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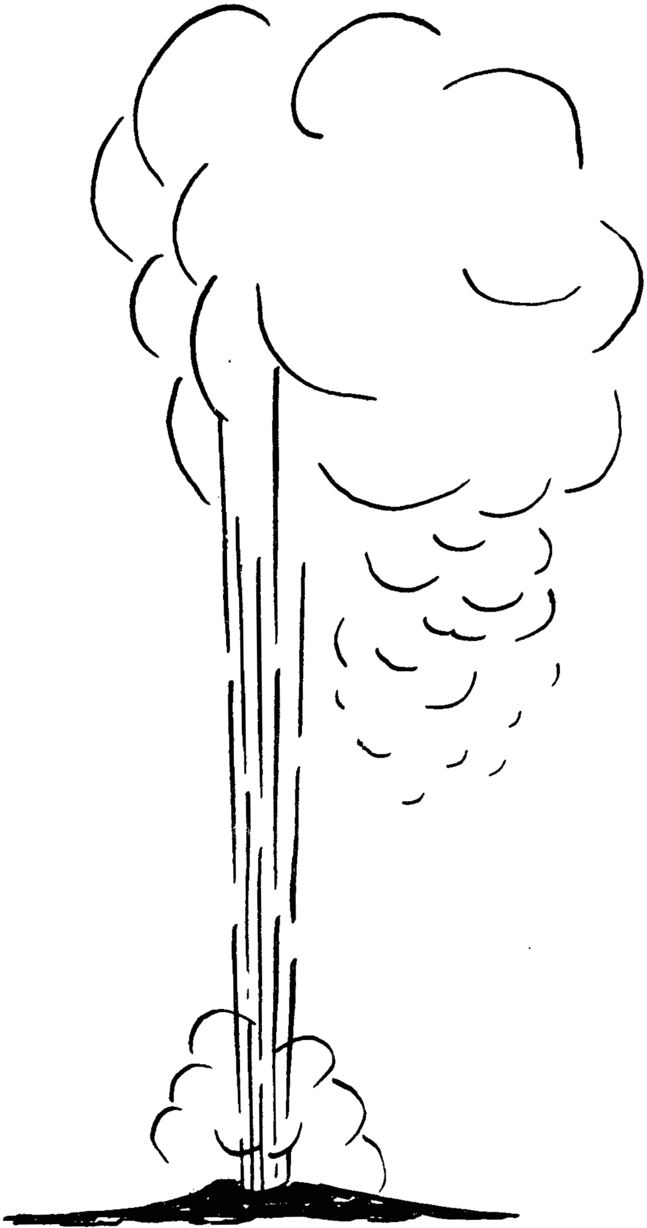

ADDENDUM TO MATERIAL SELECTION GUIDELINES FOR GEOTHERMAL ENERGY UTILIZATION SYSTEMS

Part I: Extension of the Field Experience Data Base
Part II: Proceedings of the Geothermal Engineering and Materials (GEM) Program Conference (San Diego, CA, 6–8 October 1982)

By
Carolyn S. Smith
Peter F. Ellis II

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Radian Corporation
Austin, Texas

U. S. DEPARTMENT OF ENERGY
Geothermal Energy

DISCLAIMER

New Fluorocarbon Elastomers for Seals for Geothermal and other Aggressive Environments

Earl T. Dumitru,[a] R. J. Lagow[b], and L. E. Kukacka[c]

Exfluor Research Corp.
P.O. Box 78707
Austin, Tx. 78758

ABSTRACT

Geothermal brines at 600° F which contain metallic salts, H_2S, and hydrocarbons quickly degrade conventional hydrocarbon elastomers, and hydrolyse crosslinks. Carbon-carbon and carbon-fluorine bonds are expected to be superior, but no such elastomer is now commercially available.

We have prepared crosslinked, perfluorocarbon elastomers by radiation crosslinking VDFHFP and TFEP (alternating) copolymers in film and sheet form, and then converting C-H bonds to C-F bonds with elemental Fluorine gas. EPDM elastomers became brittle on fluorination.

The best products exceeded 100 days survival at 300°C in simulated geothermal brine.

Tensile, elongation, solvent swelling, and TGA methods were used to study the products.

Geothermal Requirements

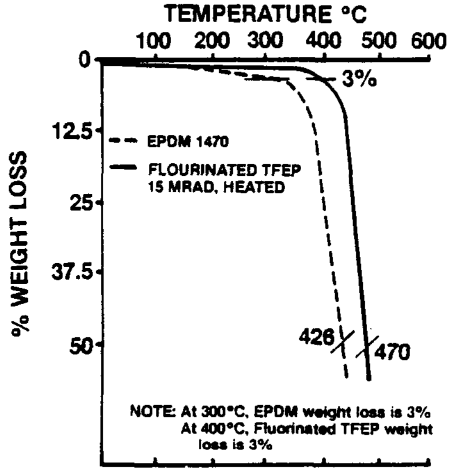
Department of Energy and Brookhaven National Laboratory have recognized[1] that a new elastomeric material superior to EPDM, VDFHFP and TFEP under geothermal conditions should excell in the following seven categories.

1. Extended use at 300°C, static applications
2. Hydrolytically stable at 300°C in presence of H_2S
3. Resist higher temperatures from heat of dynamic applications
4. Withstand chemical attack of geothermal brine constituents NaCl, $CaSO_4$, CO_2, H_2O, H_2S and O_2 and including dissolved hydrocarbons
5. Withstand chemical attack of lubricants Fluorosilicone (FS-1265, Limit 260°C)
6. Resist abrasive wear of drilling residues
7. Resist permeation by gas and liquid

Recent Geothermal Elastomeric Material (GEM) Developments

The efforts of L'Garde Corporation under the sponsorship of D.O.E. have led to a significant advance in the performance of conventional materials. The optimization of the EPDM compositions available has been successful to the point that GEM materials from L'Garde are useful at 260°C for extended periods of time. These EDPM, carbon black filled systems, are peroxide cured, post-cured, and carefully monitored for quality. It appears the EDM is successful under reducing conditions in hydrothermal brines in the absence of hydrocarbon contaminants. A glance at the TGA results for Nordel in the raw state will serve to show that the thermal stability of EPDM is close to being exhausted at 260°C. (Figure 1)

FIGURE I
THERMOGRAVIMETRIC ANALYSIS OF UNFILLED GEOTHERMAL ELASTOMERS (NITROGEN ATMOSPHERE, 10°C/MIN. DUPONT 990)



NOTE: At 300°C, EPDM weight loss is 3%
At 400°C, Fluorinated TFEP weight loss is 3%

Fluorocarbon Elastomers (300°C)

The strength of the carbon-fluorine bond and the carbon-carbon bond together promise the ultimate thermally stable composition. Polytetrafluoroethylene (TFE, "TEFLON") is thermally and chemically stable to well beyond 300°C, but is (unhappily) not elastomeric and not crosslinked. Seals made of TFE flow under pressure at elevated temperatures.

Hydrofluorocarbon elastomers such as "VITON" (VDFHFP) (DuPont) and "AFLAS" (TFEP) (ASAHI GLASS) are subject to elimination of HF or H_2 as are the EPDM elastomers. The investigations cited 3, 4, 5 have been sufficiently thorough to provide little basis for hope that the two hydrofluoro materials can be further improved.

Perfluoroelastomers based on tetrafluoroethylene copolymerized with perfluoromethylvinylether (KALREZ), are theoretically the most stable elastomers currently available.

a 10116 Aspen St. Austin, TX. 78758
b University of Texas, Austin, TX. 78712
c Brookhaven National Laboratory Upton L.I. N.Y.

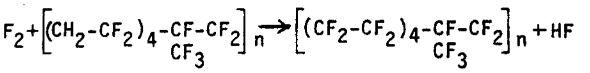
SYNTHESIS OF CROSSLINKED PERFLUOROCARBON ELASTOMERS

Direct Fluorination Method of Preparing Crosslinked Perfluoro-elastomers

Reaction of fluorine gas with hydrocarbons is known to produce HF and new C-F bonds.[6] The usually violent reaction with small molecules can be controlled by dilution techniques and low temperatures. "Teflon-like" chemical properties have been reported(6) for powdered polyethylene treated with fluorine, but the achievement of strong, macroscopic elastomeric fluorocarbon products has heretofore not been reported.

Selection of Substrate Microstructure and Chemical Compostition

Linear polyethylene and polytetrafluoroethylene molecules crystallize, with minor amounts of irregularities being segregated into amorphous domains. The structures described below may be regarded as methyl-substituted polyethylenes. The methyl substituents serve as irregularities to limit crystallization. The various stereochemical arrangements will also affect the glass transition temperature.

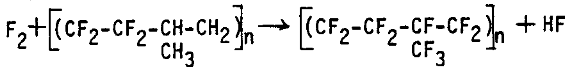


$$F_2+\left[(CH_2\text{-}CF_2)_4\text{-}\underset{CF_3}{CF}\text{-}CF_2\right]_n \rightarrow \left[(CF_2\text{-}CF_2)_4\text{-}\underset{CF_3}{CF}\text{-}CF_2\right]_n + HF$$

In the unlikely event that our new structure II is capable of crystallization, it's melting temperature must be well below the use temperature anticipated for geothermal elastomers.

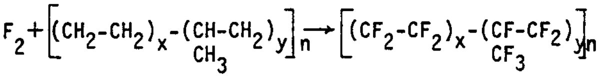
The glass temperature (T_g) of II maybe well above the T_g of structure I (-10°C) but will be well below the use temperature.

The regularly alternating structure



$$F_2+\left[(CF_2\text{-}CF_2\text{-}\underset{CH_3}{CH}\text{-}CH_2)\right]_n \rightarrow \left[(CF_2\text{-}CF_2\text{-}\underset{CF_3}{CF}\text{-}CF_2)\right]_n + HF$$

is an elastomer at room temperature (T_g = -10°C) and has one methyl group per four chain carbon atoms. The fluorinated product (IV) has a much higher proportion of CF_3 groups than (II).



$$F_2+\left[(CH_2\text{-}CH_2)_x\text{-}(\underset{CH_3}{CH}\text{-}CH_2)_y\right]_n \rightarrow \left[(CF_2\text{-}CF_2)_x\text{-}(\underset{CF_3}{CF}\text{-}CF_2)_y\right]_n$$

The compositions of these substrates are compliled in Table I.

Preparation of Films and Sheets

Solutions containing 5% polymer by weight were prepared in tetrahydrofuran, acetone, ethyl acetate, or toluene for TFEP, VDFHFP, and EPDM respectively, and cast in 20 ml. portions on 4 x 4 inch aluminum foil trays secured to 4 x 4 inch glass plates for flatness.

Thicker sheets were pressed in a 4 x 4 inch brass mold 1/8 inch think at 130° for 4 min.

Crosslinking and Post-Treatment

The cast films are separated from the glass plates, leaving them adhering to the aluminum foil. The films and sheets are then placed inside polyethylene bags which are flushed with nitrogen gas for several minutes and then sealed. The bags are then placed in shallow trays containing water at 85 C. The samples are irradiated with 1 Mev electrons at a rate of approximately 1 Mrad per minute until the required dose has been realized. The temperature remains at 85 C due to the enegy dissipated by the samples. HF and H_2 are formed during the radiation.

TABLE 1
CHEMICAL COMPOSITION of SUBSTRATES in ORDER of DECREASING FLUORINE CONTENT

Elastomer	Repeating Unit	%F	%H	Max. wt. increase %
VDFHFP	$\left[(CH_2\text{-}CF_2)_4 - (\underset{CF_3}{CF}\text{-}CF_2)_1\right]_n$	65.5	1.97	37.4
EXF-1		76.0	0	
TFEP	$\left[(CF_2\text{-}CF_2) - (\underset{CH_3}{CH}\text{-}CH_2)\right]_n$	53.5	4.22	30.2
EXF-2		76.0	0	
EPDM	$C_5H_{10}F_0$	0	14.28	271.4
EXF-3		76.0	0	
Teflon PTFE	C_2F_4	76.0	0	0

Post-irradiation treatment consists of heating the samples under nitrogen in an oven at 170 C or higher for 24 hours or longer. The weight loss by samples during this treatment is recorded. It may represent simply loss of small volatile components, or may be elimination of moieties incidental to the formation of carbon-carbon crosslinks.

Fluorination

Samples of elastomer sheet are placed on copper gauze in the fluorination reactors and subject to a flow of inert gas (helium) mixed with fluorine (F_2) in gradually increasing concentrations. The procedure begins at room temperature and may be carried out at increasing temperatures up to approximately 80°C. The concentration of fluorine is raised until pure fluorine at 35psi surrounds the samples. The procedure presently takes two to three days. At the end of the treatment, the atmosphere is replaced with helium for 8 to 24 hours and the samples are removed and weighed. This procedure is not the most expeditious, but is capable of yielding strong elastomeric products.

Evaluation of Crosslinking by Swelling in Solvents

Approximately 1" square sections of the radiated elastomers are cut and weighed. These samples are immersed in a solvent contained in a glass jar at room temperature. The samples are periodically withdrawn from the jar, quickly blotted and weighed, and replaced in the jar. The weight increase due to swelling of the sample is plotted versus the square root of time. This plot should yield a straight line at early times, and reach an asymptote at equilibrium. At equilibrium swelling, or maximum swel-

Evaluation of Fluorination Process

Changes in the weight of the elastomers represent the addition of fluorine to the structure at the expense of hydrogen. It is assumed that no carbon atoms are lost from the elastomer, and we believe this to be a reasonable assumption provided that the reaction temperature does not rise much above 100°C.

Evaluation of Fluorination by Weight Changes

Weight changes upon fluorination are recorded in Tables 2. The highest fluorination achieved so far is about 90% H replaced and efforts are continuing to achieve complete replacement of hydrogen by fluorine.

Table 2

Fluorination Extent vs. Temp of 50% loss

Sample	Mrad.	Temp.	% Fluorination
VDFHFP AHV	15	406	0.0
VDFHFP AHV	15	408	4.1
VDFHFP AHV	60	384	5.3
TFEP 150	15	421	0.0
TFEP 150	30	385	39.
TFEP 100	80	384	40.

Evaluation of Fluorination by Tensile Tests

The force and elongation at break for fluorinated samples is presented in Figures 3, 4, 5. It will be seen that the samples are strong and elastic after surviving the pure fluorine atmosphere at elevated temperature and pressure.

Evaluation of Fluorination by Swelling Tests

Swelling measurements have been performed in accordance with the procedure described, but in this case the samples have been fluorinated. The data is plotted in Figure 2. It is of course desirable to have low uptake of fluids in the fluorinated product under conditions of use.

Thermogravimetric Analysis (TGA)

TGA scans at 10°C/min. have been used to characterize the thermal stability of the fluorinated product, and to compare it wih the unfluorinated, radiated, and heated precursors. The temperature for 1%, 3%, and 50% weight loss are interesting data points for relative ranking, but are not yet correlated with performance at elevated temperatures.

EXPOSURE TO THE SIMULATED GEOTHERMAL BRINE (300°C)

Exposure to the simulated geothermal brine (300°C) has been carried out at BNL over 100 days, with indications that two of our 60 Mrad samples will survive longer than 100 days in good condition.

The samples were autoclaved in the environment of 25% simulated geothermal brine at the temperature of 300°C. The autoclaving was stopped for inspection of the samples at various intervals. After laboratory testing, the samples were returned for further autoclaving.

The laboratory tests consisted of three parts, visual inspection, IR spectra, and TGA.

The TGA analysis was performed using the DuPont 951 thermogravimetric analyzer which is a plug-in module for the 990 thermal analyzer. Used in the dynamic mode, the TGA measured the loss of weight as a function of temperature. In these tests, the samples were heated in a 90 cc/min nitrogen gas flow from room temperature to 650°C at a rate of 10°C/min.

The results were:

Seven of the twelve samples tested deteriorated beyond recognition after their first exposure. Their numbers are as follows:

1) EXF-1 (X15 F25.50.52)
2) EXF-1 (X60 F25.50.52
3) AFL 150 (30 Mrad)
4) EXF-2 (6 Mrad)
5) Viton C=10 (10 Mrad)
6) V-A35-15-H (36.25.48)
7) EXF-1 X60 (22.30.30)

TABLE 3

TEMPERATURE OF 1% and 3% WEIGHT LOSS AFTER SIMULATED GEOTHERMAL BRINE EXPOSURE at 300°C

SAMPLE #	%	CONTROL	5 Days	7 Days	14 Days	28 Days	42 Days	56 Days	70 Days	82 Days	96 Days	138 Days
DOEAC	1	200	335		400	325	350	350		365	325	270
(60MRAD)	3	340	405		435	415	415	415		420	380	367
EXF-2	1	290			415	370	385	385		370	370	290
(X60 F12.35.22)	3	345			440	435	435	445		430	425	405
A150-15H	1	185		395	380	375			100			
(16.25.48)	3	380		440	425	440			375			
EXF-2-150	1	300		400	390				360			
(X60, 22.30.30)	3	400		430	430				410			
EXF-2-100	1	275		405	395				352			
(X60,22.30.30)	3	365		440	437				404			

FIGURE 2
SWELLING OF
FLUORINATED AND UNFLUORINATED
CROSSLINKED ELASTOMER

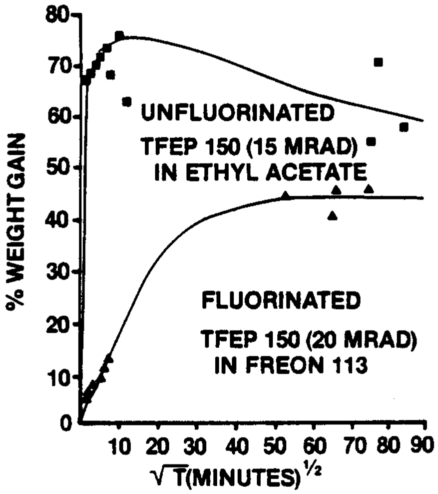


FIGURE 3
STRENGTH & ELONGATION AT BREAK
FOR FLUORINATED ELASTOMERS
(WEIGHT INCREASES AS MARKED)
(TFEP 150)

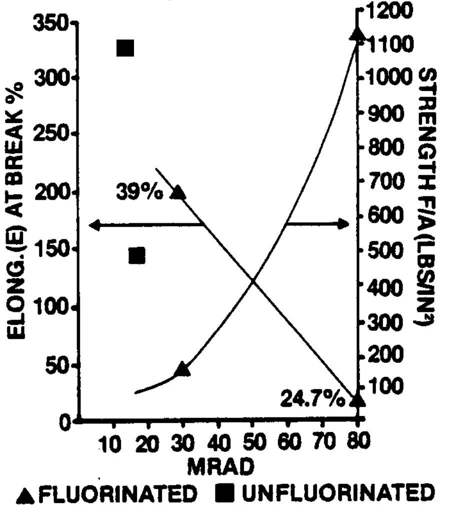


FIGURE 4
ELONGATION AT BREAK
FOR FLUORINATED ELASTOMER
(WEIGHT INCREASE AS MARKED)
(VDFHFP AHV)

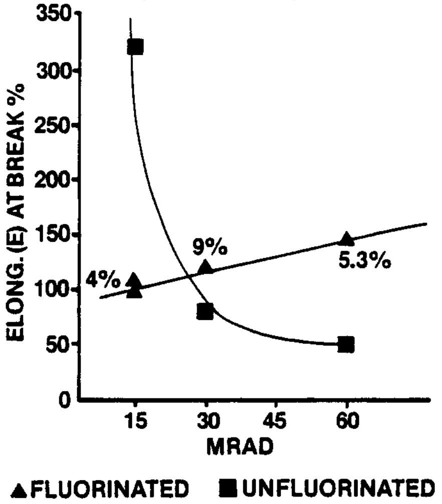
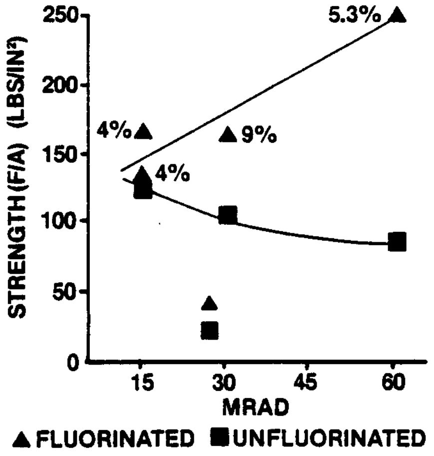


FIGURE 5
FORCE AT BREAK FOR FLUORINATED
ELASTOMER
(WEIGHT INCREASE AS MARKED)
(VDFHFP AHV)



ling, the amount of solvent uptake should be related to the cross-link density. Data for each sample is presented in Figure 2.

Samples of radiated VDFHFP frequently fragment during the swelling tests, and a post-radiation heating cycle of 24 hours at 170°C has been used to improve the physical strength of the elastomers.

Evaluation of Crosslinking by Tensile Testing

Strips approximately 3/8" wide a 3" long were cut from the radiated sheets and clamped in an Instron tester, with exactly 1" gauge length. Samples were extended at 0.5" per minute to failure while the force was recorded on the strip chart. The force at break and the elongation break are presented in Figures 3, 4, 5. The force at break divided by the area of sample in square inches is reported as the tensile strength at break. Measurements were made at room temperature and at 100°C. The extent of fluorination as measured by increase in weight is noted where appropriate.

The changes in tensile strength and elongation due to fluorination are represented in graphical form in the Figures 2, 3, 4, 5.

TABLE 4

EFFECT of FILLERS on STARTING MATERIALS (PEROXIDE CURES)

		L=N990		M=N550		H=N119	
TFEP-150		35 phr	80phr	25 phr	40 phr	25 phr	50 phr
Unfluorinated	(Hardness)	70	90	83	90	85	95
	(Tensile)	2500	2400	2600	2600	2500	2500
	(% Elongation)	160	70	110	70	240	100

		M=N550 40 phr	H=N119 40 phr
TFEP-100			
Unfluorinated	(Hardness)	93	96
	(Tensile)	2300	2800
	(% Elongation)	100	90

Two of the remaining samples, DOE-AC-60 MR and EXF-2 (60 F12 35 22) have remained together for 138 days but have detericrated to the point where they can be pulled apart with little resistance. Sample A-150-15H (36 25 48) has deteriorated after 70 days of autoclaving. Continued testing of these samples will stop. Samples EXF-2-150x60 (22 30 30) and EXF-2-100 x 60 (22 30 30) have held together for 56 days and will be further tested.

1) Visual--Samples become progressively darker in color after each period of autoclaving. The two remaining samples are still very pliable with most of the elasticity left.

2) IR--The spectra are basically the same before and after exposure except for the apparent shifting of two absorption bands, 1850 cm and 1715 cm to 1700 cm to 1700 cm and 1570 cm. This possibly could be from hydrolysis of the sample or a reaction with the salts from the brine. The two remaining samples are now too dark to test.

3) TGA--Weight loss of controls is greater than samples that were exposed to brine. It is possible that this is caused by entrapped water or processing chemicals. Table 3 gives the temperature at which 1% and 3% weight loss accrue. The two remaining samples are still being autoclaved for further testing.

Carbon Black filled compositions

The three types of fillers used at three different loading levels can be observed in the data of Table 5, and compared with the effects on the starting materials collected in Table 4.

Correlations between loading of various blacks and strengths appear to be as follows.

1. Comparing A and C(150) lower loading of the least reinforcing carbon black (N990) produce the highest tensile strength both before and after fluorination.
2. Comparing J and L(100), lower loadings of the higher reinforcing N110 also produce higher tensile strength both before and after fluorination.
3. Both low (990) and medium (568) carbon blacks are capable of forming strong cured (80 Mrad) elastomers at relatively low loadings.

TABLE 5

EFFECT of FILLERS on TENSILE STRENGTH and TEMPERATURE of 3 % WEIGHT LOSS BEFORE and AFTER FLUORINATION (RADIATION CURE)

		Strength			Temp. of Wt. Loss	
		Before	After	Filler	30 Days	60 Days
TFEP-150 80 Mrad	A	897	213	L=N990 100 phr	432	429
	C	1043	871	L=N990 33 phr	448	442
	E	997	312	M=N568 25 phr	448	390
	H	306	257	H=N110 17 phr	431	415
TFEP-100 40 Mrad	J	683	479	H=N110 10 phr		
	K			H=N110 17 phr	447	425
	L	507	328	H=N110 33 phr		
	M			M=N568 17 phr	438	427
	N	922	653	M=N568 25 phr	437	402
	Q	455	251	L=N990 50 phr	450	454
	R			L=N990	443	420

4. High loadings of the highly reinforcing black (110) produce lower strength harder compositions. They may be desireable for better compression set.

Observations of Carbon Black N568 at 25 phr in both TFEP-150 at 80 Mrad and at 40 Mrad shows a large effect on 60 day exposure tests for 3% weight loss. N990 shows the least effect. These differences are probably not due to variability in mixing.

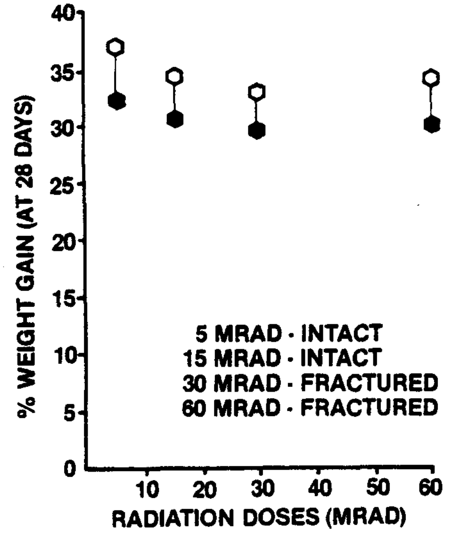
Results and Discussion

Limited swelling to constant weight may not represent thermodynamic equilibrium, but coupled with the tensile data shows that carbon-carbon crosslinks have been introduced. The dose range 5-80 MRAD covers the dose of the best samples in the simulated brine test. The VDFHFP suffers from chain scission during crosslinking, as evidenced by fragmentation during swelling. TFEP samples remain intact in the swollen state.

The data of Figure 2 is probably the first to show the successful retention of crosslinks and elastomeric properties of a polymer subjected to fluorine gas. It is clear from Figures 3,4, and 5 that the fluorinated product is strong and elastic, but not as elastic as the starting material. The leathery character of the product indicates that the glass temperature may be near room temperature.

The survival of elastic properties for 100 days at 300°C in simulated geothermal brine is remarkable.

FIGURE 6
SWELLING VS RADIATION DOSE
TFEP - 150, 1/8" THICK SHEETS
HEATED AND FLUORINATED ACETONE



CONCLUSIONS

1. We conclude that the direct fluorination of TFEP copolymers radiated with 60 Mrad is the best candidate for geothermal seak at 300°C.

ACKNOWLEDGMENTS

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We are particularly grateful to the organization and to the people of D.O.E.-Brookhaven for their willingness to support venturesome new research in a fledgling small company.

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