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POLYMER-CEMENT GEOTHERMAL-WELL-COMPLETION MATERIALS

FINAL REPORT

July 1980

MASTER

PROCESS SCIENCES DIVISION
DEPARTMENT OF ENERGY AND ENVIRONMENT

BROOKHAVEN NATIONAL LABORATORY
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FINAL REPORT

A.N. ZELDIN AND L.E. KUKACKA

Contributors: A.N. Zeldin, L.E. Kukacka, and N. Carciello

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ABSTRACT

As part of a Brookhaven National Laboratory-coordinated program for the development of improved cements specifically designed for geothermal well completion systems, a program to develop high-temperature polymer cements was performed. Several formulations based on organic and semi-inorganic binders were evaluated on the basis of mechanical and thermal stability, and thickening time. Two optimized systems exhibited properties exceeding those required for use in geothermal wells.

Both systems were selected for continued evaluation at the National Bureau of Standards and contingent upon the results, for field testing in geothermal wells.

Table of Contents

FIGURES

FIGURES (Cont'd)

FIGURES (Cont'd)

TABLES

EXECUTIVE SUMMARY

A research and development program to produce high-temperature polymer cement materials which can be used in the completion of geothermal wells has been performed. The work was performed in three parts.

In part one, assessments were made of the current state-of-the-art of the development of hydrothermally stable polymers and the use of polymer cements in oil and geothermal well completions. Screening and further evaluations on a number of monomer compositions and filler systems thought to be suitable for well cementing were performed in part two. These evaluations were performed primarily on the basis of mechanical and thermal stability.

In part three, thickening time measurements were performed on materials selected from part two.

Two polymer cement compositions have met the criteria established for use in geothermal wells[1] and were sent to the National Bureau of Standards for continued evaluation. One was based on organic binders as a mixture of styrene-acrylonitrile-acrylamide with divinyl benzene as a cross-linking agent. The second cement was based on semi-inorganic polymers such as organosiloxane. Laboratory studies have been completed for parts one and two on both these systems and the results have been published.[2-11]

The properties of the two formulations selected for additional evaluation were as follows:

	Organic PC	Inorganic PC
Compressive strength, MPa	170-200	60-80
Bonding strength, kPa	3000-4000	150-200
Permeability, millidarcy	0.002	no water penetration after 48 hr
Pumpability, hr/t°C	3/70	4/204
Density, kg/m^3	2300-2400	2,320-2,400
Materials cost, \$/m^3	600	30,000

Both formulations can be mixed and placed using American Petroleum Institute - standardized techniques.

The current cost of the inorganic PC is exceptionally high due primarily to the experimental nature of the monomers. The purchase of 200 kg quantities of the organosiloxane will result in a cost reduction of ~6%. Manufacture of the monomers on a commercial scale will result in further cost reductions. Although the PC will always be expensive when compared to more conventional cementing materials, these cost reductions may make the use of the PC in critical regions of geothermal wells cost effective.

I. INTRODUCTION

A research program to develop polymer concrete composite materials for use in the completion of geothermal wells has been performed at Brookhaven National Laboratory (BNL) under the sponsorship of the U.S. Department of Energy, Division of Geothermal Energy (DOE/DGE). The program was motivated by a 1976 assessment which indicated that the cements used at that time for well completion deteriorated in the geothermal environments, and that the life expectancy of a geothermal well and therefore, the economics of geothermal processes could be improved significantly if better materials were developed.

When the program was initiated, it was estimated that cementing materials for use in geothermal wells should have the following characteristics:

1. Compressive strength, >6.9 MPa 24 hr after placement
2. Permeability to water, <0.1 millidarcy
3. Bond strength to steel casing, >69 kPa
4. Stability, no significant reduction in strength or increase in permeability after prolonged exposure at 400°C to 25% brine solutions, flashing brine, or dry steam.
5. Placement ability, capable of 3- to 4-hr retardation at expected placement temperatures
6. Compatibility of the cement with drilling mud
7. Noncorrosive to steel well casing

BNL is assisting DOE/DGE in developing and managing a program to develop materials that meet the criteria listed above. The work involves in-house research on polymer concrete cementing materials as well as full management of an integrated program involving contract research and industrial participation. The program consists of the following phases: 1) problem definition, 2) cement research and development, 3) property verification, 4) field testing, and 5) cementing of demonstration wells. The program will culminate with the preparation of a comprehensive high-temperature geothermal well-cementing manual which will include details of down-hole equipment, pumps, cement properties, and field examples.

Phase 1 work has been completed and the results published.[12] In addition to BNL, the following organizations performed work in Phase 2: Battelle's Columbus Laboratories, Colorado School of Mines, Dowell Division of Dow Chemical U.S.A., Pennsylvania State University, Southwest Research Institute, and the University of Rhode Island. Reports for these programs are being published.[13-17] This report summarizes BNL in-house research on polymer cement systems. A status report summarizing all work in Phase 2 of the program is planned.

All the above programs with the exception of the one at the University of Rhode Island have produced one or more cementing materials which meet the property criteria given previously. These cements are currently being subjected to additional evaluation at the National Bureau of Standards; the results will be used to establish priorities for future downhole testing.

II. POLYMER CONCRETE SURVEY EXPERIMENTS

The selection of monomers for use in the production of thermostable and chemically resistant polymer concrete (PC) depends primarily on the anticipated environmental conditions. In this study, two ranges of temperature (up to 250°C and between 250° and 350°C) were selected.

A. Monomer Systems

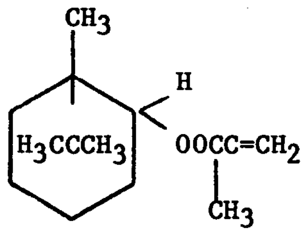
Vinyl-type monomers used in conjunction with cross-linking agents (Figure 1) were evaluated for use at temperatures up to 250°C. All materials evaluated are commercially available and were used as received.

Free radical-type initiators such as benzoyl peroxide (BPO), azobisisobutyronitrile (AIBN), and di-tert-butyl peroxide (DTBP) were used to polymerize the monomers. These initiators are readily available, require simple equipment, and yield rapid polymerization rates.

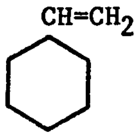
In order to increase the thermal and chemical resistance of the PC, cross-linking agents such as trimethylolpropane trimethacrylate (TMPTMA) or divinyl benzene (DVB) were mixed with the vinyl-type monomers prior to polymerization. The physicochemical properties of all the organic compounds used in the work are summarized in Table 1.

Semi-inorganic-type monomers such as organosiloxane were used to produce PC for use at temperatures >250°C. These monomers have a network consisting of -Si-O-Si- bonds which results in greater thermal stability than the -C-C- network in vinyl-type monomers. The -Si-O-Si- bond has a dissociation energy at 25°C of 190.9 [illegible] 2 kcal/mol compared to a value of 145 ± 5 kcal/mol for the C-C bond. Also, the molecular chains of siloxanes are more rigid than those of organic polymers (bond lengths of -Si-O- and -C-C- are 1.504 and 1.541 Å, respectively).

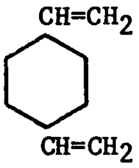
The generic term silicone is generally employed to include all monomeric or polymeric organosilicone compounds containing Si-C bonds. It has also been employed for polymers containing Si-O-Si bonds.



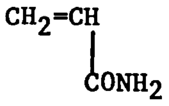
1. Isobornyl methacrylate (IBOMA)



2. Styrene (St)

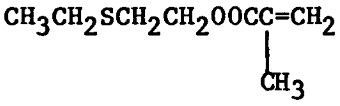


3. Divinylbenzene (DVB)



$CH_2{=}\underset{CONH_2}{\underset{|}{CH}}$

4. Acrylamide (Aa)



$CH_3CH_2SCH_2CH_2OOC\underset{CH_3}{\underset{|}{C}}{=}CH_2$

5. Ethylthioethyl methacrylate (ETEMA)

$CH_2C(CH_3)CONH_2$

6. Methacrylamide (MAa)

$CH_2C(CH_3)COOCH_3$

7. Methylmethacrylate (MMA)

$CH_2{=}CHCN$

8. Acrylonitrile (ACN)

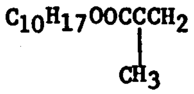
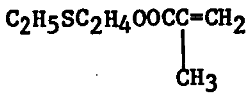
$-CH_3CH_2C(CH_2CH_3CCOOCH_2)_3$

9. Trimethylolpropane trimethacrylate (TMPTMA)

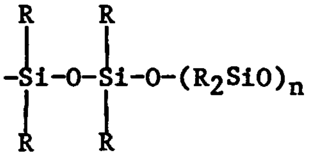
Figure 1. Vinyl-type monomers used for PC composites.

Table 1

Properties of Monomer Systems for High-Temperature PC Applications

Monomer	Structure	Molecular weight	Melting point, °C	Boiling point, °C	Flash point, °C	Condition
styrene (St)	$C_6H_5CHCH_2$	104.14	-31	146	31.1	liquid
acrylonitrile (ACN)	CH_2CHCN	53.06	-82	77.3	1.1	liquid
acrylamide (Aa)	$CH_2CHCONH_2$	71.08	84.5	125	--	solid
methacrylamide (MAa)	$CH_2CCH_3CONH_2$	85.1	111	--	--	solid
isobornyl methacrylate (IBOMA)	 $C_{10}H_{17}OOC\underset{CH_3}{\underset{\vert}{C}}CH_2$	222	--	--	127.7	liquid
ethylthioethyl methacrylate (ETEMA)	 $C_2H_5SC_2H_4OOC\underset{CH_3}{\underset{\vert}{C}}{=}CH_2$	174	--	102	79.4	liquid
methylmethacrylate (MMA)	$CH_2CCH_3COOCH_3$	100.1	-50	101	0	liquid
divinylbenzene	$C_6H_4(CHCH_2)_2$	130.1	-66.9	199.5	73.9	liquid
azobisisobutyro nitrile (AIBN)	$(CH_3)_2C(CN)NNC(CN)(CH_3)_2$	164.2	105	--	--	powder
Di-tert-butyl peroxide (DTBP)	$(CH_3)_3COOC(CH_3)_3$	146.22	-40	111.1	<27	liquid
Benzoyl peroxide (BPO)	$(C_6H_5CO)_2O_2$	242.22	104	--	--	powder

We shall define silicones as organosilicon polymers in which the silicon atoms are bound together by oxygen atoms. The silicon valences not taken up by oxygen are saturated by at least one other organic group. A simple representation of a linear polymer would be as follows:

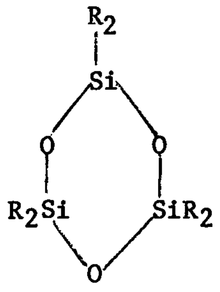


$$-\overset{R}{\underset{R}{Si}}-O-\overset{R}{\underset{R}{Si}}-O-(R_2SiO)_n$$

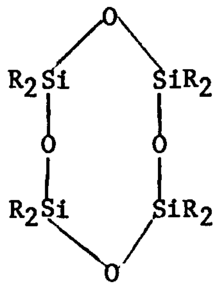
The name siloxane, from the Si-O-Si unit sil-oxane, has found general acceptance in scientific literature.[18,19] A siloxane unit is composed of an oxygen atom functioning as a link between two silicon atoms, each having a half share of the oxygen atom. This can be represented by the formula $R_nSiO_{(4-n)/2}$.

The organosiloxane units in this formula are represented by "n" values of 1 to 3. The free valences of the oxygen determine the functionality of each siloxane unit. Therefore, the organosiloxanes are mono-, di-, or trifunctional.

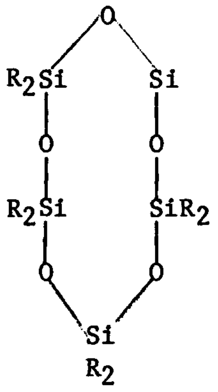
The monofunctional siloxane can combine with itself only once, giving hexaorganosiloxane $R_3Si-O-SiR_3$. The difunctional units give closed rings or combinations with one another. A ring structure containing three (a), four (b), or five (c) siloxane units may also be obtained.



(a)



(b)



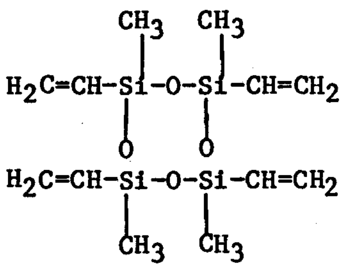
(c)

Trifunctional siloxane units combining with one another will produce polymer molecules that are cross-linked in a three-dimensional network.

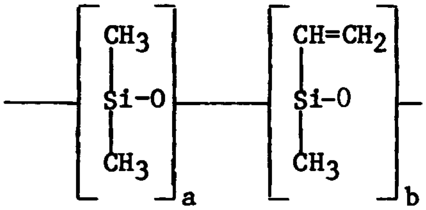
If the difunctional and trifunctional organosiloxanes containing vinyl pendant groups are copolymerized with other monomers such as styrene, methylmethacrylate, divinylbenzene, or trimethylolpropane trimethacrylate, a high-temperature stable polymer will be formed. The copolymerization reaction proceeding through the unsaturated groups will link the molecules through the Si-C bond, one of the most thermally stable structures.[18,19]

Three organosiloxanes, polymerized with DTBP, were used in this study. Their chemical structures are shown below:

1. Tetramethyltetravinylcyclotetrasiloxane (RZ)

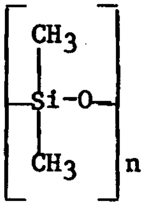


2. Dimethylpolysiloxane with pendant vinyl groups (Y-9208)



$$-\left[\begin{matrix}\mathrm{CH_3}\\ |\\ \mathrm{Si{-}O}\\ |\\ \mathrm{CH_3}\end{matrix}\right]_a-\left[\begin{matrix}\mathrm{CH{=}CH_2}\\ |\\ \mathrm{Si{-}O}\\ |\\ \mathrm{CH_3}\end{matrix}\right]_b-$$

3. Polydimethylsiloxane (V-47)



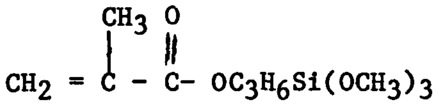
$$\left[\begin{matrix}\mathrm{CH_3}\\ |\\ -\mathrm{Si{-}O}-\\ |\\ \mathrm{CH_3}\end{matrix}\right]_n$$

B. Coupling Agents

Improvements in the mechanical and chemical resistance properties of components can be obtained by the inclusion of coupling agents.

A complex interplay of physical and chemical factors takes place in the interfacial region between polymer and filler. Practical coupling involves chemical and mechanical modification of the interface in a predictable manner.[20] To achieve this, the organofunctional group of the coupling agent should have maximum reactivity with the polymer system at the curing conditions and the orientation of the agent on the filler should allow maximum contact of the functional group with the polymer.[21] They should also have active polar groups which are capable of bonding to mineral surfaces in the presence or absence of water to form hydrolytically stable bonds.

Bifunctional silane coupling agents such as γ-methacryloxypropyl-trimethyloxysilane (A-174) meet these criteria. The chemical structure for this material which has been widely used in the formation of PC composites is as follows:



$$CH_2 = \overset{\overset{CH_3}{|}}{C} - \overset{\overset{O}{\|}}{C} - OC_3H_6Si(OCH_3)_3$$

C. Aggregate Systems

The selection of an aggregate system to produce PC composites for use in geothermal environments depends primarily on the monomer composition and its physico-chemical properties. For use in a well cement, an aggregate consisting of silica sand and portland cement was selected.

In organic PC formulations containing mixtures of St, ACN, and Aa, three sizes of silica sand (1180 μm, 600 μm and 150 μm) were mixed in the weight ratio 50-25-25, respectively, and used in conjunction with portland cement. The particle size distribution of this mixture is shown in Figure 2 and its use results in a high-strength low-porosity composite.

A mixture of silica flour, sieve size <30 μm, and portland cement was used to produce PC containing organosiloxane monomers.

The inclusion of portland cement in the aggregate significantly improves the strength and durability of PC. Studies were performed to determine the effects of concentration and cement type on the properties. The compound compositions of four cements evaluated are given in Table 2, and the results from the studies performed are given in Sections III and IV.

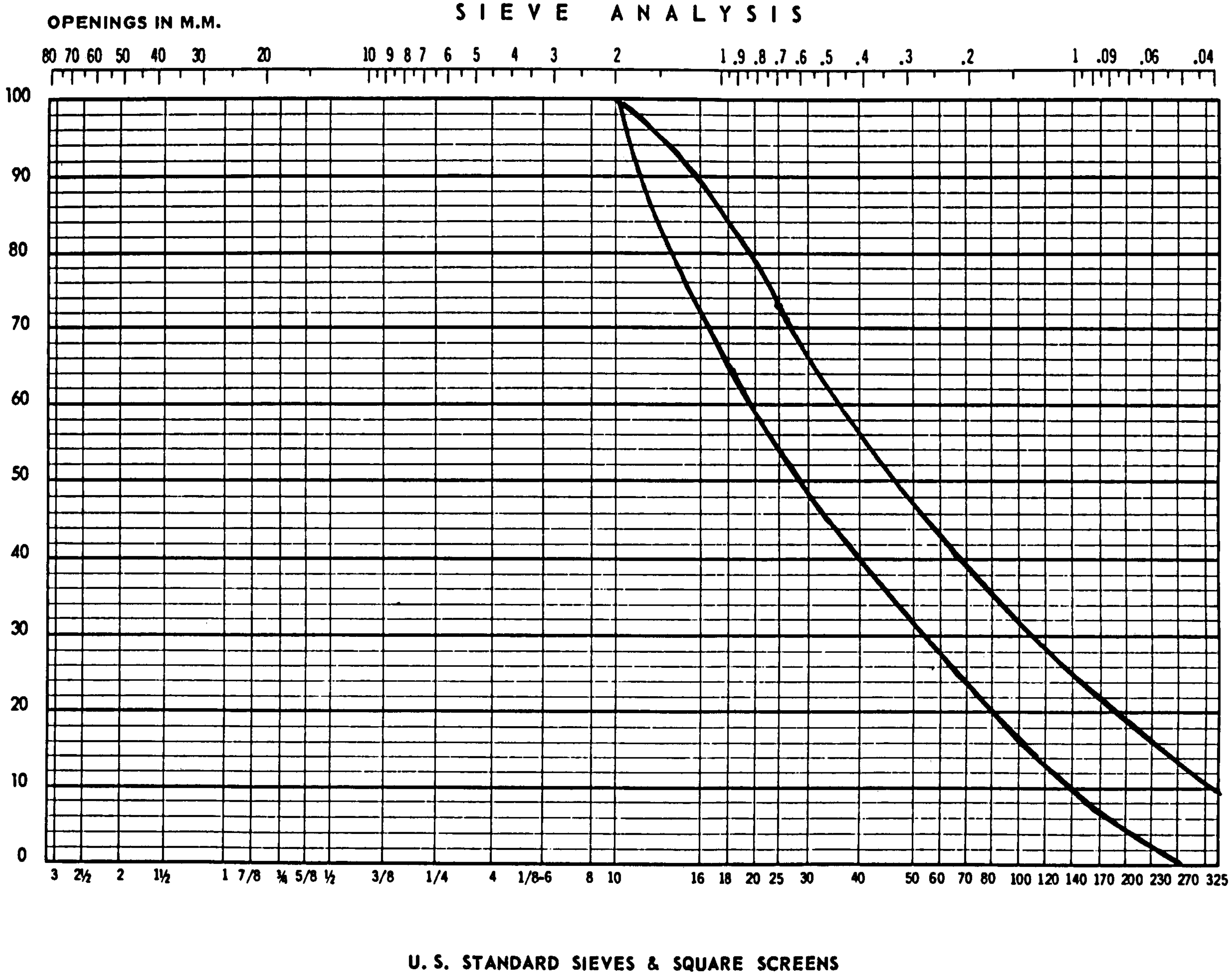


Figure 2. Typical sieve analysis for PC aggregate.

Table 2

Compound Composition of Portland Cements

Compound composition, wt%

								Calculated compounds[a]			
Cement	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Loss on ignition	C_3S	C_2S	C_3A	C_4AF
Type I	19.9	7.31	2.72	62.8	2.9	3.0	1.3	43.9	22.4	14.4	8.2
Type II	21.3	4.18	3.43	61.8	4.2	2.5	1.5	49.4	23.9	5.3	10.4
Type III	19.1	7.11	2.65	61.8	2.8	3.7	1.4	44.7	20.8	4.4	8.1
Type V	23.4	3.40	3.45	64.4	1.6	1.9	1.4	51.6	27.0	3.2	10.5

[a] In the abbreviated formula; $\hat{C} = CaO$; $S = SiO_2$; $A = Al_2O_3$, $F = Fe_2O_3$.

D. Sample Preparation

The monomers for both the organic and semi-inorganic PC formulations were mixed in glass beakers and the polymerization initiator was dissolved in the mixture. The Aa and MAa components of the organic formulations are solids at 20°C and do not readily dissolve in St and ACN. Dissolution was generally accomplished by heating the mixture to 45° or 50°C. The monomer mixture then was maintained at this temperature during the addition of fillers in order to keep the Aa and MAa in solution.

An alternative method for producing organic PC with this formulation was also used.[7] In this method the solid monomers were mixed with the aggregate at room temperature. St and ACN and cross-linking agents containing initiator were then mixed with the solids. After polymerization, PC was obtained with strength and durability properties similar to those obtained with the earlier method.

Cylindrical specimens of each formulation were prepared by filling glass tubes, whose inner surfaces were coated with a release agent, with the PC slurry. Vibration during filling was used to compact the material. The PC was then cured in an oven at the required temperature. After cooling, the samples were removed from the mold, cut to a length to diameter ratio of 2, and dried.

E. Test Procedures

Water absorption and compressive strength measurements on the PC samples were performed in accordance with ASTM standards C 373-56 and C 39-72, respectively.

Durability tests were performed in autoclaves containing a simulated 25% geothermal brine, the constituents of which are given in Table 3. In these tests, the samples were first weighed and their dimensions recorded. After exposure to brine at elevated temperature, the samples were washed in water and dried before testing.

Thermal stability measurements on the polymers were performed using a Du Pont 990 thermal analyzer equipped with a thermogravimetric (TGA) module. TGA tests were conducted in nitrogen gas flowing at a rate of 80 cc/min and a heating rate of 10°C/min.

Infrared spectroscopy (IR) measurements were performed using a Perkin-Elmer 297 infrared spectrophotometer. The KBr pellet procedure was used.

Specimens were prepared for IR analysis by mixing 200 mg of KBr with 4 mg of PC or polymer which had been crushed to a size <0.104 mm. The mixture was placed in a sample cup and evacuated to $\sim 10^{-1}$ mm Hg for 8 to 10 minutes. After evacuation, the mixture was pressurized to 125 to 140 MPa for 4 to 5 minutes to form a pellet which was then analyzed by IR.

Scanning Electron Microscopy (SEM) was used to achieve the microstructural features of PC specimens before and after hydrothermal exposure. An AMR - 1000-Å microscope was used in this work. For determination of the atomic concentration on the fractured surfaces of the PC, the SEM was equipped with an energy-dispersive x-ray Si(Li) detector.

Table 3

Chemical Constituents of 25% Brine Solution

	mol
Sodium chloride, $NaCl$	20.77
Potassium chloride, KCl	3.81
Calcium chloride, $CaCl_2$	6.53
Lithium chloride, $LiCl$	0.28
Strontium chloride, $SrCl_2 \cdot 6H_2O$	0.71
Barium chloride, $BaCl_2 \cdot 2H_2O$	0.017
Ferric chloride, $FeCl_3 \cdot 6H_2O$	0.43
Manganese chloride, $MnCl_2 \cdot 4H_2O$	0.22
Zinc chloride, $ZnCl_2$	0.069
Distilled water	440

III RESULTS - ORGANIC PC FORMULATIONS

Data were obtained for several monomer formulations: St-ACN-Aa, St-ACN-MMA, IBOMA-MMA, and IBOMA-MMA-ETEMA. Results given in Table 4 for preliminary tests indicated that formulations based upon St-ACN yielded composites with the highest strengths and chemical resistance. As a result, emphasis was placed on the development of that system.

Experiments were also performed to determine if true copolymers rather than mixtures of copolymers and/or homopolymers were formed during the polymerization reaction. The formation of copolymer was confirmed by solubility tests performed using acetone, dimethylformamide, and water. The copolymers are insoluble in these materials which are solvents for PSt, PACN, and PAa, respectively. It was also observed that homogeneous transparent films, without signs of inclusions, could be cast from the copolymer. This also was evidence of the formation of true copolymers.

A. Organic PC Cross-Linked With TMPTMA

Work was performed to optimize the monomer composition with respect to the properties of the PC. The concentration of each monomer constituent in the formulation was selected on the basis of the reactivity of the monomer. PC samples were made using a 12 wt% concentration of the monomer and 88 wt% filler. The filler consisted of 80 wt% silica sand - 20 wt% Type III portland cement. Results from property evaluations performed on these specimens are given in Table 4. These data indicate that the boiling water absorption of the specimens after 30 days' exposure to air in an oven at 240°C increases as the concentration of Aa is increased and decreases with increasing MAa content. The compressive

Table 4

Polymer Concrete Properties

Monomer system	Monomer ratio, wt%	Catalyst		Boiling water absorption, % after			Compressive strength, MPa, after			Oven at 240°C	Polymer wt loss, %, after oven at 240°C
		name	wt%	prepar.	at 240°C	autoclave	prepar.	boiling water absorption	autoclave		
St-ACN-Aa	57.5-40-2.5	AIBN	0.5	2.27	5.09[a]	1.71	141.5	72.6	75.4	21.4	18.0[a]
	60-35-5.0	AIBN	0.5	1.37	6.66	2.0	168	136.0	82.9	13.9	25.6
	55-40-5.0	AIBN	0.5	0.98	4.73	1.84	136	138.9	93.3	49.1	18.8
	55-37.5-7.5	AIBN	0.5	0.96	10.03	1.38	144.1	145.3	40.0	5.2	28.5
St-ACN-MAa	57.5-40-2.5	AIBN	0.5	2.74	6.80	3.59	105.6	89.6	40.8	12.5	25.5
	60-35-5	AIBN	0.5	1.88	4.84	2.64	117.4	92.7	74.8	21.4	18.4
	55-40-5	AIBN	0.5	1.49	5.43	1.30	130.9	132.0	49.7	37.2	15.8
	55-37.5-7.5	AIBN	0.5	0.94	2.57	1.55	153.3	102.2	61.2	37.9	9.6
IBOMA-MMA	95-5	BPO	2.0	0.16	22.70[b]	3.51	71.9	89.6	27.6	—	7.98[b]
	90-10	AIBN	0.75	0.34	15.47	3.71	84.6	91.0	46.3	—	8.79
	85-15	AIBN	0.75	0.38	17.83	4.45	79.3	79.1	40.1	—	8.76
	80-20	BPO	2.0	0.16	17.98	2.70	106.4	105.9	51.8	—	8.51
	70-30	AIBN	0.75	0.50	13.84	3.64	96.8	92.0	52.7	—	8.02
	60-40	AIBN	0.75	0.57	14.32	3.38	98.0	76.2	70.5	—	8.31
	50-50	BPO	2.0	0.37	15.46	1.66	144.4	137.5	90.5	—	7.71
IBOMA-MMA-ETEMA	94-5-1	AIBN	0.75	0.54	19.33[c]	5.22	71.4	66.2	47.5	—	8.59[c]
	84-15-1	AIBN	0.75	0.64	19.75	5.28	90.8	81.8	34.6	—	7.78
	69-30-1	AIBN	0.75	1.05	—	3.92	95.9	74.0	48.2	—	7.37
	59-40-1	AIBN	0.75	1.19	20.55	3.69	101.6	54.6	46.8	—	7.72
	49-50-1	AIBN	0.75	1.48	18.09	4.68	104.8	62.7	43.9	—	7.76
	90-5-5	AIBN	0.75	0.56	25.39	5.10	88.2	61.7	35.6	—	8.41
	80-15-5	AIBN	0.75	0.85	18.81	5.85	99.1	74.5	32.7	—	7.49
	70-25-5	AIBN	0.75	1.20	18.89	5.69	63.0	60.06	34.3	—	6.21
	70-20-10	AIBN	0.75	0.64	29.11	4.53	98.9	84.2	42.3	—	6.73
	60-30-10	AIBN	0.75	1.12	16.64	4.52	110.6	88.0	44.7	—	6.49
	50-40-10	AIBN	0.75	0.78	18.95	3.47	119.2	115.8	63.5	—	6.73

[a] After 30 days' exposure.
[b] After 1 day's exposure.
[c] After 40 days' exposure.
Monomer loading - 12 wt%; aggregate composition: sand-cement at the ratio 80-20.

strength increases with MAa concentration and decreases as the Aa concentration is increased (see Table 4).

The addition of a cross-linking agent such as TMPTMA to the monomer mixtures further improves the thermal and chemical stability of the copolymers. The results, summarized in Table 5 and Figures 3 to 5, indicate that TMPTMA concentrations ranging from 2.5 to 4.0 wt% result in a 40 to 50% decrease in polymer weight loss after exposure in 240°C air for 30 days. The change in boiling water absorption is decreased 30 to 35% and the compressive strength is increased.

The thermal stability of the 55 wt% St - 35 wt% ACN - 5 wt% Aa - 5 wt% TMPTMA system was determined and the results are given in Figure 6. The system appears stable in air at 240°C. Increasing the temperature to 275°C results in a 50% polymer weight loss in 6 days. At this temperature the thermal decomposition of [C-C=N] groups proceeds rapidly with evolution of NH_3, HCN, and H_2.

1. Styrene-Acrylonitrile Ratio. The copolymerization reactions involving St and ACN have been studied extensively, and as a result St-ACN copolymers have found wide industrial application. The properties of the copolymer obtained are directly proportional to the St-ACN-ratio in the monomer mixture. The activity ratio of both monomers is such that the curve for the copolymer composition has the appearance shown in Figure 7,[22] where it is seen that a homogeneous copolymer can be obtained only in the case of the azeotropic composition of the monomeric mixture consisting of St and ACN. The amount of ACN in the the azeotropic mixture varies between 36 and 40 mol%. When the ACN concentration is higher than that in the azeotrope, the monomeric phase is enriched by acrylonitrile.

Table 5

Summary of Results for Polymer Concrete Samples Containing Cross-linking Agents

Monomer system	Composition, wt%	Polymer weight loss, %, after 30 days at 240°C	Boiling water absorption, %, after		Compressive strength, MPa, after				Boiling water absorp after autoclave
			Preparation	32 days at 240°C	Preparation	30 days at 240°C	Autoclave for 30 days	Boiling water absorp.	
St-ACN-Aa-TMPTMA	55-35-7.5-2.5	10.0	0.33	1.71	157.3	63.5	106	189	0.83
	55-35-5.0-5.0	8.38	0.28	1.19	174.3	88.5	122	183	0.64
St-ACN-MAC-TMPTMA	50-37.5-7.5-5.0	10.5	0.28	1.54	164.1	52.6	—	155.7	—
	50-40-5.0-5.0	7.99	0.24	1.04	180	80.5	—	139.5	—
	50-42.5-2.5-5.0	6.89	0.28	0.76	180	91.8	—	170.7	—

St, styrene.
ACN, acrylonitrile.
Aa, acrylamide.
MAa, methacrylamide.
TMPTMA, trimethylolpropane trimethacrylate.

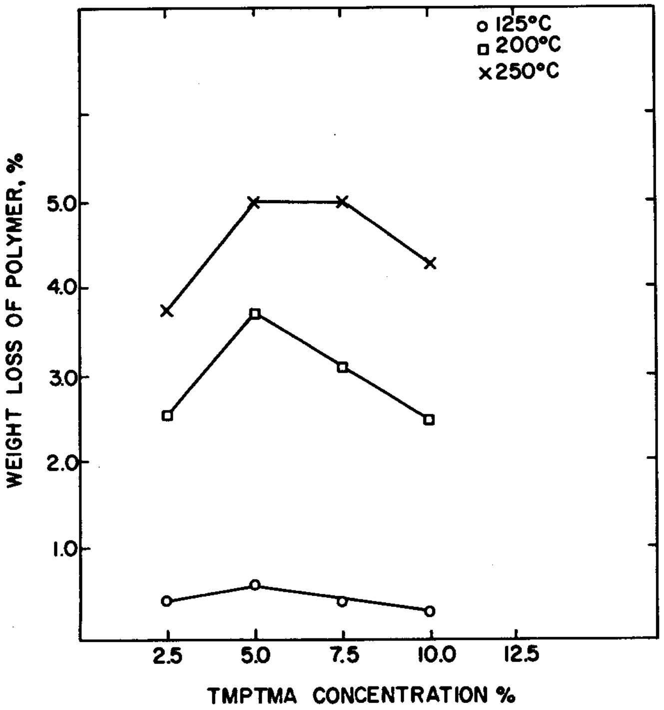


Figure 3. Weight loss of polymer as a function of cross-linking agent concentration.

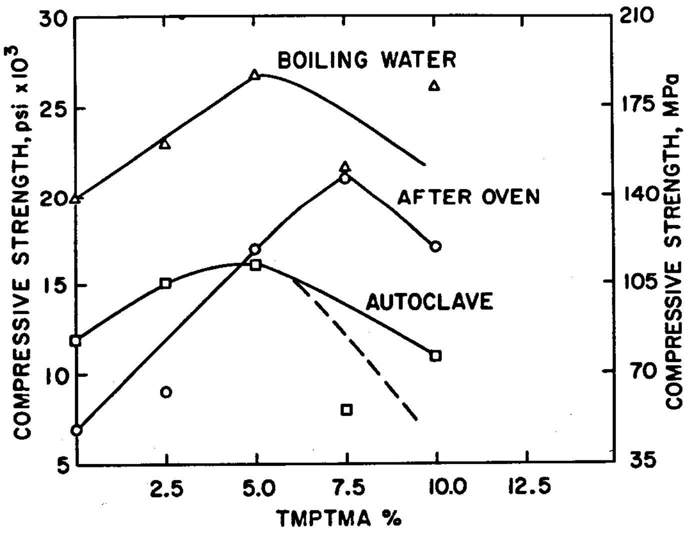


Figure 4. Compressive strength as a function of cross-linking agent concentration.

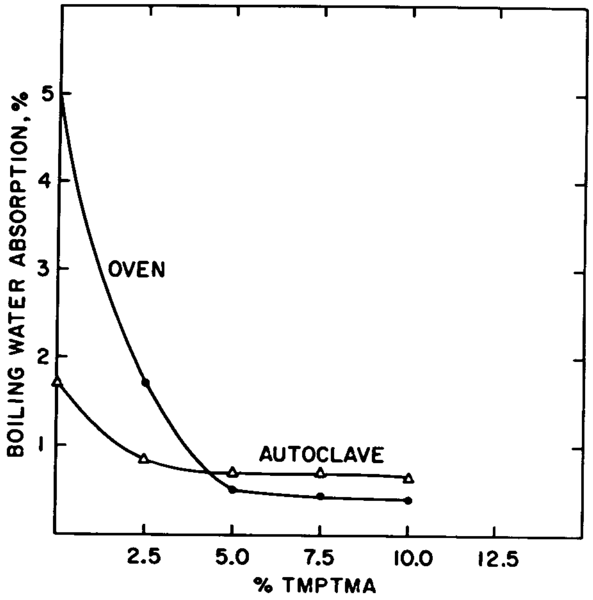


Figure 5. Boiling water absorption of PC as a function of TMPTMA concentration.

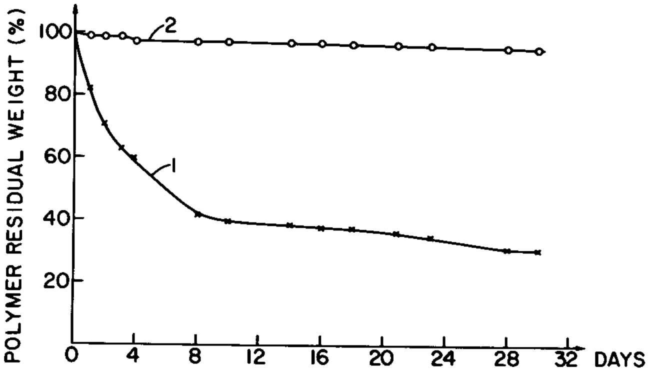


Figure 6. Effect of temperature on weight loss of polymer in PC samples. (1) 240°C; (2) 275°C. Monomer composition: 55 wt% St - 35 wt% ACN - 5 wt% Aa - 5 wt% TMPTMA

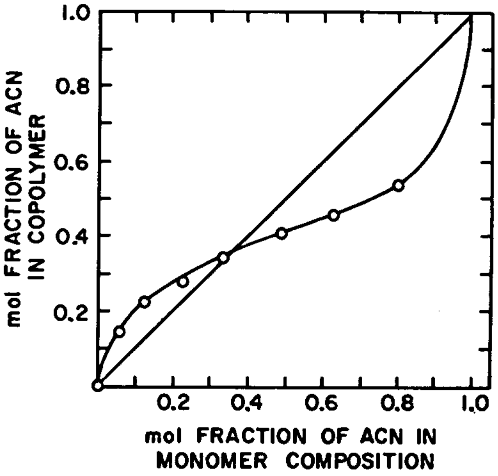


Figure 7. Monomer-polymer composition curve for styrene-acrylonitrile bulk polymerization.

Upon polymerization, the conversion to copolymer will be ~80% with the remainder PolyACN. At this time, however, a large fraction of the St is spent and the ACN-to-St ratio in the copolymer increases rapidly. If, however, the initial concentration of ACN exceeds 60 mol%, then a PolyACN will be produced at the end of polymerization. The same situation applies to styrene. If the initial concentration of ACN is <27 to 30 mol%, then a PolySt is formed at the end of polymerization. Since neither of the homopolymers mixes with the copolymer, mixtures of the monomers that are outside these limits yield a heterogeneous product.

The thermal stability of polymers depends on the molecular weight which is in turn related to the reaction temperature. Boundy[23] showed that high reaction temperature yields a low-molecular-weight copolymer, which is weak and brittle. Thus, PC samples have poor mechanical properties. On the other hand, a high-molecular-weight product is formed at low reaction temperature, but because of different reactivities of monomers, a partly nonuniform product is produced. Jones et al.[24] found that optimum products are obtained when the monomer system is polymerized in bulk at a reaction temperature in the range of 130° to 180°C. The introduction of a small amount of Aa in the molecular chain is more reactive than St but less reactive than ACN. TMPTMA has polymerization characteristics similar to those of styrene. Both Aa and TMPTMA change the St-ACN ratio at which only copolymer of a constant composition is produced, and the reaction temperature.

Without determining the parameters of copolymerization on the basis of theoretical suppositions,[25] we conducted a series of experiments to determine the effect of ACN concentration in a St-ACN-Aa-TMPTMA mixture on the properties of PC. Figure 8 shows the weight loss of a polymer measured in nitrogen by TGA at different curing conditions and ACN concentrations. The broken lines indicate that the weight loss of the polymer increases rapidly with temperature independently of ACN concentration if the maximum curing temperature of the reaction is 115°C. As shown earlier,[5] this weight loss is attributable to unreacted monomer. An increase in the reaction temperature to 160°C decreases the weight loss. As can be seen, the system containing 45 mol% of ACN in the monomer composition has a minimum weight loss. An increase in the ACN concentration increases the weight loss of the polymer, which can result in a partial formation of PolyACN at the end of the copolymerization reaction.

It was reported earlier that PC samples have high durability and thermostability when a cross-linking agent is used to obtain a three-dimensional polymer structure. The concentration of the cross-linking agent affects not only the properties of PC but also the required ACN concentration (Figure 9). The PC samples which were exposed to air at 240°C for 30 days showed a high degree of resistance to thermooxidation when the concentration of the TMPTMA cross-linking agent is in the range of 1.15 to 1.70 mol% and the ACN concentration is in the range of 45 to 55 mol%. An increase in the concentration of TMPTMA increases its ability to thermooxidize with increasing ACN concentration. Results of the study of the compressive strength of PC

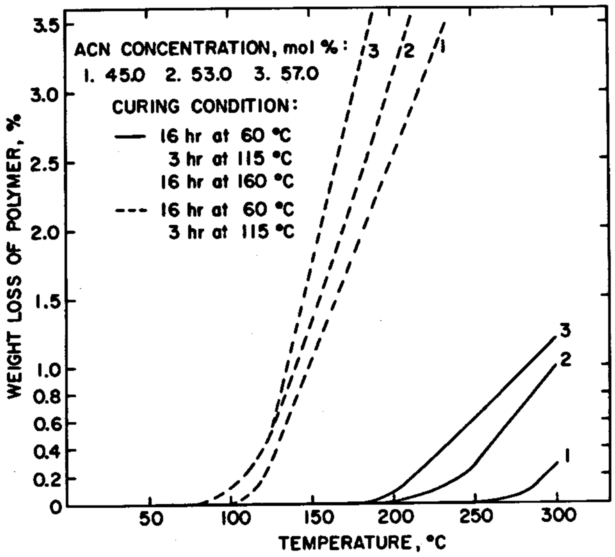


Figure 8. Polymer weight loss at elevated temperature.

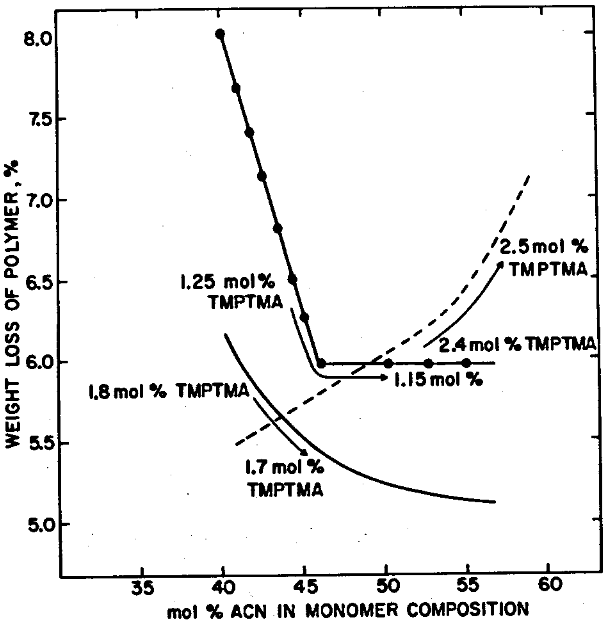


Figure 9. Weight loss of polymer in PC vs ACN concentration after 30 days' exposure to air at 240°C.

samples after their preparation and exposure to air and to a simulated geothermal brine solution at 240°C for 30 days are shown in Figures 10 through 12.

When the concentration of the cross-linking agent is in the range of 1.15 to 1.25 mol%, the compressive strength of the composite after preparation varies from 177 to 183 MPa. This also occurs when the ACN concentration increases from 40 to 55 mol% (Figure 10). Exposure of these samples for 30 days to a geothermal brine solution and to air at 240°C decreases its strength no more than 20% at an ACN concentration of 40 to 45 mol% and up to ~50% at ACN concentrations in the range 45 to 55 mol%. An increase in the concentration of the cross-linking agent from 1.7 to 1.8 mol% (Figure 11) improved the durability of the samples to thermooxidation, although, after exposure to brine, the strength decreased rapidly to ~50% at an ACN concentration of 40 mol% and continued to decrease with increasing ACN concentration. The same behavior was observed when the concentration of the cross-linking agent was increased to 2.6 mol% (Figure 12). The mechanical durability decreases with increasing ACN concentration, which results in the partial formation of ACN homopolymer. After the exposure of the samples to hot brine solutions at 240°C, this homopolymer leads to cyclic formation with evolution of gases and hence to the conjugation of the double bonds, which can be easily hydrolyzed during the exposure to hot brine. The cyclic formation increases with increasing ACN concentration.[26,27]

Thus, the results obtained show that the concentration of ACN is critical and is dependent upon the concentration of other monomers. Thus, at 40 to 45 mol% concentration of ACN, 5 to 5.5 mol% Aa, and 1.15

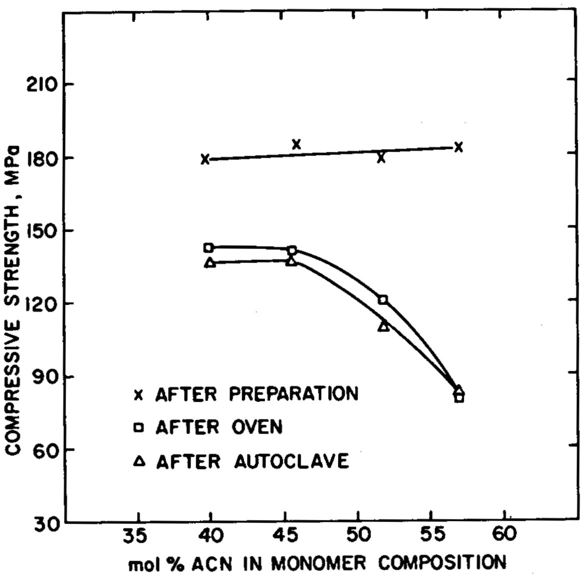


Figure 10. Compressive strength of PC vs ACN concentration. Monomer load 13 wt%; sand-cement ratio 7:3; cross-linking agent 1.15 to 1.25 mol%; Aa 5.5 mol%

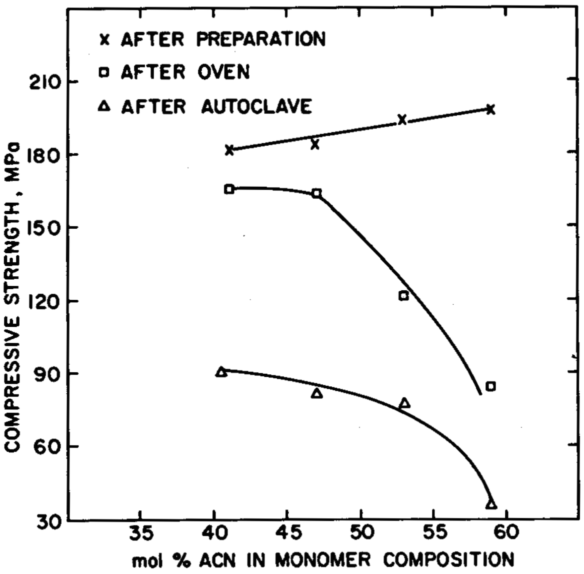


Figure 12. Compressive strength of PC vs ACN concentration. Monomer load 13 wt%; sand-cement ratio 7:3; cross-linking agent 2.4 to 2.5 mol%; Aa 6.0 mol%.

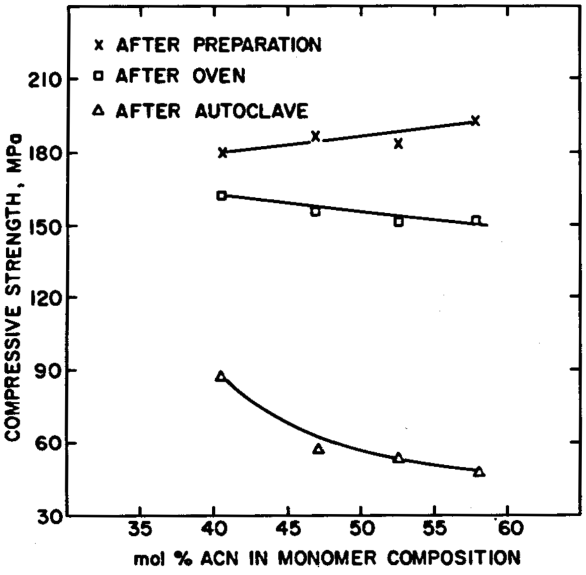


Figure 11. Compressive strength of PC vs ACN concentration. Monomer load 13 wt%; sand-cement ratio 7:3; cross-linking agent 1.7 to 1.8 mol%; Aa 5.75 mol%.

to 1.25 mol% TMPTMA, a true homogeneous copolymer is formed exclusively, which leads to the formation of highly stable, chemically resistant PC. Changes in the above concentration lead to changes in azeotropic conditions and consequently the formed PC becomes thermochemically weak. The experimental results also indicate that the inclusion of small amounts of Aa and TMPTMA into the molecular chain of St-ACN copolymers shifts the azeotrope in the direction of increasing ACN concentration, but it still occurs in the area of 40 to 45 mol%, where the homogeneous copolymer product can be obtained.

2. Curing Agent Concentration and Temperatures. As mentioned earlier,[4,6] the physical conception of a thermally stable polymer is one with a high softening or melting point. It was also mentioned that one way to increase the melting point is by the introduction of polar substituents such as C≡N and/or hydrogen bonding groups such as NH_2.

Thermal stability can also be improved by increasing the curing temperature when the molecular chain starts to grow, thereby enabling a three-dimensional structure to form. The ratio of the temperature at which the polymerization initiator starts to decompose (T_{di}) and the glass transition temperature (T_g) is very important in the selection of a curing temperature for the composite. When $T_g > T_{di}$, the curing terminates before the reaction is complete, thereby leaving unreacted monomer. Complete curing is obtained when $T_{di} > T_g$.

Two curing agents, AIBN and DTBP, and mixtures of the two were evaluated for use with a 55 wt% St - 35 wt% ACN - 5 wt% Aa - 5 wt% TMPTMA monomer system. Polymerization was performed using a two-step curing process. The first step consisted of heating at 52°C until the polymerization induction period was completed. At this point the viscosity of the monomer is essentially unchanged, but the monomer mixture begins to lose its elasticity and solubility. When the temperature was subsequently increased to ~105° or ~150°C (the second stage), a polymer with a three-dimensional structure was obtained. The method of performing these experiments and complete results have been published.[5]

Figure 13 illustrates the results from the thermogravimetric analysis performed in the dynamic mode on polymer samples. The data show the weight loss of polymer as a function of temperature for the polymers obtained at different curing temperatures (105° and 150°C) and different concentrations of free-radical initiators (AIBN and a mixture of AIBN and DTBP). The curves No. 1 and No. 2 represent the TGA data for the polymer before and after washing in ethanol, respectively. As can be seen in the figure, polymer consisting of 55 wt% St - 35 wt% ACN - 5 wt% Aa - 5 wt% TMPTMA loses weight at a temperature ranging between 50° and 150°C. Increasing the curing temperature from 105° to 150°C by a second step polymerization decreases the absolute value of the polymer weight loss from 2.7 wt% at 105°C to 1.0 wt% at a curing temperature 150°C. This is illustrated in curves No. 1 (a and d). Using a mixture of two initiators also results in a decrease in polymer weight loss. A comparison of TGA curves c and d with a and b indicates that, at the same curing temperature, the percent conversion of monomer to polymer is higher when

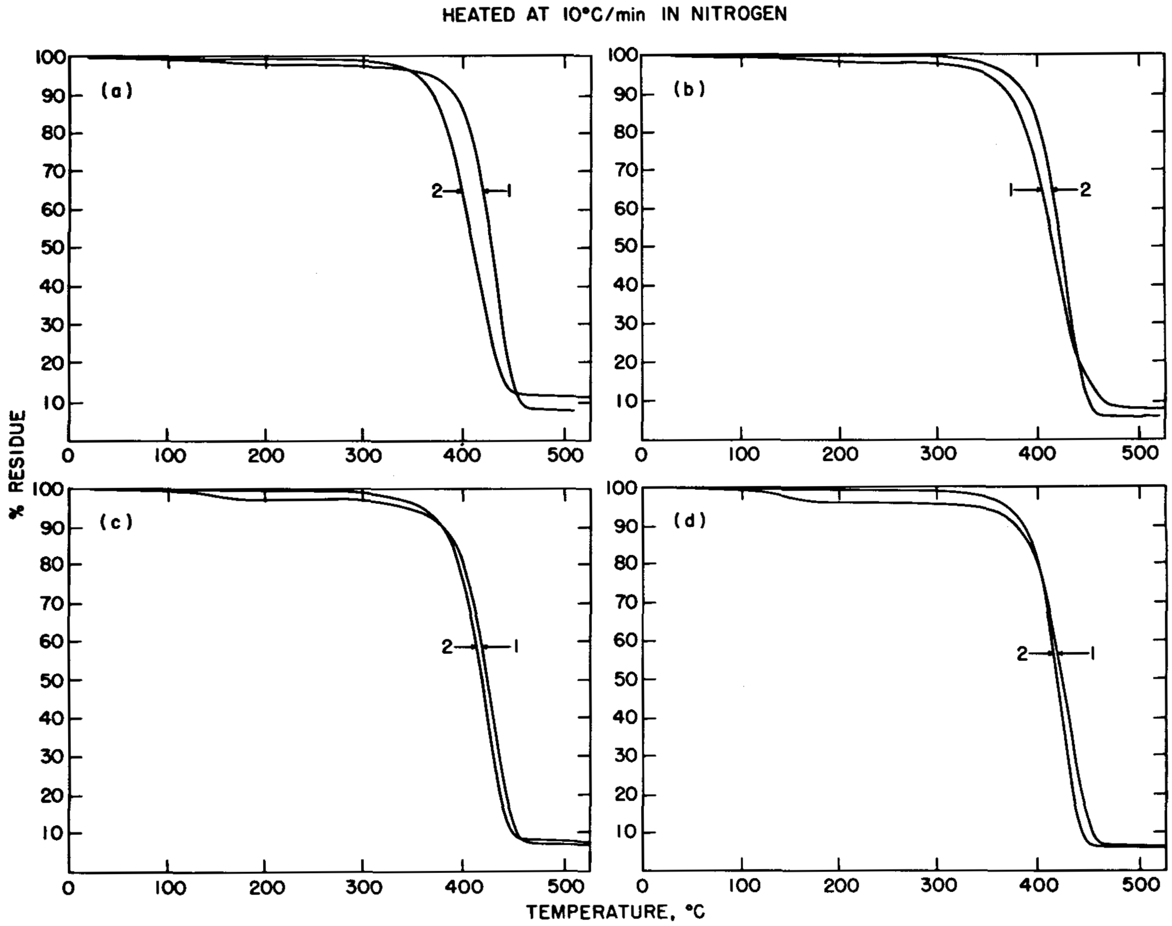


Figure 13. The influence of curing temperature and curing agent on the thermal properties of polymer.
Monomer system: 55 wt% St - 35 wt% ACN - 5 wt% Aa - 5 wt% TMPTMA
a. Curing temperatures: 52°C and 150°C
Curing agent: 0.5 wt% AIBN
b. Curing temperatures: 52°C and 150°C
Curing agents: 0.5 wt% AIBN + 0.5 wt% DTBP
c. Curing temperatures: 52°C and 105°C
Curing agents: 0.5 wt% AIBN + 0.5 wt% DTBP
d. Curing temperatures: 52°C and 105°C
Curing agent: 0.5 wt% AIBN

the mixture of two initiators is used. On the basis of the assumption that variations in weight in the temperature range 50° to 150°C are due to the presence of unreacted monomers in the system, polymer samples were evaluated after washing in ethanol. These data, shown in Figure 13 as curve 2, indicate that after treatment with ethanol the polymers are less sensitive to the temperature change.

Data from the TGA when operated in the isothermal mode are given in Figure 14. This test measured the loss of weight as a function of time at a constant temperature of 250°C. It is shown that a more thermally stable polymer is produced after washing in alcohol. The stability is independent of curing temperature and initiator concentration. It was also found that polymers produced using only one curing agent but at higher curing temperatures are more stable with time and, therefore, exhibit less weight change.

A quantitative estimate of the rate of cure for the polymers has been made using a vibrational spectroscopic method. Examination of IR spectra in the high-frequency 3000 to 1400 cm^{-1} range (see Figure 15) associated with the functional groups indicates a decrease in the absorption band of such functional groups as asymmetric and symmetric stretching vibration $-CH=CH_2$ groups (3030 cm^{-1}), asymmetric stretching vibration CH_2- groups (2930 cm^{-1}), $C\equiv N$ groups (2238 cm^{-1}), stretching vibration $-C\equiv O$ groups (1730 cm^{-1}), $CONH_2$ groups (1679 cm^{-1}), benzene rings (1602 and 1498 cm^{-1}), and unsaturated $-CH_2-$ groups (1455 cm^{-1}). Table 6 gives the values of the absorption bands for the groups found in the polymers.

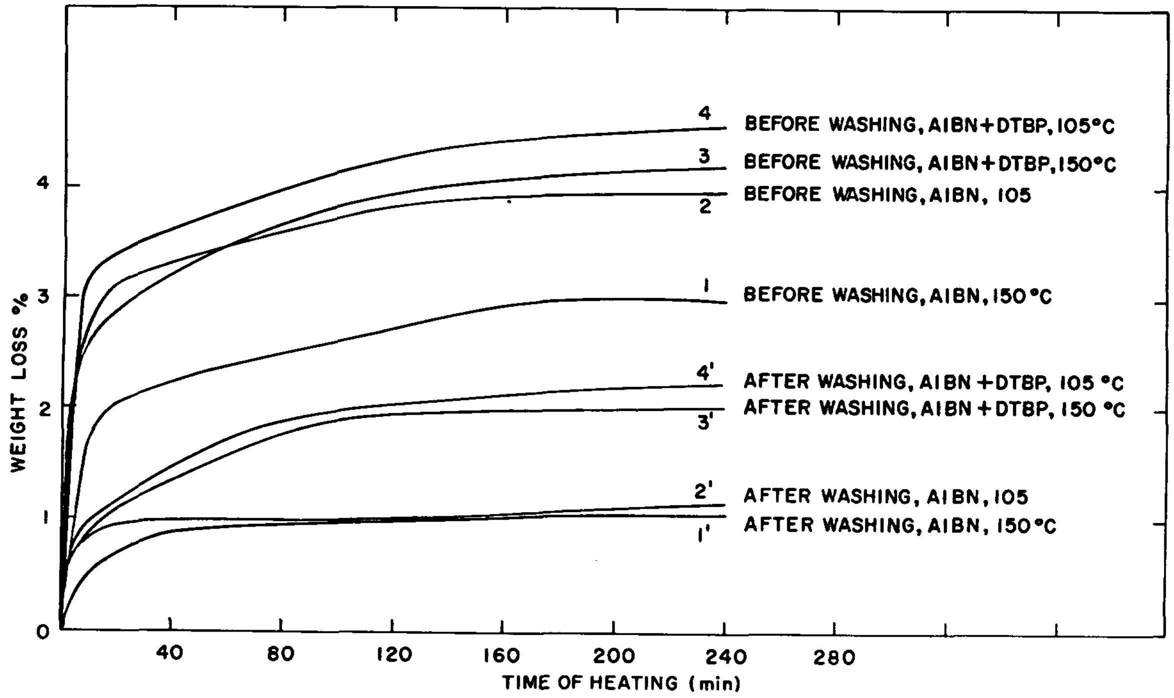


Figure 14. Isothermal weight loss of polymer in nitrogen at 250°C.

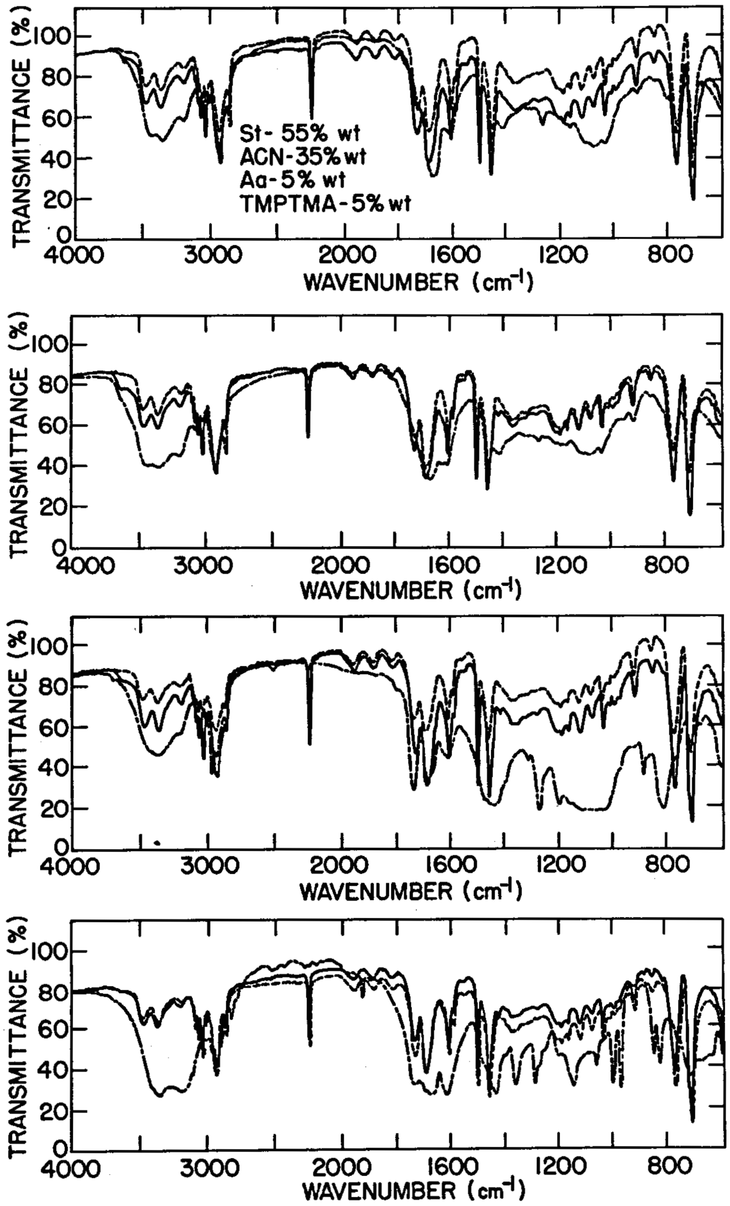


Figure 15. Infrared spectra of organic polymer systems. ——— before washing in ethanol; — — — after washing in ethanol; — — — filtrate; a, b, c, d - same as in Figure 13.

Table 6

Summary of Results of IR Spectra Analysis for St-ACN-Aa-TMPTMA Copolymer

		Absorption band $\times 10^{-1}$											
		AIBN, 105°C			AIBN, 150°C			AIBN+DTBP, 105°C			AIBN+DTBP, 150°C		
Functional group	Wavenumber, cm^{-1}	I			II			III			IV		
		A	B	C	A	B	C	A	B	C	A	B	C
asymmetric symmetric stretching vibration of vinyl groups, $-CH=CH_2$	3030	1.31	1.22	0.89	1.71	0.97	0.09	1.48	1.13	1.2	1.43	1.31	0.51
asymmetric stretching vibration $-CH_2-$	2930	2.03	1.86	2.41	2.6	1.46	0.9	2.45	1.97	7.16	2.21	2.04	2.94
C N	2238	1.88	1.85	0.1	2.6	2.4	0.1	2.21	1.85	1.92	2.05	1.93	1.15
stretching vibration $-C=O$	1730	1.33	1.33	0.03	1.74	1.27	5.62	1.57	1.31	0	1.39	1.38	0
$CONH_2$	1679	2.61	1.93	0	3.14	1.51	weak	2.59	2.16	weak	2.48	2.34	weak
benzene ring	1602	1.37	1.33	0.9	1.82	1.38	0.15	1.59	1.38	0.45	1.53	1.53	0.11
benzene ring	1498	3.38	2.86	0	4.24	2.74	0	3.71	3.11	3.8	3.3	3.3	0.02
unsaturated $-CH_2-$	1455	3.68	3.16	0	4.59	2.60	0	4.07	3.46	5.35	3.78	3.74	0.3

A - polymer before washing; B - polymer after washing; C - filtrate after washing.

When AIBN was used as a curing agent at the temperature of 105°C, the absorption peaks of such functional groups as unsaturated CH_2, benzene ring, $CONH_2$, and CN in the IR spectra of the filtrate are absent (Table 6). At the same time, the values of the absorption bands for the $-CH=CH_2$, CH_2, and C=O groups were sufficiently high. Increasing the curing temperatures to 150°C increases the amount of monomer polymerized, as can be seen from the increased values of the absorption bands for the typical functional groups. When the mixture of initiators was used, the opposite effect can be seen. Increasing the curing temperature leads to a decrease in the optical density of typical functional groups. A comparison of columns I and II in Table 6 indicates that by using the mixture of two initiators at a curing temperature 105°C, the intensity of the spectral line is increased. At the curing temperature of 150°C, the intensity of the spectral line when only one initiator was used is higher than when the mixture of two initiators was used.

The results from the study show that the use of the mixture of two initiators and high temperature produces a higher yield of cross-linked polymer. As a result, improvements in the mechanical properties are accrued. This is illustrated in Figure 16.

3. Polymer Content. Since the monomers are the most expensive components in a PC formulation, an important parameter is the effect of polymer content on the properties of the composite. To obtain information on this variable, a series of PC samples containing a monomer mixture of 55 wt% St - 35 wt% ACN - 5 wt% Aa - 5 wt% TMPTMA in conjunction with a 70 wt% silica sand - 30 wt% Type III portland cement aggregate were tested.

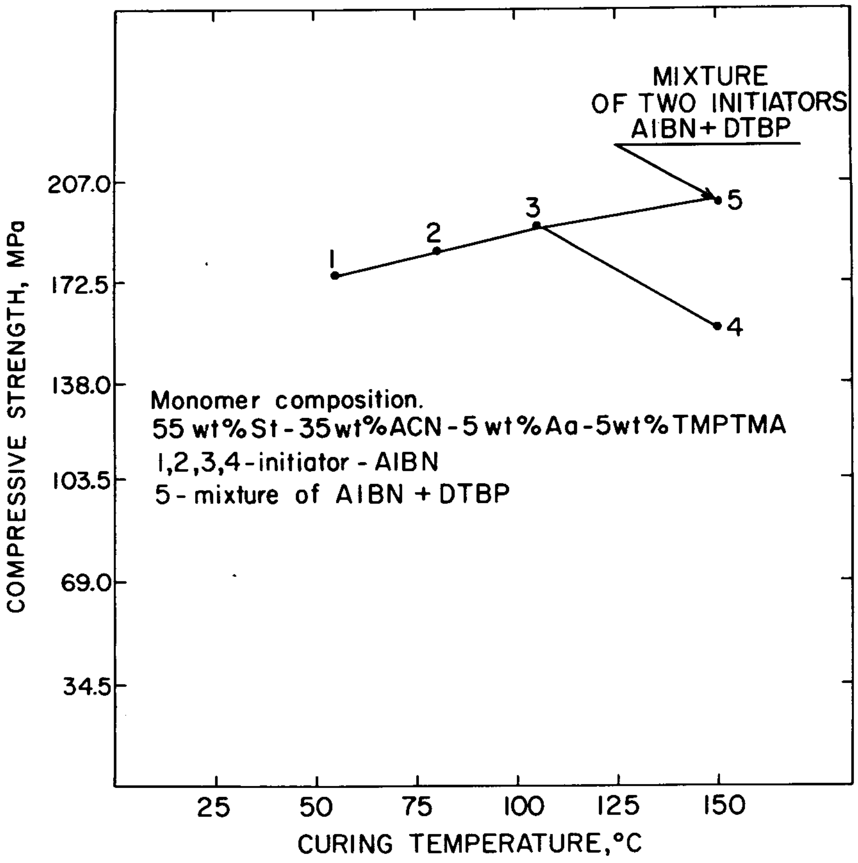


Figure 16. Compressive strength as a function of curing temperature.

Previous work[28] has indicated that with a well-compacted aggregate of the size distribution used in these tests, the addition of 12 wt% monomer generally results in a minimum excess of monomer. Therefore, the polymer loading was varied between 12 and 20 wt%. These results, summarized in Table 7, indicate that the compressive strength decreases from ~200 MPa for a sample containing 12 wt% polymer to ~120 MPa for a 20 wt% polymer loading.

If it can be assumed that a PC containing 12 wt% polymer results in the formation of a homogeneous system, further increases in polymer content will result in the formation of heterogeneous layers of polymer. These layers impede the filling of the fine voids, and thus reduce the cohesive force between the polymer and aggregate. This leads to the deterioration of the mechanical properties of the composite.

Electron microscopic studies tend to support the above assumptions. Figures 17 and 18 show fractured surfaces of PC containing 12 and 20 wt% polymer loadings, respectively. The composite containing 12 wt% polymer (Figure 17) has a more uniform surface than the sample containing 20 wt% (Figure 18). In the former, the polymer appears to be evenly filling the pore space between the sand grains and cement and a continuous three-dimensional polymeric network seems to be formed.

4. Sand-Cement Ratio. Studies were performed to determine the optimum ratio of sand to cement that should be used in the aggregate to produce PC. The results from these studies are summarized in Figure 19. The data indicate that increases in cement content from 10 to 30% result in increases in compressive strength from ~140 MPa to ~185 MPa. The water absorption remains essentially constant over the same range.

Table 7

Summary of Results for PC Systems Containing
55 wt% St - 35 wt% ACN - 5 wt% Aa - 5 wt% TMPTMA
and 70 wt% sand - 30 wt% Cement Aggregate

Property	Monomer loading, wt% 12.0	15.0	17.5	20
Compressive strength, MPa, after				
a) preparation[a]	198.1	175.1	170.4	120.3
b) boiling water	178.0	160.8	153	145.0
c) oven (30 days at 240°C)	120.8	87.15	98.5	82.4
d) autoclave (10 days, hot brine)	122.2	110.6	108.2	—
Boiling water absorption, %, after				
a) preparation[a]	0.33	0.26	0.26	0.24
b) oven (30 days at 240°C)	0.9	1.10	1.27	1.47
c) autoclave (10 days, hot brine)	0.64	0.64	0.59	—

1. Average of 4 specimens.

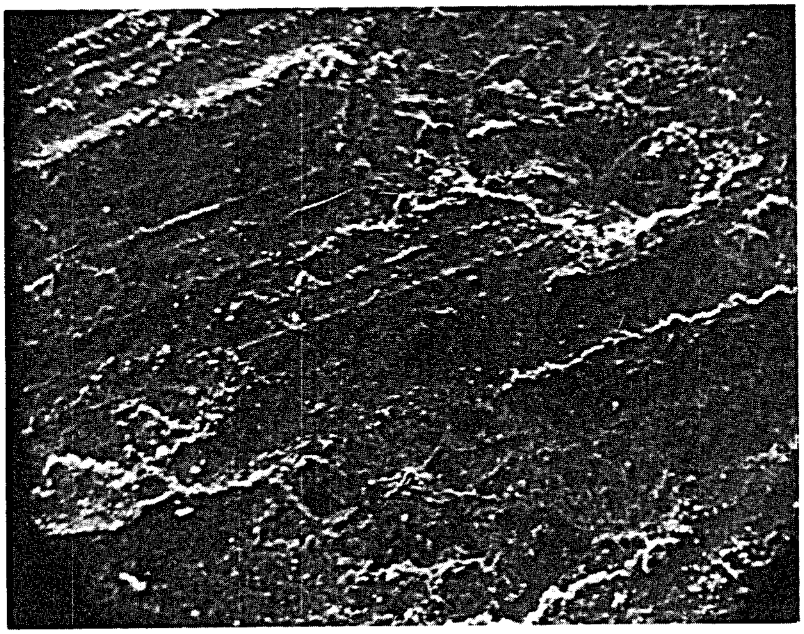


Figure 17. Scanning electron microscope picture of fractured surface of PC sample containing a 12% polymer loading.

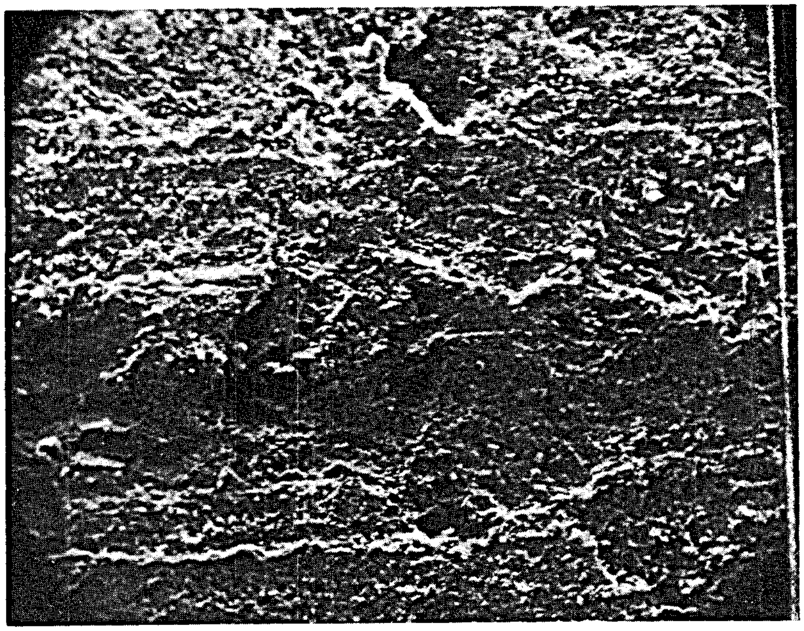


Figure 18. Scanning electron microscope picture of fractured surface of PC sample containing a 20% polymer loading.

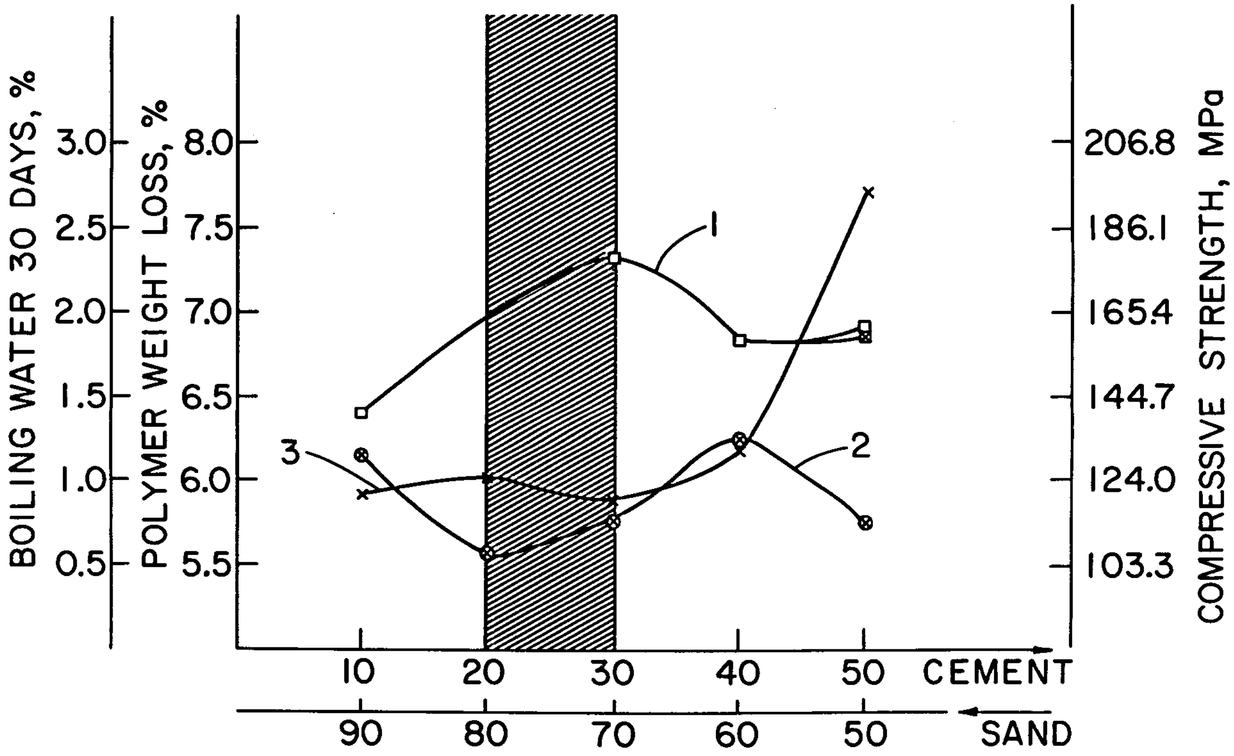


Figure 19. Effect of sand-cement ratio on the properties of PC.
1. Compressive strength after boiling water.
2. Compressive strength after oven, 30 days, (240°C).
3. Boiling water absorption after oven, 30 days.

Further increases in cement content to 50% result in an increase in water absorption and a decrease in compressive strength to ~158 MPa.

The above effects may be explained by the fact that the porosity of the aggregate is decreased as the percentage of cement is increased. This makes it difficult for the monomer to contact all of the aggregate, thus reducing the cohesive force between the polymer and the filler.

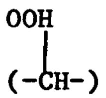
As discussed earlier,[4] an increase in the polymer content of the mix beyond 12 wt% does not compensate for the added cement fines since the resulting heterogeneous sections of copolymer lead to additional strength reductions. On the basis of these data, the optimum filler composition for use with the monomer systems is in the range 70 to 80 wt% sand and 20 to 30 wt% cement.

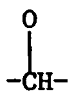
B. Organic PC Cross-Linked With DVB

1. Optimization of Monomer and PC Formulations. In a previous section, it was mentioned that one of the factors influencing thermal stability is the formation of inter- or intramolecular bonds which result in three-dimensional cross-linked structures. DVB is a commonly used cross-linking agent. When DVB was used in PC, the results indicated that the properties of the composite could be changed by varying the DVB concentration in the formulation. The probable cause is the introduction into the monomer of two vinyl groups with different reactivities. This leads to the formation of copolymers with different molecular structures.[8]

It was mentioned earlier that the properties of the copolymer and hence the PC properties are affected by the curing temperature. Dynamic TGA curves for a St-ACN-Aa monomer mixture containing various concentrations of DVB and polymerized at different curing conditions are shown in Figure 20. The results indicate decreasing polymer weight loss with increasing DVB concentration and curing temperature.

The thermooxidative stability of the PC decreases as the DVB concentration is increased. This is illustrated in Figure 21 which shows results from strength and weight determinations made after exposure for 30 days in an oven to air at 240°C. The probable cause of this is the decomposition of hydrogen peroxide groups (a)

(a)

$(\text{-}\overset{\overset{\text{OOH}}{|}}{\text{C}}\text{H-})$

(b)

$\text{-}\overset{\overset{\text{O}}{|}}{\text{C}}\text{H-}$

to form free radicals (b) which break the polymer chains. From the data given in Figure 21, it appears that for use in a thermooxidative environment the DVB concentration should be in the range of 1.0 to 2.5 wt%.

The results from property measurements performed on PC samples after exposure to brine at 240°C for 30 days are given in Figures 22 and 23. For a DVB concentration range from 2.5 to 10 wt%, the compressive strength and dimensional stability increases with increasing concentration. The water absorption also decreases as shown in Figure 23.

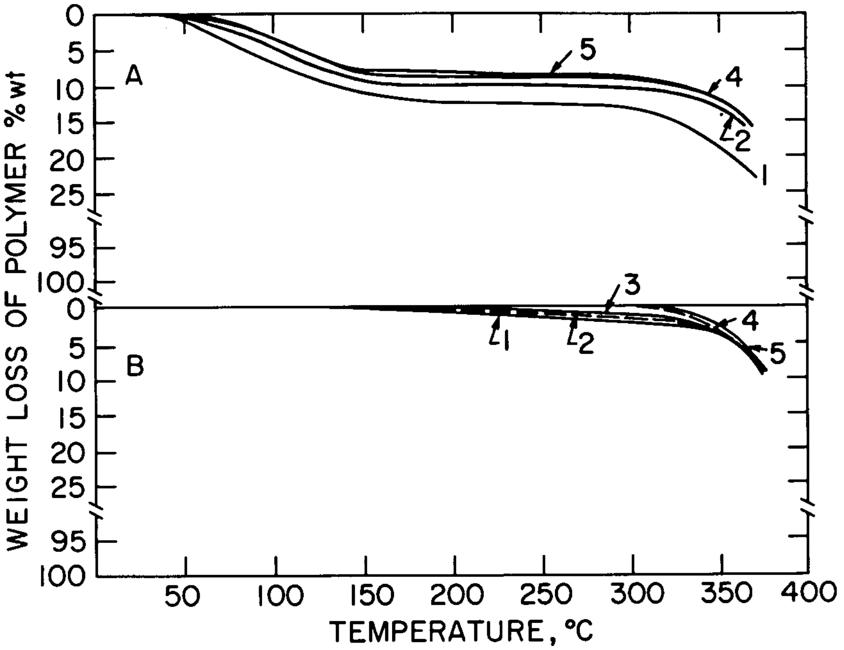


Figure 20. Dynamic weight loss of polymer vs temperature at different DVB concentrations. Monomer composition: St-ACN-Aa; cross-linking agent - DVB. Curing condition: (A) 60°C - 16 hr; 115°C - 3 hr; (B) 60°C - 16 hr; 115°C - 3 hr; 160°C - 16 hr. (1) 0 wt% DVB; (2) 2.5 wt% DVB; (3) 5.0 wt% DVB; (4) 7.5 wt% DVB; and (5) 10 wt% DVB.

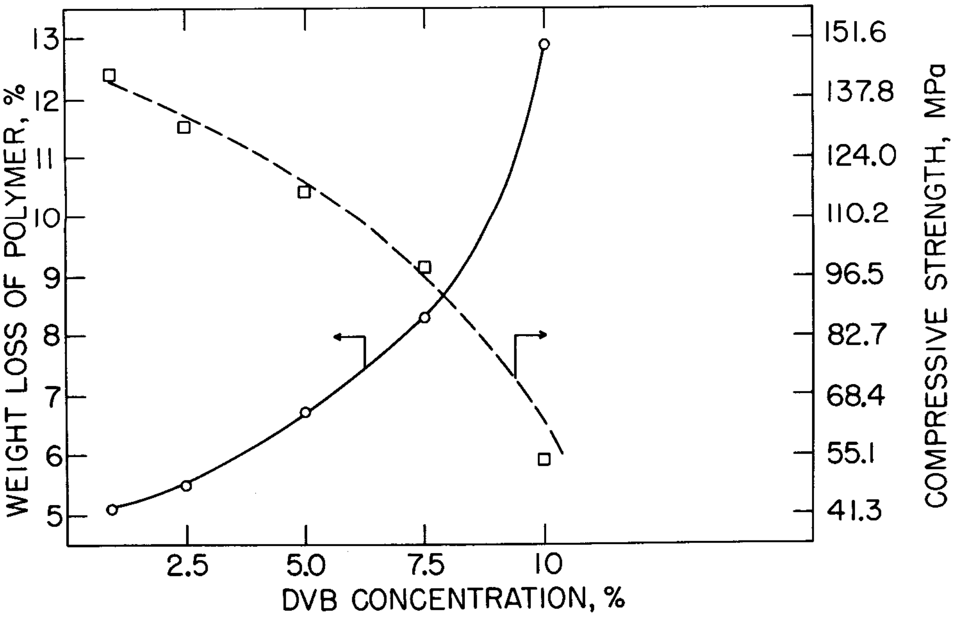


Figure 21. Weight loss of polymer and compressive strength of PC samples vs DVB concentration after 30 days' exposure to air at 240°C. Monomer mixture: St-ACN-Aa-DVB; aggregate composition: sand-Type III portland cement; monomer loading 13 wt%.

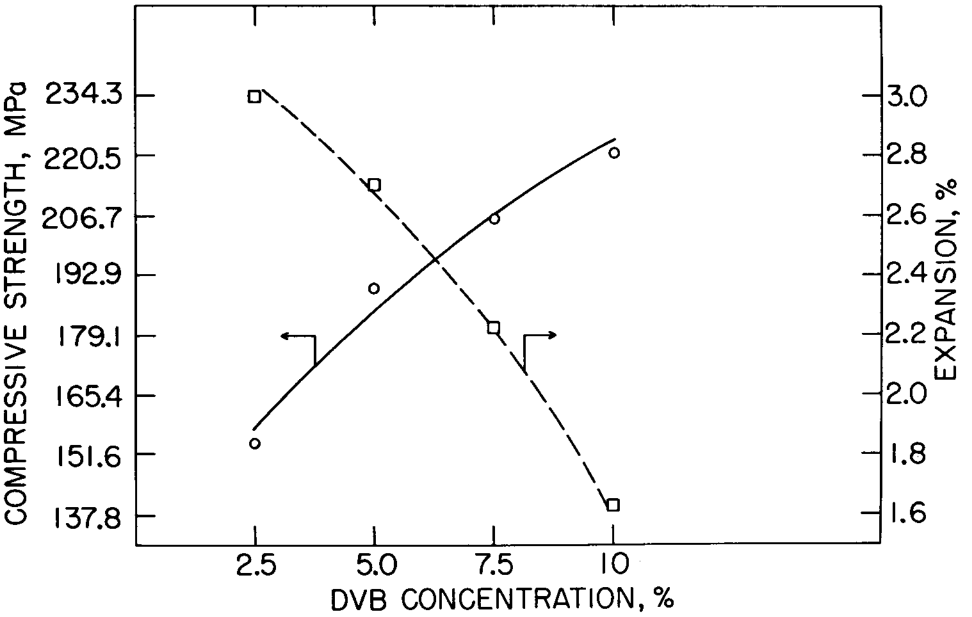


Figure 22. Compressive strength and expansion of PC samples vs DVB concentration after 30 days' exposure to brine at 240°C; monomer mixture: St-ACN-Aa; aggregate composition: sand-Type III portland cement.

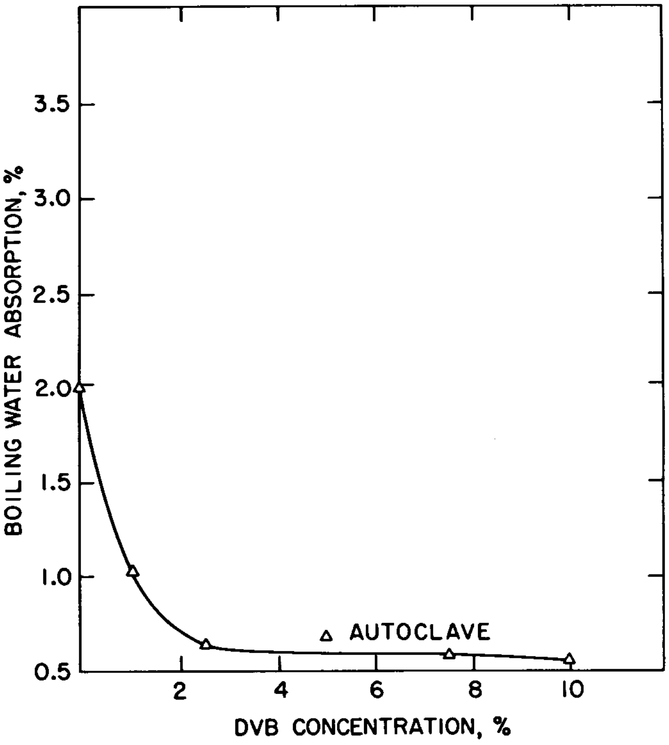


Figure 23. Boiling water absorption of PC as a function of DVB concentration.

The change in compressive strength of the PC samples measured at elevated temperatures after exposure to the brine solution for up to 90 days at 240°C is shown in Figure 24. The experimental results show that the strength decreases after a 60-day exposure as compared to a 30-day exposure, and then stabilizes and remains the same. Comparing strengths measured at the same test temperature before and after exposure, we see that the strength is increased after the exposure. This increase is a result of chemical reactions taking place in the hot brine environment.

2. PC Formation Mechanism. Portland cement is generally one of the aggregate components in PC formulations designed for use in hydrothermal environments. After exposure to hot brine, the dicalcium and tricalcium silicate compounds in the cement hydrate forming thermodynamically stable, mechanically durable needle-type tobermorite crystals[29] ($5CaO{\cdot}6SiO_2{\cdot}5H_2O$).

The slightly soluble tetraaqueous dicalcium silicate $2Ca\text{-}SiO_2\text{-}4H_2O$ and calcium hydroxide $CaO{\cdot}H_2O$ are separated as a result of the interaction of the calcium components of cement with steam. The high temperature and presence of $CaCl_2$ as one of the components of the brine facilitates acceleration of the hydrolytic decomposition of the tri- and dicalcium silicates owing to the formation of calcium hydrochloride with subsequent conversion to an insoluble product. Thus, if the first stage (formation of the composite material) involves bonding of the aggregate composition by the polymer, then the second stage (exposure to brine) involves additional hardening and formation of a microscopically inhomogeneous dispersed system. The hydrosilicate films formed under the

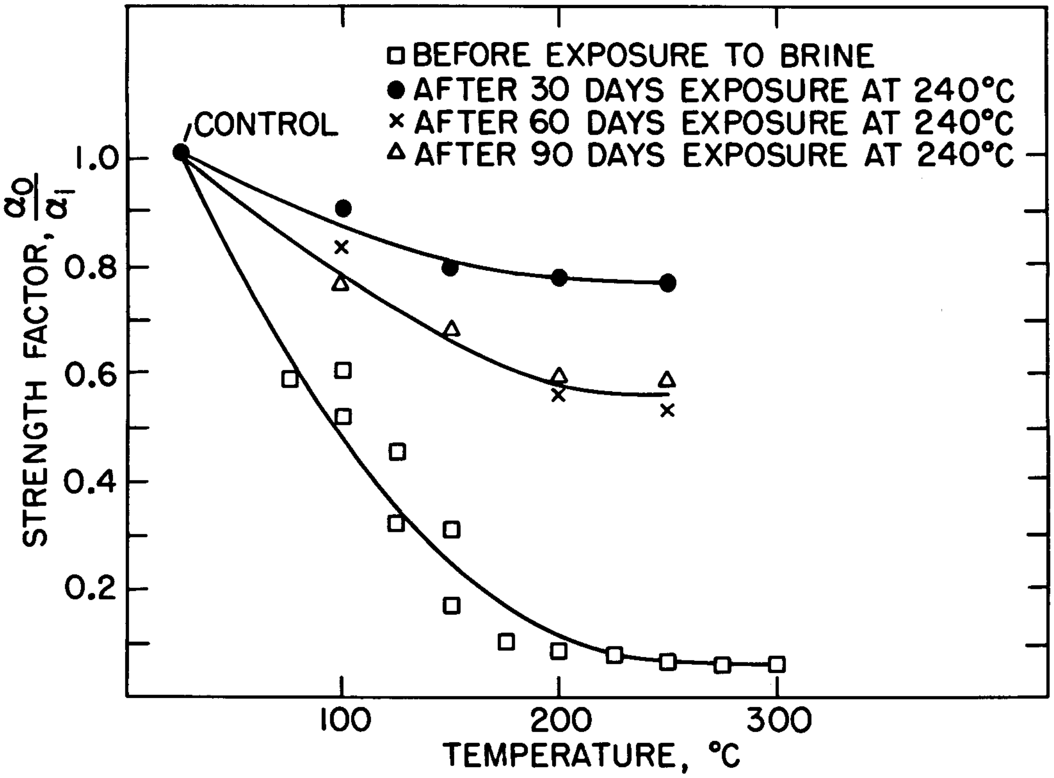


Figure 24. Strength factor for PC as a function of temperature. Monomer composition: 50 wt% St - 35 wt% ACN - 5 wt% Aa - 10 wt% DVB; aggregate composition: 70 wt% sand - 30 wt% Type III cement; monomer loading 13 wt%. α_i - initial strength; α_o - strength after exposure.

high-temperature and high-pressure conditions hinder further intensive formation of new crystals, because the recrystallization of finely divided crystals into larger crystals predominates over the process of newly formed crystals. This partially decreases the strength of the structure because of the local stress and microdefects caused by the crystal size.

3. Polymer Loading. Experiments to optimize the polymer loading with respect to the properties of the PC were performed and the results have been published.[8] The PC samples contained a monomer formulation consisting of 50 wt% St - 35 wt% ACN - 5 wt% Aa - 10 wt% DVB mixed with a 70 wt% silica sand - 30 wt% Type III portland cement aggregate. Samples containing from 13.0 to 27.5 parts of the monomer to 100 parts aggregate were tested and the results are given in Figure 25. Little change in strength and absorption was noted for polymer loadings between 13 and 20%. Further increases result in property reductions.

It is clear that the compressive strength of PC depends on the distribution of the polymer in the PC structure. To determine this influence, two PC samples with 15.0 and 27.5 parts of the monomer mixture were analyzed by using the scanning electron microscope and energy-dispersive x rays with a Si(Li) detector, which yields the atomic number concentrations ($C<Si<Ca$). Figure 26 shows the fractured surface of the PC samples which contain 15.0 parts polymer. The aggregate fills the pores, capillaries, and other voids of the tobermorite crystal, and concretions cover the newly formed crystals, which increases the strength, density, and strain-resistant characteristics of the PC composite material.

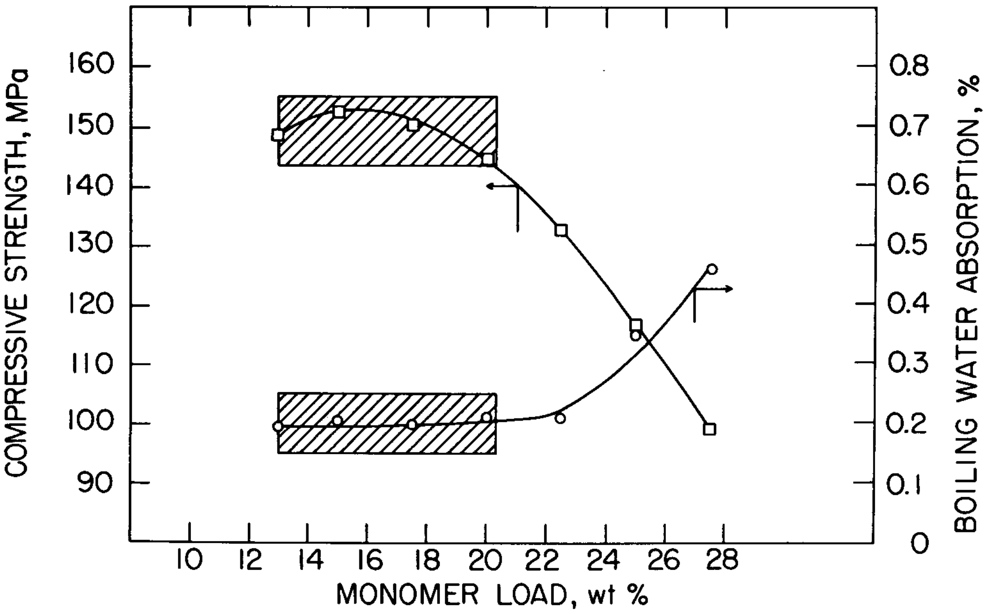


Figure 25. Effect of monomer loading on the compressive strength and boiling water absorption of PC.

Figure 26. Scanning electron microscope picture of fractured surface of PC sample containing a 15% polymer loading.

Figures 27 and 28 show the results from x-ray detector studies of two areas of this fracture. The polymer, which is distributed relatively uniformly between the Ca and Si, binds the Ca and Si (Figure 27 shows area A of Figure 26) in a continuous space lattice. As the monomer loading increases to 27.5 parts, the newly formed crystals completely separate from the thick polymer films (Figure 29), which hinders the formation of a strong crystal frame and results in regions of pure polymer. X rays show of two areas of one PC structure are shown in Figures 30 and 31. The formation of large polymer areas which divide the structure of the newly formed crystals, as seen in Figures 30 and 31, degrades the properties of the PC material.

The mechanism of PC formation at optimum monomer loading can be represented as follows. The adhesion of the aggregate particles occurs at the interface of the organic and inorganic molecules. The polymer molecules, which are absorbed by the particles of the filler, produce an oriented microlayer whose thickness depends on the mass content of the monomer in the original mixture. The energy of the adsorption bond depends on the surface energy. The carrier of high surface energy during the formation of the PC composite material is sand.

The changes in the structure and properties of PC caused by changes in the sand-to-cement ratio are shown in Figures 32 and 33, respectively. The results indicate that the strongest PC with the lowest coefficient of water absorption is produced when 65 to 90 parts of sand are used with 35 to 10 parts of cement. A further reduction in the amount of sand destroys the uniformity of contact between the carrier of high surface energy (sand) and the molecules of the polymer, and thus destroys the mechanical strength of the composite.

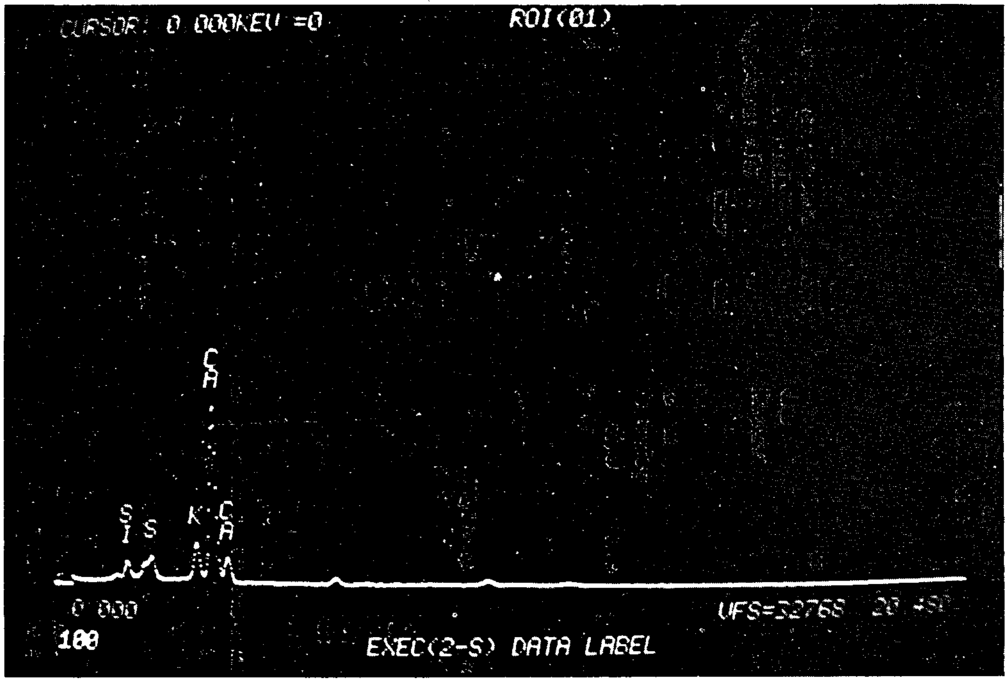


Figure 27. Energy-dispersive x-ray spectrum made with Si(Li) detector. Area A of Figure 26.

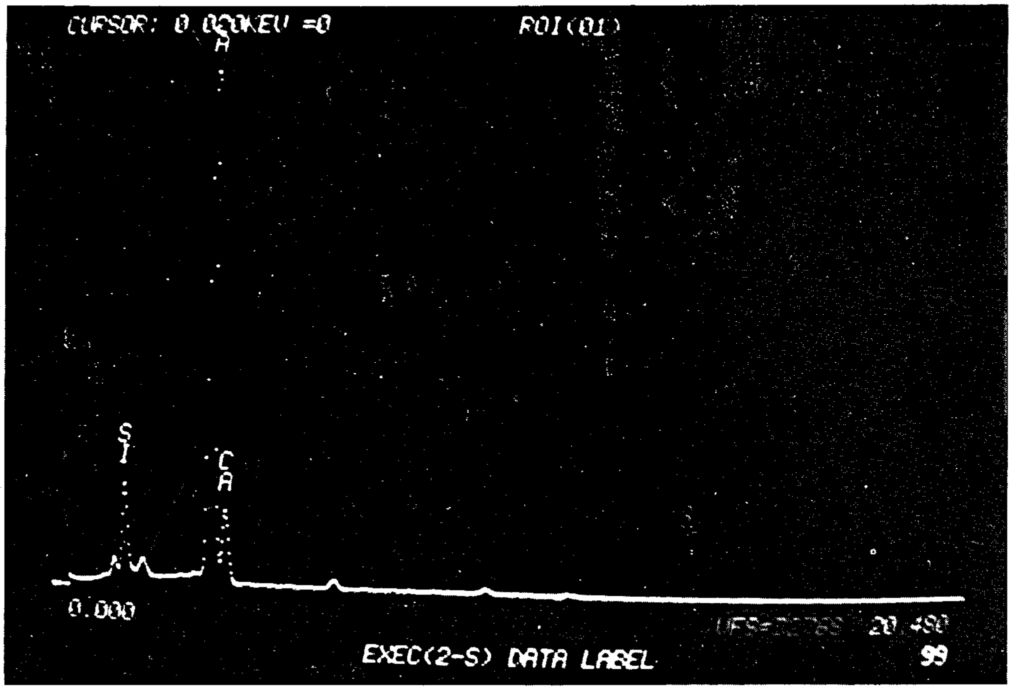


Figure 28. Energy-dispersive x-ray spectrum made with Si(Li) detector. Area B of Figure 26.

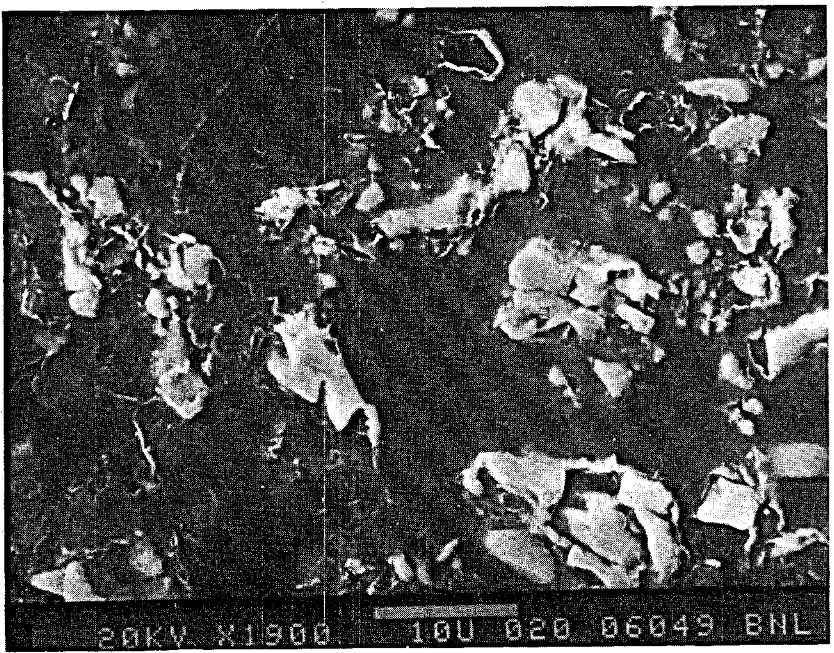


Figure 29. Scanning electron microscope picture of fractured surface of PC sample containing a 27.5% polymer loading.

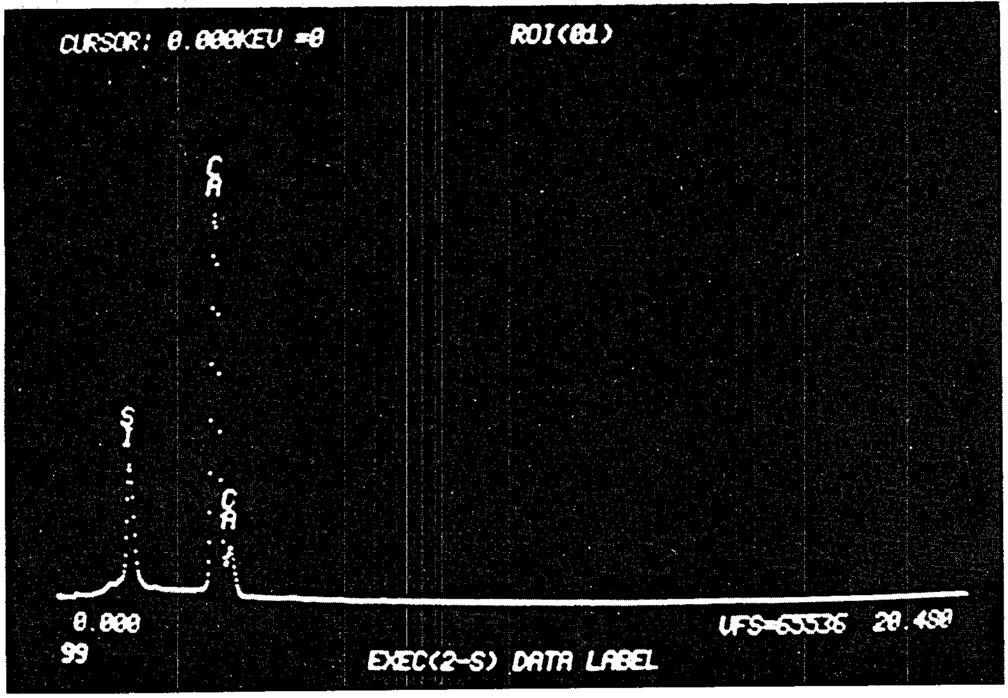


Figure 30. Energy-dispersive x-ray spectrum made with Si(Li) detector. Area B of Figure 29.

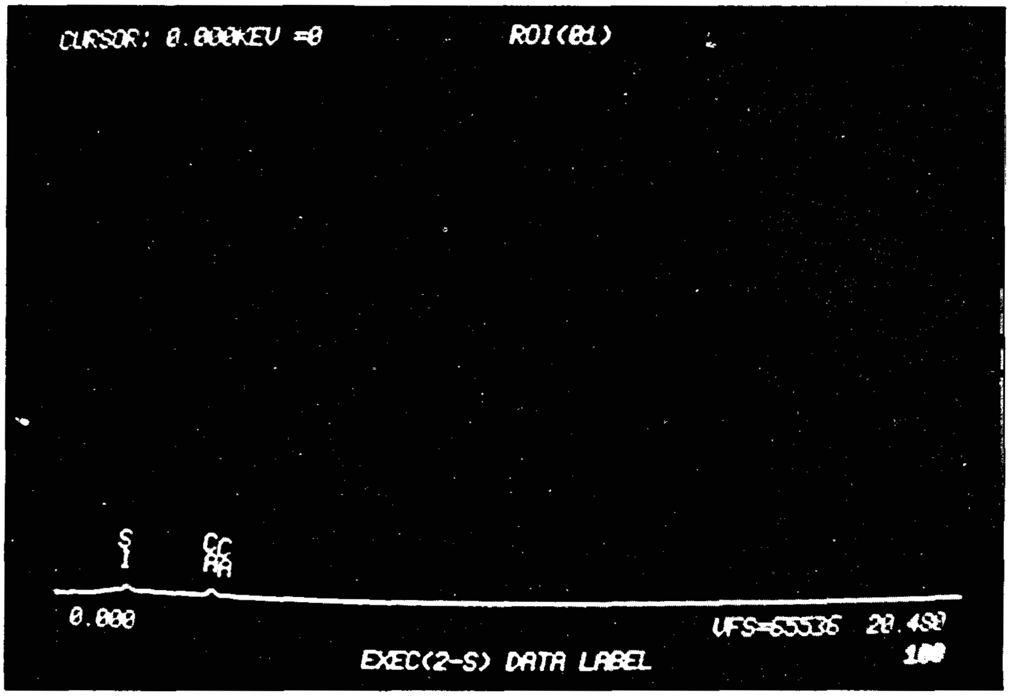
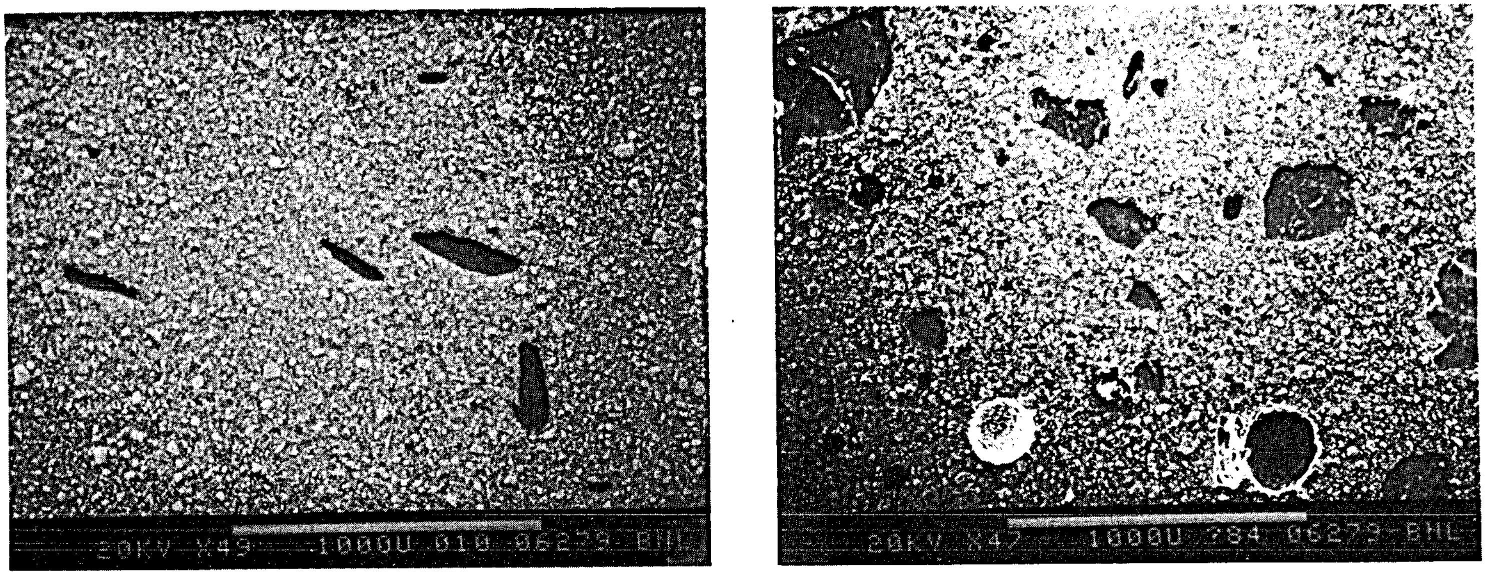
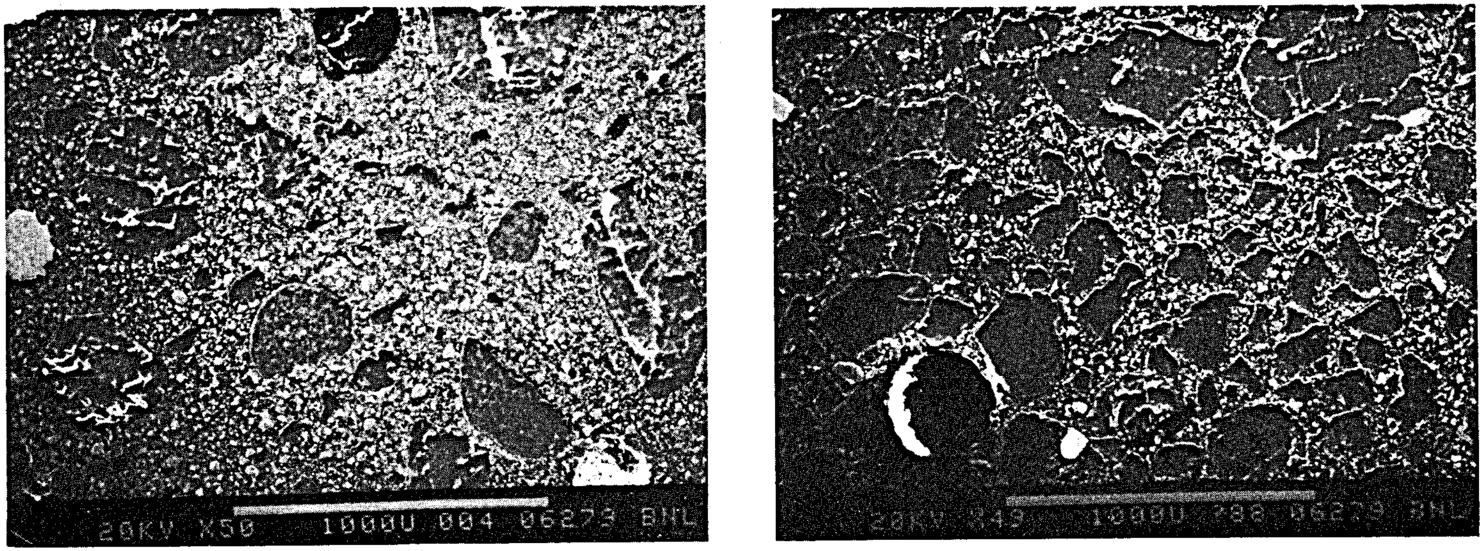


Figure 31. Energy-dispersive x-ray spectrum made with Si(Li) detector. Area A of Figure 29.



0 wt% Sand

20 wt% Sand



50 wt% Sand

80 wt% Sand

Figure 32. Effect of sand content in aggregate on the structure of PC.

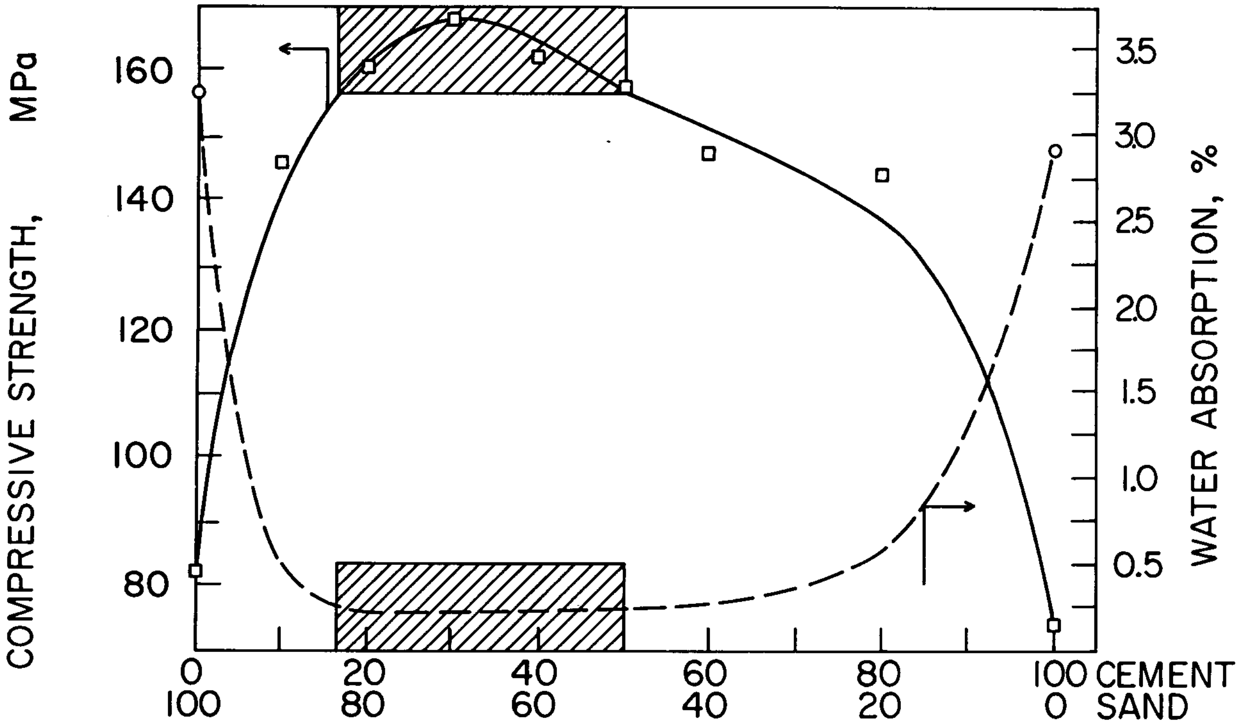


Figure 33. Effect of sand-cement ratio on the properties of PC.

C. Long-Term Durability Tests

On the basis of the results from the above studies, two PC formulations were selected for long-term exposure testing in a 25% synthetic geothermal brine at 240°C in a laboratory autoclave. The composition of the brine is given in Table 3. The formulations tested were as follows: (1) 11.5 wt% (55 wt% St - 35 wt% ACN - 5 wt% Aa - 5 wt% TMPTMA) - 88.5 wt% (70 wt% silica sand - 30 wt% Type III portland cement); (2) 11.5 wt% (50 wt% St - 35 wt% ACN - 5 wt% Aa - 10 wt% DVB) - 88.5 wt% (70 wt% silica sand - 30 wt% Type III portland cement).

Results from compressive strength tests performed after exposures up to 360 days are summarized in Figure 34. The data indicate that the strength of the DVB-containing formulation increased at an early stage of exposure and then stabilized at a value of ~230 MPa. The strength of the PC containing TMPTMA decreased from an initial value of ~195 MPa to ~90 MPa before stabilizing. This is probably caused by the low dissociation energy of the TMPTMA which results in partial degradation of the molecular chain during the hydrothermal exposure.

IV. RESULTS - ORGANOSILOXANE PC FORMULATIONS

Organosiloxanes used in this study were as follows: dimethylpolysiloxane modified with pendant vinyl groups (Y-9208), tetramethyltetravinylcyclotetrasiloxane (RZ), and polydimethylsiloxane (V-47). Filler materials used were silica sand and portland cement. PC fabrication procedures were the same as those described earlier for the organic formulations.

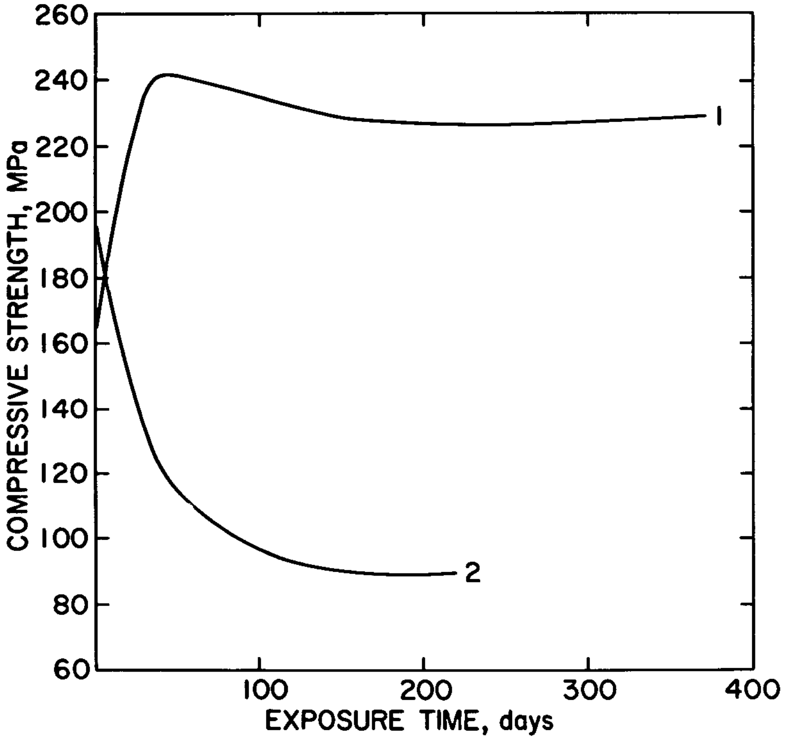
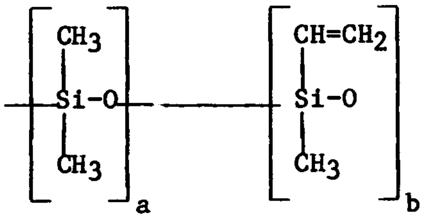


Figure 34. Compressive strength of polymer concrete after exposure to 25% brine solution at 240°C.
Monomer system: 1. 50 wt% St - 35 wt% ACN - 5 wt% Aa - 10 wt% DVB
2. 55 wt% St - 35 wt% ACN - 5 wt% Aa - 5 wt% TMPTMA
Aggregate: 70 wt% silica sand - 30 wt% Type III portland cement
Monomer load - 13 wt%

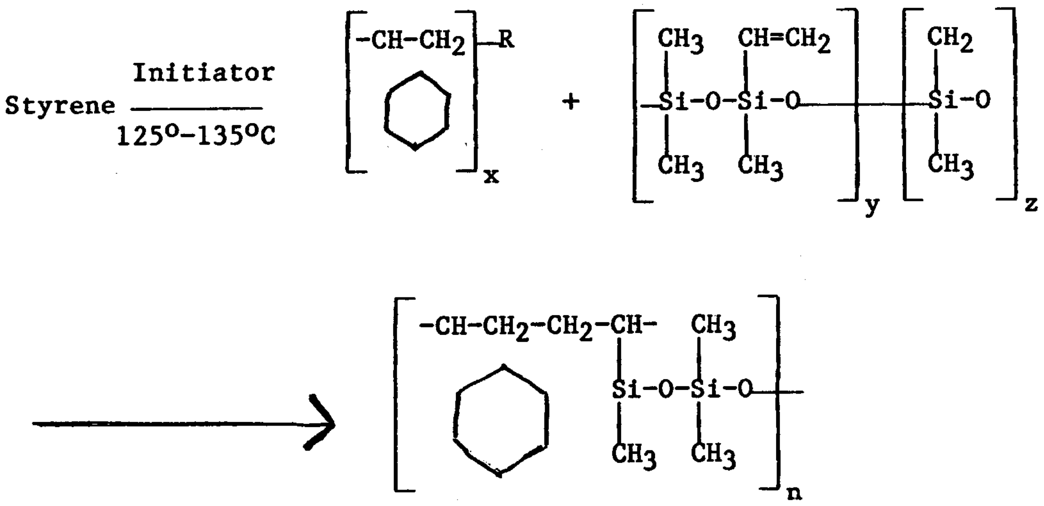
Monomer Y-9208 has the following structure:



$$-\left[\mathrm{Si(CH_3)_2{-}O}\right]_a-\left[\mathrm{Si(CH{=}CH_2)(CH_3){-}O}\right]_b-$$

where the magnitude of (a) is a function of the percentage of pendant vinyl groups (b). St, MMA, DVB, etc. can be added to the Y-9208 as comonomers in order to produce a three-dimensional structure.

Block copolymers of Y-9208 and St were prepared by a free-radical reaction initiated by DTBP. The possible reaction mechanism is given below.



Various copolymers were made and tested for thermal stability. These data are presented in Table 8. As can be seen from the results in the table, a copolymer based on a 3:1 ratio of Y-9208 to St appears to be the most thermally stable material.

As shown in Figure 35, the thermal stability is also improved by increasing the initiator concentration and curing temperature.

Table 8

Thermal Stability of Various Siloxane Copolymers

Monomer composition, wt%		Cross-linking concentration, wt%	Initiator, DTBP wt%	Curing time, hr	Curing temperature, °C	Polymer weight loss,[a] wt%			
Y-9208[b]	Styrene					250°C	300°C	350°C	400°C
100	0	0	0.5	4	155				
				and 2	185	0.02	0.05	1.0	1.03
85	15	0	0.5	16	160	0.25	0.6	1.25	3.0
80	20	0	0.5	64	150	1.25	1.3	2.48	6.25
80	20	0	1.0	64	150	0.5	0.6	1.3	5.2
75	25	0	0.5	16	100				
				and 4	155	0	0	0.4	2.7
70	30	0	0.5	64	150	1.2	1.28	3.5	9.8
60	40	0	0.5	16	145	1.4	2.5	3.75	9.5
80	0	20[c]	0.5	16	145	0.2	0.6	1.1	2.5
75	20	5[d]	0.5	16	150				
				and 2.5	200	0	0	1.8	8.4
75	23.5	1.5[e]	0.5	64	105				
				and 3	155	0.2	0.2	1.0	3.1
75	23	2[f]	0.5	64	105				
				and 3	155	1.0	1.0	1.3	5.0

[a] Measured in N_2 atmosphere with Du Pont 990 and TGA module.

[b] Y-9208 is an organosiloxane from Union Carbide.

[c] Trimethylolpropane trimethacrylate.

[d] Triallyl cyanurate.

[e] n-phenylmalimide.

[f] Divinyl benzene.

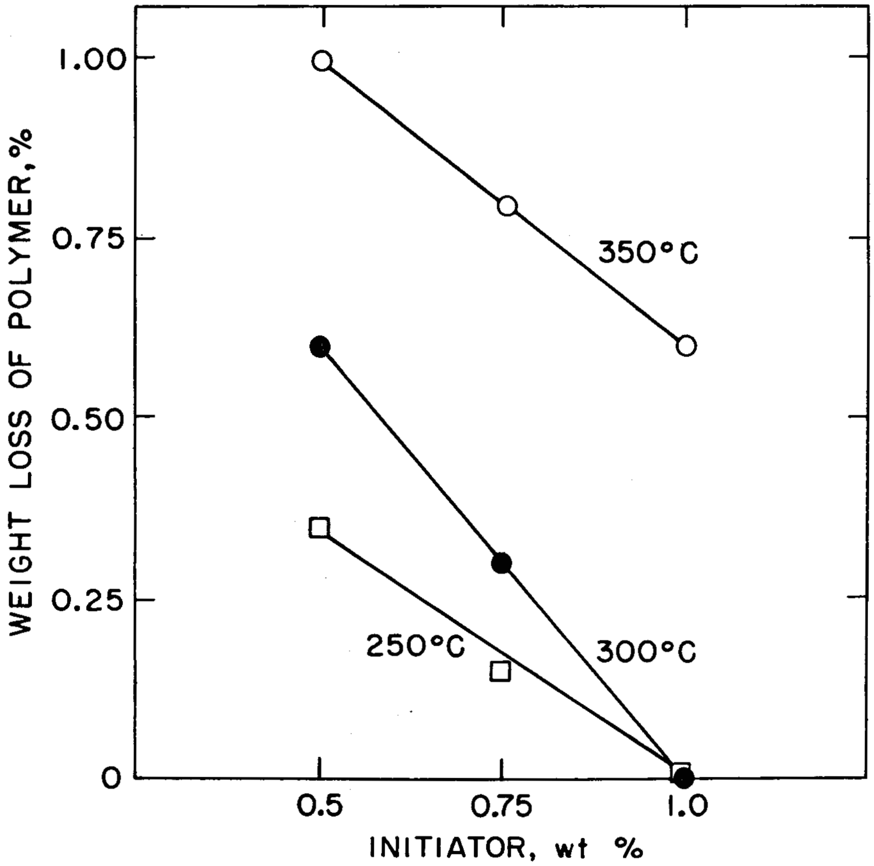
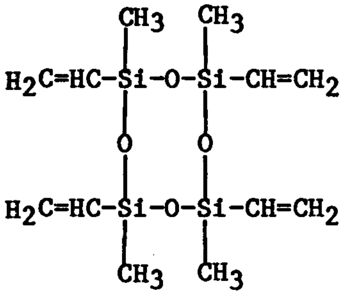


Figure 35. Effect of initiator concentration and temperature on the polymer thermal stability. Monomer system: 75 wt% Y-9208 - 25 wt% St. Polymerization conditions: 136°C for 1 hr and 70°C for 1.5 hr.

The hydrolytic stability of the copolymer consisting of 3 parts Y-9208 and 1 part St was determined by exposing samples to 25% brine at 250°C for 360 hr.

The results indicated no appreciable weight loss or deterioration. Infrared spectra made on the copolymer before and after the brine exposure indicated the formation of weak peaks in the region 3700 to 3600 cm^{-1} corresponding to free OH groups. These are shown in Figure 36. Peaks at 940 to 930 cm^{-1} corresponding to ($-CH=CH_2$) groups, decreased after exposure to brine. This small amount of hydrolysis was essentially eliminated when the polymer system was used in PC by inclusion in the aggregate of a buffer such as Mg^{2+} or Ca^{2+} ions.

The chemical structure of monomer RZ is as follows:



When the RZ was copolymerized with siloxane V-47, maximum stability occurred at an RZ concentration of 97 wt%. This is shown in Figure 37 where each point on the curve represents the average of four test specimens.

Copolymer specimens containing 97 wt% RZ - 3 wt% V-47 were exposed to a 25% brine solution at 250°C for 360 hr. No appreciable weight loss or deterioration was detected. IR analyses before and after the brine exposure showed the formation of free OH groups, indicating some hydrolysis.

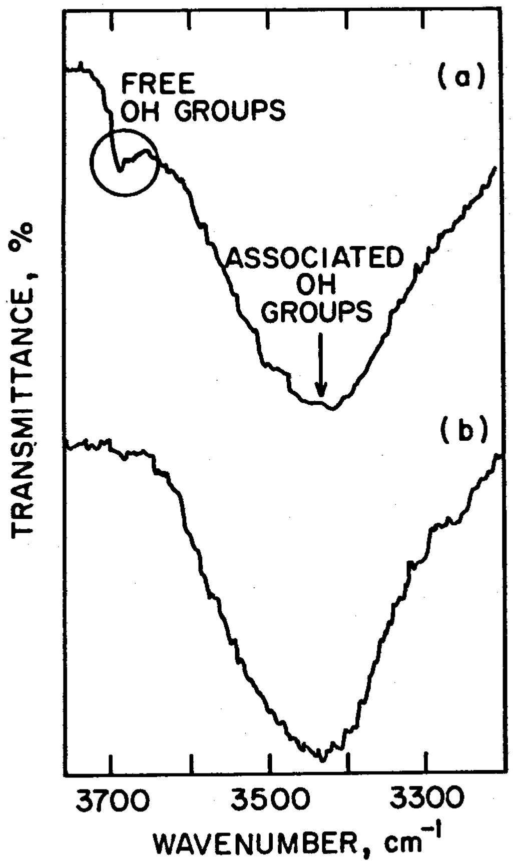


Figure 36. Infrared spectra of siloxane polymer system before and after exposure to 250°C brine. Organosiloxane monomer mixture of 75 wt% Y-9208 - 25 wt% St. (a) after exposure; (b) before exposure.

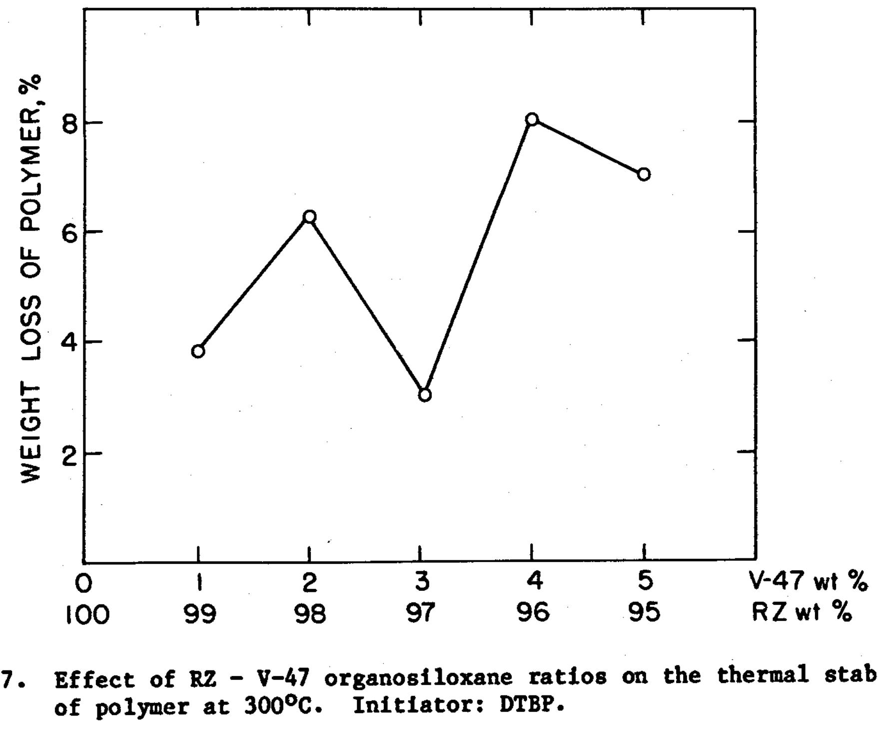


Figure 37. Effect of RZ - V-47 organosiloxane ratios on the thermal stability of polymer at 300°C. Initiator: DTBP.

Heating the Y-9208 - St copolymer in air at 260°C results in severe oxidization. However, when the copolymer is incorporated in PC containing a sand-cement filler, the resistance to oxidation is significantly improved.

A. Sand Particle Size

It is well known that the effect of the particle size of the silica sand on the properties of PC is dependent upon the viscosity of the monomer formulation. When low-viscosity (~1 cP) organic monomers are used in PC, the properties are maximized by use of a mixture of sand sizes: the monomer can easily be mixed with the filler to wet the particles and to fill the voids in the aggregate. When the viscosity of the monomer mixture is increased, the percentage of filler that the monomer wets decreases and the result is nonuniform polymer loading which decreases the durability and strength of the PC.

The effect of the sand particle size on the strength of PC containing a 75 wt% Y-9208 - 25 wt% St mixture (viscosity >100 cP) is given in Table 9. Increased strength with decreasing particle size is apparent.

B. Cement Filler Composition

As shown in Table 9, the inclusion of portland cement as a partial constituent to the aggregate in siloxane PC improves the properties of the composite. Four commercially available cements were evaluated to determine which yielded the best results. In this study, portland cement Types I, II, III, and V were used in conjunction with two siloxane systems. The results are summarized in Table 10. The data exhibit considerable scatter, and no specific trends are apparent.

Table 9

Compressive Strength of Organosiloxane as a Function of Sand Particle Size

Monomer composition, wt%[a]		Aggregate composition		Compressive strength, MP
OS[b]	St[c]	wt%	Sieve opening, µm	
75	25	100	<30	41.6
75	25	100	150	12.5
75	25	100	600	4.7
75	25	90 10	<30 Type III cement	85.2
75	25	90 10	150 Type III cement	31.6
75	25	90 10	600 Type III cement	21.8
75	25	36* 17 17 30	1180 600 150 Type III cement	40.3

---

[a] Monomer loading, 35 wt%.
[b] OS, Organosiloxane Y-9208
[c] St, Styrene.
*Aggregate composition, used for organic systems.

Table 10

Properties of PC as a Function of Cement Type

Monomer composition,[a] wt%	Aggregate composition, wt% sand[b]	cement	Cement type	Boiling H_2O absorption, %	Compressive strength, MPa	Modulus of elasticity, MPa
75 Y-9208 - 25 St[c]	90	10	I	0.075	111.8	6500
			II	0.072	46.6	4301
			III	0.03	119.3	5175
			V	0.02	100.7	4825
97 RZ - 3 V-47[d]	95	5	I	0.06	81	—
			II	0.09	111.2	—
			III	0.1	70.5	—
			V	0.09	49.1	—
	90	10	I	0.07	106.9	6826
			II	0.08	101.6	—
			III	0.05	52.9	6791
			V	0.11	74.39	7226

[a] Monomer concentration, 35 wt%.
[b] Particle size - sieve opening <30 μm.
Curing condition;
[c] 110°C, 18 hr; 165°C, 40 hr.
[d] 110°, 18 hr; 135°C, 3 hr; 170°C, 2 hr; curing agent: 1.0 wt% DTBP.

In general for the two monomer systems, the use of a 10 wt% concentration of Type I cement resulted in the highest average strength and modulus of elasticity. Little effect on the water absorption due to cement composition was apparent.

C. Sand-Cement Ratio

A study to determine the optimum ratio of sand to cement that should be used in RZ - V-47 organosiloxane PC was also performed. The results from compressive strength tests made before and after exposure of samples in autoclaves to brine at temperatures of 275° and 300°C are summarized in Table 11. The data indicate that PC samples containing cement up to a concentration of 15% are stable after exposure to brine at 275°C. Only the composites containing sand and cement in ratios of 95:5 and 90:10 showed stability at 300°C. The boiling water absorption which is indicative of the permeability shows a tendency to increase as the cement content is increased. The compressive strength appears to be at a maximum when the cement concentration is in the range 5 to 12%. The inclusion of a wetting agent (Triton X-100 from the Baker Chemical Co.) did not change these tendencies. Several samples after brine exposure at 300°C for 30 days are shown in Figure 38.

IR and SEM studies performed on the specimens before and after exposure at 300°C did not indicate changes in structure. IR results are shown in Figure 39.

Table 11

Sand-Cement Ratio for System RZ - V-47 (Ratio 97:3)

Aggregate ratio, wt%			Compressive strength, MPa after			Modulus of elasticity, MPa
Sand[a]	Cement[b]	Boiling water absorption wt%	Boiling water	30 days in autoclave at 275°C	30 days in autoclave at 300°C	After exposure to hot brine for 30 days at 300°C
100	0	0.02	49.9	48.3	—	--
95	5	0.08	74.2	55.9	79.6	8845
90	10	0.07	90.2	69.7	57.1	7963
85	15	0.04	36.2	40.6	—	--
80	20	0.54	15.2	weak	—	--
70	30	0.69	34.2	weak	—	--
95[c]	5	0.09	89.1	48.5	60.9	9100
90[c]	10	0.12	46.4	107.2	62.8	5460

Initiator 1/2 wt% DTBP; 1/2 wt% Silane A-174
Curing condition: 125°C, 16 hr;
150°C, 3 hr;
180°C, 3 hr.

[a] Particle size - sieve opening <30 μm.
[b] Portland cement Type III.
[c] These samples were made by using wetting agent.
Monomer concentration, 35 wt%.

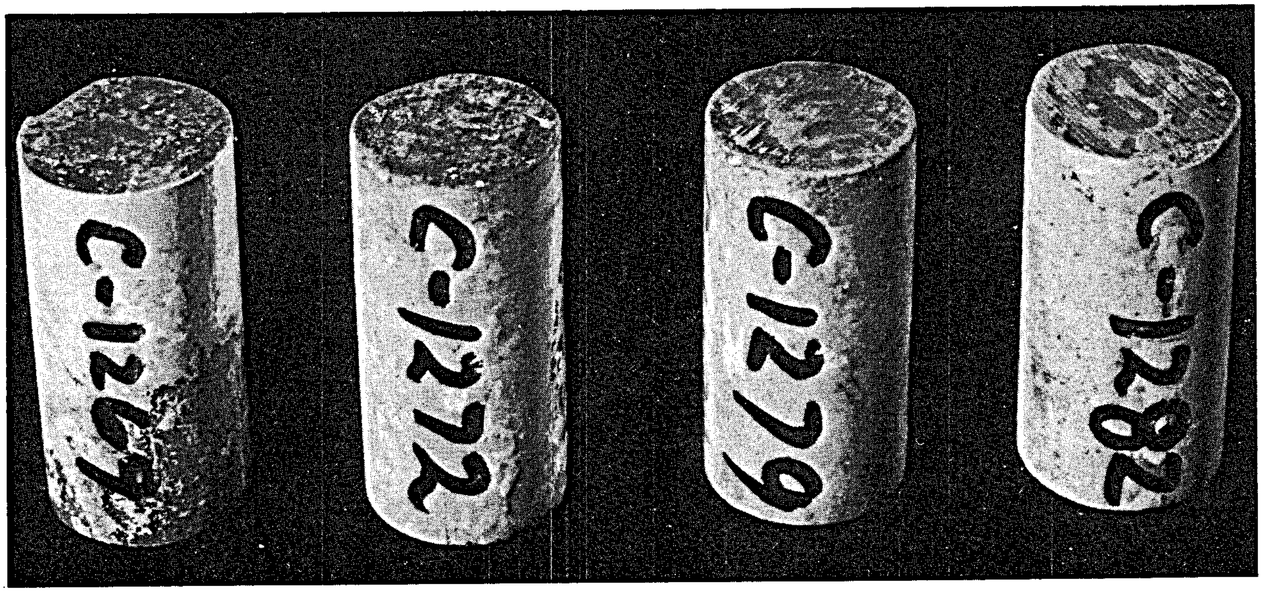


Figure 38. Organosiloxane PC samples after exposure in brine at 300°C for 30 days.

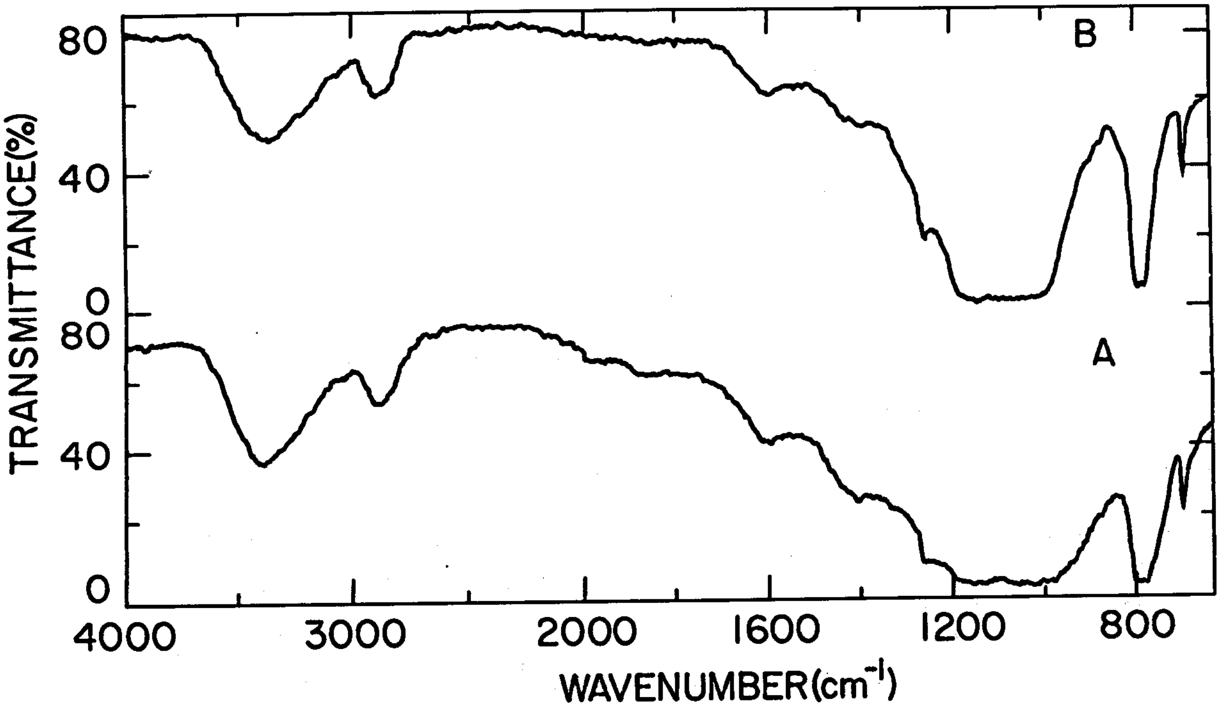


Figure 39. Infrared absorption spectra of organosiloxane PC samples before (a) and after (b) exposure to brine at 300°C.

V. WELL-CEMENTING PROPERTIES

In addition to strength and durability, there are other equally important properties that a well cement must exhibit. These include low permeability, good bond strength to steel casing, and a curing rate which allows the cement to be pumped into a well. Tests to measure these characteristics are described in this section.

A. Permeability

Three PC formulations (two organic, one semi-inorganic) were selected for testing on the basis of the results from the experimental efforts described in Sections III and IV. The compositions are as follows:

1. 12 wt% monomer (155 wt% St - 35 wt% ACN - 5 wt% Aa - 5 wt% TMPTMA)-88 wt% filler (70 wt% silica sand - 30 wt% Type III portland cement)
2. 12 wt% monomer (50 wt% St - 35 wt% ACN - 5 wt% Aa - 10 wt% DVB) - 88 wt% filler (70 wt% silica sand - 30 wt% Type III portland cement)
3. 37 wt% monomer (97 wt% RZ - 3 wt% V-47) - 63 wt% filler (90 wt% silica sand - 10 wt% Type III portland cement)

The permeability tests were conducted in accordance with the American Petroleum Institute's (API) recommended practice for testing oil-well cements and cement additives.[30] The results from the tests indicated that the organic PC formulations had an initial water permeability in the range 0.001 to 0.002 millidarcy. After exposure to a 25% brine solution at 240°C for 150 days, the permeability increased to the range 0.01 to 0.02 millidarcy, values within the design criteria for geothermal well cements.

Tests were performed using the same procedure on the organosiloxane PC before and after exposure to brine at 300°C for 120 days. After 48 hr in the permeability test equipment with a pressure differential of 344.5 kPa, no water penetration was measured.

B. Bond Strength to Steel

Currently there are no ASTM standards for measuring the shear bond strength of PC materials. The procedure used at BNL was as follows: The mold for preparing the bonding strength samples consisted of a base made of wood, carbon steel pipe measuring 42 mm o.d. x 100 mm long, and a glass tube measuring 58 mm i.d. x 100 mm. The steel pipe was placed inside of the glass tube and both were sealed to the base with silicone rubber cement. PC slurry, prepared as described earlier, was poured into the anulus betweeen the glass and the steel. The filled mold was placed in an oven at the required curing temperature to form PC composite bonded to the outer surface of the pipe.

The bonding strength test was performed by placing a metal ring on the PC portion of the test sample and applying a load on the pipe in a compression tester. The load was recorded and the stress was calculated by taking the area of the pipe surface that was covered with PC and dividing it into the load.

The results indicate that PC samples have bonding strengths in range of 3000 to 4000 kPa for the organic formulations and 150 to 200 kPa for the semi-inorganic formulations. Both systems yielded results greater than the design criteria.

C. Pumpability Tests

Two types of tests were performed to determine the pumpability of the selected PC formulations. Prior to initiating these tests, work was conducted to reduce the viscosity of the formulations to a value of 20 to 40 units of consistency, the approximate initial viscosity of inorganic cement slurries used in the completion of oil and geothermal wells. This was accomplished by increasing the monomer concentrations in the organic and semi-inorganic PC formulations to 20 and 35.5 wt%, respectively. To meet the pumpability requirements, it is essential that the viscosity of the slurry remain <100 units of consistency for ~4 hr at the placement temperature and pressure conditions.

Preliminary tests were performed in a pressure vessel equipped with a stirrer to obtain data on the curing times of both formulations as a function of pressure and temperature. Attempts were also made to correlate the stirrer speed with slurry viscosity during the polymerization reaction, but the amount of scatter made it impossible to obtain quantitative data.

The results from the preliminary pumpability tests, summarized in Table 12, indicated that the St-based formulation exhibited little change in viscosity after 4 hr at 70°C and a pressure of 264 MPa. The siloxane PC yielded similar results after 4 hr at 149°C and 68 MPa.

On the basis of these data, API pumpability tests were performed on the two systems using the high-pressure consistometer at the Dowell Division of Dow Chemical U.S.A. The results from these tests are given in Figures 40 to 43. As indicated in Figure 40, the organic PC slurry (20 wt% monomer, 80 wt% filler) had an initial viscosity in the range

Table 12

Summary of Results From Preliminary Thickening Time Tests

Monomer composition, wt%	Aggregate composition, wt%		Monomer concentration, wt%	Time, hr	Test conditions		Polymerization,	
	sand	cement			pressure, MPa (psi)	temperature, °C (°F)	yes	no
50 St - 35 ACN - 5 Aa -10 DVB	70	30	20	4	264.(3000)	70(158)		+
				4	264.(3000)	75(167)	+	
97 RZ - 3 V-47	90	10	35.5	4	68.(1000)	204(400)	+	
				4	68.(1000)	149(300)		+
				3.5	68(1000)	177(350)	+	
				2.5	264.(3000)	168(325)	+	
				0.2[a]	264.(3000)	149(300)	+	

[a] 0.1 wt% DTBP was added to the monomer mixture.

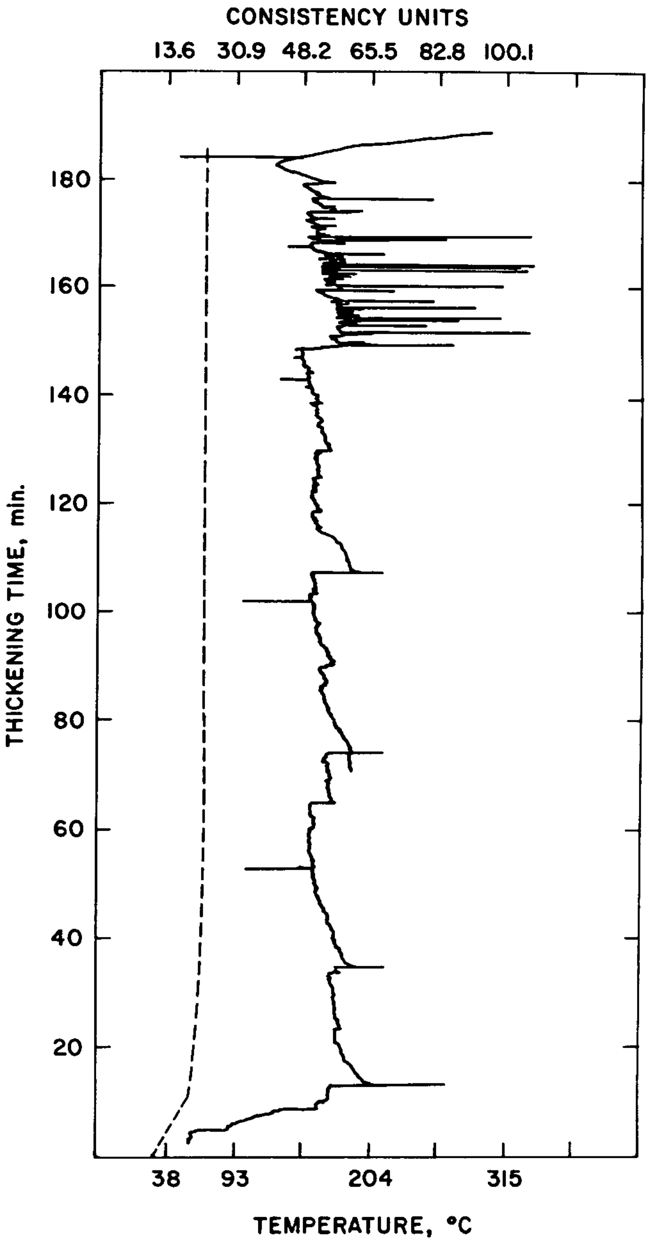


Figure 40. API thickening time test. Monomer composition: 50 wt% St - 35 wt% ACN - 5 wt% Aa - 10 wt% DVB, sand-cement ratio: 70-30. Temperature: 70°C. Monomer load: 22%. Pressure: 36.5 MPa. Temperature gradient: 3.7°C/min.
---- temperature curve
—— viscosity curve

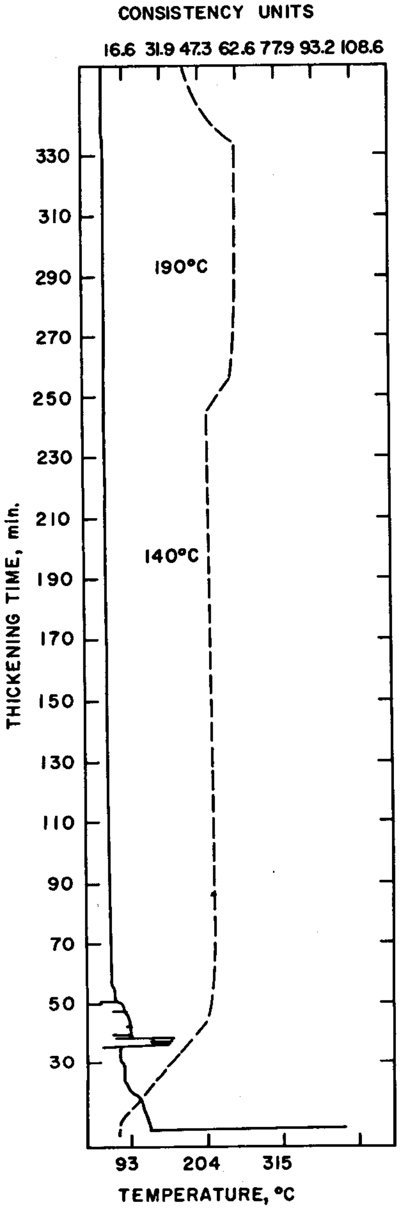


Figure 41. API thickening time test. Monomer composition: 97 wt% RZ - 3 wt% V-47; Aggregate composition: 90 wt% silica flour - 10 wt% Type III cement; Monomer load: 55 wt%; Pressure: 36.5 MPa.
---- temperature curve
—— viscosity curve

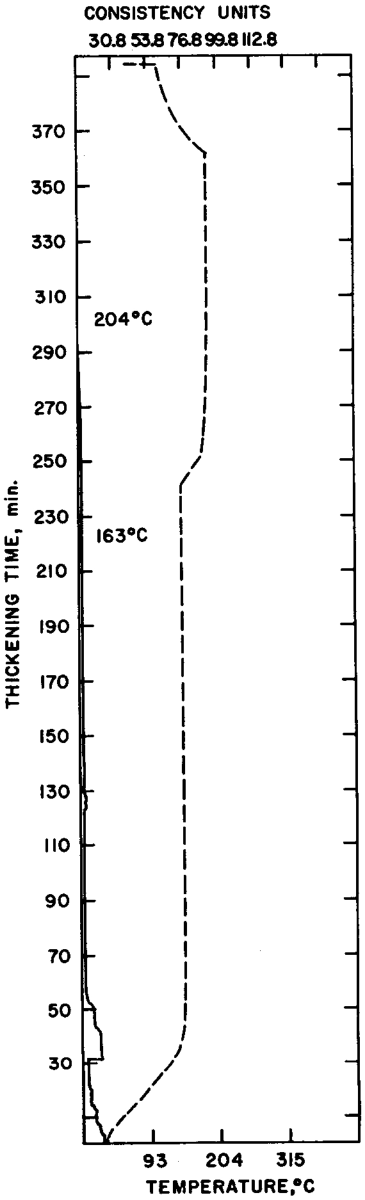


Figure 42. API thickening time test. Monomer composition 97 wt% RZ - 3 wt% V-47; Aggregate composition: 90 wt% sand flour - 10 wt% Type III cement. Monomer load: 55 wt%. Pressure: 36.5 MPa.
---- temperature curve
—— viscosity curve

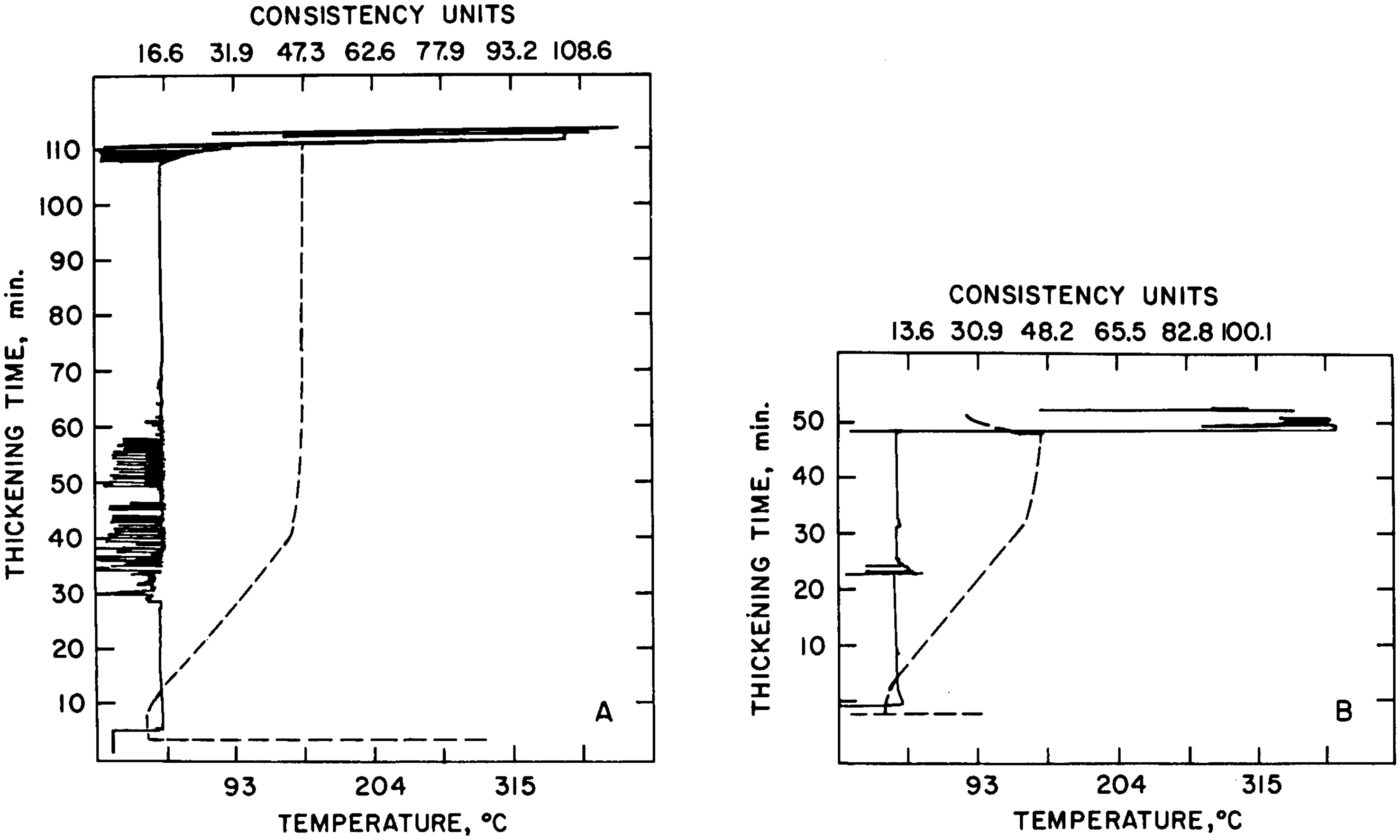


Figure 43. API thickening time test. Monomer composition: 97 wt% RZ - 3 wt% V-47; Aggregate composition: 90 wt% silica flour - 10 wt% Type III cement. Monomer load: 55 wt%. Pressure: 36.5 MPa. (A) Initiator DTBP 0.0062 wt%; (B) Initiator DTBP 0.05 wt%.
---- temperature curve
—— viscosity curve

30 to 65 consistency units. At a pressure of 36.5 MPa and a temperature of 70°C, the viscosity remained essentially constant for 180 minutes and then increased to over 100 consistency units as the PC started to gel.

The results for the siloxane (97 wt% RZ - 3 wt% V-47) PC formulation indicate that without an initiator the viscosity remains constant at a temperature in the range 149° to 163°C and a pressure of 36.5 MPa for at least 4.5 hr. These results are given in Figures 41 and 42. Increasing the temperature to 204°C resulted in a viscosity change after 4 hr.

The effects of the addition of the initiator DTBP on the pumpability are shown in Figure 43. At a temperature of 149°C and pressure of 36.5 MPa, reductions in the concentration of DTBP from 0.05 to 0.0062 wt% increase the thickening time from 50 to 110 minutes.

VI. MATERIALS COSTS

Since it appears probable that conventional equipment can be used to mix and place PC, the labor and equipment costs for well cementing are assumed to be similar to those when standard cementing materials are used. However, when compared with conventional well-cementing materials, the materials costs for PC are high. Materials costs for the two formulations selected, based on unit material cost as of November 1979, are given in Table 13.

Small quantities of the organic compositions based on St-ACN-Aa (<10 m^3) cost approximately \$600/m^3. Larger quantities of the materials will cost 10 to 15% less.

The inorganic composition based on RZ - V-47 costs approximately \$30,000/m^3. Since these materials are currently produced in only experimental quantities, their costs are exceptionally high. If this system is to be used as a well-cementing material, the manufacture

Table 13

Polymer Cement Geothermal Well Completion Materials Costs*

Material	Quantity, kg/m^3 of PC	Unit cost, \$/kg	Total, \$/m^3 of PC
Organic formulations (50 wt% St - 35 wt% ACN - 5 wt% Aa - 10 wt% DVB) (PC density, 2320 to 2400 kg/m^3)			
Sand	1040	0.092	95.68
Cement	446	0.094	41.92
Styrene	180	1.10	198.00
Acrylonitrile	115	1.09	125.35
Acrylamide	17	1.77	30.00
Divinyl benzene	33	1.35	44.55
A-174	3.3	22	72.60
		Total \$/m^3	608.20
Inorganic formulations			
RZ	624	49.20	30700.8
V-47	20	7.25	145.00
Sand	1200	0.092	110.40
Cement	120	0.094	11.28
		Total \$/m^3	30968

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*All calculations made based on m^3 of well-cementing material.

of the monomers would be on a larger scale, and it is estimated that the price could be reduced substantially.

CONCLUSIONS

The goal of this study was to develop thermally and chemically stable composites that can withstand highly reactive geothermal environments and are also pumpable. Two years of laboratory study indicate that PC consisting of a mixture of high molecular weight copolymer as a binder and silica sand - cement mixtures as a filler could be used as geothermal well-completion materials.

A number of monomers, organic and semi-inorganic, in conjunction with varying types of cement and sand particle sizes have been studied for their potential as geothermal cementing materials.

Major emphasis in this study has been given to determining the monomer ratio based on the reactivity of each component in the monomer mixture as well as sand-cement ratio. The objective of these experiments was to optimize the conditions when the combination of polymer and filler forms thermally and hydrolytically stable composites with three-dimensional structures.

On the basis of the laboratory evaluation the following systems have been selected for use in geothermal wells and will be sent to the National Bureau of Standards for continued evaluation:

1. Organic PC formulation based on 50 wt% St - 35 wt% ACN - 5 wt% Aa - 10 wt% DVB. This monomer composition in mixture with sand-cement at ratios of 7:3 appears to be suitable for use as a well-cementing material for low temperature (~240°C) applications.

2. Inorganic PC formulation based on 97 wt% RZ - 3 wt% V-47 in composition with a mixture of sand flour and cement at ratios of 9:1 can be used as a well-cementing material for high-temperature applications (~300°C).

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