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DEVELOPMENT AND EVALUATION OF ELASTOMERIC MATERIALS FOR GEOTHERMAL APPLICATIONS

Annual Report, October 1977 – December 1978

W. A. Mueller
S. H. Kalfayan
W. W. Reilly
A. H. Yavrouian
I. D. Mosesman
J. D. Ingham

Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California
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ABSTRACT

This report covers the second year of the Jet Propulsion Laboratory's development and evaluation of elastomers for geothermal applications. The first year's work was described in JPL Publication 78-69 and also in a paper presented to the American Institute of Chemical Engineers in June 1978. A copy of the latter is included, by way of review, as Appendix A to this report.

The research involves formulation of commercially available materials and synthesis of new elastomers. In the present report period, formulation studies at JPL and elsewhere produced a material having about 250-350 psi tensile strength and 30-80% elongation at 260°C for at least 24 hours in simulated brine. The relationship between these laboratory test results and sealing performance in actual or simulated test conditions is not entirely clear; however, it is believed that no conventional formation or casing packer design is likely to perform well using these materials.

The synthetic effort focused on high temperature block copolymers and development of curable polystyrene. Procedures were worked out for synthesizing these new materials. Initial results with heat-cured unfilled polystyrene "gum" at 260°C indicated a tensile strength of about 50 psi. Cast films of the first sample of polyphenyl quinoxaline-polystyrene block copolymer, which has a "graft-block" structure consisting of a polystyrene chain with pendant polyphenyl quinoxaline groups, showed elastomeric behavior in the required temperature range. Its tensile strength and elongation at 260°C were 220-350 psi and 18-36%, respectively. All of these materials also showed satisfactory hydrolytic stability.

A procedure for the synthesis of a linear block copolymer of this type has been devised, and the required new intermediates have been synthesized and characterized.

SECTION I

INTRODUCTION

A total of five types of geothermal energy resources have been defined (Ref. 1) and environmental resistance of elastomers for geothermal applications will depend on resource characteristics. The types of resources are as follows:

(1) Hydrothermal convective resources can be either vapor-dominated or liquid-dominated and are characterized by relatively high temperatures at shallow depths.

(2) Geopressured resources consist of pressurized water reservoirs in sedimentary basins. They often contain dissolved methane, and are capable of supplying both heat and mechanical energy.

(3) Hot, dry rock resources are nonmolten but very hot rock structures with insufficient water to be considered as type 1 (hydrothermal convective resources).

(4) Normal or near-normal gradient resources are conduction-dominated areas and are the result of radiogenic heat production, heat flows and the thermal conductivity of rocks. They exhibit temperatures from 15°C to about 300°C.

(5) Magma resources consist of molten rock at temperatures exceeding 650°C.

Resources (4) and (5) can be neglected at the present because their successful utilization is considered to be far in the future.

For materials applications involving resources of types (1), (2), and (3), the high temperature environment is from about 150 to 390°C or higher. In addition, salinity can be low (<1000 ppm) to high (~250,000 ppm), H_2S and CO_2 may be present, and pressures vary from about 500 psia to over 12,000 psia. The highest pressures have been found in geopressured resources. Elastomeric materials exposed to these environments may thermally, hydrolytically or chemically degrade, may absorb water or gases and later rupture at lower pressures (i.e., experience the "bends"), or they may undergo viscous flow to result in failure.

Suitable elastomers are needed for small molded items such as O-rings and other small seals, large moldings such as packers and mud motors, and for electrical insulation. The work reported here is directed toward the development of formulations for large moldings; the program structure is shown in Figure 1. The elastomer capability survey, material property specifications, and initial development work are described in the previous annual report (Ref. 2).

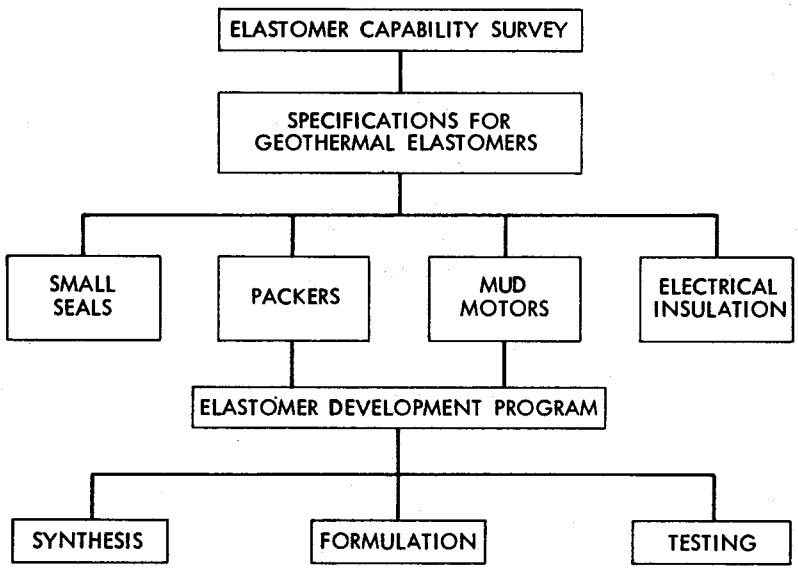

Figure 1. Geothermal Elastomers Program Structure

The development of suitable materials is being approached in two ways. One approach involves fibrous reinforcement of existing gumstocks for improved high temperature tensile strength and extrusion resistance, and the other makes use of materials having a glass transition temperature (Tg) of about 100°C. The latter approach is based upon the observation that conventional elastomers undergo a reversible decrease in tensile strength with increasing temperature that is directly proportional to the difference between the temperature at which the tensile strength is measured and the Tg of the polymer used (Ref. 3). Two avenues were pursued using high Tg materials. One was the crosslinking of plastics such as polystyrene and polyphenyl ether, and the other involved synthesis of block copolymers with individual blocks selected for the service requirements.

Brine at 260°C was selected as being a representative operating environment for geothermal applications. It is believed that under these conditions an elastomer, to be considered a test candidate, should have a tensile strength of at least 400-500 psi, an elongation of 50%, and a service life of at least 24 hours. These specifications do not represent a complete description of possibly relevant properties, but were deemed important in the absence of correlations between expected performance and compression set, extrusion resistance, etc. Chemical stress relaxation, sol-gel, and weight loss measurements were made on most samples, and it is expected that these may be useful in correlating laboratory measurements with actual performance.

SECTION II

ELASTOMER DEVELOPMENT

A. FORMULATION OF COMMERCIAL ELASTOMERS

The elastomer properties and formulation variables of interest in geothermal and petroleum applications are not necessarily the same; the objective in both cases, however, is to formulate materials that are stable and have maximum tensile strength and elongation at temperatures of 260°C and above. Parts that are to be used in oil wells at temperatures up to 149°C are most commonly made of acrylonitrile butadiene (NBR), particularly Hycar.* Parts with comparable properties can be formulated from epichlorohydrins (ECO), such as Hydrin and Herclor, but these cause some processing difficulties such as mill sticking and molding problems. Chlorinated polyethylene (CPE) elastomers do not appear to be useful because of poor mechanical properties and limited chemical resistance. Although silicones can be thermally stable at temperatures above 260°C, their mechanical properties are not very good even at room temperature and are very poor at high temperatures. Under geothermal conditions, they do not show adequate hydrolytic stability. Fluorocarbons such as Viton and Fluorel are considered the best elastomers available at reasonable cost, but molding is difficult and they have limited steam resistance. Perfluoromethylvinyl ether-tetrafluoroethylene copolymer (Kalrez) is the most stable elastomer currently available, but it is extremely expensive ($\sim$\$4000/kg) and must be molded by DuPont. Furthermore, the maximum web thickness of molded parts is limited to about 0.635 cm. Therefore, this elastomer cannot be used for packers, but can be useful for O-rings, backup rings or other small parts. Ethylene-propylene-diene (EPDM) rubbers may have merit in geothermal applications (Ref. 3). The state of the art is such, however, that any conventionally compounded material will be operating at the limits of its capability; in addition, the part for which it is used will have to be redesigned, if satisfactory results are to be obtained.

An important consideration is the fact that even though an elastomer may have good resistance to hydrolysis and heat aging during the required service period, increasing the operating temperature causes a large, essentially reversible loss in tensile strength and other properties. The magnitude of these changes in tensile strength are shown in Figure 2. These formulations all show satisfactory environmental resistance at temperature (Ref. 2), but undergo a loss of 80-90% of room temperature properties when tested at 260°C. It is interesting to note that tensile strengths at 260°C are about the same for all formulations, despite an almost twofold variation in room temperature values, an indication that caution is needed when correlating performance with measurements made at other than service conditions.

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*Manufacturers of the trade-named products mentioned in this report are identified in Appendix B.

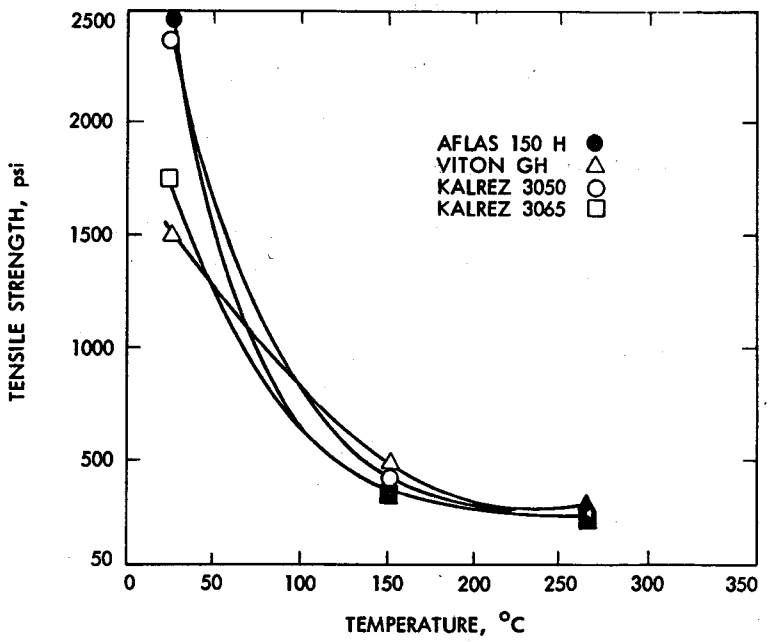

Figure 2. Tensile Strength vs. Temperature for Elastomer Formulations

With this in mind, the use of fibrous reinforcement was investigated, under the assumption that if a satisfactory balance of high temperature properties could be obtained with a fluorinated polymer such as Viton or Aflas, similar results would be obtained with another gum that might prove more suitable.

1. Reinforcement with Asbestos Fibers

Colloidal asbestos fibers were used ("Calidria HPO," Union Carbide). Untreated fibers were exposed to brine (2.5% NaCl, 0.1% CO_2, pH 4.6) for 40 hours at 260°C, resulting in a weight loss of about 3%. In order to react well with a silane coupling agent, hydrolysis of the basic magnesium hydroxide surface is necessary (Ref. 4). A description of the procedure for hydrolysis and reaction with the coupling agent is given in the previous annual report (Ref. 2, p. 14).

The formulation and cure schedule used with carbon black-filled formulations resulted in compounded elastomers which could not be molded properly when asbestos filler was used, and it was necessary to reexamine cures to establish a satisfactory procedure. The compositions of the compounds tested are listed in Table 1, and a representative carbon black-filled formulation is included for comparison.

a. Experimental Method. The experimental procedure was as follows: Gum was banded on the mill and fillers, coagent, and peroxide added, in that order. The compound was cut a number of times and refined by cigar rolling several times through a tight nip. It was then sheeted

Table 1. Composition of Asbestos-Filled Viton Compounds (Parts by Weight)

	5Gu	6Gu	7Gu	8AS6	9AS6	10[1]
Viton GH	100	100	100	100	100	100
Litharge[2]	3.0	10.0	10.0	10.0	10.0	3.0
Diak 7	1.25	1.25	0.67	1.25	1.25	2.5
Luperox 130-XL	1.25	1.25	0.67	1.25	1.25	2.5
Asbestos	-	-	-	6.0	12.0	-
Thermax	-	-	-	-	-	50
Pelletex NS	-	-	-	-	-	10
VPA #2	-	-	-	-	-	2

[1] Cf. Ref. 2, p. 12.

[2] Rubber grade, NL Industries.

off somewhat thicker than the mold dimension, molded at 177°C for 15 minutes, and postcured at 260-280°C in nitrogen for 24 hours. Rings with an O.D., I.D., and wall thickness of 0.930, 0.760, and 0.085 in., respectively, were cut from molded sheets. Ultimate tensile strength and elongation were measured in an Instron testing machine fitted with a special insulated box that allows measurements at temperatures as high as 370°C.

Aging was carried out in stainless steel pressure tubes tested to 1500 psi. They were 15 cm long and 3.2 cm OD. Rings were aged 24 hours at 252°C in 2.5% aqueous sodium chloride containing 1000 ppm carbon dioxide, at a pH of 4.6.

b. Results and Discussion. Physical properties and weight losses of unaged and aged specimens are given in Table 2, and a graph of unaged tensile strength vs. temperature is presented in Figure 3.

In general, both unfilled and filled samples show the usual large losses in tensile strength and elongation with increasing temperature, but do not show much degradation on aging in brine. It can be concluded, however, that increasing the asbestos content improves aging properties. The weight loss figures are noteworthy in that the asbestos-containing formulations have significantly higher weight loss than the unfilled compounds. However, the loss in weight by both asbestos-filled samples is about the same despite the fact that one contains twice as much asbestos as the other. Weight loss and tensile strength retention after

Table 2. Physical Properties of Asbestos-Filled Elastomers* Before and After Aging in Brine

Elastomer	Condition	Tensile Strength, psi and (Elongation, %)						Weight Loss
		25°C		150°C		260°C		
5GU	Not postcured	385	(244)	108	(65)	108	(48)	
6GU		377	(249)	117	(73)	84	(35)	
7GU		367	(281)	102	(83)	91	(38)	
5GU	Postcured	533	(223)	168	(59)	157	(48)	
6GU	280°C,N_2,24 h	715	(225)	156	(50)	173	(45)	
7GU		623	(223)	137	(54)	143	(42)	
5GU	Postcured,aged	466	(240)	146	(76)	125	(54)	1.10
7GU	252°C,Brine,24 h	479	(208)	127	(64)	143	(52)	1.70
8AS6	Postcured	1179	(169)	284	(55)	238	(41)	
9AS6	280°C,N_2,24 h	1171	(147)	280	(48)	155	(27)	
8AS6	Postcured,aged	716	(187)	117	(52)	154	(36)	3.20
9AS6	252°C,brine,24 h	1004	(165)	223	(47)	194	(34)	3.34

*Average of at least two runs.

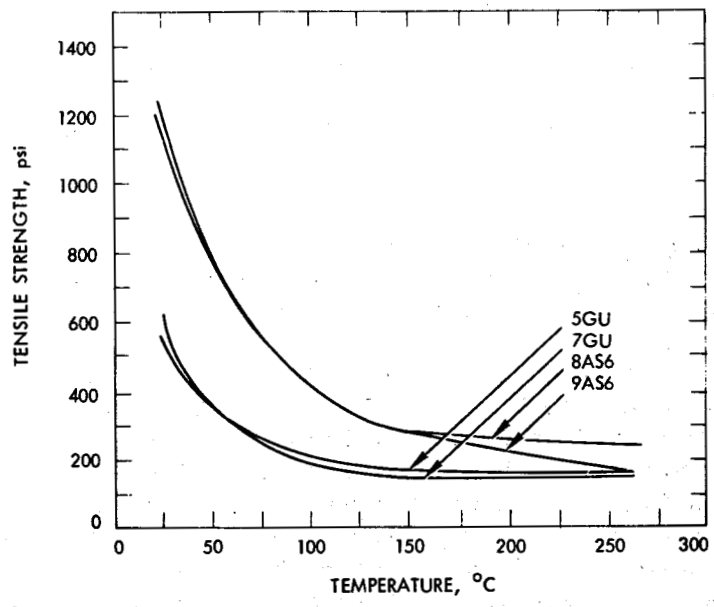

Figure 3. Temperature Dependence of the Tensile Strength of Unaged Elastomer Compositions

aging are significantly better for the asbestos-filled compounds than for the glass-filled ones (Ref. 2, pp. 25-26); perhaps longer asbestos fibers would afford a better balance of hot properties and brine resistance.

2. Testing of Miscellaneous Samples

Several aged and unaged experimental samples were submitted for high temperature testing by L'Garde, Inc., Newport Beach, California, a co-contractor on the DOE program, and a sample of a nitrile formulation was sent by Dresser Industries, Dallas, Texas, for similar tests.

Results obtained with these materials are tabulated in Table 3, and representative data are presented graphically in Figure 4. Some AFLAS 150H samples compounded at JPL are included for comparison.

The data in Table 3 and Figure 4 show the usual large losses in tensile strength and elongation as temperature is increased. The difference between aged and unaged samples in most cases is not great, the large drop in values being caused mainly by the temperature. The NBR samples, however, show irreversible hardening and embrittlement.

3. Crosslinking of Polystyrene

Polystyrene had previously been found to exhibit good resistance to geothermal conditions (Ref. 2, p. 14), and experiments were undertaken to determine the potential utility of crosslinked materials above the Tg of polystyrene ($\sim$100°C) in the region of elastomeric response.

Crosslinking was attempted by radiation and by copolymerization with vinyl toluene and butadiene to provide sites for chemical crosslinking. Some experiments were also performed with Pliolite, a commercial styrene-butadiene copolymer containing 82% styrene.

Irradiated Polystyrene: Polystyrene (M. W. 250,000, Polysciences, Inc., Warrington, PA) was molded at 150°C and cut into strips, which were placed in glass tubes and sealed under vacuum. The tubes were placed in a Co-60 source and irradiated to doses of 52, 113, 152, and 303 megarads. The sample exposed to 52 megarads was soluble; the others contained gel. Tensile strength measurements were made on these samples at 150°C in air; low tensile strength values ($\sim$ 10 psi) and high elongation (no break) were obtained. Since the literature indicated that radiation above this level would begin to degrade the polymer (Ref. 5), the radiation experiments were discontinued. Chemical crosslinking was tried using mixtures of polystyrene with (1) 3% sulfur, 1.5% sulfur; (2) 4.5% mercaptobenzthiazol (MBT); and (3) 3% sulfur and 3% MBT and curing for 1 hour at 150°C; however, no crosslinking was observed.

Pliolite 26B (Goodyear). A styrene-butadiene block copolymer (pliolite 26B, Goodyear) was also investigated. Test samples contained 0.4 and 0.8 wt% benzoyl peroxide, 0.2 wt% sulfur and 0.2 wt% MBT, and

Table 3. Tensile Strength and Elongation Data for Samples Submitted by L'Garde, Inc., and Dresser Industries* AFLAS 150H Samples Compounded at JPL

Sample No.	Tensile Strength, psi, and (Elongation, %)		
	25°C	150°C	260°C
AFLAS-5	1466 (191)	207 (93)	127 (35)
AFLAS-6	2027 (199)	296 (101)	211 (69)
AFLAS-7	1648 (168)	263 (84)	220 (59)
AFLAS-XHCL	1313 (156)	550 (71)	354 (42)
JPL 226-1 (Virgin)	1427 (267)	479 (232)	299 (185)
JPL 226-2 (Chem. aged)	1293 (275)	518 (257)	291 (174)
237-III-1 (Virgin)	1257 (97)	410 (49)	270 (30)
237-III-2 (Chem. aged)	937 (87)	245 (29)	220 (25)
JPL 242-1 (Virgin)	1210 (203)	538 (137)	320 (78)
JPL 242-2 (Chem. aged)	1000 (80)	556 (52)	336 (27)
248-II-1 (Virgin)	1392 (30)	427 (17)	197 (12)
248-II-2 (Chem. aged)	1280 (20)	98 (26)	31 (18)
JPL LOA-1 (1)	2978 (115)	705 (63)	26 (18)
NBR-1 (2)	2069 (267)	752 (138)	262 (16)

*Information supplied on these samples by L'Garde and Dresser is presented in Appendix C.

(1) L'Garde sample designation JPL LOA-1 is a nitrile formulation.

(2) Dresser Industries nitrile sample. Sample was dumbbell-shaped; other samples were ring-shaped.

0.4 wt% sulfur and 0.15 wt% MBT. They were molded at 75°C and cured at 145°C for one hour, and at 180°C for one hour. Testing for gel content indicated that degradation occured during curing when peroxide or sulfur plus MBT were present; that is, the gel content increased with each curing step for elastomers containing no peroxide, sulfur or MBT. The results (Table 4) show very poor physical properties.

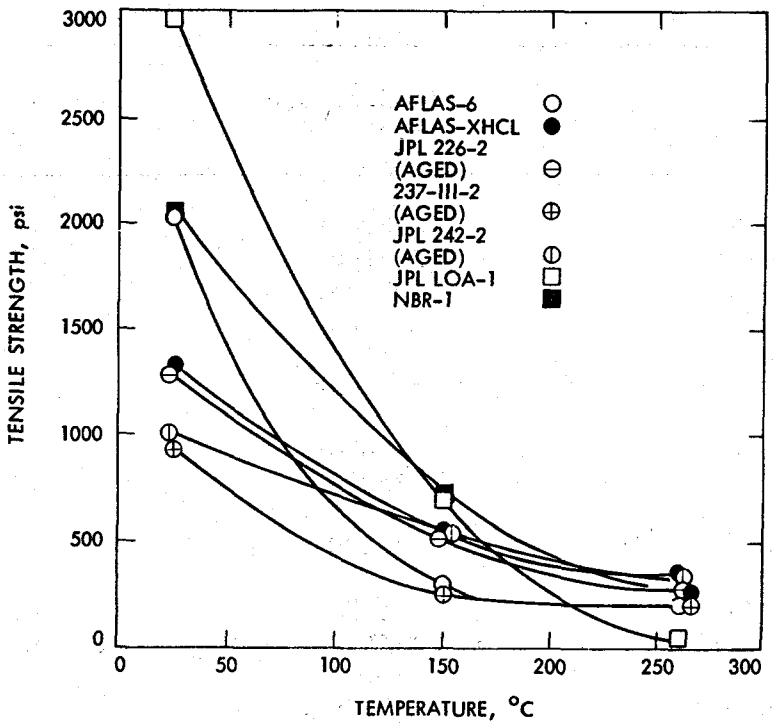

Figure 4. Tensile Strength vs. Temperature for Various Elastomers

Styrene-Ar-Methyl Styrene Copolymer. A copolymer of styrene and ar-methyl styrene was prepared. The monomers were distilled and a solution containing 10 wt% ar-methyl styrene was thermally polymerized in a sealed tube under nitrogen by heating 72 hours at 40°C, 72 hours at 50°C, 72 hours at 70°C, 168 hours at 119°C, and 48 hours at 150°C. A solution of the polymer (10.8 g) in 50 ml methylene chloride was prepared and 0.5 wt% dicumyl peroxide was added. A sheet of polymer was obtained by evaporation of the solvent and then molded at 150°C for 1 hour. The polymer was soluble, showing that no crosslinking had occurred. Similar results were obtained with Lupersol 130 and Luperco 130 XL.

Styrene-Divinyl Benzene Copolymers. Copolymers of styrene and divinyl benzene crosslinked during polymerization, but since the resulting product could not be molded, it would have very limited application as a material for geothermal seals. However, styrene-divinyl benzene polymers were prepared to attempt to determine if crosslinked polystyrene would have good properties at 260°C. (If so, then further work could be done to learn how to avoid processing difficulties.) Styrene was polymerized with 0.5, 1, and 3 wt% divinyl benzene (Ref. 6) in the presence of 0.1 benzoyl peroxide. The polymerization mixtures were cured under helium in sealed glass in an oil bath at 45°C for 96 hours, and for 48 hours each at 60, 80, 100, 125, and 150°C. The sample with

Table 4. Tensile Strength of Crosslinked Pliolite at Various Temperatures

Sample No.	Temperature Test, °C	Tensile Strength psi
346-2-07B-1	Ambient	<2500
346-2-07B-1	Ambient	2500
346-2-07C-1	Ambient	2500
346-2-07D-1	Ambient	2500
346-2-07-E	Ambient	2500
346-2-07A-1	Ambient	2500
346-2-05A-1	150°C	(1)
346-2-05B-1	150°C	(1)
346-2-05C-1	150°C	(1)
346-2-05D-1	150°C	0.13
346-2-07A-2	150°C	0.2
346-2-07B-2	150°C	0.4
346-2-07C-2	150°C	0.4
346-2-07D-2	150°C	0.5
346-2-07E-2	150°C	0.7
346-2-05A-2	260°C	(2)
346-2-05B-1	260°C	(2)
346-2-05C-2	260°C	(2)
346-2-05D-2	260°C	0.1
346-2-07A-3	260°C	0.1
346-2-07B-3	260°C	0.2
346-2-07C-3	260°C	0.2
346-2-07D-3	260°C	0.2
346-2-07E-3	260°C	0.3

(1) No break at end of travel.
(2) Sample melted.

0.5 wt% divinyl benzene had numerous small bubbles, but the two with 1 and 3 wt% divinyl benzene were free of bubbles. Tensile strength and elongation were measured for the latter (Table 5).

Styrene-Butadiene Copolymers (5%, 10% Wt% Butadiene). Styrene-butadiene copolymer containing fewer butadiene units was prepared by emulsion polymerization, using 5 and 10 wt% butadiene, according to directions in the literature (Refs. 7, 8). At 95% conversion, the polymerizations were shortstopped by the addition of five volumes of water containing 0.2 wt% hydroquinone. Rotation was continued for 30 minutes followed by coagulation with a solution of 0.2 wt% hydroquinone in

Table 5. Tensile Strength and Elongation Data for Crosslinked Styrene-Divinyl Benzene (DVB) Copolymers at 150°C*

Sample No.	% DVB	Tensile Strength psi	Elongation, %
2-17B-1	1	49	323
2-17B-2	1	47	115
2-17B-3	1	54	241
2-17B-4	1	56	250
2-17C-1	3	50	220
2-17C-2	3	70	260
2-17C-3	3	51	237

*Samples cast in dumbbell-shaped cylindrical vials. Samples were also cast with 0.5% DVB, but were not tested because of formation of numerous bubbles.

2-propanol. The resulting polymer was separated and dried at 45°C. The polymers were cured either by heat or by addition of peroxide curing agents. Curing agents were added to solutions of polymer in methylene chloride, and solvent was evaporated at room temperature. The resulting thin films were cut into squares, stacked, molded at 100°C, cured 1 hour at 175°C, and then press cooled and the samples removed. Strips were cut for testing. Tensile strength data are only available for 150°C. At room temperature, the material is a hard plastic, and the preliminary results at 150°C needed improvement before testing at 260°C would be warranted. Results are collated in Table 6.

Data in Table 6 show low tensile strength values, lower than those for the styrene-divinyl benzene materials (Table 5). Gum tensile strengths of conventional styrene-butadiene polymer are rather low, of the order of 200-300 psi, and an increase in tensile strength by a factor of 10 with carbon reinforcement is possible. One might therefore expect that carefully formulated and reinforced high-styrene materials would have a tensile strength of 500 psi at 150°C.

The copolymers listed in Tables 5 and 6 were prepared by free radical polymerization, and showed the broad molecular weight distribution characteristics of such materials, when examined by liquid chromatography. Distributions ranged from about 50,000 to several million, with peaks at about 600,000. Some improvement would probably be obtained by using ionic polymerization catalysts to obtain a narrow molecular weight distribution, but a marked improvement in properties is unlikely.

Table 6. Tensile Strength Data for Crosslinked Styrene-Butadiene Copolymers at 150°C

Sample No.	Butadiene, %	Cure System	Tensile Strength, psi (1)
346-2-18B	5	Lupersol 130, 0.3% (2)	14
346-2-19B	10	Lupersol 130, 0.3% (2)	24
346-2-21A	10	None (3)	21
346-2-21B	10	Lupersol 130, 0.3%; TAIC 0.3% (4)	24

(1) Average of at least three values.
(2) Peroxide curing agent, see Appendix B.
(3) Crosslinking by heat only.
(4) TAIC = triallylisocyanurate.

B. SYNTHESIS OF NEW HIGH TEMPERATURE ELASTOMERS

The characteristics of an elastomer for high temperature geothermal applications differ from those required for many other applications in that the operating temperature range can be limited to temperatures above 200°C. Therefore, the polymeric material can be rigid and non-elastomeric at room temperature and higher, except for certain applications; e.g., many O-ring seals where the seal must be deformed at lower temperatures for ease of assembly, as for most drill bit designs. It was planned to attempt to utilize existing high temperature polymer synthesis procedures and modify the chemical structure of such polymers so that they would be flexible at high temperatures.

Two types of materials were investigated: 1) block copolymers, and 2) crosslinkable polystyrene. The work on crosslinkable polystyrene is described in Section II-A-3.

Previous work on block copolymers, reported in the first annual report (Ref. 2), was primarily concerned with synthesis and characterization of hard and soft blocks, and included some investigation of coupling hard and soft blocks by means of the Williamson ether-forming reaction, which has given good results in certain types of block copolymer syntheses (Ref. 9).

It was not found possible to produce a satisfactory soft block from available materials such as polyethylene oxide, hydroxyl-terminated

saturated polybutadiene (Telgaen S), or a terminally difunctional polyisobutylene diol prepared by JPL. Chlorination or tosylation of end groups did not proceed in sufficient yield by the methods tried to give a material that would yield a satifactory polymer. It was therefore decided to try a commercial bromobutyl rubber (BBR, "Polysar XL") as a soft block. A model reaction was run with 1,6 dibromo hexane in solvent ethanol which gave the desired substitution product; however, reaction of the BBR gave side reactions indicating that only low molecular weight polymer would be obtained. The use of these aliphatic difunctional materials and the Williamson synthesis was unpromising, and was abandoned in favor of incorporating substituted polystyrene moieties as soft blocks.

In view of the efficiency and high yield of the quinoxaline-forming reaction, it was decided to use this reaction to couple hard and soft blocks by provision of suitable reactive entities in both types of blocks.

The first approach was to synthesize 4-vinylbenzil for copolymerization with styrene, and react the copolymer with the polyphenylquinoxaline (PPQ) hard block to form the finished polymer. This approach was thwarted by the reactivity of the intermediate 4-vinyl-benzoin, which repeatedly polymerized during purification. Polystyrene was therefore acylated with phenyl acetyl chloride and the resultant ketone oxidized with selenium dioxide. This procedure gave a polymer containing about one benzil group for every 250 styrene groups. This material was reacted by adding it to either phenylquinoxaline monomers (1,4-bis-(phenylglyoxalyl) benzene and 4,-4'-diaminobenzidine), or to preformed PPQ with terminal amine groups. The former reaction gave polymer in high yield with considerable crosslinking (gel formation), while the latter afforded a 90% yield of soluble, gel-free material.

These latter materials showed the desired properties of phase-separated block copolymers, i.e., a Tg at 100°C and another at 325°C, and softening and elastic behavior above 100°C. Thin films of this material were cast from solution. These were opaque, having the appearance of magnetic tape. A few measurements were made on these rather delicate samples; they showed tensile strengths and elongations of 220-350 psi and 18-36%, respectively, at 260°C in nitrogen. These results show that this system has the type of behavior required for the application and are in fact quite encouraging, for initial values.

These types of polymers are not linear ABAB... block copolymers, but have what is termed a "graft" block structure, since the PPQ blocks are pendant from the polystyrene chain. We believe that the ABAB... structure is likely to have better properties, particularly better thermal stability, since there will be far fewer polystyrene end groups. In order to synthesize the linear material, it is planned to use polymerized styrene in the presence of 3,3'-4-4'-tetraaminodiphenyldisulfide, which acts as a chain transfer agent and incorporates the amine moieties

as end groups in the polymer chain. The general approach is well known; however, this particular polymer has not been made. The next step would be to couple the separate blocks via the quinoxaline forming reaction to make the final block copolymer.

1. Synthesis of 3,3'-Diamino-4,4'-Dinitrophenyl Disulfide

A 1.69 g (0.022 moles) quantity of crystalline sodium sulfide was placed in a 100 ml round-bottomed flask fitted with a reflux condenser and 20 ml of ethyl alcohol added. The flask was heated on a steam bath until the sulfide dissolved. Then 0.7 g (0.022 equivalent) of finely ground sulfur was added, and the heating was continued until the sulfur dissolved, forming a brownish-red solution of sodium disulfide.

A solution of 5 g (0.0289 moles) of 3-amino-4-nitrochlorobenzene in 50 ml of ethyl alcohol was prepared and placed in 250 ml round-bottomed flask fitted with a reflux condenser. The sodium disulfide solution was added slowly to this solution through a funnel placed in the top of the reflux condenser. The mixture was then heated on a steam bath for 2 hours. After cooling, the reaction mixture was diluted to 250 ml with water, the organic disulfide was filtered off, washed several times with water, and dried.

Yield: 2.76 g (58% of theory). The material was homogeneous on thin layer chromatography and had a melting point of 172-174°C.

2. Synthesis of 3,3',4,4'-Tetraaminodiphenyl Disulfide

To a solution of 15 g (0.066 moles) of stannous chloride dihydrate in 20 ml of concentrated hydrochloric acid, 2.76 g (0.0083 moles) of 3,3'-diamino-4,4'-dinitrophenyl disulfide were added. The solution was heated on a steam bath for 20 hours, then cooled to room temperature and filtered. The filtrate was diluted with water to 50 ml and made alkaline (pH ~ 9) with 15% ammonium hydroxide. The solution was heated to 65-70°C and 12 ml of 30% hydrogen peroxide was added drop by drop over a period of about 2 hours. After the addition was finished, the temperature was maintained at 65-70°C for one more hour, then the solution was cooled to 0-5°C and the precipitated material filtered off. The product was recrystallized from water.

Yield: 0.7 g (44% of theory).

Calc. for $C_{12}H_{14}N_4S_2$ (278.39): C, 51.76%; H, 5.06%; N, 20.12%.

Found: C, 51.72%; H, 5.34%; N, 20.11%.

3. Synthesis of Benzil-Terminated Polyphenyl-quinoxalines

The polymerization was done essentially as previously described (Ref. 2) with one exception: an excess of 1,4-bis-(phenylglyoxalyl) benzene was used to ensure benzil termination.

SECTION III

CONCLUSIONS AND RECOMMENDATIONS

Current elastomeric materials, even in the absence of hydrolytic, oxidative, or other types of breakdown, undergo a reversible loss of 85-90% of their room temperature properties when heated to 260°C. If a seal or packer could be designed that would operate successfully using an elastomer having 200 psi tensile strength, 50% elongation, and compression set estimated at 60%, it could be made from presently existing elastomers and would probably operate for at least 50-100 hours at 250-260°C in brine. Since present petroleum industry tools require higher values of these properties, redesign to accommodate the lower values would be necessary. There are some types of tools, however, for which such redesign to accommodate existing materials in geothermal use would not be feasible. These include formation packers and Moyno pump stators.

Formulation of existing gumstocks is a well-explored area of increasingly marginal return. Improvement in existing formulations and tool redesign are, of course, essential if the efficiency of extraction of geothermal energy is to be increased; however, it is vital to a satisfactory ultimate solution of the materials problem that a long-term commitment to the development of new materials be made.

It is not safe to assume that developments in the petroleum area will apply to geothermal problems, since the environments are not the same. Furthermore, a material suitable for geothermal use may not find much application outside the geothermal area, and would face an uncertain market. For geothermal applications at high temperatures, it appears that it will be necessary to chemically modify existing polymers with high Tg's, or to synthesize new polymers with satisfactory mechanical properties at elevated temperatures. This is the approach JPL has taken.

If geothermal energy is perceived as a significant long-term energy source, it is recommended that a commensurate effort be made to develop satisfactory geothermal materials.

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APPENDIX A

DEVELOPMENT AND EVALUATION OF ELASTOMERIC MATERIALS FOR GEOTHERMAL APPLICATIONS (PAPER)*

*Presented to the American Institute of Chemical Engineers in June 1978.

DEVELOPMENT AND EVALUATION OF ELASTOMERIC MATERIALS FOR GEOTHERMAL APPLICATIONS

W. A. Mueller, J. D. Ingham,
S. H. Kalfayan and W. W. Reilly

Jet Propulsion Laboratory,
California Institute of Technology
Pasadena, California 91103

SUMMARY

This work includes attempts to synthesize new elastomers (block copolymers) as well as improved formulation of available materials. Constituent hard and soft blocks of candidate block copolymer compositions have been synthesized. Present work is focused on coupling them together to form the elastomer. Formulation of available elastomer gumstocks has emphasized fibrous reinforcement of fluorocarbon rubbers. Organic fiber reinforcement (Kevlar) was found to be unsatisfactory. Glass fiber reinforcement gives significant increases in tensile properties at low levels of fiber addition. Elongation is reduced, and the glass-reinforced compositions examined so far do not hold up well in the geothermal environment.

Crosslinking of plastics has not given very good results so far. A few experiments with polyphenyl ether (NORYL) gave material with low tensile strength and high compression set. The polyphenyl ether itself has good hydrolytic stability under geothermal conditions. Similar experiments are being done with polystyrene. Work carried out to date suggests that new synthetic polymers, such as those being investigated, will be required for service in geothermal environments.

INTRODUCTION

For materials applications in geothermal resources, the high temperature environment is from about 150 to 390°C (302 to 734°F) or higher. In addition, salinity can be low (< 1000 ppm) to high (∿ 250,000 ppm), H_2S and CO_2 may be present, and pressures vary from about 3.45×10^6 n/m^2 (500 psia) to over 8.27×10^7 n/m^2 (12,000 psia). Elastomeric materials exposed to these environments may thermally, hydrolytically or chemically degrade, may absorb water or gases and later rupture at lower pressures (i.e., undergo the "bends"), or undergo viscous flow to result in failure.

This paper represents one phase of research performed by the Jet Propulsion Laboratory, California Institute of Technology, sponsored by the National Aeronautics and Space Administration, Contract NAS7-100.

A very important additional consideration in the application of elastomers at high temperatures is the essentially reversible loss in tensile strength and elongation at the higher temperatures. For example, Viton may have a tensile strength of about 1.03×10^7 n/m$_2$ (1500 psi) at room temperature, but, even in the absence of degradation, the tensile strengths at 149°C (300°F) and 260°C (500°F) are only of the order of 4.14×10^6 n/m$_2$ (600 psi) and 1.72×10^6 n/m^2 (250 psi), respectively. Since this type of behavior is typical of all elastomers, there are only two ways to obtain better high temperature performance. One is to formulate or modify the base elastomer in some way that increases the high temperature tensile properties, and the other is to prepare new elastomers that are designed to have better high temperature properties. An estimate of tensile strength required was derived from a plot of tensile strength vs. differential pressure capability of oil field packers (Cf. Fig. 1).(1) Since only data for four hours in a test well and six months in oil wells were available, the middle curve for 24 hours was obtained by interpolation using log time. It can be seen that on the basis of this curve, for a differential pressure of 1.034×10^7 n/m^2 (1500 psi), the minimum tensile strength can be estimated as 2.34×10^6 n/m^2 (340 psi). To prevent cracking in a casing packer, the elongation should be greater than 50%.

On the basis of some of the above considerations, the specific objective of this work is development of one material for at least one specific application for service at 260°C ($\sim$ 500°F) and 1.034 n/m^2 (1500 psi) for 24 hours in a geothermal environment. The specific application is a casing packer.

EVALUATION OF COMMERCIAL ELASTOMERS

In most specific well applications, there are some fundamental differences between elastomer requirements for oil wells and geothermal resources. For example, oil resistance is not required for most operations in geothermal environments, and resistance to higher temperature brine may not be needed for some petroleum wells. Another difference is that, for oil production, improved elastomers are required because of the need to develop deeper wells, in which temperatures and pressures correspondingly increase.

A number of methods have been used to investigate modes of degradation of fluorinated elastomer formulations. The base elastomers included Viton and Kalrez (from DuPont), and AFLAS 150H (Asahi Glass Co., Yokahama, Japan). Test methods included stress relaxation, sol-gel determinations, swollen stress-strain measurements, weight-loss, and tensile tests after exposure to saline-carbon dioxide, saline-hydrogen sulfide solutions, and deionized water at elevated temperatures.

STRESS-RELAXATION (SR) MEASUREMENTS

Chemical SR measurements can be used to obtain information about degradation rates, scission sites, crosslink densities and nature of the degradation, i.e., whether chain scission and/or crosslinking, or both

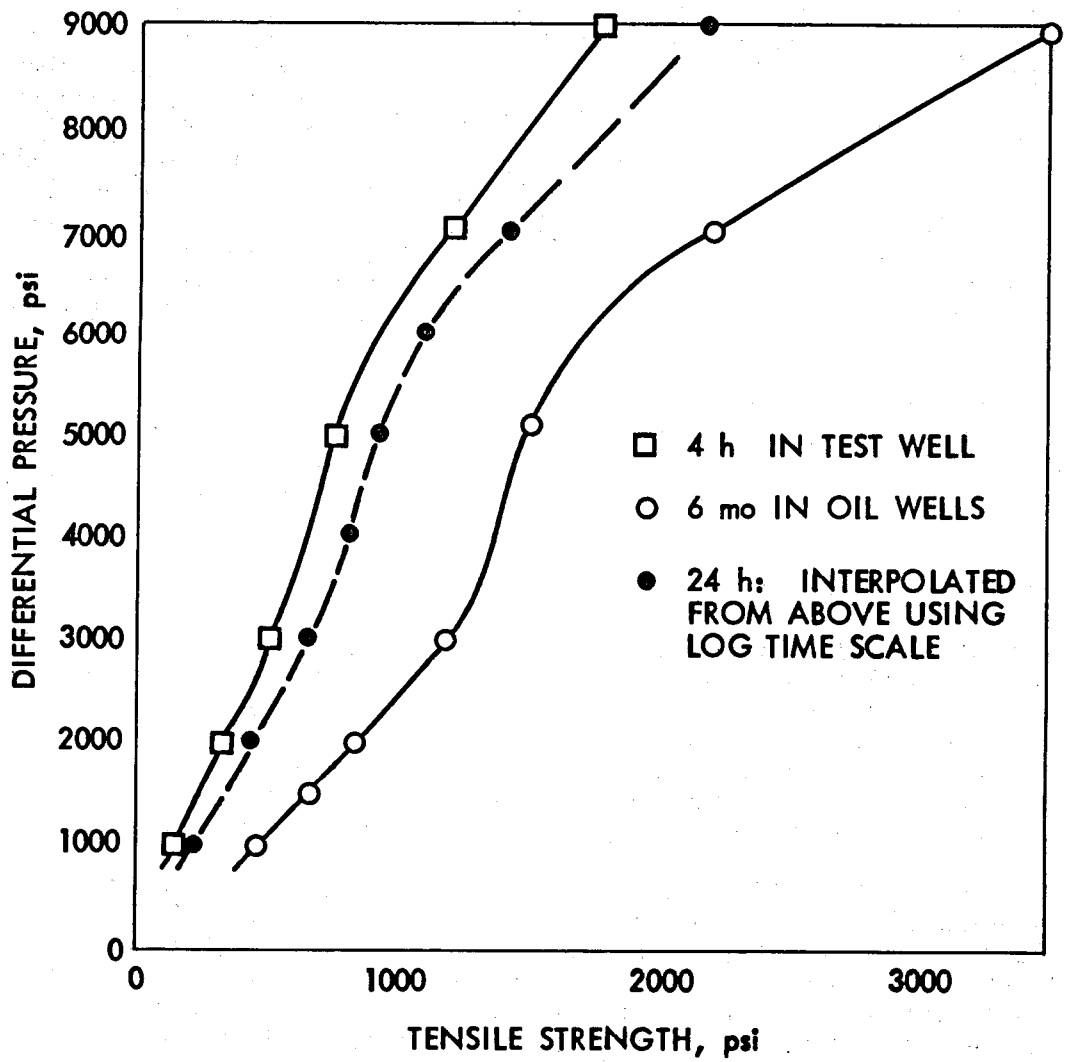


Fig. 1. Estimated Correlation of Differential Pressure Capability of Packers with Elastomer Tensile Strength

take place.[2,3] To make a measurement, the test specimen is strained a fixed distance and the force at that % strain as a function of time is recorded. Two types of SR measurements are carried out: continuous and intermittent.

Figure 2 shows SR results for Viton. Formulations were crosslinked with peroxide and triallylisocyanurate coagent. Viton 10K contains Kevlar fibers and 10G contains glass fibers. The data show that V-10 (without reinforcement) is superior to V-10K and that V-10G is the best formulation. Continuous and intermittent SR of Viton 10 and 10K in air and nitrogen are compared in Figure 3. It can be seen that these compositions undergo oxidative degradation and are significantly less stable in air than in nitrogen. It is also apparent from the wide separation of corresponding continuous and intermittent curves that, while bond scission is taking place, substantial increases in crosslinking are also observed. Figure 4 shows some similar results for Viton 10G. From SR data, this elastomer composition appears to be very stable. However, it was post cured for 24 hours at 315°C. Furthermore, although tensile data are not yet available, this composition is so highly crosslinked that it would not have sufficient elongation for normal packer operations. Figure 5 shows the decrease in SR obtained by post curing at 315°C for the same composition. For the sample that was not post cured at 315°C, further curing occurred during the test, and apparently substantially less than 24 hours is required to effect most of the post curing at 310°C.

Results for Kalrez 3065 (which contains Kevlar fibers) and Kalrez 3050 are shown in Figure 6. Kalrez behaves similarly to Viton, except that comparison of Figures 2 and 6 shows that Kalrez is significantly more thermally stable than Viton. In Figure 7, continuous and intermittent SR of Kalrez compositions are compared. Again, it is clear that both bond scission and crosslinking are taking place simultaneously.

Figure 8 shows the concentration of new crosslinks (ν_e, in moles/m^2) formed at 315°C as a function of time for Viton 10 and 10K and for Kalrez 3050. The values are derived from swelling measurements. It can be seen that crosslink density increases are greatest for Viton K and the least for Kalrez 3050. (Although not shown, crosslink density increases the most for Viton 10G.

The rates of stress relaxation of Vitons 10 and 10K and Kalrez 3050 and 3065 at 280, 295 and 310°C in nitrogen were used to calculate their activation energies (cf. Figure 9). Activation energies are high for V 10, V 10K and Kalrez 3050 (179, 168, 155 KJ, respectively), and relatively low for Kalrez 3065 (87.7 KJ).

Swelling measurements were also carried out to determine crosslink densities as a function of time of aging at 252°C in three different aqueous systems: solution 1. contained 2.5% sodium chloride and 1000 ppm carbon dioxide; solution 2. contained 2.5% sodium chloride and 300 ppm hydrogen sulfide; and solution 3. was deionized water. Swelling and sol-gel measurements were made before and after heating for 20, 40

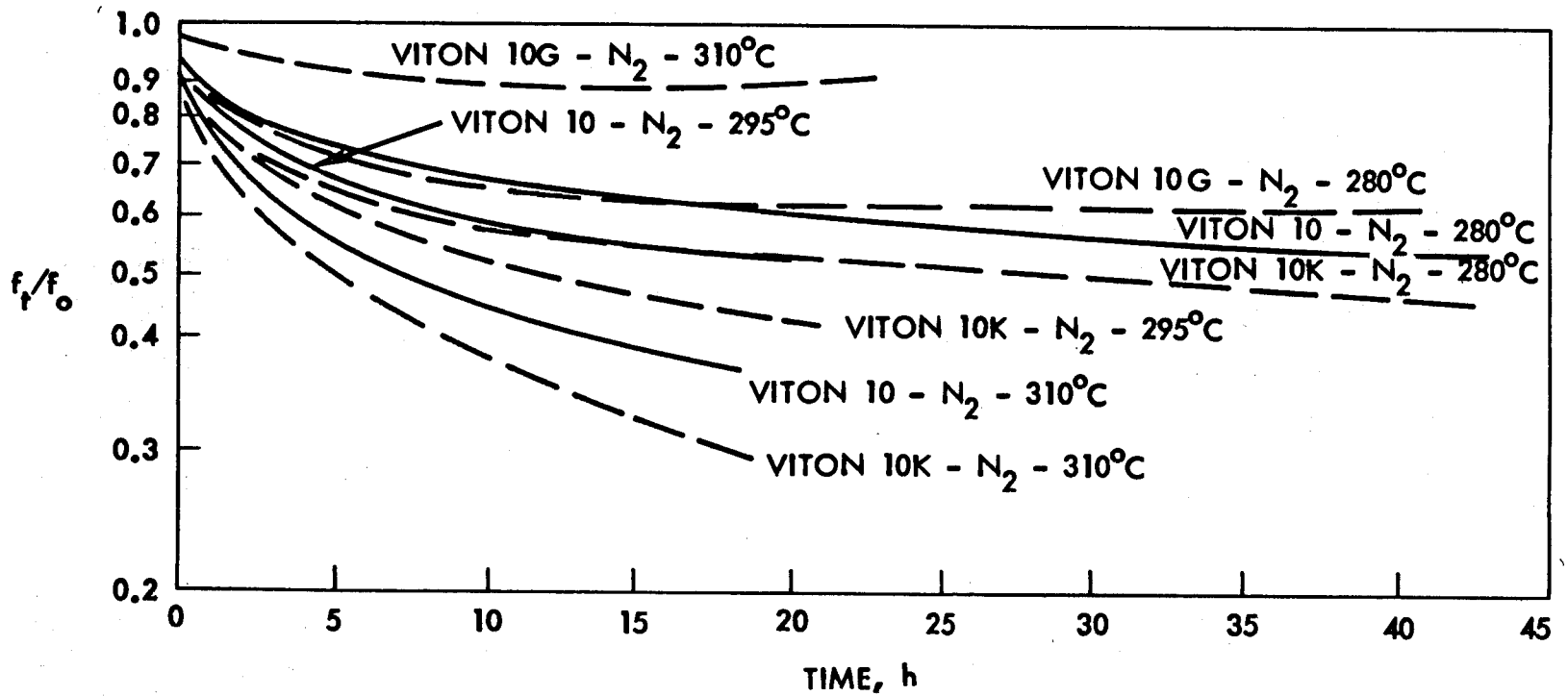


Fig. 2 Continuous Stress Relaxation of Vitons at Various Temperatures in Nitrogen Atmosphere

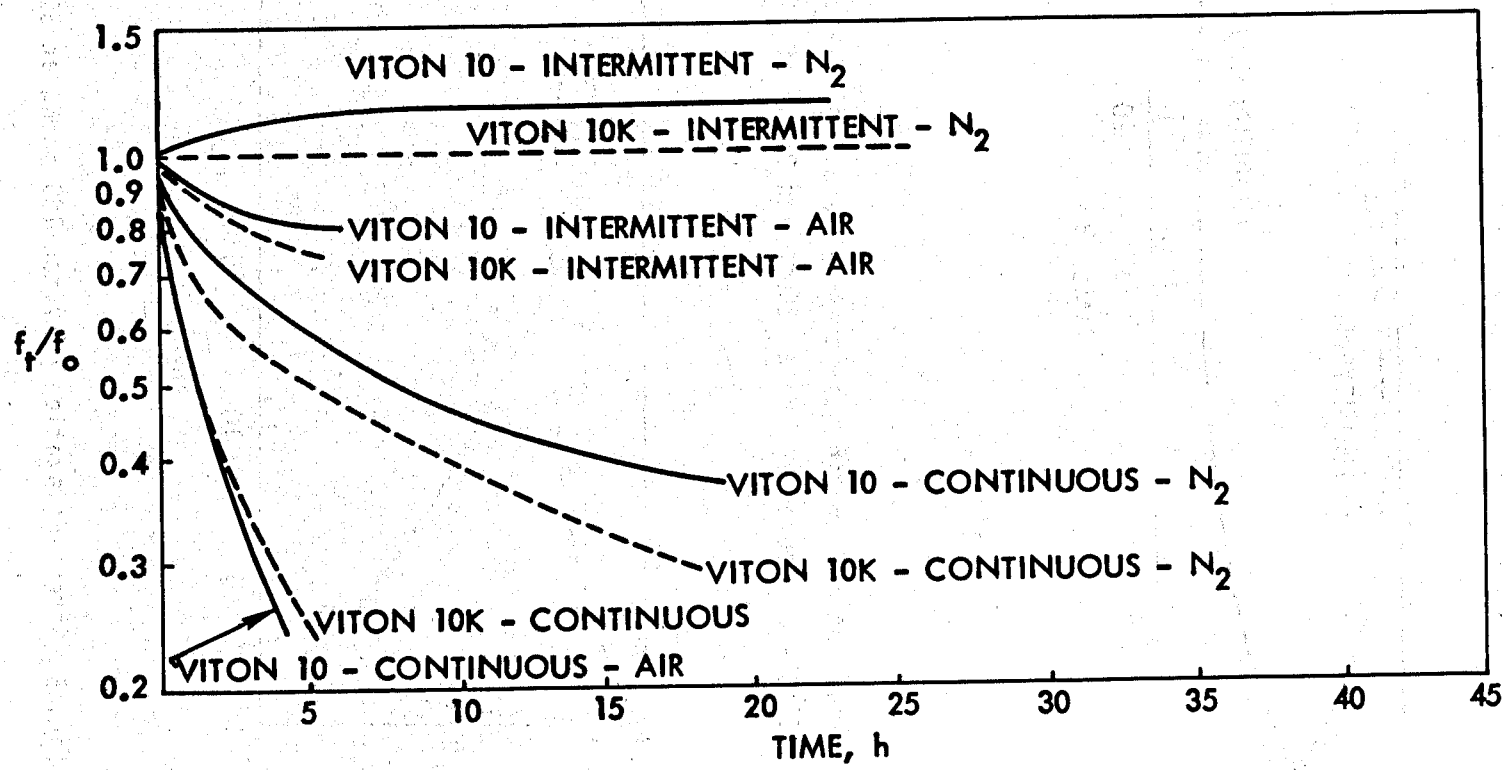


Fig. 3 Comparison of Continuous and Intermittent SR of Viton 10 and 10K in Air and Nitrogen at 310°C

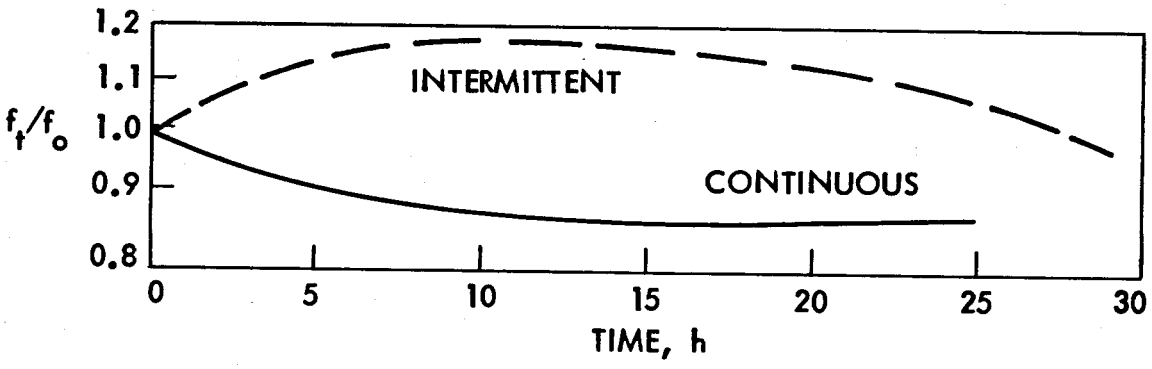


Fig. 4 Intermittent and Continuous Stress Relaxation of Viton 10G in N_2 at 310°C - Postcured 24 hr. at 260°C and 24 hr at 315°C.

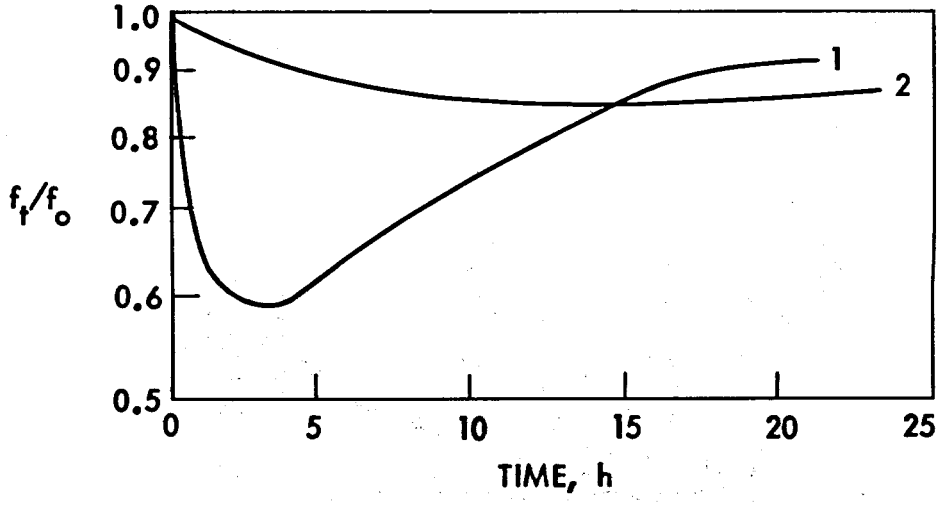


Fig. 5 Stress Relaxation of Viton 10G in N_2 at 310°C
1. Postcured at 260°C in N_2 for 24 hr.
2. Postcured at 260°C in N_2 for 24 hr and at 315°C for 24 hr.

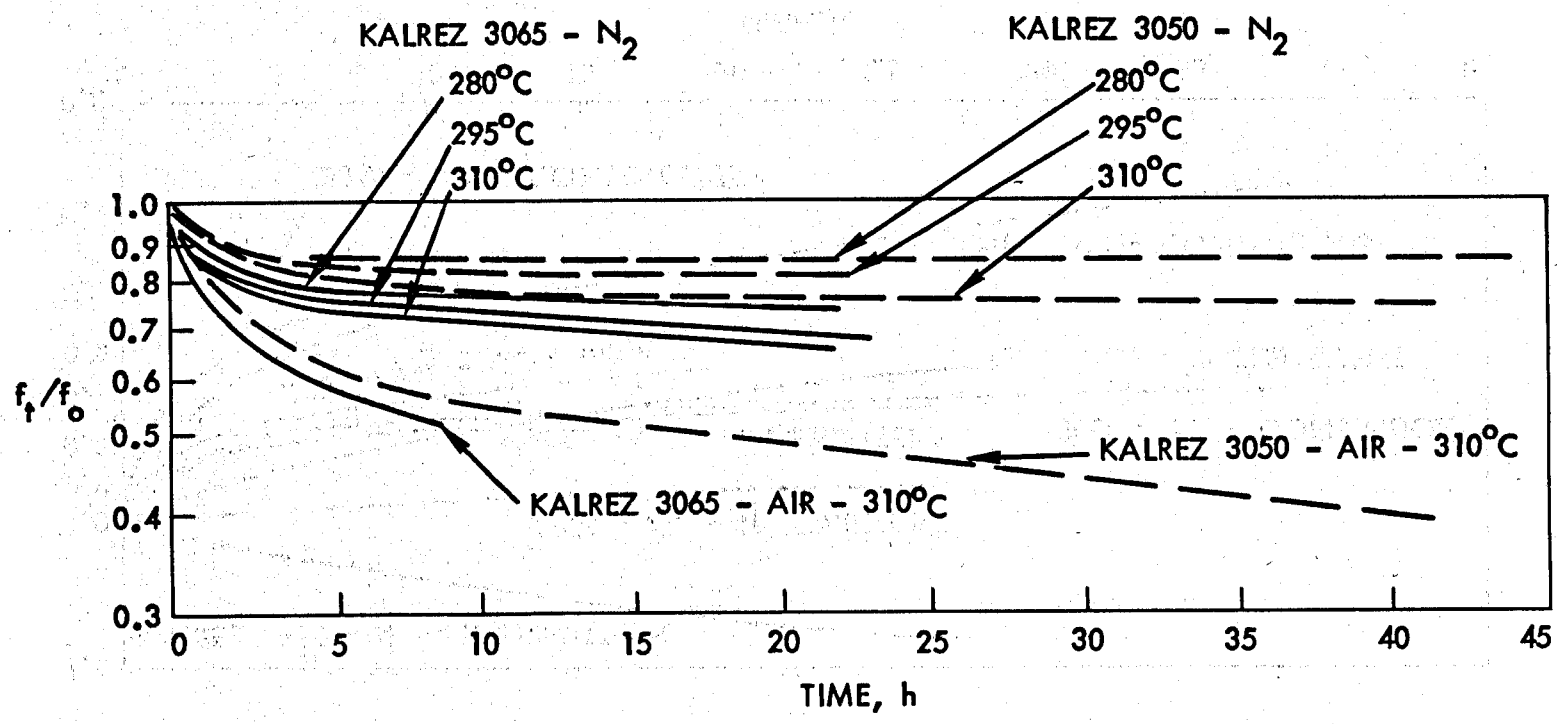


Fig. 6 Continuous SR of Kalrez 3050 and 3065 at Various Temperatures in Nitrogen and Air

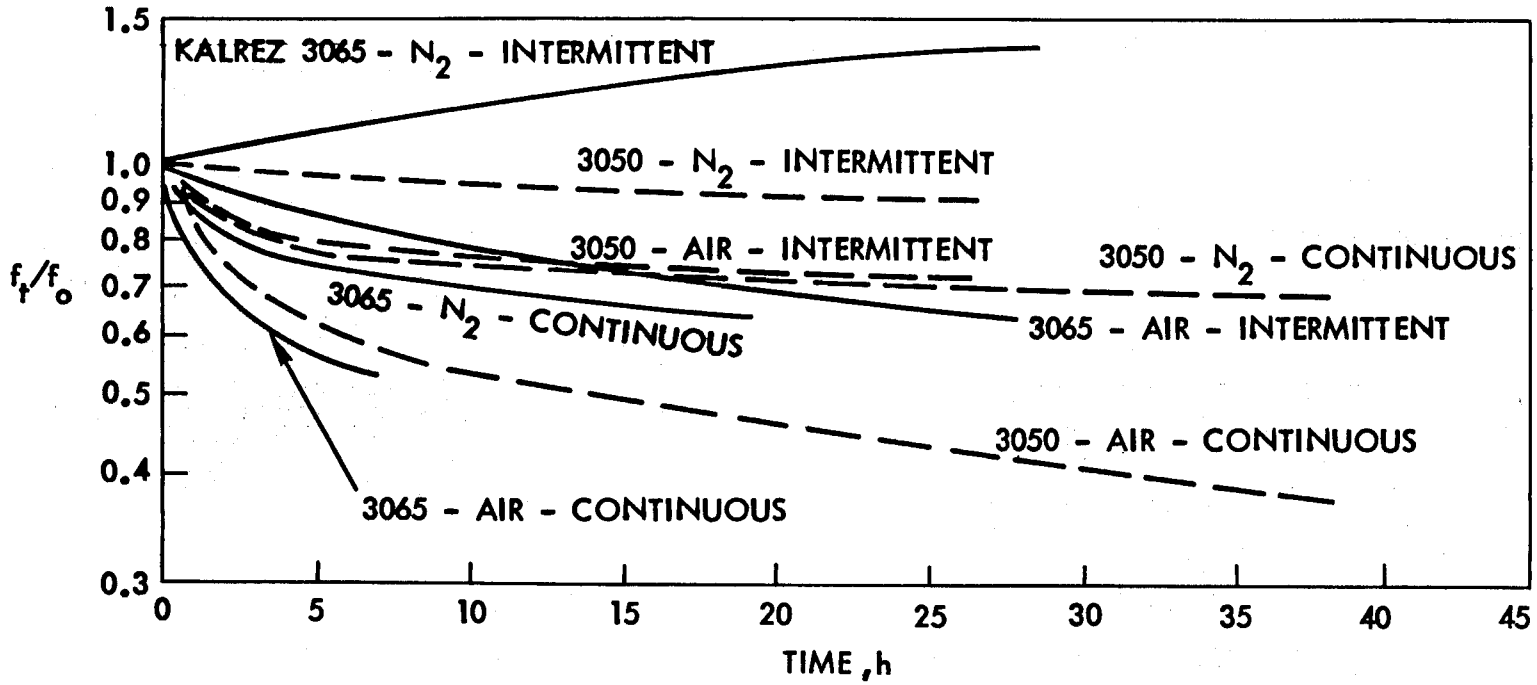


Fig. 7 Comparison of Continuous and Intermittent SR of Kalrez 3050 and 3065 in Air and Nitrogen at 310°C

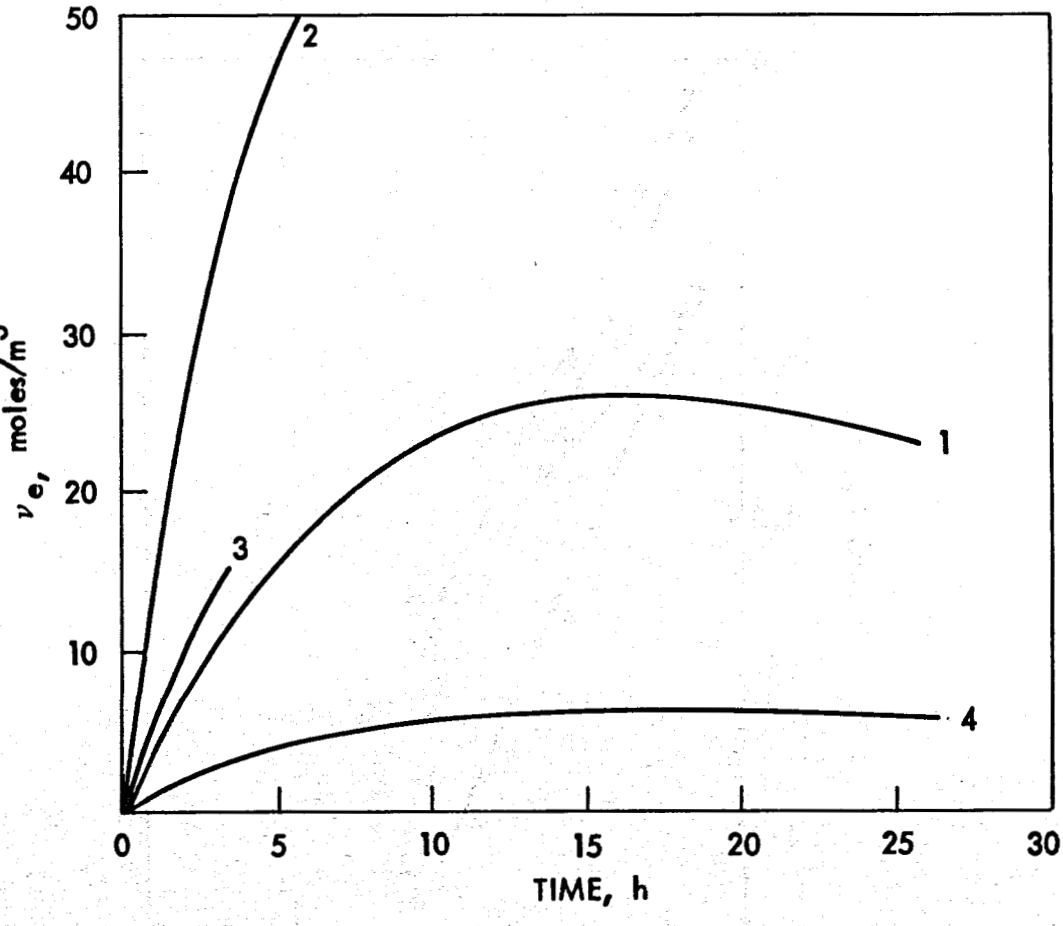


FIG. 8 ADDITIONAL CROSSLINKS FORMED AT 315°C

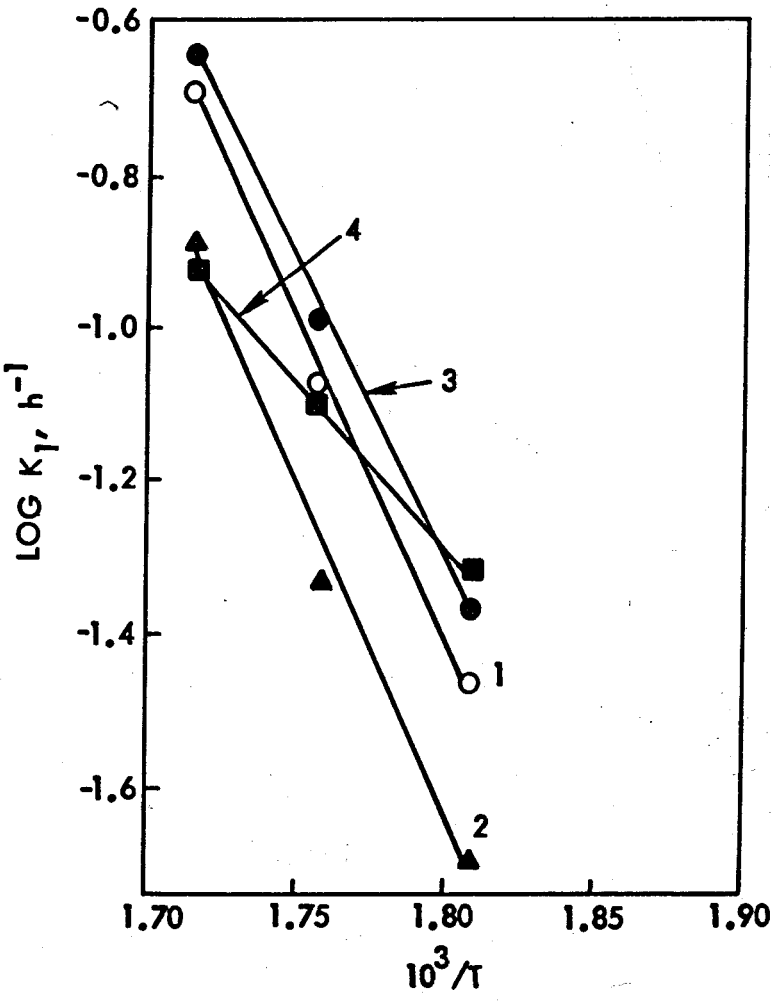


FIG. 9 TEMPERATURE DEPENDENCE OF K_1 ($K_1 = \frac{1}{t.30}$)

FOR SR OF FLUOROCARBON ELASTOMERS IN NITROGEN

and 60 hours in closed stainless steel tubes. Swollen stress-strain measurements were carried out using a beam balance to apply the force to the tensile specimens. The specimen was immersed in solvent in a glass tube and strain was measured by means of a cathetometer. The solvents were butyl acetate (Viton) and Freon TF (Kalrez). Values for K_1, calculated as described in Ref. 4, are as follows: Kalrez 3065, 0.38; Kalrez 3050, 0.44; Viton 10, -0.92; and Viton 10K, -4.98. The apparent ν_e values in Table 1 contain contributions for the highly filled Vitons (filler volume $\sim$ 55%) from the filler which cannot be taken into account, and are larger than one would normally expect. However, the values do indicate that aging in brine does not cause large changes in crosslink density.

The percent weight-loss values for Vitons, Kalrez, and AFLAS 150 were measured as a function of time on aging at 250°C in brine, are shown in Figure 10. (AFLAS 150, tetrafluoroethylene-propylene copolymer from Asahi Glass, Yokahama, Japan, was obtained only in small quantities and was not tested extensively.) Weight-loss increased from less than 1% for AFLAS 150H (after 60 hours at 250°C in solution 1.) to about 17% for Viton 10G. Although lower weight-losses, as for AFLAS 150H and Kalrez 3050, are preferred, it has generally been found that good correlations between elastomer mechanical behavior and weight-loss are difficult to establish, although these results do indicate that Kalrez and AFLAS 150 are better than Vitons, and the results are reasonably consistent with other aging data obtained.

Some mechanical properties before and after aging at 252°C in solutions 1., 2., and 3. were measured at room temperature and at 252°C for Vitons, Kalrez and AFLAS 150. The data are tabulated in Table 2, and in Figure 11. Data for aged samples are based on original dimensions. Some conclusions from these results are:

(1) Initial mechanical properties are inadequate to meet the target goal (24 hours at 260°C, pressure differential of 1.034×10^7 n/m^2 (1500 psi), in a geothermal environment) for most applications, since the estimated properties required are tensile strengths of about 2.76×10^6 n/m^2 (400 psi) and at least 50% elongation.

(2) After 40 hours in solution 3., Kalrez 3065 retains 50% of initial tensile strength and 100% of initial elongation; AFLAS 150H retains 35% of tensile and 51% of elongation, and mechanical properties retained by the remaining compositions are generally very low.

(3) Mechanical properties retained in brine-carbon dioxide and brine-hydrogen sulfide are approximately the same for specific compositions, i.e., the effects of solutions 1. and 2. are similar.

(4) Except in deionized water, Kalrez 3050 is stable in the test environment for sixty hours.

(5) Stability of AFLAS 150H is intermediate between Vitons and Kalrez.

TABLE 1. CROSSLINK DENSITIES OF AGED RUBBERS

(νe, moles/m^3)

Material	Unaged	20 h at 252°C			40 h at 252°C			60 h at 252°C		
	$\nu_{e(o)}$	Sol.1	Sol.2	Sol.3	Sol.1	Sol.2	Sol.3	Sol.1	Sol.2	Sol.3
Viton 10	1100	956	1080	942	868	986	858	924	987	868
Viton 10K	5400	4536	4543	-	4585	4522	-	4721	5059	-
Kalrez 3050	520	478	474	473	474	470	463	472	472	470
Kalrex 3065	650	562	564	525	555	551	511	550	550	507

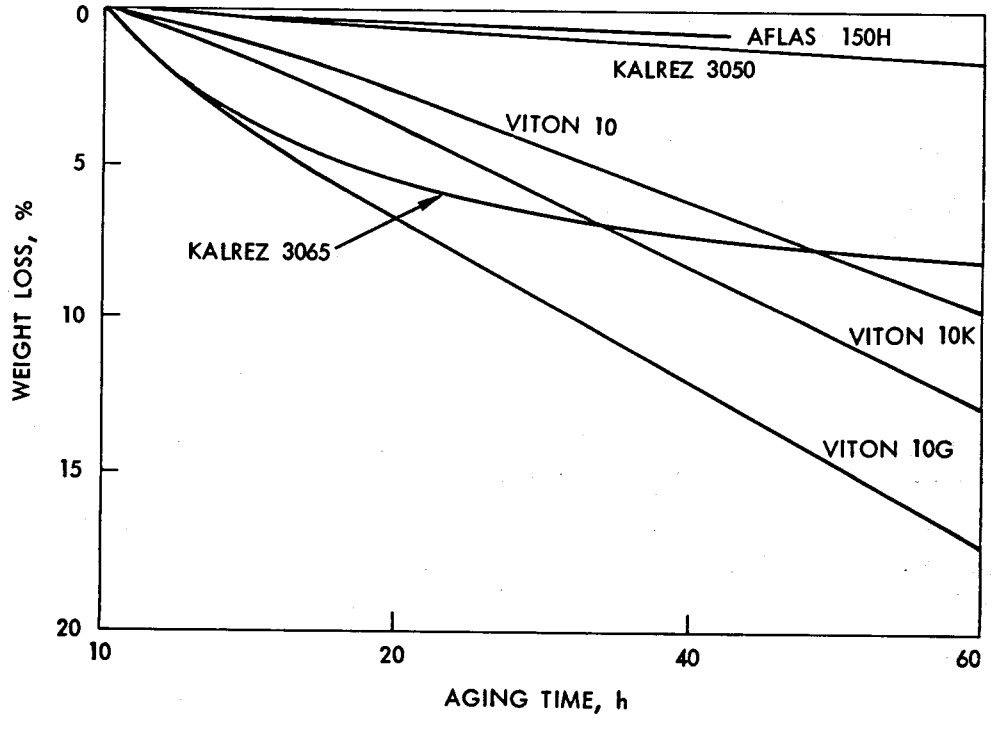


Fig. 10 Percent Wt Loss of Fluorinated Elastomers During Aging at 250°C in Brine (Sol'n 1.)

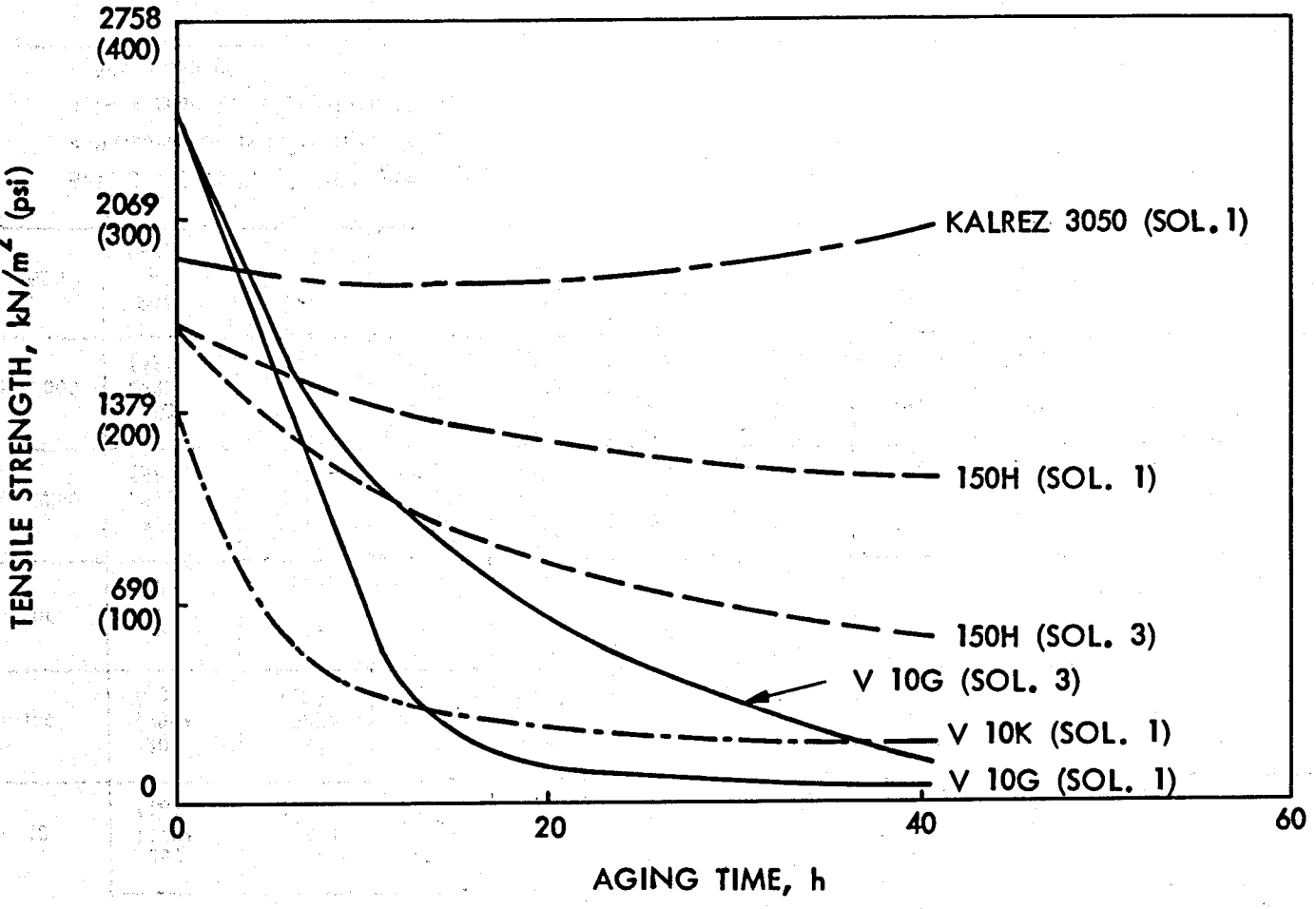


Fig. 11 Effect of Aging in Brine (Sol. 1.) and Deionized Water (Sol. 3.) on Elastomer Compositions

TABLE 2. MECHANICAL PROPERTIES OF AGED ELASTOMERS

		Tensile Strength, psi, and (Elongation, %) Measured at 260°C (500°F)								
	Unaged	20 h at 250°C			40 h at 252°C			60 h at 252°C		
	Samples	Sol. 1	Sol. 2	Sol. 3	Sol. 1	Sol. 2	Sol. 3	Sol. 1	Sol. 2	Sol. 3
Viton 10	250 1470* (18)	220 860* (27)	256 1100* (21)	101 910* (13.5)	14.5 - (18)	26 - (12)	10 - (#)	10 - (10)	13.5 - (12)	5.4 - (#)
Viton 10K	200 1090* (10)	41 920* (10)	44 850* (#)	- - (-)	30 - (#)	20 - (#)	- - (-)	23.5 - (#)	21 - (#)	- - (-)
Viton 10C	365 - (22)	14 - (14)	- - -	95 - (16)	8 - (9)	20 - (8)	- - -	- - -	- - -	- - -
Kalrez 3050	278 2470* (58)	269 2515* (53)	250 2330* (52)	152 2000* (33)	296 - (64)	298 - (62)	59 - (12)	263 - (56)	257 - (46)	32 - (10)
Kalrez 3065	280 1840* (32)	187 1780* (57)	211 1680* (56)	138 1400* (36)	202 - (57)	198 - (54)	141 - (37)	195 - (51)	194 - (50)	131 - (35)
AFLAS 150H	246 - (69)	184 - (64)	- - -	120 - (46)	163 - (60)	- - -	85 - (35)	- - -	- - -	- - -

Sol. 1 = 2.5% NaCl + 1000 ppm CO_2; Sol. 2 = 2.5% NaCl + 300 ppm H_2S; Sol. 3 = Deionized Water

* Measured at room temperature

\# Less than 10% elongation at break

\- Not measured

(6) Although Viton 10G has the best initial properties, it degrades more rapidly than the other compositions.

At present there are no candidate commercial formulations that would appear to satisfy the target requirements. Kalrez 3050 appears to be the best, but is too expensive. However, it may be applicable for small parts, e.g., O-rings, or packer backup rings. AFLAS 150H is better than Viton and studies are underway to improve the initial properties while maintaining stability. It may be that no commercially available elastomer gumstock will satisfy either anticipated geothermal or petroleum drilling and production requirements for resources operations above about 250°C.

SYNTHESIS PROGRAM

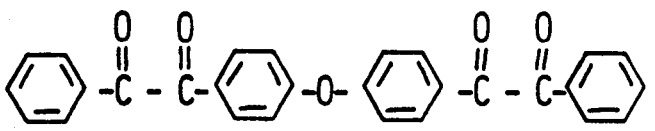
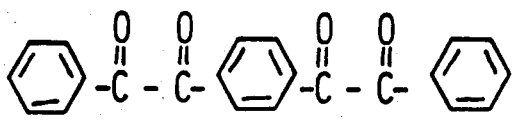
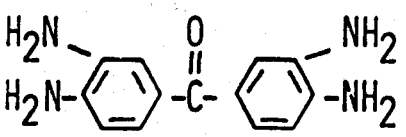
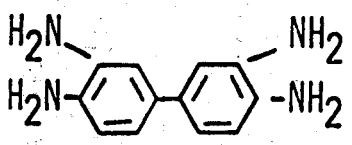
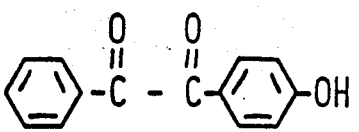
The characteristics of an elastomer for high temperature geothermal applications differ from other applications in that the operating temperature range can be limited to temperatures above 200°C. Therefore, the polymeric material can be rigid and nonelastomeric at room temperature and higher, except for certain applications, e.g., many O-ring seals where the seal must be deformed for ease of assembly, as for most drill bit designs. It was planned to attempt to utilize existing high temperature polymer synthesis procedures and modify the chemical structure of such polymers so that they would be flexible at high temperatures.

Two approaches are being pursued. One is to flexibilize high temperature polymers by incorporating the high temperature moiety in a block copolymer structure with a flexible "soft" block, and the other is to develop a curable system based on a material having a Tg of about 100°C. The block copolymer system offers the processing advantage of little or no compounding, use of thermoplastic molding techniques, and possible assembly at a reasonable temperature. The curable high Tg material should be easier to synthesize. Polyphenyl quinoxaline was selected as the hard block because of its temperature resistance and hydrolytic stability. Polystyrene was chosen for a curable high Tg system. It was tested and found to be stable for 24 hours at 250°C in brine.

The chemical structures of starting materials used in the block copolymer work are shown in Table 3. Reaction of ODB with TABP gives a phenyl quinoxaline polymer (PPQ) with a second order transition temperature of only 265°C. Therefore, a block copolymer made from these would not be usable near or above this temperature. However, these intermediates were the most readily available and preliminary work to establish synthetic methodology and procedures was carried out using ODB and TABP. A series of PPQ's was made, varying excess TABP from zero to 14 mol %. The polymer made with 2.7 mol % excess TABP could be cast as a tough, flexible thin film, indicating that the reaction conditions and methods were satisfactory and that reasonably high molecular weight PPQ polymers could be readily prepared. Reaction of pure HOB with PPQ resulted in a prepolymer with phenolic functionality.

The next step involved coupling a soft block with the phenolic-terminated PPQ. Since there are many prepolymers available that contain

TABLE 3. INTERMEDIATES FOR THE SYNTHESIS OF PPQ - ALKYL SEGMENT BLOCK COPOLYMERS

Chemical Structure	Name	Abbrev.
	Oxydibenzyl	ODB
	p-bis (phenylglyoxalyl) benzene	PGB
	3,3', 4,4' tetraaminobenzophenone	TABP
	3,3' diaminobenzidene	DAB
	4-hydroxybenzil	HOB

hydroxyl functional groups, some work was done to attempt to convert hydroxyl groups to chlorides or tosylates. These prepolymers could then be used for the soft blocks in copolymers. It was found that the chloride terminated Telagen could be reacted with bisphenol A (as a model reaction) bo obtain a polymer, indicating that the desired formation of the PPQ block copolymer should proceed satisfactorily.

It can be concluded that synthesis of the desired block copolymers is feasible. However, with respect to required mechanical behavior at high temperatures in a geothermal environment, the effects of variations in the chain lengths of hard and soft blocks cannot be fully established until those types of polymers have been synthesized. Preliminary analysis suggests that soft block lengths of the order of 10,000 may be required and further work will be done to define segment length requirements for different potential block components. In any event, it is anticipated that nearly complete reaction of the soft block segments with PPQ's will be required and that the soft block molecular weight is critical and should be relatively high. Also, saturated hydrocarbon soft blocks, such as hydroxy-terminated polybutadiene (Telagen) or butyl rubber, may not be sufficiently stable. If not, it will be necessary to prepare more stable soft blocks. These could include poly (styrene), polyphenyl ethers or fluorinated pre-polymers. (The polystyrene-PPQ polymer would be rigid at room temperature, but polystyrene has a heat distortion temperature in the vicinity of 100°C, and is normally molded at temperatures above 160°C.)

CONCLUSIONS

Current elastomeric materials, even in the absence of hydrolytic, oxidative, or other types of breakdown, undergo a reversible loss of 85 - 90% of their room temperature properties when heated to 260°C. If a seal or packer can be designed to operate successfully using an elastomer having 200 psi tensile strength, 50% elongation, and compression set estimated at 60%, such a seal could be made and would probably operate for at least 50 - 100 hours at 250 - 260°C in brine.

Under operating conditions, tensile strength and elongation of elastomers are inversely related to the difference between Tg and the temperature at which the elastomer must perform. For the case of an NBR, suitable for petroleum application, the difference between Tg and maximum operating temperature is of the order of 150°C. If it is necessary to operate at 250°C with elastomer properties similar to NBR at 150°C, an elastomer is needed with a Tg of about 100°C.

It does not appear at present that formulation changes using available gumstocks are likely to provide a material that will prove to be satisfactory in the long term. This area has been well explored, and discovery of a new formulation or ingredient that will solve the problem is not likely.

It is not safe to assume that developments in the petroleum area will apply to geothermal problems, since the environments are not the same. Furthermore, a material suitable for geothermal use is not likely to find

much application outside the geothermal area, and would face an uncertain market. Development of materials for specific applications that depart significantly from established use is a slow process, requiring a long-term commitment to achieve success. For geothermal applications at high temperatures, it appears that it will be necessary to chemically modify existing polymers with high Tg's. Alternatively, new polymers with high Tg's and adequate mechanical properties at high temperatures may be required.

REFERENCES

1. Private communication from M. B. Jett, Dresser Industries, February 22, 1976.

2. A. V. Tobolsky, T. B. Prettyman, and J. H. Dillon, J. Appl. Phys., 15, 309 (1944).

3. A. V. Tobolsky, "Properties and Structure of Polymers," John Wiley and Sons, Inc., New York, 1960.

4. S. H. Kalfayan, R. Rakutis, and R. H. Silver, Rubber Chem. and Tech., 47, 1265-74, 1974.

APPENDIX B

MANUFACTURERS' NAMES

Trade Name	Manufacturer
AFLAS	Asahi Glass Co., Yokohama, Japan
Calidria HPO	Union Carbide Corp.
Chemigum	Goodyear Tire and Rubber Co.
DIAK 7	Dupont Co.
Fluorel	3-M Co.
Freon TF	Dupont Co.
FR-N	Firestone Tire and Rubber Co.
Herclor	Hercules, Inc.
Hycar	B. F. Goodrich Co.
Hydrin	B. F. Goodrich Co.
Kalrez	Dupont Co.
Kevlar	Dupont Co.
Litharge	NL Industries, Inc.
Luperox 130-XL	Lucidol Division, Pennwalt Corp.
Lustrex	Monsanto Co.
NORYL	General Electric Co.
Paracril	Uniroyal, Inc.
Pelletex NS	R. T. Vanderbilt Co.
PNF-200	Firestone Tire and Rubber Co.
Tefzel	Dupont Co.
Telegen S	General Tire and Rubber Co.
Thermax	R. T. Vanderbilt Co.
U-Car-Sil	Union Carbide Corp.
UC A-172	Union Carbide Corp.
Vespel	Dupont Co.
Viton	Dupont Co.
VPA #2	Dupont Co.

APPENDIX C

INFORMATION ON SAMPLES SUBMITTED BY L'GARDE, INC. AND DRESSER INDUSTRIES

L'GARDE, INC.

1555 PLACENTIA AVENUE
NEWPORT BEACH, CALIFORNIA 92663
TELEPHONE (714) 546-4671 & (714) 645-4880

L-78-AH-104
May 2, 1978

Dr. W. Mueller
Jet Propulsion Laboratory
California Institute of Technology
4800 Oak Grove Drive
Pasadena, California 91103

Subject: Viton Samples for Hot Tensile Measurements

Dear Bill:

Enclosed are two Viton VT-R-4590 formulations each having a virgin ASTM sheet and one that has been chem aged. The designations are as follows:

237-III-2
248-II-1

The 237 compound is typical of our latest compounding which results in good stability through the thermochemical chem ageing, however, we do expect mechanical failures with the compound. The 248 compound is highly loaded and has survived the full pressure and temperature for 24 hours in the SIM test "cure-in-place" experiments. However, 248 is not expected to withstand the pack-off deformation in its cured state because of its low ultimate elongation (we will be testing it in the SIM test). Hopefully you will be able to run hot tensile tests on both the above, if not, we would prefer that you test 237.

Sincerely,

Alan R. Hirasuna
GEM Program Manager

ARH:pw
Enclosure

cc: R. Reeber
P. Cassidy

L'GARDE, INC.

1555 PLACENTIA AVENUE
NEWPORT BEACH, CALIFORNIA 92663
TELEPHONE (714) 546-4671 & (714) 645-4880

L-78-AH-091
April 14, 1978

Dr. W. Mueller
Jet Propulsion Laboratory
California Institute of Technology
4800 Oak Grove Drive
Pasadena, CA 91103

Subject: Rubber Samples for High Tensile Measurements

Dear Bill:

Enclosed are three formulations each having a virgin ASTM sheet and one that has been chem aged in the autoclave (except the nitrile which was hard plastic after chem ageing). The designations are as follows:

COA-1	nitrile
226-1	EPDM
242-1	EPDM/Viton Blend

We have not included any Viton samples yet, as we ran into some inconsistencies on chem ageing. The problem seems to be rooted with various lot to lot variations on the VT-R-4590. Hope to have something soon on that.

Sincerely,

Alan R. Hirasuna
GEM Program Manager

jes

cc: R. Reeber
P. Cassidy

GUIBERSON DIVISION, DRESSER INDUSTRIES, INC. P. O. BOX 1106, DALLAS, TEXAS 75221 214/421-4101 TELEX: 73-0844

November 15, 1976

Mr. William A. Mueller
Mail Stop 67-201
Jet Propulsion Lab
4800 Oak Grove Drive
Pasadena, CA 91103

Dear Mr. Mueller:

Enclosed are tensile sheets of a high durometer compound which has properties typical of those needed for sealing applications which are required to hold high pressures at elevated temperatures. The polymer used is a nitrile (NBR) elastomer. This naturally limits the high temperature capabilities to around 275° F.

Properties of the enclosed sheets are as follows (all measured at 75°):

Tensile Strength (psi)	100% Modulus (psi)	Hardness Shore A	Elongation (%)	Tear (Die C)
3200-3400	2100-2250	90-91	155-170	250

Properties measured at 300° should be as follows:

Tensile - 1500 psi Elongation - 60%

Should you require any additional samples or any information concerning these samples, please call me.

Sincerely,

Jimmy Woodson

Jimmy Woodson
Jr. Elastomer R&D Chemist

lc
Enclosure

cc: M. B. Jett