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NEW FLUOROCARBON ELASTOMERS FOR SEALS
FOR GEOTHERMAL AND OTHER AGGRESSIVE ENVIRONMENTS

FINAL REPORT

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PREPARED BY

EXFLUOR RESEARCH CORPORATION

P. O. BOX 7807

AUSTIN, TEXAS 78712

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DEPARTMENT OF ENERGY AND ENVIRONMENT

BROOKHAVEN NATIONAL LABORATORY

UPTON, NEW YORK 11973

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FOR GEOTHERMAL AND OTHER AGGRESSIVE ENVIRONMENTS

Final Report

December 1982

Dr. Richard J. Lagow, Principal Investigator
J. Christenson, E. T. Dumitru, M. A. Guerra, P. Lampack, B. J. Ziegler

Prepared by
EXFLUOR RESEARCH CORPORATION
P. O. Box 7807
Austin, Texas 78712

Under BNL Contract No. BNL-486106-S and BNL Contract No. BNL-540438-S
Phase I & II

For the
GEOTHERMAL MATERIALS GROUP
DEPARTMENT OF ENERGY AND ENVIRONMENT
BROOKHAVEN NATIONAL LABORATORY
ASSOCIATED UNIVERSITIES, INC.

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NEW FLUOROCARBON ELASTOMERS FOR SEALS
FOR GEOTHERMAL AND OTHER AGGRESSIVE ENVIRONMENTS

Summary

This is a comprehensive report of work accomplished by Exfluor Research Corporation under Contracts BNL-486106-S and BNL-540438-S, in response to BNL R.F.P. GP79-1. The object of the first contract (BNL-486106-S) was to develop and test new cross-linked perfluorocarbon elastomers produced by direct-fluorination methods. The second contract (BNL-540438-S) had the objectives of developing optimum filled compositions and fabricating new perfluorocarbon elastomer seals for use in geothermal and other severe environments.

To achieve the first contract objective, EXFLUOR screened saturated ethylenic elastomers having a range of methyl group substitution, and a range of partial fluorine substitution. Elastomers based on vinylidene fluoride hexafluoropropylene (VDFHFP) and those based on tetrafluoro-ethylenepropylene (TFEP) (alternating) were successfully cross-linked by electron-beam radiation and fluorinated to yield elastomeric products, but those based on ethylene-propylene-diene (EPDM) elastomer became brittle after fluorination. The best products were evaluated using tensile strength, elongation at break, solvent swelling, thermogravimetric analysis and infrared. The best products which have survived at least 100 days in autoclave simulated geothermal brine at 300°C are two versions of the TFEP alternating copolymer. After this extended exposure the Tg's of the elastomers differed very little from the original materials and the materials were noted to have retained their elastomeric nature.

This successful demonstration of these two fluorocarbon elastomers justified the search for effective reinforcing fillers and processing conditions for the production of O-rings.

To meet the second contract objective, EXFLUOR cross-linked a wide range of carbon-black filled compositions using the TFEP elastomer. The compositions were then fluorinated at or near room temperature for extended periods of time. After fluorination the samples were sent to Brookhaven National Laboratory where they were subjected to geothermal brine at 300°C. The best carbon-black filled composition again lasted at least 100 days in the geothermal brine. This filler-elastomer composition was chosen for use in the production of O-rings.

The O-rings were produced by compression molding using a 30 ton hydraulic press. Various sizes of O-rings were produced ranging from 0.8 to 2.0 inches in diameter and from 1/16 to 3/16 inches in width. The final O-rings were cross-linked at 40 Mrad and fluorinated under the optimized conditions developed for the samples. These O-rings have been sent to Brookhaven National Laboratory for exposure in the geothermal brine at 300°C.

It is important to note that the new perfluoro elastomer system developed in this research program represents the second class of perfluorinated elastomers ever developed. The first such perfluoro elastomers were the perfluoropolyether elastomer "Kalrez" developed by DuPont. O-rings of this material sell for over \$100 and fabricated materials can often be computed to sell for over \$10,000/lb.

Preliminary testing indicates that these new materials designated Exfluor I will exceed the performance of perfluoropolyether elastomers.

This should be so for Exfluor I (in contrast to "Kalrez") contains only carbon-carbon cross-links.

The direct fluorination technology uniquely provides a route to perfluorinated strictly one-to-one elastomeric ethylene-propylene copolymers. The "FEP" copolymer prepared from tetrafluoroethylene and hexafluoropropylene is not elastomeric because the degree of branching is inadequate to diminish polymer crystallinity. For mechanistic reasons, these copolymers have a maximum $\bar{F}$ -propylene to $\bar{F}$ -ethylene ratio of 1 to 6.

Although at least a year of further development is needed to optimize performance, we feel that the developments in this program are a major contribution to materials science. Applications of this new class of materials should extend far beyond the solution of problems in the geothermal and petroleum drilling fields.

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NEW FLUOROCARBON ELASTOMERS FOR SEALS
FOR GEOTHERMAL AND OTHER AGGRESSIVE ENVIRONMENTS

BACKGROUND

D.O.E. Sponsored Materials Research in Elastomers

The Department of Energy, Division of Geothermal Energy, has recognized the need to assemble data on the performance of materials in the extreme environments of geothermal reservoirs, and convened its first workshop-conference under the direction of Dr. R. Reeber at Lakeway⁽¹⁾ (Austin, Texas). The report, prepared by Radian Corp. (Austin, Texas) testifies to the high cost of materials failures and identifies the critical need for, among other things, superior elastomers for down-hole use. D.O.E. had already sponsored one year of a program at L'Garde (Newport Beach, California) seeking to improve known elastomers by intensive compound development and process modifications.⁽²⁾ A report of the state-of-the-art for polymers was prepared for D.O.E., Office of Energy Research, Division of Materials Science, by Texas Research Institute and Professor Patrick Cassidy of Southwest Texas State University.^(3,4)

Geothermal Requirements

Department of Energy and Brookhaven National Laboratory have recognized⁽⁵⁾ that a new elastomeric material superior to EPDM, VDFHDP and TFEP under geothermal conditions should excel in the following seven areas:

1. Extended use at 300°C, static applications
2. Hydrolytically stable at 300°C in presence of H₂S

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 Fluoro-silicone (FS-1265, Limit 260°C)
6. Resist abrasive wear of drilling residues
7. Resist permeation by gases and liquids.

Conventional Materials (200°C)

Most common elastomers are highly unsaturated, as for example polybutadiene, and their chemical resistance is severely limited by this feature of structure. Resistance to oils and elevated temperatures is improved by substitution of nitrile groups or chlorine atoms in the monomers used to make elastomers for oil well applications. The limitations of this structure are mitigated by the presence of reinforcing fillers such as carbon-black, and by carbon-carbon cross-linking introduced with peroxide curing systems. With all these palliatives, the inexpensive hydrocarbon elastomers have served usefully in energy extraction industries up to 200°C .

As discussed by Patrick Cassidy in his report,⁽⁴⁾ improvements in performance were necessary for geothermal applications of the future. Superior thermal and chemical resistance is available in elastomers having fluorocarbon bonds, and such materials were studied by the producers of rubber goods with little success. The VDFHFP and TFEP compositions were deficient in cross-link stability, especially in the presence of steam and

H₂S, and are subject to elimination of gaseous products such as HF or H₂ at elevated temperatures. The presence of fillers, and their usual effects in improving physical properties were not particularly useful in the improvements of chemical resistance under geothermal conditions. The Department of Energy set out to remedy this situation.

Recent Geothermal Elastomeric Material (GEM) Developments

(260°C)

The efforts of L'Garde Incorporated 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 around 260°C for extended periods of time. These EPDM, carbon-black filled systems, were peroxide cured, post-cured, and carefully monitored for quality. It appears that EPDM is useful under reducing conditions in hydrothermal brines. 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).

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 not elastomeric and not cross-linked. 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 H₂ as are the EPDM elastomers. The investigations cited above have been sufficiently

FIGURE 1

THERMOGRAVIMETRIC ANALYSIS OF UNFILLED GEOTHERMAL ELASTOMERS

(Nitrogen Atmosphere, 10°C/min. DuPont 990)

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. The difficulty of cross-linking such a system has not been completely solved by the producer, DuPont, and the tests at L'Garde of KALREZ O-rings have been disappointing.⁽⁵⁾ So is the high price and sole-source availability.

Efforts to produce perfluoro, cross-linked elastomers by the direct fluorination process have been funded by Brookhaven National Laboratory in anticipation that the deficiencies of materials cited above will not be present in the new product. EXFLUOR has successfully developed methods to replace the hydrogen in both TFEP and VDFHFP compositions with fluorine, while retaining intact the carbon-carbon skeleton of the cross-linked articles.

Contract Award

Under Contract No. BNL-486106-S⁽⁶⁾ awarded September 1, 1979, Exfluor Research Corporation developed novel cross-linked perfluorocarbon elastomers by direct fluorination with elemental fluorine. Brookhaven National Laboratory awarded Contract No. BNL-540438-S⁽⁷⁾ on December 1, 1980 to Exfluor Research Corporation as a continuation of Contract No. BNL-456106-S. Under the second contract, EXFLUOR was to do further testing of the new cross-linked perfluorocarbon elastomers and develop O-rings for static application at 300°C in geothermal brine.

SYNTHESIS OF CROSS-LINKED PERFLUOROCARBON ELASTOMERS

Direct Fluorination. Method of Preparing Cross-linked Perfluoroelastomers

Reaction of fluorine gas with hydrocarbons is known to produce HF and new C-F bonds.⁽⁸⁾ The usually violent reaction with small molecules can be controlled by dilution techniques and low temperatures. "Teflon-like" chemical properties have been reported⁽⁸⁾ for powdered polyethylene treated with fluorine, but the achievement of strong, macroscopic elastomeric fluorocarbon products has heretofore not been reported.

We have prepared strong, fluorinated, cross-linked elastomer films. Films of selected polymers were solvent-cast on aluminum foil which was supported by glass plates, cross-linked by 1 Mev electron-beam radiation, and fluorinated with mixtures of elemental fluorine and inert gas. The radiated films were swollen to "equilibrium" with solvents to evaluate their cross-linking density before and after fluorination. The cross-linked films were fluorinated with the direct fluorination method, and the uptake of fluorine was estimated by the weight gain assuming no loss of carbon.

Selection of Substrate Microstructure and Chemical Composition

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 stereo-chemical arrangements will also affect the glass transition temperature. The polymers were arranged in order of decreasing fluorine content, as starting materials. The fluorine

content affected both the efficiency of cross-linking by electron-beam radiation and the success of fluorination in the direct fluorination process.

An elastomer family having the following average structure fits the criteria and is readily available.

The new polymer resulting from fluorination of I above:

resembles the tetrafluoroethylene-hexafluoropropylene copolymer FEP "Teflon"^R. However, FEP (defined above) is crystalline and has a melting temperature T_M of about 270°C. The proportion of HFP (hexafluoropropylene) in FEP is thought to be 16%, the maximum which can be readily incorporated during polymerization of TFE (tetrafluoroethylene) and HFP. The HFP may not be randomly incorporated, permitting TFE sequences long enough to crystallize.

Our new structure (II) has CF_3 groups in 1/10 carbon atoms. They appear to be randomly distributed because the homopolymer of $\text{CH}_2=\text{CF}_2$ is a melting resin ($T_m = 260^\circ\text{C}$) whereas the copolymer I is an elastomer at room temperature.

In the unlikely event that our new structure II is capable of crystallization, its 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.

There are eight replaceable H atoms per average repeating unit (10 carbon atoms and 13 fluorine atoms).

The regularly alternating structure

is an elastomer at room temperature ($T_g = -10^\circ\text{C}$) 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).

If all copolymerizations are head to tail, the resulting regular structure is theoretically capable of crystallizing, as is natural rubber. However, as for (II), T_m should be low if it exists at all. The T_g may be higher than room temperature, but will be well below the use temperature in geothermal seals. There are six replaceable H atoms per four carbon atoms in Chain III, or 15 for a 10 carbon unit comparable to I.

A family of fluorinated products derived from ethylene-propylene copolymers has a variety of microstructures.

where x/y can be 1/1 to 4/1, but preferably near 1/1. The fluorinated elastomers (VI) range between (II) and (IV) in

proportion of CF_3 groups, but are random copolymers. There is little chance that the 1/1 copolymer will crystallize but the 4/1 copolymer may have long sequences of ethylene units which could possibly crystallize. If so, the crystallites would be very small and melt well below the corresponding T_m for FEP.

The compositions of these substrates are compiled in Table I.

Cross-Linking and Post-Treatment

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

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 was recorded. It may represent simply loss of small volatile components, or may be elimination of moieties incidental to the formation of carbon-carbon cross-links.

TABLE I

THEORETICAL WEIGHT INCREASE AFTER DIRECT FLUORINATION

<u>Elastomer</u>	<u>Repeating Unit</u>	<u>%F</u>	<u>%H</u>	<u>% Weight Increase</u>
<u>VDFHFP</u>	$\begin{array}{c} [(\text{CH}_2-\text{CF}_2)_4-(\text{CF}-\text{CF}_2)_1]_n \\ \\ \text{CF}_3 \end{array}$	65.5	1.97	----
<u>EXF-1</u>	$\begin{array}{c} [(\text{CF}_2\text{CF}_2)-(\text{CF}-\text{CF}_2)_1]_n \\ \\ \text{CF}_3 \end{array}$	76.0	0.0	37.4
<u>TFEP</u>	$\begin{array}{c} [(\text{CF}_2-\text{CF}_2)-(\text{CH}-\text{CH}_2)]_n \\ \\ \text{CH}_3 \end{array}$	53.5	4.22	----
<u>EXF-2</u>	$\begin{array}{c} [(\text{CF}_2-\text{CF}_2)-(\text{CF}-\text{CF}_2)]_n \\ \\ \text{CF}_3 \end{array}$	76.0	0.0	30.2
<u>EPDM</u>	$\begin{array}{c} [\text{CH}_2-\text{CH}_2]_x-(\text{CH}-\text{CH}_2)_y]_n \\ \\ \text{CH}_3 \end{array}$	0.0	14.28	0.0
<u>EXF-3</u>	$\begin{array}{c} [(\text{CF}_2-\text{CF}_2)_x-(\text{CF}-\text{CF}_2)_y]_n \\ \\ \text{CF}_3 \end{array}$	76.0	0.0	271.4

Fluorination

Samples of elastomer sheet were placed on copper gauze in the fluorination reactors and subjected to a flow of inert gas (helium) mixed with fluorine (F_2) in gradually increasing concentrations. The procedure began at room temperature and was carried out in the temperature range $20^{\circ}C$ to $85^{\circ}C$. In some instances, the temperature was slowly increased to obtain maximum diffusion rates. The concentration of fluorine was raised until pure fluorine at 35 psi surrounded the samples. The procedure usually took two to three days. At the end of the treatment, the atmosphere was flushed with helium and the samples were removed and weighed. This procedure was not an example of the most expeditious, but was capable of yielding strong elastomeric products.

Testing and Evaluation of Cross-linked Fluorinated Films

The elastomers were tested for physical properties such as tensile strength and elongation at break in an Instron Tester before and after fluorination. The thermal stability of the product at several levels of fluorine uptake was observed by thermogravimetric measurements (TGA). The temperature at which one-half of the weight loss had occurred was reported as a characteristic temperature. We believe that the onset of thermal degradation is a more interesting temperature, and temperatures for 1% and 3% weight loss are also reported in Table X.

Evaluation of Cross-linking by Swelling in Solvents

Approximately 1 inch square sections of the radiated elastomers were cut and weighed. These samples were immersed in a solvent contained in

a glass jar at room temperature. The samples were periodically withdrawn from the jar, quickly blotted and weighed, and replaced in the jar. The weight increase due to swelling of the sample was 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 swelling, the amount of solvent uptake should be related to the cross-link density. It is of course well established that highly cross-linked samples of the same polymeric materials swell to a lesser degree than samples with minimum or no cross-linking. Data for each sample is reported in Tables II, III, IV, and V.

Samples of radiated VDFHFP frequently fragment during the swelling tests, and a post-radiation heating cycle of 24 hours at 170°C has been devised to improve the physical strength of the elastomers. Data comparing post-treated samples with unheated samples is presented in Figure 2 and Table VI.

TABLE II

SOLVENTS FOR CASTING SOLUTIONS OF ELASTOMERS AND SWELLING MEASUREMENTS

Fluorinated Elastomer	Starting Elastomer	Tetrahydrofuran	Ethyl Acetate	Toluene	p-xylene	Hexanes	Acetone
EXF-I	<u>VDFHFP</u>						
	C-10	soluble	soluble				soluble(clou
	A-35	soluble	soluble				soluble(clou
	A	soluble	soluble				soluble(clou
	A-HV	soluble	soluble (cloudy)				soluble(clou
	GH	soluble	soluble (cloudy)				soluble(clou
EXF-II	<u>TFEP</u>						
	150	soluble	also soluble in Freon 113				
	100	soluble	soluble (somewhat cloudy)				
EXF-III	<u>EPDM</u>						
	1070	slightly soluble (very cloudy)	----	soluble (clear at b.p.)	soluble (clear)	insoluble (swelled)	
	1470	slightly soluble	----	soluble (clear at b.p.)	soluble (clear)	insoluble (swelled)	

TABLE III

ELASTOMERIC FILMS PREPARED FOR RADIATION CROSS-LINKING

(In order of increasing molecular weight and decreasing fluorine content.)

Starting Elastomer	Fluorinated Elastomer	Mooney Viscosity	Radiation Mrad
VDFHFP C-10	EXF-I	10 (100°C)	20, 40, 80
VDFHFP A-35		35 (100°C)	20, 40, --
VDFHFP A		65 (100°C)	20, 40, --
VDFHFP AHW		100 (150°C)	15, 30, 60
VDFHFP GH		-----	20, 40, 80
TFEP 150	EXF-II	85 (100°C)	20, 40, 80
TFEP 100		100 (100°C)	20, 40, 80
EPDM 1070	EXF-III	70 ----	20, 40, 80
EPDM 1470		70 ----	20, 40, 80

TABLE IV

SOLVENT SWELLING OF ELASTOMERS
CROSS-LINKED BY ELECTRON-BEAM RADIATION

Elastomer	Radiation Dose (Mrad)	Casting Solvent	Swelling Solvent	"Equilibrium" Wt. Gain (%)
TFEP 150	15	Freon 113	Ethyl Acetate	35
TFEP 150	15	Ethyl Acetate	Ethyl Acetate	34
TFEP 150	30	Freon 113	Freon 113	86
TFEP 150	30	Ethyl Acetate	Ethyl Acetate	31
TFEP 100	60	Freon 113	Freon 113	85
TFEP 100	60	Ethyl Acetate	Ethyl Acetate	43
VDFHFP AHV	15	Ethyl Acetate	Ethyl Acetate	294
VDFHFP AHV	15	Freon 113	Freon 113	20
VDFHFP AHV	30	Ethyl Acetate	Ethyl Acetate	28
VDFHFP AHV	30	Ethyl Acetate	Ethyl Acetate	378
VDFHFP AHV	60	Acetone	Ethyl Acetate	238
VDFHFP AHV	60	Freon 113	Freon 114	20 (Est.)

TABLE V

SOLVENT SWELLING OF ELASTOMERS CROSS-LINKED
BY ELECTRON-BEAM RADIATION AND POST-HEATED

Elastomer	Radiation Dose (Mrad)	Heat Treatment	Cast Solvent	Swelling Solvent	"Equilibrium" Wt. Gain (%)
VDFHFP GH	20	85°C - 1 hr.	Ethyl Acetate	Ethyl Acetate	197
VDFHFP GH	20	170°C - 44 hrs. flushed with N ₂ Wt. Loss=30.1%	Ethyl Acetate	Ethyl Acetate	255
TFEP 150	15	170°C - 44 hrs. flushed with N ₂ Wt. Loss=50.3%	THF	Ethyl Acetate	70

FIGURE 2

SWELLING OF POST-TREATED
CROSS-LINKED ELASTOMERS

TABLE VI

EFFECT OF POST-HEATING ON "EQUILIBRIUM" SWELLING OF VDFHFP GH FILM

(Cast from Ethyl Acetate and Swollen in Ethyl Acetate)

<u>Material</u>	<u>Radiation Dose (Mrad)</u>	<u>Temperature During Swelling (°C)</u>	<u>Time (hrs.)</u>	<u>Weight Gain (%)</u>
VDFHFP	20	170	44	250
VDFHFP	20	85	44	180
TFEP	15	150	44	80
TFEP	15	20	44	50

EVALUATION OF FLUORINATION

Weight Changes

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 could be lost from the elastomers, and we believe this to be a reasonable assumption provided that the reaction temperature does not rise much above 100°C.

Weight changes upon fluorination are recorded in Table VIII. The highest fluorination achieved so far was about 90% H replaced on EPDM test strips but in TFEP samples fluorination was 24-40%. Effort should be continued to achieve complete replacement of hydrogen by fluorine.

Solvent Swelling

Swelling measurements have been performed in accordance with the procedure described in the previous section, but in this case the samples have been fluorinated. The data is plotted in Figures 3 and 4. All swellings were carried out in Freon 113.

It is clear that the fluorination process has not destroyed the cross-linking of the elastomers, and it is also clear that Freon 113 is not a particularly good solvent for the fluorinated product. This data is probably the first to show the successful retention of cross-links and elastomeric properties of elastomers subjected to fluorine gas under pressure. It is particularly interesting to note that there is little difference in the maximum swelling for C-10, low molecular weight VDFHFP radiated with 10 Mrads and C-10 radiated with 40 Mrads (Figure 3) while the kinetics of swelling indicate that the 10 Mrad sample swelled much faster. A separate experiment was done on a 10 Mrad sample which was used as a control.

FIGURE 3

SWELLING OF FLUORINATED CROSS-LINKED ELASTOMERS

VDFHFP C-10 (40 Mrad) Ethyl Acetate
Fluorinated - 240 hrs.
% Wt. Gain = 10.37 during fluorination.
(Swelling Test - Freon 113)

% Wt. Gain
(Freon 113)

FIGURE 4

SWELLING OF FLUORINATED CROSS-LINKED ELASTOMERS

Tensile Testing

Tensile tests of the cross-linked elastomers before and after fluorination have been carried out at room temperature as described earlier, and are represented in graphical form in the Figures 5, 6, 7 and 8 and Tables VII and VIII. The extent of fluorination as measured by increase in weight is noted where appropriate. The force required to break the sample and the relative length of the sample at failure have been plotted. It is clear that the fluorinated product was still strong and elastic.

Changes in the elongation at break after fluorination may be in both directions. The samples may weaken, giving longer elongation before failure, or they may embrittle and give shorter elongations at break. The force required to break a sample may be increased if, for example, the elastomer becomes glassy at room temperature, or may decrease if cross-links are destroyed by fluorination.

Thermogravimetric Analysis (TGA)

TGA scans of 10°C/min. have been used to characterize the thermal stability of the fluorinated product, and to compare it with the unfluorinated, irradiated, and heated precursors. The temperatures for 1%, 3% and 50% weight loss are interesting data points for relative ranking (see Tables IX and X).

Thermogravimetric analysis of the starting material and the fluorinated products have been carried out on our DuPont 990 thermal analyzer. The temperature at 50% weight loss shows little variation due

to fluorination. It was expected that any remaining hydrogen in the partially fluorinated products would produce HF on heating at temperatures well below the expected thermal decomposition temperature of the fully fluorinated product. Therefore, a maximum fluorination percentage was desired.

FIGURE 5

STRENGTH AT BREAK OF FLUORINATED ELASTOMERS (wt. increase as marked)

TFEP-150
(THF Freon 113)

FIGURE 6

Elong. (E)
at break
%

ELONGATION AT BREAK OF FLUORINATED ELASTOMERS
(Wt. increases as marked)

FIGURE 7

STRENGTH AT BREAK OF FLUORINATED ELASTOMERS (Wt. increase as marked)

VDFHFP AHV
Ethyl Acetate

Δ (5.3%)

Δ (4%)

Δ (9%)

Δ (4%)

Δ (0.0%)

Δ (0.0%)

Strength
F/A
(lbs/in²)

26

250

200

150

100

50

0

15

30

45

60

MRAD

FIGURE 8

ELONGATION AT BREAK FOR FLUORINATED ELASTOMERS
(Wt. increase as marked)

VDFHFP AHV
Ethyl Acetate

Elong. (E)
at break
%

TABLE VII

STRENGTH TESTS OF CROSS-LINKED, FLUORINATED VDFHFP

Sample	Radiation Dose (Mrad)	Elong.(E) at break (%)	Force (F) at break (lbs.)	Area of Sample (A) (in. ²)	Tensile Strength at break F/A lbs./(in. ²)	Wt. Inc. (F ₂) %
<u>VDFHFP AHV</u>						
ETHYL ACETATE	15	322.0	0.279	.3774 x.0059= 2.22x10 ⁻³	125	0.0
ETHYL ACETATE	30	83.2	0.20	.3834 x.0050= 1.92x10 ⁻³	104	0.0
ACETONE	60	50.6	0.17	.3834 x.0053= 1.93x10 ⁻³	87.8	0.0
ETHYL ACETATE	15	99.0	0.63	.3663 x.0131= 4.72x10 ⁻³	133	4.1
ETHYL ACETATE	30	119.4	0.41	.3766 x.0066= 2.48x10 ⁻³	165	8.9
ETHYL ACETATE	60	145.0	0.79	.3608 x.0087= 3.13x10 ⁻³	251	5.3

TABLE VIII

STRENGTH TESTS OF CROSS-LINKED, FLUORINATED TFEP

Sample	Radiation Dose (Mrad)	Elong.(E) at break (%)	Force (F) at break (lbs.)	Area of Sample (A) (in. ²)	Tensile Strength at break F/A lbs./(in. ²)	Wt. Inc. (F ₂) %
<u>TFEP 150</u>						
THF Freon 113	15	334.0	0.863	.3340 x.0052= 1.74x10 ⁻³	497	0.0
THF Freon 113	30	215.0	0.364	.3756 x.0057= 2.14x10 ⁻³	170	39.0
THF Freon 113	80	19.8	4.80	.3750 x.0115= 4.31x10 ⁻³	1113	24.7

TABLE IX

THERMOGRAVIMETRIC ANALYSIS OF 50% WT. LOSS IN
CROSS-LINKED UNFLUORINATED AND FLUORINATED ELASTOMERS

<u>Sample</u>	<u>Mrad</u>	<u>Weight of Sample (mg)</u>	<u>Temp. at 50% Degradation (C)</u>	<u>% Fluorination</u>
<u>VDFHFP AHV</u>				
Ethyl Acetate	15	1.7	406	0.0
Ethyl Acetate	30	1.4	402	0.0
Acetone	60	2.0	399	0.0
<u>VDFHFP AHV</u>				
Ethyl Acetate	15	1.7	408	4.1
Ethyl Acetate	30	0.9	364	8.9
Ethyl Acetate	60	6.1	384	5.3
Ethyl Acetate	30	2.4	382	10.0
<u>TFEP 150</u>				
	0.0	1.5	426	0.0
<u>TFEP 150</u>				
Freon 113	15	3.0	421	0.0
Freon 113	30	8.6	385	39.0
Freon 113	80	6.3	396	24.7
<u>TFEP 100</u>				
	80	1.7	384	40.0

TABLE X

TEMPERATURE OF 1% AND 3% WEIGHT LOSS
AFTER EXPOSURE TO GEOTHERMAL BRINE 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
DOE-AC-60MR	1	200	335	---	400	325	350	350	---	365	325	270
	3	340	405	---	435	415	415	415	---	420	380	367
EXF-2 (X60F12.35.22)	1	290	---	---	415	370	385	385	---	370	370	290
	3	345	---	---	440	435	435	445	---	430	425	405
A150-15H (#6.25.48)	1	185	---	395	380	375	---	---	100	---	---	---
	3	380	---	440	425	440	---	---	375	---	---	---
EXF-2-150X60 (22.30.30)	1	300	---	400	390	---	---	---	360	---	---	---
	3	400	---	430	430	---	---	---	410	---	---	---
EXF-2-100X60 (22.30.30)	1	275	---	405	395	---	---	---	352	---	---	---
	3	365	---	440	437	---	---	---	404	---	---	---

EXPOSURE TO THE SIMULATED GEOTHERMAL BRINE (300°C)

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.

Laboratory tests consist of three parts: visual inspection, IR spectra, and TGA. A general visual inspection indicated a change in the elastic properties of the samples.

Infrared spectroscopic analysis was performed using a Perkin-Elmer Infrared Spectrometer Model 297. The thin film was placed in the sample beam with an attenuator in the reference beam.

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 measures the loss of weight as a function of temperature. In these tests, the samples are heated in a 90 cc/min nitrogen gas flow from room temperature to 650°C at a rate of 10 C/min.

Results of Geothermal Testing

Seven of twelve samples tested deteriorated beyond recognition after 30 days of 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)

Two of the remaining samples, DOE-AC-60 MR and EXF-2 (60 F12.35.22) remained together for more than 138 days but had deteriorated to the point where they could be pulled apart with little resistance. Sample A-150-15H (36.25.48) deteriorated after 70 days of autoclaving. Samples EXF-2-150 X60 (22.30.30) and EXF-2-100 X60 (22.30.30) held together for more than 56 days. General observations were made of the samples after 30 days of exposure.

- 1) Visual - Samples become progressively darker in color after each period of autoclaving. The samples were still very pliable with most of the elasticity left.
- 2) IR - The spectra were basically the same before and after exposure except for the apparent shifting of two absorption bands, 1850 cm^{-1} and 1715 cm^{-1} to 1700 cm^{-1} and 1570 cm^{-1} . This possibly could be from hydrolysis of the samples or a reaction with the seals from the brine. It was observed that toward the end of the testing period, the samples had darkened to the extent that quality infrared transmission could not be obtained due to lack of transmission.

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 X gives the temperature at which 1% and 3% weight loss occur.

RESULTS AND DISCUSSION

Limited swelling to constant weight may not represent thermodynamic equilibrium, but does show that cross-links have been successfully introduced by electron-beam radiation to both elastomer types. The swelling data over the range of 15-80 Mrads indicates that an optimum cross-link efficiency exists for each material. The TFEP samples survived the swelling tests indefinitely, with merely a change in the physical size of the sample. The VDFHFP samples fragment in one or two hours during the swelling experiment, although they do not dissolve. The fragmentation was more severe at the higher cross-link density. This indicated that the VDFHFP structure suffers radiation damage in addition to cross-linking during the radiation process, while the TFEP material was primarily cross-linked by the process. This was an expected result because the TFEP has a higher proportion of hydrogen available for the production of cross-linking sites, and was less likely to lose HF.

The post-radiation heat treatment was devised to improve the cross-linked efficiency of VDFHFP. The qualitative observation that the VDFHFP samples were much more resistant to fragmentation in the swollen state after the post-treatment supports the conclusion that the post-radiation heat treatment improves the cross-linking. The weight loss of 30% for the GH grade of VDFHFP, and 50% for TFEP on post-heating probably represents volatilization of fragments such as HF which were not driven off during the short time of the radiation treatment. The

presence of small molecules in the unheated samples probably accounts for erratic swelling versus time curves presented, as they were extracted and observed as a loss of weight.

The swelling of the fluorinated product is represented in Figure 3 for the C-10, low molecular weights grade of VDFHFP. It is clear that the fluorination process has not destroyed the cross-linking of the elastomers. Otherwise the polymer films would have dissolved. This data is probably the first to show the successful retention of cross-links and elastomeric properties of elastomers subjected to fluorine gas under pressure.

Tensile tests of the cross-linked elastomers before and after fluorination have been carried out at room temperature as described, and the data presented in Figures 5 and 7. The relative length of the sample at failure has been plotted in Figures 6 and 8. It is clear that the fluorinated product is still strong and elastic, but it is also clear that the fluorinated product is not as elastic as the starting material. It is interesting to note in the case of 150, the fluorinated product after 80 Mrad radiation is considerably stronger than the unfluorinated material at 15 Mrad and the fluorinated material at 30 Mrads. From the leathery character of the sample at room temperature, we tentatively explain this by postulating that the glass temperature of the fluorinated product was slightly above

room temperature. The low elongation at break for the 80 Mrad fluorinated sample is consistent with this interpretation.

Thermogravimetric analysis of the starting material and the fluorinated products have been carried out at Brookhaven National Laboratory and the data is recorded in Tables IX and X. The temperature at 50% weight loss in Table IX shows little variation in temperature due to fluorination. It is expected that any remaining hydrogen in the partially fluorinated products will produce HF on heating at temperatures well below the expected thermal decomposition temperature of the fully fluorinated product.

CONCLUSION

1. From the results in Table X, we conclude that our process of cross-linking and fluorinating carefully selected materials has produced the necessary chemical and physical structure for a successful elastomer in a geothermal environment at 300°C.

2. We conclude that the fluorinated TFEP copolymers radiated with 40 Mrad is the best candidate for further study, but the high molecular weight VDFHFP copolymer is also promising.

3. We conclude that the radiation method of cross-linking is adequate for TFEP copolymers and promising for VDFHFP. Radiation damage to the latter suggests peroxide cures should be investigated.

4. We conclude that the methods used to monitor our progress are valid.

The research accomplished during the first phase of this project has resulted in the development of two successful chemically distinct elastomeric fluoroelastomers, and the failure of EPDM. By success we mean that unfilled elastomers have been molded into films, cross-linked by electron-beam radiation, fluorinated by direct fluorination, and tested in 300°C brine with survival up to and surpassing 90 days.

From the data given in Tables VII, VIII, IX and X we can see that TFEP and VDFHFP are our two most promising elastomers at this point. It must be noted, however, that VDFHFP did suffer some damage due to radiation during cross-linking. We feel that this requires further investigation into the possibilities of using peroxide cures.

SELECTION OF AFLAS AS THE MOST PROMISING CANDIDATE FOR STUDY

During the first phase of the project, several criteria were used for the selection of an elastomer suitable for use in geothermal and other aggressive environments.

When VDFHFP failed to withstand the radiation cross-linking, another method of cross-linking using peroxide cures was considered. Cure systems investigated for use with VDFHFP and TFEP starting materials (the latter being tested for comparison with the radiation cross-linking) involved diallyl-isocyanurate (DIAC) and organic peroxides, and a process of heat curing and post-heating to develop permanent cross-links. This method, however, did not produce the thermally stable cross-link (this was learned from solvent swelling experiments) necessary for use in extreme environments, therefore, further testing of this elastomer was discontinued.

Due to disadvantages with the EPDM and the VDFHFP elastomers, it was decided at this time that all future testing should be carried out using the very promising elastomer TFEP.

This material, an alternating copolymer of tetrafluoroethylene with propylene (TFEP), is available in two grades having different molecular weights. The two grades are: TFEP-150 and TFEP-100. The latter was of the highest molecular weight and therefore possessed the best physical properties for extrusion resistance.

Both grades were tested with carbon-black fillers in this second phase.

TESTING WITH CARBON-BLACK FILLERS FOR COMPATIBILITY

The presence of selected carbon-black fillers in conventional elastomers is an essential part of the balance among modulus, tensile strength, elongation, hydrothermal chemical stability, abrasion resistance and lubricity of rubber products, and contributes substantially to permeation resistance, frictional properties, compression set, electrical resistance and resistance to solvent attack.

It was felt that EXFLUOR's new fluorocarbon elastomer would benefit substantially from reinforcing carbon-black fillers if the right combination could be attained. In order to find the optimum elastomer-filler combination different types of carbon-black filler were tested. Based on TGA data and preliminary tensile testing, carbon-black reinforcing fillers of ASTM designation N-990, N-568 and N-110 were used for their good processing characteristics and excellent balance of strength, hardness, and resistance to set and chemicals in conventional fluoroelastomers.

These three carbon-black fillers were compounded at three different loading levels with the two elastomers (see Table XI).

Compounding of Suitable Carbon-Black Fillers

The balance of strength, hardness, and resistance to chemicals can be varied with the amount of carbon-black present in the elastomer. For each

TABLE XI

TFEP-100 AND 150 CARBON-BLACK LOADING LEVELS

Carbon-Black	N-110	N-568	N-990
Loading Levels:	5%	10%	15%
	10%	20%	30%
	15%	30%	50%

of the three carbon-black fillers there is an optimum loading level depending on the application. Static, high pressure application requires that the composition be hard to withstand compression, and strong to resist extrusion. Dynamic application requires that the composition be pliable enough to resist the strain of cross-sectional surface movement, while maintaining surface contact. It was EXFLUOR's goal to find the optimum loading level of the correct filler to produce a filler-elastomer composition best suited for static application.

Approximately 40 gram batches of the two copolymers of tetrafluoroethylene and propylene (TFEP-150 and TFEP-100) were mixed with one of the three carbon-blacks (ASTM designations N-990, N-568, N-110) at three different loading levels as noted in Table XI.

Effect of Filler Type on Physical Properties

The three types of fillers used at 3 different loading levels [parts per hundred of rubber (phr)] can be observed in the data of Table XII, and compared with the effects on the starting materials collected in Table XIII.

Correlations between loading of various carbon-blacks and their tensile strengths appear to be as follows:

- 1) Comparing A and C (150), lower loadings of the least reinforcing carbon-black (N-990) produce the highest tensile strength both before and after fluorination.
- 2) Comparing J and L (100), lower loadings of the higher reinforcing (N-110) also produce higher tensile strength both before and after fluorination.

- 3) Both low (N-990) and medium (N-568) carbon-blacks are capable of forming strong cured (80 Mrad) elastomers at relatively low loadings.
- 4) High loadings of the highly reinforcing carbon-black (N-110) produce lower strength, harder compositions.

Samples reported here were tested for tensile strength at 100°C (see Table XIII). Samples in Table XII were fluorinated up to 20 psi pure fluorine at room temperature for 12 hours. Tensile testing of the samples in this series was performed at 20°C.

TABLE XII

EFFECT OF FILLERS ON TENSILE STRENGTH AND
TEMPERATURES OF 3% WEIGHT LOSS AFTER FLUORINATION

(Radiation Cure)

Sample	Strength (lbs/in ²) 20°C		Filler (phr*)	Temperature of 3% Wt. Loss	
	Before	After (F ₂)		30 Day Brine Exposure	60 Day Brine Exposure
<u>TFEP-150</u>					
80 Mrad					
A	897	213	L=N-990 100	432	428
C	1043	871	L=N-990 30	448	442
E	997	312	M=N-568 25	448	390
H	306	257	H=N-110 17	431	415
<u>TFEP-100</u>					
80 Mrad					
J	683	479	H=N-110 10	447	425
L	507	328	H=N-110 33	438	427
N	922	653	M=N-568 25	437	402
Q	455	251	L=N-990 50	450	454

*phr = Parts per hundred of rubber.

TABLE XIII

EFFECT OF FILLERS ON STARTING MATERIAL

(Peroxide Cure)

Unfluorinated TFEP-150	L = N-990		M = N-568		H = N-110	
	35 phr*	80 phr*	25 phr*	40 phr*	25 phr*	50 phr*
Hardness, Shore A	70	90	83	90	85	95
Tensile Strength (lbs./in ²), (100°C)	2500	2400	2600	2600	2500	2500
% Elongation	160	70	110	70	240	100

Unfluorinated TFEP-100	M = N-568		H = N-110	
	40 phr*		40 phr*	
Hardness, Shore A	93		96	
Tensile Strength (lbs./in ²), (100°C)	2300		2800	
% Elongation	100		90	

*phr = Parts per hundred of rubber.

CROSS-LINKING AND FLUORINATION OF CARBON-BLACK FILLED AFLAS/TFEP

Fabrication of Sample Sheets

The elastomers 150 and 100 were compounded at 100°C in a Brabender with the three carbon-blacks (N-110, N-568 and N-990) at three different percentages (see Table XI) and one control. They were then weighed and heated in a 4 inch by 4 inch sheet mold between platens held at 120°C for three minutes under 4,000 psi pressure. Aluminum foils were used to permit quick removal of sheets from the mold. The sheets were pressed to a thickness of 1/8 inch.

Cross-linking of Sample Sheets

The sample sheets were placed in polyethylene bags, flushed with nitrogen, sealed and placed on the conveyor belt of the Vandegraaf accelerator at Western New York Nuclear Facility (Buffalo, New York). Samples A through R were subjected to 1 Mev electrons at a dose of 2 Mrad per minute until 40 or 80 Mrad had been administered (see Table XIV).

Cross-linked samples were heated to 160°C overnight to remove volatile components.

Fluorination of Cross-linked Sample Sheets

Weighed 1 inch by 1 inch specimens of samples A through R, cross-linked with 40 Mrad of radiation were fluorinated up to 20 psi. In this instance to provide the most delicate fluorination conditions, the initial reaction temperature was -78°C. After one day of fluorination, the temperature was allowed to rise to room temperature. The final pressure was 20 psi fluorine for 12 hours at room temperature.

Similar specimens irradiated at 80 Mrad were fluorinated at room temperature with other conditions remaining the same.

TABLE XIVCOMPOSITION OF CARBON-BLACK FILLED ELASTOMERS

Polymer	Parts & Type Black phr*		Temperature at Torque Plateau
TFEP(150) - A	100	N-990 = L	110°-120°
B	50	N-990	110°
C	33	N-990	110°-130°
D	50	N-568 = M	110°-120°
E	25	N-568	110°-120°
F	17	N-568	110°-120°
G	33	N-110 = H	110°-120°
H	17	N-110	110°-120°
I	10	N-110	110°-120°
TFEP(100) - J	10	N-110	190°-200°
K	17	N-110	210°
L	33	N-110	210°
M	17	N-568	210°
N	25	N-568	210°
O	50	N-568	210°
P	33	N-990	210°
Q	50	N-990	210°
R	100	N-990	210°

*phr - Parts per hundred of rubber.

EVALUATION OF CARBON-FILLED, CROSS-LINKED, FLUORINATED AFLAS

Swelling Tests

The swelling test on Sample J was carried out in boiling, distilled water (Table XIV). The specimen a 1 inch by 1 inch sample of compound J (80 Mrad) was immersed in the water and withdrawn for weighing at times indicated in Table XV.

Reversible weight increase in boiling water indicated that the carbon-black was not thoroughly wetted with polymer during the compounding and molding steps prior to fluorination. Compounding of the elastomer with the carbon-black was continued for several hours past the torque plateau temperature in an attempt to alleviate this situation.

Figure 9 illustrates the weight percent pickup versus the square root of time. From Table XV data, it appears that 18 hours is sufficient time for reaching maximum swelling. We believe that higher fluorination levels under more severe fluorination conditions would serve to reduce this effect (Table XV), which was most probably due to unfluorinated carbon-black.

A swelling ratio of less than 10% is considered "little or no effect" for service in static O-ring applications.

Tensile Tests

Dogbone samples 2 inches long by 1/8 inch wide with 1 inch gauge length were cut from fluorinated sheets. The dogbones were tested in tension at a rate of 20 in./min. inside an environment chamber maintained at 100°C and mounted in an "Instron" Tester.

TABLE XV

BOILING WATER UPTAKE FOR FLUORINATED SAMPLE J

<u>Sample</u>	<u>Weight (grams)</u>	<u>Time (hours)</u>
J Fluorinated	1.0378	starting (sample dry)
"	1.0425	1/4
"	1.0493	1
"	1.0520	2
"	1.0657	18

Sample was left at room temperature for air drying.

J Fluorinated	1.0570	1
"	1.0526	4
"	1.0488	16

FIGURE 9

BOILING WATER UPTAKE FOR FLUORINATED SAMPLE J

The force at break, and the elongation at break were recorded (see Table XVI). Control samples were cut from post-treated sheets which were not fluorinated.

A look at Table XVI will show that some of the compounds experienced as much as a 73% loss in tensile strength after fluorination, while some of the more promising compounds experience a loss of less than 30%. Compounds experiencing a loss in tensile strength of less than 50% were chosen for further study.

Weight Increase

Sample sheets 1 inch by 1 inch were weighed both before and after fluorination (Table XVII) and a weight gain was determined.

Thermogravimetric Analysis (TGA)

Thermogravimetric weight loss measurements are characterized as the temperature for 1% and for 3% weight loss. All EXFLUOR samples tested have been found to go to at least 360°C before 1% weight loss, and to 410°C before 3% weight loss after many days exposure to geothermal brine at 300°C. Some samples reach 450°C before 3% weight loss is observed. See data reported in Table XII.

EXPOSURE TO GEOTHERMAL BRINE AT 300°C

The samples were autoclaved at Brookhaven National Laboratory in the environment of 25% simulated geothermal brine at the temperature of 300°C. The autoclaving was stopped for inspection of the samples at regular intervals of 30 days. After inspection and testing, the samples were returned for further autoclaving.

Laboratory tests at Brookhaven consist of two parts, visual inspection and TGA.

TABLE XVI

TENSILE STRENGTH AT 100°C (20 IN./MIN. AS PER ASTM D-412)

Sample Fluorinated	Strength psi	Control un- fluorinated	Elongation (%)	Loss of Tensile Strength (%)
AFLAS-150 (80 Mrad)				
A	213	897	(less than 5)	73
C	871	1043	"	20
E	312	997	"	69
H	257	306	"	16
AFLAS-100 (80 Mrad)				
J	479	683	"	30
L	328	507	"	36
N	653	922	"	29
Q	251	455	"	45

TABLE XVII

WEIGHT INCREASE ON FLUORINATION AFTER RADIATION AND POST-HEATING

Composition	Cross-links (Mrad)	Weight Increase (%)	
		A	B
A through I	40	$\frac{1}{1}$	$\frac{15}{15}$
A through I	80	1	17
J through R	40	1	15
J through R	80	1	17

This low weight gain^A indicated that the carbon-black was not fluorinated under these conditions, therefore, fluorination time was extended by 24 hours and the fluorine content adjusted to increase weight gain^B.

The TGA 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 sample 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.

EVALUATION OF RESULTS

Visual Results

After autoclaving, all of the samples held together; however, their elasticity had decreased slightly. Visual results also indicated that high carbon-black loadings of 40 to 100 phr produced compounds which were stiff after 30 days and became progressively harder with continued exposure. Lower loadings of 10 to 40 phr were softer before exposure and tend to remain so afterwards. Compounds of this nature were chosen for further study.

TGA Results

Weight loss of the controls was greater than the samples that were exposed to geothermal brine. It was suggested that this was due to an entrapment of water or processing chemicals. A bake-out process could possibly alleviate this.

Tables XVIII, XIX and XX show the temperature at which 1% and 3% weight loss occurred. Here again all EXFLUOR samples go to at least 360°C before 1% weight loss, and to 413°C before 3% weight loss after many days of exposure to geothermal brine. Some of the more promising materials

TABLE XVIII

TEMPERATURE (°C) AT 1% AND 3% WEIGHT LOSS AFTER EXPOSURE TO BRINE

Sample Number	Weight Loss (%)	Control	30 Days	60 Days	90 Days
<u>At 40 Mrad:</u>					
K (110)	1	222	404	387	395
	3	400	447	425	440
N (568)	1	335	400	350	322
	3	417	437	402	411
Q (990)	1	372	420	420	405
	3	415	450	454	452
R (990)	1	375	408	370	370
	3	435	443	420	416
<u>At 80 Mrad:</u>					
K (110)	1	210	400	350	322
	3	395	434	404	382
N (568)	1	375	410	360	372
	3	404	438	427	432

TABLE XIX

TFEP-150 AT 40 MRADTEMPERATURE (°C) AT 1% AND 3% WEIGHT LOSS AFTER EXPOSURE TO BRINE

Sample Number	Weight Loss (%)	Control	30 Days	60 Days	90 Days
A	1	355	415	387	310
	3	415	454	437	418
B	1	320	410	365	360
	3	407	447	418	421
C	1	290	410	395	345
	3	415	451	438	432
D	1	300	405	375	315
	3	415	436	422	385
E	1	335	425	395	355
	3	402	450	436	410
F	1	360	405	360	355
	3	405	443	412	408
G	1	195	423	385	372
	3	378	452	427	420
H	1	275	394	385	385
	3	405	423	427	420
I	1	300	386	382	345
	3	400	436	425	398

TABLE XX

TFEP-150 AT 80 MRAD

TEMPERATURE (°C) AT 1% AND 3% WEIGHT LOSS AFTER EXPOSURE TO BRINE

Sample Number	Weight Loss (%)	Control	30 Days	60 Days	90 Days
A	1	225	360	380	360
	3	400	432	428	416
B	1	350	389	355	325
	3	403	438	412	378
C	1	370	395	405	365
	3	418	448	442	415
D	1	300	348	370	335
	3	410	413	405	402
E	1	362	420	350	340
	3	408	448	390	390
F	1	250	357	354	365
	3	363	427	392	405
G	1	155	368	370	360
	3	374	428	415	408
H	1	167	390	375	345
	3	362	431	415	408
I	1	235	358	355	345
	3	392	417	410	390

still had 3% weight loss at temperatures of over 450°C after the 100 day exposure in the geothermal brine environment.

SELECTION OF THE MOST PROMISING FILLER-ELASTOMER COMBINATION

As stated earlier in this report, it was felt that EXFLUOR's new fluorocarbon elastomer would benefit from reinforcing carbon-black fillers if the right combination could be attained. To produce this optimum combination, EXFLUOR compared carbon-blacks of small, medium and large particle size over a wide range of "loadings" with the selected fluoroelastomers. They were then cross-linked under two different sets of conditions and fluorinated to yield test samples with a wide range of hardness and reinforcement. The fluorinated samples were then subjected to 300°C simulated geothermal brine.

After reviewing the results of the various tests it was decided that the TFEP-100 should be selected for use in the production of the final O-rings. It can be seen in Table XVI that the fluorinated samples of AFLAS-100 retained the greatest percentages of their previous unfluorinated tensile strength. It may also be noted that elongation was less than 5%. A look at Table XII indicates that the AFLAS-100 samples as a whole were able to withstand higher temperatures for a longer period of time before a weight loss of 3% occurred.

It is also clear given the results of the exposure tests that the compounds containing the AFLAS-100 elastomer were able to withstand an average temperature of 422°C after a 90 day exposure to brine before a 3% weight loss was recorded.

Observation of carbon-black (N-568) at 25 phr in both TFEP-150 at 80 Mrad and TFEP-100 at 40 Mrad shows a great effect at 60 day exposure tests

for 3% weight loss, while the (N-990) under the same conditions shows the least effect. This difference is probably not due to variability in mixing, therefore, carbon-black filler (N-990) was selected for further testing in the O-ring samples.

PRODUCTION OF FLUOROCARBON O-RINGS

After selection and testing of a suitable elastomer-filler composition was completed, EXFLUOR's final task was to produce fluorocarbon O-rings for testing under use conditions at 300°C in realistic geothermal liquids including H₂S and hydrocarbons. It was decided that the TFEP-100/carbon-black N-990 combination at 40 Mrad with 5 percent fluorine weight gain was the ideal composition for use in production of the final O-rings, and that future research would proceed in this direction.

Mold Design

EXFLUOR contracted the firm of Schaeffer's Mold & E.D.M. Service, Inc. (Fort Worth, Texas) to manufacture four chrome-plated, micropolished, mild steel compression molds for fabrication of several different size O-rings. Each mold produces one O-ring. O-ring sizes are as follows:

<u>ASTM No.</u>	<u>Diameter (inches)</u>	<u>Width (inches)</u>
568-329	2	3/16
568-222	1-3/8	1/8
568-117	13/16	3/32
568-021	15/16	1/16

See Figure 10 for general mold description.

COMPRESSION MOLD DESIGN

Processing and Molding

The selected elastomer-filler composition was blended in a small laboratory Brabender internal mixer. Five batches of approximately 40g each were produced for molding. This compounded elastomer was shredded, divided into carefully weighed samples (the weight of sample varied according to the mold size) and stored at 70°C.

The inside of each mold was coated with a lubricant (Fomblin Z) which helped to facilitate removal of the O-rings. The weighed samples were then placed inside the molds, which were put two at a time into a 30-ton press. The press was slowly heated to 150°C before full pressure was applied. At 200°C the press was allowed to begin cooling. When the molds reached 40°C they were taken from the press and cooled at room temperature. As soon as the O-rings were removed from the molds they were trimmed of excess rubber and inspected for flaws.

CROSS-LINKING OF O-RINGS

The samples were sent to Western New York Nuclear Facility for cross-linking. After receiving the prescribed dosage of radiation the samples were returned to EXFLUOR for testing. The cross-linked O-rings were tested using the same methods discussed earlier in this report.

FLUORINATION OF O-RINGS

The cross-linked samples were fluorinated up to 30 psi, with a starting temperature of approximately 25°C. The fluorine was allowed to flow over the samples in light concentration with helium gas for a period of 48 hours. During this time the amount of helium was gradually reduced

and replaced with pure fluorine. The pressure and temperature were both raised at this time for approximately 24 hours.

The cross-linked, fluorinated O-rings were sent to Brookhaven National Laboratory for further testing in the simulated geothermal brine at 300°C. Full evaluation of the O-rings produced is planned. Information derived from extensive testing will be utilized to make substantial improvements in formulation, fillers, and fluorine uptake.

CONCLUSION

Although we expect outstanding performance of the new materials, EXFLUOR is aware of a myriad of possibilities for improvement in formulation, fillers, and processing so that new developments are expected in a third phase of this program which will be proposed to Brookhaven National Laboratory.

It is remarkable indeed that with only two twelve-month periods of funding, this program was able to produce the first samples of O-rings and seals suitable for testing. It should be remembered that the O-ring samples produced at this stage are prototypes (they have been available for less than a month as this is written). They have not yet undergone the development to eliminate even obvious problems.

We are aware of certain problems and parameters which need to be improved. For example, the compression molding process seals and sinters the finished O-ring surface to a greater extent than the materials in the precursor test bars. This makes gas diffusion more difficult. Thus more vigorous fluorination conditions are necessary. The solution to this problem is at hand and at least three separate programs will be proposed to facilitate elimination of remaining hydrogen in fabricated items.

We are also very interested in the low temperature performance of these materials and feel that substantial developments will occur with such O-rings and seals in fields unrelated to geothermal applications.

It is felt that the developments discussed in this report represent a major advance in materials science, especially in the high-temperature, high-performance polymers and elastomers area. It should be obvious to

even the casual reader that the applications for such new materials extend far beyond the important applications designated in the geothermal and petroleum drilling areas.

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