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**WATER-COMPATIBLE POLYMER CONCRETE
MATERIALS FOR USE IN RAPID REPAIR
SYSTEMS FOR AIRPORT RUNWAYS**

FINAL REPORT

T. Sugama, L.E. Kukacka, and W. Horn

March 1981

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T. Sugama, L.E. Kukacka, and W. Horn

March 1981

**PROCESS SCIENCES DIVISION
DEPARTMENT OF ENERGY AND ENVIRONMENT
BROOKHAVEN NATIONAL LABORATORY
ASSOCIATED UNIVERSITIES, INC.**

**Work Performed for the U.S. Air Force
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ABSTRACT

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Formulations consisting of furfuryl alcohol, water-saturated aggregate, dry silica flour, promoters, and catalysts produced composites with properties suitable for repair purposes when mixed and polymerized at temperatures from -20° to 30°C .

Calcium-unsaturated polyester complexed PC also produced excellent properties. However, the early strength criteria [2000 psi (13.78 MPa) at 1 hr] and other requirements such as compatibility of the formulation with water and practical working times could be attained only at temperatures $>20^{\circ}\text{C}$. This system can be polymerized under water.

Studies of the polymerization reaction mechanisms, materials properties, costs, and potential placement methods were performed.

TABLE OF CONTENTS

	<u>Page</u>
Abstract	iii
Figures	vi
Tables	ix
Executive Summary	xii
 I. Introduction	 1
II. Selection of Monomers, Aggregate and Filler Systems	4
A. Literature Review	4
B. Candidate Systems	6
1. Materials	6
2. Experimental Procedure	7
3. Results and Discussions	9
C. Screening Tests	14
1. RPF and MF-PM formulations	15
a. Property Measurements	15
b. Kinetics and Reaction Mechanisms	24
2. FA-PM Formulations	32
a. Property Measurements	32
b. Kinetic Studies	39
3. Ca-UP Complexed PM Formulations	41
a. Property Measurements	41
b. Spectroscopic Studies	48
D. Cost Analysis of PM Formulations	52
E. Conclusions	52

TABLE OF CONTENTS (Cont'd)

	<u>Page</u>
III. Polymer Concrete Formulations	55
A. Aggregate Proportions	55
B. Retarders	58
C. Mixing Procedures	58
D. Optimized PC Formulations	60
1. FA-PC	60
2. Ca-UP PC	73
E. Mechanical and Physical Properties	78
F. Durability Properties	83
1. Heat Resistance	83
2. Hydrothermal Stability	83
3. Freeze-Thaw Durability	87
4. Resistance to Acid Attack	87
5. Resistance to 20% NaOH	87
6. Resistance to Chemical Attack by Acetone	88
7. Resistance to Kerosene	88
G. Reinforcement Materials	88
H. Materials Cost	88
IV. Process Technology	93
V. Conclusions and Recommendations	103
Acknowledgments	105
References	106
Appendix A	110
Appendix B	111
Appendix C	114

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FIGURES

	<u>Page</u>
1. Program outline	3
2. Typical thermograms of PM containing aggregate with a water content of ~8.0 wt%	13
3. Apparatus for flammability test	16
4. Compressive strength of RPF-PM samples containing various amounts of Type III portland cement vs time	16
5. Compressive strength of RPF-PM after a 1-hr cure time	18
6. Compressive strength of MF-PM samples containing various amounts of catalyst	22
7. Stress-strain curves for recommended PM formulations after curing for 3 days at ~24°C	22
8. DSC thermograms for RPF resin - Type III portland cement systems	25
9. Arrhenius log plots for the thermal polymerization of RPF resin combined with different amounts of Type III cement	27
10. Integral cure curves at 60°C for RPF resin combined with 5 wt% of various chemical constituents of cement	29
11. Effect of TCT catalyst content on the 1-hr compressive strength at 24°C of FA-PM containing aggregate with a water content of 7.5 wt%	33
12. Compressive strength vs water content of aggregate for FA-PM at a curing age of 1 hr	34
13. Stress-strain curves for FA-PM containing dry and wet aggregate at a curing age of ~3 hr	37
14. DSC thermograms of FA-PC containing wet aggregate	40
15. Arrhenius log plots for the thermal polymerization of FA-PM containing wet aggregate	40
16. The effect of reactive cement filler on the 1 hr compressive strength at 24°C of CP-PM containing aggregate with a water content of 7.5 wt%	43

FIGURES (Cont'd)

	<u>Page</u>
17. Compressive strength vs water content of aggregate for cement and silica flour-filled UP-PM at a curing age of 1 hr at 24°C	43
18. Infrared spectra of UP-St polymer and cement paste or silica flour paste-filled UP-St polymer	49
19. Changes in frequency from 1800 to 1300 cm^{-1} that occur at various process times for cement paste and silica flour paste-filled UP-St monomer	51
20. Interaction mechanism occurring between Ca^{2+} ions of cement grains and carboxylate anions of UP chains in an aqueous medium	51
21. Unit weight of aggregate having various F.A./C.A. ratios	57
22. Maximum water content of aggregate having various F.A./C.A. ratios	57
23. The effect of pyridine on the gel time of FA-PC	59
24. Mixture of wet aggregate with ZnCl_2 and silica flour	59
25. Mixture of initiated FA monomer with wet aggregate containing ZnCl_2 and silica flour	59
26. Frozen aggregate after exposure in air at -15°C for 24 hr	61
27. Frozen aggregate to which ZnCl_2 has been added	61
28. Effect of hooked steel fibers on the flexure strength of FA-PC containing wet aggregate	89
29. Compressive strength of FA-PC as a function of steel fiber concentration	90
30. Flexure strength of steel fiber-reinforced FA-PC as a function of cure time	90
31. Measurement of penetration depth of FA monomer into wet aggregate, and cured FA-PC after penetration to 30-cm depth	94
32. Monomer penetration in wet aggregate containing various No.30/ SiO_2 ratios as a function of ponding time	95

FIGURES (Cont'd)

	<u>Page</u>
33. The effect of No.30/SiO ₂ ratio on the early compressive strength of FA-PC	97
34. Monomer addition to prepared aggregate mix	100
35. Internal vibration of FA-aggregate mix	101
36. The effect of No.30/SiO ₂ ratio and internal vibration on the early compressive strength of FA-PC	102

TABLES

	<u>Page</u>
1. Monomer systems evaluated	8
2. Catalyst-promoter systems used for "room temperature" curing	8
3. Gel time, peak exotherm time, and compressive strength of polymer mortar specimens at ~24°C in air	10
4. Composition of RPF-PM containing different Type III portland cement contents	16
5. Composition of RPF-PM containing different water contents	18
6. RPF-PM compositions	19
7. Compressive strength of RPF-PM specimens as a function of age for the temperature range 30° to 2°C	20
8. Composition of MF-PM specimens	23
9. Measured properties of RPF and MF polymer mortars	23
10. Cure rate constants for the thermal polymerization of RPF resin combined with cement promoter	27
11. Composition of FA-PM specimens	33
12. FA-PM compositions	34
13. Compressive strength of FA-PM specimens as a function of age for the temperature range 30° to -20°C	35
14. Mechanical properties of FA-PM containing dry and wet aggregate after a 3-day cure in air at 24°C	38
15. Relative flammability of PM composites	38
16. UP-St PM compositions	42
17. Ca-UP complexed PM compositions	45
18. Compressive strength of Ca-UP PM as a function of age for the temperature range 30° to 2°C	46
19. Mechanical properties of Ca-UP PM containing wet aggregate after 3 days' curing in air at 24°C	47

TABLES (Cont'd)

	<u>Page</u>
20. Determination of the relative flammability of Ca-UP PM containing dry and wet aggregate	47
21. Polymer mortar material costs	53
22. Mechanical and physical properties of RPF, FA, and Ca-UP complexed PM in the presence of 7.5 to 8.0% water	54
23. Sieve analysis of coarse and fine aggregate used in PC	56
24. Compositions of FA-PC polymerized at 30°C	62
25. Test results, FA-PC cured at 30°C	63
26. Compositions of FA-PC polymerized at 20°C	67
27. Test results, FA-PC cured at 20°C	68
28. Compositions of FA-PC polymerized at 10°C	69
29. Test results, FA-PC cured at 10°C	70
30. Compositions of FA-PC polymerized at 1°C	71
31. Test results, FA-PC cured at 1°C	71
32. Compositions of FA-PC polymerized at -10°C	72
33. Test results, FA-PC cured at -10°C	72
34. Compositions of FA-PC polymerized at -20°C	74
35. Test results, FA-PC cured at -20°C	74
36. Summary of FA-PC formulations for use at ambient temperatures between 30° and 10°C	75
37. Summary of FA-PC formulations for use at ambient temperatures between 1° and -20°C	75
38. Compositions of Ca-UP PC polymerized at 30°C	76
39. Test results, Ca-UP PC cured at 30°C	77
40. Compositions of Ca-UP PC polymerized at 20°C	79

TABLES (Cont'd)

	<u>Page</u>
41. Test results, Ca-UP PC cured at 20°C	80
42. Compositions of Ca-UP PC polymerized at 10°C	81
43. Test results, Ca-UP PC cured at 10°C	81
44. Summary of Ca-UP PC formulations for use at ambient temperatures between 30° and 20°C	82
45. Mechanical and physical properties of FA and Ca-UP PC containing wet aggregate at a curing age of 7 days at a temperature of ~24°C in air	82
46. Shear bond strength of FA and Ca-UP PC to Type III portland cement concrete	84
47. Stability of PC in air at 100°C	84
48. Stability of PC in water at 100°C	85
49. Resistance to freezing and thawing	85
50. Resistance to chemical attack	86
51. Compositions of steel fiber-reinforced FA-PC	89
52. Material costs for PC for use at temperatures between 1° and 30°C	91
53. Material costs for PC for use at temperatures between -10° and -20°C	92
54. Composition of wet aggregate	94
55. Composition of compacted wet aggregate	98

EXECUTIVE SUMMARY

Experimental work has been performed to develop a water-compatible polymer concrete (PC) for use in rapid repair of bomb-damaged airport runways. Requirements for the material include simple and rapid placement, fast curing under all weather conditions, high strength, and good durability.

The specific goal of this project was to develop PC systems with the following characteristics: they must have a low cost and long storage life; they must be nontoxic and nonflammable; and they must exhibit compatibility with water, rapid curing (<1 hr) over the temperature range -30° to 49°C, compressive strength >2000 psi (>13.78 MPa), flexure strength >1000 psi (>6.89 MPa), and bond strength >500 psi (>3.45 MPa) (all at an age of 1 hr). Two systems meeting many of these criteria were developed and they have been characterized in terms of their properties and costs. Both formulations consist of organic polymer binders, water-saturated aggregate, and dry fillers having a size of <62 μm .

Furfuryl alcohol (FA), a non-petroleum-based monomer, was used in one PC formulation. The FA was polymerized by a condensation-type reaction initiated by the addition of acidic α,α,α -trichlorotoluene (TCT) catalyst, zinc chloride (ZnCl_2) promoter, and alkali-type pyridine retarder combinations. The FA-PC made with wet aggregate, over an ambient temperature range of 1° to 30°C, was characterized by a gel time >1 min and a 1-hr compressive strength >2000 psi (>13.78 MPa). For the temperature range -10° to -20°C, the gel time was >6 min and the 1-hr compressive strength was >3000 psi (>20.67 MPa). Other properties included a flexure strength of ~550 psi (~3.79 MPa) and a bond strength to a dry concrete surface of ~160 psi (~1.10 MPa), both at an age of 7 days. By the inclusion of hooked steel fiber reinforcement in this formulation, the flexure strength was increased to >900 psi (>6.20 MPa).

The second system showing promise was a calcium (Ca) - unsaturated polyester (UP) material. This formulation utilizes a Ca-UP complexed ionomer binder that is formed by an ionic bond occurring between Ca^{2+} ions released from portland cement paste and carboxylate anions ($-\text{COO}^-$) produced by the hydrolysis of ester groups in the UP monomer. These hydrolytically synthesized Ca-UP complexed ionomers were polymerized by an addition-type reaction initiated by the use of methyl ethyl ketone peroxide (MEKP) catalyst and cobalt naphthanate (CoN) - dimethyl aniline (DMA) promoters. When polymerized at a temperature $\geq 20^\circ\text{C}$, this formulation was characterized by a gel time >3 min, a 1-hr compressive strength >2000 psi (>13.78 MPa), a 7-day flexure strength of ~1080 psi (~7.44 MPa), and a 7 day bond strength to a dry concrete surface of ~360 psi (~2.48 MPa). However, because of its low polymerization rate at temperatures $\leq 10^\circ\text{C}$, this system does not appear to have as much potential as the FA-PC formulations.

The material costs of FA and Ca-UP complexed PC for use at ambient temperatures between 1° and 30°C were calculated to be $\sim\$510$ and $\sim\$530/\text{m}^3$ ($\sim\$390$ and $\sim\$405/\text{yd}^3$), respectively. The cost of the FA-PC composite for use in the temperature range -1° to -20°C was $\sim\$670/\text{m}^3$ ($\sim\$512/\text{yd}^3$).

Preliminary work to identify methods for practical field utilization of both formulations was performed. A method in which wet coarse and fine aggregate was prepacked into the hole prior to saturation with monomer was shown to be technically feasible and yielded the desired properties.

On the basis of these criteria - simplicity, properties, and cost both PC systems show potential for use as all-weather rapid runway repair materials. Additional work to continue the development appears warranted.

I. INTRODUCTION

Methods for the simple and rapid repair of bomb-damaged aircraft runways under all-weather conditions are needed. As part of this effort, the U.S. Air Force Engineering and Services Center (AFESC) is currently engaged in a 7-year program aimed at meeting this need.

A material currently receiving world-wide attention as a rapid patching material for concrete is polymer concrete (PC). This material consists of an aggregate and a polymeric binder. To produce PC, the aggregate is mixed with a monomer formulation and subsequently cured in place. The resultant PC has the premix characteristics of portland cement concrete (PCC) combined with high strength, long-term durability and short cure time. Although PC is expensive (materials cost ~\$523/m² [\$400/yd³]) compared to PCC, its excellent properties make it cost effective for many specialized applications.

PC can be made using a variety of materials such as epoxies, polyesters, methyl methacrylate (MMA), and mixtures of MMA with other acrylics and crosslinking agents. Considerable research and development have been performed, and the materials are being used commercially in the U.S.A., Japan, and Europe.¹⁻⁵ Of the many monomer systems tested, it has been reported that acrylic-based PC, with reactive resins as the sole binder, comes closest to meeting the long-term demands imposed on the materials system because of low shrinkage and other favorable characteristics.⁴

To provide a significantly faster runway repair technique than more conventional flexible pavement construction, PC must have curing times of 30 to 60 min. Durability and high strength are also needed. If PC is to withstand aircraft traffic, it must have a flexural strength equivalent to PCC. Flexure strengths above this value would allow the use of thinner pavement sections, thereby resulting in shorter placement times and reduced cost.

An additional requirement for use in rapid repair systems is simple and rapid placement under all weather conditions. The materials must be usable under conditions which include a wide range of temperatures and all forms of precipitation. This unique feature of all-weather repairs distinguishes the rapid runway repair requirements from conventional highway and airport routine repair, and it also presents a separate set of interesting technical problems. Even conventional PCC has placement problems in below-freezing temperatures or driving rain. The biggest obstacles for use of PC in all weather conditions are: controllable curing rates at extremely high and low temperatures, moisture tolerance, and mechanization. Each presents its own specific problems.³

Generally, acrylic-based PCs require the use of dried aggregate to yield a high-strength material. As an example, McNerney³ has reported that the compressive strength of MMA PC decreased 50% when the sand aggregate moisture content was increased from 0.2 to 0.8 wt%. Since the

moisture contents of water-saturated mixtures of fine and coarse aggregate are generally >3 wt%, the practicality of the use of conventional MMA PC formulations for all-weather repairs is doubtful.

On the other hand, synthetic rubber latexes and resin emulsions consisting of polymers dispersed in water have been widely used as water-soluble organic polymer binders for cement mortars and concretes. However, the curing of these polymer-modified hydraulic cements at an ambient temperature of ~25°C proceeds very slowly. Curing times >24 hr are generally needed to obtain a compressive strength >2000 psi (13.78 MPa).

In research sponsored by the U.S. Department of Energy, Brookhaven National Laboratory (BNL) studied the interactions that occur between organic polymers and inorganic fillers in the presence of moisture. During one study,⁶ it became apparent that several of the major criteria for airport runway patching materials could be met by the use of condensation-type polymers in PC. As a result, under sponsorship of the U.S. Air Force (Contract No. AFOSR-ISSA-80-00027), 4 resin systems, resorcinol phenol-formaldehyde (RPF), urea-formaldehyde (UF), melamine-formaldehyde (MF), and furfuryl alcohol (FA), were selected for additional evaluation.

For purposes of comparison with the condensation-type polymers, vinyl-type MMA and ester-type unsaturated polyesters (UP), representative of addition-type polymers, were also evaluated.

The specific goals of the BNL work were to identify PC systems that would exhibit the following characteristics: compatibility with water, rapid curing (<1 hr) over the temperature range -34° to 49°C, compressive strength >2000 psi (13.78 MPa) at an age of 1 hr, flexure strength >1000 psi (6.89 MPa), bond strength >500 psi (3.44 MPa), long storage life, low cost, nontoxicity, and nonflammability.

In order to accomplish the program goals within the 12-month contract period, a detailed outline and schedule for the work was prepared (see Figure 1).

Phase A was accomplished in 6 months and consisted of the measurement of the mechanical and physical properties of specimens containing water-compatible organic binders and water-saturated aggregate. Specimens 2.2 cm diam x 4.4 cm long were used in most of these screening tests, and two promising systems were selected from these studies to optimize the mix variables with respect to properties.

Additional tests to determine the physical and mechanical properties of the selected systems over a wide range of temperatures were performed in Phase B. Larger-size specimens were used in this phase of the work to determine the effects of large aggregate and steel fiber reinforcement on the properties. Preliminary studies to identify methods for the practical field utilization of the formulations were also performed in Phase B. Final program documentation was prepared in Phase C.

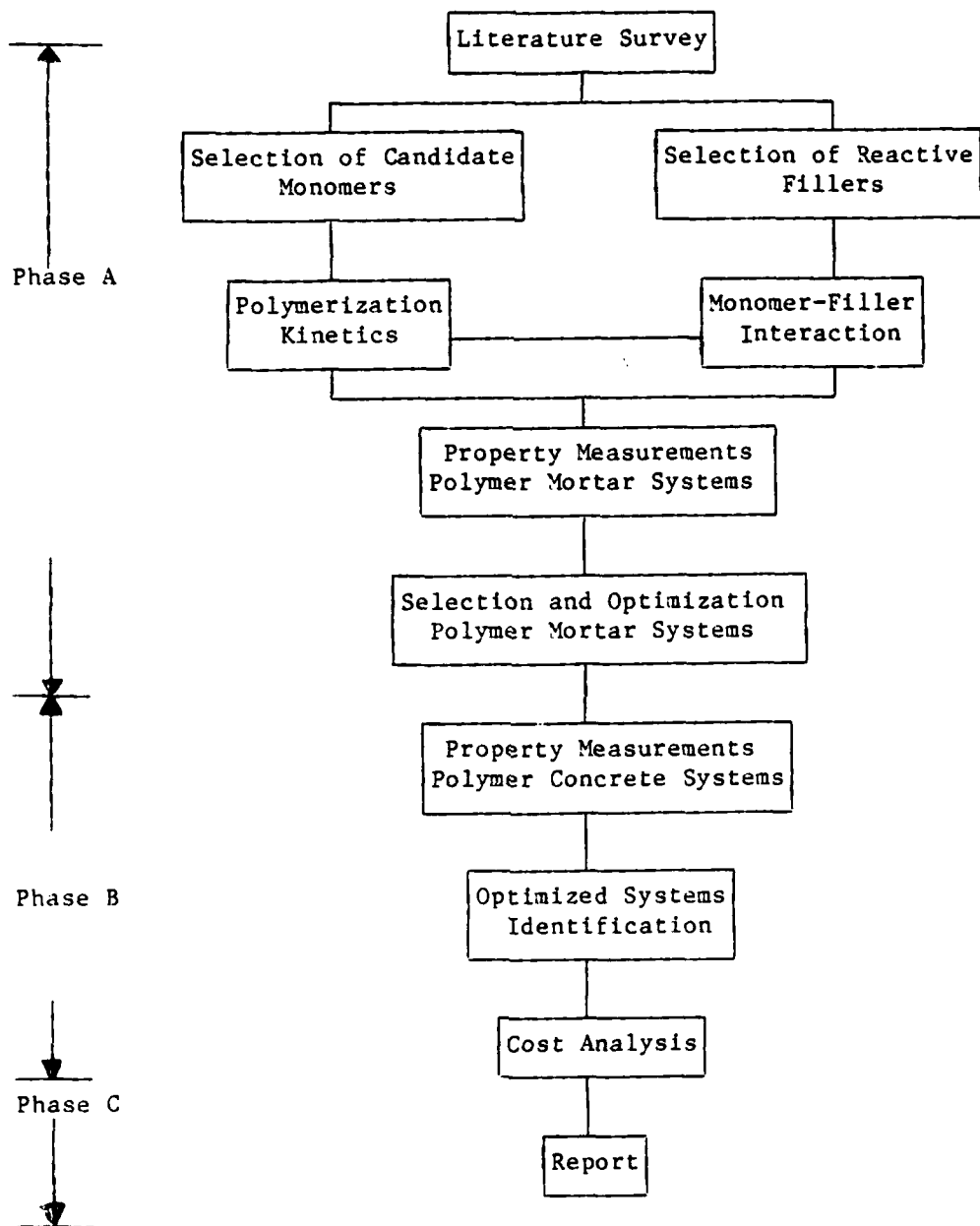


Figure 1. Program outline

II. SELECTION OF MONOMERS, AGGREGATE, AND FILLER SYSTEMS

On the basis of a literature survey, discussions with the chemical industry, and BNL expertise, the four condensation-type monomers listed previously were selected for evaluation in PC containing water-saturated aggregate. Monomer selection was based upon the following criteria: 1) ease of polymerization, 2) low-flammability, 3) shelf life, 4) miscibility with water and organic solvents, and 5) polymerization to yield high-strength chemically resistant materials.

Several types of fine aggregates and reactive filler materials were also selected. The latter act as promoters and induce chemical bonding between the polymers and water-saturated aggregate.

A. Literature Review

A literature survey was conducted to aid in the selection of organic-type polymers that could be used in the formation of PCs having compressive strengths >2000 psi (13.78 MPa) within 1 hr after mixing with aggregate containing water contents of ~8 wt%. Major findings are reported below.

When aggregate containing >3 wt% water is used in organic-type PC, a polymeric binder having an active group with a chemical affinity for moisture is required in order to obtain a strong bond at the interface between polymer and aggregate. The degree of affinity between the water and organic polymer phases depends primarily on the type of polymerization reaction (addition, condensation, emulsion, or ionic) and the number of OH and NH₂ groups in the polymer chain. The water content that is required for latex and emulsion-type polymer-modified cement concretes or mortars, prepared by emulsion polymerization, is in the range of ~8 to ~20% by weight of aggregate.^{7,8} However, the curing rates of polymer-modified hydraulic cements at temperatures of ~25°C are very slow.⁹⁻¹² Curing times >24 hr are generally needed to obtain a compressive strength >2000 psi (13.78 MPa).

When vinyl-type polymers such as MMA and unsaturated polyesters are used in PC, aggregate containing <1 wt% water is required.^{13,14}

From the literature review, it appeared that the use of emulsion, latex and addition polymerization-type monomers for rapid all-weather PC repair systems would be very difficult. As a result, attention was given to condensation-type polymer systems.

Phenol-formaldehyde (PF), melamine-formaldehyde (MF), urea-formaldehyde (UF), and furfuryl alcohol (FA) monomers contain OH and NH₂ groups in their chains which result in a strong affinity for moisture. A general characteristic of these monomers is that they yield a three-dimensional polymeric structure consisting of methylene and ether bridge formations when polymerized by a condensation-type reaction initiated by

use of acid and alkali-type catalysts. A by-product of the reaction is water.^{15,16} Furthermore, it is possible for the water to act as a plasticizer for the polymers.

PF resin as an aqueous solution is generally classified by the molecular structure: namely, the resole and novolac types, produced by the addition of alkali and acid catalysts, respectively.¹⁷ The condensation polymerization is accomplished by heating with the addition of hexamethylene tetramine.¹⁷ Resole-type PF resins are a mixture of 2,4-dimethylol-phenol, *p*-hydroxylbenzyl, and ortho-hydroxylbenzyl.¹⁸⁻²⁰

Novolac-type resins are phenol-ended chain polymers in which the phenolic nuclei are joined by methylene bridges located ortho and para to the phenolic hydroxyl groups.²¹⁻²³ Resole-type PF resin is also characterized by the one-stage polymerization which is highly reactive, when compared with the two-stage process of novolac-type PF.¹⁷ This means that the polymerization rate of the resole type is higher than that of the novolac type.

In order to assure a high degree of polymerization, the choice of a suitable alkali catalyst is very important. From the various alkali catalysts [$\text{Ca}(\text{OH})_2$, NaOH, triethylamine etc.], NaOH has been shown to be the most effective for use with the resole PF resin.^{24,25}

The formaldehyde-type condensation polymers also include MF and UF monomers which contain NH_2 groups in their molecules. Curing of these monomers is accomplished by the addition of an acid or acid-releasing catalyst. The use of ammonium salt as a strong acid catalyst will react with any uncombined formaldehyde present in the resin dispersion, as well as with the terminal methylol groups of the monomeric species, to form hexamethylenetetramine and the corresponding free acid.²⁶ The acid released from the salt acts as a catalyst to promote condensation of the monomers and intermediate polymer by elimination of water, forming straight or random chains and closed-ring structures.²⁶

FA monomer is characterized by low vapor pressure (1 mm Hg at 31.8°C), low viscosity (~ 5 cP at 25°C), low flammability (1.8 to 16.3% in air in the temperature range 72.5° to 122°C), and solubility in water. Furfural, an intermediate in the production of FA monomer, is produced from agricultural wastes such as corn cobs, oil hulls, etc.¹⁶ As a result, FA monomer is produced from a relatively stable supply source, which is low cost and energy conservative when compared to other conventional petroleum-based organic materials such as MMA, styrene (St), and UP.

The condensation polymerization of FA is normally conducted using acidic-type initiators such as benzenesulfonic acid, *p*-toluenesulfonic acid, trichloroacetic acid, α, α, α -trichlorotoluene, α, α -dichlorotoluene, and α -chlorotoluene.^{27,28} In an attempt to develop a one-step curing process, Hess²⁷ measured the gel times at 25°C of FA combined with these

acidic-type initiators. He demonstrated that gelatins could be produced within 20 hr by the addition of benzenesulfonic acid, *p*-toluenesulfonate, and α,α,α -trichlorotoluene (TCT).

In our study, TCT, which shows catalytic effects brought about by a hydrolytic reaction when water is present, was used as the acid-based initiator. However, it was very difficult to obtain a high rate of polymerization at $\sim 24^\circ\text{C}$. Therefore, the use of promoters which would accelerate the reaction was required. Several water-soluble metallic salts such as SnCl_4 , ZnCl_2 , and AlCl_3 were considered as materials to give the desired ~ 30 min cure at 24°C . Because of its low cost, ZnCl_2 was selected.

It has been reported that ZnCl_2 is widely used as a catalyst for FA monomer.²⁹ When the FA- ZnCl_2 system is activated by heating to temperatures between 60° and 85°C , it results in a smooth polymerization and a high solids yield. In our preliminary experiments, it was found that the addition of ZnCl_2 to the FA-TCT system produced a highly polymerized FA and the gel time was decreased markedly. Therefore, the use of ZnCl_2 as a promoter was adopted.

B. Candidate Systems

Based upon the results from the literature survey, a series of preliminary experiments were performed and the results were used in the selection of systems for further evaluation. In this work, polymer mortar (PM) specimens were made using formaldehyde, alcohol, vinyl, and ester-type polymers as binders and silica sand as aggregate. The moisture content of the aggregate was ~ 8 wt%.

1. Materials

Three formaldehyde-type monomers RPF, MF, and UF, were evaluated. These are commercial materials and were supplied by the Gulf Oil Chemicals Company.

The polymerization of RPF monomer was initiated by the addition of 20 wt% promoter (Gulf Oil Chemicals Company commercial name S-10) and an adequate amount of Type III portland cement which was used as a reactive filler. The major chemical constituent of S-10 is paraformaldehyde.

MF is a solid and it was first dissolved in water to produce a solution with a viscosity of 165 cP. It was then mixed with the sand aggregate.

The MF and UF monomers were polymerized using a sulfonate-type catalyst (commercial name: TWA, Gulf Oil Chemicals Company).

The FA monomer used in these preliminary tests was a commercial-grade material supplied by the Quaker Oats Company. As discussed earlier, polymerization was initiated by the use of TCT and ZnCl_2 . Since ZnCl_2 is readily soluble in water, it was easy to distribute it uniformly in the wet aggregate phase.

For the purpose of comparison with the above systems, two monomer mixtures commonly used in PC, 95 wt% MMA - 5 wt% trimethylolpropane trimethacrylate (TMPTMA), and 50 wt% UP - 50 wt% St monomer, were also evaluated. These mixtures represent vinyl- and ester-type monomers, respectively. The MMA-TMPTMA mixture was polymerized by use of benzoyl peroxide (BPO) as a catalyst and dimethyl aniline (DMA) and dimethyl toluidine (DMT) as promoters. The UP-St monomer was polymerized using methyl ethyl ketone peroxide (MEKP) catalyst, and cobalt naphthanate (CoN) and dimethyl aniline (DMA) promoters.

Some properties of these monomers are given in Table 1 and polymerization systems for each are summarized in Table 2.

Type III portland cement having a specific surface of $4920 \text{ cm}^2/\text{g}$, as measured by the Blain method, was supplied by Lone Star Industries Inc. for use as a reactive filler material. The chemical compounds in the cement were as follows:

Composition, %						Loss on
CaO	SiO_2	Al_2O_3	MgO	Fe_2O_3	SO_3	ignition, %
63.77	19.82	6.01	3.10	2.37	3.27	0.86

For purposes of comparison with the cement filler, silica flour having a particle size $<62 \mu\text{m}$ was used as a moisture-absorbing filler material.

The aggregate used in preparing the PM was a commercial silica sand having a particle size of 1.19 to 0.149 mm.

The PMs were prepared by thoroughly mixing the wet aggregate with the dry filler. The mixing was performed by hand for ~2 min. This was followed by the addition of the monomer mixture containing an adequate amount of catalyst and promoter and subsequent mixing for ~1 min.

2. Experimental Procedure

Gel times, peak exotherm times, and peak temperatures for the PM formulations were measured by inserting a thermocouple connected to a strip chart recorder into a test tube containing a 150-g mass of the PM. During polymerization the temperature was monitored on the recorder.

The compressive strength was determined for triplicate PM specimens with a curing age in air of 24 hr at a temperature of $\sim 24^\circ\text{C}$. Specimens 2.2 cm diam x 4.4 cm long were used for compressive strength tests.

Table 1			
Monomer Systems Evaluated			
Monomer	Formula ^a	Form	Viscos. at 24°C, cP
Resorcinol phenol-formaldehyde	$C_6H_4(OH)_2 - C_6H_5OH - HCHO$ (2-3) (1-1.5) (1-2)	Liquid	1760
Urea-formaldehyde	$NH_2CONH_2 - HCHO$ (1.0) (1.5-2.5)	Liquid	7150
Melamine-formaldehyde	$NH_2C:NC(NH_2):NC(NH_2):N-HCHO$ (3-4) (1-1.5)	Powder	165 ^b
Furfuryl alcohol	$OCH:CH CH:CCH_2OH$	Liquid	5
Methyl methacrylate-trimethylol- propane trimethacrylate	$CH_2:C(CH_3)COOCH_3-(CH_2=CH_3-COOCH_2)_3CCH_2CH_3$ (1.0) (0.02)	Liquid	1
Polyester-styrene	$-OCOCH:CHCOOCH_2CH_2-C_6H_5CH:CH_2$ (1.0) (1.4)	Liquid	123

^aMolar ratios of the primary ingredients.

^bObtained by dissolving powder in 30% water.

Table 2		
Catalyst-Promoter Systems Used For "Room Temperature" Curing		
Monomer	Catalyst	Promoter
Resorcinol phenol-formaldehyde	Paraformaldehyde (S-10)	Type III portland cement
Urea-formaldehyde	Sulphonate-type (TWA)	—
Melamine-formaldehyde	Sulphonate-type (TWA)	—
Furfuryl alcohol	1,1,1-trichlorotoluene (TCT)	Zinc chloride ($ZnCl_2$)
Methyl methacrylate- trimethylolpropane- trimethacrylate	Benzoyl peroxide (BPO)	Dimethyl aniline (DMA)+ Dimethyl toluidine (DMT)
Polyester-styrene	Methyl ethyl ketone peroxide (MEKP)	Cobalt naphthanate (CoN) + Dimethyl aniline (DMA)

3. Results and Discussions

Data from preliminary tests on PM systems are given in Table 3 and typical temperature-time curves are shown in Figure 2.

For PM containing RPF (Samples 1 to 4), the data indicated that the curing rate and compressive strength increased as the concentration of the Type III cement promoter was increased. Although not indicated in Table 3, the gel time of RPF-PM without the cement filler was ~10 hr. Samples containing 8.9 and 15.6% cement had gel times of ~7 and 2 min, respectively. Their compressive strengths were 2823 (19.46 MPa) and 3065 psi (21.14 MPa) at 24 hr.

Silica flour, particle size <60 μ m, was used as a dry filler in the UF specimens. As expected, the cure rate increased with increased initiator concentration. Unfortunately, the compressive strength decreased with increased curing rate and all of the formulations had strengths <2000 psi (13.78 MPa).

All MF specimens had 24-hr strengths >4000 psi (>27.56 MPa) even though the curing rates were lower than for the UF samples. As indicated in Figure 2, the low rate of cure for the MF system did not produce an appreciable exothermic peak. From these results it was apparent that special promoters and reactive fillers would have to be developed before this system could meet the program goals.

For the FA specimens, the gel times, peak times, peak temperatures, and compressive strengths were measured on samples prepared by varying the amount of ZnCl_2 promoter added while maintaining a constant FA monomer to TCT catalyst ratio of 100:3.25.

The same dry silica flour as used in UF and MF-PM specimens was used as a filler material with the FA. The data indicated that the gel and peak exotherm times decreased with increased ZnCl_2 concentration. Although not shown in Table 3, the gel time for FA specimens containing 4.0% TCT catalyst but without the ZnCl_2 was ~6 hr at 24°C.

The peak exotherm temperature and 24-hr compressive strength of FA-PM increased with ZnCl_2 concentration. Compressive strengths >2000 psi (>13.78 MPa) were obtained by the addition of >6% ZnCl_2 . At a concentration of 8.4%, the strength was 4560 psi (31.42 MPa).

The FA system also appeared to have the potential for a relatively easy placement procedure. The low-viscosity FA has a long shelf life and can be mixed conventionally. In addition, ZnCl_2 offers minimum storage problems and is compatible with water.

The use of a 50% UP - 50% St monomer system with wet aggregate would normally be avoided because of the degradation of the polymer matrix brought about by the hydrolysis of the UP polymer. However, it was found

Table 3

Gel Time, Peak Exotherm Time, and Compressive Strength of
Polymer Mortar Specimens at ~24°C in Air

Specimen No.	Composition	W/W+A, %	Gel time, min	Exothermal peak time, temperature, °C	Compressive strength after curing 24 hr in air at ~24°C, psi (MPa)
1.	$\overbrace{26.6\%RP-6.7\%(S-10)-53.2\%A-4.6\%W-8.9\% \text{ cement}}^P$	8.0	7	15 47	2823 (19.46)
2.	26.6%RP-6.7%(S-10)-49.9%A-4.4%W-12.4% cement	8.1	4	11 52	2903 (20.02)
3.	26.6%RP-6.7%(S-10)-47.0%A-4.1%W-15.6% cement	8.0	2	7 57	3065 (21.14)
4.	26.6%RP-6.7%(S-10)-44.4%A-3.9%W-18.4% cement	8.1	2	5 59	3145 (21.69)
5.	$\overbrace{22.3\%UF-1.4\%TWA-57.0\%A-5.0\%W-14.3\%SiO_2}^P$	8.1	23	—	1655 (11.41)
6.	21.4%UF-2.3%TWA-57.0%A-5.0%W-14.3%SiO ₂	8.1	15	—	1533 (10.57)
7.	19.0%UF-4.7%TWA-57.0%A-5.0%W-14.3%SiO ₂	8.1	10	—	1371 (9.46)
8.	16.6%UF-7.1%TWA-57.0%A-5.0%W-14.3%SiO ₂	8.1	6	—	1190 (8.21)
9.	$\overbrace{14.2\%MF-3.6\%H_2O-2.2\%TWA-59.9\%A-5.2\%W-14.9\%SiO_2}^P$	8.0	120	—	5726 (39.49)
10.	12.8%MF-3.2%H ₂ O-4.0%TWA-59.9%A-5.2%W-14.9%SiO ₂	8.0	96	—	5887 (40.6)
11.	11.6%MF-3.0%H ₂ O-5.4%TWA-59.9%A-5.2%W-14.9%SiO ₂	8.0	65	—	4698 (32.4)
12.	10.6%MF-2.6%H ₂ O-6.8%TWA-59.9%A-5.2%W-14.9%SiO ₂	8.0	50	—	4354 (30.03)

Table 3 (Cont'd)

Specimen No.	Composition	W/W+A, %	Gel time, min	Exothermal peak time, min	Exothermal peak temperature, °C	Compressive strength after curing 24 hr in air at ~24°C, psi (MPa)
	P					
13.	12.3%FA-0.4%TCT-61.4%A-5.4%W-5.1%ZnCl ₂ -15.4%SiO ₂	8.1	8	12	75	1200 (8.28)
14.	12.3%FA-0.4%TCT-60.7%A-5.3%W-6.1%ZnCl ₂ -15.4%SiO ₂	8.0	6	7	79	2108 (14.54)
15.	12.3%FA-0.4%TCT-59.7%A-5.2%W-7.5%ZnCl ₂ -14.9%SiO ₂	8.0	3	4	91	3910 (26.97)
16.	12.3%FA-0.4%TCT-57.1%A-5.2%W-8.4%ZnCl ₂ -14.7%SiO ₂	8.1	2	3	105	4560 (31.45)
	P					
17.	21.7%UP-St-0.2%CoN-0.1%DMA-0.5%NEKP-57.9%A-5.1%W-14.5%SiO ₂	8.1	24	—	—	831 (5.73)
18.	21.7%UP-St-0.2%CoN-0.1%DMA-0.5%NEKP-61.8%A-5.4%W-10.3% cement	8.0	24	—	—	5880 (40.55)
19.	21.7%UP-St-0.2%CoN-0.1%DMA-0.5%NEKP-57.9%A-5.1%W-14.5% cement	8.1	23	—	—	6332 (43.67)
20.	21.7%UP-St-0.2%CoN-0.1%DMA-0.5%NEKP-51.5%A-4.5%W-21.5% cement	8.0	22	—	—	6413 (44.23)
	P					
21.	15.6%MMA-1MPTMA-0.15%DMA-0.15%DMT-0.3%BPO-62.7%A-5.5%W-15.6%SiO ₂	8.1	14	21	62	1274 (8.79)
22.	15.6%MMA-1MPTMA-0.15%DMA-0.15%DMT-0.3%BPO-66.8%A-5.9%W-11.1% cement	8.1	20	—	—	182 (1.26)

Table 3 (Cont'd)

Specimen No.	Composition	W/W+A, %	Gel time, min	Exothermal peak time, min	Exothermal peak temperature, °C	Compressive strength after curing 24 hr in air at ~24°C, psi (MPa)
23.	15.6%MMA-TNPTMA-0.15%DMA-0.15%DMT-0.3%BPO-62.7%A-5.5%W-15.6% cement	8.1	20	—	—	161 (1.11)
24.	15.6%MMA-TNPTMA-0.15%DMA-0.15%DMT-0.3%BPO-55.7%A-4.9%W-23.2% cement	8.1	19	—	—	101 (0.70)

P, binder concentration including catalyst and promoters.

A, 50 wt% No. 16 sand (size, 1.19 mm)-25 wt% No. 30 sand (size, 0.595 mm)-25 wt% No. 100 sand (size, 0.149 mm).

W, water.

SiO₂, dry silica flour (size, <60 μm).

50 wt% UP ~ 50 wt% St.

95 wt% MMA - 5 wt% TNPTMA.

Average of 3 specimens. Sample size, 2.2-cm-diam x 4.4-cm-long cylinders.

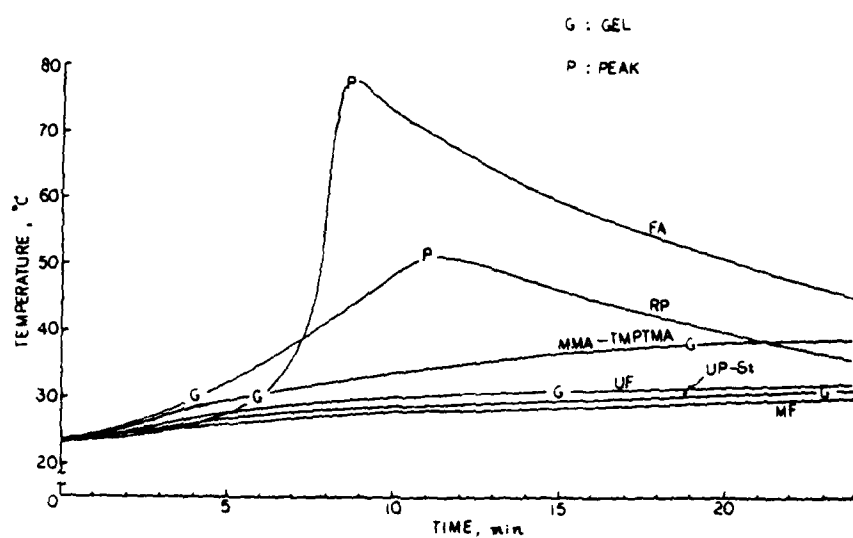


Figure 2. Typical thermograms of PM containing aggregate with a water content of 8.0 wt%

that UP-PC containing an anhydrous cement filler was converted into a Ca-UP complexed ionomer consisting of an ionic bonding between Ca^{2+} ions liberated from the cement and $-\text{COO}^-$ ions produced by the hydrolytic reaction of ester groups during exposure to water. This hydrolytically synthesized Ca-UP complexed ionomer has excellent stability which results in significant improvements in strength and durability.

On the basis of these data, anhydrous Type III portland cement was used as a reactive filler for the UP-St wet aggregate system. For purposes of comparison, silica flour filler was also evaluated. As indicated in Table 3, the compressive strength of UP-St specimens prepared by the addition of 14.5% Type III portland cement, was considerably higher (6332 psi vs 831 psi) (43.67 MPa vs 5.73 MPa) than that of specimens containing an equal amount of silica flour. The gel time of all the UP-St samples was ~23 min. However, the rate of polymerization was too slow to produce a measurable exothermal peak.

MMA monomer was found to be unsuitable for use as a binder for aggregate containing ~8% water. Strengths <1300 psi (<8.96 MPa) were obtained for all of the MMA specimens. Compared to silica flour fillers, the inclusion of portland cement with wet aggregate lowered the strength considerably.

From the results described above, the PM formulations listed below were selected for further evaluation in a series of screening tests.

- 1) RPF monomer - (S-10) catalyst - wet aggregate - Type III portland cement filler.
- 2) MF monomer - TWA catalyst - wet aggregate - silica flour filler.
- 3) FA monomer - TCT catalyst - ZnCl_2 promoter - wet aggregate - silica flour filler.
- 4) 50% UP - 50% St monomer - MEKP catalyst - CoN-DMA promoter - wet aggregate - Type III portland cement filler.

C. Screening Tests

A series of experiments intended to quantify PM formulations that would yield the properties required for rapid runway repair applications were conducted. In addition to measurements of the mechanical properties of the resulting composites, tests to determine the reaction kinetics and mechanisms were performed.

The mechanical and physical property evaluations were performed on duplicate PM specimens containing wet aggregate. Specimens 2.2 cm diam x 4.4 cm long were used for compressive strength tests. For bending strength tests, 1.25-cm-square x 7.5-cm-long beams, supported on a 5-cm span, were subjected to bending under center-point loading.

Tensile strengths were obtained using a splitting-tension test performed on 2.2-cm-diam x 4.4-cm-long specimens. Data for the modulus of elasticity were obtained using strain gages attached with epoxy to the surface of 3.4-cm-diam x 6.8-cm-long specimens. The secant modulus was obtained by calculation using data at stress levels representing 50% of the ultimate strength, as determined from the measured stress-strain curves. Water absorption was obtained by measuring the increase in weight of 2.2-cm-diam x 4.4-cm-long specimens, which were previously dried at 100°C to constant weight, after immersion in water for 7 days at ~24°C. The shear bond strength was determined from the results of the shear strength at the interface between a 7.0-cm-diam x 3.0-cm-thick cement mortar cylinder and an ~3.0-cm thickness of PM which was cast against the smoothly finished concrete surface.

The kinetics of condensation polymerizations were determined by using a DuPont 910 Differential Scanning Calorimeter (DSC) with a heating rate of 10°C/min in nitrogen gas. The area measurements of the exothermic peaks which represent the condensation reaction of the polymer were made with a planimeter.

A Perkin-Elmer Model 257 Spectrometer was used for infrared (IR) analyses. The tests were performed by using KBr discs prepared by mixing 200 mg of KBr and 3 to 5 mg of the samples crushed to <0.104 mm. The spectra were run at an 8-min scanning rate over the range 4000 to 500 cm^{-1} .

Flammability tests for PM composites, 12.7 cm long x 1.27 cm wide x 0.6 cm thick, were performed according to ASTM D635-68, "Flammability of Self-Supporting Plastics." The method is illustrated in Figure 3.

1. RPF- and MF-PM Formulations

a. Property Measurements

RPF-PM Formulations were first evaluated on the basis of compressive strength tests performed 1, 3, 5, and 20 hr after mixing with wet sand. Specimens of different compositions but with a constant water content of 8% in the aggregate were prepared according to the mix proportions given in Table 4. The ratio by weight of RPF/S-10 used was held constant at a value of 4:1.

The compressive strength results for specimens containing cement contents ranging between 6.6 and 17.5% are given in Figure 4. The data indicate that the initial strength of the specimens increases with an increase in the amount of cement promoter. Samples containing 17.5 wt% cement had a strength of 2200 psi (~15.16 MPa) at an age of 1 hr.

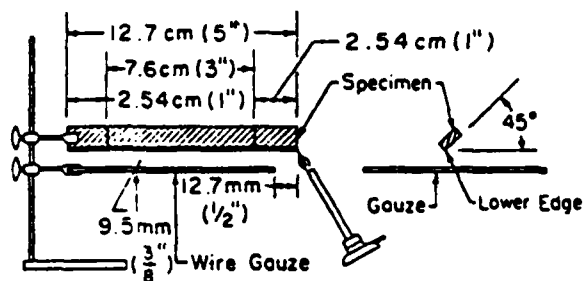


Figure 3. Apparatus for flammability test

Table 4

Composition of RPF-PM Containing Different Type III Portland Cement Contents

Specimen No.	Composition ^a	W/C, %	W/A+W, %	C/A+W+C, %
R-1	21.6%RPF-5.4%(S-10)-61.1%A-5.3%W-6.6%C	80.3	8.0	9.0
R-2	24.8%RPF-6.2%(S-10)-54.2%A-4.7%W-10.1%C	46.5	8.0	14.6
R-3	25.6%RPF-6.4%(S-10)-49.0%A-4.3%W-14.7%C	29.3	8.1	21.6
R-4	26.4%RPF-6.6%(S-10)-45.5%A-4.0%W-17.5%C	22.9	8.1	26.1

^aRPF, Resorcinol Phenol Formaldehyde; S-10 = Paraformaldehyde; A, 50 wt% No. 16 sand (size, 1.19 mm) - 25 wt% No. 30 sand (size, 0.595 mm) - 25 wt% No. 100 sand (size, 0.149 mm); W, water; C, Type III portland cement.

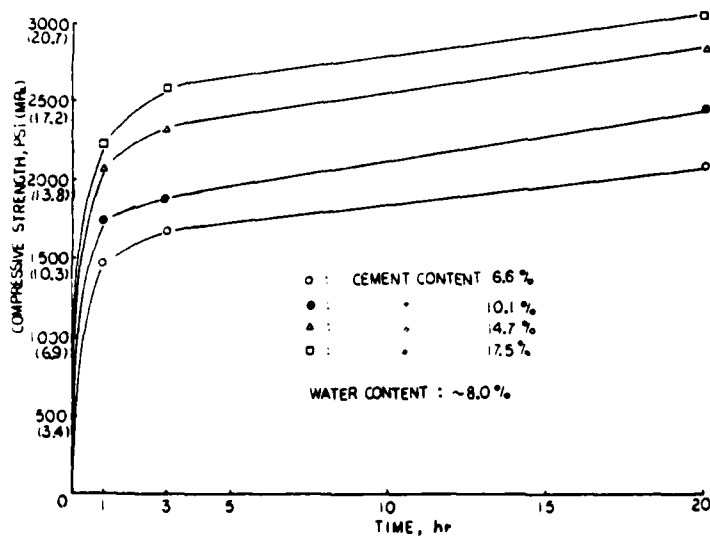


Figure 4. Compressive strength of RPF-PM samples containing various amounts of Type III portland cement vs time

To investigate the influence of water content on the mechanical properties of RPF-PM, specimens were prepared at a constant cement/aggregate + water + cement (C/A+W+C) ratio by weight of ~26%. Compositional data for these samples are given in Table 5. The water content (W/A+W) of the aggregate used was in the range of 0 to 19.3%.

Compressive strengths 1 hr after casting are given in Figure 5. Although the figure indicates that for aggregate with water contents above ~3%, the strength of the specimens decreases with an increase in the water content, this is not totally correct. As shown in Table 5, the polymer binder content was reduced as the water content was increased in order to maintain approximately the same fluidity. Therefore, the influence of the water content was estimated on the basis of a comparison of a relative value obtained from a strength/polymer content (σ_c/P_c) ratio for the different compositions of RPF-PM. These results, also given in Table 5, indicate that the σ_c/P_c ratio of RPF-PM having an aggregate water content of ~7% is slightly lower (0.44 vs 0.47) than that of specimens containing dry aggregate. This means that aggregate water contents below ~7% did not result in an appreciable reduction in the strength.

On the basis of the results described above, 3 RPF-PM formulations (see Table 6) were selected for use in tests to measure the compressive strength at several ages after casting at various temperatures. The samples were prepared by varying the amount of reactive cement filler over the range of 15.1 to 20.6 wt% while maintaining a constant RPF monomer to S-10 catalyst ratio of 80:20. Polymerization was initiated in a water bath at constant temperatures of 2°, 10°, 20°, and 30°C. Compressive strength measurements were then made at ~24°C 1, 5, and 24 hr after mixing. These results are summarized in Table 7.

At 30°C, all RPF-PM specimens containing aggregate with water contents ranging from 2.5 to 7.5 wt% had a 1-hr compressive strength >2010 psi (>13.85 MPa).

Data at a water bath temperature of 20°C indicate that the addition of <17.8 wt% reactive cement filler to RPF-PM specimens containing <7.5 wt% water does not result in adequate compressive strength. However, a 1-hr strength >2000 psi (>13.78 MPa) was obtained when 20.6 wt% cement was used. The results from these and earlier tests suggest that the initial strengths of specimens polymerized in a water bath are ~10% lower than those of specimens polymerized in air at the same temperature. This may be due to the higher heat capacity of the water and improved rate of heat transfer which results in the peak exotherm temperature being reduced.

At ambient temperatures <20°C, the strengths decrease rapidly with decreasing curing temperature. The 1-hr strength of specimens cured at 2°C was too low to be measured.

From these results, it appears that the RPF-PM system will meet the desired compressive strength criteria only at temperatures ≥20°C.

Table 5

Composition of RPF-PM Containing Different Water Contents

Specimen No.	Composition ^a	W/A+W, %	C/A+W+C, %	σ_c/P_c , ^b %
R-5	46%P-40%A-0%W-14%C	0.0	25.9	0.47
R-6	45%P-40%A-0.7%W-14.3%C	1.7	26.0	0.48
R-7	41%P-40.6%A-3.1%W-15.3%C	7.1	25.9	0.44
R-8	31%P-44.1%A-7.0%W-17.9%C	13.7	25.9	0.33
R-9	21%P-47.2%A-11.3%W-20.5%C	19.3	26.0	0.18

^aP, 80% RPF-20%(S-10); A, 50 wt% No. 16 sand (size, 1.19 mm) - 25 wt% No. 30 sand (size, 0.595 mm) - 25 wt% No. 100 sand (size, 0.149 mm); W, water; C, Type III portland cement.

^b σ_c , compressive strength; P_c , RPF resin content (wt%).

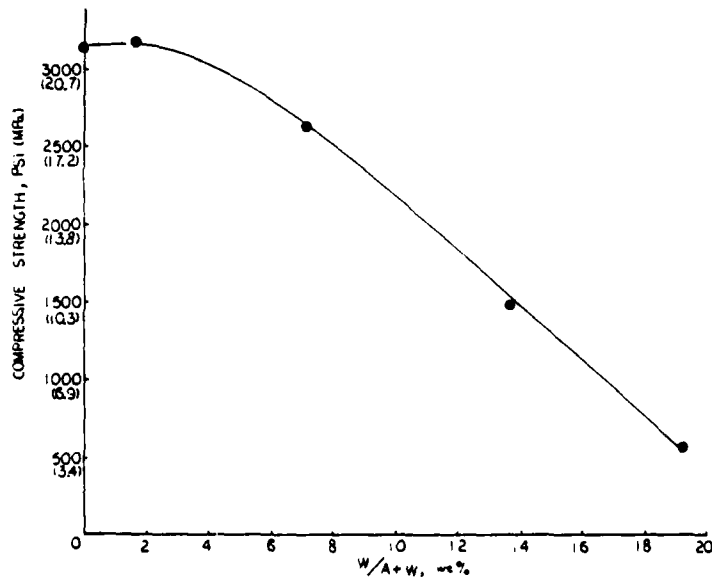


Figure 5. Compressive strength of RPF-PM after a 1-hr cure time

Table 6

RPF-PM Compositions

Specimen No.	RPF monomer, wt%	Aggregate, ^a wt%	S-10 catalyst, wt%	Type III portland cement reactive filler, wt%	Water, wt%, by weight of aggregate
A	26.4	51.9	6.6	15.1	2.5 to 7.5
B	26.4	49.2	6.6	17.8	2.5 to 7.5
C	26.4	46.4	6.6	20.6	2.5 to 7.5

^aAggregate, 50 wt% No. 16 sand (size, 1.19 mm) - 25 wt% No. 30 sand (size, 0.595 mm) - 25 wt% No. 100 sand (size, 0.149 mm).

Table 7

Compressive Strength of RPF-PM Specimens as a Function of Age for the Temperature Range 30° to 2°C

Specimen No.	Temperature, °C		Water, wt%	Cement promoter, wt%	Compressive strength, psi ^a		
	ambient	components			1 hr	5 hr	24 hr
A-1	30	24	7.5	15.1	2010	2177	2442
B-1	"	"	"	17.8	2114	2235	2619
C-1	"	"	"	20.6	2374	2538	2795
A-2	"	"	5.0	15.1	2135	2339	2869
B-2	"	"	"	17.8	2400	2661	2984
C-2	"	"	"	20.6	2794	3018	3671
A-3	"	"	2.5	15.1	2216	2661	3548
B-3	"	"	"	17.8	2636	2966	3755
C-3	"	"	"	20.6	2951	3274	4180
A-4	20	20	7.5	15.1	1410	1813	2161
B-4	"	"	"	17.8	1768	1974	2581
C-4	"	"	"	20.6	2012	2186	2598
A-5	"	"	5.0	15.1	1606	2074	2419
B-5	"	"	"	17.8	1959	2236	2658
C-5	"	"	"	20.6	2240	2596	2943
A-6	"	"	2.5	15.1	1803	2235	2695
B-6	"	"	"	17.8	1978	2471	2816
C-6	"	"	"	20.6	2295	2738	3045
A-7	10	2	7.5	15.1	368	905	1008
B-7	"	"	"	17.8	810	1014	1150
C-7	"	"	"	20.6	1058	1230	1400
A-8	10	2	5.0	15.1	740	1050	1185
B-8	"	"	"	17.8	1068	1223	1404
C-8	"	"	"	20.6	1106	1351	1689
A-9	"	"	2.5	15.1	1087	1162	1342
B-9	"	"	"	17.8	1204	1348	1510
C-9	"	"	"	20.6	1351	1666	1805
A-10	2	2	7.5	15.1	--b	--	705
B-10	"	"	"	17.8	--	--	928
C-10	"	"	"	20.6	--	208	1010
A-11	"	"	5.0	15.1	--	--	980
B-11	"	"	"	17.8	--	275	1250
C-11	"	"	"	20.6	--	460	1386
A-12	"	"	2.5	15.1	--	175	990
B-12	"	"	"	17.8	--	328	1325
C-12	"	"	"	20.6	--	500	1400

^aMPa = psi x 6.895 x 10⁻³.

^bToo low to be measured.

Compressive strength results for MF-PM specimens having the compositions indicated in Table 8 are given in Figure 6. The results indicate that the strengths for specimens containing sand with an ~8% water content are relatively lower than those for RPF-PM specimens and that a curing period >15 hr is necessary to obtain a strength >2000 psi (>13.78 MPa) in air at ~24°C.

Compressive stress-strain curves for RPF-PM and MF-PM specimens are illustrated in Figure 7. Data for the modulus of elasticity (E_c) were obtained using strain gages attached with epoxy to the surface of the cylindrical specimens. The secant modulus was obtained by calculations using data at stress levels representing 50% of the ultimate strength, as determined from the measured stress-strain curves.

The E_c value of MF-PM was 5.75×10^5 psi (3.96×10^3 MPa), ~79% higher than that of RPF-PM specimens. However, the maximum strain of MF-PM ($\sim 12 \times 10^{-3}$) was considerably lower than that of RPF-PM ($\sim 40 \times 10^{-3}$). This indicates the brittle nature of MF-PM composite materials.

The relative toughness of the materials was determined from the stress-strain curves by measuring the total area under the curves obtained by drawing perpendicular lines from the ends of the curves (representative of the complete failure of the materials) to the strain coordinates. The area for RPF-PM was relatively large when compared with the area for MF-PM. Therefore, it is apparent that RPF-PM has greater toughness than MF-PM.

RPF-PM and MF-PM specimens of the same compositions as those used in modulus of elasticity tests were used for compressive, flexure, and shear bond strength measurements and in water absorption tests. These results are summarized in Table 9.

The 3-day compressive strengths of RPF-PM and MF-PM specimens were found to be 3594 psi (24.8 MPa) and 6371 psi (43.9 MPa), respectively. Compared to the 1-hr compressive strength of RPF-PM, the improvement in strength at an age of 3 days was only ~63%. The RPF-PM specimens produced a compressive strength of >2000 psi (13.78 MPa) at ~24°C within 1 hr after mixing with an aggregate containing 8% water.

With flexure strength, it was noted that the value of 1153 psi (7.9 MPa) for RPF-PM specimens represented ~32% of its compressive strength. For MF-PM the difference was ~23%. Generally, the ratio of the flexure strength to compressive strength (f_b/f_c) for MMA and UP-PCs is ~0.21 to 0.26.³⁰ Therefore, the f_b/f_c strength ratio of 0.23 for MF-PM is quite similar to those for MMA and UP-PC specimens. The f_b/f_c ratio for RPF-PM was a relatively high 0.32.

It is well known that the density of materials has a direct effect upon the compressive strength, and that the flexure strength depends on an intermolecular force which occurs between each material phase. As a

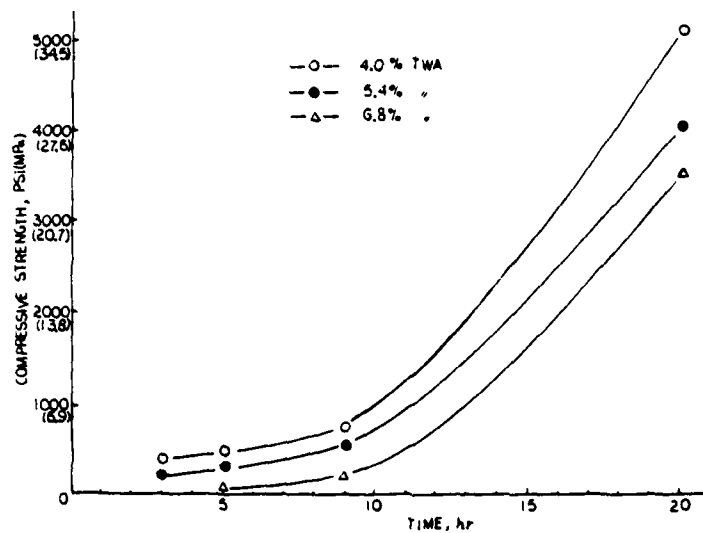


Figure 6. Compressive strength of MF-PM samples containing various amounts of catalyst

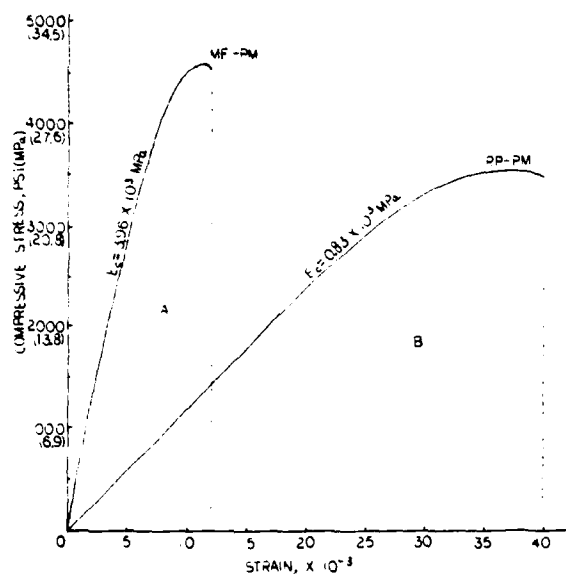


Figure 7. Stress-strain curves for recommended PM formulations after curing for 3 days at 24°C

Table 8

Composition of MF-PM Specimens

Specimen No.	Composition ^a	W/A+W, %
MF-1	12.8%MF-3.2%H ₂ O-4.0%TWA-59.9%A-5.2%W-14.9%SiO ₂	8.0
MF-2	11.6%MF-3.0%H ₂ O-5.4%TWA-59.9%A-5.2%W-14.9%SiO ₂	8.0
MF-3	10.6%MF-2.6%H ₂ O-6.8%TWA-59.9%A-5.2%W-14.9%SiO ₂	8.0

^aMF, Melamine-formaldehyde; A, 50 wt% No. 16 sand (size, 1.19 mm) - 25 wt% No. 30 sand (size, 0.595 mm) - 25 wt% No. 100 sand (size, 0.149 mm); W, water; SiO₂, dry silica flour (size, <60 μm).

Table 9

Measured Properties of RPF and MF Polymer Mortars

Type of PM ^a	Compressive strength, ^b psi (MPa)	Flexure strength, ^c psi (MPa)	Shear bond strength, ^d psi (MPa)	Water absorption, ^e wt%
RPF	3594 (24.8)	1153 (7.9)	105 (0.7)	2.64
MF	6371 (43.9)	1435 (9.9)	203 (1.4)	2.36

^aRPF, Resorcinol phenol-formaldehyde; MF, Melamine-formaldehyde.

^bSpecimen size, 2.2-cm-diam. x 4.4-cm-long cylinders; average value of three specimens.

^cSpecimen size, 1.25-cm-square x 7.5-cm-long beams; average value of three specimens.

^dAverage value of two specimens.

^eSubmerged in water at ~24°C for 3 days.

consequence, the high f_b/f_c ratio for RPF-PM may be due to the strong bonding produced between the organic polymer matrix and the inorganic aggregate phase, and the great flexibility of RPF polymer.

The shear bond strength was obtained from the results of the shear strength at the interface of a 7.0-cm-diam x 3.0-cm-thick cement mortar cylinder and an ~3.0-cm thickness of PM which was cast against the smoothly finished surface of the cement mortar. The bond strength of MF-PM was 50% higher [203 vs 105 psi (1.4 MPa vs 0.7 MPa)] than that of RPF-PM. If these PMs are cast against a concrete surface having a rough texture, it is estimated that the bond strength will be about twice as great as that with a smooth surface.

Water absorptions were obtained by measuring the increase in weight after immersion in water for 3 days. Both formulations indicated water absorption values of >2.0 wt%, high when compared with <1.0 wt% normally obtained from MMA and UP-PC samples containing dry aggregate. The high values for formaldehyde-type PM may be due to the production of capillary pores brought about by the active molecular movement of the free H_2O yielded as a by-product in the condensation-type polymerization process.

The following generalizations were drawn from the results described above:

- 1) RPF combined with portland cement could be used as a quick-setting PM binder for use with aggregate having a water content up to ~9 wt%.

- 2) MF-PM containing wet aggregate and cured for >13 hr at ~24°C, had good mechanical properties. However, it was impossible to meet the early age strength requirements needed for runway repair materials.

b. Kinetics and Reaction Mechanisms

The energetic condensation reactions occurring between the RPF resin and the cement promoter were estimated on the basis of measurements of the activation energies for the thermal polymerization. The kinetic parameters were determined by using DSC.³¹ Typical DSC thermograms obtained during the polymerization of RPF and RPF-cement mixtures are illustrated in Figure 8. The area under the curves represents the total quantity of heat liberated upon conversion of monomer to polymer by the thermal condensation polymerization.

The thermogram for RPF resin shows an exotherm corresponding to an onset temperature of polymerization of ~50°C (determined from the baseline), with a peak at ~92°C. The thermogram for RPF combined with 10% cement is characterized by an onset of polymerization at ~30°C and a peak at ~68°C. These temperatures are ~24°C lower than those for the RPF resin. Both temperatures decrease with an increase in cement content. The curves also indicate that the energy (mcal/sec) produced during the polymerization of RPF increases with increasing cement content.

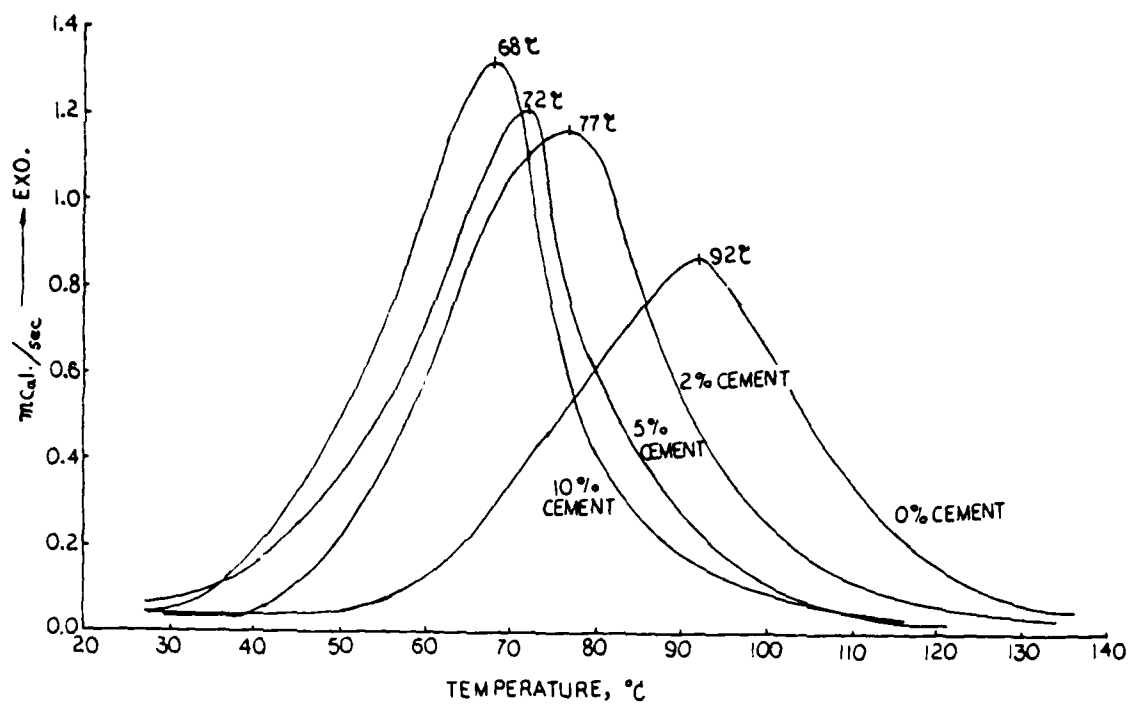


Figure 8. DSC thermograms for RPF resin - Type III portland cement systems

Calculations of the cure rate constant k for the polymerization reaction were made using Eq. (1) which was described by Borchardt and Daniels,³²

$$k = \frac{(AV/n_0)^{x-1} (dH/dt)}{(A-a)^x}, \quad (1)$$

where $A(\text{mcal})$ is the total heat of polymerization obtained from the total area under the DSC curve, $a(\text{mcal})$ is the area of departure of the DSC curve, V is the volume, n_0 is the number of moles of monomer polymerized, dH/dt (mcal/sec) is the rate of heat absorption which is plotted directly as a function of temperature, and x is the order of polymerization.

Although second-order reactions might be possible, the DSC curves used in this analysis showed only first-order reactions. Therefore, $x = 1$ and Eq. (1) reduces to the following simple form³³:

$$k = dH/dt(A-a).$$

The rate constants for the polymerization of RPF resin with different amounts of cement catalyst are given in Table 10. Comparing the results for temperatures of 70° and 80°C , the calculations indicate that k increases with cement content. This is probably due to an accelerative effect produced by the cement as a result of an increase in the condensation of active phenolic nuclei in the initial condensation polymerization rate for RPF resins.

The effect of the cement promoter on the kinetics of the thermal polymerization of RPF was evaluated on the basis of activation energies (E_a). Values for E_a were calculated from the slope of the Arrhenius plot of the logarithm of the rate constant k against the absolute temperature, $1/T$.³⁴ The first-order activation energies and a typical Arrhenius plot containing all of the available data are given in Figure 9.

The activation energy for the thermal polymerization of RPF resin was calculated to be 17.1 kcal/mole . In the presence of 2% cement the value 19.1 kcal/mole , ~12% higher than that for bulk RPF resin. The highest value of activation energy (21.7 kcal/mole) was obtained when a mixture of RPF resin with 10% cement was polymerized.

From the low value of E_a , it appears that the rate of the condensation polymerization of bulk RPF resin is very slow. As a result, the rate of thermal generation of phenolic nuclei in RPF resin is extremely small. Therefore, the addition of cement to the RPF appears to increase the concentration of active phenolic nuclei which then causes the rate of polymerization to accelerate.

Table 10

Cure Rate Constants for the Thermal Polymerization
of RPF Resin Combined with Cement Promoter

Temperature, °C	k sec ⁻¹ Cement content, wt%			
	0	2	5	10
40	--	--	0.55x10 ⁻³	0.75x10 ⁻³
50	--	0.93x10 ⁻³	1.63x10 ⁻³	2.02x10 ⁻³
60	--	2.32x10 ⁻³	4.16x10 ⁻³	6.57x10 ⁻³
70	1.58x10 ⁻³	5.64x10 ⁻³	9.54x10 ⁻³	1.33x10 ⁻²
80	3.75x10 ⁻³	1.16x10 ⁻²	2.57x10 ⁻²	4.25x10 ⁻²
90	7.79x10 ⁻³	2.84x10 ⁻²	--	--
100	1.46x10 ⁻²	--	--	--
110	2.53x10 ⁻²	--	--	--

Heating rate, 10°C/min.

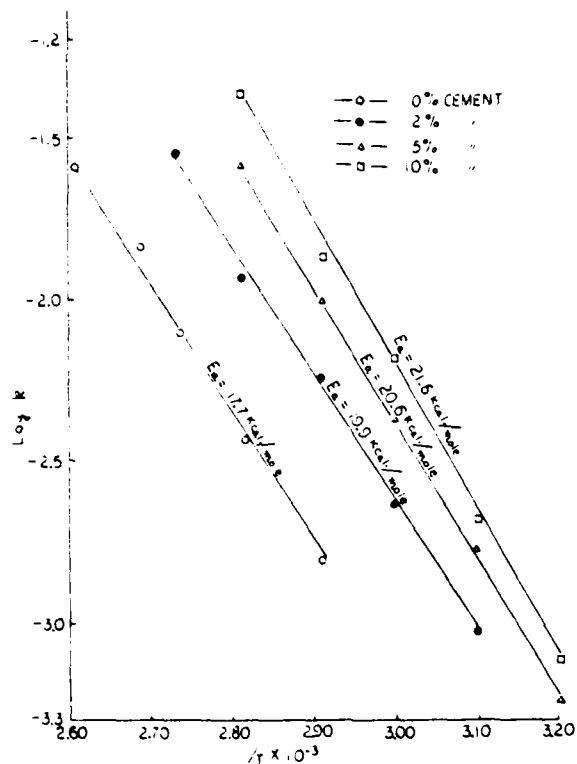


Figure 9. Arrhenius log plots for the thermal polymerization of RPF resin combined with different amounts of Type III cement

In order to determine which of the chemical constituents of cement affect the polymerization of RPF resin, the catalytic effects of CaO , MgO , Al_2O_3 , SiO_2 , Fe_2O_3 , and $\text{Ca}(\text{OH})_2$ were evaluated by a study of their thermograms. The relative degree of cure was calculated using the following equation.

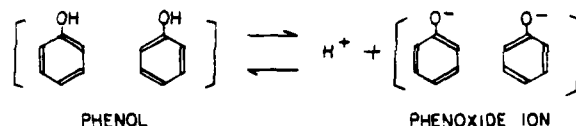
$$Q = \frac{H}{H_T} \times 100,$$

where $H_T(\text{mcal/mg})$ is the maximum isothermal heat of cure, and $H(\text{mcal/mg})$ is the cumulative heat generated in the isothermal heat of cure.

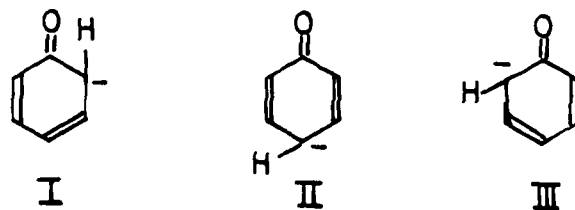
The reaction rate curves were integrated in order to obtain curves which depict the time dependence of the relative degree of cure, Q .³⁵ A comparison between the integral cure curves for the various chemical constituents of portland cement in an amount of 5 wt% added to RPF resin, is presented in Figure 10. As is evident from the figure, the pronounced effects on the curing process of RPF resin containing CaO , MgO , and Ca(OH)_2 , which produce electropositive bivalent metal ions in an aqueous medium, were far greater than those from Al_2O_3 and Fe_2O_3 which have trivalent metallic ions. The results corresponded to those reported by Fraser et al.²¹ and Pizzi.³⁶ Thus, the high rate of the condensation reactions of RPF resin in the presence of cement is due to the active calcium and magnesium metallic cations. It is also obvious that CaO , the major chemical constituent of portland cement, has the greatest effect on the curing process.

On the basis of the condensation reaction mechanisms between phenol and formaldehyde catalyzed by bivalent metallic cations, as described by Fraser et al.,²² theoretical work was performed to develop a hypothetical reaction mechanism for the orientation effect of the Ca^{2+} ions released from cement pastes.

It is well known that the phenol must be a hybrid of a Kekule structure³⁷ which consists of the phenol and phenoxide ion, as illustrated below.



The electronic chemical structure of phenoxide ions can be represented by the formation of three resonant structures possessing a negative charge at the ortho or para position in the structure I-III.³⁸



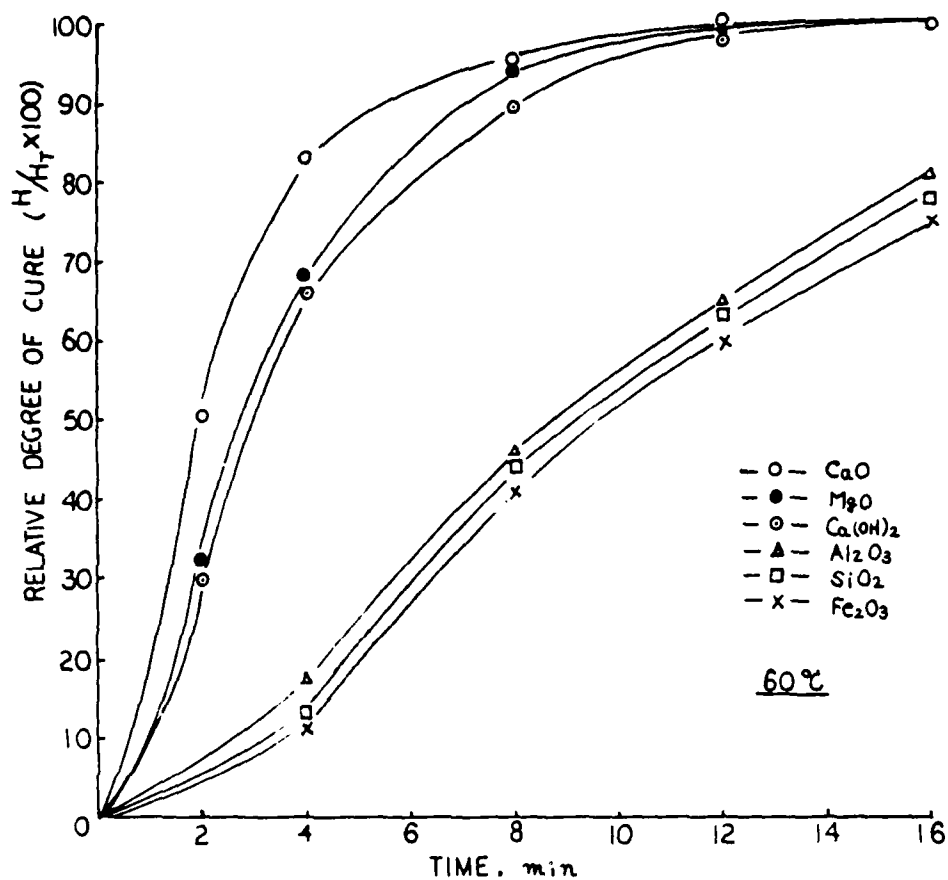
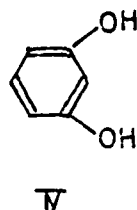
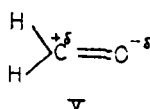


Figure 10. Integral cure curves at 60°C for RPF resin combined with 5 wt% of various chemical constituents of cement

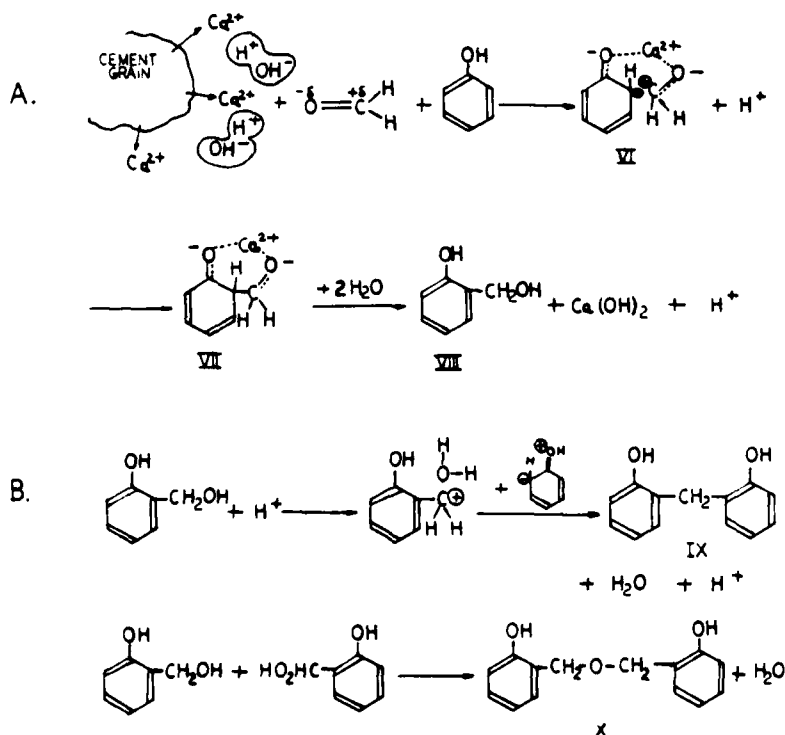


Resorcinol (see structure IV above), which has two OH groups in the benzene ring, has a more reactive structure than phenol which has one OH group. This means that resorcinol reacts readily in a condensation reaction with electrophilic formaldehyde reagents.

On the other hand, it is characteristic of the formaldehyde molecule structure (see structure V) that the oxygen is strongly attracted to the more electronegative atom in the carbonyl group (-C=O). Thus, formaldehyde carrying both the electronegative oxygen and the electropositive carbon in its molecule acts strongly as an electrophilic reagent.



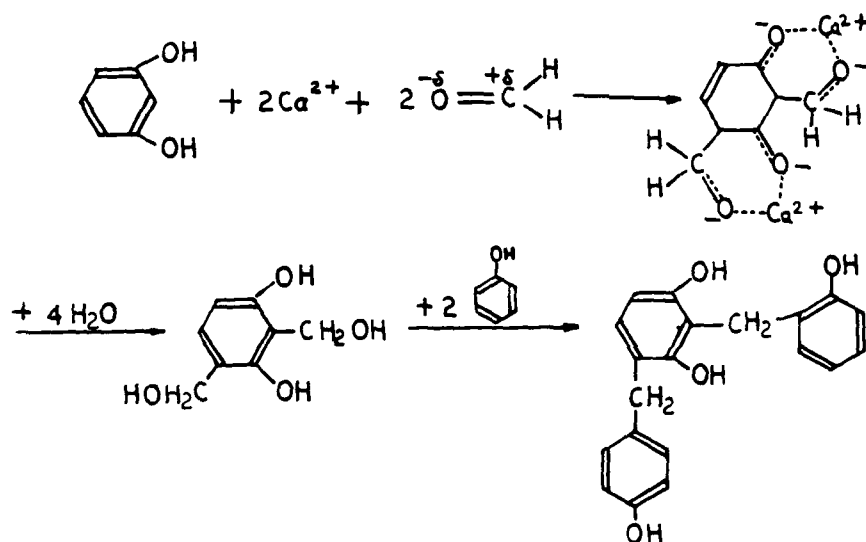
On the basis of the structural characteristics of each molecule in the resorcinol phenol-formaldehyde resin, the catalytic functions of Ca^{2+} ions released from cement pastes on the condensation reactions of RPF resin may be illustrated by the following hypothetical mechanisms:



In the first process A, the Ca^{2+} ions released from the cement paste produce a protonation with the electronegative oxygen atoms of the formaldehyde, and simultaneously add to the oxygen in nucleophilic phenoxide ion reagents of the resonant hybrid of the phenol. The cross-linking of Ca^{2+} ions acting to connect phenoxide ions and formaldehyde may have a specific function which induces both the negative charge in the ortho position of phenol rings and the positive charge of the carbon atom in formaldehyde (see structure VI). Furthermore, the intermolecular bonding of these opposite charges forms the activated Ca^{2+} chelate complexed rings as shown in structure VII. The activated complex then undergoes a hydrolytic reaction with two water molecules to produce hydroxymethyl phenol, $\text{Ca}(\text{OH})_2$, and hydrogen (H^+) ions liberated from the ortho position in the phenolic rings (see structure VIII).

In process B, the carbonyl groups formed by formaldehyde in the hydroxymethyl phenol structure react with a phenolic ring hydrogen having a proton atom. The carbon atom of the carbonium ion thus acquires a positive charge to form dihydroxy diphenylmethane (structure IX) due to the condensation with another phenol molecule at the ortho or para position. The condensation reactions of methylol phenols with themselves may also produce dibenzol ether links, as shown in structure X.

On the other hand, resorcinol, a nucleophilic reagent which is far more reactive than phenol, easily reacts with Ca^{2+} ions and formaldehyde in a condensation reaction, and subsequently causes the formation of dihydroxymethyl resorcinol. This reaction is assumed to occur because of a process similar to that of the phenol as described above. This mechanism is as follows:



As demonstrated in the results described above, when resorcinol and phenol are treated with formaldehyde in the presence of electropositive metallic Ca^{2+} ions, a high-molecular-weight polymer is obtained in which the phenolic rings may be connected by bridge formations of $-\text{CH}_2-$ and $-\text{CH}_2-\text{O}-\text{CH}_2-$ groups.

2. FA-PM Formulations

a. Property Measurements

In order to determine the quantity of acidic TCT catalyst required to obtain a compressive strength >2000 psi (>13.78 MPa) within 1 hr after mixing FA monomer with aggregate containing 7.5 wt% water, FA-PM specimens combined with different amounts of TCT were prepared according to the mix proportions given in Table 11. The ratio by weight of FA monomer to ZnCl_2 promoter was held constant at 10:6. Compressive strength results at $\sim 24^\circ\text{C}$ are summarized in Figure 11.

The data indicate that the 1-hr strength of the specimens increases with an increase in the amount of TCT catalyst, and a strength >2000 psi (13.78 MPa) is obtained by the addition of >1.0 wt% catalyst. A strength of 3650 psi (25.15 MPa) was obtained when 3.0 wt% catalyst was used. This value is only $\sim 14\%$ greater than the strength obtained by the addition of 1.5 wt% TCT. Thus, 1.5 wt% is considered to be an adequate amount of TCT catalyst for use with FA-PM at a temperature of $\sim 24^\circ\text{C}$. The gel time of >7 min for this formulation also appears practical for field use.

Investigations to determine the influence of the water content on the compressive strength were also conducted. In this work, samples having a water content [water (W)/aggregate (A) + water (W) ratio by weight] in the range of 0 to 10 wt% were prepared according to the compositions given in Table 11. The TCT catalyst content was 1.5% by weight of FA monomer.

The 1-hr compressive strength results for these specimens are given in Figure 12. The data indicate that the strength decreases with increases in water content. The 1 hr compressive strength for specimens prepared by directly adding the finely powdered ZnCl_2 promoter to dry aggregate (0% water content) was determined to be 5200 psi (35.83 MPa). The strength reduction when the water content was 2.5 wt% was $\sim 5.8\%$. The 3200 psi strength (22.05 MPa) at 1 hr for specimens containing 7.5 wt% water corresponds to a reduction of $\sim 38.5\%$. The curve also suggests that water contents up to ~ 8.5 wt% will yield the necessary properties.

On the basis of the data described above, two compositions (see Table 12) were chosen for use in compressive strength tests after casting at temperatures from -20° to 30°C . These data are listed in Table 13.

The data indicate that the strength criteria can be achieved over the entire temperature range by varying the TCT/ ZnCl_2 ratio. When the aggregate water content is 7.5 wt% and the temperature $>10^\circ\text{C}$, the required strength can be achieved by using 7.8 wt% ZnCl_2 . Over the temperature range 2° to -20°C , the addition of 10.3 wt% ZnCl_2 to the formulation containing 7.5 wt% water is required. The data also suggest that the addition of >8 wt% TCT by weight of FA monomer has no effect on the initial strength of specimens containing wet aggregate over the temperature range -10° to -20°C .

Table 11

Composition of FA-PM Specimens

FA concentration, wt%	Aggregate, ^a wt%	Dry silica flour ^b filler, wt%	ZnCl ₂ promoter, wt%	Water, % by weight of aggregate
13.2	63.2	15.7	7.9	0-10

^aAggregate, 50 wt% No. 16 sand (size, 1.19 mm)-25 wt% No. 30 sand (size, 0.595 mm)-25 wt% No. 100 sand (size, 0.149 mm).

^bParticle size <62 μ m.

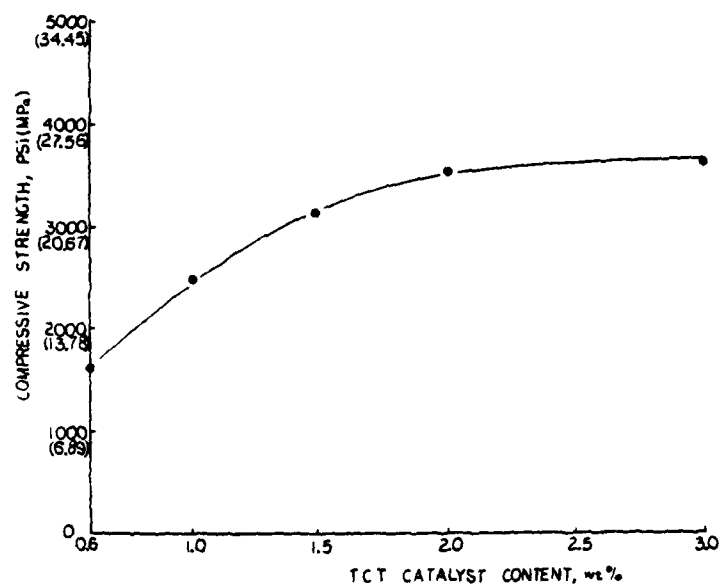


Figure 11. Effect of TCT catalyst content on the 1-hr compressive strength at 24°C of FA-PM containing aggregate with a water content of 7.5 wt%.

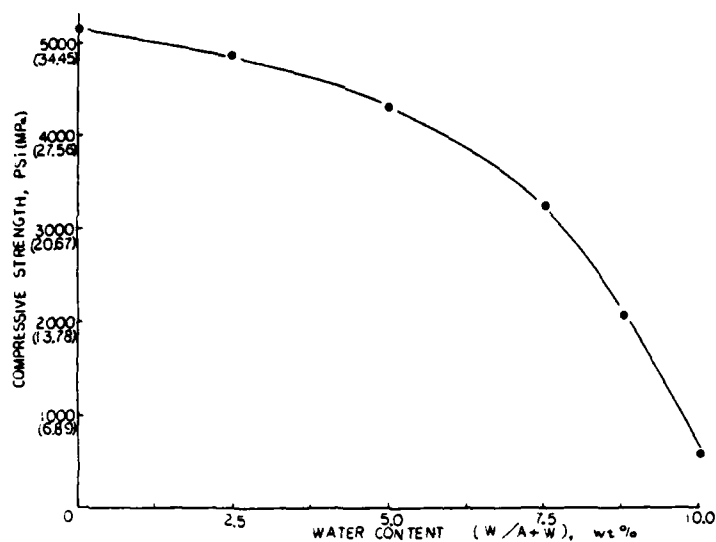


Figure 12. Compressive strength vs water content of aggregate for FA-PM at a curing age of 1 hr

Table 12

FA-PM Compositions

Specimen No.	FA monomer, wt%	Aggregate, ^a wt%	ZnCl ₂ promoter, wt%	Silica flour filler, wt%	TCT catalyst, wt%, by weight of FA monomer	Water, wt% by weight of aggregate
D	13.2	63.2	7.8	15.8	1.5 to 12	2.5 to 7.5
E	13.2	61.2	10.3	15.3	3 to 12	2.5 to 7.5

^aAggregate, 50 wt% No. 16 sand (size, 1.19 mm) - 25 wt% No. 30 sand (size, 0.595 mm) - 25 wt% No. 100 sand (size, 0.149 mm).

Table 13

Compressive Strength of FA-PM Specimens as a Function of Age for the Temperature Range 30° to -20°C

Specimen No.	Temperature, °C		Water, wt%	TCT catalyst, wt%	ZnCl ₂ promoter, wt%	Compressive strength, psi ^a		
	ambient	components				1 hr	5 hr	24 hr
D-1	30	24	7.5	2	7.8	1960	2048	2563
D-2	"	"	"	3	"	2763	2998	3354
D-3	"	"	"	4	"	3983	4209	4765
D-4	"	"	5.0	1.5	7.8	2640	2763	3286
D-5	"	"	"	2	"	3850	4058	4355
D-6	"	"	"	3	"	Quick setting <1 min		
D-7	20	20	7.5	2	7.8	1758	1963	2340
D-8	"	"	"	3	"	2453	2716	3159
D-9	"	"	"	4	"	3718	3985	4620
D-10	"	"	5.0	1.5	7.8	2164	2580	2904
D-11	"	"	"	2	"	3629	3826	4113
D-12	"	"	"	3	"	Quick setting <1 min		
D-13	10	2	7.5	3	7.8	1965	2264	2305
D-14	"	"	"	4	"	2823	2830	2916
D-15	"	"	"	5	"	2903	2984	3065
D-16	"	"	5.0	2	7.8	2984	3065	3583
D-17	"	"	"	3	"	3871	4032	4113
D-18	"	"	"	4	"	3952	4114	4274
E-1	2	-5	7.5	4	10.3	2371	2694	2935
E-2	"	"	"	8	"	3825	3925	4080
E-3	"	"	"	12	"	2647	2883	3056
D-19	"	"	5.0	3	7.8	927	1210	2581
D-20	"	"	"	4	"	2419	2823	3065
D-21	"	"	"	8	"	3468	3548	3710
D-22	"	"	2.5	2	7.8	1980	2686	3600
D-23	"	"	"	3	"	3520	4160	4820
D-24	"	"	"	4	"	4432	5081	5565
E-4	-10	-15	7.5	4	10.3	1371	1694	1935
E-5	"	"	"	8	"	2903	2984	3100
E-6	"	"	"	12	"	1884	1967	2050
D-25	"	"	5.0	3	7.8	484	1129	2097
D-26	"	"	"	4	"	2017	2151	2372
D-27	"	"	"	8	"	2903	2984	3274
D-28	"	"	2.5	2	7.8	1290	1829	2253
D-29	"	"	"	3	"	3226	3580	3926
D-30	"	"	"	4	"	3629	4186	4600
E-7	-20	-15	7.5	4	10.3	995	1268	1488
E-8	"	"	"	8	"	2742	2903	3058
E-9	"	"	"	12	"	1260	1408	1625
E-10	"	"	5.0	3	10.3	870	1481	2068
E-11	"	"	"	4	"	2140	2387	2451
E-12	"	"	"	6	10.3	2984	3077	3417
D-31	"	"	2.5	4	7.8	1150	1742	1985
D-32	"	"	"	8	"	2988	3090	3600
D-33	"	"	"	12	"	2154	2417	2866

^aMPa = psi x 6.895 x 10⁻³.

The FA monomer-TCT catalyst-ZnCl₂ promoter compositions used in the above study could not be used practically at temperatures $\geq 10^{\circ}\text{C}$ with aggregate containing < 2.5 wt% water because of the very short gel time of < 1 min. Therefore, the addition of an adequate amount of water to the aggregate is necessary to establish the working time within practical limits.

Tests to measure other mechanical and physical properties of the FA-PM formulations were performed. The results are given below.

The compressive stress-strain curves at a curing age of ~ 3 hr for specimens containing dry or wet aggregate are illustrated in Figure 13. Using data at stress levels representing 50% of the ultimate strength, the secant modulus (E_c) of FA-PM containing dry aggregate was calculated to be 3.38×10^5 psi (2.33×10^3 MPa). The E_c of wet aggregate-filled samples was $\sim 26\%$ lower.

The relative ductility of the two systems was determined by comparison of the ultimate strains. For the wet aggregate the strain was $\sim 24 \times 10^{-3}$, $\sim 37\%$ higher than that for the dry aggregate PM. The high ductility of the PM containing wet aggregate may be due to viscoelastic effects caused by physical or chemical interactions between the water phase surrounding the surface of the aggregate and the organic FA polymer phase. The reaction products were not identified.

The results from compressive, flexure, tensile, shear bond strength, and water absorption measurements for FA-PM after a 3-day cure in air at $\sim 24^{\circ}\text{C}$ are summarized in Table 14. The compressive strength for specimens containing dry aggregate was 7600 psi (52.36 MPa), only 1.4 times higher than that obtained with aggregate having a 7.5 wt% water content. Similar trends were noted in the results from the other strength tests.

The water absorption of dry aggregate-filled FA-PM specimens was somewhat lower (1.20 vs 1.85%) than for specimens containing wet aggregate. Both values were relatively high compared to the $< 1\%$ normally obtained for vinyl-type PC specimens. This is believed to be due to the free H₂O produced as a by-product of the FA polymerization process. The free H₂O under the high reaction temperatures may then produce an active molecular movement which in turn produces many capillary pores in the PM.

Flammability tests were performed according to ASTM D635-68, Flammability of Self-Supporting Plastics. The samples were 12.7 cm long x 1.27 cm wide and 0.6 cm thick. For purposes of comparison, vinyl-type MMA and 60% St - 40% TMPTMA, and vinyl ester-type 50% UP - 50% St PC composites were also evaluated.

As summarized in Table 15, the FA-PM did not support combustion after removal of the flame source. This is probably due to the three-dimensional network of the heterocyclic furan ring, by-product H₂O molecules from the polymerization process, and the chlorine portions of the TCT and ZnCl₂ molecules, which act as flame retardants.

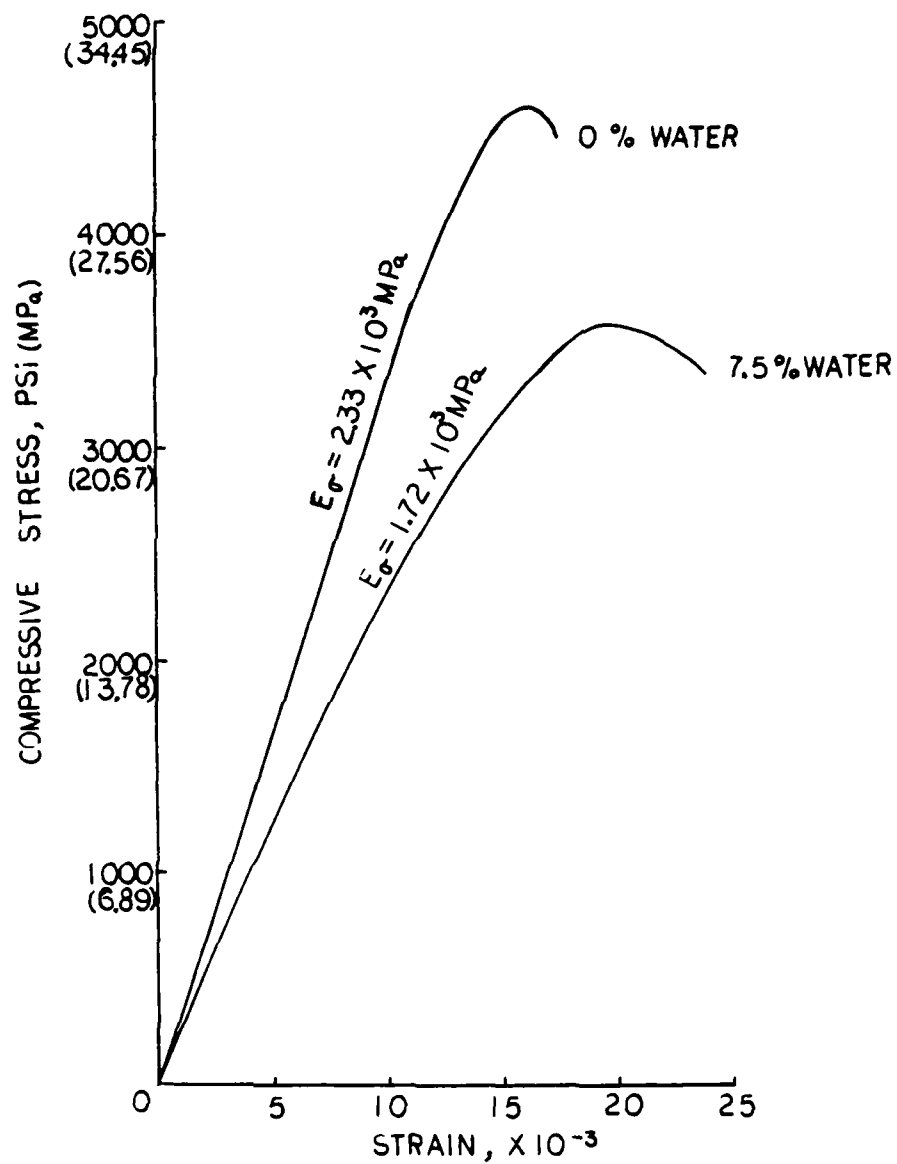


Figure 13. Stress-strain curves for FA-PM containing dry and wet aggregate at a curing age of 23 hr

Table 14

Mechanical Properties of FA-PM Containing Dry and Wet Aggregate
(7.5% water content) After a 3-Day Cure in Air at 24°C

W/A+W, %	Compressive ^a strength, psi (MPa)	Flexure ^b strength, psi (MPa)	Tensile ^a strength, psi (MPa)	Shear bond strength, psi (MPa)	Water ^c absorption, %
0	7600 (52.36)	1680 (11.58)	962 (6.63)	220 (1.52)	1.20
7.5	5410 (37.28)	1452 (10.00)	769 (5.30)	185 (1.28)	1.85

^aSpecimens, 2.3-cm-diam x 4.4-cm-long cylinders.

^bSpecimens, 1.25-cm-square x 7.5-cm-long beams.

^cImmersed in water for 7 days at 24°C.

Average values of three specimens.

Table 15

Relative Flammability of PM Composites

Polymer	Polymer conc., wt%	Remarks ^a
furfuryl alcohol	13.2	Nonburning by this test, two 30-sec ignitions
methyl methacrylate	11.0	Self-extinguishing flame; travels ~2.0 cm in 1.0 min
60% styrene-40% TMPTMA	12.1	Self-extinguishing flame; travels ~2.4 cm in 1.5 min
50% polyester-50% styrene	18.0	Self-extinguishing flame; travels ~3.0 cm in 2.0 min

^aThe extent of burning is equal to the average of ten specimens.

The other PCs were either self-extinguishing or did not burn at all. This may be due to the aggregate which acts as a heat sink. However, disintegration occurred at the point of application when the flame was sustained for 30 sec. A portion of the polymer pyrolyzed, and the remainder which consisted primarily of aggregate dropped off the specimen. After removal of the burner flame, deformation was noted to the extent of burning.

b. Kinetic Studies

The kinetics of polymerization of the FA-PM system were also studied. This study has been published³⁹ and the results are summarized below.

Since water has a relatively high thermal conductivity ($\sim 6.00 \text{ cal g hr}^{-1} \text{ cm}^{-1} \text{ }^{\circ}\text{K}^{-1}$), its presence in uncured FA-PM specimens may restrain the initial polymerization rate. This is due to the ready absorption by water of energy produced in the polymerization process of FA-PM. It appears that the restrictive action of the free water increases with an increase in the amount of water used. Therefore, approximate estimates for the quantity of the heat of polymerization absorbed by the free water were made by use of a DSC technique which appears to be the most effective method for obtaining quantitative information on the curing process of thermosetting resins.⁴⁰⁻⁴²

The effect of 2.5 and 5.0 wt% water contents on the kinetics of thermal polymerization of FA-PM was evaluated from the values of the activation energies, E_a , for the polymerization. The amount of TCT catalyst used was 1.5 wt% by weight of FA monomer. Typical DSC thermograms obtained during these experiments are illustrated in Figure 14. The area under the exothermic peaks represents the total quantity of heat liberated during the polymerization reaction. The results for specimens having a 5 wt% water content show an exotherm corresponding to an onset temperature of $\sim 32^{\circ}\text{C}$. The peak exotherm energy of $\sim 4.5 \text{ mcal/sec}$ occurred at 43°C .

The thermogram for samples containing 2.5 wt% water indicates an onset of polymerization at $\sim 17^{\circ}\text{C}$, the exothermal kinetic energy peak at $\sim 28^{\circ}\text{C}$, and a peak of $\sim 5.8 \text{ mcal/sec}$. The energy produced during the polymerization of samples containing 2.5 wt% water was $\sim 27\%$ greater than that when the water content was 5.0 wt%. This seems to demonstrate that the polymerization rate of FA-PM is dependent on the amount of water in the aggregate.

On the basis of the areas of the exothermic peaks as determined from the baseline, a cure rate constant was calculated. The values of the activation energies (E_a) were calculated from the slope of the straight line of the Arrhenius plot of the logarithm of the rate of polymerization (k) against the absolute temperature, $1/T$. The first-order activation energies and a typical Arrhenius plot containing all of the available data are given in Figure 15.

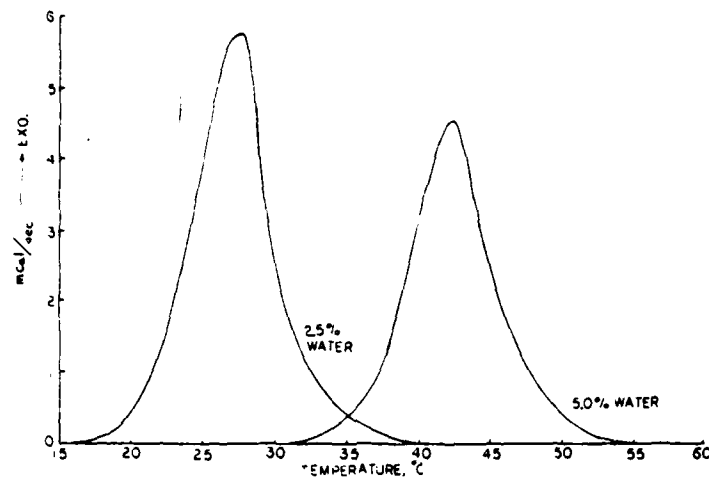


Figure 14. DSC thermograms of FA-PC containing wet aggregate

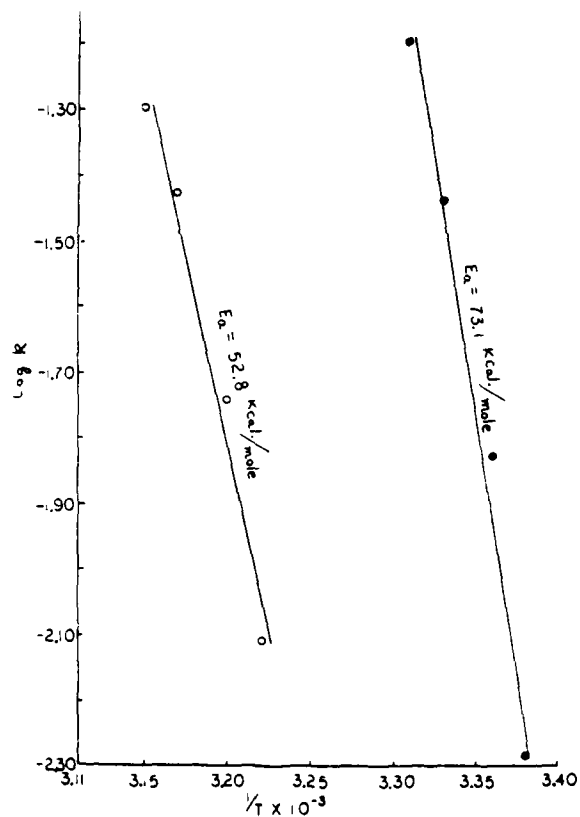


Figure 15. Arrhenius log plots for the thermal polymerization of FA-PM containing aggregate with 2.5 wt% (—○—) and 5.0 wt% (—●—) water.

Ea for the thermal polymerization of FA-PM in the presence of 5.0 wt% water was calculated to be 52.8 kcal/mole. The value of Ea (73.1 kcal/mole) obtained for samples having a water content of 2.5 wt% was 20.3 kcal/mole higher. This means that the added presence of 1 wt% water caused an ~8.0 kcal/mole change in the total polymerization energy released during the thermal reaction. It is evident from these data that the presence of free water acts as an inhibitor in the FA-TCT-ZnCl₂ polymerization system. Therefore, the addition of a relatively large amount of a water-soluble-type catalyst and promoter to the FA-PM system is required for a rapid and complete condensation-type polymerization reaction to occur.

3. Calcium-UP Complexed PM Formulations

a. Property Measurements

The effect of the inclusion of Type III portland cement fillers on the compressive strength of UP-PM was evaluated from the results of the 1-hr strength at ~24°C. The PM specimens contained aggregate with a water content [water/aggregate+water (W/A+W)] of 7.5 wt% and were prepared according to the compositions given in Table 16. The data shown in Figure 16 indicate that the strength of the specimens increases with an increase in the amount of reactive cement filler. The 1-hr strength of a 10 wt% cement-filled PM [2665 psi (18.36 MPa)] was slightly lower than the 2720 psi (18.74 MPa) of the sample containing 16 wt% cement. This means that values close to the maximum strength for PM specimens containing aggregate with water contents ~7.5 wt% can be obtained by the addition of 10 wt% cement.

The effect of the water content on the initial compressive strength was also investigated. Specimens containing aggregate with water contents ranging from 0 to 10 wt% were prepared; the PM formulation consisted of 20 wt% UP-St monomer - 70 wt% aggregate - 10 wt% Type III portland cement (Series No. 3 in Table 16). For purposes of comparison, samples containing a dry silica flour filler having a particle size <62 µm were also tested.

The 1-hr compressive strength results at 24°C for UP-PM specimens are presented in Figure 17. As illustrated the curve for the cement-filled PM specimens indicates that the strength gradually decreases as the water content of the aggregate is increased. A maximum strength of 6800 psi (46.85 MPa) was obtained for specimens containing dry aggregate. Specimens containing 10 wt% water had a strength of 1900 psi (13.09 MPa). The curve suggests that the program goal strength of >2000 psi (>13.78 MPa) at an age of 1 hr can be obtained if the water content is <9.0 wt%.

Table 16

UP-St PM Compositions

Specimen No.	UP-St monomer, ^a	Aggregate, ^b	Type III portland cement or silica flour filler, wt%	Water, wt% by weight of aggregate
1	20	77	3	0 to 10
2	20	74	6	"
3	20	70	10	"
4	20	64	16	"

^aMonomer; 50 wt% UP - 50 wt% St, polymerized by adding 2 wt% methyl ethyl ketone peroxide catalyst - 2 wt% cobalt naphthanate promoter - 0.5 wt% dimethyl aniline promoter.

^b50 wt% No. 16 sand (size, 1.19 mm) - 25 wt% No. 30 sand (size, 0.595 mm) - 25 wt% No. 100 sand (size, 0.149 mm).

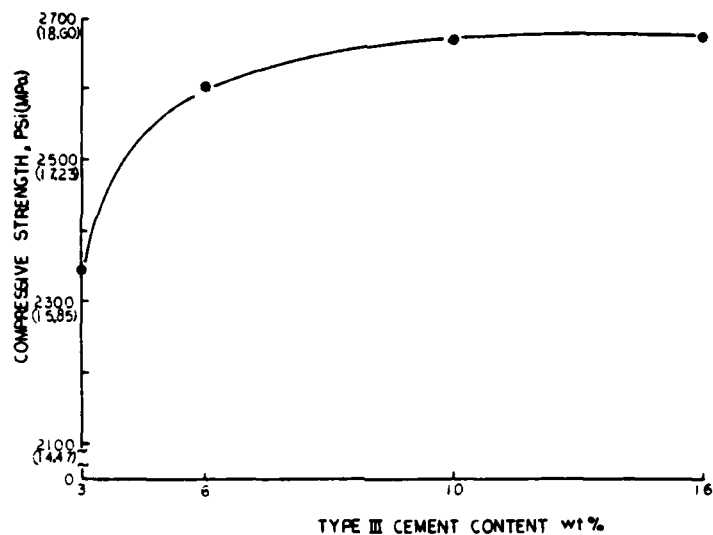


Figure 16. The effect of reactive cement filler on the 1 hr compressive strength at 24°C of UP-PM containing aggregate with a water content of 7.5 wt%

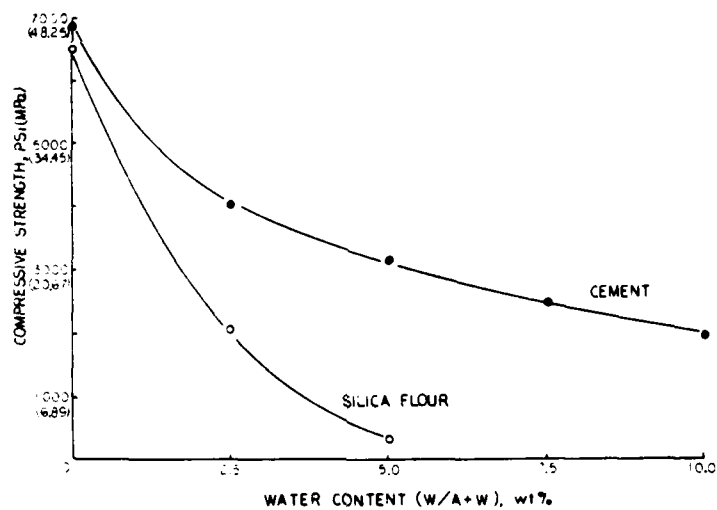


Figure 17. Compressive strength vs water content of aggregate for cement and silica flour-filled UP-PM at a curing age of 1 hr at 24°C

It is apparent from Figure 17 that the compressive strength of specimens containing silica flour decreases more rapidly with increased water content than cement-filled PMs. The initial strength of silica flour-filled PM containing dry aggregate was almost equivalent [6500 psi (44.79 MPa) vs 6800 psi (46.85 MPa)] to that of cement-filled PM. However, the strength was reduced by ~70% when the water content was increased to 2.5 wt%. In contrast, the strength reduction of cement-filled PM with a similar water content was ~40%. The 1-hr strengths of flour-filled samples containing >5 wt% water were too low to be measured.

On the basis of these initial results, three compositions (see Table 17) were selected for continued evaluation over the temperature range 2° to 30°C.

As shown in Table 17, in order to prepare a UP-PM slurry of uniform consistency, the UP-St monomer loading was decreased as the water content of the aggregate was increased. The UP-St monomer to reactive cement filler ratio was held constant at 2:1 by weight.

The compressive strength results for these formulations at 1, 5, and 24 hr after mixing are summarized in Table 18. The data indicate results similar to those from RPF-PM specimens. The specimens containing wet aggregate had high initial strengths at ambient temperatures >20°C, but extremely low strengths at temperatures <10°C.

It appears from the results that the optimum catalyst-promoter system for use with UP-PM is 2 wt% MEKP, 2 wt% CoN, and 2 wt% DMA. The addition of 4 wt% MEKP catalyst results in decreased strength.

Additional mechanical property tests on UP-PM formulations consisting of 20 wt% UP-St monomer, 70 wt% aggregate with a water content of 7.5 wt%, and 10 wt% Type III portland cement were performed after 3 days' curing in air at 24°C. These results are summarized in Table 19. The resulting values were 6150 psi (42.37 MPa) compressive strength, 1672 psi (11.52 MPa) flexure strength, 906 psi (6.24 MPa) tensile strength, 205 psi (1.41 MPa) shear bond strength, 1.16% water absorption, and 6.93×10^5 psi (4.77×10^3 MPa) modulus of elasticity.

Flammability tests in accordance with ASTM D635-68 were also conducted. In these studies, specimens containing aggregate with water contents ranging from 0 to 7.5 wt% were prepared. The formulation consisted of 20 wt% UP-St monomer, 70 wt% aggregate, and 10 wt% cement. Results of the relative flammability characteristics are summarized in Table 20.

With all of these PMs, disintegration occurred at the point of flame application after the burner flame was sustained for 30 sec. A portion of the polymer pyrolyzed, and the remainder melted and dropped off the test specimen along with the aggregate. After removal of the flame, the deformation was noted as the extent of burning.

Table 17

Ca-UP Complexed PM Compositions

Specimen No.	UP-St monomer, wt%	Aggregate, ^a wt%	Type III portland cement filler, wt%	MEKP catalyst, wt%, by weight of UP-St monomer	CoN promoter, wt% by weight of UP-St monomer	DMA promoter, wt% by weight of UP-St monomer	Water, wt% by weight of aggregate
F	20.0	70.0	10.0	2 to 4	2	1 to 2	7.5
G	24.3	63.5	12.2	2 to 4	2	1 to 2	5.0
H	26.3	60.5	13.2	2 to 4	2	1 to 2	2.5

^aAggregate, 50 wt% No. 16 sand (size, 1.19 mm) - 25 wt% No. 30 sand (size, 0.595 mm) - 25 wt% No. 100 sand (size, 0.149 mm).

Table 18

Compressive Strength of Ca-UP PM as a Function of Age for the
Temperature Range 30° to 2°C

Specimen No.	Temperature, °C		Water, wt%	MEKP catalyst, wt%	CoN promoter, wt%	DMA promoter, wt%	Compressive strength, psi ^b		
	ambient	components					1 hr	5 hr	24 hr
F-1	30	24	7.5	2	2	1	1955	3226	3952
F-2	"	"	"	2	2	2	2174	3665	4229
F-3	"	"	"	4	2	2	1806	2823	3145
G-1	"	"	5.0	2	2	1	2823	3468	4313
G-2	"	"	"	2	2	2	2903	3710	5116
G-3	"	"	"	4	2	2	2258	3226	4274
H-1	"	"	2.5	2	2	1	3883	4113	5019
H-2	"	"	"	2	2	2	4083	4435	5323
H-3	"	"	"	4	2	2	3306	3710	4355
F-4	20	20	7.5	2	2	1	1223	1984	2161
F-5	"	"	"	2	2	2	1860	2258	2906
F-6	"	"	"	4	2	2	1057	1466	1825
G-4	"	"	5.0	2	2	1	1824	2984	4161
G-5	"	"	"	2	2	2	2145	3145	4919
G-6	"	"	"	4	2	2	1481	2742	3861
H-4	"	"	2.5	2	2	1	2306	3871	4623
H-5	"	"	"	2	2	2	2855	3952	5000
H-6	"	"	"	4	2	2	2048	3387	4165
F-7	10	2	7.5	2	2	1	-- ^a	264	1060
F-8	"	"	"	2	2	2	--	686	1535
F-9	"	"	"	4	2	2	--	190	1016
G-7	"	"	5.0	2	2	1	--	690	1925
G-8	"	"	"	2	2	2	98	1318	2486
G-9	"	"	"	4	2	2	--	466	1238
H-7	"	"	2.5	2	2	1	181	1810	2451
H-8	"	"	"	2	2	2	975	2258	3058
H-9	"	"	"	4	2	2	180	1532	2173
H-10	2	2	2.5	2	2	1	--	--	1435
H-11	"	"	"	2	2	2	--	795	2097
H-12	"	"	"	4	2	2	--	--	1020
H-13	"	"	0.0	2	2	1	1935	2468	3053
H-14	"	"	"	2	2	2	2581	2885	3915
H-15	"	"	"	4	2	2	2419	2783	3735

^aToo weak to be measured.

^bMPa = psi x 6.895 x 10⁻³.

Table 19

Mechanical properties of Ca-UP PM Containing Wet Aggregate
(7.5% Water Content) After 3 Days' Curing in Air at 24°C

Compressive ^a strength, psi (MPa)	Flexure ^b strength, psi (MPa)	Tensile ^a strength, psi (MPa)	Shear bond strength, psi (MPa)	Water ^c absorption, %	Modulus of ^d elasticity, psi (MPa)
6150	1672	906	205	1.16	6.93x10 ⁵
(42.37)	(11.52)	(6.24)	(1.41)		(4.77x10 ³)

^aSpecimens, 2.2-cm-diam x 4.4-cm-long cylinders.

^bSpecimens, 1.25-cm-square x 7.5-cm-long beams.

^cImmersed in water for 7 days at 24°C.

^dSpecimens, 3.4-cm-diam x 6.8-cm-long cylinders.

Average values of three specimens.

Table 20

Determination of the Relative Flammability of Ca-UP PM
Containing Dry and Wet Aggregate

Water content of aggregate, wt%	Remarks ^a
0	Self-extinguishing flame; travels ~3.0 cm in 2.0 min
2.5	Self-extinguishing flame; travels ~1.19 cm in 1.48 min
5.0	Self-extinguishing flame; travels ~1.2 cm in 1.36 min
7.5	Self-extinguishing flame; travels ~0.8 cm in 1.25 min

^aThe extent of burning is equal to the average of three specimens.

The specimens containing dry aggregate burned continuously for ~2.0 min after removal of the flame at the end of 30 sec. However, the specimens did not burn to the 10.2-cm mark which was judged to be "burning by this test" after the first ignition. Thus, it was judged to be "self-extinguishing by this test." This self-extinguishing phenomenon may be due to the aggregate which acts as a heat sink, and the heat resulting from combustion not being sufficient to sustain pyrolysis.

The data indicate that the burning times and the extent of burning for PM specimens decrease with an increase in the water content of the aggregate. The extent of burning of the Ca-UP complexed PM with a water content of 7.5 wt% was measured to be only ~0.8 cm, compared to ~3.0 cm for the specimen containing dry aggregate. It is apparent from the results that the chemically coordinated H₂O molecules and Ca²⁺ ions formed in Ca-UP complexed PM have a great effect as a flame retarder.

b. Spectroscopic Studies

In order to determine why portland cement paste acts to restrain strength regression in UP-PM specimens, an IR spectroscopy analysis was performed. Spectra from three pellets of bulk UP-St polymer and UP-St PM samples consisting of 42 wt% UP-St polymer, 16 wt% water, and 42 wt% Type III cement or silica flour are given in Figure 18.

The IR spectrum for bulk polymer samples (Sample No. a) is characterized by absorption bands which indicate a stretching and scissor vibration of CH₂ groups at 2940 and 1450 cm⁻¹, a stretching vibration of C=O groups at 1710 cm⁻¹, a skeletal n-plane vibration of the benzene ring at 1600 and 1490 cm⁻¹, an asymmetric and symmetric vibration of esters at 1260 and 1130 cm⁻¹, and a C=C stretching vibration of phenyl at 750 and 700 cm⁻¹. The spectrum of UP-St polymer containing silica flour paste (Sample No. b) shows three new bands appearing at 3370, 1630, and 1080 cm⁻¹. The band at 3370 cm⁻¹ is a stretching vibration of OH groups from the water existing in the samples. The small bands at 1630 cm⁻¹ seem to indicate that some carboxylic esters of UP molecules are converted into

carboxylate anion $\left(\begin{array}{c} \diagup \text{O} \\ \text{C} \diagdown \\ \diagdown \text{O} \end{array} \right)^{\ominus}$ groups brought about by hydrolytic

reactions. Si-O groups of the silica flour filler are represented by the prominent band at 1080 cm⁻¹.

The spectrum for cement paste-filled UP-St polymer (Sample No. c) reveals two prominent new bands at 1530 and 1400 cm⁻¹. These bands represent asymmetric and symmetric stretching vibrations of the -COO⁻(Ca) groups, and are probably due to ionic bonding occurring between the Ca²⁺ ions produced from cement paste and the carboxylate anions (-COO⁻) produced from esters. These spectra do not exhibit the typical band at 1630 cm⁻¹ which represents carboxylate anions produced by the hydrolysis of esters. The relatively wide band indicating OH groups at 3370 cm⁻¹ may be due to neutral H₂O molecules coordinated to Ca²⁺ ions formed in the Ca-UP complexes, and free water existing in the samples.

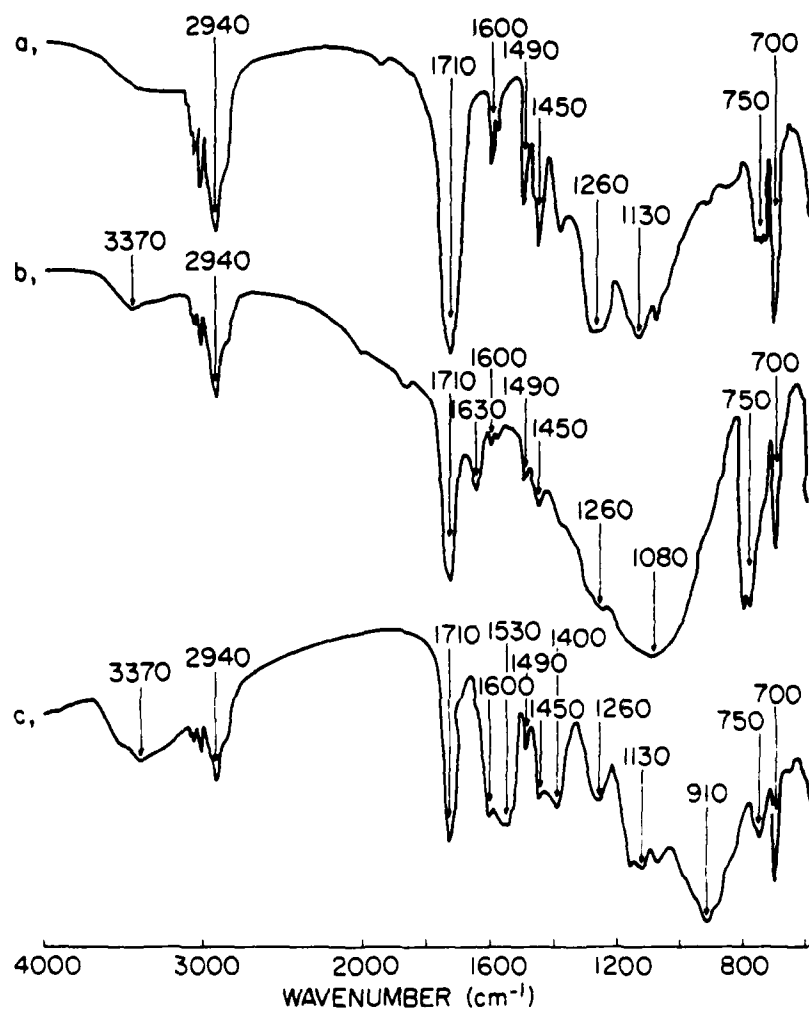


Figure 18. Infrared spectra of UP-St polymer and cement paste or silica flour paste-filled UP-St polymer: (a) Bulk UP-St polymer; (b) Silica flour paste-filled UP-St polymer; (c) Cement paste-filled UP-St polymer.

In a published paper⁴³ it was mentioned that the calcium cation in a salt bridge of the type $\text{-COO}^- \dots \text{Ca}^{2+} \dots \text{-OOC-}$ will complex up to 6 molecules of H_2O in the form of an octahedral structure. The strong band at 910 cm^{-1} is due to the Type III portland cement used as a reactive filler material.

The interaction processes of Ca-UP complexed products in UP-St PM consisting of 42 wt% UP-St monomer, 16 wt% water, and 42 wt% cement or silica flour fillers, but without the addition of catalysts and promoters, were investigated. Evaluation was performed on the basis of the change in IR bands occurring in the frequency range of 1800 to 1300 cm^{-1} at various times after mixing at room temperature. Results are illustrated in Figure 19. As shown in the figure, it is obvious from the presence of the typical carboxylate anion (-COO^-) band at 1630 cm^{-1} that the hydrolytic reaction of UP monomer occurs within 10 min after mixing of the cement and silica flour paste with UP-St monomer.

For the cement paste-filled monomer samples, the spectrum at 5 hr is characterized by the appearance of a new shoulder band at $\sim 1560 \text{ cm}^{-1}$. The shoulder band seems to demonstrate the beginning of the formation of ionic bonds between the -COO^- anions and the Ca^{2+} ions ~ 5 hr after mixing. The spectrum at 10 hr indicates that the carboxylate anion (-COO^-) band at 1630 cm^{-1} tends to shorten with a growth of the -COO^- (Ca) band at 1560 cm^{-1} . Furthermore, it appears from the presence of a prominent band at 1560 cm^{-1} and the disappearance of the -COO^- band at 1630 cm^{-1} , as indicated in the 3-day spectrum, that the number of Ca^{2+} ion complexed bridges of the type $\text{-COO}^- \dots \text{Ca}^{2+} \dots \text{-OOC-}$ increases with time at room temperature. This means that all carboxylate anions (-COO^-) produced by the hydrolysis of esters existing in the main chains of UP monomer are converted into -COO^- (Ca) groups consisting of ionic bonds formed by the attack of the nucleophilic Ca^{2+} ions released from cement paste.

On the other hand, the spectrum at 3 days for silica flour paste-filled UP-St monomer samples exhibits bands similar to those obtained at 10 min and 10 hr after mixing. Thus, it is clear from the presence of the typical carboxylate anion band at 1630 cm^{-1} , due to the hydrolytic reactions of esters, that the addition of silica flour paste cannot prevent the scission of UP molecules brought about by the hydrolysis of esters.

From the IR analysis results of cement paste-filled UP-St monomers described above, the following interaction mechanisms may be hypothetically illustrated as the formation process of Ca-UP complexed ionomer. These are shown in Figure 20.

In the first stage A, the strongly nucleophilic Ca^{2+} ions are released rapidly from the surface of the cement grains during mixture of cement filler, water, and UP-St monomer. The carboxylic esters existing in the main chains of UP molecules are easily converted into carboxylate

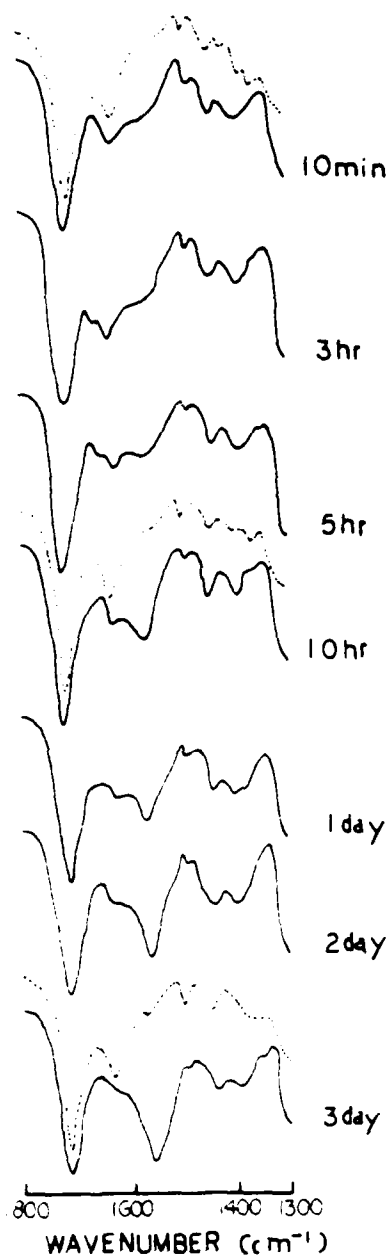


Figure 19. Changes in frequency from 1800 to 1300 cm^{-1} that occur at various process times for cement paste (—) and silica flour paste (---)-filled UP-St monomer.

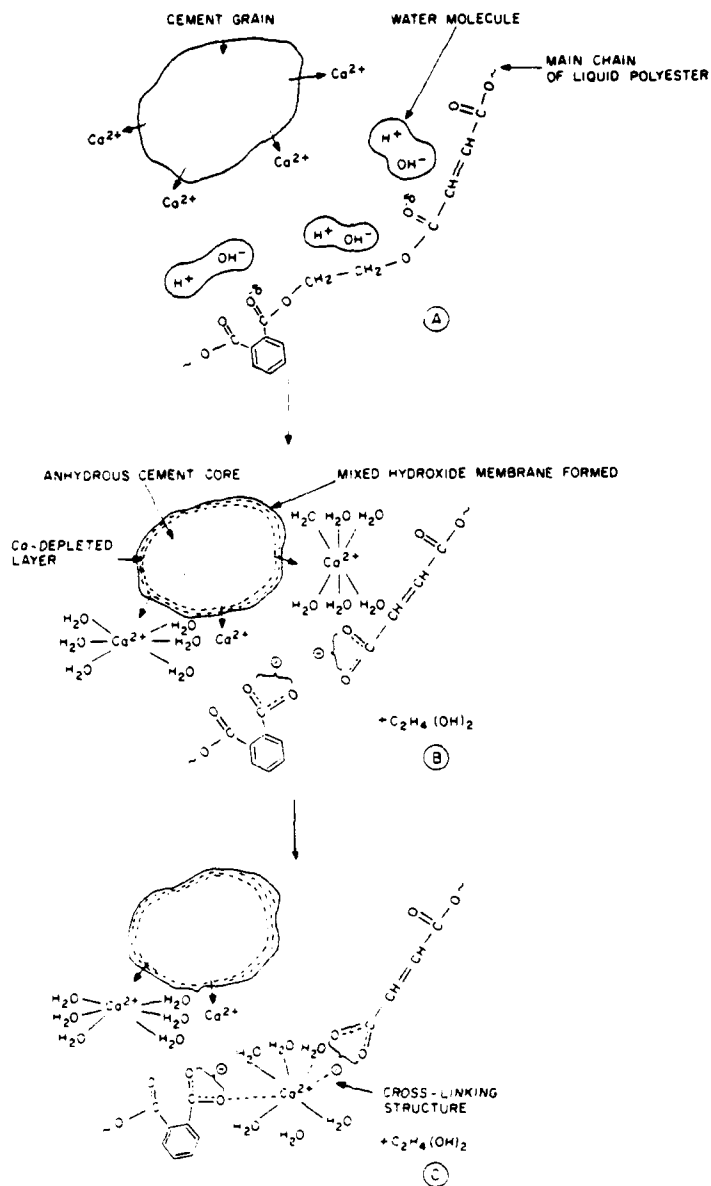


Figure 20. Interaction mechanism occurring between Ca^{2+} ions of cement grains and carboxylate anions of UP chains in an aqueous medium

ions (-COO^-) brought about by a hydrolytic reaction. Ethylene glycol [$\text{C}_2\text{H}_4(\text{OH})_2$] is simultaneously produced as a by-product (see stage B). Ca^{2+} ions produced in an aqueous medium, complex up to 6 molecules of water in the form of an octahedral structure. The neutral H_2O molecules coordinated to Ca^{2+} ions are stable enough to remove water vapor from ordinary air at ambient temperature.

For the final stage C, the Ca-UP complex consisting of the Ca^{2+} salt bridge structure is consequentially synthesized by the formation of an ionic bond between the Ca^{2+} ions having 6 coordinated H_2O ligands and the carboxylate anions (-COO^-) from the ester. The chemical effect of Ca^{2+} bivalent metallic ions may be presumed to be intermolecular cross-linking, acting to connect two -COO^- groups formed in the main chains of UP molecules. It is further assumed that the Ca-UP complex contributes to the prevention of the scission of the molecular chains caused by the hydrolysis of esters.

D. Cost Analysis of PM Formulations

The cost of the materials in each of the PM compositions was calculated and the results are shown in Table 21. The PM density is $\sim 2350 \text{ kg/m}^3$. The cost of the solvent which is required to clean up the mixers and tools is not included in this table. Unless the binders have thickened considerably because of partial curing, methanol and trichloroethane can be used to clean tools used with the RPF and Ca-UP complexed PM, respectively. Water may be used as a solvent for the FA-PM system.

The estimate indicates that as of January 1981, the cost of RPF-PM was $\sim \$1206/\text{m}^3$. The costs of Ca-UP complexed PM and FA-PM were calculated to be 603 and $\$688/\text{m}^3$, respectively. The cost of the FA-PM is only $\sim 14\%$ higher than that of Ca-UP complexed PM. However, if the amount of trichloroethane required for use as a solvent is added to the material cost of Ca-UP complexed PM, the total cost is almost equal to that of FA-PM where water can be used as a solvent.

E. Conclusions

The mechanical and physical properties of the RPF, FA, and Ca-UP complexed PM are compared in Table 22. MF-PM is not included since its compressive strength at 1 hr was below the design criteria. From these results and the cost estimates described above, RPF-PM has inferior characteristics when compared to those of FA and Ca-UP complexed PM. Therefore, the following two binder formulations were selected for further development of polymer concrete (PC) containing wet coarse aggregate:

- 1) FA monomer-TCT catalyst- ZnCl_2 promoter
- 2) 50% UP - 50% St monomer-MEKP catalyst-CoN-DMA promoter-Type III portland cement reactive filler.

Table 21

Polymer Mortar Material Costs

Material	Quantity, kg/m ³	Unit cost, \$/kg	Cost, \$/m ³
----------	--------------------------------	---------------------	----------------------------

RPF-PM

PM formulation: 26.4 wt% RPF monomer 6.6 wt% (S-10) catalyst-46.4 wt%
wet sand-20.6 wt% Type III portland cement filler
Density: ~2350 kg/m³

Sand	1090.4	0.015	16.36
RPF	620.4	1.498	929.36
S-10	155.1	1.542	239.16
Cement	484.1	0.044	21.30
Total \$/m ³			1206.18
s/yd ³			922.23

FA-PM

PM formulation: 13.2 wt% FA monomer-63.2 wt% wet sand-7.8 wt% ZnCl₂
promoter-15.7 wt% silica flour filler
Density: ~2350 kg/m³

Sand	1501.7	0.015	22.53
FA	310.2	1.322	410.08
ZnCl ₂	183.3	0.991	181.65
TCT ^a	6.2	5.397	33.46
Silica flour	369.0	0.110	40.59
Total \$/m ³			688.31
s/yd ³			526.27

Ca-UP Complexed PM

PM formulation: 20 wt% UP-St monomer-70 wt% wet sand-10 wt%
Type III portland cement filler
Density: ~2350 kg/m³

Sand	1645	0.015	24.68
UP-St	470	1.045	491.15
MEKP ^b	9.4	2.313	21.74
CoN ^c	9.4	3.106	29.20
DMA ^d	9.4	2.775	26.09
Cement	235	0.044	10.34
Total \$/m ³			603.20
s/yd ³			461.20

^aTCT catalyst: 2.0 wt% by weight of FA monomer.

^bMEKP catalyst: 2.0 wt% by weight of UP-St monomer.

^cCoN promoter: 2.0 wt% " " " " " "

^dDMA promoter: 2.0 wt% " " " " " "

Table 22

Mechanical and Physical Properties of RPF, FA, and Ca-UP Complexed PM
in the Presence of 7.5 to 8.0% Water

Property	RPF	Polymer Mortar	
		FA	Ca-UP Complex
1-hr compressive strength ^a at 20°C, psi	2012	3718	1824
1-hr compressive strength ^a at -20°C, psi	--8	2742	--8
3-day flexure strength ^b at 24°C, psi	1153	1452	1672
3-day tensile strength ^a at 24°C, psi	476	769	906
3-day modulus of elasticity ^c at 24°C, (10 ⁵ psi)	1.21	2.50 ^h	6.93
3-day shear bond strength ^d at 24°C, psi	105	185	205
Water absorption, ^e wt%	2.64	1.85	1.16
Relative flammability ^f ,	nonburning	nonburning	self-extinguishing flame

^aSpecimens, 2,2-cm-diam x 4.4-cm-long cylinders.

^bSpecimens, 1.25-cm-square x 7.5-cm-long beams.

^cSpecimens, 3.4-cm-diam x 6.8-cm-long cylinders.

^dShear strength at the interface of a 7.0-cm-diam x 3.0-cm-thick cement mortar cylinder and an ~3.0-cm thickness of PM which was cast against the smooth-finished surface of the cement mortar.

^eImmersed in water for 7 days at 24°C.

^fASTM D635-68, "Flammability of Self-Supporting Plastics."

^gToo low to be measured.

^hModulus at a curing age of ~3 hr.

III. POLYMER CONCRETE FORMULATIONS

Practical field use as a rapid repair material will require the inclusion of large-size aggregate in the mixture of monomer and fillers. Therefore, on the basis of the studies described in Section II, work was performed to modify the PM formulations in order to produce a polymer concrete (PC). In this work the formulations consisted of monomer, coarse aggregate (size, 9.5 to 2.38 mm), fine aggregate (size 1.19 to 0.149 mm), a filler (size <62 μ m), and water.

Initially, experiments were performed to determine the proper proportion of coarse and fine aggregates that would yield a PC with high bulk density. In these tests, the water content was based on the assumption that the aggregate would be stored unprotected in an area where frequent rain occurs. After these tests were completed, measurements of the gel time (working time) and the 1-hr compressive strength of the PC specimens were performed over the temperature range -20° to 30°C. On the basis of these data, the optimum FA and Ca-UP complexed PC formulations were determined. In addition, other mechanical, physical, and durability properties were measured at 24°C.

A. Aggregate Proportions

U.S. sieve analysis data for the coarse and fine aggregates used in this study are given in Table 23. The coarse aggregate (C.A.) was composed of limestone, and a silica sand with a silicate content >98% was used as the fine aggregate (F.A.).

The optimum F.A./C.A. ratio was determined in accordance with ASTM C29-69 "Unit weight of Aggregate." Results are illustrated in Figure 21. The curve indicates that an aggregate mixture consisting of 40 parts F.A. to 60 parts C.A. by weight has the greatest unit weight and therefore the highest density. It was assumed that PC specimens containing this aggregate mixture would have the best mechanical properties. Therefore, this was used in the preparation of all PC specimens.

In an attempt to estimate the maximum water content of aggregate that could be expected in the field after a heavy rain, the aggregate was completely saturated by soaking in water for 24 hr. The aggregate was subsequently filtered through a filter paper for 1 hr at ~24°C to remove any excess water existing on the surface of the aggregate. This is illustrated in Figure 22. The water content of the wet aggregate was then measured by using a Moisture Determination Balance. The values obtained are given in Figure 22 and they were assumed to be the maximum possible water contents of the various aggregate mixtures. The data indicate that the maximum water content of the aggregate decreases with an increase in the C.A. content. The water content of 100% F.A. having a particle size <1.19 mm was measured to be ~11.5 wt%. A 40/60 F.A./C.A. mixture had a water content of 3.5%, ~70% lower than that of the 100% F.A. The lowest water content (~0.8%) resulted from the use of 100% C.A.. On the basis of these results, a water content of 3.5% was included in all PC samples in which an aggregate F.A./C.A. ratio of 40/60 was used.

Table 23

Sieve Analysis of Coarse and Fine Aggregate Used in PC

Coarse Aggregate (C.A.)

<u>U.S. Sieve Size</u>	<u>Percent passing</u>
3/4 in. (18.8 mm)	100
1/2 in. (12.5 mm)	95
3/8 in. (9.5 mm)	50
1/4 in. (6.3 mm)	28
No. 4 (4.76 mm)	4
No. 8 (2.38 mm)	0

Fine Aggregate (F.A.)

<u>U.S. Sieve Size</u>	<u>Percent passing</u>
No. 8 (2.38 mm)	100
No. 16 (1.19 mm)	50
No. 30 (0.595 mm)	25
No. 100 (0.149 mm)	0

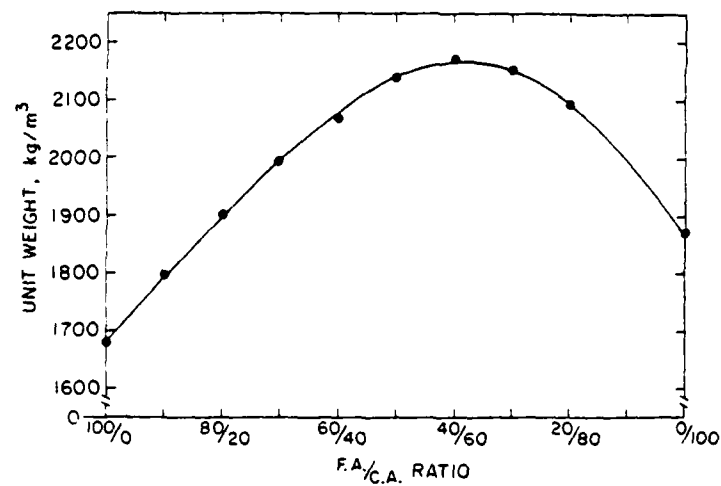


Figure 21. Unit weight of aggregate having various F.A./C.A. ratios

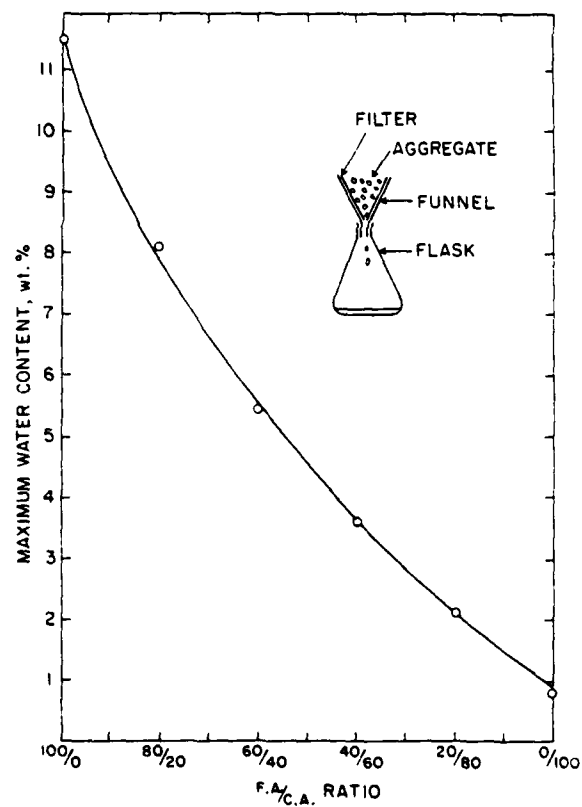


Figure 22. Maximum water content of aggregate having various F.A./C.A. ratios

B. Retarders

Work was performed to identify materials that could retard the rate of polymerization of FA in order to allow sufficient time for placement and compaction of the PC.

It is well known that the condensation polymerization of FA monomer occurs because of the catalytic function of a strong acid such as ZnCl_2 , HCl , H_2SO_4 , P_2O_5 , etc. Therefore, it was reasoned that the polymerization could be inhibited by the addition of a suitable basic reagent ($\text{pH} > 7$). It was found that pyridine reagent is widely used for this purpose. The pyridine is readily soluble in FA and is relatively inexpensive.

The effect of the addition of pyridine on the gel time of FA-PC is illustrated in Figure 23. As shown, the gel time increases with the pyridine concentration. The addition of 20% pyridine by weight of TCT results in the gel time being ~1 min longer than that for samples without pyridine. A gel time >10 min can be achieved by the addition of 70 wt% pyridine. The results also appear to indicate that the addition of pyridine could possibly be used as a method to extend the storage life of FA monomer.

The data in Figure 23 also suggest that the peak exotherm times which are indicative of the polymerization times increase with an increase in the gel time. The peak exotherm time for specimens containing 70% pyridine was ~21.5 min. The gel time for this formulation was ~10.5 min.

C. Mixing Procedures

The mixing procedures used were dependent upon the temperature. For the range 1° to 30°C , FA-PC specimens were produced using the mix procedures given below. Prior to mixing, all of the components were equilibrated at the desired mix temperature.

- 1) The required amount of the powdered ZnCl_2 promoter was added directly to the water-saturated aggregate, and then mixed for ~2 min to achieve a uniform distribution and complete dissolution of the ZnCl_2 (see Figure 24).

- 2) The dry silica flour filler was then mixed with the mixture of wet aggregate and ZnCl_2 promoter. The appearance of this mixture is shown on the right in Figure 24.

- 3) FA monomer, containing the appropriate amounts of TCT catalyst and pyridine retarder, was then added to the mixture of wet aggregate, ZnCl_2 , and silica flour (see Figure 25). The PC formulation was then placed in paper forms 7.6 cm diam x 20.0 cm long. The mix was not compacted in the forms.

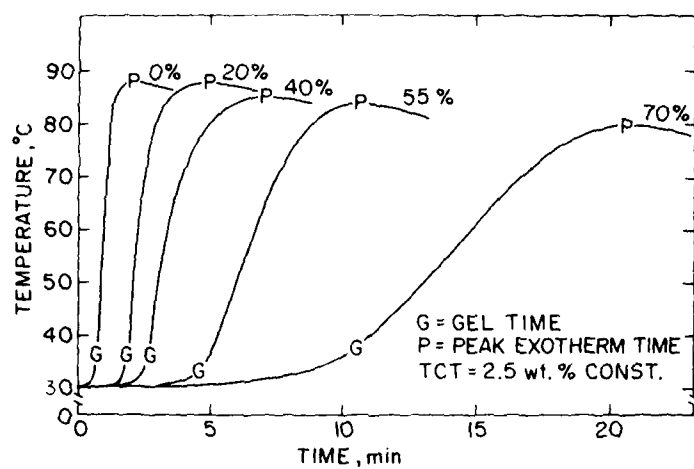


Figure 23. The effect of pyridine on the gel time of FA-PC

Figure 24. Mixture of wet aggregate with zinc chloride (left), and silica flour (right).



Figure 25. Mixture of initiated FA monomer with wet aggregate containing zinc chloride and silica flour.

4) Polymerization was performed in a water bath controlled to $\pm 1.1^{\circ}\text{C}$ over the operating temperature range of 1° to 30°C .

Ca-UP complexed PC specimens were produced in a similar manner except that different promoters, initiators, and fillers were used.

In addition to accelerating the polymerization of FA, at temperatures $< 0^{\circ}\text{C}$ the ZnCl_2 acts as a de-icing material. Heat resulting from the exothermic reaction between ZnCl_2 and water results in the melting of any ice that may be present in the frozen aggregate. At temperatures $< 0^{\circ}\text{C}$, specimens were produced in accordance with the following mix procedures:

1) The required amount of powdered ZnCl_2 promoter was added directly to the frozen aggregate (see Figure 26), and then mixed for ~ 3 min to achieve a uniform distribution and complete dissolution of the ZnCl_2 (see Figure 27).

2) Dry silica flour filler was then mixed with the wet aggregate - ZnCl_2 mixture.

3) FA monomer containing the appropriate amounts of TCT catalyst and pyridine retarder was then added to the mixture of wet aggregate, ZnCl_2 , and silica flour.

4) Polymerization was performed in an alcohol bath controlled to $\pm 1.1^{\circ}\text{C}$ over the operating temperature range of 0°C to -20°C .

D. Optimized PC Formulations

In order to establish an optimized water-compatible PC formulation for use over the temperature range -20° to 30°C , measurements of the 1-hr compressive strength and the gel times were performed. Test cylinders 7.6 cm diam x 15.2 cm long were used in this work.

The temperature of each specimen was monitored continuously during the curing period by means of a thermocouple connected to a strip chart recorder. The gel time is defined as the point at which the monomer converts into a gelatin state and therefore represents the maximum allowable time between mixing and finishing.

1. FA-PC

Compositions summarized in Table 24 were selected for use in tests to measure the PC properties after curing at 30°C . The results from these tests (see Table 25) indicate that the early strength is dependent upon the catalyst, promoter, and retarder concentrations, and the aggregate water content. Without the use of pyridine retarder, the required strength of > 2000 psi (13.78 MPa) is easily attainable. However, the resulting gel times of < 1 min are too short to be practical for field application and the use of pyridine retarder is required. Unfortunately, high concentrations of retarder cause strength reductions.



Figure 26. Frozen aggregate after exposure in air at -15°C for 24 hr



Figure 27. Frozen aggregate to which ZnCl_2 has been added

Table 24

Compositions of FA-PC Polymerized at 30°C

Specimen No.	FA monomer, wt%	Aggregate, wt%	ZnCl ₂ promoter, wt%	Silica flour filler, wt%	TCT catalyst, % by weight of FA monomer	Pyridine retarder, % by weight of TCT catalyst	Water, % by weight of aggregate
F-A	8.0	68.0	7.0	17.0	0.5 to 1.0	0 to 140	3.5
F-B	8.0	68.8	6.0	17.2	1.0 to 1.5	0 to 90	3.5
F-C	8.0	69.6	5.0	17.4	1.0 to 6.0	0 to 80	3.5
F-D	8.0	69.6	6.0	17.3	1.0 to 1.5	0 to 110	2.5
F-E	8.0	69.6	5.0	17.4	1.0 to 3.0	0 to 90	2.5
F-F	9.0	68.3	5.6	17.1	0.5 to 1.5	0 to 90	1.5
F-G	10.0	68.0	5.0	17.0	0.25 to 1.0	0 to 95	0.75
F-H	10.0	69.0	3.8	17.2	1.0 to 3.0	0 to 90	0.0

^aAggregate, 60 wt% coarse (size, 9.5 to 2.38 mm) - 40 wt% fine (size, 1.19 to 0.149 mm).

Table 25

Test Results, FA-PC Cured at 30°C

Specimen No.	Temperature, °C		Water, wt%	TCT catalyst, wt%	Pyridine ^a retarder, wt%	ZnCl ₂ promoter, wt%	Gel time, min:sec	1-hr compressive strength, psi ^b
	ambient	mix components						
F-A-1	30	24	3.5	0.5	0	7.0	0:10	2,347
F-A-2	30	24	3.5	0.5	50	7.0	0:30	2,122
F-A-3	30	24	3.5	0.5	90	7.0	1:10	1,743
F-A-4	30	24	3.5	0.5	110	7.0	1:40	1,586
F-A-5	30	24	3.5	0.5	140	7.0	2:05	811
F-A-6	30	24	3.5	1.0	70	7.0	0:50	1,899
F-A-7	30	24	3.5	1.0	90	7.0	1:30	1,495
F-B-1	30	24	3.5	1.0	0	6.0	0:15	2,119
F-B-2	30	24	3.5	1.0	50	6.0	1:35	1,771
F-B-3	30	24	3.5	1.0	70	6.0	2:00	1,159
F-B-4	30	24	3.5	1.0	90	6.0	3:05	477
F-B-5	30	24	3.5	1.5	50	6.0	0:38	2,460
F-B-6	30	24	3.5	1.5	70	6.0	1:15	2,134
F-B-7	30	24	3.5	1.5	90	6.0	2:20 _c	1,466
F-C-1	30	24	3.5	1.0	0	5.0		_c
F-C-2	30	24	3.5	1.5	0	5.0	1:12	1,230
F-C-3	30	24	3.5	2.0	0	5.0	0:30	2,020
F-C-4	30	24	3.5	2.5	0	5.0	0:18	2,201
F-C-5	30	24	3.5	3.0	50	5.0	1:54	1,430
F-C-6	30	24	3.5	3.0	60	5.0	3:15	846
F-C-7	30	24	3.5	3.0	70	5.0	5:20	576
F-C-8	30	24	3.5	4.0	60	5.0	1:30	1,579
F-C-9	30	24	3.5	4.0	70	5.0	3:15	932
F-C-10	30	24	3.5	6.0	70	5.0	1:40	832
F-C-11	30	24	3.5	6.0	80	5.0	2:00	633
F-D-1	30	24	2.5	1.0	0	6.0	0:15	2,610
F-D-2	30	24	2.5	1.0	50	6.0	0:50	2,496
F-D-3	30	24	2.5	1.0	70	6.0	1:15	2,400
F-D-4	30	24	2.5	1.0	90	6.0	2:00	2,269
F-D-5	30	24	2.5	1.0	110	6.0	3:05	1,750

Table 25 (Cont'd)

Specimen No.	Temperature, °C		Water, wt%	TCR catalyst, wt%	Pyridine ^a retarder, wt%	ZnCl ₂ promoter, wt%	Gel time, min:sec	1-hr compressive strength, psi ^b
	ambient	mix components						
F-D-6	30	24	2.5	1.5	90	6.0	1:35	2,482
F-D-7	30	24	2.5	1.5	110	6.0	2:10	2,283
F-E-1	30	24	2.5	1.0	0	5.0	1:12	1,977
F-E-2	30	24	2.5	1.5	0	5.0	0:20	2,788
F-E-3	30	24	2.5	1.5	30	5.0	1:06	2,461
F-E-4	30	24	2.5	1.5	50	5.0	3:40	1,637
F-E-5	30	24	2.5	2.0	30	5.0	0:30	2,817
F-E-6	30	24	2.5	2.0	50	5.0	1:20	2,568
F-E-7	30	24	2.5	2.0	60	5.0	2:15	2,226
F-E-8	30	24	2.5	2.0	70	5.0	3:25	1,680
F-E-9	30	24	2.5	2.0	80	5.0	6:00	939
F-E-10	30	24	2.5	3.0	60	5.0	1:00	2,660
F-E-11	30	24	2.5	3.0	70	5.0	1:50	2,504
F-E-12	30	24	2.5	3.0	80	5.0	2:20	2,084
F-E-13	30	24	2.5	3.0	90	5.0	3:45	1,188
F-F-1	30	24	1.5	0.5	0	5.6	3:30	1,472
F-F-2	30	24	1.5	1.0	0	5.6	0:15	3,371
F-F-3	30	24	1.5	1.0	50	5.6	3:10	2,419
F-F-4	30	24	1.5	1.0	60	5.6	3:55	1,265
F-F-5	30	24	1.5	1.0	70	5.6	7:10	c
F-F-6	30	24	1.5	1.5	50	5.6	0:50	3,771
F-F-7	30	24	1.5	1.5	60	5.6	2:30	2,648
F-F-8	30	24	1.5	1.5	70	5.6	4:15	1,090
F-F-9	30	24	1.5	1.5	80	5.6	6:05	498
F-G-1	30	24	0.75	0.25	0	5.0	1:55	1,814
F-G-2	30	24	0.75	0.50	0	5.0	1:00	3,158
F-G-3	30	24	0.75	0.50	50	5.0	2:40	2,091
F-G-4	30	24	0.75	0.50	70	5.0	3:15	1,977
F-G-5	30	24	0.75	0.50	90	5.0	4:40	327
F-G-6	30	24	0.75	1.0	80	5.0	2:20	3,485
F-G-7	30	24	0.75	1.0	90	5.0	3:25	2,263

Table 25 (Cont'd)

Specimen No.	Temperature, °C		Water, wt%	TCT catalyst, wt%	Pyridine ^a retarder, wt%	ZnCl ₂ promoter, wt%	Gel time, min:sec	1-hr compressive strength, psi ^b
	ambient	mix components						
F-G-8	30	24	0.75	1.0	95	5.0	3:50	2,176
F-II-1	30	24	0.0	1.0	50	3.8	3:05	1,444
F-II-2	30	24	0.0	2.0	50	3.8	1:55	3,677
F-II-3	30	24	0.0	2.0	70	3.8	3:10	2,553
F-II-4	30	24	0.0	2.0	90	3.8	5:20	782
F-II-5	30	24	0.0	3.0	0	3.8	1:05	3,908
F-II-6	30	24	0.0	3.0	50	3.8	2:20	3,734
F-II-7	30	24	0.0	3.0	70	3.8	3:05	3,208
F-II-8	30	24	0.0	3.0	80	3.8	4:15	2,200
F-II-9	30	24	0.0	3.0	90	3.8	6:00	1,501

^aBy weight of TCT.^bMPa = psi x 6.895 x 10⁻³.^cToo low to be measured.

The data also indicate that the gel time increases with a decrease in the aggregate water content. The longest gel time at the maximum water content of 3.5 wt% that results in a PC with adequate strength is ~1 min 15 sec (Specimen No. F-B-6). This was attained by the addition of a reagent formulation consisting of 1.5% catalyst by weight of monomer, 70% retarder by weight of catalyst (TCT) and 75% promoter by weight of monomer. If a gel time >2 min was required, 90% retarder by weight of catalyst was needed. However, the strength (Specimen No. F-B-7) at 1 hr was only 1466 psi (10.10 MPa), ~31% lower than that of PC with 70 wt% retarder. At a water content of 2.5 wt%, the gel time was ~2 min 20 sec and the strength was >2000 psi (>13.78 MPa). PCs made with water contents <1.5 wt% had gel times >3 min and excellent early strength. These results suggest that even if it is possible to use dry aggregate and the temperature is a relatively high 30°C, a gel time of ~5 min would be required to meet the compressive strength criteria.

Compositions and test results for specimens cured at 20°C are given in Tables 26 and 27, respectively. When compared to those used for the 30°C samples, these compositions are characterized by an appreciably increased amount of TCT catalyst.

The results are similar to those obtained at 30°C. Namely, the gel times tend to increase gradually with a decrease in water content. For a water content of 3.5 wt%, a strength of 2304 psi (15.88 MPa) was developed by use of 2.0% catalyst by weight of monomer, 60% retarder by weight of catalyst, and 75% promoter by weight of monomer. The gel time was 1 min, 40 sec. Gel times >2 min and adequate strengths were obtained when the water content was <2.5 wt%.

The compositions of specimens cured at 10°C are given in Table 28. By comparison with samples cured at 20°C, the formulations are characterized by the use of a somewhat decreased amount of retarder. The test results, summarized in Table 29, indicate that the desired properties can be obtained with aggregate having water contents up to 3.5 wt%. All of these formulations have gel times between ~1 and 4 min.

The properties of specimens cured at 1°C and consisting of the mix compositions listed in Table 30 are given in Table 31. Compared to the PC cured at 10°C, the 1°C formulations contain increased amounts of catalyst and promoter. The data indicate that a 1-hr compressive strength >1000 psi (6.89 MPa) can be obtained with samples containing 3.5 wt% water. The gel time is ~2 min 15 sec. At 10°C, strengths <500 psi (3.44 MPa) were normally obtained for samples with similar gel times.

The results at -10°C for PC specimens of compositions listed in Table 32, are given in Table 33. As shown in Table 32, the required quantities of FA monomer, promoter, and catalyst are considerably higher than those used at 1°C. Since the viscosity of FA monomer at -10°C is significantly greater than at 1°C, monomer contents ≥10 wt% are required to achieve mix consistencies similar to those for formulations used at >1°C. The addition of >7.5 wt% ZnCl₂ and 5.0 wt% TCT is also required to attain the desired early strength.

Table 26

Compositions of FA-PC Polymerized at 20°C

Specimen No.	FA monomer, wt%	Aggregate, ^a wt%	ZnCl ₂ promoter, wt%	Silica flour filler, wt%	TCT catalyst, % by weight of FA monomer	Pyridine retarder, % by weight of TCT catalyst	Water, % by weight of aggregate
F-I	8.0	68.8	6.0	17.2	1.5 to 2.0	50 to 80	3.5
F-J	8.0	69.6	5.0	17.4	2.0	60 to 90	2.5
F-K	9.0	68.8	5.0	17.2	1.5 to 2.0	60 to 90	1.5
F-L	10.0	68.0	5.0	17.0	1.0 to 1.5	30 to 70	0.75
F-M	10.0	68.0	5.0	17.0	1.5	50 to 80	0.0

^aAggregate, 60 wt% coarse (size, 9.5 to 2.38 mm) - 40 wt% fine (size, 1.19 to 0.149 mm).

Table 27

Test Results, FA-PC Cured at 20°C

Specimen No.	Temperature, °C		Water, wt%	TCT catalyst, wt%	Pyridine ^a retarder, wt%	ZnCl ₂ promoter, wt%	Gel time, min:sec	1-hr compressive strength, psi ^b
	ambient	mix components						
F-I-1	20	20	3.5	1.5	50	6.0	1:18	2,198
F-I-2	20	20	3.5	1.5	60	6.0	2:20	1,712
F-I-3	20	20	3.5	1.5	70	6.0	4:20	598
F-I-4	20	20	3.5	2.0	50	6.0	1:00	2,519
F-I-5	20	20	3.5	2.0	60	6.0	1:40	2,304
F-I-6	20	20	3.5	2.0	70	6.0	2:30	1,593
F-J-1	20	20	2.5	2.0	60	5.0	1:35	2,489
F-J-2	20	20	2.5	2.0	70	5.0	2:10	2,262
F-J-3	20	20	2.5	2.0	75	5.0	2:30	1,970
F-J-4	20	20	2.5	2.0	80	5.0	4:15	1,408
F-J-5	20	20	2.5	2.0	90	5.0	8:10	419
F-K-1	20	20	1.5	1.5	60	5.0	1:45	3,364
F-K-2	20	20	1.5	1.5	70	5.0	2:30	1,522
F-K-3	20	20	1.5	1.5	80	5.0	4:25	785
F-K-4	20	20	1.5	2.0	70	5.0	1:40	3,208
F-K-5	20	20	1.5	2.0	80	5.0	2:25	2,845
F-K-6	20	20	1.5	2.0	90	5.0	4:18	1,050
F-L-1	20	20	0.75	1.0	30	5.0	4:20	1,575
F-L-2	20	20	0.75	1.0	50	5.0	4:55	1,038
F-L-3	20	20	0.75	1.5	50	5.0	2:10	3,385
F-L-4	20	20	0.75	1.5	60	5.0	2:45	3,087
F-L-5	20	20	0.75	1.5	70	5.0	3:05	2,304
F-M-1	20	20	0.0	1.5	50	5.0	1:02	4,780
F-M-2	20	20	0.0	1.5	60	5.0	2:15	3,462
F-M-3	20	20	0.0	1.5	70	5.0	3:45	2,145
F-M-4	20	20	0.0	1.5	80	5.0	5:55	780

^aBy weight of TCT.^bMPa = psi x 6.895 x 10⁻³.

Table 28

Compositions of FA-PC Polymerized at 10°C

Specimen No.	FA monomer, wt%	Aggregate, ^a wt%	ZnCl ₂ promoter, wt%	Silica flour filler, wt%	TCT catalyst, % by weight of FA monomer	Pyridine retarder, % by weight of TCT catalyst	Water, % by weight of aggregate
F-N	8.0	68.8	6.0	17.2	2.0	10 to 50	3.5
F-O	8.0	69.6	5.0	17.4	2.0 to 2.5	10 to 60	2.5
F-P	9.0	68.8	5.0	17.2	2.0	30 to 60	1.5
F-Q	10.0	68.0	5.0	17.0	1.5 to 2.0	10 to 60	0.75
F-R	10.0	68.0	5.0	17.0	1.5	10 to 50	0.0

^aAggregate, 60 wt% coarse (size, 9.5 to 2.38 mm) - 40 wt% fine (size, 1.19 to 0.149 mm).

Table 29

Test Results, FA-PC Cured at 10°C

Specimen No.	Temperature, °C		Water, wt%	TCT catalyst, wt%	Pyridine ^a retarder, wt%	ZnCl ₂ promoter, wt%	Gel time, min:sec	1-hr compressive strength, psi ^b
	ambient	mix components						
F-N-1	10	5	3.5	2.0	10	6.0	1:10	2,440
F-N-2	10	5	3.5	2.0	30	6.0	1:40	2,048
F-N-3	10	5	3.5	2.0	50	6.0	2:45	985
F-O-1	10	5	2.5	2.0	10	5.0	1:00	2,824
F-O-2	10	5	2.5	2.0	30	5.0	2:20	1,792
F-O-3	10	5	2.5	2.0	50	5.0	3:15	298
F-O-4	10	5	2.5	2.5	40	5.0	1:12	3,120
F-O-5	10	5	2.5	2.5	50	5.0	2:25	2,269
F-O-6	10	5	2.5	2.5	60	5.0	3:05	1,275
F-P-1	10	5	1.5	2.0	30	5.0	1:10	3,450
F-P-2	10	5	1.5	2.0	40	5.0	2:00	2,795
F-P-3	10	5	1.5	2.0	50	5.0	3:10	2,042
F-P-4	10	5	1.5	2.0	60	5.0	4:50	656
F-Q-1	10	5	0.75	1.5	10	5.0	1:32	3,528
F-Q-2	10	5	0.75	1.5	30	5.0	3:10	1,780
F-Q-3	10	5	0.75	1.5	50	5.0	5:18	896
F-Q-4	10	5	0.75	2.0	40	5.0	1:35	4,182
F-Q-5	10	5	0.75	2.0	50	5.0	2:50	3,713
F-Q-6	10	5	0.75	2.0	60	5.0	3:45	1,968
F-R-1	10	5	0.0	1.5	10	5.0	1:25	4,694
F-R-2	10	5	0.0	1.5	30	5.0	2:35	3,442
F-R-3	10	5	0.0	1.5	40	5.0	3:30	1,523
F-R-4	10	5	0.0	1.5	50	5.0	4:25	764

^aBy weight of TCT.^bMPa = psi x 6.895 x 10⁻³.

Table 30

Compositions of FA-PC Polymerized At 1°C

Specimen No.	FA monomer, wt%	Aggregate, a wt%	ZnCl ₂ promoter, wt%	Silica flour filler, wt%	TCT catalyst, % by weight of FA monomer	Pyridine retarder, % by weight of TCT catalyst	Water, % by weight of aggregate
F-S	8.0	68.8	6.0	17.2	2.5	30 to 60	3.5
F-T	8.0	69.2	5.5	17.3	2.5	0 to 50	2.5
F-U	9.0	68.4	5.5	17.1	2.5	10 to 50	1.5
F-V	10.0	67.6	5.5	16.9	2.0	0 to 20	0.75
F-W	10.0	67.6	5.5	16.9	2.0	0 to 30	0.0

aAggregate, 60 wt% coarse (size, 9.5 to 2.38 mm) - 40 wt% fine (size, 1.19 to 0.149 mm).

Table 31

Test Results, FA-PC Cured at 1°C

Specimen No.	Temperature, °C	ambient	mix components	Water, wt%	TCT catalyst, wt%	Pyridine ^a retarder, wt%	ZnCl ₂ promoter, wt%	Gel time, min:sec	1-hr compressive strength, psi ^b
F-S-1	1	1	3	3.5	2.5	30	6.0	0:45	2749
F-S-2	1	1	3	3.5	2.5	40	6.0	1:35	2288
F-S-3	1	1	3	3.5	2.5	50	6.0	2:15	1275
F-S-4	1	1	3	3.5	2.5	60	6.0	7:50	900
F-T-1	1	1	3	2.5	2.5	0	5.5	0:25	3376
F-T-2	1	1	3	2.5	2.5	10	5.5	1:40	3048
F-T-3	1	1	3	2.5	2.5	30	5.5	2:10	2860
F-T-4	1	1	3	2.5	2.5	50	5.5	5:20	1050
F-U-1	1	1	3	1.5	2.5	10	5.5	0:55	4274
F-U-2	1	1	3	1.5	2.5	30	5.5	2:45	3561
F-U-3	1	1	3	1.5	2.5	50	5.5	5:50	1688
F-V-1	1	1	3	0.75	2.0	0	5.5	1:40	3892
F-V-2	1	1	3	0.75	2.0	10	5.5	3:50	2336
F-V-3	1	1	3	0.75	2.0	20	5.5	6:00	1765
F-W-1	1	1	3	0.0	2.0	0	5.5	1:50	4082
F-W-2	1	1	3	0.0	2.0	10	5.5	4:10	2955
F-W-3	1	1	3	0.0	2.0	30	5.5	6:20	2280

^aBy weight of TCT.

^bMPa = psi x 6.895 x 10⁻³.

Table 32

Compositions of FA-PC polymerized at -10°C

Specimen No.	FA monomer, wt%	Aggregate, wt%	ZnCl ₂ promoter, wt%	Silica flour filler, wt%	TCT catalyst, % by weight of FA monomer	Pyridine retarder, % by weight of TCT catalyst	Water, % by weight of aggregate
F-F-A	10.0	64.8	9.0	16.2	5.0	0 to 30	3.5
F-F-B	10.5	64.8	8.5	16.2	5.0	0 to 40	2.5
F-F-C	11.0	64.8	8.0	16.2	5.0	10 to 50	1.5
F-F-D	11.5	64.8	7.5	16.2	5.0	10 to 30	0.75
F-F-E	11.5	64.8	7.5	16.2	5.0	10 to 30	0.0

^aAggregate, 60 wt% coarse (size, 9.5 to 2.38 mm) - 40 wt% fine (size, 1.19 to 0.149 mm).

Table 33

Test Results, FA-PC Cured at -10°C

Specimen No.	Temperature, °C	Water, wt%	TCT catalyst, wt%	Pyridine ^a retarder, wt%	ZnCl ₂ promoter, wt%	Gel time, min:sec	1-hr compressive strength, psi ^b
F-F-A-1	-10	3.5	5.0	0	9.0	0:45	4050
F-F-A-2	-10	3.5	5.0	10	9.0	2:30	3974
F-F-A-3	-10	3.5	5.0	20	9.0	6:25	3811
F-F-A-4	-10	3.5	5.0	30	9.0	8:10	3490
F-F-B-1	-10	2.5	5.0	0	8.5	1:40	4188
F-F-B-2	-10	2.5	5.0	10	8.5	4:30	4060
F-F-B-3	-10	2.5	5.0	30	8.5	6:50	3900
F-F-B-4	-10	2.5	5.0	40	8.5	9:35	2860
F-F-C-1	-10	1.5	5.0	10	8.0	2:50	4690
F-F-C-2	-10	1.5	5.0	30	8.0	8:50	4843
F-F-C-3	-10	1.5	5.0	50	8.0	22:00	3077
F-F-D-1	-10	0.75	5.0	10	7.5	5:45	4420
F-F-D-2	-10	0.75	5.0	20	7.5	8:50	4630
F-F-D-3	-10	0.75	5.0	30	7.5	15:00	4350
F-F-E-1	-10	0.0	5.0	10	7.5	6:00	5983
F-F-E-2	-10	0.0	5.0	20	7.5	9:10	5698
F-F-E-3	-10	0.0	5.0	30	7.5	15:30	4843

^aBy weight of TCT.^bMPa = psi x 6.89 x 10⁻³.

The test results at -10°C show an interesting relationship between the gel time and the 1-hr strength. Even if the specimens have a maximum water content of 3.5 wt%, an early strength of 3490 psi (24.05 MPa) can be obtained at a relatively long gel time of ~8 min 10 sec. PC having the same water content and polymerized by the addition of 5.0 wt% TCT and 9.0 wt% ZnCl_2 , but without pyridine retarder, had an excellent early strength of >4000 psi (>27.56 MPa). However, its gel time was only ~45 sec. The gel time for a PC with a 1-hr strength >3000 psi (>20.67 MPa) increases with a decrease in the water content of the aggregate. The results also suggest that the strength of samples containing a wet aggregate can be controlled by varying the catalyst, promoter, and retarder concentrations.

At -20°C , the mix compositions listed in Table 34 were used. For PC formulations containing <3.5 wt% water, the quantities of retarder used were somewhat lower than those used at -10°C . The test results, summarized in Table 35, indicate that a 1-hr strength >2500 psi (>17.23 MPa) can be produced with a PC formulation containing 3.5 wt% water and 10 wt% ZnCl_2 . The gel time is ~12 min (Specimen No. F-F-F-3), practical for field application. For PC specimens made with aggregate having a water content <2.5 wt%, the desired properties can be obtained at a gel time >8 min.

Summarizing the results from the above tests, FA formulations containing aggregate with water contents up to 3.5 wt% appear suitable for use over the temperature range 30° to -20°C . These compositions are listed in Tables 36 and 37.

2. Ca-UP PC

To determine the optimum formulations to produce Ca-UP complexed PC over the temperature range 10° to 30°C , tests similar to those described above for FA-PC were performed.

The gel time and 1-hr compressive strength results at 30°C for PC specimens made according to the mix compositions listed in Table 38 are presented in Table 39. These data indicate that the addition of DMA promoter in conjunction with MEKP catalyst and CoN promoter has a significant effect on the early strength of specimens made with wet aggregate. The 1-hr strength increases with increasing levels of DMA and the gel time decreases. It is possible to obtain a strength >2000 psi (>13.78 MPa) for PC containing aggregate with a water content of 3.5 wt% while maintaining a gel time >3 min. For water contents <2.5 wt%, the gel times are longer than for samples containing 3.5 wt%. The maximum gel time that will still yield a PC with the desired early strength seems to be ~5 min. Using dried aggregate, the strength requirements could not be met if the gel time was >5 min.

Table 34

Compositions of FA-PC polymerized at -20°C

Specimen No.	FA monomer, wt%	Aggregate, wt%	ZnCl ₂ promoter, wt%	Silica flour filler, wt%	TCT catalyst, % by weight of FA monomer	Pyridine retarder, % by weight of TCT catalyst	Water, % by weight of aggregate
F-F-F	10.0	64.0	10.0	16.0	5.0	0 to 30	3.5
F-F-G	10.5	64.8	8.5	16.2	5.0	0 to 30	2.5
F-F-H	11.0	64.8	8.0	16.2	5.0	0 to 20	1.5
F-F-I	11.5	64.8	7.5	16.2	6.0	0 to 20	0.75
F-F-J	11.5	64.8	7.5	16.2	6.0	0 to 20	0.0

^aAggregate, 60 wt% coarse (size, 9.5 to 2.38 mm) - 40 wt% fine (size, 1.19 to 0.149 mm).

Table 35

Test Results, FA-PC Cured at -20°C

Specimen No.	Temperature, °C	ambient	mix components	Water, wt%	TCT catalyst, wt%	Pyridine ^a retarder, wt%	ZnCl ₂ promoter, wt%	Gel time, min:sec	1-hr compressive strength, psi ^b
F-F-F-1	-20	-10	-10	3.5	5.0	0	10.0	3:50	3992
F-F-F-2	-20	-10	-10	3.5	5.0	10	10.0	6:40	3490
F-F-F-3	-20	-10	-10	3.5	5.0	30	10.0	12:00	2542
F-F-G-1	-20	-10	-10	2.5	5.0	0	8.5	5:10	3419
F-F-G-2	-20	-10	-10	2.5	5.0	10	8.5	6:50	2650
F-F-G-3	-20	-10	-10	2.5	5.0	20	8.5	8:20	2200
F-F-H-1	-20	-10	-10	1.5	5.0	0	8.0	6:50	3235
F-F-H-2	-20	-10	-10	1.5	5.0	10	8.0	7:30	3454
F-F-H-3	-20	-10	-10	1.5	5.0	20	8.0	10:45	3068
F-F-I-1	-20	-10	-10	0.75	6.0	0	7.5	1:35	3850
F-F-I-2	-20	-10	-10	0.75	6.0	10	7.5	3:15	3697
F-F-I-3	-20	-10	-10	0.75	6.0	20	7.5	8:30	3128
F-F-J-1	-20	-10	-10	0.0	6.0	0	7.5	2:00	4110
F-F-J-2	-20	-10	-10	0.0	6.0	10	7.5	4:00	4024
F-F-J-3	-20	-10	-10	0.0	6.0	20	7.5	6:10	3633

^aBy weight of TCT.^bMPa = psi x 6.895 x 10⁻³.

Table 36

Summary of FA-PC Formulations^a for Use at
Ambient Temperatures Between 30° and 100°C

Water content, wt%	FA monomer, wt%	Aggregate, ^b wt%	ZnCl ₂ promoter, wt%	Silica flour filler, wt%	TCT catalyst, % by weight of FA monomer	Pyridine retarder, % by weight of TCT catalyst
3.5	8.0	68.8	6.0	17.2	1.5 to 2.0	30 to 70
2.5	8.0	69.6	5.0	17.4	2.0 to 2.5	50 to 70
1.5	9.0	68.3	5.0 to 5.6	17.1 to 17.2	1.0 to 2.0	50 to 80
0.75	10.0	68.0	5.0	17.0	1.0 to 2.0	50 to 90
0.0	10.0	68.0 to 69.0	3.8 to 5.0	17.0 to 17.2	1.5 to 3.0	30 to 80

^aFormulations selected have 1-hr compressive strengths >2000 psi and gel times >1 min.

^bAggregate, 60 wt% coarse (size, 9.5 to 2.38 mm) - 40 wt% fine (size, 1.19 to 0.149 mm).

Table 37

Summary of FA-PC Formulations^a for Use at
Ambient Temperatures Between 1° and -20°C

Water content, wt%	FA monomer, wt%	Aggregate, ^b wt%	ZnCl ₂ promoter, wt%	Silica flour filler, wt%	TCT catalyst, % by weight of FA monomer	Pyridine retarder, % by weight of TCT catalyst
3.5	8.0 to 10.0	64.0 to 68.8	6.0 to 10.0	16.0 to 17.2	2.5 to 5.0	0 to 40
2.5	8.0 to 10.5	64.8 to 69.2	5.5 to 8.5	16.2 to 17.3	2.5 to 5.0	0 to 40
1.5	9.0 to 11.0	64.8 to 68.4	5.5 to 8.0	16.2 to 17.1	2.5 to 5.0	0 to 50
0.75	10.0 to 11.5	64.8 to 67.6	5.5 to 7.5	16.2 to 16.9	2.0 to 6.0	0 to 30
0.0	10.0 to 11.5	64.8 to 67.6	5.5 to 7.5	16.2 to 16.9	2.0 to 6.0	0 to 30

^aFormulations selected have 1-hr compressive strength >2000 psi and gel times >1 min 30 sec.

^bAggregate, 60 wt% coarse (size, 9.5 to 2.38 mm) - 40 wt% fine (size, 1.19 to 0.149 mm).

Table 38

Compositions of Ca-UP PC Polymerized at 30°C

Specimen No.	UP-St monomer, wt%	Aggregate, a wt%	Type III portland cement filler, wt%	MEKP catalyst, % by weight of UP-St monomer	CoN promoter, % by weight of UP-St monomer	DMA promoter, % by weight of UP-St monomer	Water, % by weight of aggregate
U-A	19.0	70.9	10.1	0.5 to 2.0	1.0 to 2.0	0 to 1.0	3.5
U-B	19.0	70.9	10.1	1.0	2.0	0 to 1.0	2.5
U-C	20.0	70.0	10.0	1.0	1.5	0 to 1.0	1.5
U-D	20.0	70.0	10.0	1.0	1.5	0 to 0.5	0.75
U-E	20.0	70.0	10.0	1.0	1.5	0 to 0.3	0.0

a Aggregate, 60 wt% coarse (size, 9.5 to 2.38 mm) - 40 wt% fine (size, 1.19 to 0.149 mm).

Table 39

Test Results, Ca-UP PC Cured at 30°C

Specimen No.	Temperature, °C		Water, wt%	MEKP catalyst, wt%	CoN promoter, wt%	DMA promoter, wt%	Gel time, min:sec	1-hr compressive strength, psi
	ambient	mix components						
U-A-1	30	24	3.5	0.5	2.0	0.0	17:30	377
U-A-2	30	24	3.5	1.0	1.0	0.0	9:25	725
U-A-3	30	24	3.5	1.0	2.0	0.0	4:10	1,508
U-A-4	30	24	3.5	1.0	2.0	0.2	3:30	2,432
U-A-5	30	24	3.5	1.0	2.0	0.5	2:15	2,774
U-A-6	30	24	3.5	1.5	2.0	0.0	3:35	1,873
U-A-7	30	24	3.5	2.0	2.0	0.0	2:40	1,988
U-A-8	30	24	3.5	2.0	2.0	0.2	2:15	2,634
U-A-9	30	24	3.5	2.0	2.0	0.5	1:45	3,220
U-A-10	30	24	3.5	2.0	2.0	1.0	1:20	3,848
U-B-1	30	24	2.5	1.0	2.0	0.0	4:50	917
U-B-2	30	24	2.5	1.0	2.0	0.1	4:00	2,297
U-B-3	30	24	2.5	1.0	2.0	0.2	3:20	2,376
U-B-4	30	24	2.5	1.0	2.0	0.5	3:00	2,731
U-B-5	30	24	2.5	1.0	2.0	1.0	2:25	2,800
U-C-1	30	24	1.5	1.0	1.5	0.0	5:15	1,529
U-C-2	30	24	1.5	1.0	1.5	0.1	3:50	2,255
U-C-3	30	24	1.5	1.0	1.5	0.2	3:05	2,404
U-C-4	30	24	1.5	1.0	1.5	0.5	2:10	2,994
U-C-5	30	24	1.5	1.0	1.5	1.0	1:40	3,691
U-D-1	30	24	0.75	1.0	1.5	0.0	5:40	1,869
U-D-2	30	24	0.75	1.0	1.5	0.1	5:00	2,255
U-D-3	30	24	0.75	1.0	1.5	0.3	4:30	2,411
U-D-4	30	24	0.75	1.0	1.5	0.5	1:20	3,293
U-E-1	30	24	0.0	1.0	1.5	0.0	12:50	519
U-E-2	30	24	0.0	1.0	1.5	0.05	4:40	2,089
U-E-3	30	24	0.0	1.0	1.5	0.1	2:25	4,267
U-E-4	30	24	0.0	1.0	1.5	0.3	1:00	8,250

MPa = psi x 6.895 x 10⁻³.

At 20°C, the mix compositions listed in Table 40 were used. As shown in this table, the quantities of catalyst and promoter used were somewhat higher than those used at 30°C. These test results, summarized in Table 41, are similar to those obtained for PM specimens. They indicate that we could not obtain the required early strength without gel times <1 min if the aggregate water content was >2.5 wt%. This is probably due to the water acting as a heat sink which results in a decreased polymerization rate. For water contents in the range >0 <1.5 wt%, PC with gel times <2 min yielded acceptable strengths. A 1-hr strength >3000 psi (>20.67 MPa) could not be obtained for water contents >0.75 wt%. PC containing dry aggregate (<0.1 wt% water) had a strength of >2000 psi (>13.78 MPa) and a gel time of ~3 min.

At 10°C, the mix compositions listed in Table 42 were tested and the results are summarized in Table 43. All samples containing aggregate with water contents ranging from 3.5 to 0.75 wt% had 1-hr strengths <1000 psi (<6.89 MPa). Because of the need to use relatively high catalyst and promoter concentrations in this test series, the gel times were only ~15 sec, too short to be practical.

The data suggest that PC made at 10°C with dry aggregate is capable of yielding an early strength >3000 psi (>20.67 MPa). However at <10°C, the Ca-UP complexed PC containing wet aggregate does not appear to have potential for rapid runway repair.

From the results of the above tests, Ca-UP complexed PC containing aggregate with water contents up to 3.5 wt% were selected for use in the temperature range 20° to 30°C. These compositions are summarized in Table 44.

E. Mechanical and Physical Properties

Additional tests to further characterize the FA and Ca-UP complexed systems were performed. Compressive, flexure, tensile, and shear bond strength tests were made, and bulk density and water absorption measurements were taken. These results are summarized in Tables 45 and 46.

The relative strength of Ca-UP complexed PC at ~24°C was ~2.0 times as great as that of FA-PC. The flexure and tensile strengths were 1080 psi (7.44 MPa) and 875 psi (6.03 MPa), respectively. The water absorption of FA-PC was approximately 48% lower than that of Ca-UP complexed PC. This is probably due to the relatively high bulk density of 2.45 g/cm³, when compared to that of Ca-UP complexed PC.

The shear bond strength was obtained from measurements of the shear strength at the interface between a smoothly finished surface of a 7.0-cm-diam x 3.0-cm-thick cement concrete disc and an ~3.0-cm thickness of PC containing either wet or dry aggregate which was cast against the concrete. As indicated in Table 46, the bond strength of Ca-UP complexed PC was much larger than that of the FA-PC specimens. Also, the degree of

Table 40

Compositions of Ca-UP Polymerized at 20°C

Specimen No.	UP-St monomer, wt%	Aggregate, a wt%	Type III portland cement filler, wt%	MEKP catalyst, % by weight of UP-St monomer	CoN promoter, % by weight of UP-St monomer	DMA promoter, % by weight of UP-St monomer	Water, % by weight of aggregate
U-F	19.0	70.9	10.1	1.0 to 1.5	2.0	0 to 0.3	3.5
U-G	19.0	70.9	10.1	1.0 to 1.5	2.0	0 to 0.2	2.5
U-H	20.0	70.0	10.0	1.5	2.0	0.05 to 0.2	1.5
U-I	20.0	70.0	10.0	1.5	2.0	0.05 to 0.1	0.75
U-J	20.0	70.0	10.0	1.5	2.0	0 to 0.1	0.0

^aAggregate, 60 wt% coarse (size, 9.5 to 2.38 mm) - 40 wt% fine (size, 1.19 to 0.149 mm).

Table 41

Test Results, Ca-UP PC Cured at 20°C

Specimen No.	Temperature, °C		Water, wt%	MEKP catalyst, wt%	CON promoter, wt%	DMA promoter, wt%	Gel time, min:sec	1-hr compressive strength, psi
	ambient	mix components						
U-F-1	20	20	3.5	1.0	2.0	0.0	4:50	541
U-F-2	20	20	3.5	1.0	2.0	0.05	3:10	1,088
U-F-3	20	20	3.5	1.0	2.0	0.1	2:35	1,331
U-F-4	20	20	3.5	1.0	2.0	0.2	1:50	1,878
U-F-5	20	20	3.5	1.0	2.0	0.3	0:40	2,165
U-F-6	20	20	3.5	1.5	2.0	0.0	2:35	839
U-F-7	20	20	3.5	1.5	2.0	0.1	2:00	1,629
U-F-8	20	20	3.5	1.5	2.0	0.2	1:30	1,906
U-F-9	20	20	3.5	1.5	2.0	0.3	0:25	2,338
U-G-1	20	20	2.5	1.0	2.0	0.0	3:20	690
U-G-2	20	20	2.5	1.0	2.0	0.1	2:30	1,489
U-G-3	20	20	2.5	1.0	2.0	0.2	1:40	1,905
U-G-4	20	20	2.5	1.5	2.0	0.0	2:30	906
U-G-5	20	20	2.5	1.5	2.0	0.05	2:15	1,004
U-G-6	20	20	2.5	1.5	2.0	0.1	1:25	1,738
U-G-7	20	20	2.5	1.5	2.0	0.2	0:40	2,064
U-H-1	20	20	1.5	1.5	2.0	0.05	2:00	1,970
U-H-2	20	20	1.5	1.5	2.0	0.1	1:30	2,176
U-H-3	20	20	1.5	1.5	2.0	0.2	0:50	2,490
U-I-1	20	20	0.75	1.5	2.0	0.05	1:30	2,205
U-I-2	20	20	0.75	1.5	2.0	0.1	1:05	2,458
U-I-3	20	20	0.75	1.5	2.0	0.15	0:40	2,590
U-J-1	20	20	0.0	1.5	2.0	0.0	6:30	1,260
U-J-2	20	20	0.0	1.5	2.0	0.02	3:00	2,200
U-J-3	20	20	0.0	1.5	2.0	0.05	1:15	3,142
U-J-4	20	20	0.0	1.5	2.0	0.1	0:40	5,680

MPa = psi x 6.895 x 10⁻³.

Table 42

Compositions of Ca-UP PC Polymerized at 10°C

Specimen No.	UP-St monomer, wt%	Aggregate, ^a wt%	Type III portland cement filler, wt%	MEKP catalyst, % by weight of UP-St monomer	CoN promoter, % by weight of UP-St monomer	DMA promoter, % by weight of UP-St monomer	Water, % by weight of aggregate
U-K	19.0	70.9	10.1	2.0	2.0	0.2 to 0.7	3.5
U-L	19.0	70.9	10.1	2.0	2.0	0.2 to 0.7	2.5
U-M	20.0	70.0	10.0	2.0	2.0	0.3 to 1.0	1.5
U-N	20.0	70.0	10.0	2.0	2.0	0.05 to 0.3	0.75
U-O	20.0	70.0	10.0	1.5	2.0	0.1 to 0.3	0.0

^aAggregate, 60 wt% coarse (size, 9.5 to 2.38 mm) - 40 wt% fine (size, 1.19 to 0.149 mm).

Table 43

Test Results, Ca-UP PC Cured at 10°C

Specimen No.	Temperature, °C	ambient	mix components	Water, wt%	MEKP catalyst, wt%	CoN promoter, wt%	DMA promoter, wt%	Gel time, min:sec	1-hr compressive strength, psi
U-K-1	10	5	5	3.5	2.0	2.0	0.2	15:00	199
U-K-2	10	5	5	3.5	2.0	2.0	0.5	9:50	350
U-K-3	10	5	5	3.5	2.0	2.0	0.7	7:35	157
U-L-1	10	5	5	2.5	2.0	2.0	0.2	7:20	228
U-L-2	10	5	5	2.5	2.0	2.0	0.5	5:40	520
U-L-3	10	5	5	2.5	2.0	2.0	0.7	3:20	292
U-M-1	10	5	5	1.5	2.0	2.0	0.3	3:20	370
U-M-2	10	5	5	1.5	2.0	2.0	0.5	2:40	780
U-M-3	10	5	5	1.5	2.0	2.0	1.0	1:50	320
U-N-1	10	5	5	0.75	2.0	2.0	0.05	4:15	349
U-N-2	10	5	5	0.75	2.0	2.0	0.1	3:55	399
U-N-3	10	5	5	0.75	2.0	2.0	0.3	3:10	548
U-O-1	10	5	5	0.0	1.5	2.0	0.1	3:50	1,346
U-O-2	10	5	5	0.0	1.5	2.0	0.2	2:30	3,620
U-O-3	10	5	5	0.0	1.5	2.0	0.3	1:40	6,552

^aMPa = psi x 6.895 x 10⁻³.

Table 44

Summary of Ca-UP PC Formulations^a for Use at Ambient Temperatures Between 30° and 20°C

Water content, wt%	UP-St monomer, wt%	Aggregate, wt%	Type III portland cement filler, wt%	MEKP catalyst, % by weight of UP-St monomer	CoN promoter, % by weight of UP-St monomer	DMA promoter, % by weight of UP-St monomer
3.5	19.0	70.9	10.1	1.0	2.0	0.2
2.5	19.0	70.9	10.1	1.0 to 1.5	2.0	0.1 to 0.2
1.5	20.0	70.0	10.0	1.0 to 1.5	1.5 to 2.0	0.1
0.75	20.0	70.0	10.0	1.0 to 1.5	1.5 to 2.0	0.05 to 0.1
0.00	20.0	70.0	10.0	1.0 to 1.5	1.5 to 2.0	0.02 to 0.05

^aFormulations selected have 1-hr compressive strengths >1800 psi and gel times >1 min.

^bAggregate, 60 wt% coarse (size, 9.5 to 2.38 mm) - 40 wt% fine (size, 1.19 to 0.149 mm).

Table 45

Mechanical and Physical Properties of FA and Ca-UP PC Containing Wet Aggregate (3.5 wt% Water Content) at a Curing Age of 7 days at a Temperature of ~24°C in Air

PC	Bulk density, g/cm ³	Compressive strength, psi (MPa)	Flexure ^b strength, psi (MPa)	Tensile ^a strength, psi (MPa)	Shear ^c strength, psi (MPa)	Water ^d absorption, %
FA	2.45	3150 (21.70)	502 (3.46)	400 (2.76)	764 (5.26)	0.95
Ca-UP	2.21	5405 (37.24)	1080 (7.44)	875 (6.03)	1378 (9.49)	1.84

^aSpecimens, 7.5-cm-diam x 15.0-cm-long cylinders; average value of two specimens.

^bSpecimens, 5.0-cm-square x 30.0-cm-long beams; average value of two specimens.

^cSpecimens, 7.3-cm-diam x 10.0-cm-long cylinders; average value of two specimens.

^dSubmerged in water at ~24°C for 7 days.

dryness of the concrete had a greater effect on the shear strength than the moisture content of the PC. Against a wet surface, the Ca-UP PC containing a wet aggregate exhibited a bond strength of 236 psi (1.63 MPa) compared to only 27 psi (0.19 MPa) for similar FA-PC samples. When the concrete surface was dry, the bond strength increased.

F. Durability Properties

Although not of primary importance for runway repair materials, the durability of the PC formulations in a variety of aggressive environments was determined. These data may serve to identify other potential applications for the USAF.

FA and Ca-UP PCs containing wet aggregate were tested for heat resistance, hydrothermal durability, freeze-thaw durability, and resistance to chemical attack by acids, sodium hydroxide, acetone, and kerosene. The acid tests included 20% H_2SO_4 and 20% HCl. Test results are given in Tables 47 to 50.

1. Heat Resistance

Change in weight and length, and the compressive strengths were determined after exposure to air at 100°C for periods up to 60 days. Test results are given in Table 47. FA-PC specimens show a gradual weight loss with time. This ranged from 1.34% after 10 days to 1.85% after 60 days. The weight loss is probably due to the evaporation of free water from the PC. Length change measurements show a slight expansion with increasing exposure time, ranging from 0.02% for 10 days to 0.14% for 60 days. The compressive strength after 10 days' exposure was 4430 psi (30.52 MPa), significantly greater than the control value of 2910 psi (20.05 MPa). This suggests that the degree of polymerization of FA monomer is enhanced by the heating. Additional heating for 60 days did not affect the strength, indicating that at 100°C the polymerization reaction is completed within the first 10 days and that the PC is thermally stable.

Ca-UP complexed PC specimens exposed to air at 100°C also show a small continuous decrease in weight due to the evaporation of free water. Length change measurements indicate progressive shrinkage with increasing exposure time. The strength improved from a control value of 5320 psi (36.66 MPa) to an average of 6190 psi (42.65 MPa) after 10 days exposure. After 60 days, it was 6342 psi (43.70 MPa). No visual signs of deterioration were apparent.

2. Hydrothermal Stability

The PC specimens were exposed to boiling water in an enclosed recirculating system. After 10, 30, and 60 days' exposure, the specimens were tested for weight and length changes, and compressive strength.

Table 46

Shear Bond Strength of FA and Ca-UP PC
to Type III Portland Cement Concrete

PC	Aggregate ^a	Condition of cement concrete surface	7-day bond strength, psi (MPa)	Failure mode
FA	wet	dry	160 (1.10)	joint
FA	wet	wet	27 (0.19)	joint
FA	dry	dry	235 (1.62)	joint
FA	dry	wet	32 (0.22)	joint
Ca-UP	wet	dry	358 (2.47)	cement concrete failure
Ca-UP	wet	wet	236 (1.63)	joint
Ca-UP	dry	dry	1081 (7.45)	cement concrete failure
Ca-UP	dry	wet	381 (2.63)	joint

^aWater content of aggregate, 3.5 wt%.

Table 47

Stability of PC in Air at 100°C

PC	Exposure, days	Weight change, %	Length change, %	Compressive strength, psi (MPa)
FA	0	0	0	2910 (20.05)
FA	10	-1.34	+0.02	4430 (30.52)
FA	30	-1.54	+0.13	4433 (30.54)
FA	60	-1.85	+0.14	4437 (30.57)
Ca-UP	0	0	0	5320 (36.66)
Ca-UP	10	-1.77	-0.26	6190 (42.65)
Ca-UP	30	-1.79	-0.29	6200 (42.72)
Ca-UP	60	-1.94	-0.36	6342 (43.70)

Table 48

Stability of PC in Water at 100°C

PC	Exposure, days	Weight change, %	Length change, %	Compressive strength, psi (MPa)
FA	0	0	0	2910 (20.05)
FA	10	+0.02	+0.72	2240 (15.43)
FA	30	+0.02	+0.68	2170 (14.95)
FA	60	+0.04	+0.68	2180 (15.02)
Ca-UP	0	0	0	5320 (36.66)
Ca-UP	10	+4.21	+2.14	3500 (24.12)
Ca-UP	30	+4.23	+2.13	3020 (20.81)
Ca-UP	60	+4.28	+2.14	3794 (26.14)

Table 49

Resistance to Freezing and Thawing

PC	Number of test cycles	Weight change, %	Compressive strength, psi (MPa)
FA	0	0.00	2,759 (19.01)
FA	50	-2.21	2,536 (17.47)
Ca-UP	0	0.00	5,560 (38.31)
Ca-UP	50	0.00	5,841 (40.24)

Table 50

Resistance to Chemical Attack

PC	Environment	Compressive strength, psi (MPa)		Strength reduction, %
		before exposure,	after 60 days	
FA	20% H ₂ SO ₄	2910 (20.05)	1770 (12.20)	39.18
FA	20% HCl	2910 (20.05)	1367 (9.42)	53.02
FA	20% NaOH	2910 (20.05)	2308 (15.90)	20.69
FA	acetone	2910 (20.05)	262 (1.81)	91.00
FA	kerosene	2910 (20.05)	2887 (19.89)	0.79
Ca-UP	20% H ₂ SO ₄	5320 (36.66)	2968 (34.23)	6.62
Ca-UP	20% HCl	5320 (36.66)	4643 (31.99)	12.73
Ca-UP	20% NaOH	5320 (36.66)	3251 (22.40)	38.89
Ca-UP	acetone	5320 (36.66)	— ^a	100.00
Ca-UP	kerosene	5320 (36.66)	5318 (36.64)	0.04

^aDisintegrated, removed from test.

The results are presented in Table 48. As shown in the table, the FA-PC specimens had no significant change in weight. Length change measurements indicate an expansion of 0.72% after 10 days and stabilization beyond that time. The compressive strength decreased ~25% within the first 30 days. No further reduction was noted.

The Ca-UP PC showed a relatively high weight increase of 4.21% and an increase in length of 2.14% after 10 days. These are probably due to absorption of water. Little changes were noted for longer exposure times. The compressive strength of the PC after exposure for 30 days indicates a trend toward decreased strength with increased exposure time. Values ranged from 5320 psi (36.66 MPa) before exposure to 3020 psi (20.81 MPa) after 30 days. Thereafter, the strength increased to 3794 psi (26.14 MPa) after 60 days. This increase was probably due to the hydration products of the cement filler formed during exposure to the boiling water.

3. Freeze-Thaw Durability

In this test, specimens were immersed in water and alternately frozen at -15°C and thawed at 24°C at the rate of about 7 cycles per week. The test results after 50 cycles are given in Table 49. FA-PC containing wet aggregate had a weight loss of 2.21% after 50 cycles. The compressive strength decreased from an average of 2759 psi (19.10 MPa) for the control to 2536 psi (17.49 MPa) after 50 cycles. During this period, the specimens developed a brown color on the surface.

The Ca-UP PC samples containing wet aggregate appeared to be in good condition after 50 cycles. No weight change was observed. The compressive strength after 50 cycles was higher than that for the controls.

4. Resistance to Acid Attack

Specimens were immersed for 60 days in 20% H_2SO_4 and 20% HCl at room temperature. Compressive strength results are given in Table 50. In 20% H_2SO_4 , the FA-PC specimens had a strength reduction of 39.18%. The Ca-UP PC specimens showed significantly greater acid resistance. The strength reduction was only 6.62%.

After similar exposure to 20% HCl , the FA-PC exhibited appreciable deterioration as indicated by a strength reduction of 53%. The Ca-UP PC lost 12.73%, thereby indicating far greater resistance. However, it should be noted that the FA-PC specimens were slightly absorptive and that lime-type aggregate is readily attacked by acids. Therefore, the use of more acid-resistant aggregate would significantly increase the durability.

5. Exposure to 20% NaOH

Specimens were tested for resistance to 20% NaOH at room temperature for 60 days. The test results (see Table 50) indicated that the loss in strength of Ca-UP PC is higher (38.89% vs 20.69%) than for FA-PC.

6. Resistance to Chemical Attack by Acetone

Results of accelerated acetone attack tests are also given in Table 50. After about 10 days exposure, the Ca-UP PC completely disintegrated. The resistance of FA-PC specimens was somewhat greater, but still very poor. After 60 days' exposure, the specimens had a strength of only 262 psi (1.81 MPa).

7. Resistance to Kerosene

Test specimens were also immersed in kerosene at room temperature for 60 days. As seen in Table 50, all specimens showed no visible signs of deterioration and the strengths remained constant.

G. Reinforcement Materials

The use of steel fiber reinforcement as a means of increasing the flexure strength of FA-PC at an age of 1 hr to at least 500 psi (3.45 MPa) was investigated. In these studies, the specimens were prepared in accordance with the mix compositions given in Table 51. Each composition had a F.A./C.A. ratio of 40/60 and a maximum water content of 3.5 wt%. Observations of the workability during the mixing of the PC indicated that the maximum concentration of fiber should be limited to the range of ~5 to 7% by weight of aggregate.

The flexure and compressive strength results for steel fiber reinforced specimens at a curing age of 7 days in air at ~24°C are summarized in Figures 28 and 29. These curves indicate that both strength properties increase with an increase in fiber concentration. Using 9 wt%, the flexure and compressive strengths were ~2.1 and 1.2 times greater than those of unreinforced PC.

The flexure strength results for samples containing 7.0 wt% steel fiber as a function of the cure time at ~24°C are given in Figure 30. The data indicate a maximum strength at a cure time of ~7 hr. The 30-min strength for the reinforced PC was 519 psi (3.58 MPa), ~67% higher than that of the unreinforced PC. The maximum strength at an age of 7 hr was 910 psi (6.27 MPa). This corresponds to an improvement of ~75% over specimens at a 30 min age.

H. Materials Cost

The cost for the materials in the steel fiber reinforced PC compositions needed for use in the temperature range 1° to 30°C and -10° to -20°C were calculated and the results are shown in Tables 52 and 53. The cost of solvents was not included in these calculations. Unless the binder has thickened considerably because of partial curing, acetone or trichloroethane can be used to clean tools used with the Ca-UP PC. Water is used as a solvent for the FA-PC compositions. The quantity of steel fiber used in the cost estimates was 7% by weight of aggregate.

Table 51

Compositions of Steel Fiber-Reinforced FA-PC

FA	ZnCl ₂	C.A.	F.A.	SiO ₂	Wt%		Pyridine retarder, by weight of catalyst	Steel fiber, by weight of aggregate
					Water, by weight of aggregate	TCT catalyst, by weight of monomer		
8	6	41.3	27.5	17.2	3.5	1.5	60	0 to 9

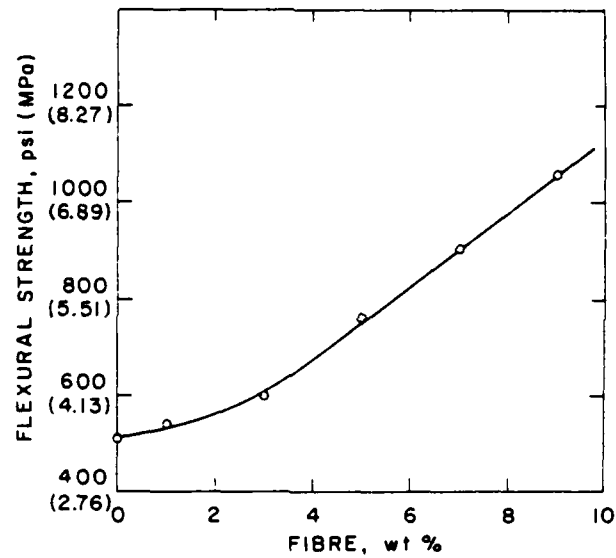


Figure 28. Effect of hooked steel fibers on the flexure strength of FA-PC containing wet aggregate

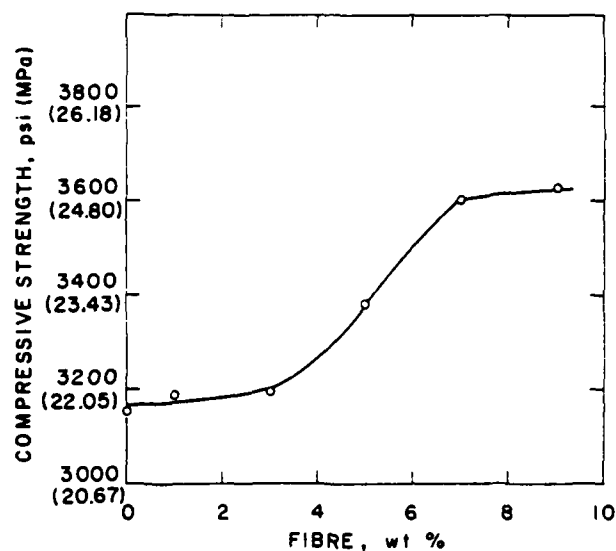


Figure 29. Compressive strength of FA-PC as a function of steel fiber concentration

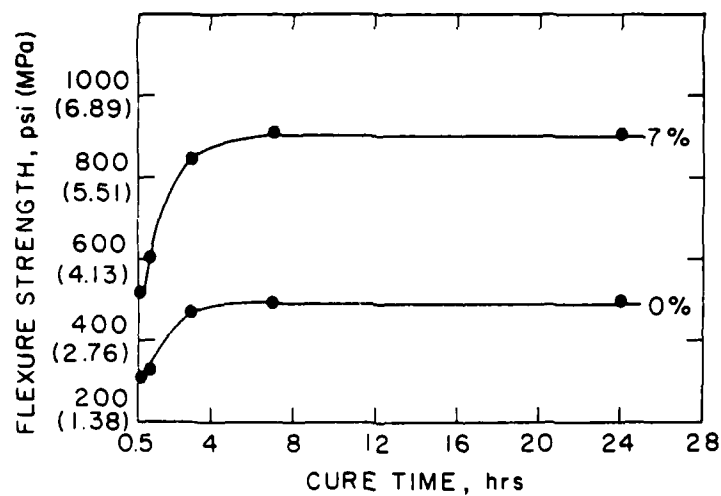


Figure 30. Flexure strength of steel fiber-reinforced FA-PC as a function of cure time

Table 52

Material Costs for PC for Use at Temperatures Between 1° and 30°C

Material	Quantity, kg/m ³	Unit cost, \$/kg	Cost, \$/m ³
<u>FA-PC^a</u>			
FA	196.0	1.322	259.11
aggregate	1690.5	0.015	25.36
ZnCl ₂	147.0	0.933	137.15
silica flour	416.5	0.110	45.82
TCT ¹	3.9	5.397	21.05
pyridine ²	2.3	9.775	22.48
steel fiber ³	118.3	1.110	131.31
total \$/m ³			642.28
\$/yd ³			491.08
<u>Ca-UP complexed PC^b</u>			
UP-St	419.9	1.045	438.8
aggregate	1566.9	0.015	23.5
cement	223.2	0.044	9.8
MEKP ⁴	8.4	2.313	19.4
CoN ⁵	8.4	3.106	26.1
DMA ⁶	4.2	2.775	11.7
steel fiber ³	109.7	1.110	121.8
total \$/m ³			651.1
\$/yd ³			497.8

^aPC formulation, 8.0 wt% FA monomer - 69.0 wt% wet aggregate - 6.0 wt% ZnCl₂ promoter - 17.0 wt% silica flour filler.

Density: 2450 kg/m³.

^bPC formulation, 19 wt% UP-St monomer - 70.9 wt% wet aggregate - 10.1 wt% Type III portland cement filler.

Density: 2210 kg/m³.

¹TCT catalyst, 2.0% by weight of FA monomer.

²Pyridine retarder, 60.0% by weight of TCT catalyst.

³Steel fiber, 7.0% by weight of aggregate.

⁴MEKP catalyst, 2.0% by weight of UP-St monomer.

⁵CoN promoter, 2.0% by weight of UP-St monomer.

⁶DMA promoter, 1.0% by weight of UP-St monomer.

Table 53

Material Costs for PC for Use at Temperatures Between -10° and -20°C

<u>FA-PC^a</u>			
Material	Quantity, kg/m^3	Unit Cost, \$/kg	Cost, \$/ m^3
FA	236.0	1.322	311.99
aggregate	1529.3	0.015	22.94
ZnCl_2	212.4	0.933	198.17
silica flour	382.3	0.110	42.05
TCT ¹	11.8	5.397	63.69
pyridine ²	3.5	9.775	34.21
steel fiber ³	107.1	1.110	118.88
		total s/m^3	791.93
		s/yd^3	605.50

^aPC formulation: 10.0 wt% FA monomer - 64.8 wt% wet aggregate - 9.0 wt% ZnCl_2 promoter - 16.2 wt% silica flour filler.
Density: 2360 kg/m^3 .

¹TCT catalyst: 5.0% by weight of FA monomer.

²Pyridine retarder: 30.0% by weight of TCT catalyst.

³Steel fiber: 7.0% by weight of aggregate.

IV. PROCESS TECHNOLOGY

In order to establish the feasibility of field use, preliminary process technology work was performed.

A premix method in which the monomer and the aggregate are added together in a mixer has generally been used to produce high-quality FA-PC. A primary consideration has been to reduce the void volume in the aggregate mass in order to minimize the required quantity of the expensive monomer. The fact that the water-soluble monomer completely wets the surface of the wet aggregate during mixing is an important advantage of this technique. This results in good bonding between the polymer and the aggregate phases, thereby enhancing the mechanical properties.

The penetration of FA monomer into a pre-packed wet aggregate matrix can be considered as an alternative method for producing FA-PC. With this method it is not necessary to mix the monomer with aggregate in a mixer, therefore it is less complicated and permits the use of formulations with short gel times.

Preliminary information regarding the rate of penetration of monomer into a wet aggregate matrix was obtained. Because of the relatively high early strength of FA-PC, it was assumed that a penetration depth of 30 cm would be adequate for most applications.

As shown in Figure 31, the measurements of the penetration rate of FA monomer into a 30-cm column of wet aggregate were performed in a 6.0-cm-diam x 40.0-cm-long glass cylinder. Saturation was performed by ponding the FA under atmospheric pressure. The aggregate had a F.A./C.A. ratio of 30/70 and a moisture content of 2.8 wt%. After curing, compressive strength tests on specimens cut from the saturated cylinders were performed in accordance with ASTM C39. These results are discussed later.

Although FA is water-soluble monomer, it appeared that the presence of entrapped water in the void spaces decreased the rate of penetration into the aggregate matrix. A mixture of filler materials consisting of dry No. 30 silica sand and dry silica flour was therefore added as a moisture absorbing material in this test series. The filler concentration was 19 wt%.

Wet aggregate consisting of the mix proportions indicated in Table 54 was placed to a height of ~30 cm in the glass cylinder. The aggregate was not vibrated or compacted by tamping. Monomer was then ponded onto the surface.

As illustrated in Figure 32, the penetration rate in aggregate mixtures containing various No.30/SiO₂ ratios was evaluated. The curves indicate that the rate of penetration was rapid for approximately the first 10 sec. Thereafter, the rate of penetration could be represented

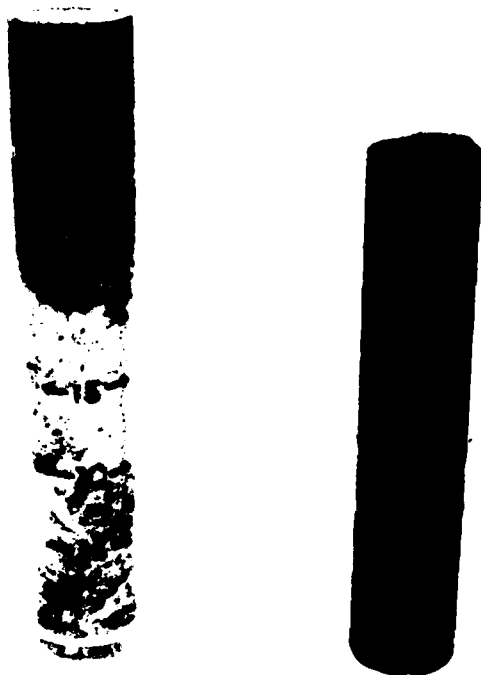


Figure 31. Measurement of penetration depth of FA monomer into wet aggregate (left), and cured FA-PC after penetration to 30-cm depth (right).

Table 54

Composition of Wet Aggregate

F.A./C.A. Ratio	C.A. ^a , wt%	F.A. ^b , wt%	ZnCl ₂ , wt%	Water ^c , % by weight of aggregate	No.30 dry silica sand ^d , + dry silica flour (SiO ₂) ^e , wt%
30/70	52.9	22.6	5.5	2.8	19.0

^aCrushed bluestone coarse aggregate (size, 12.5 to 2.38 mm).

^bSilica fine aggregate (size, 1.19 to 0.149 mm).

^cMaximum water content.

^dParticle size, 0.595 mm.

^eParticle size, <62 μ m.

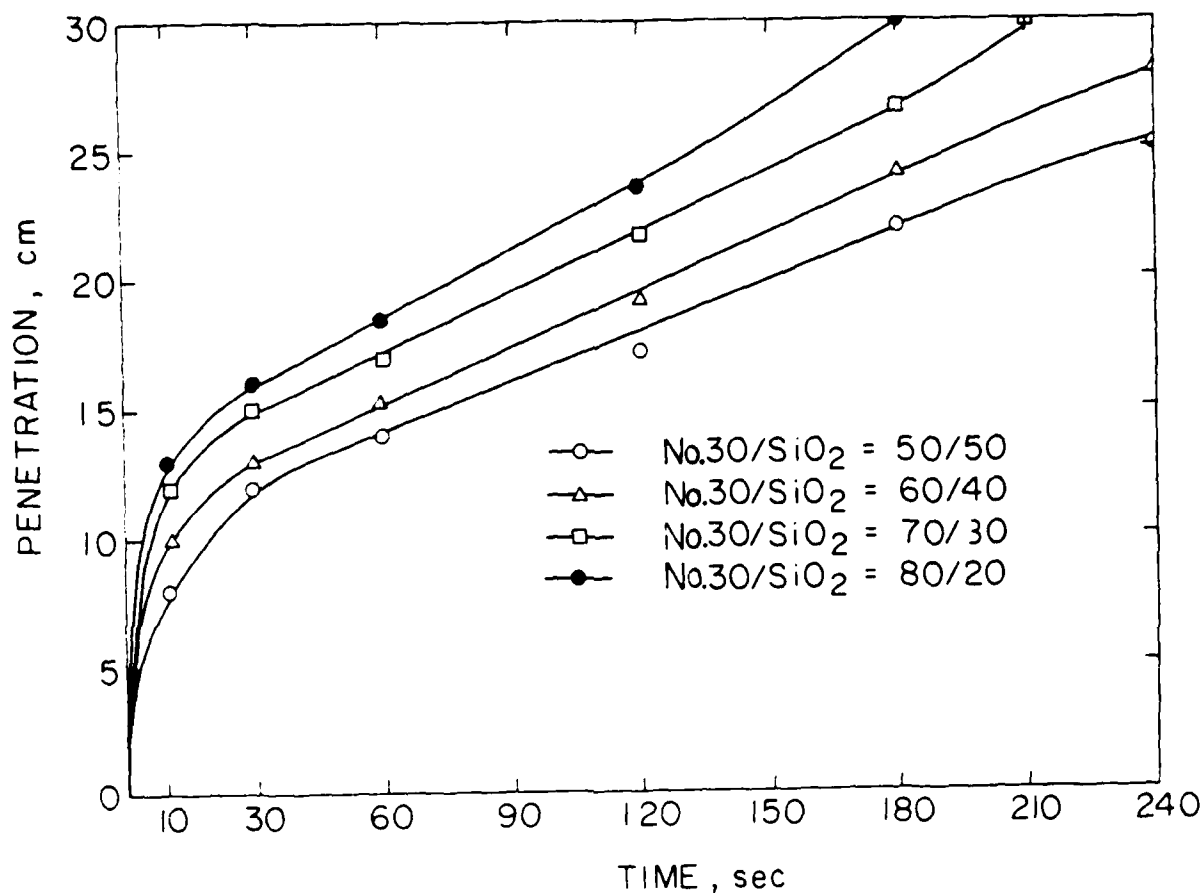


Figure 32. Monomer penetration in wet aggregate containing various No. 30/SiO₂ ratios as a function of ponding time.

by an almost straight line. It was also observed that settling of the aggregate phase upon monomer addition decreased with an increase in the amount of finely powdered silica flour which was used as a moisture-absorbing additive.

The curves also indicate that the penetration depth of monomer as a function of time tends to decrease with an increase in the amount of silica flour. A penetration depth >20 cm in ~30 sec was obtained with an aggregate system having a No.30/SiO₂ ratio of 80/20. This impregnation time represents the shortest penetration period in this test series. Thus, it is assumed that this aggregate system has a relatively large pore size distribution. The impregnation time when a No.30/SiO₂ ratio of 50/50 was used is approximately twice that for the 80/20 ratio. Although it is not shown in Figure 32, a No.30/SiO₂ ratio of 40/60, a very compact aggregate system, could not be penetrated in <4 min.

To determine the compressive strength at a cure age of 1 hr, FA-PC specimens containing wet aggregate with various No.30/SiO₂ ratios were prepared in the following manner. The appropriate amount of the wet aggregate containing moisture-absorbing additives and the ZnCl₂ promoter was placed to a height of ~15 cm in a 7.4-cm-diam x 20-cm-long cylindrical paper mold, and then FA monomer containing 1.5 wt% TCT catalyst by weight of monomer and 60 wt% pyridine retarder by weight of catalyst was added by ponding under atmospheric pressure for ~1 min 30 sec. Subsequently, a small quantity of the wet aggregate system consisting of the same ingredients was added to fill up the ~3- to 4-cm deep void space at the top produced by the shrinkage of the initial aggregate phase. Monomer was then added until this aggregate was saturated with monomer. The material was then compacted by the use of table vibration for ~10 sec. The total impregnation time was generally in the order of 2 min 30 sec.

The effect of the No.30/SiO₂ ratio on the strength of FA-PC specimens compacted using table vibration is illustrated in Figure 33. As is evident from the figure, the strength of specimens at ~24°C increases with an increase in the amount of SiO₂ flour. The maximum strength of ~1760 psi (~12.13 MPa) was obtained when a 50/50 ratio was used. Thus, it appears that the addition of SiO₂ flour to wet aggregate has a great effect on the early strength of FA-PC specimens prepared by use of the pre-packed method.

It was also observed that FA-PC specimens compacted on a vibrating table after being saturated to a depth of ~20 cm by use of the ponding technique did not give the desired compressive strength. However, this can be corrected by use of internal vibration.

In a final series of experiments, compacted wet aggregate having compositions listed in Table 55 was used. The PC specimens were prepared in the following manner. The appropriate amounts of wet aggregate, moisture-absorbing additives, and ZnCl₂ promoter were placed to a height of ~22 cm in a 10-cm x 10-cm x 23-cm metal can. FA monomer containing 1.5%

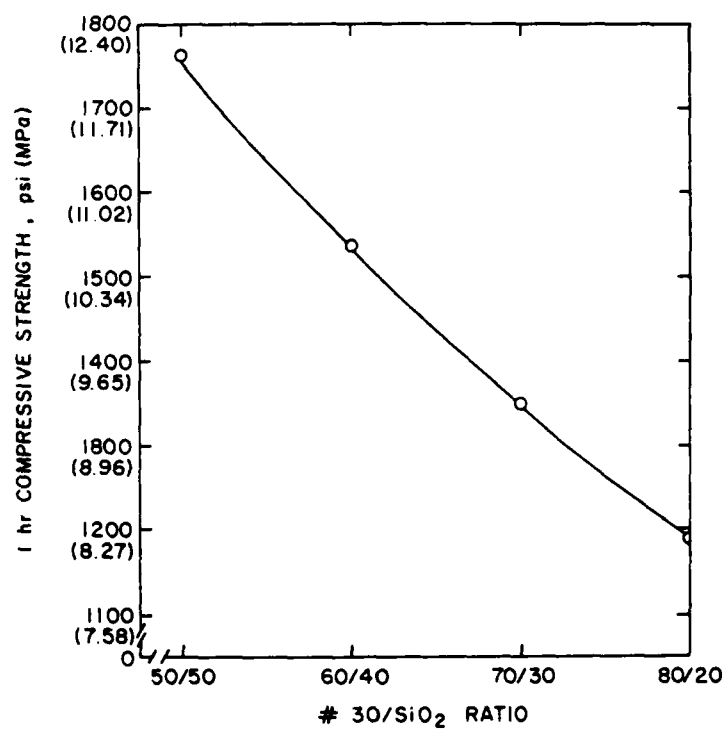


Figure 33. The effect of No.30/SiO₂ ratio on the early compressive strength of FA-PC

Table 55

Compositions of Compacted Wet Aggregate

Specimen No.	C.A., wt%	FA, wt%	ZnCl ₂ promoter, wt%	Water, by weight of aggregate, wt%	Moisture-absorbing additive		
					Dry No.30 silica sand, wt%	Dry silica flour (SiO ₂), wt%	No.30/SiO ₂
P-78	52.9	22.7	5.4	2.8	9.5	9.5	50/50
P-79	52.9	22.7	5.4	2.8	7.6	11.4	40/60
P-80	52.9	22.7	5.4	2.8	5.7	13.3	30/70
P-81	52.9	22.7	5.4	2.8	3.8	15.2	20/80

TCT catalyst by weight of monomer and 60% pyridine retarder by weight of catalyst was then ponded on the surface for 1.5 min (see Figure 34). Subsequently, a small quantity of the reactive aggregate system was added to fill the 2- to 3-cm deep void produced by the compaction of the initial aggregate phase. Monomer was then added until this additional aggregate was saturated. The monomer-saturated wet aggregate was finally compacted by the use of an internal vibrator for ~20 sec as shown in Figure 35. The total saturation time was ~2 min 40 sec.

The effect of the No.30/SiO₂ ratio on the improvement in strength of FA-PC specimens prepared by the pre-packed method and the use of internal vibration is illustrated in Figure 36. The curve shows the relation between the 1 hr strength and the No.30/SiO₂ ratio and is characterized by a peak at a No.30/SiO₂ ratio in the range of 40/60. A strength of ~2310 psi (~15.92 MPa) was obtained when a No.30/SiO₂ ratio of 40/60 was used. The curve suggests that the addition of a mix containing a high ratio of silica flour (SiO₂) to wet aggregate results in a decrease in early strength. This may be due to poor penetration of monomer into the very compact aggregate system. Thus it appears that the use of a moisture-absorbing additive having a No.30/SiO₂ ratio of 40/60 has a significant effect on the strength of specimens prepared by this method.



Figure 34. Monomer addition to prepared aggregate mix

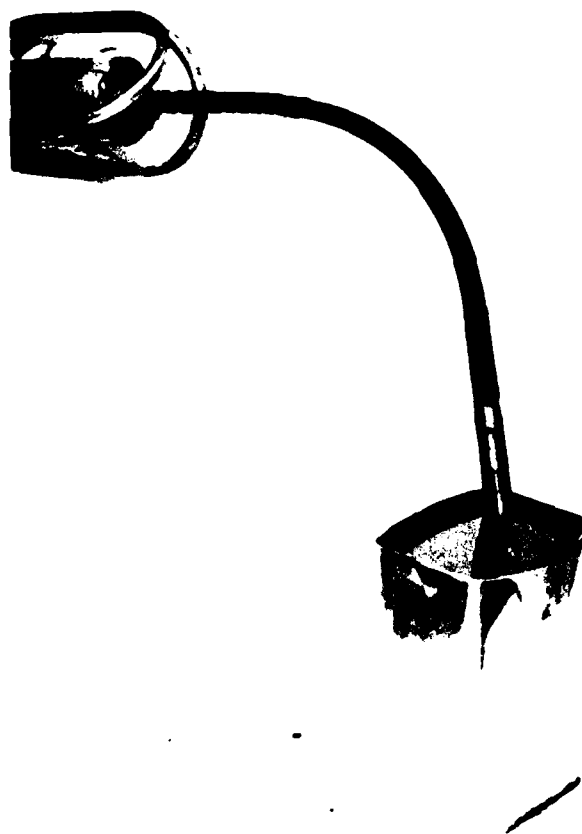


Figure 35. Internal vibration of FA-aggregate mix

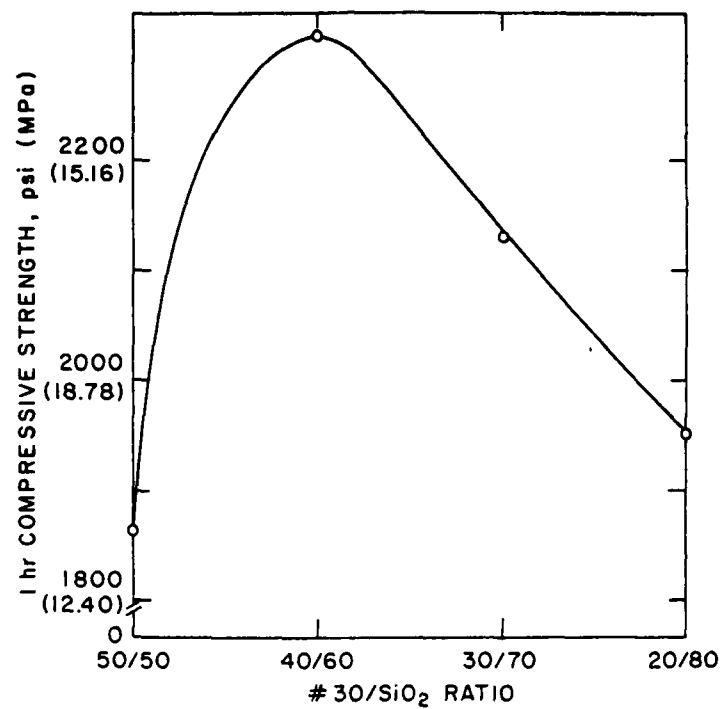


Figure 36. The effect of No.30/SiO₂ ratio and internal vibration on the early compressive strength of FA-PC

V. CONCLUSIONS AND RECOMMENDATIONS

FA-PC formulations that yield most of the properties needed for rapid runway repair purposes were developed. These properties cannot be produced over the temperature range -20° to 30°C with a single PC formulation, and, therefore, it is necessary to vary the concentrations of TCT catalyst, ZnCl_2 promoter, and pyridine retarder in the PC. Composites made from water-saturated aggregate exhibited a working time >6 min and a 1-hr strength >3000 psi (>20.67 MPa). The maximum flexure strength was <600 psi (<14.13 MPa). If necessary, the latter can be increased by the utilization of steel fiber reinforcement. Results from preliminary tests indicated that $\sim 7\%$ by weight of total aggregate concentration of hooked steel fibers [0.4 mm diam x 30 mm long (0.016 in. x 1.18 in.)] in FA-PC resulted in an ultimate flexure strength >900 psi (76.2 MPa). A detailed study to optimize the FA-PC formulation for use with fiber reinforcement is needed.

FA-PC does not bond to portland cement concrete as well as vinyl-type PCs. Bond strengths to smoothly finished concrete surfaces of ~ 160 psi (1.1 MPa) were measured, considerably less than the goal of >500 psi (3.45 MPa). Structural analysis studies are needed to verify the amount of bonding that is needed, and if ~ 200 psi (1.38 MPa), the use of primer coats and coupling agents should be investigated.

Preliminary work to identify methods for practical field utilization of the FA-PC formulations was performed. One method is to prepack wet aggregate containing ZnCl_2 promoter and steel fiber into the hole to be repaired and then to saturate the aggregate with FA containing TCT catalyst. A >20 -cm (7.9-in.) penetration depth was obtained by ponding for ~ 1 min under atmospheric pressure. The 1-hr compressive strength was >2000 psi (13.79 MPa).

For use at temperatures $<20^{\circ}\text{C}$, Ca-UP complexed PC does not appear to have as much potential as FA-PC because of the low curing rates which result in inadequate strengths at an age of 1 hr. However, when this system was polymerized at temperatures $>20^{\circ}\text{C}$, it produced excellent properties. The system also has the advantage of being capable of polymerization under water.

The costs of both PC systems appear reasonable for runway repair applications. For temperatures in the range 1° to 30°C , the costs of steel fiber-reinforced FA and Ca-UP complexed PC systems are $\$642$ and $\$651/\text{m}^3$, respectively ($\$491$ and $\$498/\text{yd}^3$). Without steel fiber the costs would be reduced by $\sim 18\%$. For use at temperatures $<1^{\circ}\text{C}$, the cost of the FA formulations would be increased by $\sim 23\%$.

From the results obtained in the current program, steel fiber reinforced FA and Ca-UP complexed PC formulations appear suitable for use as rapid runway repair materials. Additional work to continue their development appears warranted. Topics requiring additional work are summarized below.

1. Effects of aggregate size and composition on the resulting PC properties.
2. Compatibility of the PC with asphalt.
3. Methods for the storage and mixing of the components and safe simple rapid placement of the PC formulations.
4. Structural analysis to define minimum structural slab thickness, required reinforcement, and necessary compaction of the backfill as a function of wheel loading and crater size.
5. Field testing to determine if laboratory properties can be reproduced in the field, to identify field placement problems, and to determine placement costs.

ACKNOWLEDGMENTS

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APPENDIX A

Required Materials and Sources of Supply

Furfuryl alcohol monomer (FA): Minimum purity 98.0%.

Supplier: Quaker Oats Company

Polyester-styrene: A mixed monomer-polymer system consisting of ~50 wt% GR511 (a flexible polyester) and ~50 wt% styrene monomer.

Supplier: Marco Division of W.R. Grace Company, Blend LB 183-13.

Zinc chloride ($ZnCl_2$): Granular, minimum purity 98%.

Suppliers: Mineral Research Development Corporation, Ashland Chemical Corporation.

α,α,α -Trichlorotoluene (TCT):

Supplier: Eastman Kodak Company.

Pyridine:

Suppliers: Eastman Kodak Company, Mallinckrodt, Inc.

N,N, Dimethyl aniline (DMA):

Suppliers: American Cyanamid Company, Berton Plastic, Inc., Polysciences Inc.

Methyl ethyl ketone peroxide (MEKP): Active oxygen content, 60%.

Suppliers: Berton Plastic Inc., Lucidol Division of Penwalt Corporation, Reichold Chemical.

Cobalt naphthanate (CoN):

Suppliers: Berton Plastic Inc., Polyscience Inc., Sartomer Company.

APPENDIX B

Safety Information

The chemicals required for producing polymer concrete (PC) are not normally used in field applications. It is, therefore, essential that users have a good understanding of their properties, their hazards, and the safety precautions required. Practice has shown that safety can be achieved in large-scale projects if sound practices are followed. The manufacturers' instructions and safety procedures should be carefully followed whenever the materials are used. The safety aspects of these chemicals will be discussed individually.

FA Monomer:

FA is a pale-yellow, low-viscosity liquid soluble in water and many organic solvents. It is very sensitive to acids and polymerizes readily. Its flammability is comparable to that of kerosene, and fire may be controlled by use of water, foam, carbon dioxide, or dry chemicals. No ICC precautionary label is required for the drum or bulk shipment of FA. In the presence of concentrated mineral acids or strong organic acids, furfuryl alcohol reacts with explosive violence; therefore, precaution should be taken to avoid contact of such material with the alcohol. Good ventilation should be provided and contact with the skin avoided. If spilled on the body, it should be washed off promptly with water. Rubber protective gloves and chemical goggles should be used.

Polyester-styrene Monomer:

Polyester-styrene is a volatile, combustible, and toxic liquid. However, practice has shown that prolonged stability and safety can be achieved by following recommended practices in storage and handling. Manufacturers provide safety and handling guidelines which should be carefully observed.

The principal factors that influence the stability of monomers and determine the methods to be used for safe handling are:

1. level and effectiveness of inhibitors,
2. storage temperature,
3. flammability and combustibility,
4. toxicity,
5. effect of construction materials with which they are used.

Secondary considerations include odor, sensitivity to light, moisture, and oxygen.

To prevent premature polymerization, the monomers contain an inhibitor when they are shipped by manufacturers. In general, inhibitors are free-radical scavengers. More specifically, they serve two functions. First, they can react with and deactivate the free radicals in growing polymer chains. Second, they can act as antioxidants and prevent polymerization by reacting with oxidation products that may be formed in the storage vessel through contamination or through the formation of peroxides from oxygen in the air. Polyester-styrene may be inhibited with t-butyl pyrocatechol at levels of 10 to 20 ppm. The inhibitor level should be maintained above a minimum concentration at all times. If the concentration is allowed to drop below this danger level, the amount remaining may not be adequate to prevent a premature or runaway polymerization. For example, the danger level for styrene is ~4 to 5 ppm. Excessive inhibitor concentrations, however, can pose problems with polymerization rates when polymerization is desired.

The time required for initial inhibitor concentrations to fall to a critical level varies greatly with storage and handling conditions. Factors affecting the depletion of inhibitor are heat, water, and air, with heat being the most important. In hot climates [normal temperatures], the bulk monomer should be cooled.

Drums of monomer should not be allowed to stand in the sun for only a short time. As soon as possible after being received, monomer should be placed in a cool, shaded area. In hot weather, drums can be cooled by water spray. It is also advisable to keep inventories to a minimum during hot weather and to use them in the order received so that monomer is not stored any longer than necessary.

Personnel responsible for handling and mixing the monomers should wear respirators equipped with chemical filters, safety eye glasses, and impervious gloves and aprons. All personnel should be thoroughly trained in accordance with the material manufacturers' recommendations.

1,1,1-Trichlorotoluene (TCT) Initiator:

TCT is a colorless to yellowish liquid with a very strong, acidic, penetrating odor. It is non flammable and insoluble in water. Contact with skin or mucous membranes can cause local irritation. Proper protective clothing such as rubber gloves and goggles should be worn.

Methyl Ethyl Ketone Peroxide (MEKP) Initiator:

MEKP is generally used as a 60% solution in a plasticizer. It is relatively safe but is still considered hazardous by the ICC and must be packaged and shipped according to ICC regulations. The flash point ranges from 52° to 82°C, and as such it is not considered flammable by the ICC. However, once ignited, MEKP solutions will burn vigorously, even more so than gasoline.

Larger amounts of MEKP solutions are reasonably stable and may be kept for long periods of time, although they should never be stored in sealed glass bottles. The material can be decomposed by heat, sunlight, and many chemicals. It is not completely stable in the presence of many metals, including iron, and for this reason the solution should never be shipped or stored in a metal container.

In handling MEKP: (1) store in a cool area away from sunlight in original container; (2) keep away from heat, open flame, or sparks; (3) prevent contamination with oxidizable materials; (4) do not add to hot materials; and (5) avoid contact with body or clothing.

Zinc Chloride (ZnCl_2) Promoter:

ZnCl_2 is a free-flowing white powder containing essentially no insoluble matter and is completely soluble in water up to 81 g/100 ml at room temperature. It is commonly used as a promoter of FA in industry. It has no flash point and is rated as non flammable by O.S.H.A. The material is deliquescent and corrosive, causing burns to the skin, eyes, etc. in both solid and liquid forms; therefore adequate safety precautions such as rubber or plastic gloves and chemical safety goggles should be taken to avoid contact.

Cobalt Naphthanate (CoN) and N,N, Dimethyl Aniline (DMA) Promoter:

Cobalt naphthanate is generally used in conjunction with MEKP for rapid curing of polyester-styrene. DMA is used individually or together with MEKP to polymerize monomers such as polyester-styrene.

Promoters are used in quantities small compared with the amount of monomer. However, their handling should be similar to that of monomers. They should be stored in a cool place out of direct sunlight and not in the same area as the peroxide initiators. They should be treated as combustible and toxic materials.

Particular care must be taken to avoid mixing promoters directly with peroxide initiators because the mixture can react explosively. Promoters should first be added to the monomer and dispersed thoroughly. Then and only then should the peroxide be added.

Pyridine Retarder:

Pyridine is a slightly yellowish or colorless liquid with a sharp penetrating odor. It is soluble in water and most common organic solvents. It has a moderate toxicity level and is irritating to the skin. Flammability is high and it will form explosive mixtures with air. Adequate ventilation and skin protection should be provided at all times.

APPENDIX C

Program Patent Applications and Publications

Patent Applications Submitted

- . Sugama, T., Kukacka, L.E., and Horn, W., Quick Setting Water-Compatible Furfuryl Alcohol Polymer Concrete. July, 1980.
- . Sugama, T., Kukacka, L.E., and Horn, W., Electropositive Bivalent Metallic Ion-Unsaturated Polyester Complexed Polymer Concrete. October, 1980.

Papers Presented

- . Sugama, T., and Kukacka, L.E., The Cross-Linking and Catalytic Effects of Ca^{2+} Ions Released from Cement on the Properties of Unsaturated Polyester and Resorcinol Phenol-Formaldehyde Polymer Concrete. Materials Research Society Annual Meeting, Boston, November 17-18, 1980.

Publications in Press

- . Sugama, T., Kukacka, L.E., and Horn, W., The Catalytic Effect of a Portland Cement Filler on the Cure of a Water-Compatible Resorcinol Phenol-Formaldehyde Polymer Concrete. Journal of Applied Polymer Science, Vol. 26, No. 5 (1981).
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