Polymer Systems in Geothermal Applications

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Synopsis

The feasibility of using a copolymer composed of styrene, acrylonitrile, and acrylamide or methacrylamide in the formation of a high-strength thermally and chemically stable polymer concrete for use in geothermal environments has been demonstrated. Specimens produced with the copolymer in conjunction with an aggregate containing sand and portland cement had compressive strengths in the range of 25,000 to 30,000 psi at 20°C and were thermally stable up to ~240°C. A study of the effect of monomer concentration on the properties of the polymer concrete indicated that the optimum concentration is in the range of 12 to 13 wt. %. Increased monomer concentrations lead to a nonuniform polymer distribution within the composite, resulting in a deterioration of the properties. The optimum properties are obtained when the monomer is used in conjunction with an aggregate containing 70 to 80 wt. % silica sand and 20 to 30 wt. % portland cement. The results from laboratory and field evaluations in progress indicate that the materials can be used for pipe or as protective liners on pipe and vessels in electric generating and direct utilization geothermal processes.

INTRODUCTION

In recent years, researchers from many countries have devoted a great deal of attention to the problem of developing high-strength, chemically stable cements which can be used for high-temperature applications. One type of material being investigated is formed by combining organic and inorganic materials to produce a series of composites called concrete polymer materials. These materials have strength and durability characteristics far superior to those of portland cement concrete. As a result, two of the materials, polymer-impregnated concrete and polymer concrete, are beginning to be utilized throughout the world in applications where portland cement cannot be used or where severe maintenance problems occur. Recent results from laboratory and field tests indicate that the composites may be applicable to many parts of the geothermal processes.

Polymer-impregnated concrete (PIC) consists of a precast portland cement concrete impregnated with a monomer system that is subsequently polymerized *in situ.* The polymer tends to fill the porous void volume of the concrete, which results in significant improvement in strength and durability properties. For a concrete mix that produces specimens with a compressive strength of 5000 psi, compressive strengths larger than 20,000 psi have been measured after impregnation. Similarly, large improvements in other structural and durability properties have also been obtained.

Polymer concrete (PC) consists of an aggregate mixed with a monomer or resin that is subsequently polymerized in place. The techniques used for mixing and placement are similar to those used for portland cement concrete. After curing, a high-strength (>10,000 psi) durable material is produced.

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A third type of material, a further development of PIC, is also being applied. This is a precast concrete that has been partially impregnated to a finite depth with a monomer that is subsequently polymerized.

The monomers used to produce concrete polymer materials usually polymerize by a free-radical mechanism. Two methods used to initiate the polymerization are ionizing radiation (x-rays, gamma rays) and chemical initiators. The principal advantage of radiation-induced polymerization is that the reaction can be initiated at room temperature and at a uniform rate within relatively thick concrete sections. Detrimental features include the high cost and complexity of radiation facilities and the low polymerization rates. The latter, when combined with the radiation attenuation due to the thick sections and high density, results in large radiation requirements and long processing times.

Chemical initiators have been used extensively to polymerize monomers for producing PIC and PC. The advantages of this method are that relatively simple equipment is required and the polymerization rates are rapid. If promoters are used in conjunction with the initiators, the polymerization can be conducted at temperatures at least as low as 0°C.

The most widely used initiators for the production of PIC and PC are benzoyl peroxide (BPO) and azobisisobutyronitrile (AIBN). Crosslinking agents such as trimethylolpropane trimethacrylate (TMPTMA) or divinylbenzene (DVB) are also added to the monomers prior to polymerization in order to increase the thermal and chemical resistance properties.

The feasibility of using concrete polymer composites as materials of construction for handling hot brine and steam was demonstrated in 1972. As part of this work, the concrete liner on a vertical tube evaporator at the Office of Saline Water Desalting Facility in Freeport, Texas, was partially impregnated to a depth of ~0.25 in. The results from these tests indicated that the composites had long-term stability in seawater at 177°C and in acid solutions. On the basis of these results, a research program to develop the composites for use in geothermal systems was started in April 1974. To date several high-temperature PC systems have been formulated, and laboratory and field tests have been performed in brine, flashing brine, and steam at temperatures up to 240°C. In this paper, studies to determine the possibility of using styrene–acrylonitrile–amide mixtures to produce high-strength thermal and chemically stable PC materials are described.

POLYMER CONCRETE (PC) PREPARATION METHODS

Materials such as polyester, methyl methacrylate, and styrene are being widely used in the preparation of PC for ambient-temperature (0 to 40°C) applications.[1] The present work at BNL is focused on the development of high-temperature systems for use in geothermal environments.

Two monomer systems which are currently under development consist of mixtures of styrene (St) and acrylonitrile (ACN) in conjunction with either acrylamide (Aa) or methacrylamide (MAa). The physicochemical properties of these materials are summarized in Table I.

Earlier work[2] has indicated that a silica sand mixture consisting of 50 parts by weight of sieve size No. 16, 25 parts of No. 30, and 25 parts of No. 100 has the proper particle size distribution to produce a high quality PC with a minimum

TABLE I
Properties of Organic Materials Used 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)	$CH_2C(CH_3)CONH_2$	85.1	111	—	—	solid
Trimethylolpropane trimethacrylate (TMPTMA)	$(CH_2CCH_3COOCH_2)_3CCH_2CH_3$	338.39	—	—	>300	liquid

polymer content.   For high-temperature applications, Type III portland cement is added to this mixture to enhance the resistance to brine and steam.   Possible explanations for this effect are discussed in a previous report.[3]

The monomers are mixed in a glass beaker and polymerization initiator is added and dissolved.   If acrylamide or methacrylamide is to be added to the St–ACN mixture, the mixture is heated to 50°C prior to the addition of initiator (azobisisobutyronitrile) to dissolve the solid monomer.   The formulation is mixed with the sand–cement aggregate and placed in a glass tube which is coated with a release agent.   Vibration is used to compact the PC.   The samples are cured in an oven at 60°C for 16 hr and for 2 hr at 85°C.   After cooling, the samples are removed from the form.   Prior to testing, they are cut to a length-to-diameter ratio of 2 and dried for 18 hr at 105°C.

Several monomer formulations have been used previously to produce high-temperature PC formulations.   The systems studied include mixtures of St–trimethylolpropane trimethacrylate (TMPTMA), St–ACN–TMPTMA, St–triallyl cyanurate (TAC)–polyphenylene oxide (PPO), isobornyl methacrylate (IBOMA)–methyl methacrylate (MMA), IBOMA–MMA–ethylthioethyl-methacrylate (ETEMA), St–ACN–acrylamide (Aa), and St–ACN–methacrylamide (MAa).   Preliminary tests have indicated that the last two systems produced a PC with the best high-temperature and chemical resistance properties.   As a result, emphasis has been placed on the development of these systems.

Experiments were performed to determine if copolymers rather than mixtures of St, ACN, Aa, or MAa homopolymers or mixtures of copolymers and homo-polymers were formed during the free-radical polymerization process.   The formation of copolymers was confirmed by solubility tests.   In these tests the copolymers were found to be insoluble in solutions for polystyrene, polyacrylo-nitrile, polyacrylamide, and polymethacrylamide such as acetone, dimethyl-formamide, and water, respectively.   It was also noted that homogeneous transparent films without signs of inclusions were produced when the copolymers were press molded.   This also is evidence of the formation of true copoly-mers.

The copolymerization of the St–ACN system has been investigated extensively for many years.[4,5]   The activity ratio of both monomers is such that a homoge-neous copolymer is formed when the ACN monomer concentration is in the range 36 to 39 mol-%.   It was also reported[6–8] that the inclusion of small quantities of Aa or MAa and a crosslinking agent into the polymer chain increases the thermal and chemical stability of the copolymer.   This is verified by the infrared spectra of the copolymers shown in Figure 1.   All of the absorption bonds characteristic of polymers of St, ACN, Aa, and MAa (3400–3500, 3040, 2930, 2220, 1600, 1500, and 1450 cm^{-1}) are present in the spectra.   By comparing spectra (a) and (c) in Figure 1, it is evident that the optical density of the copolymer St–ACN–Aa–TMPTMA (curve c) is greater than that of the St–ACN copolymer (curve a) in the absorption region 2930, 2200, 1600, and 1500 cm^{-1}.   This is indicative of a crosslinked structure which results in improved physical properties of the co-polymer.

The reactivities of all the components in the reaction have not been measured.   However, on the basis of the St–ACN ratio in the mixture and the reaction rate, it appears that they are close to the values calculated by use of the Alfrey–Price semiempirical equation.[9]
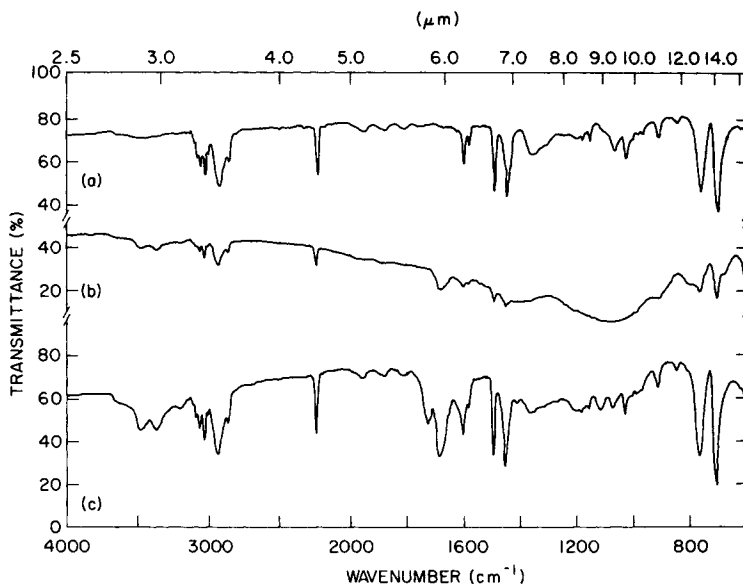
Fig. 1. Infrared absorption spectra of the copolymers: (a) styrene–acrylonitrile; (b) styrene–acrylonitrile–acrylamide; (c) styrene–acrylonitrile–acrylamide–trimethylolpropane–trimethacrylate.

RESULTS

Monomer Composition

Tests were performed to optimize the monomer composition with respect to the properties of the PC. As stated above, the concentrations of each monomer constituent in the formulations were selected on the basis of the reactivity of each monomer. PC samples were made containing 12 wt. % of the monomer formulations and 88 wt. % of filler composed of an 80–20 silica sand–Type III portland cement mixture. The results from property evaluations performed on these specimens are given in Table II. These data indicate that the boiling water absorption after exposure of the specimens in an oven at 238°C for 32 days increases as the concentration of Aa is increased and decreases with increasing MAa content. These data are plotted in Figure 2. The compressive strength increases with increased MAa and decreases as the Aa concentration is increased (Fig. 3).

The addition of a crosslinking agent such as TMPTMA to the monomer mixtures further improves the thermal and chemical stability of the copolymers. The results, shown in Table III, indicate that TMPTMA concentrations ranging from 2.5 to 5.0 wt. % result in a 40% to 50% decrease in weight loss of polymer after exposure in air for 32 days at 238°C and in boiling water absorption of 30% to 35%. The compressive strength of the PC composite is also increased.

The temperature limitations of the system have been studied. From the data given in Figure 4, it is apparent that the system is stable to a temperature of ~240°C. At a temperature of 275°C the polymer exhibits a weight loss approaching 50% after 6 days in an oven. At this temperature the thermal destruction of the [C—CN] group proceeds very rapidly with the evolution of NH_3, HCN, and H_2.

TABLE II

Summary of Properties for Polymer Concrete Containing St–ACN–Aa and St–ACN–MAa[a]

Monomer system	Composition, wt. %	Polymer weight loss after 30 days at 238°C, %	Boiling water absorption, % after			Compressive strength, psi, after			
			Preparation	32 days at 238°C	Autoclave	Preparation	Boiling water absorp.	32 days in oven at 238°C	Autoclave
St–ACN–Aa	57.5–40–2.5	18.0	2.27	5.09	1.71	20,542	10,542	3111	10.942
	60–35–5.0	25.6	1.37	6.66	2.0	24,375	19,750	2013	12,030
	55–40–5.0	18.8	0.98	4.73	1.84	19,750	20,167	7128	13,547
	55–37.5–7.5	28.5	0.96	10.03	1.38	20,917	21,083	752	5,812
St–ACN–MAa	57.5–40–2.5	25.5	2.74	6.80	3.59	15,333	13,000	1812	5,919
	60–35–5	18.4	1.88	4.84	2.64	17,042	13,458	3111	10,855
	55–40–5	15.8	1.49	5.43	1.30	19,000	19,167	5396	7,222
	55–37.5–7.5	9.6	0.94	2.57	1.55	22,250	14,833	5496	8,889

[a] Monomer loading, 12 wt. %; sand–cement ratio, 80–20; initiator, azobisisobutyronitrile (AIBN); St, styrene; ACN, acrylonitrile; Aa, acrylamide; MAa, methacrylamide.
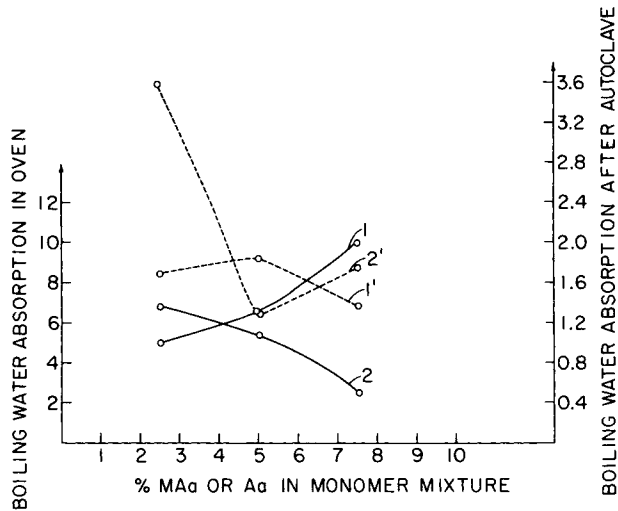
Fig. 2. Effect of monomer composition on the boiling water absorption of PC: (———) boiling water absorption after oven; (- - -) boiling water absorption after autoclave; (1) St–ACN–Aa; (2) St–ACN–MAa.
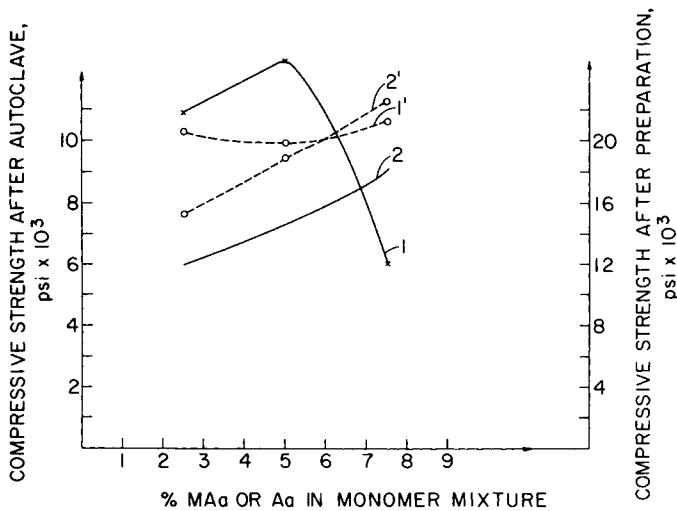
Fig. 3. Effect of monomer composition on the compressive strength of PC: (———) compressive strength after preparation; (- - -) compressive strength after autoclave; (1) St–ACN–Aa; (2) St–ACN–MAa.

IR examination of samples after exposure to brine at 238°C indicated the formation of weak peaks in the 2920 cm^{-1} absorption region which corresponds to the stretching vibrations of the end carboxyl group. The presence of this region indicates that a partial hydrolysis of the amide group occurs in the basic medium. The rate of hydrolysis increases with increasing temperature. This has been confirmed by literature data.[10,11]

TABLE III
Summary of Results for Polymer Concrete Samples Containing Crosslinking Agents

Monomer system[a]	Composition, wt. %	Polymer weight loss after 30 days at 238°C, %	Boiling water absorption, %, after		Compressive strength, psi, after			Boiling water absorp.	Boiling water absorp. after autoclave
			Preparation	32 days at 238°C, %	Preparation	30–32 days at 238°C	Autoclave for 30 days		
St-ACN-Aa-TMPTMA	55-35-7.5-2.5	10.0	0.33	1.71	22,832	9,217	15,420	27,434	0.83
	55-35-5.0-5.0	8.38	0.28	1.19	25,310	12,852	17,743	26,594	0.64
St-ACN-MAC-TMPTMA	50-37.5-7.5-5.0	10.5	0.28	1.54	23,826	7,641	—	22,609	
	50-40-5.0-5.0	7.99	0.24	1.04	26,174	11,692	—	20,261	
	50-42.5-2.5-5.0	6.89	0.28	0.76	26,174	13,333	—	24,783	

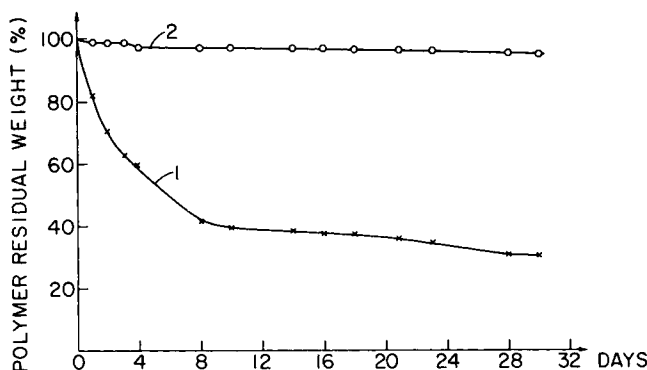[a] St, styrene; ACN, acrylonitrile; Aa, acrylamide; MAa, methacrylamide.

Fig. 4. Effect of temperature on weight loss of the polymer in PC samples: (1) 240°C; (2) 275°C.

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.

Previous work[12] 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 IV, indicate that the compressive strength decreases from ~28,000 psi for a sample containing 12 wt. % polymer to ~17,000 psi 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.

TABLE IV

Summary of Test Results for Polymer–Concrete Systems Containing 55 wt. % St–35 wt. % ACN–5 wt. % Aa–5 wt. % TMPTMA and 70 wt. %–30 wt. % Sand–Cement Aggregate

Property	Monomer loading, wt. %			
	12.0	15.0	17.5	20
Compressive strength, psi, after				
Preparation[a]	28,319	25,421	24,737	17,457
Boiling water	25,841	23,333	22,193	21,053
Oven (30 days at 238°C)	17,537	12,649	14,297	11,955
Autoclave (10 days, hot brine)	17,743	16,052	15,704	—
Boiling water absorption, %, after				
Preparation[a]	0.33	0.26	0.26	0.24
Oven (30 days at 238°C)	0.9	1.10	1.27	1.47
Autoclave (10 days, hot brine)	0.64	0.64	0.59	—

[a] Average of four specimens.

Electron-microscopic studies tend to support the above assumptions. Figures 5 and 6 show fractured surfaces of PC containing 12 and 20 wt.% polymer loadings, respectively. The composite containing 12 wt. % polymer (Fig. 5) has a more uniform surface than the sample containing 20 wt. % (Fig. 6). 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.

Sand–Cement Ratio

Studies are also in progress 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 Table V and Figure 7. The data indicate that increases in cement content from 10% to 30% result in increases in compressive strength from 20,000 psi to 27,000 psi. The water absorption remains essentially constant over the same range. Further increases in cement content to 50% result in an increase in water absorption and a decrease in compressive strength to 23,000 psi.

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, an increase in the polymer content of the mix beyond 12 wt. % does not compensate for the
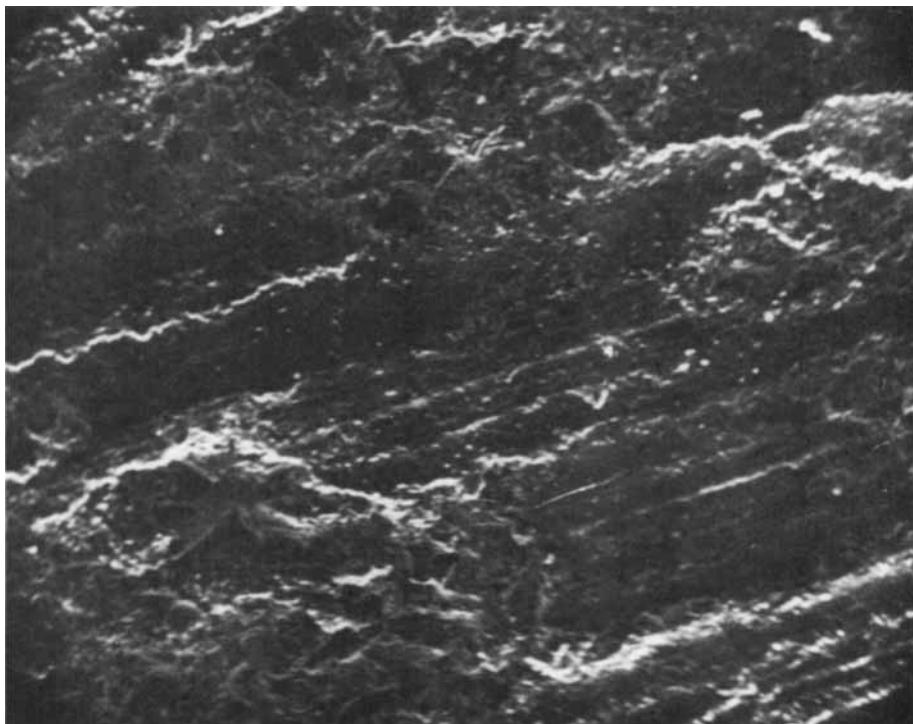

Fig. 5. Scanning electron microscope picture of fractured surface of PC sample containing a 12% polymer loading.
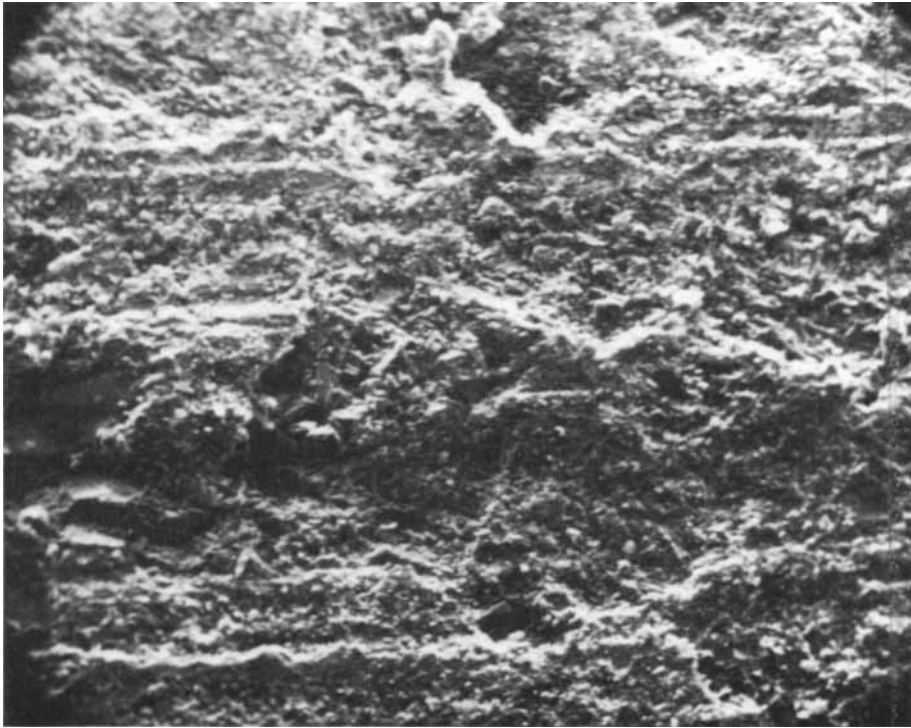
Fig. 6. Scanning electron microscope picture of fractured surface of PC sample containing a 20% polymer loading.
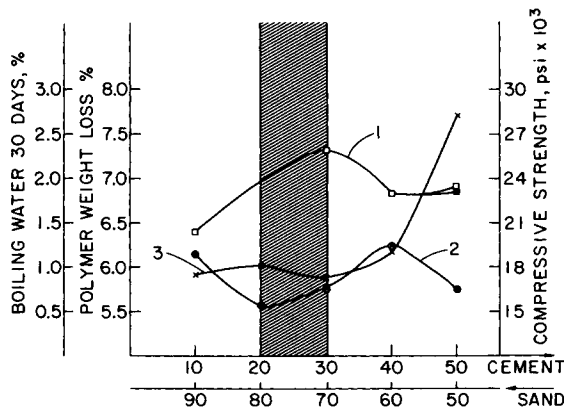

Fig. 7. Effect of sand–cement ratio on the properties of PC: (1) compressive strength after boiling water; (2) compressive strength after oven, 30 days, 460°F; (3) boiling water absorption after oven, 30 days.

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.

TABLE V
Properties of Polymer Concrete as a Function of Sand–Cement Composition

	90–10 wt. %[a]	80–20 wt. %	70–30 wt. %	60–40 wt. %	50–50 wt. %
	55 wt. % St–35 wt. % ACN–5 wt. % Aa–5 wt. % TMPTMA				
Boiling water absorption, %, after					
Preparation	0.78	0.62	0.85	0.38	0.42
Oven (30 days, 460°F)	0.90	1.02	0.87	1.18	2.69
Compressive strength, psi, after					
Preparation	22,212	24,248	28,319	20,620	26,549
Boiling water	20,266	—	27,841	22,920	23,028
Oven (30 days, 238°C)	18,926	15,537	17,547	19,174	16,694
	55 wt. % St–37.5 wt. % ACN–7.5 wt. % MAa				
Boiling water absorption, %, after					
Preparation	2.05	1.25	1.41	2.33	2.63
Oven (30 days, 238°C)	5.57	3.82	4.06	7.21	7.42
Compressive strength, psi, after					
Preparation	14,655	15,080	18,620	13,327	7,168
Boiling water	10,779	19,097	15,027	6,478	5,699
Oven (30 days, 238°C)	3,652	4,300	2,209	1,565	973

a Sand–cement composition.

SUMMARY AND CONCLUSIONS

A study has been performed to determine the suitability of using copolymers obtained by the free-radical polymerization of mixtures of St and ACN with either Aa or MAa to produce PC for use in geothermal environments. A cross-linking agent, TMPTMA, and a polymerization initiator, AIBN, were also added to the systems.

The properties of the PC were measured as a function of the concentrations of Aa and MAa, polymer concentration, and aggregate composition. The optimum properties result when a 12 to 13 wt. % concentration of a 55 wt. % St–35 wt. % ACN–5 wt. % Aa–5 wt. % TMPTMA monomer mixture is used in conjunction with an aggregate containing 87 to 88 wt. % of a 70 wt. % sand–30 wt. % portland cement mixture. After exposure to a 25% brine solution at 240°C for 30 days, the compressive strength of the composite was ~17,700 psi. The control strength was ~25,000 psi.

On the basis of these laboratory results, field tests have been started but results have not yet been obtained.

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