mixtures and the strengths of the PCC's made from them; results are best when the solid-particle dimensions are 1 to 5μ.

Stabilization, that is, preventing of premature coagulation of latexes and emulsions when they are mixed with cement, is one of the chief problems encountered in formulating polymer-cement concretes with emulsions. Therefore, the possibility of obtaining a good polymer-mineral binding, and thus the good quality of the concrete product, depends on the type and amount of stabilizer selected. The simple addition of cement to latex leads to breakdown of the latter, with separation of the polymer particles. Rapid coagulation is induced by the multivalent ions (chiefly Ca^{+++}) formed from the cement and by the incompatibility of the particles of cement and polymer, which are oppositely charged. The addition of stabilizers keeps emulsions and latexes from separating out before the concrete has started to set. A good discussion of stabilizers is presented in a paper by Solomatov. (25)

The addition of polyvinyl acetate and some other emulsions to concrete mixtures changes their rheological properties. (99-102) Plastification of the mixture is accompanied by an increase in viscosity. Concretes with a 1/3 cement-aggregate ratio, containing 20% vinyl acetate-dibutyl maleate copolymer and having a w/c varying from 0.46 to 0.5 by weight, were so fluid that there was no point in determining the consistency by the slump-cone method. However, when the mixture was placed in forms and subjected to heavy vibration at standard frequencies, the voids in the samples were not completely removed.

There are reports that with polyvinyl chloride latexes the amount of water may be decreased by a factor of 3 without decreasing the mobility of the mixture. For cement-sand compositions with a ratio of 1/3, identical mobilities were obtained by adding to the mixture 15 and 25% polychloroprene, which resulted in, respectively, 40 and 60% decrease in the w/c as compared with a similar mixture but without polymer. When natural latex was used (P/C = 0.2), the indicated mobility was obtained with a w/c value lower by a factor of 2.

The maximum strength of PCC's with a cement-aggregate ratio of 1/3 is obtained with 15 to 20 wt.% polymer. This value, which has been repeatedly confirmed in studies on concretes containing thermoplastics and rubbers, has a physical basis, since with it the continuity of the cement gel in the structure is maintained, but the polymer fills the small pores and capillaries and covers the cement concretions and filler particles. With an increase in the P/C ratio, the polymer binder becomes the predominant material, and the new formations in the concrete create irregular inclusions that affect the strength. For polyvinyl acetate-cement concretes with a cement/sand ratio of 1/5 and lower, optimum properties are found with an increase in the P/C ratio; with fatty compounds the tendency is reversed.

A PCC containing only a few-percent polymer is no stronger--and may even be weaker--than a concrete with no polymer. (103)(104) The effect of very small amounts (less than 1%) of polyvinyl acetate-vinyl acetate copolymer emulsions is similar to that of the commonly used concrete plasticizers.

The use of a suitable polymer emulsion has particularly beneficial effects on the flexural, tensile and bond strengths of the PCC. For instance, the DOW Latexes 460 and 464 (105) as well as other similar latex emulsions (106-110) can, reportedly, increase these strengths up to 200 percent or even more despite the fact that the modulus of elasticity of the concrete is reduced significantly by these emulsions. Several pertinent results are shown in Table 2.

The change in the compressive strength is less significant than the change in the flexural strength; in fact, in many cases dry polyvinyl acetate-cement concrete is not so strong as ordinary concrete cured under wet conditions. (98) These facts indirectly indicate a limited hydration of the cement upon its combination with polyvinyl acetate.

The strength of polyvinyl acetate-cement concrete cured in very humid air or in water decreases continuously as the polymer content increases. Excess moisture hinders the adhesive hardening of the conglomerate and causes swelling

TABLE 2

Typical Mechanical Properties of DOW Latex-Modified Mortars (105)

Properties and Cure Time	DOW Latex 460 Formulations 10% Latex in psi**	15% Latex in psi	20% Latex in psi	Unmodified Control in psi*	DOW Latex 464 Formulations 15% Latex in psi	20% Latex in psi	25% Late in psi
Shear Bond Strength							
2 day	390	330	280	---	280	510	500
3 "	---	390	300	---	---	600	510
4 "	480	500	440	---	500	>650	>650
5 "	---	530	>650	---	---	>650	>650
6 "	---	600	>650	---	---	>650	>650
7 "	620	>650	>650	---	530	>650	>650
14 "	630	>650	>650	---	560	>650	>650
28 "	630	>650	>650	50-200	>650	>650	>650
28 "/7 Wet	300	330	370	50-200	400	>650	>650
Compressive Strength							
2 day	1940	1670	2080	1560	2330	3300	2420
4 "	2980	2630	2760	2720	3540	4570	3620
7 "	3380	3220	3360	3500	4300	5770	4400
14 "	3730	3750	4150	4200	5160	7150	8000
28 "	4000	4130	4800	4480	6180	8430	9670
28 "/7 Wet	2890	3000	3680	4430	3960	7150	7560
Tensile Strength							
2 day	390	400	480	220	340	470	600
4 "	480	600	640	270	540	750	790
7 "	550	670	750	320	670	810	880
14 "	600	740	830	350	760	870	970
28 "	630	790	870	380	820	910	1000
Flexural Strength Modulus of Rupture							
1 day	---	850	740	---	---	910	970
2 "	950	1080	1070	---	1040	1190	1280
4 "	1010	1210	1330	450	1340	1360	1490
7 "	1090	1380	1510	660	1520	1550	1600
14 "	1120	1520	1680	740	1710	1740	1770
28 "	1130	1620	1730	820	1750	1820	1900
28 "/7 Wet	640	790	770	980	1200	1100	1150
Elastic Modulus (all values are $x10^6$)							
1 day	---	1.38		---	---	1.32	1.35
2 "	---	1.43		---	---	1.68	1.62
4 "	---	1.55		2.74	---	1.82	1.65
7 "	---	1.72		2.85	---	2.10	1.77
14 "	---	1.80		3.04	---	2.24	1.99
28 "	---	1.92		3.40	---	2.52	2.25
28 "/7 Wet	---	1.40		3.74	---	2.44	1.98

28 day/7 Wet=28 days dry cured at 73°F and 50% relative humidity followed by 7 days water immersion at 75°F; tested wet. Other specimens were dry cured at 73°F and 50% relative humidity; tested dry.

*The unmodified control mortar has a sand to cement to water ratio of 3 to 1 to 0.50 by weight. These samples were cured at 73°F and 100% relative humidity.

**Note for metrication: 100 psi is equivalent with 690 kPa in SI units.

and loosening of hydrophilic polymer within the structure. Especially characteristic is the decrease in compressive strength ; for instance, with a 20% polymer content, the compressive strength is only a third or a fourth of the value of that cured in dry air.

Moist heat and heat alone have a stimulating effect on the curing of concretes containing thermoplastics and elastomers. Steaming intensifies hydration, but the products are not so strong as those cured in dry air. A 2- 3-hr. steam treatment of a polychloroprene-cement concrete with subsequent curing dry air proved to be feasible. Polychloroprene-cement concrete cured in dry air at 40°C was 30% stronger at the end of 28 days than when cured at 20°C.

Curing of PCC's is accompanied by significant shrinkage. When small amounts of latex SKS-65 were introduced in a test run, the shrinkage occurred in the first 10 days and did not exceed values typical for ordinary concrete, but at P/C values of 0.2 and higher, shrinkage increased sharply.

Temperature dependence of the strength of concretes containing thermoplastics and elastomers is expected since the properties of these plastics depend on the temperature of the medium. For instance, heating to 45°C of concrete containing a thermoplastic decreases the modulus of elasticity and bending strengths 2-fold. The hardening at lower temperature is less marked than in ordinary concrete, apparently because of incomplete freezing of the bound water and the elasticity of the polymer in this temperature range.

The properties of hardened PCC's are determined largely by the curing regime, or, more precisely, by the heat and moisture conditions. In contrast to ordinary concrete, high strength and improvements in other physical and mechanical properties of the product concrete result from curing in dry air, and these properties decrease with increasing humidity. However, quantitative relations have not been established.

Polymers usually slow down the process of structure formation in the cement paste. The setting time of mixtures containing plasticized polyvinyl acetate is 1.3 times that of ordinary concrete when $P/C = 0.05$ and 1.6 times when $P/C = 0.2$. The rate of setting of mixtures of rubber and cement, i.e., the kinetics of their structure formation, is determined by the type of stabilizer used. They are stiffening rapidly when electrolytes (e.g., potash) are used which is accelerated even more by addition of calcium chloride. Addition of 1 and 4% $CaCl_2$ has been shown to decrease the setting time of polychloroprene-cement composites ($P/C = 0.2$) 2- and 3-fold, respectively.

At room temperature, creep deformation in PCC samples is more than twice that in ordinary concrete. When loads were placed on PCC's at 50°C, deformation increased catastrophically, and they failed rapidly. Creep increases also sharply in PCC's when they are moistened because of swelling and plastification of the polymer.

The water resistance of PCC's frequently decreases with increasing penetrability. Water that penetrates concrete has both a physical and a chemical action on the material. Polyvinyl acetate swells in water, and in an alkaline medium the saponifiable ester bond, -CO-O-, reacts to form polyvinyl alcohol, which dissolves in the water.

Polyvinyl acetate-cement concretes cured under optimum dry-air conditions decrease in strength when immersed in water. Decreases in bending and tensile strength are especially high, and these strengths may reach levels typical for ordinary concrete. Subsequent drying restores the strength to its initial value, but significant volume deformations occur in the transformation, probably not without affecting final concrete properties.

Some of the PCC's made with polymer emulsion show improved resistance to freezing, while others deteriorate more rapidly, especially under continuously wet conditions. Similarly, the resistance of PCC's to chemicals depends primarily on the type and amount of polymer added.

The wear resistance and the impact resistance of PCC's are usually increased significantly by using suitable polymer emulsions. (101-102)

A summary of the properties of PCC's made with suspensions of premix polymerization is given in Table 3 after Kreijger. (96) He presents also a wealth of other related test results in the same paper.

2. Water-solutions of Polymers. The mechanism of combination of water-soluble resins with cement differs theoretically from that described above for high-polymer emulsions. The kinetics of the setting process are controlled so as to convert the resin to an insoluble solid inside the hardening cement paste. The synthetic polymers added to concrete as aqueous solutions are chiefly thermosetting resins. An exception is the polyvinyl alcohol which is a water-soluble thermoplastic polymer.

Experiments have been done on introducing carbamide (urea-formaldehyde) resins into concrete as water solutions. Fine-grained concrete (1/3) has been made with portland cement and aqueous resin solutions of densities of 1.04, 1.05, 1.07, 1.10, and 1.14 g/ml. The samples were cured under moist conditions for 14 days, after which they were heated for 7 days at 60°C. Results were best with resin solutions of density 1.05 g/ml. With the higher resin concentrations--1.10 and 1.14 g/ml--the strength of the formed concrete decreased sharply. With the optimum amount of resin, the compression strength at 28 days was 30 to 50% greater than that of controls, and the tensile strength was 60 to 70% greater. Further, the pentrability of the resin-containing samples was lower and the stability greater than that of ordinary concrete.

Interesting work has been done recently in the Soviet Union on addition of

TABLE 3

Ratios of Properties of PCC's With Suspension to Those of the Reference Mortars (Concretes) of the Same Workability. (96)

Properties	PVAc		VC		PVP
	$\frac{P}{c} \gtrsim 0.015$	$\frac{P}{c} \gtrsim 0.1\text{-}0.2$	$\frac{P}{c} = 0.1\text{-}0.2$		$\frac{P}{c} = 0.1\text{-}0.2$
	concrete	mortar	Vinylidene chloride	Vinyl-vinylidene chloride	
(1)	(2)	(3)	(4)	(5)	(6)
time of setting	-	increased	increased	-	increased strongly
w/c reduction	= 0.15	= 0.10	0.54-0.60	0.45-0.34	0.15
air content	increased	not changed	increased strongly	-	increased strongly
flexural strength-dry 28d	1.0-1.1	1.24-2.42	1.33-1.50	1.80-2.67	1.80-2.47
" " -wet 28d	0.92-1.39	0.25-0.75	0.53-0.60	0.78-1.65	1.00-1.10
compressive strength-dry 28d	0.90-1.29	0.59-1.55	0.69-0.80	2.10-2.34	1.20-1.25
" " -wet 28d	0.89-1.28	0.25-0.85	0.27-0.33	0.95-1.10	0.68-0.86
bending-28 days-dry	-	3.10-4.75			
bending-28 days-wet	1.35-2.09	-			
compression-28 days-dry	-	1.50-1.85			
compression-28 days-wet	1.67-1.75	-			
tension-28 days-dry		0.66			
tension-28 days-wet		1.25			
shrinkage-28 days	0.96-1.37	1.2-2.17	1.10-1.40	0.90-0.95	1.20-1.40
swelling-28 days	-	4.5-11.75	2.15-3.5	-	2.15-2.95
water absorption	-	0.48-0.74	increased	0.22-0.79	reduced
adhesion strength-dry	-	0.90-1.90	2	1.36-2.35	2.20
" " -wet	1.14-1.30	0.70-1.25	1.5	-	1.30
abrasion resistance	1.00	2.00	2	increased strongly	4
shock resistance	-	1.6-2.8	-	1.45-2.10	increased
durability-indoors	good	good?	good	good	good
durability-outdoors	good?	bad	bad	bad	good?

TABLE 3 (continued)

	AC $\frac{p}{c}$ = 0.1-0.2		Ethylene glycol $\frac{p}{c}$ = 0.02	Rubbers $\frac{p}{c}$ = 0.1-0.2				Epoxy $\frac{p}{c}$ = 0.10
Properties	Methyl-meta-crylate (7)	Polyacrylate ester (8)	(9)	NR (10)	SB (11)	NBR (12)	CR (13)	(14)
time of setting	decreased	-	-	-	increased	-	-	-
w/c reduction	0.46-0.52	0.34-0.50	-	0.53-0.38	0.26-0.56	0.21-0.36	0.04-0.29	-
air content	increased strongly	-	-	-	increased sometimes	-	-	-
flexural strength-dry 28d	1.80-2.00	2.03-3.00	-	0.67	1.15-3.06	2.2-2.3	1.4-3.0	1.06-1.9
" " -wet 28d	0.43-0.47	0.95-1.00	1.25	0.4-1.3	0.6-1.3	1.1-1.5	0.7-1.1	0.9-1.3
compressive strength-dry 28d	1.05-1.10	2.19	-	0.5	0.6-2.7	1.9	2.3	0.64-1.6
" " -wet 28d	0.13-0.33	0.72	1.17	0.25	0.3-1.4	2.0	1.1	0.9-1.3
bending-28 days-dry			1.39					
bending-28 days-wet			1.12					
compression-28 days-dry								
compression-28 days-wet								
tension-28 days-dry								
tension-28 days-wet								
shrinkage-28 days	1.10-1.20	1.33	0.44	0.9-1.1	0.8-1.2	0.4	1.3	0.9
swelling-28 days	2.10-3.05	-	-	-	4.2-9.0	-	-	-
water absorption	reduced	0.21-0.68	water tightness increased strongly	0.32-0.83	0.11-0.86	0.2-0.7	0.6-1.0	-
adhesion strength-dry	3	3	-	0.9-2.7	1.6-3.8	2.2-2.5	0.7-1.4	-
" " -wet	1.85	-	-	-	1.0	-	-	-
abrasion resistance	3	increased	-	increased strongly	increased strongly	increased strongly	increased strongly	-
shock resistance	-	1.81-2.5	-	3.9-10.4	2.3-9.4	3.6-3.0	2.3-5.2	-
durability-indoors	good	good	good	good	good	good	good	good
durability-outdoors	bad	good?	good	bad	good?	good	good?	good?

water-soluble carbamide resin S-89 and epoxy resins DEG-1 and TEG-17 to concrete. Mechanical properties of these concretes are best when the amount of resin is 2% of the weight of the cement, i.e., a smaller amount of resin than is used in PCC's containing aqueous dispersions of polymers. Addition of water-soluble resins allows a decrease in the water-cement ratio to 0.29 without detriment to the workability characteristics of the mixtures. (25)

A distinctive property of PCC's containing water-soluble carbamide and epoxy resins is their capability of being rapidly cured under wet conditions. Even with aqueous curing, the strength of these concretes increases more rapidly than that of concretes without polymers. Results are better when the curing regime consists of an initial period in water or in air with a 90% or high R.H. and then in air with a 50 to 70% R.H.

Water-soluble resins, which harden as the cement sets, increase the elasticity of concrete but do not increase its deformability under a compressing load. Wet curing does not decrease the strength of PCC's containing these resins, and tensile strengths are high. It has been shown that addition of S-89 resin to the mix increases the deformation limit of fine-grained concrete almost 3-fold. Modulus-of-elasticity values that have been found for such PCC's are in kg/cm^2 (kPa): 256,000 (25.1 x 10^3) for concrete without polymer; 107,500 (14.3 x 10^3) with 16.6% latex SKS-65-GP.

Information on creep in PCC's containing water-soluble resins is limited. Concrete containing S-89 and DEG-1 resins showed creep at load values that were 50% or even 25% of those for ordinary concrete.

Polymer-Cement Concrete with Post-Mix Polymerization

This is a PCC where polymerizable components of a monomer system or prepolymer system either in the form of emulsion or solution, are mixed integrally with the fresh concrete and the polymerization is obtained along with the hydration of the cement. According to the reviewed literature, to date investigations concerning this type of PCC have been confined to small-scale feasibility studies of limited success. The reasons for this are that (a) the alkali enviroment of the fresh cement paste may have reactions with the monomers that interfer with the hydration of the cement; and (b) the presence of water in the PCC may interfer with the polymer-aggregate bond.

1. Use of Emulsion Systems. Several experiments are reported in the literature for mixing various monomers to the fresh cement paste or mortar where the polymerization was produced either by irradiation or by heat treatment of the concrete. (10)(18)(111) Disappointing initial results as well as the complexity of the technology have precluded further investigations and make it unnecessary to deal with the results here in details.

Another, much simpler approach is to produce the polymerization of the monomers in the concrete by chemical means, that is, without any irradiation or treatment. Quite a few monomers, initiators and promoters have been tried out but according to the reported results, only epoxy resins have shown some promise of increasing the strength of concrete. A few pertinent experimental results with various monomers are shown in Table 4 but resorcinol-formaldehyde systems or acrylamide catalyst systems did not provide better results either. (112) Several experiments with epoxy systems are discussed below.

Lezy (113) first mixed the epoxy resin and:

a) part of the cement and mixed this mixture with cement paste for grout;

b) siliceous or clacareous aggregate material and mixed this mixture with standard mortar and 45% reduced water content.

The amount of epoxy he used in concrete varied from 4.6 to 9.2 percent of the weight of the cement. Under wet curing conditions ($20^{\circ}C/95\%$ rel. hum.) the use of suitable epoxies produced increases of 1 to 17 percent in the compressive

TABLE 4

PCC With Various Monomers (112)

Sand: 100 g; Cement + monomer: 40 g; Water: g cement/2.

Monomer (1)	% Monomer (of Cement + Monomer) (2)	Treatment and Remarks (3)	Compressive Strength in psi (kPa) (4)
None	--	6 days R.T. 7 hrs. 100°C	5,660 (39,000)
Laminac EPX 289-4 + Norox W-60 (Lupersol DSW) (believed to be MEK peroxide)	10	6 days R.T. 7 hrs. at 100°C (required several days to harden)	3,380 (23,300)
Laminac DP 289-4 + Benzoyl Peroxide	10	6 days R.T. 7 hrs. at 100°C (soft for several days)	1,730 (11,900)
Laminac EPX 295-1 + Norox W 60	10	6 days R.T. 7 hrs. at 100°C (soft for several days)	1,685 (11,600)
Styrene	10	6 days R.T. 7 hrs. at 100°C (concrete set overnight)	5,000 (34,500)
Styrene	50	6 days R.T. 7 hrs. 100°C (liq. sep. out on surface initially, before setting of concrete)	1,530 (10,500)
Styrene + Divinylbenzene (5%)	10	6 days R.T. 7 hrs. 100°C	5,000 (34,500)
Styrene + Divinylbenzene (5%)	25	6 days R.T. 7 hrs. 100°C (some liq. sep. out initially, before setting of concrete)	2,950 (19,600)

TABLE 4 (continued)

Monomer (1)	%Monomer (of Cement + Monomer) (2)	Treatment and Remarks (3)	Compressive Strength in psi (kPa) (4)
Styrene (70%) Polystyrene (30%)	50	6 days R.T. 7 hrs. 100°C (sticky on bottom. Hardened in 7 hrs. at 100°C.)	3,800 (26,200)
Acrylonitrile	10	6 days R.T. 7 hrs. 100°C (Liq. sep. out for several days)	4,500 (31,100)
Methyl Methacrylate + 1% Ethyleneglycol Dimethylacrylate (80%) + Polymethyl Methacrylate (lucite) (20%)	10	6 days R.T. 7 hrs. 100°C	3,300 (22,800)
"	20	6 days R.T. 7 hrs. 100°C	1,300 (9,000)
"	25	6 days R.T. 24 hrs. 50°C 24 hrs. 80°C	samples broke when removed from mold
"	50	6 days R.T. 24 hrs. 50°C 24 hrs. 80°C (soft after 24 hrs.)	1,600 (11,000)
"	75	6 days R.T. 24 hrs. 50°C 24 hrs. 80°C (soft after 24 hrs.)	1,420 (9,800)
"	100	6 days R.T. 8 hrs. 40°C 24 hrs. 80°C (soft after 6 days)	17,000 (117,200)

strength of his concrete, and 30 to 57 percent in the flexural strength at the age of 28 days.

Valenta (114) used epoxy- emulsions with different types of emulsifiers, different concentrations of these emulsifiers, different resin contents in the emulsion and different accelerators and other agents. It was found that the moment the accelerator is added, has an importent effect on the strength properties.

Under dry curing conditions (20°C/60% rel. hum.) with the best type of emulsion (5% concentration of emulsifying agent and 10% epoxy in the emulsion), the flexural strength at 90 days was increased by 60 percent, the compressive strength decreased by 12%, and the shrinkage at 56 days decreased by 38 percent. After 28 days these values were 6, 36, and 18 percent respectively.

Valenta reported also a decrease of 18 percent and 26 percent in shrinkage after 28 and 56 days, respectively. Lezy reported at 28 days a decrease in shrinkage varying from 5 percent to 40 percent.

Also the water permeability was reduced by the epoxy as in this case no permeability took place at 60 bars, while for the reference mortar at 30 bars after 1.05 hours water came through these specimens.

Frost resistance of mortars with epoxy was increased after 50 cycles (-20°C- +20°C each 6 h); no decrease in strength was measured when epoxy was used, while for the reference the strength was reduced by 30 to 40 percent. No remarks are made regarding the physico-chemical behaviour. (113)

Raff reports (112)(115) that the incorporation of at least 30 percent of the cement as epoxy resin improves the compressive strength of cured mortar (Table 5), especially if the cured sample is heat treated to post cure the resin. The compressive strength curve shows a dip at 12.5 percent to 25 percent resin below the control specimen (fig. 2). This may be due to the fact that when the amount of resin is too small to form a continuous phase, the resin merely acts as an impurity and thus decreases the compressive strength. When sufficient

TABLE 5

PCC With Epon 828 (19, 112)

Cement in wt. % (1)	Epon 828 in wt. % (2)	Treatment of Specimen (3)	Compressive Strength in psi (kPa) (4)
100	0	6 days 100% R.H., R.T. 7 hrs. 212°F	5,660 (39,000)
75	25	6 days 100% R.H., R.T. 7 hrs. 212° F	4,500 (31,000)
50	50	6 days 100% R.H., R.T. 7 hrs. 212°F	7,780 (53,600)
25	75	6 days 100% R.H., R.T. 7 hrs. 212°F	11,100 (76,500)
25	75	Overnight at R.T. 2 hrs. 149°F 4 hrs. 302°F	13,600 (93,700)
0	100	6 days 100% R.H., R.T. 7 hrs. 212°F	4,525 (31,200) ("Explodes" on testing)
0	100	Overnight at R.T. 2 hrs. 149°F 4 hrs. 302°F	19,100 (132,000)

All specimens contained sand (100 g), cement plus Epon 282 (40 g) and water (g cement/2).

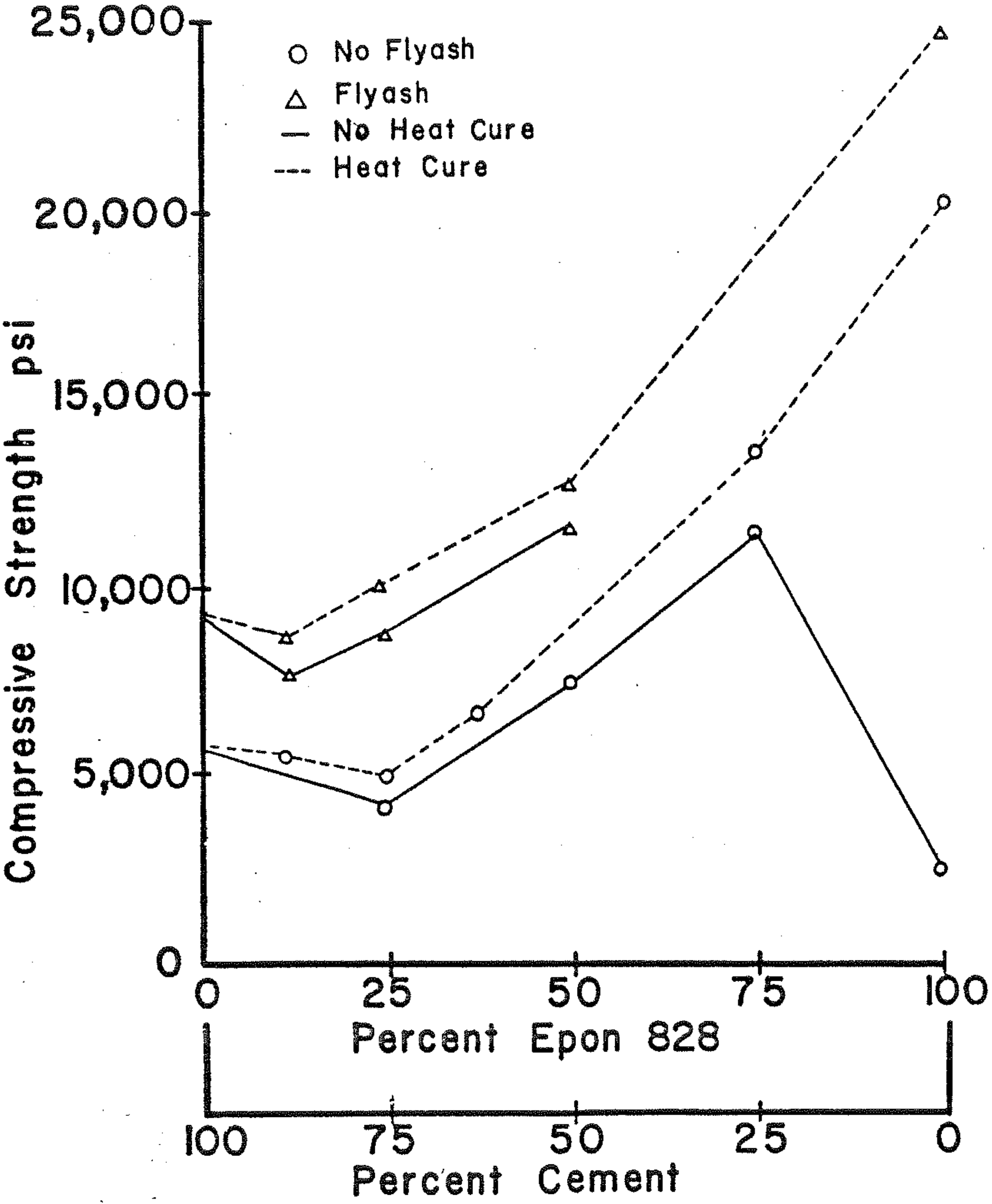

Figure 2. Effect of cement-epoxy ratio on the compressive strength of polymer-cement mortar. (19)(115)

resin is present to form a continuous phase, the strength of the concrete markedly increases.

Samples containing flyash showed significantly improved compressive strengths even when no epoxy resin was present. The addition of resin above 25 percent still further improved the excellent compressive strength gained by the addition of flyash. (Table 6). The effect of other fillers is less advantageous on the mortar strength. (Table 7) While the values he obtained for the degree of hydration are not really consistent, the values are high enough to indicate that the presence of epoxy does not appreciable inhibit the hydration of portland cement.

The Celanese Coatings Company has also developed a two-part epoxy for commercial purposes, called Epi-Top PC-10. This is emulsifiable without any extra surfactant and is compatible with portland cement paste. (116) A more detailed description of this epoxy is given in Part II of this report. Their experiments show sizable increases in strengths, particularly in the tensile and flexural strengths of concretes made with this epoxy. Some of the pertinent test results are presented in Table 8 and in Figure 3.

2. Use of Water Solutions. Extensive laboratory work has been done in the Soviet Union on concrete containing furfuryl alcohol. (25)(117) Aniline hydrochloride reacts with furfuryl alcohol to form an insoluble polymer inside the cement. Upon addition of the optimum amount of aniline hydrochloride--about 15 percent in furfuryl alcohol--the process of structure formation in the cement paste is slowed down as a result of the surface activity of the furfuryl alcohol (FA) and decrease in the pH. The addition of $CaCl_2$ compensates this slowing down.

Solomatov reports also an experiment in which concrete containing aniline and furfuryl alcohol was prepared in standard equipment used in concrete technology. Calcium chloride was added to water and then the aniline hydrochloride-furfuryl alcohol solution. This mixture was used in making the concrete. Spade vibrators

TABLE 6

PCC With Epon 828 Plus Flyash (19, 112)

Cement in g	Epon 828		Water in g	Flyash in g	Treatment of Specimen		Compressive Strength in psi*
(1)	in g (2)	in% (3)	(4)	(5)	6 days R.T. 100% R.H. 7 hrs. 212° (6)	4 hrs. 302°F (7)	(8)
40	--	---	22.0	30	X		9,700
35	5	12.5	19.0	30	X		8,150
35	5	12.5	19.0	30	X	X	9,700
30	10	25	16.0	30	X		9,200
30	10	25	16.0	30	X	X	10,200
20	20	50	10.5	30	X		11,800
20	20	20	10.5	30	X	X	12,600
--	40	100	----	30	X	X	24,800

All samples contained 100 g sand.

* Note for metrication: 100 psi is equivalent with 690 kPa in SI units.

TABLE 7

Effect of Fillers on Epon-828-Cement Concrete (112)

Filler (30 g) (1)	Epon in g (2)	Cement in g (3)	Water in g (4)	Compressive Strength in psi* (5)	Filler Particle Size in μ (6)
None	10	30	15	4,500	----
Flyash	10	30	16	9,200	10-20
Min-U-Sil	10	30	25	7,800	5
Pptd. Silica	10	30	20	6,000	10-50
Magnesium Oxide	10	30	40	4,700	10-30
Idaho Clay	10	30	30	4,900	5-20
Mica	10	30	40	1,750	30-50
Silica Gel	10	30	17	3,500	5-20

All samples contained 100 g sand.

*Note for metrication: 100 psi is equivalent with 690 kPa in SI units.

TABLE 8

Properties of Concrete Containing Epi-Top PC-10 Versus Control (116)

Property (1)	With Epi-Top PC-10 (2)	Control (3)
Workability:		
Slump in inches, (cm)	6 (15)	1 (2.5)
Working Life (minutes)		
@ 75°F	90	80
@ 100°F	50	35
Strengths (1):		
Tensile in psi (kPa)		
Tested Dry	820 (5650)	440 (3030)
Tested Wet (2)	730 (5050)	460 (3170)
Flexure in psi (kPa)		
Tested Dry	1650 (11,400)	850 (5860)
Tested Wet (2)	1620 (11,200)	860 (5930)
Compressive in psi (kPa)		
Tested Dry	7500 (51,700)	5500 (38,000)
Tested Wet (2)	7000 (48,300)	6100 (42,100)
Modulus of Elasticity in psi (kPa)	$2.7x10^6$ $(18.6x10^6)$	$3.1x10^6$ $(21.5x10^6)$
Miscellaneous Properties (1):		
Coefficient of Linear Thermal Expansion in./in./°F or cm/cm	$8x10^{-6}$	$6x10^{-6}$
Salt Scaling Resistance	No effect @ 50 Cycles	Pronounced Scaling @ 20 Cycles
Acid Resistance, 15% HCl	Slow Effervescence	Rapid Disintegration
Wear Resistance, Steel Wheel (3) No. Wheel Passes for 3/8" Wear	7700	2400

(1) Concrete with Epi-Top PC-10 cured 28 days @ 77°F & 50% RH. Control Cured 28 days @ 77°F & 95% RH.

(2) After an additional 28 days water soak @ 77°F.

(3) A 1-5/8" wide steel sheel loaded with 400 lbs. (182 kg)

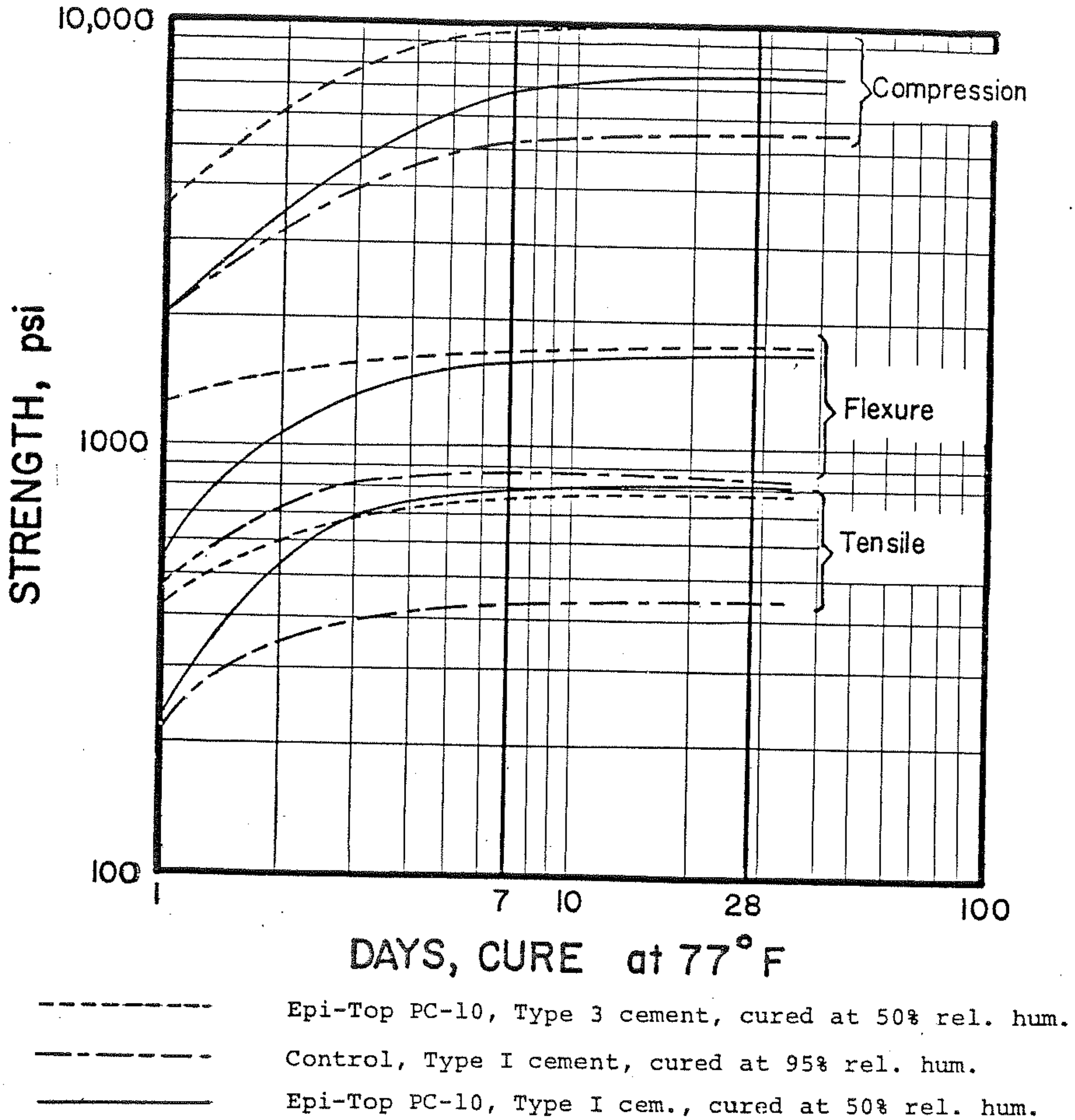

Figure 3. Strength deveopment of concretes made with Epi-Top PC-10 (116)

were suitable for compacting it.

Curing of concrete, containing furfuryl alcohol in moist air is accompanied by shrinkage (0.35 to 0.40 mm/m); to avoid crack formation in products during the curing steps, a wet state must be maintained. A 45-day curing time is recommended for this type of concrete, during which time its tensile strength increases greatly. Steam curing accelerates the hardening in the initial period but has little effect on the final properties of the material. (Table 9)

In other experiments by Raff (118)(119) the first tests made were for the purpose of determining the effect of various catalysts while using a constant five percent of furfuryl alcohol in all formulations. The amount of catalyst used was determined by adding enough catalyst to the furfuryl alcohol-water solution to lower the pH to the value obtained with 0.24 percent aniline hydrochloride (about 3.2). Subsequent formulations were determined first by seven-day compressive strength, then by 28-day compressive strength, and finally by resistance to sulfuric acid attack.

The durability test tried was resistance to hot distilled water. It soon became evident that a more aggressive test would be necessary if the test for durability was to be of any value in the selection of the optium formulation. Testing was, therefore, shifted to sulfuric acid solution for seven days at room temperature using continuous immersion in 15 percent H_2SO_4 as described in Ref (18). However, specimens were not tested to total failure but were washed, dried, and weighed, dried and weighed after seven days of exposure.

For a more thorough study, first a few screening tests were made and small number of catalysts were selected. Elimination of a catalyst from the group was made on the basis of low early strength, the difficulty of handling the catalyst, or the hazard involved. The catalysts selected for further studies were benzenesulfonyl chloride, aluminum sulfate, acetic acid and formic acid. For comparison

TABLE 9

Strength of Concrete Containing Furfuryl Alcohol (25)

Curing Condition	Compressive Strength kgf/cm^2 *					Tensile Strength kgf/cm^2					Flexural Strength kgf/cm^2				
	1 day	28 days	45 days	90 days	1 yr.	1 day	28 days	45 days	90 days	1 yr.	1 day	28 days	45 days	90 days	1 yr.
Moist medium	---	247	255	292	330	--	18	21	23	27	--	37	45	46	55
Fast steaming	140	267	274	332	364	10	17	18	21	27	20	34	36	42	54
Steaming	140	224	230	254	300	6	14	16	24	27	13	28	33	47	54
Moist medium	---	227	251	310	380	--	18	22	25	32	--	36	44	49	65
Fast steaming	190	278	283	302	383	16	20	22	24	33	32	40	45	48	66
Steaming	200	267	280	313	387	15	18	--	--	30	30	36	--	--	60

*Note for metrication: 100 kg/cm^2 is equivalent with 9810 kPa in SI units.

several tests were also made with aniline hydrochloride as the catalyst.

Calcium chloride was used to obtain high early mortar strength with furfuryl alcohol regardless of the catalyst used. In evaluating some of the variables, tests were made with furfuryl alcohol in mortar but without adding catalyst. It was found that when calcium chloride was used, the high early strength was obtained without the use of a catalyst.

There are a few cases in the report by Raff where very high strengths were obtained. Attempting to duplicate these reported results ended in failure leading to the assumption that an error may have been made in the original batching proceedure.

Good results were obtained using benzenesulfonyl chloride as catalyst with five percent FA and varying amounts of calcium chloride. At seven days the strength and the acid resistance were generally decreased as the FA content was increased to seven percent and ten percent. At 28 days the strength was better at the three percent calcium chloride level but dropped at high calcium chloride levels (4% and 5%).

With aluminum sulfate catalyst the highest seven day strength and acid resistance was obtained with ten percent FA. The highest 28 day strength was obtained with five percent FA and three percent calcium chloride. At this level the acid resistance is not maximum but the weight loss was approximately 50 percent of that of the control speciments.

Acetic acid produced relatively low strength at seven days with all concentrations of FA. The highest 28 day strength was with five percent FA, with the best acid resistance at ten percent FA. The change in both strength and acid resistance seem to be quite dependent on the quantity of acid used. When no FA or no calcium chloride is used, the resistance to sulfuric acid attack is approximately the same as for the control.

The best resistance to sulfuric acid attack with formic acid catalyst was with the highest FA content (15%). At this level, increasing the amount of catalyst increased the strength. Comparatively low strength was obtained at both seven and 28 days when using aniline hydrochloride catalyst. Acid resistance was also very low, with some improvement showing with higher amounts of FA (10% and 15%).

When calcium chloride was used without catalyst, good acid resistance and strength were obtained with five percent furfuryl alcohol. Both strength and acid resistance dropped with increased FA content (10% and 15%). (119)

That is, the furfuryl alcohol in portland cement was found to produce PCC with considerably increased acid resistance and a marginal increase in compressive strength above that obtained with calcium chloride alone.

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Conclusions of the Literature Search

From the standpoint of the present research project the topic of which is a preliminary investigation toward polymer and concrete combinations suitable for pavements and other field purposes, the most important findings of the literature search are that

(a) up to 1973 only preliminary investigations have been reported in the literature with polymer and concrete composites that are suitable technically and economically for field use because

(b) the unfavorable results of these investigations discouraged further, detailed research concerning a simple, useable technology for polymer and concrete combinations.

These findings should be kept in mind in order to appreciate our own investigations properly.

PART II

Experiments with Commercially Available Monomer Systems in Concrete

The following four series of our own experiments are presented in this part:

1. Experiments with four monomer systems produced by Dupont;
2. PCC experiments with the addition of monomer + catalyst systems;
3. Experiments with polyvinyl acetate emulsion; and
4. Concrete experiments with polymer-coated aggregates.

Further experiments, namely, experiments with the addition of urea-formaldehyde systems to portland cement mortars are discussed in Part III of this report. Due to time and funding limitations, these experiments have been exploratory in nature.

Materials

Portland Cement

Commercially available "Phoenix" Type II portland cement produced by the Phoenix Cement Company, Clarkdale, Arizona, was used in all of our experiments. It was homogenized and stored in sealed barrels to maintain the same quality throughout the testing.

Aggregates

The gravel and concrete sand used in the tests were commercially available materials from the Camp Verde, Arizona, area. The light-weight aggregates were obtained from the Flagstaff, Arizona, area.

The coarse aggregates and concrete sand were separated into fractions by sieving; then the fractions were reblended in predetermined proportions. The combined grading for the concrete experiments is as follows:

Fraction Size	Quantity
Pan - Sieve #16	25% by weight
Sieve #16 - Sieve # 4	30" " "
1/2" sieve-3/4" sieve	30" " "
3/4" sieve-1" sieve	15" " "
Total	100% by weight

Chemicals

Various chemicals, primarily monomer systems, were used. Their descriptions are given later in connection with their effects on the properties of cement pastes, mortars or concretes.

Test Methods

Generally accepted test methods were used for the experiments. When ASTM methods were available, they were used and are referred to in this report by name and ASTM Designation number. When non-standard methods were applied, the methods are described in detail when presented in this report.

In order to increase the reliability of the test results, many tests were repeated.

Experiments with Four Monomer Systems of Dupont

Description of the Monomer Systems

The following monomer systems were tested:

(1) LR3-412-Toluene-2,4-diisocyanate ("Hylene" TM) in ethyl acetate (50/50 weight basis).

(2) LR3-414-Toluene-2,4-diisocyanate ("Hylene" TM) in tetrahydrofuran (50/50 weight basis).

(3) LR3-413-"Adiprene" L-100 in ethyl acetate (50/50 weight basis).

(4) LR3-415-"Adiprene" L-100 in tetrahydrofuran (50/50 weight basis).

All four systems were produced by Dupont. They all polymerized with water. The manufacturer provided the following information about these systems:

Toluene-2,4-diisocyanate is the simple monomer from which, by reaction with glycols, many commercial polyurethanes are manufactured. "Adiprene" L-100 reaction product with water is more rubbery with decreased hydrogen-bonding capabilities.

The samples were provided with both a water immiscible solvent (ethyl acetate) and a water miscible solvent (tetrahydrofuran) since water compatibility should be an influential parameter in rate of reaction, degree of penetration, etc.

Experiments with monomer + Cement + Water Systems

(1) LR3-412

First the mixture of 25 grams of monomer with 50 grams of water was observed. The mixture immediately formed 3 layers with the middle layer being the more concentrated LR3-412. This middle layer was fairly reactive, giving gas bubbles. The reaction increased somewhat with time. After 5 minutes the mixture had settled into 2 layers with the reactions on top. After 30 minutes white flock started forming on top. Three and one half (3 1/2) hours later white flock had covered the bottom of the plastic container, allowing most of the liquid to drain out. Twenty hours later all the remaining liquid had evaporated or been absorbed allowing the crystals to completely dry and then harden.

Another test consisted of placing a small amount of LR3-412 on a large square of plastic sheeting. It was then allowed to dry at room temperature. After 4 hours a few crystals had formed but the LR3-412 was still very runny. It dried over night and at 20 hours had become a patch of white crystals.

(2) LR3-413

Again the mixture of 25 grams of LR3-413 with 50 grams of water was observed. This was the least reactive of the 4 monomers but some gas was still given off.

Initially, most of the monomer collected on top and seemed to "race around" on the surface. After 3 hours most of the monomer had settled to the bottom in a gel; some had coated the sides of the container and hardened. There was a small amount of movement on the surface. After 20 hours the movements had stopped and the gel had become rubbery.

The second test consisted of placing a small amount of LR3-413 on a square plastic sheet. After 10 minutes of air drying the LR3-413 had dried and thickened a little. After 4 hours it had become thick and sticky but not hard. Twenty-four hours later there was no change. Days later it became hard.

In another test, observation was made to see how LR3-413 would behave with cement paste. Several different amounts of water were used trying to obtain a specimen showing "normal consistency" (ASTM C 187 - 68) but this effort was unsuccessful. Even a mixture of 30 grams of LR3-413 with 150 cc water and 500 grams of cement proved to stiffen too quickly, within minutes. The longer the mixture was mixed and worked with, the stiffer it became. After stiffening, the paste was not as strong as a comparable paste but without LR3-413.

(3) LR3-414

First a mixture of 25 grams of monomer with 50 grams of water was observed. LR3-414 was the most reactive of the 4 monomers. It settled into 2 layers very soon with gas bubbles being released from the monomer on the bottom. The speed of the bubbling increased with time. The container became warm to the touch very soon. After about 7 minutes, white flock started crystallizing within 25 minutes. After 4 hours the flock had covered the top, bottom and sides and had hardened. Later tests repeating the above showed that all the reactions occurred faster if the mixture was continually stirred. A test was also made to determine how the LR3-414, the most reactive, would behave with cement paste. Again, the mixture stiffened too fast, within minutes, even when the mixture consisted of 50 grams LR3-414 with 150 cc of water and 500 grams of cement. The specimen was covered with wet towels as it dried. After 20 hours white flock crystalls had formed on the outside of the specimen. The specimen itself was relatively soft.

(4) LR3-415

A mixture of 25 grams of monomer and 50 grams of water settled into 2 layers within 5 minutes with the concentrated chemical on top, by giving off gas. This reaction continuted for 45 minutes. After 3 hours the LR3-415 had gelled on the bottom, top and sides of the container and was very sticky. After 20 hours it had become a bit more rubbery.

In another test, a small amount of monomer was placed on a plastic sheet. After 10 minutes the LR3-415 had thickened a little. After 4 hours it had thickened more but was not hard. After 20 hours there was no more visible change.

It appears that none of the four tested monomer systems are suitable for mixing them with fresh concrete because they make the cement paste set within a few minutes.

Simple impregnation of mortars with the monomer systems.

Standard Ottawa sand mortar cubes (ASTM C 109-70T) were cured in the fog room for 28 days and subsequently in the air for 14 more days for drying. After that the specimens were divided into four groups and each group was gradually submerged into one of the four liquid monomer systems described below. The specimens were kept in the liquids for four days and then either tested for compressive strength or cured for one more week and then tested. The objective was to see whether these simple impregnation processes would increase the strength of the mortar. Details and related test results are shown in Table 10.

It can be seen that the effects of these impregnations on the compressive strengths were negative; that is, most of the compressive strengths were reduced by the impregnation. Especially harmful was the impregnation with

TABLE 10

Compressive Strength of Ottawa Sand Mortar Cubes with and without Impregnation with Monomer System

Monomer System	Curing	Age at testing, days	Compressive Strength in psi (kPa)
None (Control)	28 days wet 14 days dry	42	6,750 (46,500)
"Hylene" TM in ethyl acetate	28 days wet 14 days dry 4 days impregn. 7 days dry	53	5,500 (38,000)
"Hylene" TM in tetrahydrofuran	------"------	53	5,650 (39,000)
------"------	28 days wet 14 days dry 4 days impregn.	46	5,500 (38,000)
"Adiprene" L-100 in ethyl acetate	same as above + 7 days wet	53	2,100 (14,500)
------"------	28 days wet 14 days dry 4 days impregn. 7 days dry	53	3,200 (22,000)
"Adiprene" L-100 in tetrahydrofuran	28 days wet 14 days dry 4 days impregn. 7 days wet	53	4,800 (33,000)
------"------	28 days wet 14 days dry 4 days impregn.	46	2,900 (20,000)

"Adiprene" L-100 both in ethyl acetate in tetrahydorfuran: most of the cubes impregnated with these two systems showed more than 50 percent strength reduction.

PCC Experiments with the Addition of Monomer + Catalyst Systems

Experiments with Epi-Top PC-10

Description of the Epoxy (116) Epi-Top PC-10 is a water-dispersible epoxy produced by the Celanese Coatings Company. It is furnished in two parts: part A is a reactive, liquid epoxy resin, more specifically a poly-epoxide based on the condensation product of polyhydroxy compounds with epichlorohydrine; and part B is a reactive, amido-amine type curing agent. It includes also an integral non-ionic dispersing agent. Other details and chemical characteristics of the composition are not available since Epi-Top PC-10 is the property of the Celanese Coatings Company. However, general descriptions of such type of epoxies can be found in the literature. (120)(121)

Epi-Top PC-10 was selected for the experiments presented below because that was the only commercially available water-dispersible epoxy we could find. In addition, the properties of this epoxy, as described by the manufacturer appeared quite attractive both in pure state and in combination with portland cement concrete.

Just prior to use, parts A and B should be combined in the proportion of 3 to 1 by volume, thoroughly blended and dispersed in water by agitation. Epi-Top PC-10 functions as a plastifier and also as an air-entraining agent during mixing. Therefore a defoamer was added to it to regulate entrained air within the usual limits. In certain mixes we also used silanes as coupling agents. Typical properties of the uncombined components and a freshly mixed blend are listed in Table 11, and those of a cured system are in Table 12.

The epoxy resin and converter have been specifically developed for easy water dispersibility in the liquid state but minimum water sensitivity in the cured state, chemical compatibility with the alkali content of portland cement and its complex

TABLE 11

Typical Properties of Uncured Epi-Top PC-10 Binder (116)

Property	Component A (Resin)	Component B (Converter)	Mixed System (1)
Viscosity @ 77°F (cps) ASTM D 445-65	3600	700	2,000
Weight per Gallon (lbs.) ASTM D 1475-60	9.65	8.20	9.2
Specific Gravity	1.15	0.98	1.10
Color (Gardner-Holdt) ASTM D 1544-67T	3	12	10
Weight per Epoxide	200	---	---
Amine Content (2)	---	500-550	---
Hazard Potential (SPI Classification)	3-4	4	4
Storage Stability	>1 year (3)	>1 year (3)	Reactive

(1) Combined in the weight ratio of 100 parts A and 35 parts B.

(2) Milligrams of KOH equivalent to the amine content of 1 gram of converter. A detailed test method is available upon request.

(3) In original, sealed containers.

TABLE 12

Typical Properties of Cured Epi-Top PC-10 Binder (116)

Binder System: Undiluted

Property (1)	Value
Tensile Strength (psi)	9,200
Tensile Elongation (%)	4
Flexure Strength (psi)	14,100
Flexural Modulus (psi)	0.46×10^6
Compressive Yield Strength (psi)	12,600
Izod Impact Strength (ft.-lbs./inch notch)	0.51
% Weight Change	
24 hours in water	0.20
24 hours in 5% Acetic Acid	0.81

(1) Properties determined on 1/8" thick casting cured 2 weeks at 77°F.

hydration mechanism, and optimized cured state properties. The following benefits can be expected from the addition of Epi-Top PC-10 to a fresh concrete:

1. Resin rich surface layer which retains water, resulting in less dependency on plastic films, wet burlap, membrane coatings and other external moisture barriers for complete hydration.
2. Water demand is reduced by 30-50% at comparable slump, resulting in commensurate strength increases.
3. More viscous consistency at equivalent slump reduces or eliminates segregation during horizontal movement and vibratory compaction. A combination of factors 1 & 3 virtually eliminates laitance formation when epoxy binder/portland cement ratios are 0.15 or higher.
4. Reduced permeability to water and aqueous solutions increases resistance to salt scaling dramatically, even when compared to air entrained standards. Increased protection of reinforcing steel from corrosion in decks subjected to frequent applications of deicing salts is anticipated. Acid attack is greatly retarded.
5. Abrasion resistance and wear resistance are improved by a factor of 2 or more.
6. Coefficient of linear thermal expansion (8×10^{-6} in./in./^{0}F) is a closer match to that of reinforcing steel.

The present cost of epoxy and the necessitated additional mixing limits the initial use of Epi-Top PC-10 concretes to problem areas, such as bridge decks, or treatment tanks for any industrial detergents, ammonia, cleaning solutions, solvents, etc.

A mixing procedure for Epi-Top PC-10 concrete suggested by the manufacturer is as follows:

1. Load the cement, sand, and coarse aggregate into the concrete mixer.

2. Weigh or volumetrically measure the prescribed amount of Epi-Top PC-10 Component A and add to a mixing tank or pail. The capacity of this mixing vessel should be at least four times larger than the volume of Component A.
3. Weigh or volumetrically measure the specified amount of Component B and combine with Component A in the mixing vessel. The temperature of the Epi-Top PC-10 binder components should be between 55 and 100°F, preferably between 70 and 85°F.
4. Blend the two components together thoroughly with power agitation. About 3 minutes of mixing with a motor powered agitator of proper size will provide a homogeneous blend of resin and converter. For small batches, manual mixing may be employed provided that care is taken to repeatedly scrape the sides and bottom of the mixing container.
5. Promptly add a portion of the total mixing water approximately equal in volume to that of the blended binder and follow with the prescribed amount of defoamer. Continue mixing until a creamy white, uniform emulsion is formed. The agitator should be of sufficient size and speed to form a vortex and circulate unmixed material from the walls and bottom of the container. As in step no. 4, blending of small batches may be done manually with the aid of a paddle; however, care must be exercised to mix completely.
6. Pour or pump the water dispersed epoxy binder into the concrete mixer and mix; then add the remaining water, if any.
7. Mix until all components of the concrete are uniformly dispersed. A minimum of 70 drum revolutions is standard practice for rotary drum mixers. About 2 to 5 minutes mixing in a revolving blade or paddle mixer is generally sufficient.

8. Dump the mixed batch and place the concrete.

Water will effectively clean up mixers and tools, unless the epoxy binder has thickened considerably (partially reacted). If this should occur, all ungelled binder can usually be dissolved in Cellosolve (glycolether) solvents.

Description of Silanes. In some of our epoxy-cement mortar and concrete experiments special chemicals, so-called silanes, were also added to the mixture to explore the applicability of these chemicals in PCC. Silanes can act as coupling agents, or adhesive promoters, in composite mixtures.

Coupling agents are monomeric silanes characterized by dual functionality. In the general silane structure, $R'\ Si(OR)_3$, two distinctly different reactive groups may be noted. R' represents a common organo-functional group such as amino, mercapto, vinyl, epoxy, methacryloxy, etc. and OR represents a hydrolyzable alkoxy group attached to silicon. R' is usually bonded to the silicon atom by a short alkyl chain.

In use, the alkoxy groups hydrolyze to form silanols which can react with or otherwise condense in the presence of active silica, clay or metal oxide surfaces. At the other end of the silane molecule, the functional organic groups such as vinyl, epoxy and amino are capable of reaction with the organic matrix resin. To be effective in any given system, the silane coupling agent must be reactive with both the matrix resin and the filler to some degree. In actual use, the silane may be applied to the filler in a separate pre-treatment step or it may be added directly to the resin where it eventually migrates to the filler-resin interface. (40) The silane coupling agents commonly used in composites as well as their applications are discussed extensively in the literature. (37-39)(122)

Three silanes produced by Union Carbide were tried out in our experiments. These were:

A-186: beta-(3, 4-Epoxycyclohexyl) ethyltrimethoxysilane, A-187: gamma-Glycidoxypropyltrimethoxysilane,

A-1100: gamma-Aminopropyltriethoxysilane.

Silane coupling agents are used in a wide range of applications because of their unique ability to bond polymers with dissimilar materials such as inorganic oxides-i.e., silica and alumina. The bond thus formed has good initial strength as demonstrated by failure of the composite by polymer rupture, and the bond exhibits excellent retention of strength even after severe environmental aging. The siliceous matter or metal may be in the form of fibers, particulate fillers, or massive structures.

Almost every type of organic polymer is compatible with silane coupling agents, ranging from thermoset resins through elastomers to thermoplastic resins. The silane may be applied to the substrate as a pretreatment or, in many systems, the silane may be added to the resin (14)(16) where it migrates to the substrate during normal mixing and application procedures. The application of silane coupling agents to promote bonding has led to improved physical properties of composite materials such as filled and reinforced resins, filled elastomers, caulks for adhesion of metal and glass, and resin-coated and painted metal. Use of silane coupling agents in glass reinforced plastics has resulted in a particularly notable improvement of materials performance.(35)

Silane coupling agents are also used in many commercial sand-epoxy-type composites such as those used for sand consolidation in oil wells, seamless flooring and in highway patching kits. Typically, sand responds extremely well to silane treatment in an epoxy composite providing retention of physical properties under high humidity conditions or when immersed in water.

In sand consolidation, it has been shown that as little as one percent A-1100 added to an anhydride-cured epoxy system will more than double core strength.

Significant improvements in the physical property result from the use of epoxy- and amino-functional silanes with metals (aluminum needles and powder, iron powder) and Wollastonite in epoxy composites. The data for the aluminum needles clearly shows the dramatic improvements obtained with three silanes (A-187, A-186, A-1100). Approximately 100% improvement is noted in dry flexural strength with complete retention being obtained after the 72-hour boiling test. Aluminum and iron powders are also shown to respond well to A-1100 addition providing significant increases in tensile strength. Both A-186 and A-187 are effective in the Wollastonite-filled epoxy formulation providing improvements of some 35-55% in flexural strength over the control after wet conditioning.

It has been found that the use of A-186, the cycloaliphatic epoxy silane provides significant reinforcing properties in the epoxy composite filled with hydrated alumina. (20) Using a 50/50 blend of ERRA-4090 and ERL-4221 and alumina hydrate treated with 1 part A-186, tensile strength is increased by over 50% and elongation is increased over 100%. Toughness as measured by the area under a stress-strain curve is increased by over 300%. A-186 is also shown to improve the erosion resistance, and the arc-tracking properties of the composite remain excellent.

Results were also published that were obtained in phenolic composites using very high loadings of three different fillers: glass spheres, Al_2O_3 abrasive grit for grinding wheels, and foundry sand for shell molding. In all cases, the silane was integrally added to a resin system at very low levels. A-1100 silane is generally effective with all three fillers, providing dramatic improvements in the wet strength retention. In many applications such as phenolic foundry binders, the resin content can be reduced considerably if a silane coupling agent is used.

With melamine and furan resins, the amino-functional silanes are specified to provide maximum wet strength protection to the mineral-filled composites. The silane effect is particularly dramatic with furan resins as used in the no-bake foundry binder systems: the use of only 0.4% A-1100 in a furan binder resin provides improvements in tensile strength ranging from 100-400%. Similar furan resin-aminosilane systems are used in sand consolidation of oil wells. (40)

The exact reaction mechanism of the adhesion promotion by silanes is not known yet but it is likely that more than one process take place simultaneously. (36)

Tests with Ottawa-Sand Mortar Cubes

Two-inch cubes were made of Ottawa-sand mortars in the standard way as specified in ASTM C 109-70T (cement-sand ratio = 1:2.75 by weight, etc.). There were three discrepancies from the standard method: (a) apart from the control series, a portion of the mixing water was substituted by the 3:1 blend by weight of A and B portions of Epi-Top PC-10 + a small amount of defoamer in the form of emulsion as recommended by the manufacturer and described earlier in this report; (b) in certain series the temperature of the water and emulsion was raised and/or they were used with a delay; (c) the cubes with epoxy were cured in the fog room rather than under water because of the high water-sensitivity of the epoxy.

In most cases the flow of the mortars was also determined by the standard method described in ASTM C 109-70T and C 230-68. It should be noted in this connection that the epoxy mortars displayed a high degree of plasticity and excellent work ability even when the standard flow was less than 50 percent. The test results are shown in Table 13.

It can be seen from these data that despite the reduced water-cement ratio, the compressive strengths of the wet-cured epoxy-cement mortars, in most cases, were far below the strength of the controls specimens even when the epoxy emulsion was heated. According to the literature, this inferior strength can be attributed to the wet curing. To check this out, the AA series was repeated but after three days of wet curing the cubes were stored in air until testing. The 7- and 28-day compressives strengths of these specimens were practically indentical with the

TABLE 13

Composition, Flow and Compressive Strength of Epoxy-Cement Mortars

Standard 2-in. cubes of Ottawa-sand mortars. Cement-sand ratio = 1:2.75 by weight. Epoxy: emulsified Epi-Top PC-10 75% A + 25% B by weight. The epoxy emulsion contained a small amount of defoamer. Wet curing. The ratios are expressed by weight.

Series	Water Cement Ratio	Epoxy Cement Ratio	Flow		Compressive Strength psi			Remarks
			in	%	2-d	7-d	28-d	
Control	0.485	---	6.5	62.5	1,610	3,080	4,620	
AA	0.35	0.20	6.25	56.3	440	1,530	1,870	
AB	0.35	0.20	---	---	120	490	1,450	0.5 g of A-186 silane was added
AC	0.35	0.20	5.5	37.5	740	1,600	2,200	Hot water was used for the epoxy emulsion
AD	0.35	0.20	---	---	1,210	3,450	3,890	Both epoxy and water were heated to 6.°C
AE	0.35	0.20	6.25	56.3	500	1,200	1,640	Repetition of AA
AF	0.35	0.20	5.5	37.5	650	1,530	2,040	Delayed addition (2min) of the epoxy emulsion
AG	0.35	0.20	5.75	43.8	560	1,630	2,320	Delayed addition (5min) of the epoxy emulsion
AI	0.35	0.20	5.5	37.5	610	1,500	2,320	Delayed addition (10min) of the epoxy emulsion
AJ	0.35	0.20	6.0	50.0	710	2,410	3,140	Delayed addition (30min) of the epoxy emulsion
X-1	0.35	0.20	5.3	32.5	390	840	960	As AI but with emulsion of 50°C

TABLE 13 (Continued)

Series	Water Cement Ratio	Epoxy Cement Ratio	Flow in	Flow %	Compressive Strength psi 2-d	Compressive Strength psi 7-d	Compressive Strength psi 28-d	Remarks
X-2	0.35	0.20	5.3	32.5	770	2,280	2,340	As AJ but with emulsion of 50°C
X-3	0.35	0.20	6.0	50.0	790	2,000	---	As AF but with emulsion of 50°C
X-4	0.35	0.20	5.3	32.5	960	1,580	2,000	As X-3 but with emulsion of 75°C
X-5	0.35	0.20	5.5	37.5	830	2,120	2,250	Repetition of X-3
X-9	0.35	0.20	5.0	25.0	1,120	1,690	2.2%	As X-3 but the water was added to the epoxy after 30 sec. waiting
X-10	0.35	0.20	6.25	56.3	800	1,300	1,890	As X-3 but the water was added to the epoxy after 1 min waiting
X-11	0.35	0.20	5.0	25.0	1,700	2,710	4,410	As X-3 but the water was added to the epoxy after 2 min waiting
X-12	0.35	0.20	5.0	25.0	1,140	2,910	4,130	Repetition of X-11
X-13	0.35	0.20	5.0	25.0	790	2,410	3,880	Repetition of X-3
X-14	0.35	0.20	5.0	25.0	750	2,150	3,810	------"------
X-15	0.35	0.20	5.0	25.0	830	1,260	1,890	As X-11 but with longer delay
X-16	0.35	0.20	---	---	850	2,480	4,020	As X-3 but with longer mixing
X-17	0.35	0.20	---	---	660	1,260	1,760	As X-3 but with shorter mixing

control strengths.

Compressive Strength of Epoxy-Cement Concretes. Specimens were made from fixed basic concrete combined with emulsions of A and B portions of Epi-Top PC-10 in 3:1 ratio by weight, and a small amount of defoamer. The amount of epoxy used was 20 percent of the weight of cement in accordance with the recommendation of the manufacturer. The combined grading of the concrete sand and gravel was given at the beginning of Part II in this report. The cement-aggregate ratio applied was 1:5.5 by weight. In several cases silane was also mixed with the fresh concrete as an attempt to improve the bond between the hardened cement paste and the aggregate surface. Most of the epoxy-cement concretes displayed good workability.

Each of these concrete combinations was tested for consistency by using the slump test according to ASTM C 143-71, and for compressive strength, by using 3" by 6" cylinders, according to ASTM C 192-69 and C 39-72. The strengths were determined at the ages of 2, 7, and 14 days, and in several cases at 28 days. The purpose of these tests was to find a combination and technology of Epi-Top PC-10 with concrete that provides compressive strengths superior to the strength of comparable control specimens. The results of these tests are presented in Table 14.

It can be seen from these data that

(a) the addition of Epi-Top PC-10 to fresh concrete did not result in increases of the compressive strength under the applied conditions despite the reduced water-cement ratio; as a matter of fact, the strengths were reduced considerably at the early ages;

(b) the addition of any of the three silanes to the fresh concrete caused serious strength reductions in the epoxy-cement concretes; this can be attributed to the interference of the silane with the hydration of portland cement. When however, silane was used for the pretreatment of the aggregate, strength reduction did not take place.

TABLE 14

Composition, Slump and Compressive Strength of Epoxy-Cement Concretes

Standard 3" x 6" cylinders. Cement-aggregate ratio = 1:5.5 by weight. Epoxy: same as in Table 13. Wet curing. The ratios are expressed by weight.

Series	Water-Cement Ratio	Epoxy-Cement Ratio	Silane-Aggregate	Slump in.	Compressive Strength, psi				Remarks
					2-d	7-d	14-d	28-d	
Control	.55	---	---	1.5	1,620	3,100	4,420	5,230	
A	.32	.20	---	1.0	770	3,100	4,250	5,330	
B	.40	.20	---	3.5	500	2,600	3,670	5,150	Good workability.
C	.40	.20	0.001 of A-186	2	127	590	680	---	Poor workability.
D	.40	.20	0.001 of A-187	3.75	200	590	650	---	Good workability.
E	.40	.20	0.001 of A-1100	3.25	160	420	---	---	------"------
F	.40	.20	---	---	910	2,830	4,020	---	Coarse aggregate coated with Concresive 1078 + sand.
G	.40	.20	0.0005 of A-187	---	200	810	860	---	------"------
H	.40	.20	0.0005 of A-1100	---	180	350	440	---	------"------
J	.40	.20	---	---	970	2,880	---	---	As B but with reduced quantity of defoamer.
K	.40	.20	---	---	930	2,940	4,170	---	As B but with increased quantity of defoamer
L	.40	.20	0.0002 of A-187	---	230	780	1,220	---	

Experiments with Furfuryl Alcohol

Description of the Chemicals. Furfuryl alcohol (FA) is a member of the "furan " group, that is, it contains a heterocycylic component, the furan ring, in the molecular structure. The polymerization of pure FA occurs very rapidly when catalyzed with strong acids but the polymerization rate can be reduced by the use of weak acid catalysts and/or low temperature. The problem involved in catalyzing FA in portland cement paste is to obtain an acid catalyst that can work in the presence of the alkaline portland cement. A solution to this problem can be the use of aniline hydrochloride which in theory slowly releases hydrochloric acid, or some other acid catalyst, e.g., $CaCl_2$, to catalyze the FA in the hardening cement paste during polymerization, imparting to it a number of valuable improvements in its mechanical properties. Spectroscopic and X-ray structural analyses have established that a furfuryl-aniline polymer forms upon interaction of furfuryl alcohol and aniline hydrochloride. The process of polymerization and hardening of the resin in an alkaline medium occur much more slowly than in acid media.

FA in not too high concentrations in water (up to 20 percent) does not impede the hydration and hardening of cement. High concentrations, however, slow down these processes. The optimum amount of aniline hydrochloride is 12 to 15 percent of the weight of FA. Higher concentrations of aniline chloride result in unstable resin structures. (117)

Compressive Strength of Concretes with Furfuryl Alcohol. The same basic concrete was combined with furfuryl alcohol in this series that was used in connection with the Epi-Top PC-10 experiments. That is, both the aggregate and the grading and the aggregate-cement ratio (5.5 by weight) were the same. The amount of FA was 5 percent of the weight of the cement in accordance with the recommendation in the literature.

Each of the differing concrete mixtures was tested for compressive strength, by using 3" x 6" cylinders, according to ASTM C 192-69 and C 39-72. The results of these tests are presented in Table 15.

It can be seen from these data that

(a) the addition of furfuryl alcohol to the fresh concrete did not increase the compressive strength under the applied circumstances. That is, the strengths of the FA-cement concretes made with calcium chloride are below the strengths of the comparable concrete with calcium chloride but without FA; and the strengths of concretes made with FA but without calcium chloride are below the control strengths even when a catalyst and/or water of elevated temperature was used for mixing.

(b) the addition of FA does not permit the reduction of the water-cement ratio without impairing the workability of the fresh concrete.

Experiments with Polyvinyl Acetate Emulsion

A modified version of a polyvinyl acetate (PVA) emulsion is produced by the Adhesive Engineering Company, San Carlos, California, under the brand name of "Concresive 1069." According to the Manufacturer, this "is a material for bonding wet cementitious materials to dry surfaces. It is a fluid, aqueous, resinous emulsion which is especially formulated to dry to a thin, flexible film. The film is ageless, non-toxic and is not affected by the alkalinity of gypsum, lime-putty or portland cement mixes. It is resistant to most acids and will not deteriorate in a temperature range from -65°F to +300°F. Concresive 1069 may be applied by brush, spray or roller to the surface over which cementitious material is to be applied. It may also be mixed into certain materials such as grout, mortar and neat cement."

In order to test the effectiveness of this polyvinyl acetate emulsion in PCC, 2-in. cubes were made of Ottawa-sand mortars so that, apart from the control series, a portion of the mixing water was substituted by Concresive 1069. Otherwise the standard procedure was followed as described in ASTM C 109-70T. The

TABLE 15

Composition and Compressive Strength of Furfuryl Alcohol-Cement Concretes

Standard 3" x 6" cylinders. Cement-aggregate ratio = 1:5.5 by weight. Monomer: furfuryl slcohol. Wet curing. The ratios are expressed by weight.

Series	Water-Cement Ratio	Monomer-Cement Ratio	$CaCl_2$-Cement Ratio	Compressive Strength psi		Remarks
				2-d	7-d	
Control	0.55	---	---	1,620	3,100	
27	0.55	---	0.03	2,790	4,920	As control but with 3% $CaCl_2$.
28	0.52	0.05	0.03	1,770	3,710	Consistency is stiff.
29	0.55	0.05	0.03	2,090	3,640	As 28 but with more water.
30	0.55	0.05	---	1,780	3,010	Water of about 70°C was used for mixing.
35	0.55	0.05	---	1,770	3,380	As 30 but aniline hydrochloride was added to the mixing water (5% of FA).

amount of PVA used was 20 percent of the weight of cement. The flow of the mortars was also determined by the standard method. The test results are shown in Table 16.

It can be seen from these data that the compressive strengths of the tested PVA-cement mortars are far below the strengths of the control specimens. This can be attributed again to a large extent to the wet curing of the mortar specimens, and also to the relatively early testing ages.

Experiments with Coated Aggregates

Background

The purpose of this test series was to investigate how much the concrete strengths are increased when mineral aggregate is used the coarse particles of which were coated with a layer of adhesive material (polymer) or adhesive promoter (silane) with or without containing embedded small, solid particles.

The theoretical framework of this approach is that the surface conditions of the mineral aggregate applied have a considerable effect on the various strengths of the hardened concrete through influencing the adhesion of the cement paste to the aggregate particles. (35)(89-95)(113)(123-126) Since it is desirable in many cases to produce a concrete having increased strengths, especially increased flexural and tensile strengths, without substantially increasing the cement content, or decreasing the water content of the fresh concrete, or without using any special treatment of the concrete, it appeared to be a logical method to improve the technically important surface characteristics of the aggregate by a suitable coating. Only the coating of Coarse aggregate was considered since the adhesion to smaller particles is usually not a problem due to the larger specific surface of the fine aggregate.

Description of the Chemicals

Epi-Top Pc-10, the silanes and Concresive 1069 have been described earlier in

TABLE 16

Composition, Flow and Compressive Strength of PVA-Cement Mortars

Standard 2-in. cubes of Ottawa-sand mortars. Cement-sand ratio = 1:2.75 by weight. Polymer: Concresive 1069 which is a modified polyvinyl acetate emulsion. Wet curing. The ratios are expressed by weight.

Series	Water-Cement Ratio	PVA-Cement Ratio	Flow in	Flow %	Compressive Strength psi 2-d	Compressive Strength psi 7-d	Compressive Strength psi 28-d
Control	0.485	---	6.5	62.5	1,610	3,080	4,620
X-6	0.40	0.20	6.25	56.3	410	910	1,510
X-7	0.45	0.20	6.8	70.0	210	550	1,130
X-8	0.42	0.20	6.5	62.5	330	630	1,350

Part II of this report. The characteristics of the other three polymers applied for aggregate coating were taken from the technical bulletins of the manufacturer, The Adhesive Engineering Company, San Carlos, California.

Both Concresive 1001 Regular and Concresive 1001 LPL (Long Pot Life) are high-strength, two-component epoxy adhesives for bonding new concrete to old. They are said to bond well to damp concrete, and to be applicable easily. Details concerning the chemical compositions of these epoxies are not available since these are patented materials. The other characteristics of the blended epoxies are as follows:

Concresive 1001 Regular:

Consistency:	thin liquid
Color:	medium grey
Recommended blending proportion:	5 parts of A to 2 parts of B by volume
Pot life:	25 minutes (one quart mass at 75°F)
Set time:	5 hours (1/8" film at 75°F)
Cure time at 75°F:	12 hours for gentle handling, 3 days for normal service.

Concresive 1001-LPL:

Consistency:	viscous liquid
Color:	medium grey
Density:	10.1 lbs/gal
Recommended blending proportion:	2 parts of A to 1 part of B by volume
Pot Life (1 gal):	3 hours at 40°F, 2 hours at 70°F, 40 minutes at 100°F.
Tack time:	4 hours at 40°F, 2-1/2 hours at 70°F, 60 minutes at 100°F.
Cure time at 75°F:	48 hours for light loads, 5 days for complete cure
Shelf life:	1 year.

Concresive 1078 is a two-component, 100% solids epoxy resin paste designed for coating, sealing or bonding surfaces which are wet, or which are completely submerged in water. It is relatively insoluble, even in fresh water. Therefore, water is displaced from the bond line when Concresive 1078 is pressed against materials. Some other characteristics of the blended epoxy are as follows:

Consistency:	paste
Color:	yellow
Density:	11.7 lbs/gal
Recommended blending proportion:	3 parts of A to 1 part of B by volume
Pot life:	40 to 60 minutes (1/4 gal. mass at 75°F)
Set time:	2 hours at 80°F, 4-1/2 hours at 60°F
Cure time at 75°F:	about a week
Shelf Life:	at least one year.

Strengths of Concretes Made with Coated Aggregate

In order to see the effectiveness of various coatings on different aggregates, comparable concrete specimens were made with coated and uncoated coarse aggregates. The basic concrete was similar to the one that was used in connection with the Epi-Top PC-10, and with the furfuryl alcohol experiments. That is, both the aggregate grading and the aggregate-cement ratio (6.6 by absolute volume which is 5.5 by weight for normal-weight aggregate) were the same.

Each of the differing mixtures was tested for compressive strength by the standard methods using 4" x 8" cylinders. Slump was also determined in many cases. In addition, some of the mixtures were tested for splitting strength on 4" x 8" cylinders according to ASTM C 496-71, while some others were tested for flexual strength according to ASTM C 192-69 and C 78-64 using 4" x 4" x 14" beams and third-point loading.

The coating of coarse aggregate particles took place by hand: The particles were washed and dried, and then covered with a thin layer of the premixed polymer.

or silane or both. In certain cases this primary coating was also covered with another layer consisting of portland cement or fine sand. Then the concrete was made with the coated aggregate in the usual manner. Additional details along with the compositions of the tested concretes and with the slump and strength results are presented in three tables. More specifically,

1) in Table 17 data are summarized concerning the effect of various coatings on the compressive strength of concrete made with the same kind of normal-weight aggregate from Camp Verde, AZ, that was used in our previous experiments;

2) Table 18 shows similar data with two additions: it presents splitting strength results of the concretes, and it deals also with lightweight aggregate concrete. The light weight coarse aggregate used was a greyish cinder of good quality from the Flagstaff area. Its specific gravity (saturated-surface-dry), and its water absorption determined according to ASTM C 127-73 were 1.87 and 6.3 percent, respectively;

3) the results summarized in Table 19 demonstrate the influence, or lack of influence, of the type of the coated aggregate on the compressive and flexural strengths of the concrete. In addition to the previously described normal-weight aggregate from Camp Verde, and the greyish cinder from Flagstaff, the following three coarse aggregates were used in these tests:

1) a dark grey cinder of poor quality from the Flagstaff area. Its specific gravity (saturated-surface-dry) and water absorption are 1.50 and 14.9 percent, respectively;

2) crushed glass obtained from empty beer bottles. Its specific gravity is 2.52;

3) gravel from the Salt River, AZ. Its specific gravity 2.63. This gravel has provided probably the strongest concrete and the best service record in Arizona.

TABLE 17

Effects of Aggregate Coatings on the Compressive Strength of Concrete

Standard 4" x 8" cylinders. Cement-aggregate ratio = 1:5.5 by weight. Average cement content: 560 lbs/cu yd. (552-567). Average air content: 1% (0-2.0). Average slump: 4 in. (3 1/2-4 1/2) for w/c = 0.6; and 2 in. (1 3/8-2 1/4) for w/c = 0.55 by weight. Wet curing.

Series	Water-Cement Ratio	Coating	Compressive Strength psi 2-d	Compressive Strength psi 7-d	Remarks
Control	0.60	---	1,360	2,610	
2	0.60	C* 1001 Reg.	1,290	2,670	Concrete was mixed 3 hrs after coating.
3	0.60	"	180	1,210	Coarse aggregate was precoated with Silane A-186.
4	0.60	"	900	2,140	Coarse aggregate was precoated with Silane A-186 and sprayed with water.
5	0.60	"	---	1,760	Same as 4 but Silane A-187 was used.
7	0.60	"	10	1,000	Same as 4 but Silane 1100 was used
11	0.60	"	1,000	1,980	Coarse aggregate was precoated with Silane A-186 and a little silane was also added to the mixing water.
Control	0.55	---	1,450	3,030	
13	0.55	C 1001 LPL	990	2,380	Concrete mixed 3 hrs after coating.
14	0.55	C 1078	1,010	2,510	"
17	0.55	C 1001 LPL	1,235	2,570	The epoxy coating was covered with fine sand 1/2 hr after coating. The concrete was made next day.
18	0.55	C 1078	1,600	3,000	"
19	0.55	C 1001 Reg.	1,520	2,250	"

* C stands for Concresive.

TABLE 17 (Continued)

Series	Water-Cement Ratio	Coating	Compressive Strength psi 2-d	7-d	Remarks
20	0.55	Epi-Top PC-10	1,080	1,940	The epoxy coating was covered with fine sand 1/2 hr after coating. The concrete was made next day.
23	0.55	C* 1001 LPL	1,660	3,180	The epoxy coating was covered with portland cement 1/2 hr after coating. The concrete was made two days later.
24	0.55	C 1001 LPL	1,240	3,150	Essentially the same as 17.
25	0.55	C 1078	1,750	3,750	Similar to 23.
26	0.55	"	1,840	3,590	Similar to 17.
31	0.55	C 1001 Reg	1,550	3,180	Similar to 23.
32	0.55	"	1,900	3,350	Similar to 17.
33	0.55	Epi-Top PC-10	1,360	2,920	Similar to 23.
34	0.55	"	1,700	3,440	Similar to 17.
37	0.55	"	1,315	3,190	Epoxy coating was covered with portland cement. The concrete was made 4 days later.
38	0.55	"	1,370	3,390	Epoxy coating was covered with sand. Otherwise the same as 37.
39	0.55	"	1,520	3,450	Coarse aggregate was sprayed with Silane A-186 diluted in ethenol. Otherwise the same as 37.
40	0.55	"	1,430	3,085	Epoxy coating was covered with sand. Otherwise the same as 39.
41	0.55	C 1078	1,600	3,365	Similar to 39.
42	0.55	"	1,820	3,660	Similar to 40.
43	0.55	"	1,670	3,220	Similar to 37.
44	0.55	"	1,700	3,600	Similar to 38.
46	0.55	C 1069	1,130	1,770	Similar to 40.
47	0.55	"	1,105	1,940	No silane treatment. Otherwise same as 46.
49	0.55	"	1,170	2,100	Polymer coating was not covered with anything.

TABLE 18

Composition, Compressive and Splitting Strengths of Concretes

Made with Lightweight and Normal-Weight Coated Aggregates

Standard 4" x 8" cylinders. Cement-aggregate ratio = 1:6.6 by absolute volume (= 1:5.5 by weight for normal-weight aggregates). Average cement content: 560 lbs/cu yd. Average air content: 1%. Average slume: 1 3/4 in for w/c = 0.55 by weight, and 2 1/4 in. for w/c = 0.58.

Series	Water-Cement Ratio	Coating	Compressive Strength psi			Splitting Strength psi			Remarks
			2-d	7-d	28-d	2-d	7-d	28-d	
Control	0.55	---	1,590	3,440	5,670	295	445	566	
54	0.55	C 1001 LPL	1,600	3,190	4,650	273	437	530	Concrete was mixed the next day after coating.
56	0.55	C 1078	1,600	2,820	5,510	301	413	576	Concrete was mixed 3 days after coating.
Control	0.58	---	1,510	3,410	5,160	186	402	528	
Control	0.58	---	1,870	3,460	5,060	263	405	473	Coarse aggregate is a local cinder of good quality.
60	0.58	C 1078	1,770	3,300	4,960	286	386	477	Similar to the lightweight control above but the coarse aggregate was coated.
64	0.58	"	1,520	3,210	5,020	220	425	579	Epoxy coating was covered with sand. The concrete was made 4 days later.
68	0.58	"	1,570	3,130	4,570	235	478	508	Epoxy coating was covered with sand. Concrete was made the next day.
70	0.58	"	1,670	3,300	4,530	226	398	557	" Otherwise similar to 60.

TABLE 19

Composition, Compressive and Flexural Strengths of Concretes Made with Various Coated Aggregates

Standard 4" x 8" cylinders and 4" x 4" x 14" beams with third-point loading. Cement-aggregate ratio = 1:6.6 by absolute volume (= 1:5.5 by weight for normal-weight aggregates). Average cement content: 560 lbs/cu yd. Average air content: 1%. Average slump: 2 1/2 in. Wet curing.

Series	Water Cement Ratio	Coating	Compressive Strength psi			Flexural Strength psi			Remarks
			7-d	14-d	28-d	7-d	14-d	28-d	
Control	0.58	---	3,240	4,050	4,980	658	---	890	The two day strengths were: 1,650 and 348 psi, respectively.
Control	0.58	---	3,040	4,390	4,730	682	689	808	Coarse aggregate is a local cinder of good quality.
(2)	0.58	C 1078	3,400	3,920	4,810	608	527	665	Epoxy coating was covered with sand. Concrete was made the next day.
(5)	0.58	"	---	3,930	---	--	581	--	Air-cured after 7 days. Otherwise similar to (2).
(6)	0.58	"	2,740	---	---	469	--	637	Similar to the lightweight control above but coarse aggregate was coated.
Control	0.69	---	1,870	---	4,030	513	--	666	Coarse aggregate is a local cinder of poor quality.

TABLE 19 (Continued)

Series	Water-Cement Ratio	Coating	Compressive Strength psi 7-d	Compressive Strength psi 14-d	Compressive Strength psi 28-d	Flexural Strength psi 7-d	Flexural Strength psi 14-d	Flexural Strength psi 28-d	Remarks
(10)	0.69	C 1078	2,940	---	4,370	497	--	629	Same as control above but coated coarse aggregate was used.
(12)	0.58	C 1078	980	---	1,710	367	--	417	Coarse aggregate is broken glass. Most of the glass particles reveled out of the broken surfaces because the hardened epoxy layer stuck to the concrete rather than to the glass.
(13)	0.58	"	3,220	---	4,610	544	--	760	Coarse aggregate is Salt River gravel. Otherwise similar to (2).

It can be seen from these tables that the use of a silane reduces the concrete strength but otherwise the type of coating has little effect on the strength of concrete. It is true that the coating consisting of Concresive 1078 with fine sand seems to provide the highest strengths; however, these increases in the compressive, splitting and flexural strengths over the strengths of the comparable control specimens are so small that they are insignificant from a practical standpoint. The strength improvement is not better either when lightweight coarse aggregate or special aggregate, such as crushed glass, is coated and used in the concrete.

Thus, under the tested conditions the use of polymer-coated aggregates does not seem to increase the strength of concrete. It is still possible, however, that under other conditions the aggregate coating will prove to be beneficial for the concrete strength. Several new approaches will be tested in the continuation (Study II) of this project. Another aspect of the aggregate coating is discussed in the next paragraph.

Water Absorption Measurements

Although the conditions under which polymer coating of aggregate strengthens the concrete is yet to be found, it is worthwhile to consider that aggregate coating may be beneficial in improving the durability of concretes made with aggregates of marginal quality. In order to obtain a preliminary picture of this possibility, water absorption measurements were preformed on three coarse aggregates in coated and uncoated states according to ASTM C 127-73, as well as on concrete made with these aggregates. The three aggregates tested were the previously described ones, namely gravel from Camp Verde, Arizona, the greyish cinder and the dark cinder, both of them from the Flagstaff area. The concrete specimens tested for water absorption were portions of the beams of 4" x 4" cross section that remained after the completion of the flexural tests. That is, the compositions of these concretes were the same as described in connection with Table 19.

The processes of water absorption of the various aggregates are shown in Figure 4. The water absorptions of the corresponding concretes are shown in Table 20.

It can be seen from these data, especially from Figure 4, that epoxy coating slows down as well as reduces the water absorptions of porous aggregates considerably. This reduction can be significant from the standpoint of concrete durability in the case of aggregates of marginal quality.

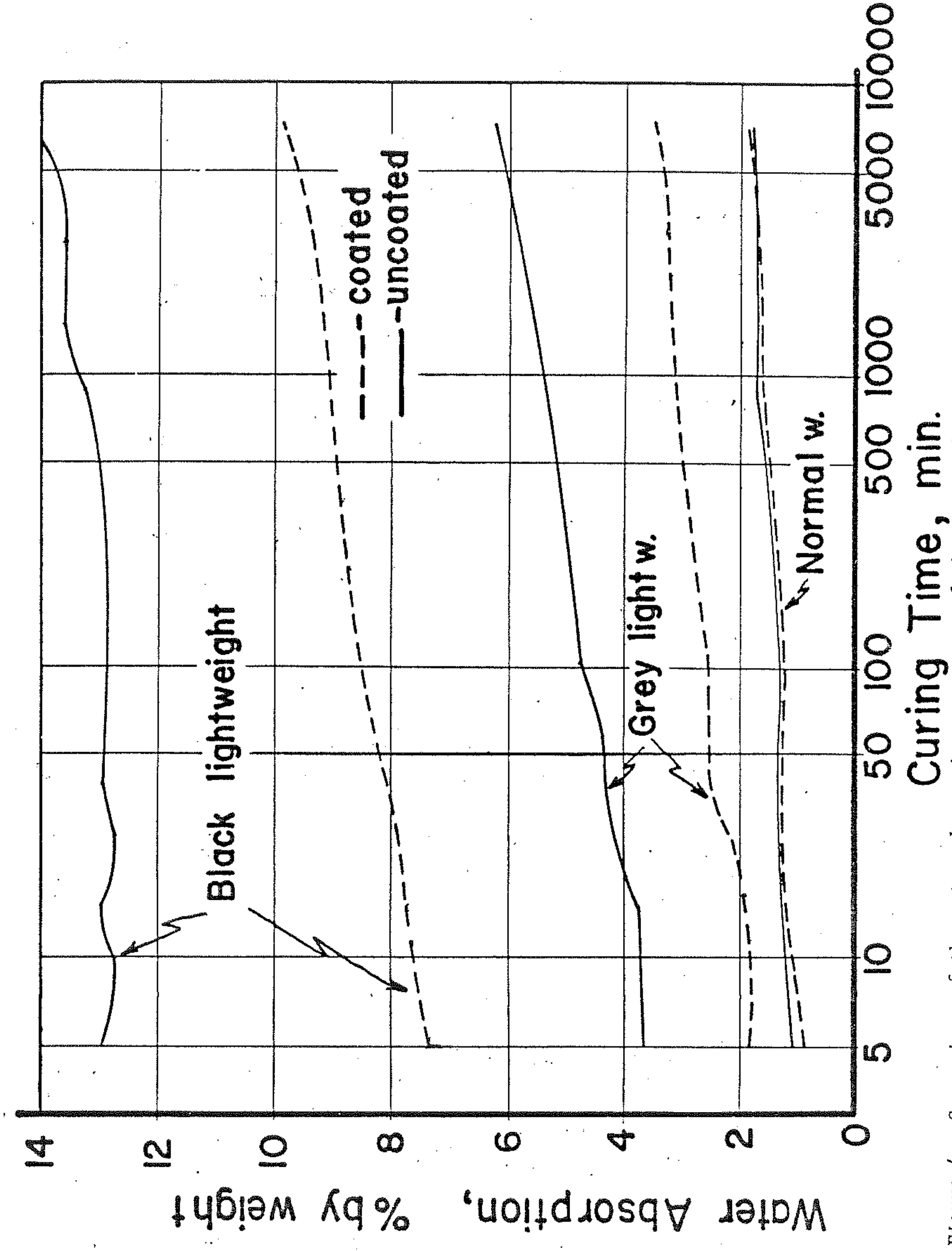

Figure 4. Comparison of the water absorption processes of three coated and uncoated coarse aggregates.

TABLE 20

Comparison of the Water Absorptions of Concretes Made with Polymer-Coated and Uncoated Coarse Aggregates

Aggregate in Concrete	Coating	Water Absorption, % by wt.	
		Coated ag.	Uncoated ag.
Camp Verde (normal-weight) gravel	C 1078	3.5	3.7
Greyish (lignt-weight) cinder	---"---	6.8	7.1
Dark grey (black) cinder	---"---	7.5	7.9

PART III

Experiments with Urea-Formaldehyde Systems in Portland Cement Mortars

This Part III of the report and the work covered by it, particularly the work related to polymer chemistry, were contributed by Dr. Leslie L. Turai as consultant. Also, the presented comparison and analysis of the data as well as the conclusions concerning the strength increases produced by the polymers express his opinion unless it is indicated otherwise. Due to time and funding limitations the work reported here has been again exploratory in nature.

Description of the Materials

The same Type II portland cement was used in these experiments as in those described in Part II. The aggregate used was standard Ottawa sand ASTM C 109.

Formaldehyde (CH_2O) is a member of the aldehydes group which is characterized by the presence of the functional group -CHO. It was used in the form of an approximately 40% aqueous solution. Urea, that is $CO(NH_2)_2$, can be obtained from ammonium cyanate by heating. Urea can react with formaldehyde under different conditions forming different products. In alkaline solutions the condensation reaction appears to take place primarily between hydroxymethyl units. (127-129)

The cement and sand were mixed in the proportion of 1:2.75 by weight. To this the mixture of water and water-solution of urea-formaldehyde prepolymer was added. The cement mortar was prepared in a standard mixer and then 2"-cubes were made, again in the standard manner as described in ASTM C 109. The cubes were cured in the fogroom until the time of the determination of compressive strength.

Research Approach and Results

A research approach was developed which made it possible to select from the multitude of existing polymers a narrow group, members of which would be the most likely to interact with cement in a water medium and reinforce its role as a binder in a concrete composition. Accordingly, the writer suggested that the experimental work be concentrated on monomers, which are: (1) water-soluble, (2) form water-soluble or water-dispersible pre-polymers, and (3) capable of cross-linking and forming water-insoluble polymers in the presence of cement and aggregates.

The first monomer system which was selected for trial was urea-formaldehyde, a water-soluble pre-polymer of which was prepared in the laboratory. This solution was used to replace part of the water in an ASTM standard mortar mix and to produce 2" x 2" x 2" mortar cubes for testing. Test results on these cubes showed approximately 70% higher, 7-day compressive strength and approximately 100% higher 14-day compressive strength than the cubes made from ASTM standard mortar formulation without the pre-polymer. Further test results indicated that the strength improvement was depended on the degree of polymerization of the pre-polymer. When the polymerization proceeded too far the prepolymer was not water-soluble any longer; and when the degree of polymerization was too low, the pre-polymer did not polymerize any further when added to the mortar mix. Both conditions resulted in a decrease rather than an increase in compressive strength. The problem was to stop the reaction at the right degree of polymerization. However, once the over-polymerization had started, it ran to completion within a few seconds.

A clue toward the solution of the problem was found when it was noted that after filtering off the water-insoluble polymer, the filtrate still contained some water-soluble pre-polymer. By filtering and collecting the water-soluble portion of the polymerization products from several reaction mixtures, it was possible to come close to the duplication of previous results. This pointed toward the possibility of slowing down the reaction (and thereby controlling it) by the dilution of the reaction mixture with water. Again, this led to results close to the initial compressive strength values.

The addition of water to the reaction mixture had the effect of increasing the time interval between the completion of the pre-polymerization phase and the initiation of the over-polymerization phase from a few seconds to several minutes. While this allowed the addition of the pre-polymer solution to the mortar mix in the laboratory, the time interval was still too short for practical field application.

The completion of the pre-polymerization phase of the reaction is indicated by the appearance of a light haze, while over-polymerization is shown by the precipitation of the water-insoluble polymer. It was found that by pouring the reaction mixture into cold water (of about 1/3 of the volume of the reaction mixture), after the haze appeared, it was possible to completely stop further polymerization. Any slight amount of insoluble polymer which precipitated was filtered off. The filtered solution was stable and free from further polymerization for at least 24 hours. Compressive tests obtained on test cubes made by using the above pre-polymer showed approximately 40% increase in 7-day test and 70% increase in 14-day test over the ASTM standard mortar formulation. (See table 21, second series, cube No. 161-163).

It was noted during these experiments that the addition of the pre-polymer to the mortar mix allowed a reduction in the water cement ratio ranging from 10 to 18% depending on the amount of pre-polymer used.

In another series of experiments, the effect of pH on the polymerization reaction was investigated. Increasing the pH by the addition of ammonia or potassium hydroxide (to about pH = 8) resulted in water-soluble polymers of a very viscous nature indicating high molecular weights. The use of these polymers in standard mortar formulations resulted in a decrease in compressive strengths. In this connection further investigations should be made to find out whether the negative results are due to the pH effects on the cement or to the degree of polymerization in an alkaline medium.

In several experiments unreacted urea or formaldehyde was left in the reaction mixture. Either one of these conditions caused a very drastic reduction in compressive strength. In case of a slight excess of urea, the addition of an equivalent amount of formaldehyde to the mortar mix improved the compressive strength.

In the last series of experiments the effect of the pre-polymer - cement ratio was investigated. Since the efficiency of the pre-polymer formation was unknown, the urea - cement ratio was used as a yard stick. Preliminary results indicate that 4-6% urea (based on the weight of cement used) gives optimum results. Investigation should be extended below the 4% urea - cement ratio.

Experimental Procedures

Preparation of Pre-polymer: The desired amounts of urea, formaldehyde solution, and water are placed in a three-neck flask equipped with reflux condenser, stirrer, and thermometer. The three-neck flask is placed in an electric heating mantle and slowly heated-while stirring to boiling then until a slight haze appears. (The haze usually appears within a few minutes after boiling starts.) Then the mixture is quickly filtered from the small amount of precipitate which is formed. The filtrate is then diluted with water to the desired volume.

An alternate method is to dilute the reaction mixture with the desired amount of water before filtration.

Sample formulation: 30 grams of urea, 50 ml. of 37% formaldehyde solution, and 40 cc of water is placed in a three-neck flask and treated as described above. Then the filtrate is diluted with water to a volume of 195 ml. The pre-polymer solution so prepared is used to replace all the water in the standard mortar formula for six specimens as described in ASTM Standard C-109-70T.*

Tabulation of Results: Experimental runs resulting at least 25% improvement in 14 and/or 28 day compressive tests over the standard mortar formulation are tabulated in Table 21.

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Conclusions of Part III

Urea-formaldehyde water-soluble pre-polymer was found to be a practical and effective additive for increasing the compressive strength of mortar. For optimum results, the pre-polymer is prepared by reacting 1 mole of urea with 1.1-1.4 moles of formaldehyde according to the procedure described under Preparation of Pre-polymer.

Recommendations for Further Research with the Urea-formaldehyde System

1. Extend the investigation from the pre-polymer - cement - sand - water system to pre-polymer - cement - sand - coarse aggregate - water system.
2. Investigate the effect of urea-formaldehyde pre-polymer on the water penetration, chemical resistance, sulfate resistance, freeze-thaw resistance, and abrasion resistance of mortar and concrete. An improvement in all of these properties is expected.
3. Further investigate urea-formaldehyde polymerization in an alkaline medium.
4. Investigate the effect of urea - cement ratio below the 4% level as indicated in Paragraph 10.

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* In other words, Dr. Turai compares the strength of a no-polymer-cement mortar of 0.48 water-cement ratio to the strength of a polymer-cement mortar of 0.39 water-cement ratio. (S.P.)

TABLE 21

Compressive Strength of Ottawa Sand Mortar Cubes with and without Addition of Urea-Formaldehyde Pre-Polymer

Cube No.	Notebook Reference Date	Age of cube at Testing Date	Compressive Strength psi	Remarks*
Standard Mortar Cubes	Control	7	3125	
		14	3650	
		28	4625	
		90	5475	
214 1st series	Aug. 1, 1973	7	5250	
216 "	"	14	8475	
244 "	Aug. 10, 1973	7	2600	While the 7-day test is low, the 28 and 41-day tests are 45% higher than those of the control
245 "	"	28	6825	
246 "	"	41	7550	
361 "	Sept. 27, 1973	7	4400	
363 "	"	7	4050	
362 "	"	14	5275	
364 "	"	21	6025	
365 "	"	28	6325	
366 "	"	54	7925	
111 2nd series	Jan. 14, 1974	2	1100	
112 "	"	7	4500	
113 "	"	14	6675	
114 "	"	36	7100	
115 "	"	63	9550	
161 "	Jan. 24, 1974	7	4100	
162 "	"	28	8675	
163 "	"	53	9450	
164 "	Jan. 24, 1974	7	2300	7-day test is low, but 28 and 53-day tests are more than 50% higher than those of the control
165 "	"	28	7400	
166 "	"	53	8150	
171 "	Jan. 30, 1974	21	5850	Cubes No. 173 and 184 were aged 27 days in the fog room for 1 day air dried--For 7 and 14 day tests, compressive tester was out of order.
172 "	"	28	7125	
173 "	"	28	8675	
174 "	"	47	7350	
182 "	Jan. 31, 1974	21	6275	
183 "	"	28	7775	
184 "	"	28	8400	
185 "	"	46	8250	

* The water-cement ratio of the control mortar used here for comparison was 0.48 while that of the polymer-cement mortars was usually 0.39 or 0.40, by weight. (S. P.)

CONCLUSIONS

1. Polymer-cement concrete (PCC) is hardly mentioned in the technical literature. The overwhelming majority of the publications related to the combinations of polymer and concrete deals either with the polymer-impregnated concrete (PIC) or with the polymer concrete (PC).

2. As of 1973, the few reported investigations concerning the incorporation of a polymerizable product into fresh concrete have been confined to limited and small-scale feasibility studies because disappointing results have precluded further thorough investigations.

3. None of the four monomer systems produced by Dupont seems suitable for either mixing them with fresh concrete or impregnate a hardened concrete with them.

4. The addition of the A and B portions of Epi-Top PC-10 epoxy in the form of emulsion to a fresh mortar or concrete permits the reduction of the water-cement ratio without impairing the workability; nevertheless, the compressive strengths of such wet-cured PCC's are below the strengths of comparable specimens but without the epoxy emulsion. The addition of furfuryl alcohol to fresh concrete in various combinations did not increase the compressive strength either.

5. Similar statement can be made concerning the compressive strength of wet-cured cement mortar specimens combined with a polyvinyl acetate emulsion.

6. Polymer-Coated aggregates have not provided significantly higher concrete strengths than comparable concretes with uncoated aggregates. It is still possible, however, that new approaches will produce higher concrete strengths with coated aggregates. This would be all the more desirable since epoxy coating reduces the water absorption of porous aggregates considerably. Thus, coating may improve the durability of concretes made with aggregates of

marginal quality.

7. The addition of certain urea-formaldehyde systems increased the compressive strength of standard Ottawa sand mortars considerably. Thus, this approach seems promising for the development of a polymer-cement concrete suitable for field construction. However, much more work is needed in this direction before a definite evaluation of the method can be made.

8. Further research is recommended primarily with the urea-formaldehyde system because of the positive nature of the obtained results. However, the procedure is not ready for implementation at this time.

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