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ORGANOSILOXANE POLYMER CONCRETE FOR GEOTHERMAL ENVIRONMENTS

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Abstract

The feasibility of using the products of free-radical copolymerization of modified organosiloxane in the formation of a thermally stable and chemically resistant polymer concrete for use in geothermal environments has been demonstrated. Specimens have been produced using mixtures of organosiloxane containing pendant vinyl groups and styrene or different silicone fluids as a comonomer in conjunction with a free-radical initiator and several aggregate materials. The use of these monomers in conjunction with materials such as SiO_2 and portland cement to form polymer concrete results in composites with high compressive strength (80 to 100 MPa) and thermal and hydrolytic stability. The results from studies to determine the effect of variables such as sand-particle size, type of cement, and sand-cement ratio are discussed.

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Introduction

For the last ten years, researchers from many countries have devoted a great deal of attention to the problem of developing high-strength, chemical-resistant cements which can be used for high temperature applications. One type of material, which has been investigated at Brookhaven National Laboratory (BNL) since 1971,[1] is formed by combining organic and inorganic materials to produce a series of composites called concrete polymer materials. As a result of this work, 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. Extensive work on these composites is being conducted in Germany, Japan, and the USSR.[2]

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. For a concrete mix that produces specimens with a compressive strength of 35.0 MPa, compressive strength > 130.0 MPa has 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 (> 75 MPa) durable material is produced.

The filler materials used in the production of PC include sand, limestone, slag, and expanded clay. Resins such as polyester, polyurethane, polymethyl methacrylate, polystyrene, and carbamide find application as the bonding agent.

Results from laboratory and field tests indicate that one of the areas where these composites can be used is in geothermal processes.[3] The feasibility of these applications was demonstrated in 1972 when tests of a PC liner on a vertical tube evaporator in Freeport, Texas indicated that the composites had long-term stability in seawater at 177°C and in acid solutions.[4] 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 performed in brine, flashing brine, and steam at temperatures up to 250°C.[3,5] In all of the systems tested, organic resins were used as the binding agent.

It is well known that organic networks consist of carbon-carbon bonds, which are cleaved at temperatures near 250°C. As a result, the use of organic binders in PC is limited to temperatures below 250°C.

Above this temperature, PC samples become soft, swell, and crack because of the evolution of gas.

This paper deals with new semiinorganic polymer compositions which have a network consisting of -Si-O-Si bonds. This bond has a dissociation energy at 25°C of 190.9 ± 2 kcal/mol compared to the 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 -Si-O- and -C-C are 1.504 Å and 1.541 Å, respectively). Thus it is believed that siloxanes in composition with various fillers should be stable at temperatures up to 350°C.[7]

Experimental

Materials

Materials used in this study were as follows: dimethylpolysiloxane modified with pendant vinyl groups (Y-9208), supplied by the Union Carbide Corporation, silicone fluids RZ-4035 and V-47 supplied by the Rhodia Corporation, and styrene from the Dow Chemical Company. These materials were used as bonding materials and sand and cement were used as fillers. The curing agent for the polymerization was di-*tert*-butyl peroxide (DTBP). Thermal polymerization was used to polymerize the monomer composition.

Sample Preparation

PC samples were made by blending 25 to 30 wt% of the comonomers and 0.5 to 1.0 wt% of a free-radical initiator, and the formulation was mixed with the appropriate aggregate mixture. The slurry was then evacuated to remove entrapped air. The monomer concrete slurry was vibrated into 25-mm-diam glass cylinders and cured in these cylinders.

When the PC was removed from the glass tubes, it was cut into cylinders that measured 25 mm in diam by 50 mm in length. These cylinders were used in property measurements.

Test Methods

The water absorption and compressive strength tests for the PC samples were performed in accordance with ASTM standards.[6] The absorption indicates the percentage of liquid that is drawn into and tends to fill permeable pores in a porous solid body and is calculated as follows:

$$\frac{W_2-W_1}{W_1}\,(100\%),$$

where

W_1 = weight of the dried sample before test,
W_2 = weight of the sample after test.

Compressive strength tests were performed on PC samples before and after exposure to 25% brine solutions at elevated temperatures.

Durability tests in autoclaves containing a simulated geothermal brine were also performed. In these tests the samples were first weighed and dimensionally measured. They were then installed in high pressure autoclaves containing 25% brine solutions at room temperature. The autoclaves were brought up to temperature and the pressure recorded. After the desired testing time was reached, the vessel was opened and the samples were washed in H_2O and dried before testing.

Analytical equipment used to evaluate the PC include an AMR Model 1000A Scanning Electron Microscope equipped with LaB_6 and a Perkin-Elmer Infrared (IR) Spectrophotometer 297. The KBr pellet procedure was used for the IR analysis.

Results and Discussion

In an earlier paper[7] the possibility of using organosiloxanes with organics or different siloxane fluids as a means of producing high temperature mechanically and chemically stable PC was discussed. This work indicated that in contrast to PC containing organic polymers which showed a marked decrease in strength with temperature, the strength of the organosiloxane-styrene PC decreased at a much slower rate and at 350°C the compressive strength was ∿ 25 MPa (see Figure 1).

The goal of the current study was to optimize the monomer and aggregate compositions and to determine the properties of the PC as a function of sand-particle size, type of cement, monomer composition, sand-cement ratio, and concentration of coupling agent. Partial results from these studies are reported below.

1. Sand-Particle Size

As shown earlier,[8] the particle size of sand has an effect on the properties of PC and is dependent upon the viscosity of the monomer composition. The best results for the organic binders with viscosities close to the viscosity of water were obtained when a mixture of sand sizes was used.[8] In this case, the low viscosity monomer could 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. The result, therefore, is nonuniform polymer loading which decreases the durability and strength of the PC. Table 1 illustrates the effect of sand-particle size on the compressive strength of PC composites. Decreasing the particle size of the sand for a 75 wt% organosiloxane - 25 wt% styrene system increased strength of the PC samples from 4.7 to 41.6 MPa. It is also apparent from the data in Table 1 that the addition of portland cement results in improved strength. When 10 wt% Type III portland cement was added to the filler, compressive strength of the material increased to 85.2 MPa.

2. Type of Cement

As indicated above, the addition of cement significantly improves the strength and durability of siloxane-PC (SPC) composites. A study to determine the influence of various types of cement on the properties of PC is in progress. Four different commercially available types of cement which were included as a partial constituent of the aggregate were tested: Types I, II, III, and V. Compound compositions[9] of these materials are given in Table 2.

The properties of PC as a function of cement type are summarized in Table 3 for a 75 wt% Y-9208 - 25 wt% styrene monomer system and in Table 4 for a 97 wt% RZ - 3 wt% V-47 system. PC samples containing Types I and III cements in conjunction with the Y-9208 - styrene monomer system had high strengths (Figure 2). Type II cement used with the RZ - V-47 system also yielded high strength (Figure 3). The sand-cement ratios were 90 to 10 and 95 to 5, respectively. The amount of water absorbed was lowest for samples containing Types III and V cement (Figures 2 and 3). Stress-strain curves (Figures 4 and 5) indicate that PC samples containing Types I and II cement are more brittle than PC containing the other cements. This brittleness can be reduced slightly by using Type III cement. Greater reductions can be obtained with Type V cement. The reasons for these variations may be the differences in the chemical composition of the cements. The feasibility of increasing the elasticity of PC could be useful in developing high temperature sealing materials for the geothermal industry.

Sand-Cement Ratio

Studies are also in progress to determine the optimum ratio of sand to cement that should be used in the PC composites. 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 5 and Figure 6. 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 to 5 and 90 to 10 showed stability at 300°C (Figure 7).

Infrared spectroscopy analyses (Figure 8) and scanning electron microscopy (Figure 9) studies of the structure of PC samples before and after exposure to brine at 300°C did not indicate changes in structure and composition. As indicated in Figure 9, some fragments of the resin adhering to the filler surface have been observed. These observations support the presence of adhesion between the polymer and filler. The boiling water absorption, which is representative of the PC density, has a tendency to increase with increasing amounts of cement. Figure 6 indicates that maximum strength is obtained when the cement concentration used is in the range of 10 to 15 wt%. Further increases in the cement concentration lead to strength reductions and increases in elasticity (Figure 10). The use of a wetting agent (Triton X-100 from the Baker Chemical Co.) does not change this tendency (see Table 5 and Figure 10) but improves the particle-particle packing of the various mixtures of monomer and aggregate.

Summary and Conclusion

A study has been performed to determine the suitability of using copolymers obtained by the free-radical polymerization of mixtures of organosiloxane with different silicone fluids or with styrene to produce thermostable polymer concrete composites for use in geothermal environments. The properties of the PC were measured as a function of sand-particle size, cement type, and sand-cement ratio for 75 wt% Y-9208 - 25 wt% styrene and 97 wt% RZ - 3 wt% V-47 monomer system. The optimum properties result when sand flour with a sieve opening < 30 μm is used in conjunction with Type II or III cement in the ratio 90 to 10 or 95 to 5.

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3. Kukacka, L. E., Polymer Concrete Materials for Use in Geothermal Energy Processes, Second International Congress on Polymers in Concrete, Oct. 1978, Austin, Texas.
4. Kukacka, L. E. et al, Alternate Materials of Construction for Geothermal Applications, Progress Report No. 14, Brookhaven National Laboratory, BNL 50751, Sept. 1977.
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6. Annual Book of ASTM Standards, Part 14.
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9. Concrete Manual, US Bureau of Reclamation, 1975.

Table 1

Compressive Strength of Organosiloxane as a Function of Sand Particle Size

Monomer composition, wt%		Aggregate Composition		Compressive strength, MPa
OS	St	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	< 30	
		10	Type III cement	85.2
75	25	90	150	
		10	Type III cement	31.6
75	25	90	600	
		10	Type III cement	21.8
75	25	36*	1180	
		17	600	40.3
		17	150	
		30	Type III cement	

OS, Organosiloxane.
St, Styrene.
*Aggregate composition, used for organic systems.
Monomer concentration, 35 wt%.

Table 2

Compound Composition of Portland Cements

Type of cement	Compound composition, %							
	C_3S	C_2S	C_3A	C_4AF	$CaSO_4$	Free CaO	MgO	Ignition loss
I	49	25	12	8	2.9	0.8	2.4	1.2
II	46	29	6	12	2.8	0.6	3.0	1.0
III	56	15	12	8	3.9	1.3	2.6	1.9
V	43	36	4	12	2.7	0.4	1.6	1.0

Table 3

Properties of PC as a Function of Cement Type

Aggregate composition, wt%					
Sand[a]	Cement	Cement type	Boiling H_2O absorption, %	Compressive strength, MPa	Modulus of elasticity, MPa
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
80	70	I	0.12	66.2	--
		II	0.05	63.8	--
		III	0.06	42.5	--
		V	0.07	95.1	--
70	30	I	0.09	60	--
		II	0.08	105.3	--
		III	0.12	73.8	--
		V	0.05	104.2	--

[a] Particle size - sieve opening < 30 µm.

Monomer composition: 75 wt% Y-9208 - 25 wt% styrene.

Curing agent: 1.0 wt% di-*tert*-butyl peroxide.

Curing condition: 110°C, 18 hr; 165°C, 4 hr.

Monomer concentration, 35 wt%.

Table 4

Properties of PC as a Function of Cement Type

Aggregate composition, wt%		Cement type	Boiling H_2O absorption, %	Compressive strength, MPa	Modulus of elasticity, MPa
Sand[a]	Cement				
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	7526
85	15	I	0.11	86.1	--
		II	0.08	102.9	--
		III	0.08	72.2	--
		V	0.13	70.85	--
80	20	I	0.22	47.5	--
		II	0.12	71.6	--
		III	0.19	72.7	--
		V	0.14	68.2	--

[a] Particle size - sieve opening < 30 μm.

Monomer composition: 97 wt% RZ - 3.0 wt% V-47.

Curing agent: 1.0 wt% Di-*tert*-butyl peroxide.

Curing condition: 110°C, 18 hr 135°C, 3 hr; 170°C, 2 hr.

Monomer concentration, 35 wt%.

Table 5

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 Captions

Figure 1. Polymer weight loss and PC compressive strength at various temperatures.

Figure 2. Compressive strength and boiling water absorption as a function of cement type. Monomer composition: 75 wt% Y-9208 - 25 wt% St. Sand-cement ratio:(1) 90:10; (2) 80:20; and (3) 70:30.

Figure 3. Compressive strength and boiling water absorption as a function of cement type. Monomer composition: 97 wt% RZ - 3 wt% V-47; Sand-cement ratio: (1) 95:5; (2) 90:10; and (3) 85:15.

Figure 4. Compressive stress-strain curves for siloxane PC after preparation as a function of cement type. Monomer composition: 75 wt% Y-9208 - 25 wt% styrene. Aggregate composition: 90 wt% flour sand - 10 wt% cement. (1) Type I cement; (2) Type II; (3) Type III; and (4) Type V.

Figure 5. Compressive stress-strain curves for PC after preparation as a function of cement type. Monomer composition: 97 wt% RZ - 3 wt% V-47. Aggregate composition 90 wt% flour sand - 10 wt% cement. (1) Type I cement; (2) Type II, (3) Type III; and (4) Type V.

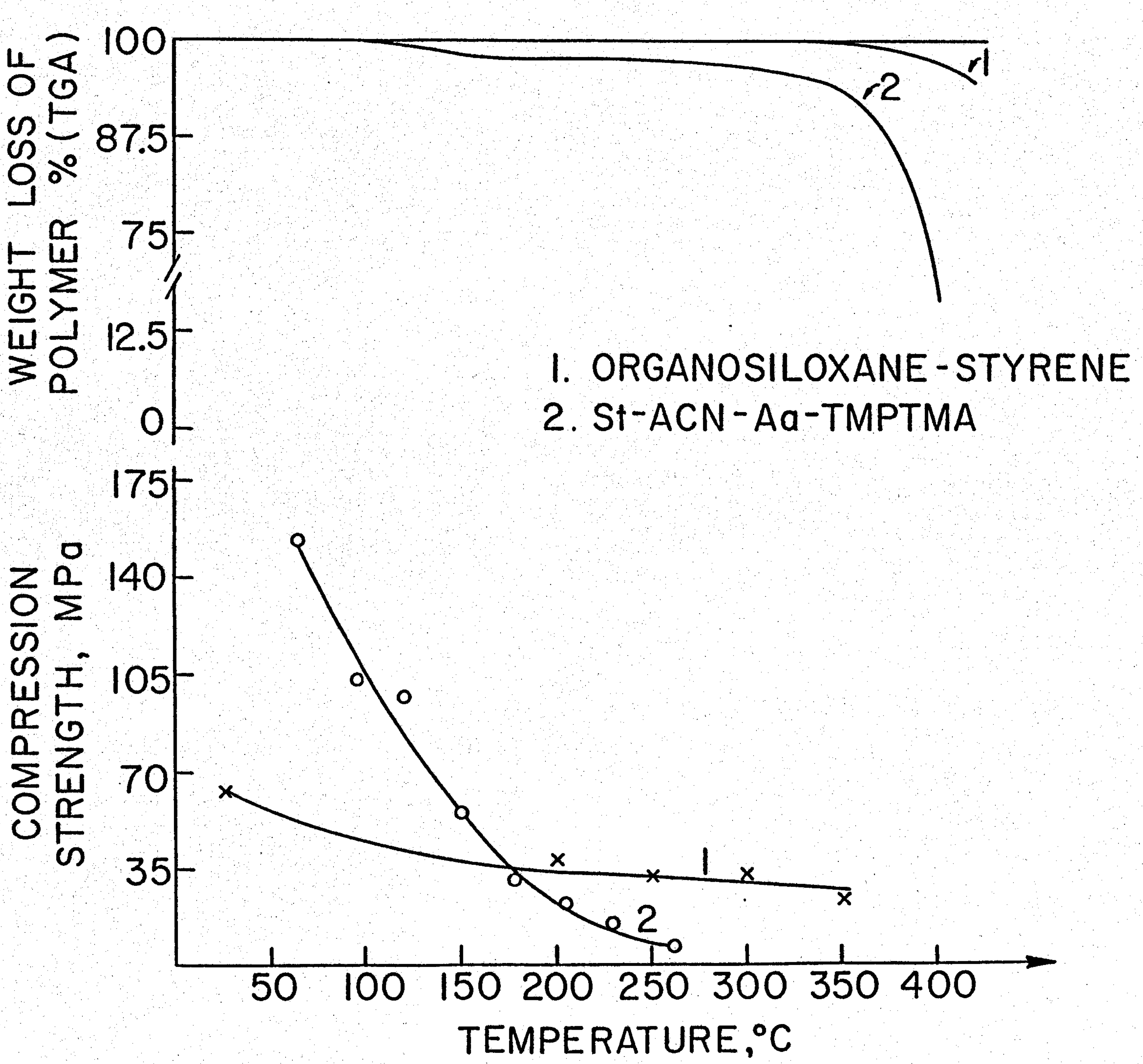
Figure 6. Compressive strength as a function of sand-cement ratio. Monomer composition: 97 wt% RZ - 3 wt% V-47. Aggregate composition: sand-sieve opening < 30 μm; cement-Type III. (1) After boiling water; (2) after exposure to brine at 275°C; and (3) after exposure to brine at 300°C.

Figure 7. PC samples after exposure to brine at 300°C.

Figure 8. Infrared absorption spectra of the PC samples before (A) and after (B) exposure to brine at 300°C.

Figure 9. Scanning electron microscope pictures of fractured surface of PC samples before (A) and after (B) exposure to brine at 300°C.

Figure 10. Compressive stress-strain curve for PC after 30 days' exposure to brine at 300°C. Monomer composition: 97 wt% RZ 3 wt% V-47. (1) Sand-cement ratio 95:5; (2) sand-cement ratio 90:10; (3) same as 1 plus wetting agent; and (4) same as 2 plus wetting agent.



12-1248-78

Figure 1

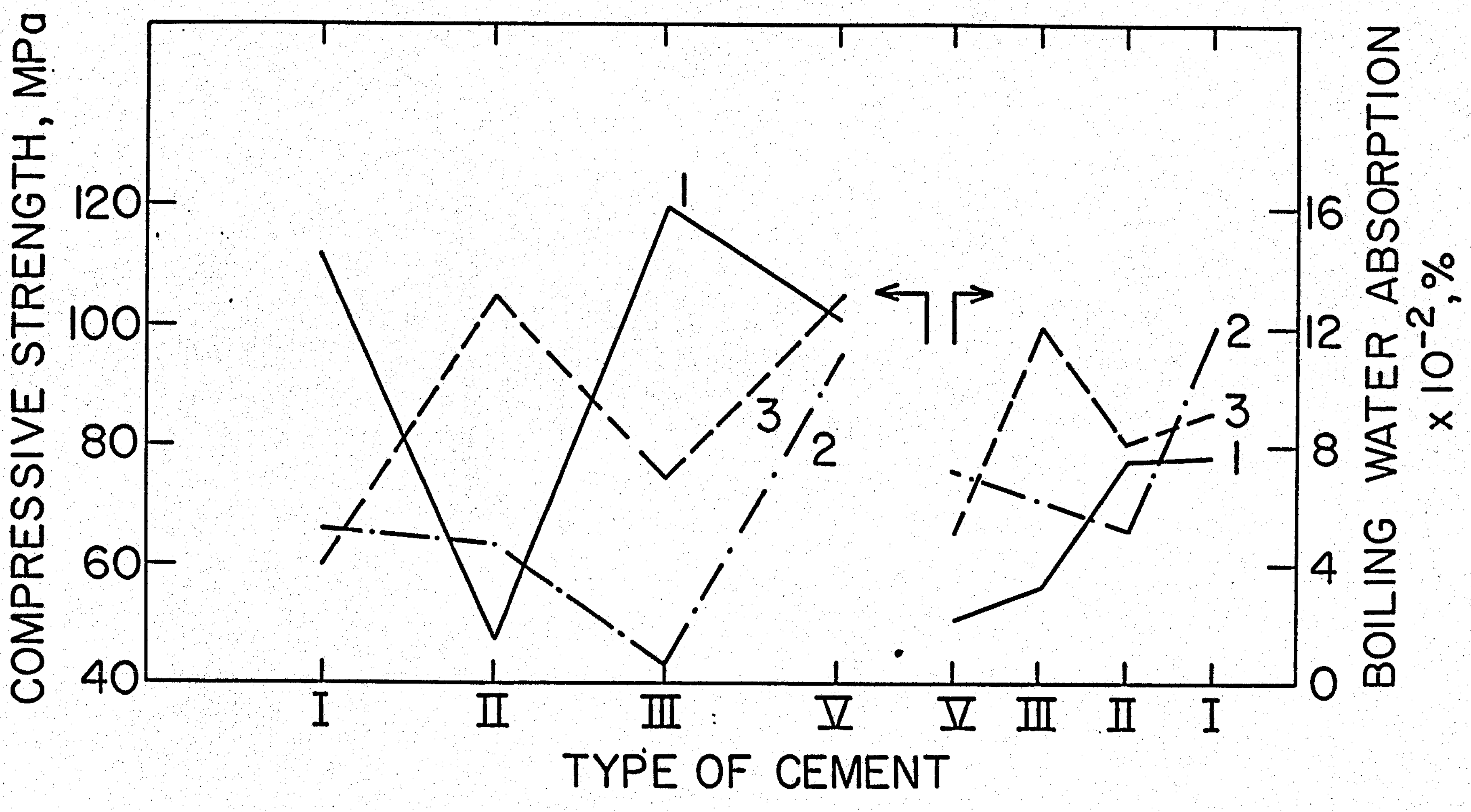
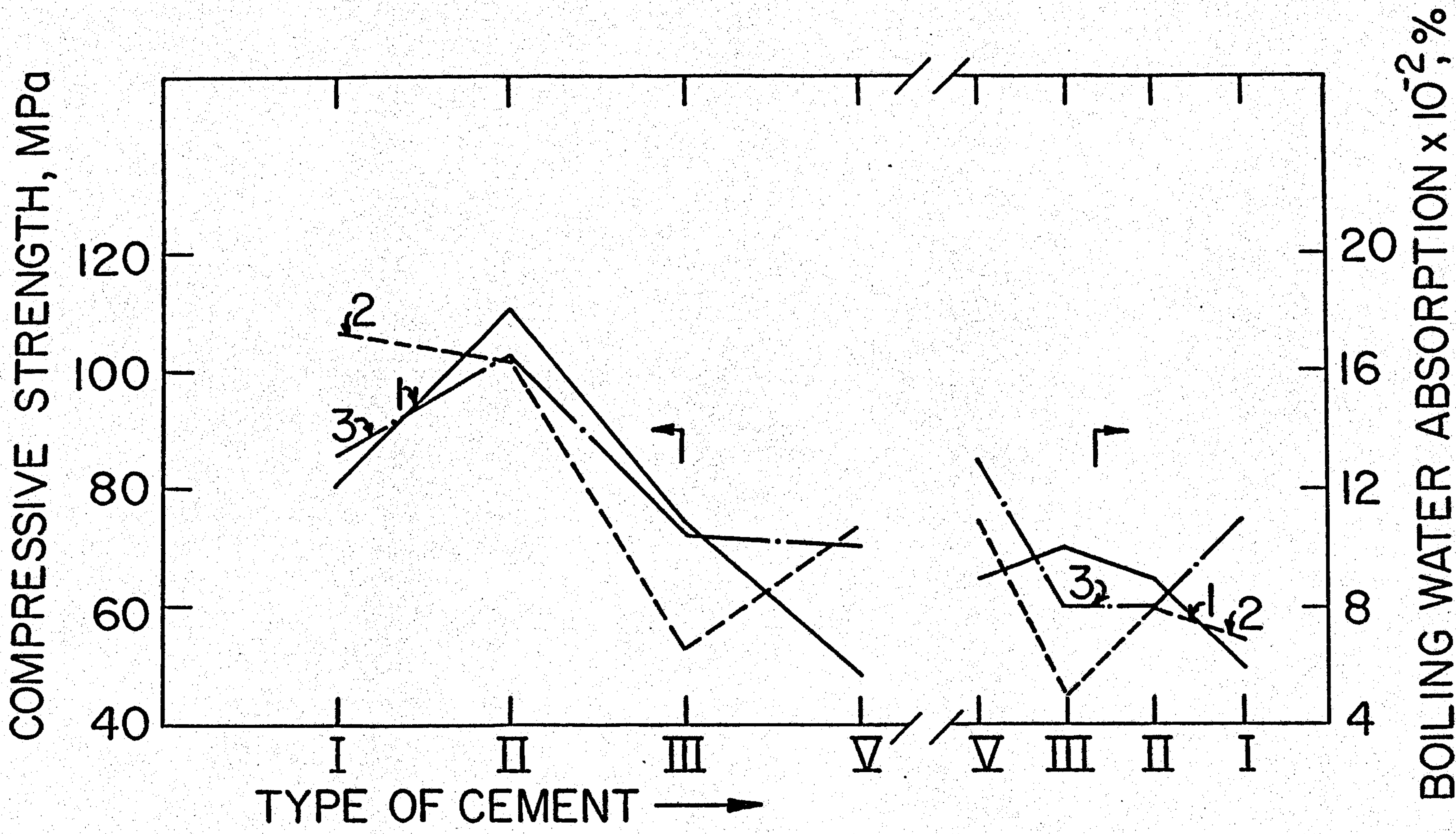

COMPRESSIVE STRENGTH, MPa
120
100
80
60
40
BOILING WATER ABSORPTION x 10^-2, %
16
12
8
4
0
1
2
3
I
II
III
V
V
III
II
I
TYPE OF CEMENT

Figure 2



1-1128-79

Figure 3

1-1518-79

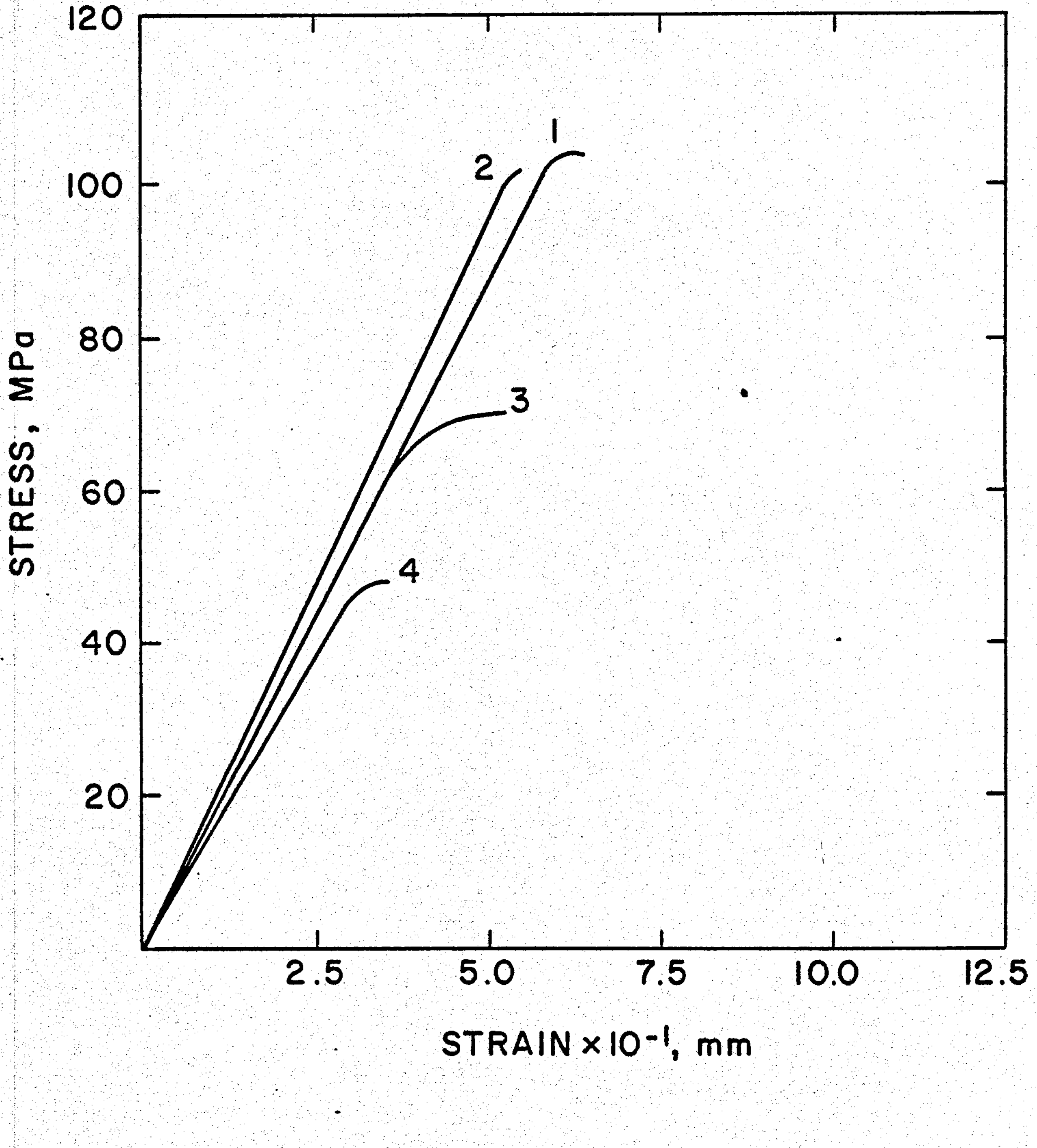


Figure 4

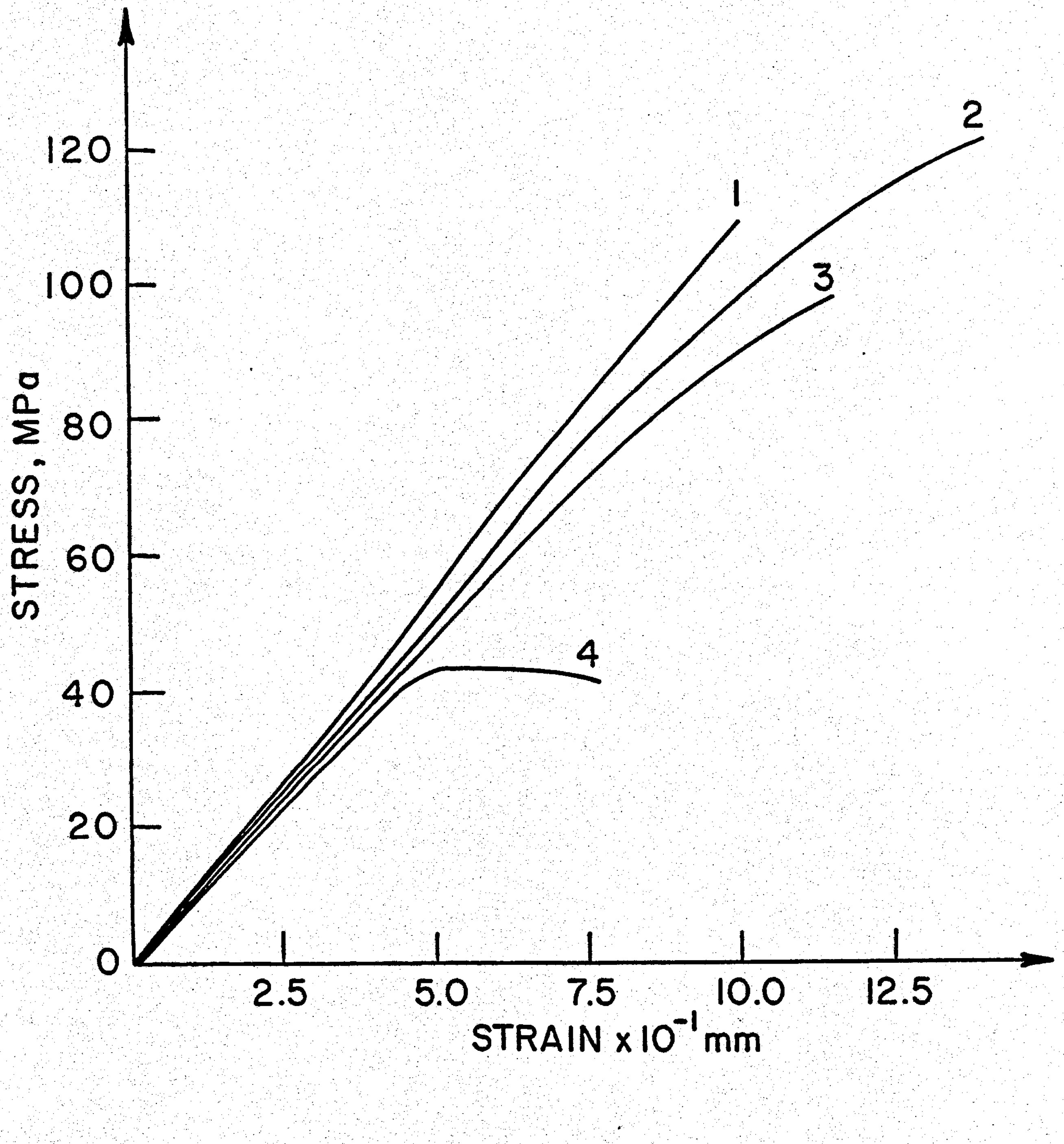

STRESS, MPa
120
100
80
60
40
20
0
2.5
5.0
7.5
10.0
12.5
STRAIN x 10^{-1} mm
1
2
3
4

Figure 5

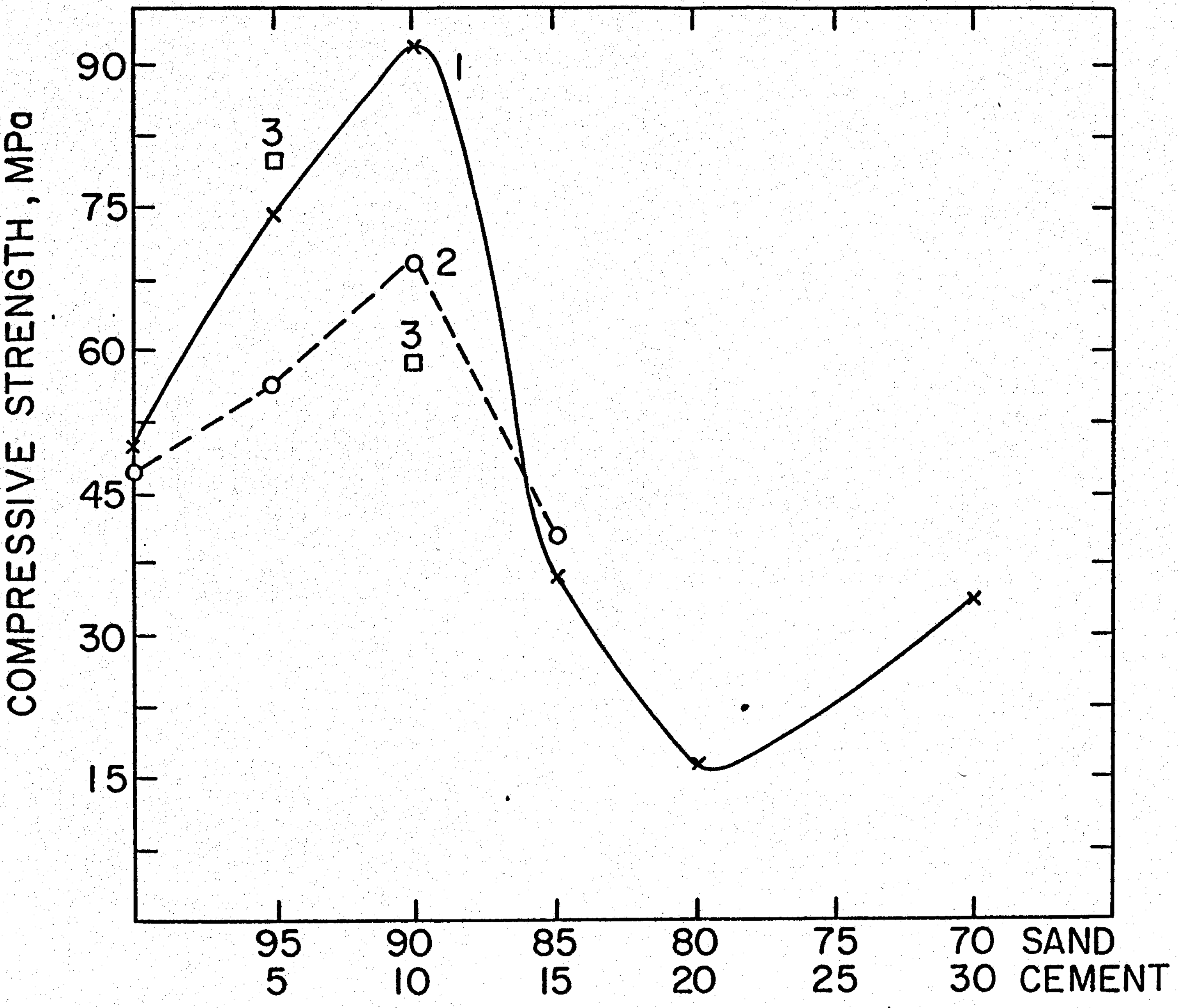


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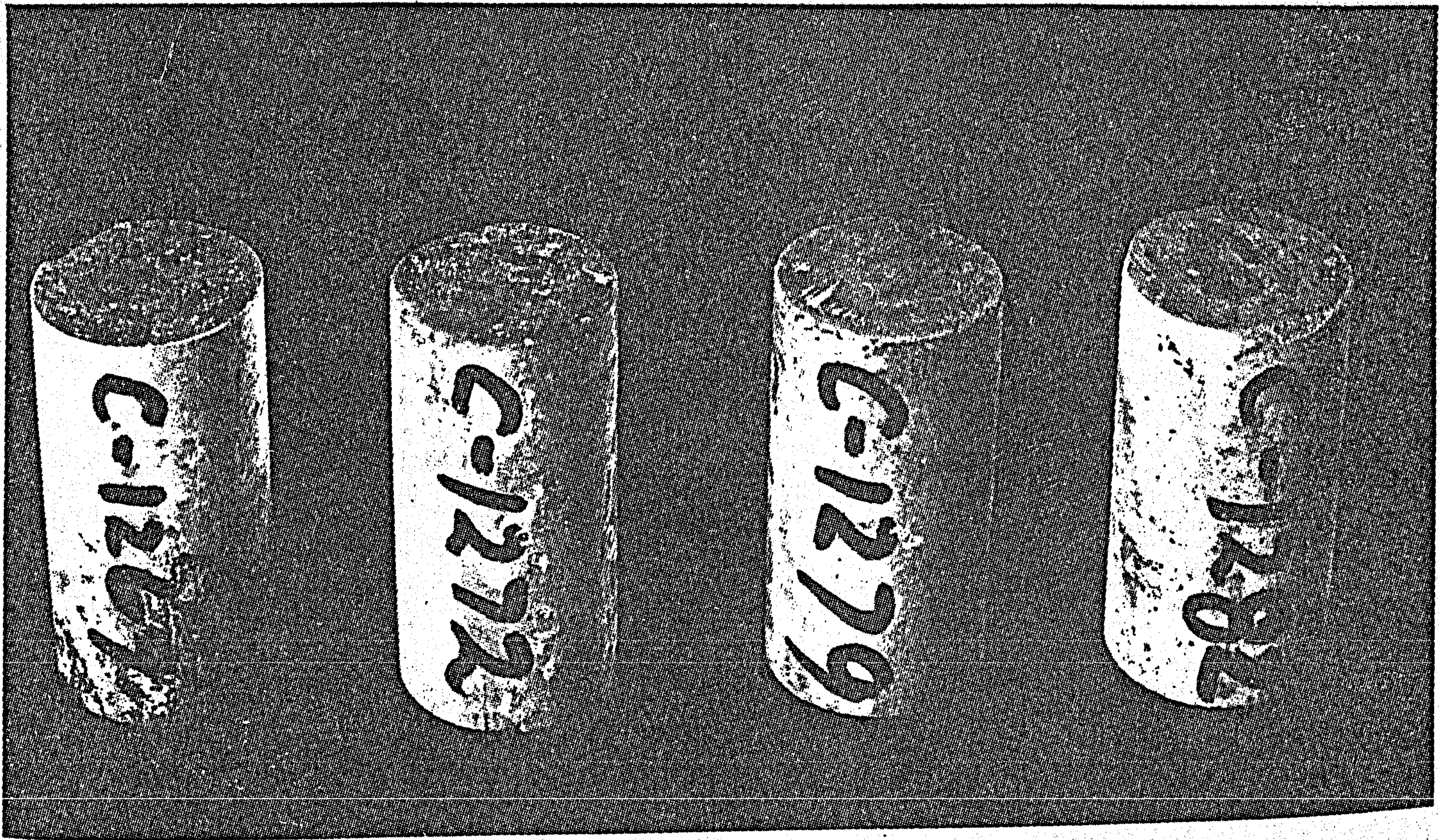
Figure 6



ORGANOSILOXANE PC SAMPLES FROM R7 AND V-47 IN RATIO 97:3 AFTER EXPOSURE IN HOT BRINE SOLUTIONS FOR 30 DAYS AT 300°C.

CN12-102-78

Figure 7

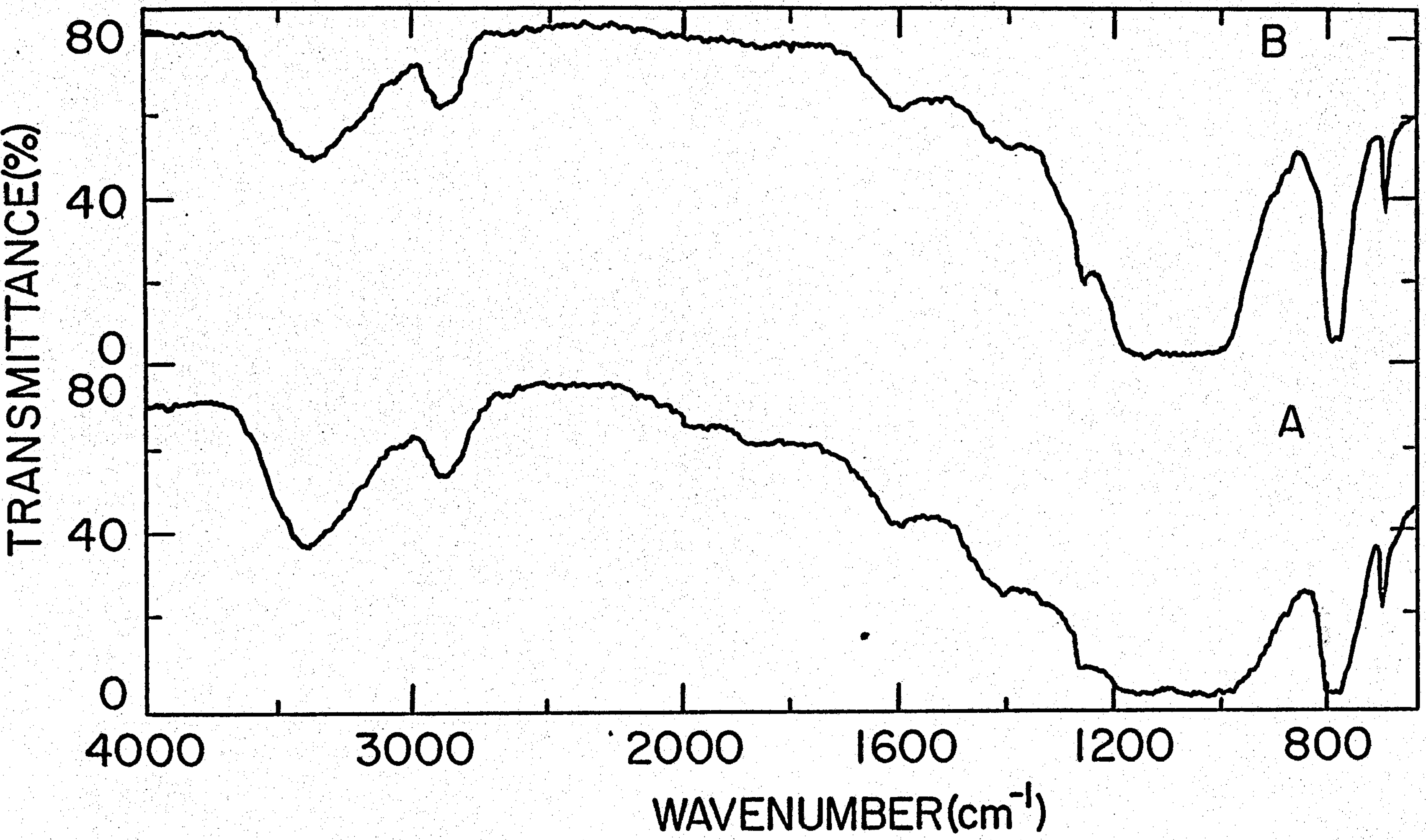


Figure 8

1-1512-79

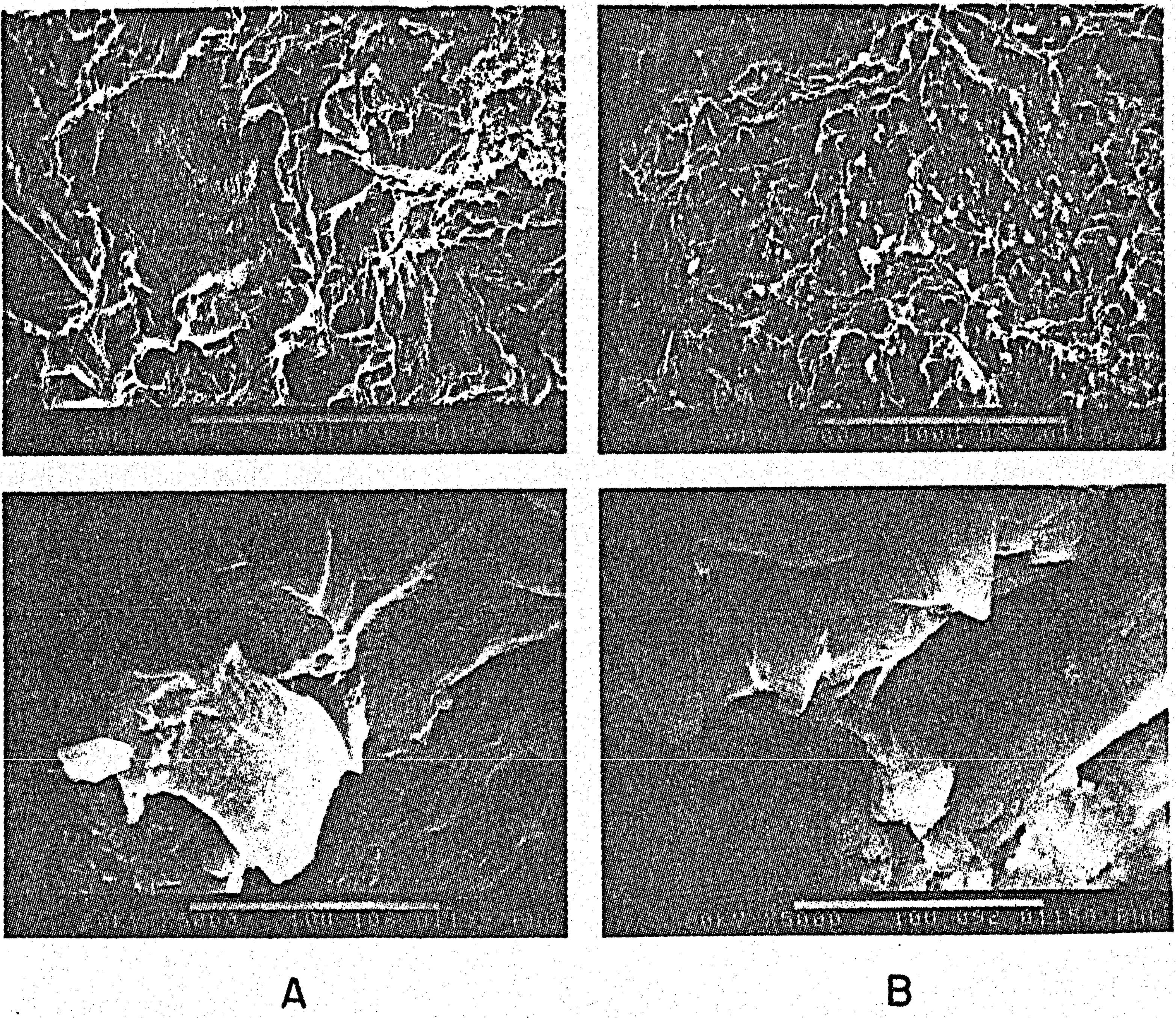


Figure 9

1-1511-79

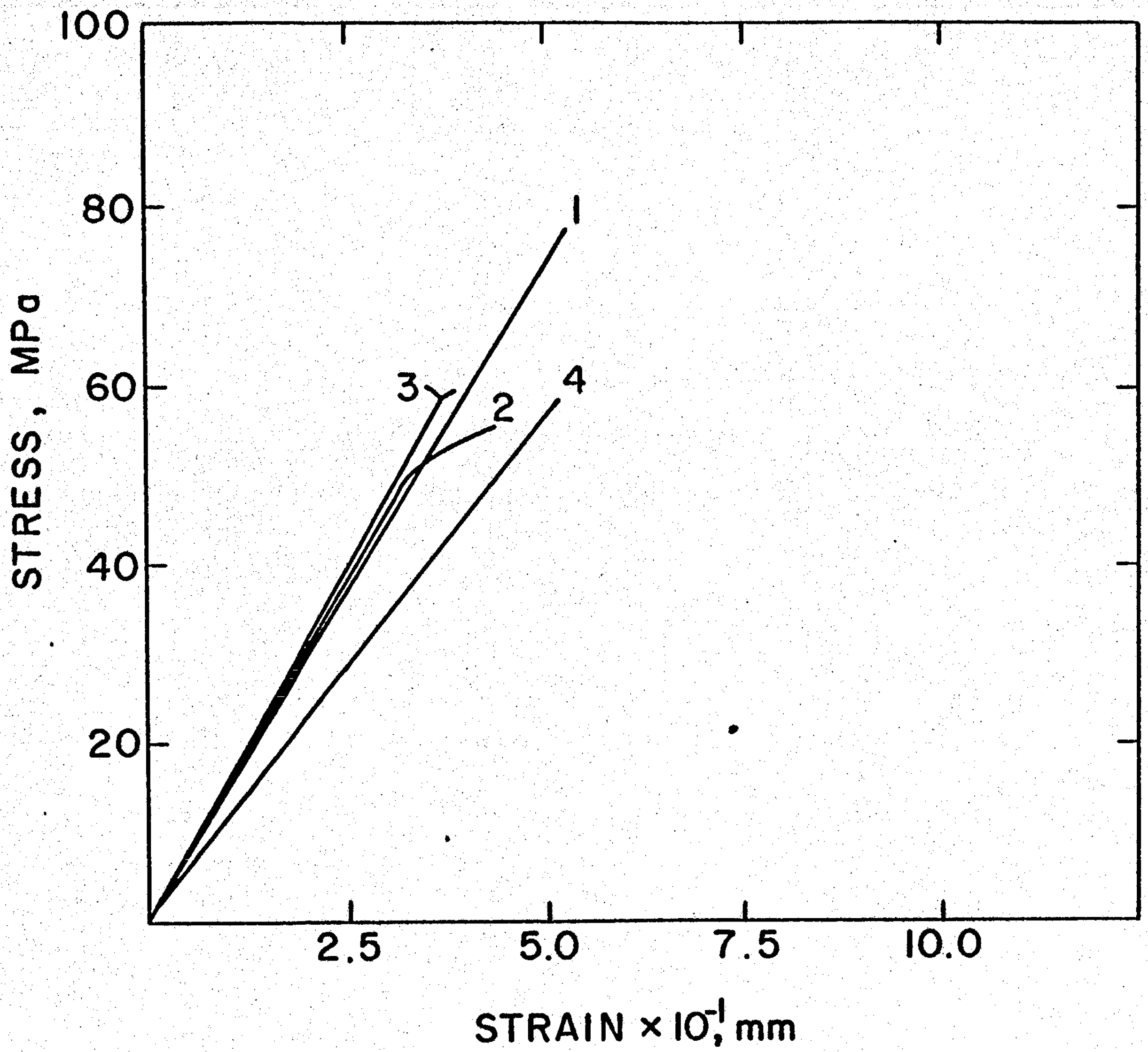


Figure 10