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(71) Applicant *(for all designated States except US)*: **DUPONT DOW ELASTOMERS L.L.C.** [US/US]; 300 BELLEVUE PARK WAY, Wilmington, DE 19809 (US).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **HUNG, Ming-Hong** [US/US]; 601 Andover Road, Wilmington, DE 19803 (US). **SCHMIEGEL, Walter, Werner** [US/US]; 7 Haslet Way, Wilmington, DE 19807 (US).

(74) Agent: KIRVAN, George, E.; Du Pont Dow Elastomers LLC, Legal Patent Records Center, 4417 Lancaster Pike, Wilmington, DE 19805 (US).

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(54) Title: FLUOROELASTOMER COMPOSITION HAVING EXCELLENT LOW TEMPERATURE PROPERTIES

(57) Abstract: Compositions containing fluoroelastomers, curative and a fluorinated polyether of the general formula $-[CF_2CFH-O-R_fCF_2CH_2O]_n-$, wherein n is such that the weight average molecular weight, M_w, is between 2000 and 100,000 and R_f is selected from the group consisting of a) $-(CF_2)_s-$, wherein s is 1 to 10; and b) $-[CF_2CF(CF_3)O]_t(CF_2)_u-$, wherein u is 1 to 10 and t is 1 to 20, exhibit excellent low temperature properties.

TITLE OF INVENTION

FLUOROELASTOMER COMPOSITION HAVING EXCELLENT LOW TEMPERATURE PROPERTIES

FIELD OF THE INVENTION

This invention relates to fluoroelastomer compositions, and in particular to the enhancement of the low temperature properties of such compositions.

BACKGROUND OF THE INVENTION

Elastomeric fluoropolymers (i.e. fluoroelastomers) exhibit excellent resistance to the effects of heat, weather, oil, solvents and chemicals. Such materials are commercially available and are most commonly copolymers of vinylidene fluoride (VF_2) with hexafluoropropylene (HFP) and, optionally, tetrafluoroethylene (TFE). Other known fluoroelastomers include copolymers of TFE with a perfluoro(alkyl vinyl ether) such as perfluoro(methyl vinyl ether) (PMVE), copolymer of TFE with propylene (P) and, optionally VF_2, and copolymers of ethylene (E) with TFE and PMVE. Often, these fluoroelastomers also contain copolymerized units of a cure site monomer to facilitate vulcanization. While these copolymers have many desirable properties, including low compression set and excellent processability, their low temperature flexibility is not adequate for all end use applications. One particularly desirable improvement would be a reduction in glass transition temperature (T_g) with an accompanying extension of service temperature to lower temperatures. T_g is often used as an indicator of low temperature flexibility because polymers having low glass transition temperatures maintain elastomeric properties at low temperatures.

U.S. Patent No. 4,894,418 discloses vinylidene fluoride based fluoroelastomer compositions which contain processing adjuvants that are perfluorinated polyethers having an hydroxyl group at one or both chain ends. Among the benefits listed for such adjuvants is improved low temperature properties. Being perfluorinated, the polyethers disclosed in the '418 patent are not very compatible with vinylidene fluoride based fluoroelastomers which contain polar hydrogen atoms. Such incompatibility may cause processability problems and lead to the ready extraction of the polyether by solvents.

U.S. Patent No. 5,268,405 discloses compositions of TFE/PMVE copolymers which also contain a perfluoropolyether (e.g. DuPont's Krytox® fluorinated oil) for reducing the T_g of the composition.

At high temperatures, the perfluoropolyethers employed in all the above compositions tend to be fugitive. As the level of perfluoropolyether in the compositions decreases, the physical properties of the compositions revert to those of compositions containing no perfluoropolyether.

It would be an improvement to have a fluoroelastomer composition wherein the fluorinated polyether is less fugitive than the above perfluoropolyethers.

SUMMARY OF THE INVENTION

The present invention is directed to a curable composition comprising

A. a fluoroelastomer copolymer;

B. a fluorinated polyether having a general formula of $—[CF_2CFH\text{-}O\text{-}R_f\text{-}CF_2CH_2O]_n—$, wherein n is such that M_w is between 2000 and 100,000 and R_f is selected from the group consisting of a) $—(CF_2)_s—$, wherein s is 1 to 10 ; and b) $—[CF_2CF(CF_3)O]_t(CF_2)_u—$, wherein u is 1 to 10 and t is 1 to 20; and

C. a curing agent.

DETAILED DESCRIPTION OF THE INVENTION

The fluoroelastomers employed in the compositions of the present invention are capable of undergoing crosslinking reactions with any of the known curatives for fluoroelastomers such as, but not limited to polyhydroxy compounds such as bisphenol AF, diamines such as 1,6-hexamethylenediamine or its dicarbamate, the combination of organic peroxides and polyfunctional coagents, organotin (U.S. Patent No. 5,789,489), bis(aminophenols) such as diaminobisphenol AF (U.S. Patent No. 6,211,319 B1), aromatic tetraamines such as 3,3'-diaminobenzidene, and ammonia generating compounds such as urea and other compounds disclosed in U.S. Patent No. 6,281,296 and WO 01/27194.

The resulting cured elastomeric compositions exhibit good low temperature properties without the loss of other important properties such as tensile strength and compression set resistance. Furthermore, the fluorinated polyethers employed in the compositions of the invention are relatively compatible with the fluoroelastomer and stable to heat. The polyethers do not volatilize out of the crosslinked compositions at typical service temperatures (i.e. 250°- 270°C).

One type of fluoroelastomer which may be employed in the compositions of this invention is based on vinylidene fluoride (VF_2). In addition to copolymerized units of VF_2, this type of fluoroelastomer contains copolymerized units of at least one other fluorine-containing monomer. Examples of such monomers include, but are not limited to hexafluoropropylene (HFP), tetrafluoroethylene (TFE), chlorotrifluoroethylene (CTFE), fluorinated vinyl ethers (FVE) and perfluoro(alkyl vinyl) ethers (PAVE) such as perfluoro(methyl vinyl ether). In addition, the fluoroelastomers may optionally contain copolymerized units of methyl vinyl ether, or an olefin such as ethylene (E) or propylene (P). Peroxide curable fluoroelastomers which contain copolymerized units of vinylidene fluoride, perfluoro(methyl vinyl ether) and tetrafluoroethylene are especially preferred.

Another type of fluoroelastomer which may be employed in this invention is based on tetrafluoroethylene (TFE). In addition to copolymerized units of TFE, this type of fluoroelastomer contains copolymerized units of at least one other monomer such as a PAVE, a FVE, methyl vinyl ether, E, or P.

Fluorinated vinyl ethers (FVE) suitable for use as monomers in the fluoroelastomers employed in this invention include those of the formula

$$CF_2=CFO-(CF_2)_m-(CH_2)_n-[O(CF_2)_x]_y-O-A$$

where m is an integer between 0 and 4; n is an integer between 0 and 2; x is an integer between 1 and 3; y is an integer between 0 and 6; and A is selected from the group consisting of C_1-C_4 perfluoroalkyl groups, C_1-C_6 perfluoroalkoxy groups, and C_1-C_4 alkyl groups containing between 0 and 8 fluorine atoms.

Perfluoro(alkyl vinyl ethers) (PAVE) suitable for use as monomers include those of the formula

$$CF_2=CFO(R_{f'}O)_n(R_{f''}O)_mR_f \quad (I)$$

where $R_{f'}$ and $R_{f''}$ are different linear or branched perfluoroalkylene groups of 2-6 carbon atoms, m and n are independently 0-10, and R_f is a perfluoroalkyl group of 1-6 carbon atoms.

A preferred class of perfluoro(alkyl vinyl ethers) includes compositions of the formula

$$CF_2=CFO(CF_2CFXO)_nR_f \quad (II)$$

where X is F or CF_3, n is 0-5, and R_f is a perfluoroalkyl group of 1-6 carbon atoms.

A most preferred class of perfluoro(alkyl vinyl ethers) includes those ethers wherein n is 0 or 1 and R_f contains 1-3 carbon atoms. Examples of such perfluorinated ethers include perfluoro(methyl vinyl ether) (PMVE) and perfluoro(propyl vinyl ether) (PPVE). Other useful monomers include compounds of the formula

$$CF_2=CFO[(CF_2)_mCF_2CFZO]_nR_f \quad (III)$$

where R_f is a perfluoroalkyl group having 1-6 carbon atoms,

$m = 0$ or 1, $n = 0$-5, and $Z = F$ or CF_3.

Preferred members of this class are those in which R_f is CF_3, $m = 1$, $n= 1$, and $Z = F$; and R_f is C_3F_7, $m = 0$, and $n = 1$.

Additional perfluoro(alkyl vinyl ether) monomers include compounds of the formula

$$CF_2{=}CFO[(CF_2CF\{CF_3\}O)_n(CF_2CF_2CF_2O)_m(CF_2)_p]C_xF_{2x+1} \quad (IV)$$

where m and n independently = 0-10, p = 0-3, and x = 1-5.

Preferred members of this class include compounds where n = 0-1, m = 0-1, and x = 1.

Additional examples of useful perfluoro(alkyl vinyl ethers) include

$$CF_2{=}CFOCF_2CF(CF_3)O(CF_2O)_mC_nF_{2n+1} \quad (V)$$

where n = 1-5, m = 1-3, and where, preferably, n = 1.

The fluoroelastomers employed in the compositions of this invention may also contain a cure site for facilitating crosslinking.

Suitable cure sites for crosslinking by organic peroxide/polyfunctional coagent curing systems include, but are not limited to bromine endgroups, iodine endgroups, or a combination thereof. Such cure sites may be introduced to the fluoroelastomer polymer chain by polymerization in the presence of a bromine- or iodine-containing chain transfer agent (U.S. Patent No. 4,243,770). Cure sites may also be introduced by copolymerization of the fluoroelastomer with cure site monomers that contain a bromine or iodine atom such as fluorinated olefins or fluorinated vinyl ethers. Such cure site monomers are well known in the art (e.g. U.S. Patent Nos. 4,214,060; 5,214,106; and 5,717,036). Specific examples include, but are not limited to bromotrifluoroethylene (BTFE); 4-bromo-3,3,4,4-tetrafluorobutene-1 (BTFB); and 4-iodo-3,3,4,4-tetrafluorobutene-1 (ITFB). Bis-olefins may also be employed as cure site monomers in peroxide curable fluoroelastomers (U.S. Patent No. 5,585,449)

Suitable cure sites for crosslinking by polyhydroxy curing systems include, but are not limited to trifluoroethylene; 3,3,3-trifluoropropene-1; 1,2,3,3,3-pentafluoropropylene; 1,1,3,3,3-pentafluoropropylene; 2,3,3,3-tetrafluoropropene.

Suitable cure sites for crosslinking by organotin, diaminobisphenol AF, 3,3'-diamonobenzidinene, or ammonia generating curatives include, but are not limited to comonomers such as fluorovinyl ethers or fluoroolefins containing pendent nitrile groups. Examples include perfluoro(8-cyano-5-methyl-3,6-dioxa-1-octene) (8-CNVE) and the nitrile-containing cure site monomers disclosed in U.S. Patent No. 6,211,319 B1.

Specific examples of fluoroelastomers suitable for use in the compositions of this invention include, but are not limited to elastomers comprising copolymerized units selected from the group consisting of a) VF_2/HFP, b) VF_2/HFP/TFE, c) VF_2/PMVE, d) VF_2/PMVE/TFE, e) VF_2/TFE/P; f) TFE/P; g) E/TFE/PMVE and h) TFE/PMVE. Preferably, these elastomers further comprise at least one type of cure site described above. Most preferably, the fluoroelastomers employed in the compositions of this invention further comprise both iodine endgroups and copolymerized units of an iodine-containing cure site monomer. An especially preferred fluoroelastomer comprises copolymerized units of vinylidene fluoride, perfluoro(methyl vinyl ether) tetrafluoroethylene and ITFB. The latter elastomer also contains iodine endgroups.

The fluorinated polyethers contained in the compositions of this invention are disclosed in U.S. Patent No. 5,134,211. The polyether consists essentially of the repeat unit

$$—[CF_2CFH\text{-}O\text{-}R_f\text{-}CF_2CH_2O]_n— ,$$

wherein n is such that the weight average molecular weight (M_w) is between 2000 and 100,000 (preferably between 15,000 and 45,000) and R_f is selected from the group consisting of a) $—(CF_2)_s—$, wherein s is 1 to 10; and b) $—[CF_2CF(CF_3)O]_t(CF_2)_u—$, wherein u is 1 to 10 and t is 1 to

20. Preferably, both t and u are 1, or s is 1-3. Most preferably, t and u are 1 so that the fluorinated polyether contains the repeat unit

$$—[CF_2CFH\text{-}O\text{-}CF_2CF(CF_3)OCF_2CF_2CH_2O]_n—.$$

These fluorinated polyethers have $CF_2CFH\text{-}O—$ as one terminal group and $—CH_2OH$ as the other terminal group.

Compositions of this invention contain between 2 and 30 parts by weight fluorinated polyether per 100 parts by weight fluoroelastomer (i.e. 2 to 30 phr – parts per hundred parts rubber). Preferably, compositions contain between 2 and 20 phr fluorinated polyether. As shown in the above structures, the fluorinated polyethers employed in this invention contain polar hydrogen atoms in the repeat units, making this polyether more compatible with vinylidene fluoride based fluoroelastomers than are perfluorinated polyethers.

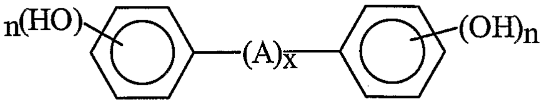
These fluorinated polyethers may be made by the catalytic anionic polymerization of 9,9-dihydro-9-hydroxy-perfluoro(3,6-dioxa-5-methyl-1-nonene) (EVE-OH) as disclosed in U.S. Patent 5,134,211. Suitable catalysts include, but are not limited to cesium carbonate, cesium fluoride, tetraalkylammonium chloride, potassium carbonate, potassium t-butoxide, and tetraphenylphosphonium chloride. EVE-OH is readily prepared (U.S. Patent 4,982,009) by the reduction of methyl perfluoro(5-methyl-4,7-dioxa-8-nonenoate) (EVE) which is commercially available from DuPont. Sodium borohydride is a preferred reducing agent.

The curable compositions of the invention may, optionally, also contain an acid acceptor such as a strongly basic amine (e.g. ProtonSponge®, available from Aldrich), a divalent metal oxide (e.g. magnesium oxide, zinc oxide, calcium oxide, or lead oxide), a divalent metal hydroxide; or a mixture of an oxide and hydroxide. The level of the acid acceptor in the compositions of the invention is generally 1-15 phr, with 2-10 parts being preferred.

The compositions of the present invention also contain a curing agent. One preferred curing agent is an organic peroxide/polyfunctional coagent system. Useful organic peroxides are those which generate free radicals at curing temperatures. A dialkyl peroxide or a bis(dialkyl peroxide) which decomposes at a temperature above 50°C is especially preferred. In many cases it is preferred to use a ditertiarybutyl peroxide having a tertiary carbon atom attached to a peroxy oxygen. Among the most useful peroxides of this type are 2,5-dimethyl-2,5-di(tertiarybutylperoxy)hexyne-3 and 2,5-dimethyl-2,5-di(tertiarybutylperoxy)-hexane. Other peroxides can be selected from such compounds as dicumyl peroxide, dibenzoyl peroxide, tertiarybutyl perbenzoate, and di[1,3-dimethyl-3-(t-butylperoxy)butyl]carbonate. Generally, about 1-3 phr peroxide is used.

The polyfunctional coagent employed with an organic peroxide is a polyunsaturated compound that is capable of cooperating with the peroxide to provide a useful cure. These coagents can be added in an amount equal to 0.1 and 10 phr, preferably between 2-5 phr. The coagent may be one or more of the following compounds: triallyl cyanurate; triallyl isocyanurate; tri(methallyl)isocyanurate; tris(diallylamine)-s-triazine; triallyl phosphite; N,N-diallyl acrylamide; hexaallyl phosphoramide; N,N,N′,N′-tetraalkyl tetraphthalamide; N,N,N′,N′-tetraallyl malonamide; trivinyl isocyanurate; 2,4,6-trivinyl methyltrisiloxane; and tri(5-norbornene-2-methylene)cyanurate. Particularly useful is triallyl isocyanurate (TAIC).

The curable compositions of the invention may also be cured with a polyhydroxy curing agent. Such compositions contain between 0.1 to 20 parts by weight (preferably 1-3 parts) of polyhydroxy crosslinking agent (or a derivative thereof) per 100 parts fluoroelastomer. Typical polyhydroxy cross-linking agents include di-, tri-, and tetrahydroxybenzenes, naphthalenes, and anthracenes, and bisphenols of the formula



where A is a difunctional aliphatic, cycloaliphatic, or aromatic radical of 1-13 carbon atoms, or a thio, oxy, carbonyl, sulfinyl, or sulfonyl radical; A may optionally be substituted with at least one chlorine or fluorine atom; x is 0 or 1; n is 1 or 2; and any aromatic ring of the polyhydroxylic compound may optionally be substituted with at least one chlorine or fluorine atom, an amino group, a -CHO group, or a carboxyl or acyl radical. Preferred polyhydroxy compounds include hexafluoroisopropylidene-bis(4-hydroxy-benzene) (i.e. bisphenol AF or BPAF); 4,4′-isopropylidene diphenol (i.e. bisphenol A); 4,4′-dihydroxydiphenyl sulfone; and diaminobisphenol AF. Referring to the bisphenol formula shown above, when A is alkylene, it can be for example methylene, ethylene, chloroethylene, fluoroethylene, difluoroethylene, propylidene, isopropylidene, tributylidene, heptachlorobutylidene, heptafluorobutylidene, pentylidene, hexylidene, and 1,1-cyclohexylidene. When A is a cycloalkylene radical, it can be for example 1,4-cyclohexylene, 2-chloro-1,4-cyclohexylene, cyclopentylene, or 2-fluoro-1,4-cyclohexylene. Further, A can be an arylene radical such as m-phenylene, p-phenylene, o-phenylene, methylphenylene, dimethylphenylene, 1,4-naphthylene, 3-fluoro-1,4-naphthylene, and 2,6-naphthylene.

Additional polyhydroxy curing agents include alkali metal salts of bisphenol anions, quaternary ammonium salts of bisphenol anions, tertiary sulfonium salts of bisphenol anions and quaternary phosphonium salts of bisphenol anions. For example, the salts of bisphenol A and bisphenol AF. Specific examples include the disodium salt of bisphenol AF, the dipotassium salt of bisphenol AF, the monosodium monopotassium salt of bisphenol AF and the benzyltriphenylphosphonium salt of bisphenol AF.

Quaternary ammonium and phosphonium salts of bisphenol anions are discussed in U.S. Patents 4,957,975 and 5,648,429. Bisphenol AF salts (1:1 molar ratio) with quaternary ammonium ions of the formula $R_1R_2R_3R_4N^+$, wherein R_1-R_4 are C_1-C_8 alkyl groups and at least three of R_1-R_4 are C_3 or C_4 alkyl groups are preferred. Specific examples of these preferred compositions include the 1:1 molar ratio salts of tetrapropyl ammonium-, methyltributylammonium- and tetrabutylammonium bisphenol AF. Such salts may be made by a variety of methods. For instance a methanolic solution of bisphenol AF may be mixed with a methanolic solution of a quaternary ammonium salt, the pH is then raised with sodium methoxide, causing an inorganic sodium salt to precipitate. After filtration, the tetraalkylammonium/BPAF salt may be isolated from solution by evaporation of the methanol. Alternatively, a methanolic solution of tetraalkylammonium hydroxide may be employed in place of the solution of quaternary ammonium salt, thus eliminating the precipitation of an inorganic salt and the need for its removal prior to evaporation of the solution.

Vulcanization accelerators are typically employed in polyhydroxy curable compositions of the invention. Typical accelerators include tertiary sulfonium salts such as $[(C_6H_5)_2S^+(C_6H_{13})][Cl]^-$, and $[(C_6H_{13})_2S(C_6H_5)]^+[CH_3CO_2]^-$ and quaternary ammonium, phosphonium, arsonium, and stibonium salts of the formula $R_5R_6R_7R_8Y^+\ X^-$,where Y is phosphorous, nitrogen, arsenic, or antimony; R_5, R_6, R_7, and R_8 are individually C_1-C_{20} alkyl, aryl, aralkyl, alkenyl, and the chlorine, fluorine, bromine, cyano, -OR, and -COOR substituted analogs thereof, with R being C_1-C_{20} alkyl, aryl, aralkyl, alkenyl, and where X is halide, hydroxide, sulfate, sulfite, carbonate, pentachlorothiophenolate, tetrafluoroborate, hexafluorosilicate, hexafluorophosphate, dimethyl phosphate, and C_1-C_{20} alkyl, aryl, aralkyl, and alkenyl carboxylates and dicarboxylates. Particularly preferred are benzyltri-phenylphosphonium chloride, benzyltriphenylphosphonium bromide, tetrabutylammonium hydrogen sulfate, tetrabutylammonium hydroxide, tetrapropylammonium hydroxide, tetrabutylammonium bromide, tributylallylphosphonium chloride, tributyl-2-methoxypropylphosphonium chloride, 1,8-diazabicyclo[5.4.0]undec-7-ene, and benzyldiphenyl(dimethylamino) phosphonium chloride. Other useful accelerators include methyltrioctylammonium chloride, methyltributylammonium chloride, tetrapropylammonium chloride, benzyltrioctylphosphonium bromide, benzyltrioctylphosphonium chloride, methyltrioctylphosphonium acetate, tetraoctylphosphonium bromide, methyltriphenylarsonium tetrafluoroborate, tetraphenylstibonium bromide, 4-chlorobenzyltriphenyl phosphonium chloride, 8-benzyl-1,8-diazabicyclo(5.4.0)-7-undecenonium chloride, diphenylmethyltriphenylphosphonium chloride, allyltriphenyl-phosphonium chloride, tetrabutylphosphonium bromide, m-trifluoromethyl-benzyltrioctylphosphonium chloride, and other quaternary compounds disclosed in U.S. Patent Nos. 5,591,804; 4,912,171; 4,882,390; 4,259,463; 4,250,278 and 3,876,654. The amount of accelerator used is between 0.1 and 20 parts by weight per hundred parts by weight fluoroelastomer. Preferably, 0.5-3.0 phr is used.

Other curatives which may be employed in the compositions of the invention include diamines, carbamates thereof, bis(aminophenols) such as diaminobisphenol, tetraamines, organotin and compounds which decompose to produce ammonia at curing temperatures. When present in the compositions of this invention, typically, 0.1 to 7 phr of any one of the latter curatives is employed.

Other additives may be compounded into the fluoroelastomer to optimize various physical properties. Such additives include carbon black, stabilizers, plasticizers, lubricants, pigments, fillers (e.g. mineral fillers such as silicas, alumina, barium sulfate, titanium dioxide), and processing aids typically utilized in perfluoroelastomer compounding. Any of these additives can be incorporated into the compositions of the present invention, provided the additive has adequate stability for the intended service conditions.

Carbon black is used in elastomers as a means to balance modulus, tensile strength, elongation, hardness, abrasion resistance, conductivity, and processability of the compositions. Carbon black is generally useful in amounts of from 5-60 phr.

In addition, or in the alternative, fluoropolymer fillers may be present in the composition. Generally from 1 to 50 phr of a fluoropolymer filler is used, and preferably at least about 5 phr is present. The fluoropolymer filler can be any finely divided, easily dispersed plastic fluoropolymer that is solid at the highest temperature utilized in fabrication and curing of the perfluoroelastomer composition. By solid, it is meant that the fluoroplastic, if partially crystalline, will have a crystalline melting temperature above the processing temperature(s) of the perfluoroelastomer(s). Such finely divided, easily dispersed fluoroplastics are commonly called micropowders or fluoroadditives. Micropowders are ordinarily partially crystalline polymers.

The fluorinated polyether, crosslinking agent, and optional other additives are generally incorporated into the polymer by means of an internal mixer or on a rubber mill. The resultant composition is then cured, generally by means of heat and pressure, for example by compression transfer or injection molding.

The curable compositions of the present invention are useful in production of gaskets, tubing, seals and other molded components. Such articles are generally produced by molding a compounded formulation of the curable composition with various additives under pressure, curing the part, and then subjecting it to a post cure cycle. The cured compositions have excellent low temperature flexibility and processability as well as excellent thermal stability and chemical resistance. They are particularly useful in applications such as seals and gaskets requiring a good combination of oil resistance, fuel resistance and low temperature flexibility, for example in fuel injection systems, fuel line connector systems and in other seals for high and low temperature automotive uses.

The invention is now illustrated by certain embodiments wherein all parts and percentages are by weight unless otherwise specified.

EXAMPLES

TEST METHODS

Cure Characteristics

Unless otherwise noted, cure characteristics were measured using an Alpha Systems model MDR 2000E moving die rheometer (MDR), under the following conditions (ISO 6502):

Moving die frequency: 1.66 Hertz
Oscillation amplitude: ±0.5°
Temperature: 180°C
Sample size: 6 to 10 g
Duration: 12 minutes

The following cure parameters were recorded:

M_H: maximum torque level, in units of dN·m
M_L: minimum torque level, in units of dN·m
Delta M: difference between maximum and minimum torque, in units of dN·m
t_s2: minutes to a 2.26 dNm rise above M_L
tc50: minutes to 50% of maximum torque
tc90: minutes to 90% of maximum torque

Tensile Properties

The following physical property parameters were recorded; test methods are in parentheses:

M_{100}: modulus at 100% elongation in units of MPa (ISO 37 T2)
T_B: tensile strength in units of MPa (ISO 3 T2)
T_S: tear strength in units of kN/m (ISO 34, Die B)

E_B: elongation at break in units of % (ISO 37 T2)

TR-10: temperature of retraction (ISO 2921)

According to the TR test method, a standard test piece of length 50 mm is stretched at room temperature and then cooled in a bath (usually filled with isopropanol) to a temperature of about 10°C less than the T_g of the polymer. The test piece is then allowed to retract freely while the test temperature is raised at a rate of 1°C per minute. Readings of the retracted length are taken every 2 minutes until the retraction reaches 75%. TR-10 is the temperature at which a retraction of 10% is achieved.

Hardness (Shore A, ISO 868)

Compression set of small pip samples (ISO 815)

Glass Transition temperature (T_g) was measured by Modulated Differential Scanning Calorimetry (MDSC) at 10°/minute heating rate in nitrogen.

<u>The following polymers were used in the Examples:</u>

The fluorinated polyether (FPE-1) employed in the examples was prepared by a 2-step process wherein methyl perfluoro(5-methyl-4,7-dioxa-8-nonenoate) (EVE), commercially available from DuPont, was first converted to 9,9-dihydro-9-hydroxy-perfluoro-(3,6-dioxa-5-methyl-1-nonene) (EVE-OH) and then the EVE-OH was homopolymerized.

(1). Preparation of EVE-OH [$CF_2=CFO-CF_2CF(CF_3)O-CF_2CF_2-CH_2OH$]:

To a dry flask was charged EVE® (211 g, 0.50 mole) in absolute ethanol (300 ml). Sodium borohydride(11.34 g, 0.30 mole) was added slowly. The reaction was somewhat exothermic and the reaction flask was kept at about 10°C by external cooling. After the addition of sodium borohydride was completed, the reaction mixture was stirred for 1 hour at ambient temperature. The reaction mixture was then dumped into an ice water/6N HCl (600mL/600 ml) mixture. The bottom (product) layer was separated, washed with water and distilled to give EVE-OH as a clear, colorless liquid. Boiling point: 68°C/25 mm Hg. Yield: 168.7 g (85.6 %). ^{1}H NMR ($CDCl3$): δ4.00 (dt, J = 1.0 Hz, 13.5 Hz, 2H), 2.12 (s, br, 1H); ^{19}F NMR ($CDCl_3$, F-11 internal standard): -80.4 s, br, 3F), -84.2 (s, br, 2F), -85.3 (m, br, 2F), -126.6 (t, J =14 Hz, 2F), -145.7 (t, J =21.8 Hz, 1F), -113.4, -113.7, -113.8, -114.2 (4s, 1F), -121.6, -112.1, -122.2, -122.7 (4t, J = 5.2 Hz, 1F), -135.3, -135.6, -135.9, -136.2 (4t, J =5.8 Hz, 1F).

(2). Homopolymerization of EVE-OH:

EVE-OH (50 g, 0.127 mole) and cesium carbonate (0.5 g) were charged into a 400 ml shaker tube. The tube was sealed and cool-evacuated. It was then was heated at 125-130°C for 16 hours. After cooling, the highly viscous oily product was collected. Yield: 40 g (80%). ^{1}H NMR (acetone-d_6): δ6.60 (d, J = 52 Hz, 1H, CHF), 4.62 (t, J = 13 Hz, 2H, internal CF_2CH_2O); ^{19}F NMR (acetone-d_6); -79.6 (m, 3F), -83.1 to –84.7 (m, 4F), -90.3 (m, 2F), -125.3 (m, 2F, internal CF_2CH_2O), -145.2 (m, 1F), -145.4 (m, 1F). The spectral properties matched the homopolymer structure $—[CF_2CFHO\text{-}CF_2CF(CF_3)O\text{-}CF_2CF_2\text{-}CH_2O]_n—$ (FPE-1). The weight average molecular weight (M_w) of the polyether was determined by gel permeation chromatography (in THF solvent) to be 20,200, with a dispersion factor of 3.70. Thermal gravimetric analysis (TGA) (20°C/min) of a similarly prepared sample showed onset of thermal decomposition at ca. 300°C (air) and 400 °C (N_2). DSC exhibited a T_g at –65.7 °C.

The fluoroelastomers employed in the Examples were

FE-1: an iodine-containing copolymer of vinylidene fluoride, perfluoro(methyl vinyl ether), and tetrafluoroethylene, commercially available from DuPont Dow Elastomers as Viton® GBLT-S.

FE-2: a copolymer of ethylene, tetrafluoroethylene and perfluoro(methyl vinyl ether) having iodine and bromine cure sites, commercially available from DuPont Dow Elastomers as Viton® ETP-S.

FE-3: a copolymer of vinylidene fluoride and hexafluoropropylene also containing bisphenol AF curative, commercially available from DuPont Dow Elastomers as Viton® A201C.

FE-4: a copolymer of vinylidene fluoride, hexafluoropropylene and tetrafluoroethylene also containing bisphenol AF curative, commercially available from DuPont Dow Elastomers as Viton® B601C.

Examples 1-5 and Comparative Examples A and B

Compositions of the invention (Examples 1-5) and control compositions (Comparative Examples A and B), not containing a fluorinated polyether, were made by compounding the ingredients in a conventional manner on a 2-roll mill. The ingredients and proportions are shown in Table I.

Table I

Formulation, phr	Comp. Ex. A	Ex. 1	Ex. 2	Ex. 3	Ex .4	Ex. 5	Comp. Ex. B
Fluorinated Polyether FPE-1	0	5	10	20	15	20	0
Carbon Black[1]	30	30	30	30	50	50	50
Fluoroelastomer FE-1	100	100	100	100	100	100	100
Zinc Oxide[2]	3	3	3	3	3	3	3
TAIC[3]	3	3	3	3	3	3	3
Luperox 101 XL 45[4]	1.5	1.5	1.5	1.5	1.5	1.5	1.5

[1] MT Thermax N 990 (available from Lehmann & Voss Co.)

[2] Extrox 100 (available from Elementis Specialties UK Ltd.)

[3] triallyl isocyanurate (available from DuPont Dow Elastomers as Diak 7)

[4] organic peroxide (available from Atofina)

Cure characteristics of the above compositions and physical properties of cured test specimens (180°C press cure for 10 minutes, followed by post cure in an air oven at 230°C for 2 hours) were measured according to the Test Methods. Results are shown in Table II.

Table II

Example	Comp. A	1	2	3	4	5	Comp. B
Curing Characteristics							
ML (dNm)	1.44	1.22	1.09	0.77	1.26	1.11	2
MH (dNm)	29.74	25.01	21.72	17.06	24.04	21.42	39.82
Delta M (dNm)	28.3	23.79	20.63	16.29	22.78	20.31	37.82
Ts2 (min.)	0.47	0.48	0.5	0.51	0.43	0.43	0.39
Tc 50 (min.)	0.76	0.75	0.76	0.74	0.69	0.68	0.73
Tc90 (min.)	1.32	1.3	1.28	1.23	1.32	1.24	1.43
Peak rate (dNm/min)	49	44	36	30	42	38	61
Physical Properties							
T_B (MPa)	16.7	12.9	13.5	12.8	12.7	11.3	17.7
E_B (%)	224	213	292	313	211	214	192
M_{100} (MPa)	4.4	3.5	2.6	2.1	4.4	3.4	7.8
Hardness Shore A (pts)	68.9	65.5	61.5	55.2	67.1	63.7	77.3
T_S (kN/m)	16	16.6	17.3	15	16	15.3	21.8
Comp Set (%) (70 hrs @ 200°C)	22	23	24	25	21	21	19
TR-10 (°C)	-27	-28	-28	-30	-28	-29	-27
T_g start (°C)	-22.4	-24.2	-24.7	-27.2	-26.9	-26.4	-23.3
T_g inflection (°C)	-24.8	-26.1	-27.6	-30.5	-33.1	-28.7	-25
T_g end (°C)	-27.8	-30.9	-31.8	-34.2	-34.6	-33.9	-28.4

The effect of heat aging (168 hours @250°C) on physical properties of the above samples was measured. Results are contained in Table III. The Δ values reported refer to the percent (tensile strength, elongation and modulus) or absolute (hardness) difference between the original values reported in Table II and the values measured after heat aging.

Table III

Example	Comp. A	1	2	3	4	5	Comp. B
ΔT_B (%)	-21.0	-15.5	-31.9	-46.1	-43.3	-44.2	-31.6
ΔE_B (%)	80.4	108.9	62.0	90.1	87.2	84.6	54.2
ΔM_{100} (%)	-40.9	-42.9	-30.8	-42.9	-50.0	-47.1	-48.7
ΔHardness (pts)	-1.2	-0.6	-1.2	-2.3	1.2	0.6	0.6
Weight Change (%)	-3.7	-4	-4.4	-5.3	-4.8	-5.6	-3.7
T_g start(°C)	-23.6	-24.3	-26.2	-28.2	-27	-27.7	-23.3
T_g inflection (°C)	-24.7	-26	-29	-31.4	-29.9	-30.5	-24.8
T_g end (°C)	-28.2	-30.9	-33.5	-34.9	-34.8	-35.5	-29.9

Some of the original (i.e. not heat aged) examples were soaked in M-15 fuel for 168 hours at 23°C. The effect of the fuel on physical properties vs. the original properties reported in Table II is shown in Table IV.

Table IV

Example	**4**	**5**	**Comp. B**
ΔT_B (%)	-26	-25	-29
ΔE_B (%)	-19	-18	-19
ΔM_{100} (%)	-14	-6	-15
ΔHardness (pts)	-9.2	-8.2	-9.0
Weight Change (%)	6.6	6.6	6.5
Volume Change (%)	17.7	18.3	15.6

Example 6

A composition of the invention (Example 6) and control composition (Comparative Example C), not containing a fluorinated polyether, were made by compounding the ingredients in a conventional manner on a 2-roll mill. The ingredients and proportions are shown in Table V.

Table V

Formulation, phr	Example 6	Comp. Ex. C
Fluorinated Polyether FPE-1	20	0
MT Carbon Black[1]	15	15
Furnace Carbon Black[2]	30	30
Fluoroelastomer FE-2	100	100
Zinc Oxide[3]	3	3
TAIC[4]	3	3
Luperox 101 XL 45[5]	3	3

[1] MT Thermax N 990 (available from Lehmann & Voss Co.)

[2] Regal SRF N772 (available from Cabot GmbH, Germany)

[3] Extrox 100 (available from Elementis Specialties UK Ltd.)

[4] triallyl isocyanurate (available from DuPont Dow Elastomers as Diak 7)

[5] organic peroxide (available from Atofina)

Cure characteristics of the above compositions and physical properties of cured test specimens (180°C press cure for 5 minutes, followed by post cure in an air oven at 230°C for 16 hours) were measured according to the Test Methods. Results are shown in Table VI.

Table VI

Example	Example 6	Comp. Ex. C
Curing Characteristics		
ML (dNm)	1.42	2.46
MH (dNm)	20.08	33.05
Delta M (dNm)	18.66	31.05
Ts2 (min.)	0.5	0.5
Tc 50 (min.)	0.85	1.0
Tc90 (min.)	1.94	2.7
Peak rate (dNm/min)	24	39
Physical Properties		
T_B (MPa)	14.4	20.7
E_B (%)	254	124
M_{100} (MPa)	5.4	15.2
Hardness Shore A (pts)	78	87
T_S (kN/m)	22.3	23.7
Comp Set (%) (70 hrs @ 200°C)	57	55
TR-10 (°C)	-13	-9

Examples 7 and 8

Compositions of the invention (Examples 7 and 8) and control compositions (Comparative Example D and E), not containing a fluorinated polyether, were made by compounding the ingredients in a conventional manner on a 2-roll mill. The ingredients and proportions are shown in Table VII.

Table VII

Formulation, phr	Ex. 7	Comp. Ex. D	Ex. 8	Comp. Ex. E
Fluorinated Polyether FPE-1	20	0	20	0
Fluoroelastomer FE-3	100	100	0	0
Fluoroelastomer FE-4	0	0	100	100
MT Carbon Black[1]	45	45	45	45
Furnace Carbon Black[2]	10	10	10	10
Magnesium Oxide[3]	3	3	3	3
Calcium Hydroxide[4]	1.6	1.6	1.6	1.6

[1] Thermax Floform N990 (available from Lehmann & Voss Co.)

[2] Regal SRF N772 (available from Cabot GmbH, Germany)

[3] Elastomag 170 99% (available from Morton Performance Chemicals, Inc.)

[4] Rhenofit CF (available from Rhein Chemie Rheinau GmbH, Germany)

Cure characteristics of the above compositions and physical properties of cured test specimens (180°C press cure for 10 minutes, followed by post cure in an air oven at 230°C for 24 hours) were measured according to the Test Methods. Results are shown in Table VIII.

Table VIII

Example	Example 7	Comp. Ex. D	Example 8	Comp. Ex. E
Curing Characteristics				
ML (dNm)	0.94	1.01	2.02	3.12
MH (dNm)	34.52	41.28	27.73	43.89
Delta M (dNm)	33.58	40.27	25.71	40.77
Ts2 (min.)	1.17	1.05	1.47	1.15
Tc 50 (min.)	1.63	1.4	2.49	2.38
Tc90 (min.)	3.07	2.73	3.52	3.6
Peak rate (dNm/min)	61	110	25	54
Physical Properties				
T_B (MPa)	10.5	15.8	10.3	16.7
E_B (%)	157	135	182	169
M_{100} (MPa)	7.34	12.35	6.36	10.69
Hardness Shore A (pts)	89	94	89	93
Comp Set (%) (70 hrs @ 200°C)	50	46	56	44
TR-10 (°C)	-18	-17	-18	-14

WHAT IS CLAIMED IS:

1. A curable composition comprising

A) a fluoroelastomer copolymer;

B) a fluorinated polyether having a general formula of $—[CF_2CFH\text{-}O\text{-}R_f\text{-}CF_2CH_2O]_n—$, wherein n is such that M_w is between 2000 and 100,000 and R_f is selected from the group consisting of a) $—(CF_2)_s—$, wherein s is 1 to 10; and b) $—[CF_2CF(CF_3)O]_t(CF_2)_u—$, wherein u is 1 to 10 and t is 1 to 20; and

C) a curing agent.

2. A curable composition of Claim 1 wherein said fluorinated polyether has a M_w between 15,000 and 45,000.

3. A curable composition of Claim 2 wherein said fluorinated polyether has an R_f group having said formula $—(CF_2)_s—$ and wherein s is 1-3.

4. A curable composition of Claim 2 wherein said fluorinated polyether has an R_f group having said formula $—[CF_2CF(CF_3)O]_t(CF_2)_u—$ and wherein both t and u are 1.

5. A curable composition of Claim 1 wherein said fluoroelastomer comprises copolymerized units selected from the group consisting of a) vinylidene fluoride and hexafluoropropylene; b) vinylidene fluoride, hexafluoropropylene and tetrafluoroethylene; c) vinylidene fluoride and perfluoro(methyl vinyl ether); d) vinylidene fluoride, perfluoro(methyl vinyl ether) and tetrafluoroethylene; e) vinylidene fluoride, tetrafluoroethylene and propylene; f) tetrafluoroethylene and propylene; g) ethylene, tetrafluoroethylene and perfluoro(methyl vinyl ether); and h) tetrafluoroethylene and perfluoro(methyl vinyl ether).

6. A curable composition of Claim 5 wherein said fluoroelastomer further comprises cure sites selected from the group consisting of iodine endgroups; bromine endgroups; copolymerized iodine-containing cure site monomers; bromine-containing cure site monomers;

bis-olefin cure site monomers; nitrile group-containing cure site monomers; trifluoroethylene; 3,3,3-trifluoropropene-1; 1,2,3,3,3-pentafluoropropylene; 1,1,3,3,3-pentafluoropropylene; 2,3,3,3-tetrafluoropropene; and combinations thereof.

7. A curable composition of Claim 1 wherein said curing agent is selected from the group consisting of organic peroxides, polyhydroxy compounds, bis(aminophenols), tetraamines, organotin compounds and ammonia generating compounds.

8. A curable composition of Claim 1 further comprising an acid acceptor selected from the group consisting of metal oxides, metal hydroxides and a combination thereof.

INTERNATIONAL SEARCH REPORT

International Application No
[illegible]T/US2004/016411

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08L27/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08L C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 894 418 A (STREPPAROLA EZIO ET AL) 16 January 1990 (1990-01-16) cited in the application the whole document	1-8
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A	EP 0 842 980 A (DYNEON LLC) 20 May 1998 (1998-05-20) the whole document	1-8
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

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Date of the actual completion of the international search	Date of mailing of the international search report
3 September 2004	14/09/2004

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Baekelmans, D

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Information on patent family members

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