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(21) International Application Number: PCT/US93/04380 (22) International Filing Date: 7 May 1993 (07.05.93) (30) Priority data: 07/879,390 7 May 1992 (07.05.92) US (71) Applicant: E.I. DU PONT DE NEMOURS AND COM- PANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). (72) Inventors: HUNG, Ming-Hong ; 601 Andover Road, Wil- mington, DE 19803 (US). OJAKAAR, Leo ; 8 Jacqueline Drive, R.D. 1, Hockessin, DE 19707 (US). (74) Agents: HUNTLEY, Donald, W. et al.; E.I. du Pont de Ne- mours and Company, Legal/Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).		(81) Designated States: JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the</i> <i>claims and to be republished in the event of the receipt of</i> <i>amendments.</i>
(54) Title: PERFLUOROELASTOMERS WITH ENHANCED PROPERTIES		
(57) Abstract The mechanical properties of cured perfluoroelastomers are enhanced by incorporating into compounds of uncured perfluoropolymer a fluoropolymer containing a hydroxyl group. The modified fluoropolymer can be either a fluoroplastic or a fluoroelastomer. A preferred hydroxy-containing monomer for preparation of the fluoropolymer is $CF_2 = CFOCF_2CF(CF_3)OCF_2CF_2-CH_2OH$.		

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PERFLUOROELASTOMERS WITH ENHANCED PROPERTIES

Background of the Invention

5 Perfluoroelastomers such as those described in U.S. Patents 3,682,872, 4,281,092, 4,487,903 and 4,983,697 have properties that make them attractive for use under unusually severe conditions. These materials are suitable for applications requiring the characteristics of an elastomer and at the same time tolerance for exposure to high temperatures or to aggressive chemicals.

10 The mechanical properties of perfluoroelastomers, in common with other elastomers, are conventionally adjusted by varying the ratios of perfluoromonomers in the polymers, by varying the amount of carbon black and other compound ingredients, and by varying the curing, or vulcanizing, chemistry. Certain uses, however, require combinations of properties not
15 attainable by known means. One particularly desirable improvement would be the increase of tensile strength and modulus without sacrifice of compression set.

Summary of the Invention

20 The present invention provides cured perfluoroelastomers which exhibit enhanced mechanical properties through the incorporation into the compound of a fluoropolymer modified with a monomer containing a hydroxyl group.

Specifically, the instant invention provides a polymer blend comprising, complementally,

- 25 (a) at least one perfluoroelastomer of tetrafluoroethylene, perfluoroalkyl perfluoro(vinyl ether) and at least one cure site moiety, and
(b) about from 2 to 20 parts by weight of at least one hydroxy-containing fluoropolymer, the fluoropolymer containing about from 0.2 to 20 mole percent of units derived from at least one hydroxy-containing
30 vinyl ether monomer of the formula

$CF_2=CF[OCF_2CF(CF_3)]_n(O)_p(CF_2)_mCH_2OH$ wherein p is 0 or 1; m is 0 to 10 and n is 0 to 20; and provided that when m is 0, p is 0; and when m is greater than 0, p is 1; and further provided that at least one of n and m is at least 1.

Detailed Description of the Invention

Perfluoroelastomers used in the present invention are prepared from tetrafluoroethylene, perfluoroalkyl perfluoro(vinyl ether) and at least one cure site moiety. For purposes of the present invention, minor portions of the tetrafluoroethylene can be replaced by other perhaloolefins, such as chlorotrifluoroethylene. Perfluoro(alkyl vinyl ethers) preferred for use in the present invention include perfluoro(methyl vinyl ether) (PMVE) and perfluoro(propyl vinyl ether) (PPVE). Small concentrations of monomers which are not perfluorinated can also be used without significantly changing the desirable characteristics of these perfluoroelastomers. Normally, such monomers are incorporated as cure site moieties to obtain desirable crosslinking characteristics and may be present in concentrations up to about 3 mol%. Such monomers can include, for example, bromotetrafluorobutene, bromotrifluoroethylene, and monomers containing cyano groups. Alternatively or additionally, chain transfer agents which are not perfluorinated can be used in the polymerization reaction to introduce desirable fragments into the polymer for curing purposes, and are considered cure site moieties or monomers in the context of the present invention. Such agents include di-iodo compounds that result in bound iodine in the polymer, commonly at the end of the molecule. Representative perfluoroelastomers are illustrated in U.S. Patents 3,467,638, 4,281,092, 4,487,903, 4,529,784, 4,948,853 and 4,983,697, each of which is hereby incorporated by reference.

In accordance with the present invention, the perfluoroelastomer is blended with about from 2 to 20 parts by weight of at least one hydroxy-containing fluoropolymer, the fluoropolymer containing about from 0.2 to 20 mole percent of units derived from at least one hydroxy-containing vinyl ether monomer of the formula $CF_2=CF[OCF_2CF(CF_3)]_n(O)_p(CF_2)_mCH_2OH$ wherein p is 0 or 1; m is 0 to 10 and n is 0 to 20; and provided that when m is 0, p is 0; and when m is greater than 0, p is 1; and further provided that at least one of n and m is at least 1. Hydroxy-containing monomers which can be used in the preparation of these fluoropolymers are described in detail in U.S. Patents 4,982,009 and 5,059,720. Among these fluoro(vinyl ethers), a preferred monomer is

$\text{CF}_2=\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{-CH}_2\text{OH}$ (EVE-OH).

The fluoropolymers used in this invention, in addition to the units derived from the hydroxy-containing vinyl ether monomer, contain at least one other fluoromonomer. These fluoromonomers include
5 fluoroolefins and fluoro(vinyl ethers). Preferred fluoromonomers include TFE, hexafluoropropylene (HFP), PPVE, and PMVE. Monomers that do not contain fluorine, such as ethylene (E), can be used in conjunction with a fluorinated monomer. Partially fluorinated monomers such as
10 perfluorobutyl ethylene (PFBE) can also be used. One illustrative combination with a hydroxy-containing monomer is E/TFE/PFBE. Preferred combinations with the hydroxy-containing monomer include TFE alone, TFE/HFP, TFE/PPVE, and TFE/PMVE. These polymers can be prepared by conventional copolymerization techniques.

The hydroxy-containing fluoropolymers can be either partially-
15 crystalline and classified as fluoroplastics or non-crystalline and classified as fluoroelastomers, depending on the monomers chosen and their proportions, as known to those skilled in the art. If the hydroxy-modified fluoropolymers are elastomeric, they may also contain cure site monomers or fragments with desirable curing characteristics derived from chain transfer agents in
20 polymerization, as discussed above.

The units in the fluoropolymer derived from hydroxy-containing monomer will constitute about 0.2-20 mol% of the modified fluoropolymer. If the fluoropolymer is a fluoroplastic, the units derived from the hydroxy-containing monomer will constitute about 3-20 mol% and
25 preferably about 5-15 mol% of the hydroxy-modified fluoropolymer. If the fluoropolymer is a fluoroelastomer, the units derived from the hydroxy-containing monomer will constitute about 0.2-10 mol% and preferably about 0.5-5 mol% of the hydroxy-containing fluoropolymer.

The amount of hydroxy-containing fluoropolymer used in the
30 present polymer blends is about from 2 to 20 parts by weight, per 100 parts by weight of the polymer blend. Preferably, the hydroxy-modified fluoropolymer will be about from 5 to 15 parts by weight of the blend. The blending of the polymeric components of the present invention and compounding of the blends with other components of the compounds can be

carried out by conventional blending and compounding techniques. The blends of the present invention are typically compounded with one or more of the additives known to be useful in perfluoropolymer compositions, such as pigments, fillers, pore-forming agents and plasticizers. It is particularly advantageous to add carbon black to the fluoroelastomer to increase its modulus. Usually, amounts of about 5-50 parts by weight per hundred parts of the fluoroelastomer blends are used, the particular amount being determined from the particle size of the carbon black and the desired hardness and modulus of the cured composition.

One component of the compounded elastomer is a cure accelerator. The particular cure accelerator is generally determined by the particular cure site monomer used in the fluoroelastomer. For those perfluoroelastomers in which the cure site monomer consists essentially of perfluoro-(8-cyano-5-methyl-3,6-dioxo-1-octene), tetraphenyltin is customarily used. In the blends of the present invention, it has been found that, with these cure site monomers, triphenyltin hydride is particularly effective.

The blends of the present invention, through the incorporation of the hydroxy-containing fluoropolymer, exhibit significantly increased tensile strength and modulus, without sacrifice of other desirable elastomeric characteristics, such as compression set.

In the following Examples and Control Examples, parts and percentages are by weight unless otherwise indicated.

In these Examples and Control Examples, the following polymers were used, and prepared according to the indicated techniques.

Polymer A

A 2-liter reactor was purged with nitrogen, and then charged with 1250 ml of deionized water, 50 ml of 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113), and 50 ml of 4% aqueous ammonium persulfate initiator solution. TFE (60 g) and 20 g of $\text{CF}_2=\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{-CH}_2\text{OH}$ (EVE-OH) were then transferred into the reactor, the temperature was increased to 60°C, and the agitator speed was set at 175 rpm. Continuous feed of TFE at the rate of 20 g/hr was then started. Polymerization continued at autogenous pressure for 4 hr,

after which TFE feed was stopped and the reactor was cooled. The polymer emulsion was discharged from the reactor and was coagulated by addition of concentrated nitric acid accompanied by vigorous stirring. The precipitated polymer was collected by filtration, was washed thoroughly with warm water, and dried for 24 hr in a vacuum oven at 150 mmHg and 100°C. The yield was 135 g of a white powder designated as Polymer A. Polymer A had a molar composition of TFE/EVE-OH = 86.1/13.9 as determined by ^{19}F nuclear magnetic resonance (NMR) spectroscopy at high a temperature of 330°-340°C. The polymer was a partially crystalline fluoroplastic with a melting point of 279°C as determined by differential scanning calorimetry (DSC).

Polymer B

Eight batches of TFE/EVE-OH partially-crystalline fluoropolymer were made by the above procedure for Polymer A. The eight batches were combined to yield 1040 g of Polymer B. Polymer B had the molar composition TFE/EVE-OH = 88.5/11.5 by ^{19}F NMR spectroscopy and a DSC melting point in the range 280°-285°C.

Polymer C

A modified perfluoroelastomer was made in a well-stirred 5.4-liter reactor by continuous emulsion polymerization at 70°C. Two aqueous solutions were fed to the reactor. The first solution was fed at the composition rate of 120 ml/hr of water, 1.92 g/hr of ammonium persulfate, 1.3 g/hr of disodium hydrogen phosphate heptahydrate, and 1.4 g/hr of ammonium perfluorooctanoate ("Fluorad" FC-143 from 3M Co.). The second solution was fed at the composition rate of 150 ml/hr of water, 1.6 g/hr of sodium sulfite, and 1.7 g/hr of FC-143. TFE, perfluoro (methyl vinyl ether) (PMVE) and EVE-OH monomers were fed simultaneously at the rates of 62 g/hr for TFE, 76 g/hr for PMVE, and 2.34 ml/hr for EVE-OH. The polymer was isolated by coagulation with magnesium sulfate aqueous solution, then washed and dried in an oven at 80°C for 48 hr. About 5.5 kg of Polymer C obtained in this way had molar composition TFE/PMVE/EVE-OH = 65.1/34.3/0.64 by ^{19}F NMR spectroscopy. Polymer C had a glass transition temperature (T_g) of -5°C and no discernible crystalline melting point by DSC.

In the Examples and Control Examples, compounds of perfluoroelastomer and hydroxy-modified fluoropolymer with other ingredients specified were prepared on a standard two-roll rubber mill with the rolls heated to about 90°C. Ingredients were weighed out, premixed, and then milled for 20-30 minutes.

The compounded blends were converted to a form suitable for physical testing by compression molding into sheet 15 cm square and 1.9 mm thick. Unless otherwise specified, the sheet was press-cured at 210°C for 10 minutes, and then post-cured in a circulating air oven at 90°C for 6 hr followed by a uniform transition to 305°C over 10 hr and in turn followed by 26 hr at 305°C. Specimens for physical testing were die-cut from the sheet as called for by the test methods summarized in Table 1.

Table 1. Physical Test Methods

<u>Symbol</u>	<u>Property</u>	<u>Method</u>
M ₁₀₀	Modulus at 100% elongation (psi)	ASTM D-412
T _b	Tensile strength at break (psi)	ASTM D-412
E _b	Elongation at break (%)	ASTM D-412
H	Hardness (Shore A, pellet)	ASTM D-395
CS	Compression Set (% , 70 hr/200°C, pellet)	ASTM D-395

Examples 1-2 and Control A

Polymer A was compounded with a fluoroelastomer identified as Polymer D and other ingredients listed in Table 2. Polymer D was a TFE/PMVE/8-CNVE perfluoroelastomer prepared according to the general procedures described in U.S. Patent 4,281,092. 8-CNVE is the cure site monomer perfluoro-(8-cyano-5-methyl-3,6-dioxa-1-octene), The compound was molded and tested according to the procedures described above, and the results are summarized in Table 2. As can be seen from the test results in Table 2, the incorporation of Polymer A in the blend enhanced modulus with modest sacrifice of compression set and tensile strength, a desirable combination of properties.

Examples 3-8 and Control B

Polymer B was compounded with Polymer D and other ingredients as listed in Table 3, using the same procedures as in Examples 1-2. The compounds were tested as before, and the results are similarly summarized in Table 3.

5 **Examples 9-12 and Control C**

Polymer B and Polymer D were compounded with other ingredients including two different curing accelerators as listed in Table 4. While both accelerators in conjunction with Polymer B show enhanced modulus and hardness with little or no sacrifice of compression set and little
10 loss of elongation, the data show triphenyltin hydride to be superior in preserving low compression set.

Control Examples D-E

Polymer D was blended with a commercial non-melt-fabricable TFE polymer (PTFE) of the type known as fine powder, available
15 as Teflon® TFE fluorocarbon resin grade 6C (Du Pont Co.), and other ingredients as listed in Table 5. After milling, molding and curing, the elastomeric sheet lacked integrity, being delaminated and showing visible cracks and blisters, so properties were not measured. These examples indicate that fluoropolymers without hydroxy modification are ineffective in
20 enhancing properties.

Examples 13-14 and Control F

Polymer C was blended with Polymer E and other ingredients as listed in Table 6. Polymer E, prepared generally as described in U.S. Patent 3,467,638, was an elastomeric copolymer of TFE and PMVE with 5-
25 pentafluorophenoxy-perfluoro-(5-methyl-3-oxa-1-pentene) as a cure site monomer. The molded sheet was press-cured at 190°C for 30 minutes, then post-cured in a circulating air oven first at 90°C for 6 hr followed by a 10-hr transition to 288°C and finally at 288°C for 26 hr. The test results in Table 6 show that addition of the hydroxy-modified fluoroelastomer enhanced
30 mechanical properties without sacrifice of compression set.

Examples 15-18 and Control G

Polymer C was blended with Polymer F and other ingredients as listed in Table 7. Polymer F was a copolymer of TFE, PMVE, and BTFB in which BTFB is cure site monomer 4-bromo-3,3,4,4-tetrafluorobutene.

Perfluoroelastomers of this type and their preparation are described in U.S. Patent 4,035,565. After milling and molding by the general procedures described above, the sheet was press-cured at 170°C for 10 minutes, then post-cured in a circulating air oven at 90°C for 2 hr followed by a 6-hr
5 transition to 250°C and finally at 250°C for 18 hr. The test results in Table 7 show enhancements of modulus and tensile strength with little change of hardness and modest loss of elongation. Three of the samples exhibit favorable reductions in compression set.

Table 2. Compounds with Hydroxy-Modified Fluoroplastic

Example	Control A	1	2	
Formulation:				
5	Polymer A	0	10	10
	Polymer D	100	90	90
	Carbon Black	12 ^a	12 ^b	12 ^a
	18-crown-6 ^c	0.3	0.3	0.3
	Ph ₄ Sn ^d 3	3	3	
10	Properties:			
	M ₁₀₀	1300	1449	1862
	T _b	2700	1786	2146
	E _b	150	121	109
	H	77	82	86
15	CS	20	36	36

^a SAF type carbon black

^b SRF type carbon black

^c Aldrich Chemical Co.

20 ^d Tetraphenyltin

Table 3. Compounds with Hydroxy-Modified Fluoroplastic

Example	B	3	4	5	6	7	8	
Formulation:								
5	Polymer B	0	12.5	10	7.5	5	3.75	15
	Polymer D	100	87.5	90	92.5	95	96.25	85
	SAF Carbon	12	12	12	12	12	12	12
	18-crown-6	0.3	0.3	0.3	0.3	0.3	0.3	0.3
	Ph ₄ Sn	3	3	3	3	3	3	3
10	Properties:							
	M ₁₀₀	1300	1602	1621	---	1446	1169	1738
	T _b	2700	2473	2600	2444	2410	2246	2903
	E _b	150	106	114	---	117	115	121
	H	77	89	89	88	87	87	90
15	CS	20	35	29	22	21	19	37

Table 4. Compounds with Different Cure Accelerators

Example	C	9	10	11	12	
Formulation:						
5	Polymer B	0	5	7.5	5	7.5
	Polymer D	100	95	92.5	95	92.5
	SAF Carbon	12	12	12	12	12
	18-crown-6	0.3	0.3	0.3	0.3	0.3
	Ph ₄ Sn	3	3	3	---	---
10	Ph ₃ SnH ^a	---	---	---	3	3
Properties:						
	M ₁₀₀	1300	1784	1925	1965	1965
	T _b	2700	2423	2246	2199	2190
	E _b	150	117	108	107	107
15	H	77	87	88	88	89
	CS	20	22	25	20	21

^a Triphenyltin Hydride

Table 5. Compounds with Unmodified Fluoroplastic

<u>Example</u>	<u>D</u>	<u>E</u>	
Formulation:			
5	PTFE 6C	12.5	5
	Polymer D	87.5	95
	SAF Carbon	12	12
	18-crown-6	0.3	0.3
	Ph ₄ Sn	3	3
10			

Table 6. Compounds with Hydroxy-Modified Fluoroelastomers

<u>Example</u>	<u>F</u>	<u>13</u>	<u>14</u>	
Formulation:				
5	Polymer C	0	5	10
	Polymer E	100	95	90
	SAF Carbon	10	10	10
	18-crown-6	4	4	4
	MgO	4	4	4
10	K ₂ AF	3	3	3
Properties:				
	M ₁₀₀	1370	1571	1429
	T _b	1699	1944	1975
	E _b	116	115	125
15	H	80	80	79
	CS	51	45	51

^a Dipotassium salt of bisphenol-AF

Table 7. Compounds with Hydroxy-Modified Fluoroelastomer

Example	G	15	16	17	18	
Formulation:						
5	Polymer C	0	5	10	15	20
	Polymer F	100	95	90	85	80
	SAF Carbon	10	10	10	10	10
	18-crown-6	4	4	4	4	4
	MgO	4	4	4	4	4
10	K ₂ AF	3	3	3	3	3
Properties:						
	M ₁₀₀	775	889	995	1035	835
	T _b	2262	2448	2303	2196	2311
	E _b	217	195	172	163	199
15	H	79	78	79	81	77
	CS	55	46	52	51	71

I CLAIM:

1. A polymer blend comprising, complementally,
 - (a) at least one perfluoroelastomer of tetrafluoroethylene, perfluoroalkyl perfluoro(vinyl ether) and at least one cure site moiety, and
 - (b) about from 2 to 20 parts by weight of at least one hydroxy-containing fluoropolymer, the fluoropolymer containing about from 0.2 to 20 mole percent of units derived from at least one hydroxy-containing vinyl ether monomer of the formula
$$\text{CF}_2=\text{CF}[\text{OCF}_2\text{CF}(\text{CF}_3)]_n(\text{O})_p(\text{CF}_2)_m\text{CH}_2\text{OH}$$
 wherein p is 0 or 1; m is 0 to 10 and n is 0 to 20; and provided that when m is 0, p is 0; and when m is greater than 0, p is 1; and further provided that at least one of n and m is at least 1.
2. A polymer blend of Claim 1 wherein the fluoropolymer is a plastic and contains at least about 3 mole percent of units derived from the hydroxy-containing vinyl ether.
3. A polymer blend of Claim 2 wherein the fluoropolymer contains about from 5 to 15 mole percent of units derived from the hydroxy-containing vinyl ether.
4. A polymer blend of Claim 1 wherein the fluoropolymer is an elastomer and contains about from 0.2 to 10 mole percent of units derived from the hydroxy-containing vinyl ether, and the fluoropolymer further comprises units derived from tetrafluoroethylene and perfluoroalkyl perfluoro(vinyl ether).
5. A polymer blend of Claim 4 wherein the hydroxy-containing fluoropolymer contains about from 0.5 to 5 mole percent of units derived from the hydroxy-containing vinyl ether.
6. A crosslinkable composition comprising a polymer blend of Claim 1 in about from 1 to 5 parts by weight of at least 1 cure accelerator.

7. A crosslinkable composition of Claim 6 wherein the cure site monomer in the perfluoroelastomer consists essentially of perfluoro-(8-cyano-5-methyl-3,6-dioxa-1-octene).

5 8. A crosslinkable composition of Claim 7 wherein the cure accelerator consists essentially of tetraphenyltin.

9. A crosslinkable composition of Claim 7 wherein the cure accelerator consists essentially of triphenyltin hydride.

10

10. A cured perfluoroelastomer prepared from the crosslinkable composition of Claim 6.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 93/04380

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)⁶

According to International Patent Classification (IPC) or to both National Classification and IPC
 Int.Cl. 5 C08L27/12; //(C08L27/12,27:18)

II. FIELDS SEARCHED

Minimum Documentation Searched⁷

Classification System	Classification Symbols
Int.Cl. 5	C08L ; C08K

Documentation Searched other than Minimum Documentation
 to the Extent that such Documents are Included in the Fields Searched⁸

III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹

Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	US,A,4 982 009 (DU PONT) 1 January 1991 cited in the application see column 4, line 29 - line 48; examples 8,9,11	1-3
A	---	
A	EP,A,0 186 186 (ASAHI GLASS) 2 July 1986 see claims 1,2,4; example 1	1,6
A	---	
A	EP,A,0 225 792 (DU PONT) 16 June 1987	1,6

¹⁰ Special categories of cited documents :

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IV. CERTIFICATION

Date of the Actual Completion of the International Search 26 AUGUST 1993	Date of Mailing of this International Search Report 07.09.93
International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer ENGEL S.L.

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9304380
SA 73872

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on
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26/08/93

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