

Catalytic Effect of a Portland Cement Filler on the Cure of Water-Compatible Resorcinol Phenol-Formaldehyde Polymer Concrete*

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Synopsis

Aggregate with a water content <1 wt % is normally needed for the production of polymer concrete (PC). This increases the cost and complexity of the process. In this study, PC with a compressive strength of >2000 psi (>13.78 MPa) at an age of 1 hr at 24°C was produced by mixing resorcinol phenol-formaldehyde (RPF) resin with portland cement and aggregate containing 1–10% water. The addition of ~ 14.7 – 17.5 % type III portland cement to the PC formulation produced an acceleration in the rate of the condensation-type polymerization reaction and improved the properties of the composite. The cause of the accelerative effect was found to be the electropositive bivalent metallic ions of calcium and magnesium released from the cement grains in an aqueous medium. Conversely, the trivalent metallic ions from cement such as Al^{3+} and Fe^{3+} have no effect on the rate of polymerization of RPF resin.

INTRODUCTION

At present, vinyl-type methyl methacrylate (MMA) and ester-type unsaturated polyester (UP) polymer concretes combined with aggregate containing <1 wt % moisture are being used as rapid repair materials for deteriorated concrete bridge decks and highways.^{1–3} When aggregate having ~ 8 % water content is used in these polymer concrete systems, however, a compressive strength of >2000 psi (13.78 MPa) cannot be obtained within 24 hr after mixing. This is due to phase separation and a hydrolytic reaction at the interface between the organic polymer and the moisture existing on the surface of the aggregate. Therefore, MMA and UP polymers should be avoided for use as a binder of wet aggregate.

On the other hand, it is well known from several U.S. patents^{4–7} that synthetic rubber latexes [styrene-butadiene rubber (SBR), acrylonitrile-butadiene rubber, methyl methacrylate-butadiene rubber (MBR)] and resin emulsions [polyacrylic ester (PAE), poly(vinyl acetate) (PVAC), vinylidene chloride-vinyl chloride copolymer (PVDC), poly(vinyl propionate) (PVP), epoxy resin] consisting of polymers dispersed in water have been successfully applied as water-soluble organic polymer binders in cement mortars and concretes. The most important characteristics of these polymer-modified cement mortars (concretes) is their reduced water permeability and improved physical properties. This is attributed to the formation of a polymer skin connecting the hydration products of cement and aggregate.^{8–10} Curing of the latex and emulsion polymer-modified mortar

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at an ambient temperature of $\sim 25^{\circ}\text{C}$, however, proceeds very slowly. Thus, it is impossible to obtain a compressive strength above 2000 psi (13.78 MPa) with a curing age under approximately 24 hr. Therefore, it is doubtful that latex or emulsion polymers could fully satisfy the quick setting conditions required for use in rapid repair systems for bridge decks and highways where restoration of traffic within 2 hr is often required.

The objective of the current study was to develop an organic-type polymer binder, a reactive filler, and an optimum composition of PC which will meet these criteria. Design specifications include compatibility with wet aggregate and a compressive strength >2000 psi (13.78 MPa) at an age of 1 hr.

A resorcinol phenol-formaldehyde (RPF) resin having OH groups possessing a strong affinity for moisture was especially chosen for this study as a polymer which would adequately satisfy the conditions mentioned above. This type of polymer has a three-dimensional structure consisting of methylene and ether bridge formations produced by the condensation polymerization occurring through the use of acid or alkaline-type catalysts.^{11,12} Water molecules as by-products are yielded simultaneously during the process of polymerization. The addition of water can be utilized as a way of reducing viscosity thereby making mixing and placement of the composition easier.

In order to obtain a quick set of RPF resin, particular attention must be paid to the formaldehyde-to-phenol ratio (F/P)^{11,13-15} of the liquid resin and the choice of an active catalyst¹⁶⁻¹⁸ having electropositive bivalent metal ions produced in an aqueous medium. The curing of resin having a F/P ratio in the range of 1.25-1.35 is initiated by the addition of ~ 3 to $4N$ sodium hydroxide, used as an alkaline catalyst, and takes place in ~ 24 hr at a temperature of 60°C .^{11,12} Resin of this type is generally called a water-soluble resin by the manufacturing industry.¹¹ In contrast, resin containing a high F/P ratio of 2.5 is called a casting resin and requires a curing time of ~ 3 to ten days at temperatures of 70 - 80°C when used with an alkaline catalyst.¹¹ King et al.¹⁴ showed from the results of nuclear magnetic resonance (NMR) and gel permeation chromatograph (GPC) analysis that a resin with a low F/P ratio of 1.3 and polymerized using NaOH as a catalyst is in a more advanced state of condensation than one with a high F/P ratio of 1.7. Therefore, all RP resins, used in this study were adjusted to a F/P ratio of 1.3.

The catalytic effects of the metallic cation on the condensation reaction between phenol and formaldehyde have been described by Fraser et al.¹⁶ and Pizzi.¹⁸ They found that the presence of electropositive bivalent metallic ions such as Mn^{2+} , Zn^{2+} , Cd^{2+} , Mg^{2+} , Co^{2+} , Ca^{2+} , and Ba^{2+} has a catalytic effect on the production 2- and 2,6-substituted phenolic nuclei in the resulting novolak resins. Pizzi¹⁸ proved that the bivalent metallic salts apparently also accelerate both the reaction of formaldehyde with the phenolic nuclei and condensation of methylolphenols with other phenolic nuclei in the preparation of resins. He also mentioned that the trivalent metallic ions such as Al^{3+} , Cr^{3+} , Fe^{3+} , Mn^{3+} , and Co^{3+} do not show this catalytic effect at all but tend to slow down the reaction.

On the basis of the results of the literature survey regarding the catalysis of resin as described above, a conventional type III portland cement containing 63.77% CaO and 3.1 MgO as chemical constituents may be used as a catalyst of RPF resin. The fine type III cement having a specific surface of 4920 cm^2/g is also considered to function effectively as a filler material of RPF-PC.

In this report, the catalytic effect of type III portland cement was evaluated on the basis of the mechanical properties of RPF-PC and the kinetics of condensation polymerization. The mechanical evaluation performed consisted of measuring compressive strength and the modulus of elasticity. The kinetic analysis of the thermal polymerization of RPF resin was performed from the exothermal peaks on the thermograms obtained by using differential scanning calorimetry (DSC). Furthermore, in order to find the most effective catalyst from among the various chemical constituents of type III cement such as CaO, SiO₂, Al₂O₃, MgO, and Fe₂O₃, a thermal behavior study of RPF resin combined with 5 wt % of these constituents was performed by using DSC.

EXPERIMENTAL

Materials

The resorcinol phenol-formaldehyde (RPF) used in this study was a commercial-type RP-20 supplied by the Gulf Oil Chemical Co. The chemical composition of RP-20 consists of the following molar ratios: resorcinol, 2-3; phenol, 1-1.5; and formaldehyde, 1-2. The polymerization was initiated at ~24°C by the addition of 20 wt % promoter (commercial name S-10; obtained from Gulf Oil Chemical Co.) and type III portland cement as the catalyst. Cement concentrations above 6.0 wt % were used. The major chemical constituent of S-10 is paraformaldehyde. The cement catalyst consisted of the following chemical compounds and was supplied by Lone Star Industries, Inc.: CaO (63.77%); SiO₂ (19.82%); Al₂O₃ (6.01%); MgO (3.10%); Fe₂O₃ (2.37%); SO₃ (3.27%); and loss on ignition (0.86%).

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

PCs were prepared by thoroughly mixing the wet aggregate and anhydrous type III cement by hand for ~2 min. This was followed by the addition of the mixture of RPF resin with S-10 promoter and subsequent mixing for ~1 min.

Test Methods

The compressive strength was determined for triplicate RPF-PC specimens with a curing age of 1, 3, and 24 hr at a temperature of ~24°C. Specimens 2.2 cm in diameter and 4.4 cm in length were used for compressive strength tests.

Data for the modulus of elasticity were obtained using strain gauges attached with epoxy to the surface of cylindrical specimens, 3.4 cm diam × 6.8 cm long. 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.

The kinetics of the condensation polymerization of PC were determined by using a du Pont 910 differential scanning calorimeter (DSC) with a heating rate of 10°C/min in nitrogen gas. The DSC samples ranged in weight from 10 to 20 mg and were crushed to a size to pass through a 0.104-mm sieve. The area measurements of the exothermic peaks which represent the condensation reaction of the polymer were made with a planimeter.

RESULTS AND DISCUSSION

Compressive Strength and Modulus of Elasticity

In order to determine the quantity of alkaline cement catalyst required to produce a composite with a compressive strength >13.78 MPa within 1 hr after mixing the RPF resin with wet aggregate, RPF-PC specimens of different compositions but with a constant water content of 8% in the aggregate were prepared. The mix proportions are given in Table I. A 4:1 ratio by weight of RPF/S-10 was used for all samples.

Compressive strength results for RPF-PC specimens containing cement contents ranging from 6.6 to 17.5% are given in Figure 1. The data indicate that the initial strength of the specimens increases with an increase in cement content. The compressive strength of the RPF-PC containing 17.5% cement had a strength of ~ 2200 psi (~ 15.16 MPa) at an age of 1 hr. This value is $\sim 33\%$ higher than that of PC specimens containing 6.6% cement. It appears therefore that it is possible to obtain compressive strengths of >2000 psi ($>>13.78$ MPa) within

TABLE I
Composition of RP-PC Containing Different Amounts of Type III Cement

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

^a RP, 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.

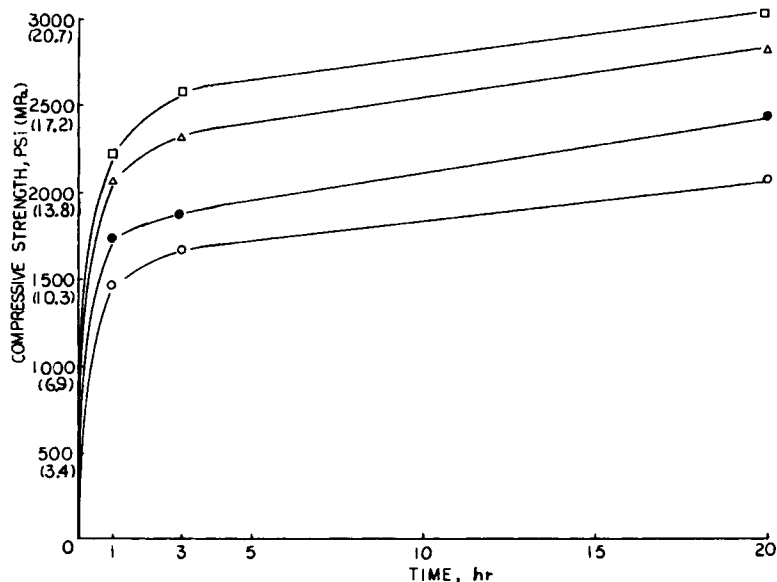


Fig. 1. Effect of cement as active catalyst on the initial compressive strength of RP-PC. Cement content: (O) 6.6%; (●) 10.1%; (Δ) 14.7%; (□) 17.5%. Water content: $\sim 8.0\%$.

1 hr at $\sim 24^{\circ}\text{C}$ by the inclusion of above $\sim 15\%$ cement in the RPF-PC formulation.

The data in Figure 2 also suggest that the compressive strength of cement-filled RPF-PC increases gradually with a lengthening in curing age. Thus, the PC containing the lowest cement content of 6.6% also exhibited a strength above 13.78 MPa at an age of ~ 20 hr.

Compressive stress-strain curves of RPF-PC containing 10.1 and 17.5% cement and cured for three days are illustrated in Figure 2. The elastic modulus of 17.5% cement-filled RPF-PC was 0.83×10^3 MPa, 43% greater than the 0.58×10^3 MPa obtained for samples containing 10.1% cement.

As shown in Figure 2, both formulations resulted in ductile composites with maximum strains $> 37 \times 10^{-3}$. Generally the compressive maximum strains of vinyl-type PCs such as MMA,²¹ styrene,²² and unsaturated polyester²³ are in the range $(\sim 5-14) \times 10^{-3}$, which indicates that these materials are of a brittle nature. The strain of RPF-PC, therefore, is considerably higher than that of vinyl-type PC, which seems to indicate that the RPF-PC can withstand greater impact. This is an important property for concrete repair materials.

Assuming that the superior ductility noted above may be more closely related to the bending strength of PC than to its compressive strength, bending strength tests of beams 1.25 cm² wide \times 7.5 cm long, supported on a 5-cm span, were performed using a center-point loading. Generally, the bending strengths of optimized PMMA and PST-PCs are $\sim 23\%$ of their compressive strengths.^{21,22} The bending strength of RPF-PC at a curing age of three days was 7.94 MPa, $\sim 32\%$ of its compressive strength.

From the above results, it appears that the anhydrous cement alkaline catalyst has not only an accelerative effect on the polymerization reaction but also a significant effect on the mechanical properties of the resulting PC.

The effect of water content on the mechanical properties of RPF-PC was also studied. In these studies, the ratio of cement to aggregate + water + cement $[C/(A + W + C)]$ was held constant at ~ 0.26 , while the water content $[W/(A +$

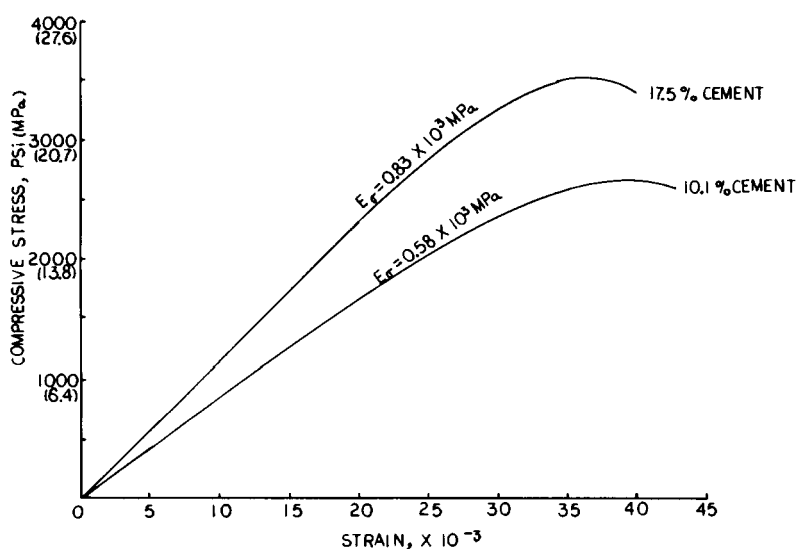


Fig. 2. Stress-strain curves for RPF-PC containing cement as reactive filler.

W)] was varied from 0 to 0.193. The compositions of each of the specimens are given in Table II.

The compressive strengths for the samples at an age of 1 hr are given in Figure 3. For water concentrations up to $\sim 2\%$, little effect on strength was noted. Beyond 2% water, the strengths decreased as the water content was increased. It should be noted, however, that other factors may have contributed to the strength reduction. As shown in Table II, the polymer content was decreased as the concentration of water was increased. This was necessary in order to maintain approximately constant fluidity. Therefore, the influence of the water content was examined by comparing relative values obtained from a strength/polymer content (σ_c/P_c) ratio for the different RPF-PC compositions. The results are presented in Table II. The data indicate that the σ_c/P_c ratios for RPF-PC containing a water content below $\sim 7\%$ have almost equivalent values

TABLE II
Compositions of RP-PC Containing Different Amounts of Water

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	0.48
R-8	31% P-44.1% A-7.0% W-17.9% C	13.7	25.9	0.39
R-9	21% P-47.2% A-11.3% W-20.5% C	19.3	26.0	0.25

^a P, 80% RP-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 , RP resin content (wt %).

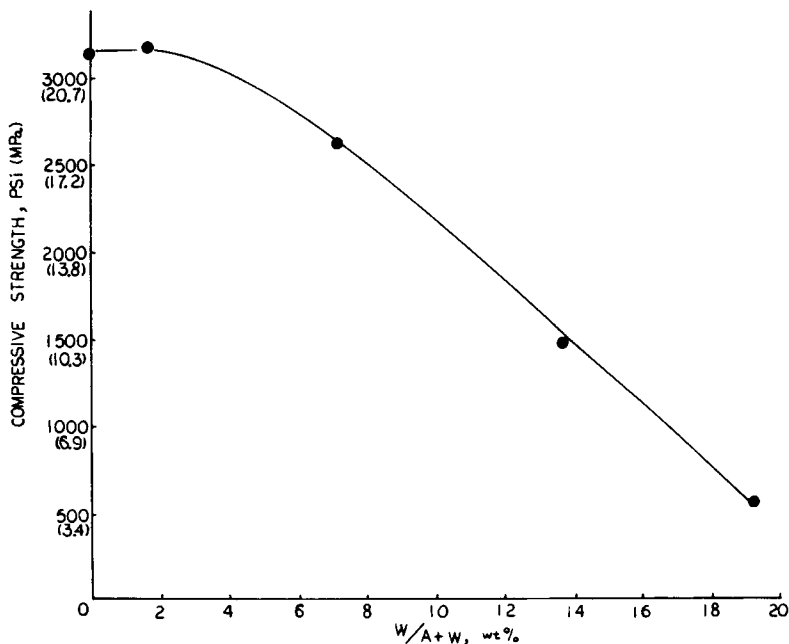


Fig. 3. Compressive strength vs. water content of aggregate for RP-PC at a curing age of 1 hr.

of ~ 0.48 . This means that below $\sim 7\%$ the reduction in strength of RPF-PC is not primarily due to water content.

Polymerization Kinetics

The energetic condensation reactions occurring between the RPF resin and the cement catalyst were estimated on the basis of the results obtained from the activation energies for the thermal polymerization. The kinetic parameters can be determined by using DSC.²⁴

Typical DSC thermograms obtained during the polymerization of RPF and RPF-cement mixtures are illustrated in Figure 4. The area under the exothermic peaks represents the total quality of heat liberated upon conversion of monomer to polymer by a thermal condensation polymerization.

The thermogram of the thermally induced polymerization of RPF resin shows an exotherm corresponding to an onset temperature of polymerization of $\sim 50^\circ\text{C}$ (determined from the baseline), with a peak at $\sim 92^\circ\text{C}$. The thermogram of RPF resin combined with 10% cement catalyst is characterized by an onset of polymerization at $\sim 30^\circ\text{C}$ and a peak at $\sim 68^\circ\text{C}$. These temperatures are $\sim 24^\circ\text{C}$ lower than those for the RPF resin. The peak and onset of polymerization temperatures for the RPF-cement systems decrease with an increase in cement content. The curve also indicates that the exothermal kinetic energy (mcal/sec) produced during the thermal condensation polymerization of RPF resin with a high cement content is greater than that for a lower cement content. This seems to demonstrate that the condensation rate of RPF resin in the presence of cement is dependent on the amount of cement catalyst added.

On the basis of the areas of these exothermic peaks, determined from the baseline, the cure rate constant k can be calculated from eq. (1), which is described by Borchardt and Daniels²⁵:

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

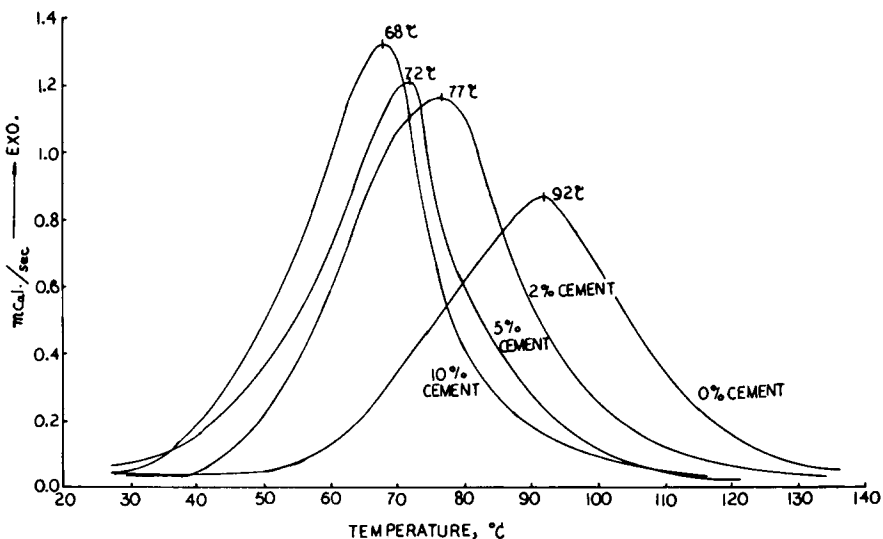


Fig. 4. DSC thermograms for RP resin-type III portland cement systems.

where A (mcal) is the total heat of polymerization obtained from the total area under the DSC curve, a (mcal) is the area of departure of the DSC curve, V is the volume, n_0 is the initial number of moles of polymerization, 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 form²⁶:

$$k = \frac{dH}{dt/(A - a)} \quad (2)$$

The rate constants for the polymerization of RPF resin with different amounts of cement catalyst are given in Table III.

From a comparison of the cure rate constants at temperatures of 70 and 80°C, the values indicate that the addition of cement catalyst to RPF resin results in a higher cure rate constant than for RPF resin without cement. This is 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 active cement catalyst on the kinetics of thermal polymerization of RPF resins was evaluated on the basis of activation energies (E_a). The values of E_a were calculated from the slope of a straight line of the Arrhenius plot of the logarithm of the rate k of polymerization against the absolute temperature, $1/T$.²⁷ The first-order activation energies and a typical Arrhenius plot containing all of the available data are given in Figure 5.

The activation energy for the thermal polymerization of RPF resin without cement catalyst was calculated to be 17.1 kcal/mole. The highest value of activation energy (21.7 kcal/mole) was obtained when a mixture of RPF resin with 10% cement was polymerized. The activation energy of RPF resin in the presence of 2% cement was calculated to be 19.1 kcal/mole, ~12% higher than that for bulk RPF resin. It is assumed from the lowest value of E_a that the condensation polymerization of bulk RPF resin is very slow. This means that the rate of thermal generation of phenolic nuclei in RPF resin is extremely small. Therefore, the addition of the cement to the RPF appears to increase the concentration of active phenolic nuclei which then causes the rate of polymerization to accelerate.

TABLE III
Cure Rate Constants for the Thermal Polymerization of RP Resin Combined with Cement Catalyst at a Heating Rate of 10°C/min

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

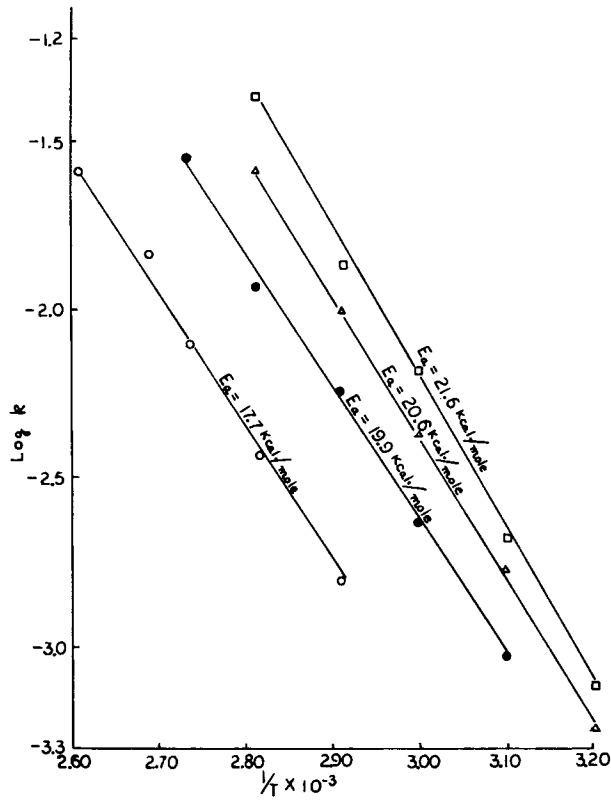


Fig. 5. Arrhenius log plots for thermal polymerization of RP resin combined with different amounts of type III cement. Cement content: (○) 0%; (●) 2%; (△) 5%; (□) 10%.

In order to determine which of the chemical constituents of cement affect the polymerization of RPF resin, the catalytic effects of CaO, MgO, Al₂O₃, SiO₂, Fe₂O₃, and Ca(OH)₂ were evaluated by the study of thermograms. The relative degree of cure was calculated according to the following equation:

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

where H_T (mcal/mg) is the maximum isothermal heat of cure and H (mcal/mg) is the cumulative heat generated in the isothermal heat of cure.

The reaction rate curves can be integrated so as to obtain a curve depicting the time dependence of the relative degree of cure, Q .²⁸ A comparison between the integral cure curves for the various chemical constituents in an amount of 5 wt % added to RPF resin is presented in Figure 6.

As is evident from Figure 6, the pronounced effects on the curing process of RPF resin brought about by the addition of CaO, MgO, and Ca(OH)₂, which produce electropositive bivalent metal ions in an aqueous medium, are far greater than those of Al₂O₃ and Fe₂O₃, which have trivalent metallic ions. The results correspond to those obtained by Fraser et al.¹⁶ and Pizzi.¹⁸ 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 from a comparison between the isothermal curves that CaO, the major chemical con-

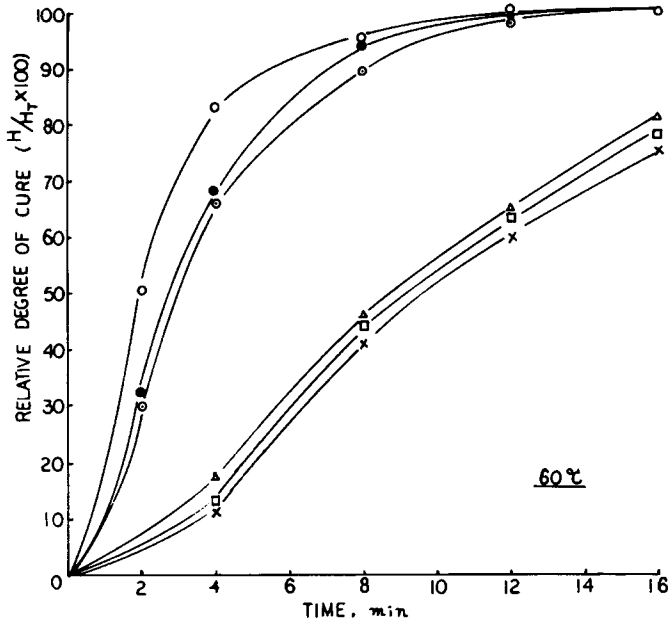


Fig. 6. Integral cure curves at 60°C for RP resin combined with 5 wt % of various chemical constituents of cement: (○) CaO; (●) MgO; (○) Ca(OH)₂; (Δ) Al₂O₃; (□) SiO₂; (X) Fe₂O₃.

stituent of portland cement, has the greatest effect on the curing process of RPF resin.

Additional clarification of the condensation reaction mechanisms of RPF resin in the presence of Ca²⁺ is currently being performed by using infrared spectroscopy.

CONCLUSIONS

The following generalizations can be drawn from the results described above:

(1) Resorcinol phenol-formaldehyde (RPF) resin combined with portland cement can be used as a setting binder in PC for use with aggregate having a water content up to ~8 wt %.

(2) A compressive strength of >2000 psi (13.78 MPa) for PC containing aggregate with a water content of 8 wt % is obtained within 1 hr at 24°C by the addition of above ~14.7% type III portland cement.

(3) A maximum strain $>37 \times 10^{-3}$ was obtained from the compressive stress-strain curves of RPF-cement composites. The PC is characterized as producing a material with superior ductility making it suitable for use in rapid repair systems for deteriorated concrete bridge decks and highways.

(4) The anhydrous portland cement has a very significant effect on the accelerative functions of the condensation polymerization of RPF resins and produces an improvement in mechanical properties when used as a reactive filler.

(5) The active catalytic effect of cement is due to the electropositive bivalent metallic ions of calcium and magnesium released from the cement grains in an aqueous medium.

(6) The trivalent metallic ions of cement such as Al^{3+} and Fe^{3+} have no effect on the accelerative function of RPF resin.

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