BROOKHAVEN NATIONAL LABORATORY
Associated Universities, Inc.
Upton, New York

DEPARTMENT OF APPLIED SCIENCE
Informal Report

CONCRETE-POLYMER COMPOSITE MATERIALS AND ITS POTENTIAL
FOR CONSTRUCTION, URBAN WASTE UTILIZATION
AND NUCLEAR WASTE STORAGE

by
Meyer Steinberg

May 1973

THIS DOCUMENT CONFIRMED AS
UNCLASSIFIED
DIVISION OF CLASSIFICATION
BY J. L. Caschiera / am
DATE 8/8/73

N O T I C E

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

S1028

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

fy

CONCRETE-POLYMER COMPOSITE MATERIALS AND ITS POTENTIAL
FOR CONSTRUCTION, URBAN WASTE UTILIZATION
AND NUCLEAR WASTE STORAGE

by
Meyer Steinberg
Department of Applied Science
Brookhaven National Laboratory
Upton, New York 11973

Abstract

A wide range of concrete-polymer composite materials are under investigation. The old technology of hydraulic cement concrete is combined with the new technology of polymers. Polymer impregnated precast concrete (PIC) is the more developed of the composites and exhibits the highest degree of strength and durability. Polymer concrete (PC), an aggregate bound with polymer is potentially a most promising material for cast-in-place applications. PC with solid waste aggregate holds out interesting possibilities for converting urban waste into valuable construction materials of commerce. PIC and PC also show potential for immobilizing radioactive waste from the nuclear power industry for long term engineered storage.

CONCRETE-POLYMER COMPOSITE MATERIALS AND ITS POTENTIAL
FOR CONSTRUCTION, URBAN WASTE UTILIZATION
AND NUCLEAR WASTE STORAGE

by
Meyer Steinberg
Department of Applied Science
Brookhaven National Laboratory
Upton, New York 11973

May 1973

Introduction

The concrete-polymer composite materials program at Brookhaven National Laboratory is directed at developing both improved and new concrete materials by combining the ancient technology of hydraulic cement concrete formation with the more modern technology of polymer chemistry. A wide range of concrete-polymer composites are being investigated as follows.

Polymer Impregnated Concrete Materials Development

Polymer impregnated concrete (PIC) is a precast and cured hydrated cement concrete which has been impregnated with a low viscosity 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/cm²) to a value of 20,000 psi (1410 Kg/cm²). Water absorption is reduced by 99% and the freeze-thaw resistance is enormously improved. With high silica cement, strong basaltic aggregate, and high temperature steam curing, strength increases from 12,000 psi (845 Kg/cm²) to over 38,000 psi (2630 Kg/cm²) can be obtained. The tensile

strength of PIC is approximately ten times less than the compressive strength similar to conventional concrete. A maximum 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 dried concrete) are obtained. A photograph of a freeze-thaw test of PIC is shown in Figure 1 and resistance to chemical attack by acids is shown in Figure 2.

In contrast to conventional concrete, PIC exhibits essentially zero creep properties. Furthermore by polymer impregnating concrete, conventional concrete is transformed from a plastic material to essentially an elastic material with an increase of at least 2 times in the modulus of elasticity. This is indicated by the linearity of the stress-strain plot for PIC in Figure 3. 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. This may be achieved by adding plasticizers to the monomer systems or varying the type and shape of aggregate, i.e. steel fiber aggregate.

PIC is basically formed by drying cured conventional concrete by the most convenient and economical processing technique (i.e. hot air, oven, steam, dielectric heating, etc.), displacing the air from the open cell void volume (vacuum or monomer displacement and pressure), diffusing a low viscosity monomer ($<10 \text{ cps}$) 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 (i.e. radiation, heat or chemical initiation). A schematic flow sheet of the simplest process is given in Figure 4, which indicates underwater thermal-catalytic polymerization (curing).

Mainly the free-radical vinyl type monomers, i.e. methyl methacrylate, styrene, acrylonitrile, t-butyl styrene, and other thermoplastic monomers are used. For increased thermal stability crosslinking agents and thermosetting monomers such as styrene-trimethylol propane trimethacrylate (TMPTMA) and polyester-styrene are used. The more important process criteria are that the monomer should be 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 five years in the U.S. ⁽¹⁻⁴⁾ Table 1 gives a brief summary and classification of the PIC materials and properties. A U.S. patent has also been issued on the production of PIC. ⁽⁷⁾

Polymer Cement Concrete

Polymer cement concrete (PCC) is a premixture of hydrated cement paste and aggregate to which a monomer is added prior to setting and curing. The introduction of various organic materials to a concrete mix has been tried numerous times in the past by others ⁽⁸⁾ as well as by BNL. The results obtained are either disappointing or relatively modest in improvements of strength and durability. In many cases materials poorer than concrete are obtained. Under the best conditions compressive strength improvement over conventional concrete of $\approx 50\%$ are obtained with relatively high polymer concentrations in the order of $\approx 30\%$. Polyester-styrene, epoxy-styrene, furans and vinylidene chloride have been used in PCC with limited success. This is explained by the fact that most organic materials are incompatible with aqueous systems and in many cases polymerization either is inhibited by the alkalinity of the cement phase or interfere with the cement hydration process. In addition porosity develops due to shrinkage during the curing

process which remains unfilled. With PIC, the polymer fills the voids and the strength which is a direct function of the unfilled pore fraction is greatly reduced, and the strength is thus increased to a high degree.

The incentive to attain an improved premix concrete material is that it can be cast-in-place for field applications, whereas PIC requires a precast structure.

A variation of PCC is the addition of a modest amount of polymer latex such as styrene-butadiene or polyvinylidene chloride emulsion to the fresh concrete mix. The amount of polymer added to the mix is less than 4% by weight to the total mix. No polymerization takes place, however, the polymer particles coalesce during the concrete curing process and coats the pore structure of the concrete. Maximum strength only increases by a factor of 2, but durability is significantly increased⁽⁹⁾.

The answer for cost in place concrete-polymer materials lies in PC development.

Polymer Concrete Materials Development

Polymer-concrete (PC) is an aggregate bound with a polymer binder. 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 about 1¼¢/lb in the U.S. 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. 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 mainly 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. In one method monomer is then diffused up through the mixed aggregate and the polymerization is initiated by either radiation or chemical means. Conventional concrete mixing equipment can also be used for making up the mix. Safety precautions need to be observed handling flammable monomer. 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 hydraulic cement which forms voids and cracks on hydration in binding the stone aggregate. Water can intrude and crack the concrete, and the alkaline cement is attacked by acidic media and causes severe deterioration. 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 resist chemical attack. As shown in summary Table I, PC compressive strengths can be achieved as high as with PIC ($\approx 20,000$ psi (1410 Kg/cm^2)) with monomer loadings in the order of 6%. A silane coupling agent is added to the monomer to improve the bond strength between the polymer and the aggregate. The main problems arise from the viscoelastic properties of the polymer. Polymers usually have a low modulus of elasticity which means they are flexible and exhibit 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 an important

new class of high benefit to cost ratio materials. It is interesting to note, from the open literature, that investigators in the USSR⁽⁶⁾ have advanced the development of PC to a greater extent than the U.S., whereas PIC is much more advanced in the U.S. than in the USSR. Much more investigation and experience are required with PC to make it a reliably acceptable material of construction.

Aggregate Compositions

Consideration can be given to the aggregate in the binder-aggregate concretes or composites. The definition of an aggregate is any readily available bulk material. The cheapest and most abundantly available aggregates are natural stone and sand which are widely used throughout the world. There are a number of types and grades of stone aggregates which basically relate to igneous (granite), metamorphic (slate) and sedimentary (sandstone) stone. Aggregates are also classified as standard weight, structural lightweight and insulating lightweight. Among the various lightweight polymer impregnated concrete materials, perlite or expanded shale which has essentially no structural properties, has been used for producing a material which is lighter than wood and compressively as strong as concrete. This opens up possibilities for producing lightweight structurally strong mortars and concretes which are buoyant and have a high strength to weight ratio.

Table 1 briefly summarizes the properties of the various concrete-polymer materials produced to date, including surface coated (SC) and partially penetrated PIC referred to as coated in-depth concrete (CID). An attempt at rating the strength and durability and the manufacturing cost with a benefit/cost ratio are given for each of the materials given in Table 1.

Urban Waste Utilization

Aggregates can also include urban solid waste discarded by man, such as garbage, refuse, sewage, paper, glass and metal. Sewage and solid waste refuse-polymer concrete (SRPIC) has been produced using garbage as aggregate and sewage as the hydrating media for the cement, setting and curing the concrete followed by drying, impregnating and in-situ polymerizing the monomer in the precast concrete mix by radiation. Compressive strengths as high as conventional concrete can be obtained, as shown in Table 2.

Flat paper newsprint has been soaked in monomer and polymerized in-situ under pressure to produce a material called paper polymer (PPC) or paper plywood because it has very good tensile strength along the plane of the paper (7500 psi, 510 Kg/cm²).

Non-returnable glass bottles have been crushed and graded and the mixed particulate glass filled with monomer in a manner similar to PC. The polymer bound broken glass is almost as strong as PIC and highly resistant to attack by corrosive media. The various size glass particles and a sample of the composite material are shown in Figure 5. An application of this material is for sewer pipe, especially when handling acid wastes or when aerobic conditions oxidizes the hydrogen sulfide gas coming from sewage to sulfuric acid. We call this material glass-polymer composite (GPC) and the sewer pipe, ecopipe. Conventional concrete is unsuitable for this purpose so that asbestos cement and vitreous clay or cast iron pipe are usually specified for this service.

Bricks and facings which also has decorative value for buildings can also be made from GPC. Incinerator ash has also been used as aggregate to produce a structurally sound material.

Table 2 summarizes some of the solid waste refuse polymer-concrete material properties. Hopefully this materials development work will lead to converting a negative ecological value into a positive asset in the form of valuable construction materials. This is of great importance in recycling and reuse of man's solid waste.

Applications Development

A number of applications of concrete-polymers are being investigated. For the U.S. Federal Highway Administration (FHWA) advanced prestressed-post tensioned bridge deck designs⁽⁸⁾ are being investigated using high strength PIC which leads to some highly interesting streamlined designs. The U.S. Office of Saline Water (OSW) has been investigating corrosion resistant PIC for constructing economical and durable distillation vessels used in producing fresh water from the sea. The U.S. Bureau of Mines (USBM) is investigating the chemical stabilization of coal mine roof supports by impregnation of stone⁽⁵⁾ with monomers followed by in-situ polymerization and also in developing a pumpable roof bolt. PIC tunnel linings are another application of interest to the U.S. Bureau of Reclamation (USBR). The U.S. Navy has been interested in the use of PIC for underwater buoys and piling. PIC is also being investigated for beams and building blocks for durable housing. The American Concrete Pipe Association (ACPA) in cooperation with the U.S. Atomic Energy Commission (USAEC) and the USBR is investigating the use of PIC for sewer and pressure pipe. There is also interest in PIC railroad crossties. A number of industry associations in the U.S. are investigating concrete-polymer materials for their own particular applications.

In Japan an industrial construction company together with a chemical company is reported to have constructed a 15 ton/day pilot plant for experimental production of PIC using thermal-catalytic initiation. The material has been named powercrete and beams, panels, and pipe have been produced, and a number of structural and durability tests have been performed.

A firm in the Union of South Africa is reported to have constructed a pilot plant for the thermal-catalytic production of PIC using a special type of concrete with smooth surfaces called mirror concrete. In addition to pipe and building concrete, a market for domestic sanitaryware (i.e. wash basins, bathtubs, sinks, etc.) is being explored.

A cement association in Italy and the University of Rome is collaborating in developing a PIC using a high silica cement for high strength concrete. High pressure steam cured concrete using underwater polymer curing is being used. Possibilities exist for construction of ship plate, sewer pipe and PIC for producing nuts and bolts and such items as screw ended concrete sewer pipe.

Investigators in Norway, Denmark, Belgium, France, Spain, England, and Israel are known to be exploring PIC applications, including heated road panels, curbing, base plates for pumps, window sills, etc.

Extensive work has been conducted in the USSR on developing and applying polymer-concrete (PC) which is aggregate bound with a polymer binder. The Russian literature⁽⁶⁾ indicates significant advances in a number of applications including tunnel supports. PC is also being investigated in the U.S., however to a much lesser extent than PIC. Interestingly enough, the Russian literature indicates little work on PIC in the USSR.

A number of universities around the world have initiated studies on concrete-polymer materials.

In addition to conventional design procedures sophisticated three-dimensional finite element computer code structural analysis has been developed at Brookhaven National Laboratory (BNL) (9) and is being applied to aid in the design and analysis of structures utilizing these new concrete-polymer materials.

Preliminary cost estimates indicate that PIC materials cost could be competitive with other conventional materials of construction. The feeling is that concrete-polymer which mates an ancient materials technology (concrete) with a new materials technology (polymer) is a growing and exciting one. Given the opportunity of additional investigation, demonstration and experience it is believed that concrete-polymers can become an important class of construction materials.

Storage of Nuclear Waste Materials

Another potentially important application for hydraulic cement concrete, in combination with the polymers in PIC and PC is the storage of long-lived radioactive waste from the nuclear industry. A major unsolved problem facing the exponentially growing nuclear power industry is the safe disposal of fission product wastes. A technically and economically reasonable approach taken by the AEC is immobilizing fissionable and fission products in long-term durable materials in an engineered storage system. Concrete appears to be an attractive material for accomplishing this goal. The material must be stored for periods of 1000 years before it can be considered biologically safe. There is experience with concrete in some environments for much longer periods of time. Also concrete ingredients are low cost and readily available. Adding the new dimension of PIC and PC can insure additional durability and strength factors. The radioactive waste materials

requiring storage are in the form of soluble salts, aqueous solution (nitrates), oxides, glasses, and contaminated process equipment. At BNL, the USAEC has established a program for investigating conventional concrete, PIC and PC formulations for determining the radiation stability, leachability, thermal stability and structural integrity of promising formulations for incorporating radioactive waste materials. Much more will have to be learned about this ancient material of concrete so that it can be confidently recommended to last a thousand years or more. Some promising formulations of aqueous nitrates with calcium aluminates, in high early strength mortars and concretes have been produced and impregnated with styrene-divinyl benzene and have shown radiation stability to 10^{10} rads which is the total integrated dose expected for 1000 years exposure. Crosslinked polystyrene is especially radiation resistant. The compressive strength of these materials run to about 13,000 psi. Also oxide materials incorporated in styrene-divinyl benzene for PC composites have been prepared and show promise.

References

1. Steinberg, M. et al., "Concrete Polymer Materials, First Topical Report", BNL 50134, Brookhaven National Laboratory, Upton, New York, (December 1968).
2. Steinberg, M. et al., "Concrete Polymer Materials, Second Topical Report", BNL 50218, Brookhaven National Laboratory, Upton, New York (December 1969).
3. Dikeou, J. et al., "Concrete Polymer Materials, Third Topical Report", BNL 50275, Federal Center, Denver, Colorado, (January 1971).

4. L.E. Kukacka et al., "Concrete-Polymer Materials, Fourth Topical Report", BNL 50328, Federal Center, Denver, Colorado, (January 1972).
5. M. Steinberg and P. Colombo, "Preliminary Survey of Polymer Impregnated Stone", BNL 50255, Brookhaven National Laboratory, Upton, New York (September 1970).
6. N. A. Moshchanskii and Y. V. Patureov, "Structural Chemically Stable Polymer Concretes" (translated from Russian by NSF TT 71-50007) Moscow, USSR (1970).
7. M. Steinberg, P. Colombo and L. E. Kukacka, assignors to USAEC "Method of Producing Plastic Impregnated Concrete" U.S. Patent 3,567,496 (March 2, 1971).
8. H. B. Wagner, ChemTech 105-118 (February 1973).
9. M. Reich, B. Koplick and J. M. Hendrie, "Finite Element Approach to Polymer Concrete Bridge Deck Designs and Analysis", BNL 16890, Brookhaven National Laboratory, Upton, New York, (May 1972).
10. G. L. Enig, "Latex Polymer Cement Concrete-Structural Properties and Applications" presented at ACI Seminar on Concrete with Polymers, Denver, Colorado (April 24-26, 1973).

List of Figures and Tables

Figure 1 Freeze thaw test on Polymer Impregnated-Concrete PIC (contains 6% by wt. PMMA), lost 0.5% by weight. Control conventional concrete lost 26.5% by weight.

Figure 2 Resistance to chemical attack - 15% hydrochloric acid. PIC lost 7% by weight after 497 days. Conventional concrete loses 25% by weight in 105 days.

Figure 3 Compressive Stress-Strain Curve for PMMA-impregnated concrete. Impregnated shows elastic behavior. Unimpregnated shows plastic behavior.

Figure 4 Creep strain characteristics of PIC.

Figure 5 Schematic of PIC Process.

Figure 6 Glass-Polymer Composite (GPC) indicating combination of various particle size mixtures and specimen of GPC in lower right hand corner. Composition: 90% crushed waste glass - 10% styrene-polyester.

Figure 7 Glass-Polymer Composite (GPC) "Ecopipe" for sewer lines.

Table 1 Classification of Concrete-Polymer Materials

Table 2 Solid Waste and Sewage Containing Polymer Concrete

Figure 1
Freeze thaw test on polymer impregnated
concrete-(PIC) (contains 6% by wt PMMA),
lost 0.5% by weight. Control con-
ventional concrete lost 26.5% by weight.

Figure 3
Compressive stress-strain curve for
PMMA-impregnated concrete. Impregnated
shows elastic behavior. Unimpregnated
shows plastic behavior.

Figure 4
Creep strain characteristics of PIC

PRODUCTION OF POLYMER IMPREGNATED CONCRETE

PIC

Figure 5
Schematic of PIC process.

Figure 6
Glass-Polymer Composite (GPC) indicating combination of various particle size mixtures and specimen of GPC in lower right hand corner. Composition: 90% crushed waste glass - 10% styrene-polyester.

Figure 7
Glass-Polymer Composite (GPC) "Ecopipe"
for sewer lines

Table 1

CLASSIFICATION OF CONCRETE-POLYMER MATERIALS

	Polymer loading, wt % PMMA	Density lbs/ft ³		Compressive strength, lbs/in. ²		Strength weight ratio	Durability	Benefit cost index
		(gm/cc)		(Kg/cm ²)				
1. Conventional concrete control	0.0	150	(2.40)	5,000	(353)	33	Poor	1.0
2. Surface Coating (SC) paint or overlay	0.0	150	(2.40)	5,000	(353)	33	Limited	1.1
3. Coating in Depth (CID)	1.0	150	(2.40)	6,000	(423)	40	Good	1.3
4. Polymer Cement Concrete (PCC) premix								
a. Monomer premix	35.0	130	(2.08)	7,500	(528)	58	Fair	0.4
b. Polymer premix	1.0	150	(2.40)	10,000	(705)	49	Better	1.5
5. Polymer Impregnated Con- crete (PIC)								
Standard aggregate								
a. Undried-dipped	2.0	153	(2.45)	10,000	(705)	49	Fair	1.4
b. Dried-evac.-filled	6.0	159	(2.55)	20,000	(1410)	126	Very good	2.0
c. Hi-Silica steam cured	8.0	159	(2.55)	38,000	(2680)	240	Very good	3.0
Lightweight aggregate								
a. Struct. lt. wt. concr.	15.0	130	(2.08)	25,000	(1760)	193	Very good	2.5
b. Insul. lt. wt. concr.	65.0	60	(0.96)	5,000	(353)	84	Very good	2.5
6. Polymer Concrete (PC) cementless	6.0	150	(2.40)	20,000	(1410)	133	Excellent	4.0

Table 2

SOLID WASTE AND SEWAGE CONTAINING POLYMER CONCRETE

Type	Composition - wt. %				Compressive strength, psi	Tensile strength, psi
	Water	Portland Cement	Aggregate	Polymer ⁽¹⁾ loading		
Standard concrete	6	14	80 ⁽⁴⁾	0	4,500	450
Sewage-cement concr.	38	46	16 solids ⁽²⁾	0	2,200	-
Sewage-cement-polymer concrete	28	60	12 solids ⁽²⁾	24	11,300	-
Refuse-cement-polymer concrete	17	33	50 refuse	10	4,000	-
Sewage-refuse-cement polymer concrete (SRPIC)	18	28	54 refuse ⁽²⁾	10	3,700	-
Glass-polymer composite ⁽³⁾ (GPC)	0	0	100 glass bottles	7	16,000	1,200
Paper polymer composite (PPC) paper plywood	0	0	100 newsprint	23	7,300	7,500

(1) Polymethyl methacrylate, wt. % of unloaded dried material

(2) Content of sewage sludge (70% water, 30% solids)

(3) Acid resistance 5 weeks, 5% H₂SO₄, 0.2% weight gain
Water absorption 5 weeks, no gain

(4) 33% sand, 67% stone