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An Investigation of the Properties of Polymer Concrete

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Synopsis:

An investigation of various formulations of polymer and aggregate composites was undertaken in order to determine possible applications of these new materials in building construction. A number of polyester-styrene-methyl methacrylate resin systems were mixed with combinations of sand, gypsum, gravel, clay and chopped glass fibers, cast and cured, and the resulting materials were then tested. No portland cement was used. Maximum compressive strength obtained was 21,100 psi ($145.6N/mn^2$) and maximum splitting tensile strength was 2,210 psi ($15.2N/mn^2$); unit weights ranged from 122 to 145 pcf ($1,970 - 2,350 kg/m^3$) and modulus of elasticity ranged from 1,460,000 to 3,300,000 psi (10.1 to 22.8kN/mm²). Rapid curing at ambient temperatures was possible. The addition of a chlorendic anhydride improved polymerization at both ambient and elevated temperatures.

Detailed formulations are presented for the most promising systems investigated. These polymer composites cost more than portland cement concretes for equal volumes of material but compare well on a strengthto-cost basis. Specific applications of these new materials will require additional development and testing. However, in many instances, they offer an attractive alternative to conventional concretes with regard to physical properties and architectural aesthetics.

<u>Keywords</u>: aggregates; <u>compressive strength</u>; concretes; curing; fiber reinforced concretes; <u>mix proportioning</u>; modulus of elasticity; polyester resins; <u>polymer concrete</u>; stress-strain relationships; tensile strength.

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I. INTRODUCTION

This work investigates the formulation of various composite materials, consisting of a polymeric matrix with mineral fillers, for application as building materials. Our approach seeks to utilize the higher tensile strength and lower density of polyester and acrylic polymers (as compared to portland cement) and the variety of colors and textures that can be obtained by combining these resins with different mineral fillers, to create new materials for certain structural and architectural applications.

Specifically we sought to optimize the formulation of resin-aggregate systems, capable of curing at ambient temperatures under field conditions, to give materials with high strengths in flexure and compression. Specialty formulations, which achieve certain colors and textures of architectural interest, were also explored. Specimens from the most promising formulations were tested in compression and flexure and compared with respect to physical properties and cost with ordinary concrete.

II. PREVIOUS WORK

The development of polymer-aggregate concretes is relatively recent but is continuously increasing in scope and intensity. One of the main difficulties concerns the adaptation of polymer formulation and curing techniques, developed for controlled temperature and humidity to field applications, where these conditions vary widely. The following paragraphs provide a summary of the investigations to date.

Dennard (1) studied the complete replacement of portland cement in

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concrete with a polyester resin. Optimum formulations contained 12% by weight resin and were oven cured at 350° F. They showed flexural strengths of approximately 800 psi and a compressive strength of nearly 16,000 psi. Jejcic (3) compared various epoxy and polyester resins. Epoxy was found superior to polyester chiefly for its moisture tolerance, but its cost was about six times higher. The problem of grading of the aggregate was also recognized in obtaining optimum mechanical properties from the material and minimizing the quantity of resin.

L'Hermite and Jejcic (5) listed the special properties of resin concretes and described their appearance as quite similar to ordinary concrete. Gebauer and Coughlin (2) compared polymer cement and polymer mortar composites based on styrene and methyl methacrylate. Radiation techniques were used to create a prepolymer cement paste and mortar which was cast and polymerized with either thermal-catalytic or gamma radiation means. Methyl methacrylate samples using pure cement powder showed the greatest compressive strengths and the lowest water absorption. Smith and Waling (7) evaluated several resin binders for use with lightweight aggregates.

Kukacka and DePuy (4) reported significant improvements in polymer concretes with the use of various acrylic resins. Strengths up to 17,000 psi at polymer loadings of up to 15% were obtained with conventional aggregates. With Type II portland cement and Number 30-mesh Ottawa sand, specimens with a compressive strength of 23,500 psi were obtained. Ohama (6) reports the first systematic study of resin-mineral proportions of polyester resin concrete. Compressive strength was found to be considerably higher in samples cured at elevated temperatures. The water content of the aggregate was also shown to affect the strength.

Previous work in the Author's laboratories revealed several novel aspects of polymer-aggregate concretes. These were:

- Methyl methacrylate polymers or copolymers that may be cured at ambient temperatures without irradiation.
- 2. The compounding of polymer and aggregate materials to achieve aesthetically desirable structures.
- The casting of highly crystalline mineral aggregate with a clear polymer binder in thin sections to achieve a translucent material for controlling light.

III. EXPERIMENTAL

A. Materials

The following is a comprehensive list of components, from which we selected the various formulations for the composite systems, investigated in this work.

- 1. Resin System
 - (a) unsaturated polyester resins (Diamond Shamrock Co., Dow Chemical Co.*)
 - (b) styrene (Dow Chemical Co.*)

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- (c) methyl methacrylate (Rohm and Haas Co.*)
- (d) crosslinking agents: Divinylbenzene; Trimethylol Propane
- Trimethacrylate
- (e) fire retardant (also crosslinking agent): Chlorendic Anhydride
- (f) silane coupling agent (for aggretate binding): γ-Methacryloxypropyltrimethoxysilane
- (g) catlysts: Methyl Ethyl Ketone Peroxide, Azobisisobutyronitrile
- (h) accelerators: N-N-Dimethylaniline; Cobalt Napthenate
- 2. Aggregates
 - (a) natural aggregates (sand and gravel) normally used in ordinary concrete
 - (b) sea sand
 - (c) gypsum
 - (d) various clays
 - (e) Ottawa sand
 - (f) chopped glass fibers

B. Procedure

The components of the resin system were premixed in the proper proportions, in the order listed above, just prior to mixing with the prepared aggregates.

The aggregates were air-dried with the exception of the gypsum powder which was heated in a 2-inch layer at 75° for two hours then cooled and stored in a sealed container at room temperature. The glass strands were chopped by hand to approximately 3/8 inch with standard scissors.

Two methods were adopted for mixing the aggregate with the resin. The principal method was to first thoroughly wet the sand, gravel and chopped glass fiber, then manually mix in the gypsum and clay powders. The ratio of resin to the aggregate components was determined by the amount of resin necessary to produce a stiff, workable paste. This paste was cast by placing it into a suitable mold with rodding at appropriate intervals. Several sharp taps were also administered on the mold surface while filling the mold.

The second method was used exclusively when sand fines were the sole aggregate component. The sand was poured directly into the mold and rodded at intervals to compaction. The resin system was then introduced at the base of the mold and allowed to diffuse up through the

^{*}Polymeric materials need to be identified by manufacturer because of variations in formulation

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sand under atmospheric pressure until it was saturated.

Samples produced with the second method were placed in an oven and heated to 75° C for twelve hours, then removed from the oven and cooled to room temperature. This was done to speed up the polymerization process without using accelerators with the catalysts which could prematurely polymerize the binder before the aggregate was completely saturated.

Samples produced with the first method were cured at room temperature, 20° C, for twenty-four hours using a combination of catalysts and accelerators.

C. Testing Procedures

All material tests followed standardized ASTM procedures where possible. Any variance from accepted ASTM procedure was undertaken to facilitate screening rather than full scale verification. A listing of material test procedures follows:

- 1. Flexural Strength; Modulus of Elasticity
 - (a) ASTM* C293-68, using a cylindrical beam
 - (b) Specimen size: 2 in. diameter x 8 in. cylinder
 - (c) Instrumentation: Instron Universal Testing Machine, synchronized chart; load vs. time, deflection vs. time.
- 2. Compressive Strength (a) ASTM C116-68
 - (b) Specimen size: 2 in. diameter x 4 in. cylinder
- 3. Splitting Tensile Strength (a) ASTM C496-71
 - (b) Specimen size: 2 in. diameter x 4 in. cylinder

IV. RESULTS AND DISCUSSION

Initially methyl methacrylate alone was used for the resin matrix. It suffered in these ways: the monomer volatility was too high, producing noxious vapors in the mixing phase and excessive evaporation before complete polymerization; also polymerization at ambient temperatures could only be achieved by gamma radiation, considered to be impractical for field application.

Polyester and styrene were then studied as an alternative resin system. They had better handling characteristics and polymerization could be achieved at ambient temperatures with chemical catalysts. However, the composites did not have the high quality finish, strength or weathering characteristics of the composites with methyl methacrylate.

*1973 Annual Book of ASTM Standards, American Soceity for Testing and Materials, Philadelphia.

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In an effort to optimize the polymerization characteristics and physical properties of our resin, we developed various combinations of polyester-styrene and methyl methacrylate. These are described in Table I, together with the aggregates used in the composite systems.

A. Optimization of Resin Formulations

Using the four resin formulations described in Table 1, a number of chemical additives were introduced to accelerate the polymerization process and improve the composite strength. A set of forty samples was prepared with either a fine or coarse sand mixture. The amount of polymer required to produce a workable, mud-like mix was noted, and the mix was cast in glass tubes 0.655 in. in diameter x 6 in. long. They were then cured at either room temperature or in an oven. Following the cure, the forms were removed and the surface quality of the specimens was noted. They were then tested in flexure. Typical results are shown in Table 11.

Because of the relatively high viscosity of the unsaturated polyester resin, formulations that were high in this component required greater proportions of resin to aggregate in order to achieve a workable paste. However, only the resin formulations high in polyester (over 40%) were capable of curing at room temperature. The formulations with 20% polyester failed to get an initial set at room temperature and were subsequently placed in an oven to cure (Table 11).

Increased use of styrene in the resin mix was found to have a tendency to decrease the flexural modulus and strength of the composite. Thus composites made with Resin Mix C, which contains 25% styrene, develop flexural moduli of 2,250,000 psi (15.5 kN/mm²) and flexural strengths of 5,750 psi (39.7 N/mm²) versus 2,070,000 (14.3 kN/mm²) and 5,250 psi (36.2 N/mm²) respectively for systems with Resin Mix D, which has 60% styrene.

The amount of methyl methacrylate in the Resin Mix was found to contribute most directly to the appearance of the composite. Increases in methyl methacrylate content gave composites with glossier surfaces and reduced darkening of the aggregate.

A chlorendic anhydride was added to the resin mix to promote polymerization and enhance fire resistance of the system. The anhydride did improve the polymerization rate at room temperature. It was also useful in achieving a flaw-free composite, with a tack-free finish on exposed surfaces.

The resin-to-catalyst ratio was important in determining both the rate and extent of the polymerization. Either too much or too little catalyst resulted in flawed materials. Generally, the specimen's shape, size and percentage of resin as well as the cure temperature controlled the catalyst requirements. Less catalyst was required with high resin loadings due to increased polymerization exotherms per unit volume. Less catalyst was also required with larger or more compact sections because of lower heat dissipation rates, due to the lower surface-to-volume ratios of the specimen.

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The use of additional accelerators significantly increased the rate of polymerization, making rapid cures at room temperature possible even with small samples. The higher cure rates also reduced evaporation of the resin from the specimen. However, excess accelerator often introduced flaws in the polymeric matrix and surface finish, such as unpolymerized areas and discoloration in the specimen.

As expected, specimens cured in the oven at 75° C developed higher flexural strengths (by 10 to 15%) than those cured at ambient temperature (20° C). However the most dramatic effects of the oven cure were observed in the flexural moduli, which were 35 to 50% higher than those of the same formulations, cured at 20° C.

Resin Mix C was selected as the optimum polymer formulation, and was used as the resin basis for the composite systems, listed in Table III. The addition of an azo catalyst and reduction in the quantity of accelerator in the optimum formulation improved the rate and extent of the polymerization at room temperature. The addition of larger quantities of crosslinking agents and a silane coupling agent improved the physical properties of the polymer matrix, resulting in stronger and stiffer composites. Test results for these materials are shown in Table IV.

B. Aggregate Systems

In the initial testing of the resin binders, two aggregate mixtures were studied. The first combination consisted of the resin mix with conventional concrete sand and gypsum filler. The second combination consisted of the resin binder with sea sand and gypsum filler. The difference between the two aggregate systems was, principally, particle size. The concrete sand was smoothly graded with a maximum particle size of 0.150 inches. The sea sand was smoothly graded with a maximum size of 0.0150 inches.

In these initial tests, specimens with sea sand showed an average polymer content 16% greater than specimens with concrete sand. The specimens showed significant differences in their flexural strengths and moduli of elasticity. Those with sea sand were almost 12% stronger than those with concrete sand. The reverse was true with respect to their moduli of elasticity. Specimens with concrete sand were almost 10% stiffer than specimens with sea sand.

Using the polymer binder shown in Table III, a subsequent test series was conducted. These systems were formulated and tested in order to investigate a wider range of aggregate sizes, to incorporate some new materials, and to clarify the contributions of gypsum to the properties of the composite. A number of aggregate gradings were selected with a range of particle sizes from sand fines to gravels. Chopped glass and Ottawa sand were also studied in separate tests. Clay was added to some formulations. The materials were either premixed or the resin was introduced after placement as described in the Experimental section. Specimen sizes were increased to allow for the coarse materials. With the exception of the specimens that had the resin introduced after placement in the mold, all specimens were cured

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at room temperature. A discussion of the results follows.

The influence of particle size on resin loadings was clearly demonstrated in these experiments. The specimen with sand fines and gypsum required twice as much resin to achieve a workable mix as a similar specimen with 50% gravel (Table IV, System II and System V).

Gypsum was used to produce plasticity in the aggregate-resin mix. Handling qualities were similar to conventional concrete when gypsum was added. The gypsum gave a smooth molded finish in the cast materials, and was a desirable medium for enhancing the aggregate colors. The resin absorbency of the gypsum was significantly reduced by heating it in an oven as described.

A sand-and-resin specimen was studied in comparison to a sand-resin gypsum specimen. A special procedure of diffusing the resin through the packed sand (see Experimental section) was adopted to achieve an even distribution of polymer in the specimens without gypsum. This procedure eliminated voids in the material normally incurred with batch techniques. The specimen without gypsum showed an increase in compressive strength of slightly more than 10%, and a decrease in stiffness of more than 50%. The specimen also showed a 20% increase in amount of polymer required over the comparable specimen with gypsum (Table IV, Systems 1 and 11).

Ottawa sand as filler produced a particularly unique material. The highly crystalline Ottawa sand was remarkably translucent when combined with the clear polymer binder. Cast in sections from 1/16 to 1/4 inch thick a number of panels were produced with different degrees of translucence. The fine spherical sand diffused light uniformly, and cast a slightly golden hue because of its faint straw color.

Fiber glass strand was cut into 3/8 in. lengths in an investigation of fiber reinforcement, and added to the material during the mixing phase. The chopped fiber was added in what was considered to be the maximum limit for a good, workable mix. The fiberglass increased the polymer requirements of the material by more than 50% of comparable materials without fiber. The stress-strain curve of this material was unique; it was not perfectly brittle, having some elastic deformation (fiber failure) before rupture (Fig. 1). The compressive strength was lower, by 33% (Table 1V, System II and System V!).

Red and grey clay powders were tried in a few material formulations. They were very effective in imparting a natural earth color to the polymer-aggregate materials. Adding 5% clay (by aggregate weight) during the mixing produced materials with an especially attractive appearance.

V. ECONOMICS

The polymer binder represents a considerable increase in material costs when compared with conventional portland cement binder. However, an "inplace" cost analysis of several polymer concrete formulations, summarized in Table V, indicates that in certain cases they might well

be competitive with conventional concrete in terms of the total cost of field-constructed structures.

For lack of better information, this analysis assumes similar placing and forming costs for the polymeric and conventional concrete, based on average figures for cast-in-place column, beam and slab costs for a reinforced concrete building. In Table V one column of data shows the cost of that amount of polymer concrete equivalent to one cubic yard of portland cement concrete, assuming the volume is reduced in proportion to the increase in compressive strength. This assumption is valid if the size of the structural member is based on compressive strength. If the size of the member is based on the concrete strength in tension, the volume reduction would be even greater. If the size of the member is based on stability considerations or on strength of reinforcement, then of course the volume reduction would be less. We arrive thus at estimated total costs for equivalent structures, using the various polymer formulations under development, which compare favorably with the corresponding cost of portland cement concrete.

Table V also shows the equivalent structure weight of the various concrete systems. The weight of the polymer concrete structures ranged from only 24 to 46% of that of the portland cement structure. Consequently, in design, the cost of the polymer concrete structure could be reduced even further to reflect reduction in the structure's dead load with a corresponding reduction of frame and foundation requirements.

This rough estimate does not take into account other advantages of polymer concrete, such as its faster curing time (1 day versus 28 days) for faster construction and recycling of formwork, or its various aesthetic aspects, which may eliminate finishing or decorative operations necessary with conventional concrete.

VII CONCLUSIONS

On the basis of this investigation, a number of conclusions appear valid:

1. Maximum individual values of strength obtained were as follows:

Compressive strength	21,100 psi	(145.6 N/mm ²)
Flexural tensile strength	6,000 psi	(41.4 N/mm ²)
Splitting tensile strength	2,210 psi	(15.2 N/mm ²)

- Modulus of elasticity ranged from 1,460,000 psi (10.1 kN/mm²) to 3,300,000 psi (22.8 kN/mm²).
- Unit weights ranged from 122 to 145 pcf (1,970-2,350 kg/m³).
- Rapid curing at ambient temperatures was possible. The addition of a chlorendic anhydride improved polymerization at both ambient and elevated temperatures.
- 5. The addition of methyl methacrylate monomer to a polyesterstyrene resin improved the resin for use in polymer aggregate systems by imparting a hard clear mirror finish to the cast

materials. It reduced the viscosity of the polyester-styrene resin for a workable mix with less resin without reducing the strength. It also formed a co-polymer with enhanced weathering characteristics.

- 6. The selected proportions of polyester-styrene-methyl methacrylate gave resin systems, suitable for making casting pastes with low resin requirements or diffusing through compacted sands under atmospheric pressure. These systems cure quickly, with negligible monomer evaporation.
- 7. The aggregate particle size and distribution affected the strength and resin requirements of the composite system. Fine sands produced a more workable mix which may be cast in relatively thin sections and sawn and sanded with hand power tools. The addition of coarser sands and gravels produced the most economical mix but with a corresponding reduction in strength and homogeneity.
- A pre-heated gypsum powder was instrumental in obtaining an economical, workable mix for casting with equipment and procedures similar to those of conventional concrete construction.
- 9. The polymer concretes investigated cost more than conventional concretes for equal volumes of material but compare well with conventional concretes on a cost-to-strength basis.

Specific applications of these new materials will require additional testing, but there would appear to be a wide range of potential applications for these materials.