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(54) **Title:** SILANE-CROSSLINKABLE FLUOROPOLYMERS

(57) **Abstract:** The present invention pertains to a process for the manufacture of a silane-crosslinkable fluoropolymer [polymer (FS)], said process comprising processing in molten phase a composition [composition (F)] comprising: (A) at least one fluoropolymer [polymer (F)] comprising recurring units derived from: (a) chlorotrifluoroethylene (CTFE) and (b) at least one hydrogenated monomer selected from the group consisting of C₂-C₈ alkenes, (B) at least one vinyl silane compound of formula (I): CH₂=CH-SiR₁R₂R₃ (I) wherein R₁ is a hydrolysable group and R₂ and R₃, equal to or different from each other, are independently C₁-C₄ alkyl groups or hydrolysable groups R₁ and (C) at least one organic initiator. The present invention also pertains to use of said silane-crosslinkable fluoropolymer in a process for the manufacture of a silane-crosslinked fluoropolymer and to extruded articles comprising said silane-crosslinkable fluoropolymer and/or said silane-crosslinked fluoropolymer.



Description**Silane-crosslinkable fluoropolymers**

[0001] This application claims priority to European application No. EP 14179531.0 filed on August 1st, 2014, the whole content of this application being incorporated herein by reference for all purposes.

Technical Field

[0002] The present invention pertains to a silane-crosslinkable fluoropolymer, to use of said silane-crosslinkable fluoropolymer in a process for the manufacture of a silane-crosslinked fluoropolymer and to extruded articles comprising said silane-crosslinkable fluoropolymer and/or said silane-crosslinked fluoropolymer.

Background Art

[0003] Crosslinkable polyolefin resins, in particular crosslinkable polyethylene resins, are commonly manufactured by copolymerization or grafting of a polyolefin resin such as a polyethylene resin in the presence of a vinyl alkoxy silane compound.

[0004] Crosslinkable polyolefin resins are advantageously used in the manufacture of electrical insulating articles because of their excellent electrical properties such as low dielectric constant and high dielectric strength.

[0005] Crosslinking is typically accomplished by exposing to moisture, under suitable conditions, the articles so obtained until the desired degree of crosslinking is reached.

[0006] However, crosslinked polyolefin resins still suffer from low thermo-mechanical resistance properties which make them unsuitable for use in cable jacketing applications.

[0007] There is thus still the need in the art for curable polymer compositions exhibiting enhanced mechanical properties at high temperatures.

Summary of invention

[0008] It has been now surprisingly found that by using specific fluoropolymers it is possible to manufacture silane-crosslinked fluoropolymers advantageously exhibiting enhanced mechanical properties at high temperatures as compared with uncrosslinked fluoropolymers.

- [0009] In a first instance, the present invention pertains to a process for the manufacture of a silane-crosslinkable fluoropolymer [polymer (FS)], said process comprising processing in molten phase a composition [composition (F)] comprising:
- (A) at least one fluoropolymer [polymer (F)] comprising recurring units derived from:
 - (a) chlorotrifluoroethylene (CTFE) and
 - (b) at least one hydrogenated monomer selected from the group consisting of C₂-C₈ alkenes,
 - (B) at least one vinyl silane compound of formula (I):
$$\text{CH}_2=\text{CH}-\text{SiR}_1\text{R}_2\text{R}_3 \text{ (I)}$$
wherein R₁ is a hydrolysable group and R₂ and R₃, equal to or different from each other, are independently C₁-C₄ alkyl groups or hydrolysable groups R₁ and
 - (C) at least one organic initiator.
- [0010] For the purpose of the present invention, the term “hydrolysable group” is intended to denote a group which is able to undergo hydrolysis in the presence of water.
- [0011] For the purpose of the present invention, the term “organic initiator” is intended to denote any organic compound which can generate free radicals in the polymer (F) under the operating conditions.
- [0012] Non-limiting examples of organic initiators suitable for use in the process of the invention are selected from the group consisting of organic peroxides, peresters and diazo compounds. Organic peroxides are preferred. Good results have been obtained with alkylperoxides such as 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane, 3,3,5,7,7-pentamethyl-1,2,4-trioxepane and dicumyl peroxide.
- [0013] The composition (F) typically comprises:
- (A) at least one polymer (F),
 - (B) from 1.0% to 2.5% by weight, preferably from 1.5% to 2.4% by weight, based on the weight of the polymer (F), of at least one vinyl silane compound of formula (I) and
 - (C) from 0.04% to 0.15% by weight, preferably from 0.05% to 0.12% by

weight, based on the weight of the polymer (F), of at least one organic initiator.

- [0014] The composition (F) typically comprises from 20% to 99.99% by weight, preferably from 40% to 99% by weight of at least one polymer (F), based on the total weight of said polymer (F) and the vinyl silane compound of formula (I).
- [0015] The composition (F) of the process of the invention is advantageously free from at least one crosslinking catalyst.
- [0016] The process of the invention is carried out in molten phase at a temperature typically comprised between 70°C and 300°C, preferably between 120°C and 280°C, more preferably between 120°C and 220°C.
- [0017] The skilled in the art will typically select the temperature of the process of the invention as a function of the melting point of the polymer (F).
- [0018] The composition (F) is typically processed in molten phase by melt blending, usually at a temperature comprised between 70°C and 300°C, preferably between 120°C and 280°C, more preferably between 120°C and 220°C. The mixing time usually varies from 2 seconds to 20 minutes. The melt blending may be carried out in any device known for this purpose such as internal or external mixers. The mixing is preferably carried out in a continuous mixer, more particularly in an extruder.
- [0019] The composition (F) may be also processed in molten phase by melt extrusion, preferably using a single screw extruder or a twin screw extruder, usually at a temperature comprised between 120°C and 280°C, preferably between 120°C and 220°C.
- [0020] The process for the manufacture of a polymer (FS) typically comprises:
(i) processing in molten phase by melt extrusion the composition (F) thereby providing an extruded article comprising at least one polymer (FS) and
(ii) pelletizing the extruded article provided in step (i) thereby providing a polymer (FS) in the form of pellets.
- [0021] Under step (i) of the process of the invention, the composition (F) is typically processed in molten phase by melt extrusion thereby providing rods comprising at least one polymer (FS).

- [0022] The pellets provided in step (ii) of the process of the invention may be optionally micronized thereby providing a polymer (FS) in the form of powder particles.
- [0023] In a second instance, the present invention pertains to a silane-crosslinkable fluoropolymer [polymer (FS)] obtainable by the process of the invention.
- [0024] The silane-crosslinkable fluoropolymer [polymer (FS)] of the invention typically comprises, preferably consists of:
- (a') at least one main chain comprising recurring units derived from chlorotrifluoroethylene (CTFE) and from at least one hydrogenated monomer selected from the group consisting of C₂-C₈ alkenes and
 - (b') at least one pendant group of formula (I-A):
-CH₂-CH₂-SiR₁R₂R₃ (I-A)
wherein R₁ is a hydrolysable group and R₂ and R₃, equal to or different from each other, are independently C₁-C₄ alkyl groups or hydrolysable groups R₁.
- [0025] The polymer (FS) is typically in the form of pellets.
- [0026] In a third instance, the present invention pertains to a process for the manufacture of a silane-crosslinked fluoropolymer [polymer (FS-c)], said process comprising:
- (i') processing in molten phase by melt extrusion a composition [composition (FS)] comprising:
 - (A') at least one polymer (FS) and
 - (B') optionally, at least one crosslinking catalystthereby providing an extruded article comprising at least one polymer (FS) and
 - (ii') contacting the extruded article provided in step (i') with water or atmosphere having a water vapour content of more than 0.001% v/v.
- [0027] The Applicant thinks, without this limiting the scope of the invention, that the polymer (FS) of the composition (FS) is crosslinked by a condensation reaction and hydrolysed in the presence of water thereby providing the polymer (FS-c).
- [0028] For the purpose of the present invention, the term "crosslinking catalyst" is

intended to denote any catalyst which makes it possible to accelerate the crosslinking of the polymer (FS) when it undergoes hydrolysis and/or condensation reaction.

- [0029] The crosslinking catalyst is usually selected from the group consisting of metal carboxylates, organometallic compounds, organic or inorganic bases and organic or inorganic acids.
- [0030] The crosslinking catalyst is preferably selected from the group consisting of metal carboxylates and more particularly from lead, cobalt, iron, nickel, zinc and tin carboxylates. Organic and inorganic tin carboxylates are particularly preferred. Good results have been obtained with dialkyltin carboxylates and more particularly with dioctyltin dilaurate.
- [0031] The composition (FS) typically comprises from 0.05% to 0.47% by moles, preferably from 0.08% to 0.2% by moles of at least one crosslinking catalyst, based on the total moles of the pendant groups of formula (I-A) in the polymer (FS).
- [0032] The crosslinking catalyst is advantageously added to the composition (FS) in the form of a masterbatch. This masterbatch usually contains from 0.1% to 10% by weight of at least one crosslinking catalyst, based on the weight of the polymer (FS). The masterbatch typically further comprises at least one polymer, said polymer usually acting as a carrier for said crosslinking catalyst. The choice of the polymer in the masterbatch is not particularly limited provided that it is compatible with the polymer (FS).
- [0033] The crosslinking catalyst or the crosslinking catalyst masterbatch can be added to the composition (FS) during processing of said composition (FS) in molten phase by melt extrusion under step (i') of the process of the invention.
- [0034] The Applicant thinks, without this limiting the scope of the invention, that the crosslinking catalyst may also be generated in situ, under specific operating conditions, in the process for the manufacture of a polymer (FS-c).
- [0035] The composition (FS) may further comprise at least one crosslinking promoter.
- [0036] For the purpose of the present invention, the term "crosslinking promoter"

is intended to denote any compound which makes it possible to accelerate the process for the manufacture of the polymer (FS).

- [0037] The crosslinking promoter is typically selected from the group consisting of polyolefines, preferably from the group consisting of polyethylenes such as ethylene homopolymers or copolymers of ethylene with another hydrogenated monomer selected from the group consisting of C₄-C₈ alkenes, preferably from the group consisting of C₄-C₆ alkenes.
- [0038] The composition (FS) typically comprises from 70% to 99.9% by weight, preferably from 80% to 99.9% by weight, based on the total weight of the composition (FS), of at least one polymer (FS).
- [0039] The composition (FS) preferably comprises:
(A') from 70% to 99.9% by weight, preferably from 80% to 99.9% by weight, of at least one polymer (FS) and
(B') from 0.1% to 30% by weight, preferably from 0.1% to 20% by weight, of at least one crosslinking catalyst.
- [0040] Under step (i') of the process of the invention, the composition (FS) typically comprises at least one polymer (FS) in the form of pellets.
- [0041] Under step (i') of the process of the invention, the composition (FS) is processed in molten phase by melt extrusion, preferably using a single screw extruder or a twin screw extruder, usually at a temperature comprised between 100°C and 300°C, preferably between 120°C and 280°C, more preferably between 120°C and 220°C.
- [0042] The skilled in the art will typically select the temperature of the process of the invention under step (i') as a function of the melting point of the polymer (FS).
- [0043] According to a first embodiment of the invention, under step (i') of the process of the invention, the extruded article is a cable comprising at least one layer comprising at least one polymer (FS).
- [0044] According to a second embodiment of the invention, under step (i') of the process of the invention, the extruded article is a tube comprising at least one layer comprising at least one polymer (FS).
- [0045] According to a third embodiment of the invention, under step (i') of the process of the invention, the extruded article is a film comprising at least

one layer comprising at least one polymer (FS).

- [0046] For the purpose of the present invention, the term “cable” is used according to its usual meaning and is intended to denote either an electrical cable or a communication cable.
- [0047] Under step (ii') of the process of the invention, the extruded article provided in step (i') is typically contacted with water or atmosphere having a water vapour content of more than 0.001% v/v at a temperature comprised between 20°C and 95°C, preferably between 70°C and 95°C.
- [0048] Under step (ii') of the process of the invention, the extruded article provided in step (i') is typically contacted with water or atmosphere having a water vapour content of more than 0.001% v/v during a period of from 30 minutes to 24 hours.
- [0049] In a fourth instance, the present invention pertains to a silane-crosslinked fluoropolymer [polymer (FS-c)] obtainable by the process of the invention.
- [0050] The polymer (FS-c) typically comprises, preferably consists of:
- (a'') organic domains consisting of chains obtainable by the main chain of the polymer (FS) and
 - (b'') inorganic domains consisting of residues obtainable by hydrolysis and/or condensation of the pendant groups of formula (I-A):
$$-\text{CH}_2-\text{CH}_2-\text{SiR}_1\text{R}_2\text{R}_3 \text{ (I-A)}$$
wherein R_1 is a hydrolysable group and R_2 and R_3 , equal to or different from each other, are independently C_1 - C_4 alkyl groups or hydrolysable groups R_1 .
- [0051] In a fifth instance, the present invention pertains to a cable comprising at least one layer comprising at least polymer (FS) and/or at least one polymer (FS-c).
- [0052] Should the cable be an electrical cable, the electrical cable typically comprises a core made of an electrical conductor coated with at least one layer comprising at least one polymer (FS) and/or at least one polymer (FS-c).
- [0053] Should the cable be a communication cable, the communication cable typically comprises a core made of one or more optical fibers coated with at least one layer comprising at least one polymer (FS) and/or at least one

polymer (FS-c).

[0054] In a sixth instance, the present invention pertains to a tube comprising at least one layer comprising at least one polymer (FS) and/or at least one polymer (FS-c).

[0055] In a seventh instance, the present invention pertains to a film comprising at least one layer comprising at least one polymer (FS) and/or at least one polymer (FS-c).

[0056] Polymers (F) wherein the fluorinated monomer is chlorotrifluoroethylene (CTFE) and the hydrogenated monomer is ethylene (E) will be identified herein below as ECTFE copolymers.

[0057] By the term “fluorinated monomer”, it is hereby intended to denote an ethylenically unsaturated monomer comprising at least one fluorine atom.

[0058] The term “at least one fluorinated monomer” is understood to mean that the polymer (F) may comprise recurring units derived from one or more than one fluorinated monomers. In the rest of the text, the expression “fluorinated monomers” is understood, for the purposes of the present invention, both in the plural and the singular, that is to say that they denote both one or more than one fluorinated monomers as defined above.

[0059] By the term “hydrogenated monomer”, it is hereby intended to denote an ethylenically unsaturated monomer comprising at least one hydrogen atom and free from fluorine atoms.

[0060] The term “at least one hydrogenated monomer” is understood to mean that the polymer (F) may comprise recurring units derived from one or more than one hydrogenated monomers. In the rest of the text, the expression “hydrogenated monomers” is understood, for the purposes of the present invention, both in the plural and the singular, that is to say that they denote both one or more than one hydrogenated monomers as defined above.

[0061] The polymer (F) typically comprises recurring units derived from:
(a) chlorotrifluoroethylene (CTFE) and
(b) at least one hydrogenated monomer selected from the group consisting of C₂-C₈ alkenes, preferably from the group consisting of C₂-C₆ alkenes such as ethylene (E), propylene, butylene and hexene.

[0062] The polymer (F) typically comprises:

- (a) from 50% to 70% by moles, preferably from 55% to 65% by moles of recurring units derived from chlorotrifluoroethylene (CTFE) and
- (b) from 30% to 50% by moles, preferably from 35% to 45% by moles of recurring units derived from at least one hydrogenated monomer selected from the group consisting of C₂-C₈ alkenes, preferably from the group consisting of C₂-C₆ alkenes such as ethylene (E), propylene, butylene and hexene.

[0063] The polymer (F) may further comprise one or more additional comonomers, typically in amounts of from 0.01% to 30% by moles, based on the total moles of recurring units derived from CTFE and the hydrogenated monomer(s).

[0064] The polymer (F) more preferably comprises:

- (a) from 50% to 70% by moles, preferably from 55% to 65% by moles of recurring units derived from chlorotrifluoroethylene (CTFE),
- (b) from 30% to 50% by moles, preferably from 35% to 45% by moles of recurring units derived from at least one hydrogenated monomer selected from the group consisting of ethylene (E) and
- (c) optionally, from 0.01% to 10% by moles, preferably from 0.1% to 5% by moles, based on the total moles of recurring units derived from monomers (a) and (b), of one or more additional comonomers.

[0065] The comonomer (c) may be a fluorinated monomer different from chlorotrifluoroethylene (CTFE) or an additional hydrogenated monomer.

[0066] Non-limiting examples of suitable fluorinated monomers different from chlorotrifluoroethylene (CTFE) are selected from the group consisting of:

- C₃-C₈ perfluoroolefins such as hexafluoropropylene;
- C₂-C₈ hydrogenated fluoroolefins such as vinylidene fluoride, vinyl fluoride, 1,2-difluoroethylene and trifluoroethylene;
- perfluoroalkylethylenes complying with formula CH₂=CH-R_{f0}, wherein R_{f0} is a C₁-C₆ perfluoroalkyl group;
- bromo- and/or iodo-C₂-C₆ fluoroolefins;
- (per)fluoroalkylvinylethers complying with formula CF₂=CFOR_{f1}, wherein R_{f1} is a C₁-C₆ fluoro- or perfluoroalkyl group, e.g. CF₃, C₂F₅, C₃F₇;

- $\text{CF}_2=\text{CFOX}_0$ (per)fluoro-oxyalkylvinylethers, wherein X_0 is a $\text{C}_1\text{-C}_{12}$ alkyl group, a $\text{C}_1\text{-C}_{12}$ oxyalkyl or a $\text{C}_1\text{-C}_{12}$ (per)fluorooxyalkyl group having one or more ether groups such as perfluoro-2-propoxy-propyl group;
- (per)fluoroalkylvinylethers complying with formula $\text{CF}_2=\text{CFOCF}_2\text{OR}_{f2}$, wherein R_{f2} is a $\text{C}_1\text{-C}_6$ fluoro- or perfluoroalkyl group, e.g. CF_3 , C_2F_5 , C_3F_7 or a $\text{C}_1\text{-C}_6$ (per)fluorooxyalkyl group having one or more ether groups such as $-\text{C}_2\text{F}_5\text{-O-CF}_3$;
- functional (per)fluoro-oxyalkylvinylethers complying with formula $\text{CF}_2=\text{CFOY}_0$, wherein Y_0 is a $\text{C}_1\text{-C}_{12}$ alkyl or (per)fluoroalkyl group, a $\text{C}_1\text{-C}_{12}$ oxyalkyl group or a $\text{C}_1\text{-C}_{12}$ (per)fluorooxyalkyl group having one or more ether groups and Y_0 comprises carboxylic or sulfonic acid group, in its acid, acid halide or salt form;
- (per)fluorodioxoles, preferably perfluorodioxoles.

- [0067] Non-limiting examples of suitable additional hydrogenated monomers are selected from the group consisting of $\text{C}_2\text{-C}_8$ alkenes, vinyl monomers such as vinyl acetate, (meth)acrylic monomers and styrene monomers.
- [0068] The polymer (F) typically has a heat of fusion of from 15 to 90 J/g, preferably of from 15 to 65 J/g, more preferably of from 15 to 45 J/g, as measured by Differential Scanning Calorimetry (DSC), at a heating rate of $10^\circ\text{C}/\text{min}$, according to ASTM D3418.
- [0069] The polymer (F) typically has a melt flow index comprised between 0.01 and 75 g/10 min, preferably between 0.1 and 50 g/10 min, more preferably between 0.5 and 30 g/10 min, as measured according to ASTM D1238 standard procedure at 225°C and 2.16 Kg.
- [0070] Among polymers (F), ECTFE polymers are preferred.
- [0071] ECTFE polymers suitable in the process of the invention typically have a melting temperature of at most 250°C . The ECTFE polymer typically has a melting temperature of at least 120°C , preferably of at least 150°C .
- [0072] The melting temperature is determined by Differential Scanning Calorimetry (DSC), at a heating rate of $10^\circ\text{C}/\text{min}$, according to ASTM D3418.
- [0073] ECTFE polymers which have been found to give particularly good results are those consisting of recurring units derived from:

(a) 55% to 65% by moles of chlorotrifluoroethylene (CTFE) and

(b) 35% to 45% by moles of ethylene (E).

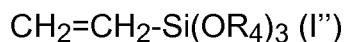
[0074] End chains, defects or minor amounts of monomer impurities leading to recurring units different from those above mentioned can be still comprised in the preferred ECTFE, without this affecting properties of the material.

[0075] The vinyl silane compound of formula (I) is preferably of formula (I'):



wherein R'₁, R'₂ and R'₃, equal to or different from each other, are independently hydrolysable groups selected from the group consisting of alkoxy, acyloxy, oxime, epoxy and amine groups, preferably from the group consisting of C₁-C₆ alkoxy groups, more preferably from the group consisting of C₁-C₄ alkoxy groups.

[0076] The vinyl silane compound of formula (I) is more preferably of formula (I''):



wherein R₄ is a methyl or an ethyl group.

[0077] The polymer (FS) typically comprises from 0.5% to 2.5% by weight of at least one pendant group of formula (I-A) as defined above.

[0078] The content of pendant groups of formula (I-A) in the polymer (FS) may be determined according to techniques generally known in the art.

[0079] The polymer (FS) typically comprises, preferably consists of:

(a') at least one main chain comprising:

- from 50% to 70% by moles, preferably from 55% to 65% by moles of recurring units derived from chlorotrifluoroethylene (CTFE) and
- from 30% to 50% by moles, preferably from 35% to 45% by moles of recurring units derived from at least one hydrogenated monomer selected from the group consisting of C₂-C₈ alkenes, preferably from the group consisting of C₂-C₆ alkenes such as ethylene (E), propylene, butylene and hexene and

(b') at least one pendant group of formula (I-A):



wherein R₁ is a hydrolysable group and R₂ and R₃, equal to or different from each other, are independently C₁-C₄ alkyl groups or hydrolysable groups R₁.

[0080] The polymer (FS) preferably comprises, more preferably consists of:

(a') at least one main chain comprising:

- from 50% to 70% by moles, preferably from 55% to 65% by moles of recurring units derived from chlorotrifluoroethylene (CTFE) and
- from 30% to 50% by moles, preferably from 35% to 45% by moles of recurring units derived from at least one hydrogenated monomer selected from the group consisting of C₂-C₈ alkenes, preferably from the group consisting of C₂-C₆ alkenes such as ethylene (E), propylene, butylene and hexene and

(b') at least one pendant group of formula (I'-A):



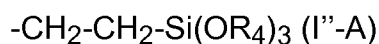
wherein R'₁, R'₂ and R'₃, equal to or different from each other, are independently hydrolysable groups selected from the group consisting of alkoxy, acyloxy, oxime, epoxy and amine groups, preferably from the group consisting of C₁-C₆ alkoxy groups, more preferably from the group consisting of C₁-C₄ alkoxy groups.

[0081] The polymer (FS) more preferably comprises, even more preferably consists of:

(a') at least one main chain comprising:

- from 50% to 70% by moles, preferably from 55% to 65% by moles of recurring units derived from chlorotrifluoroethylene (CTFE) and
- from 30% to 50% by moles, preferably from 35% to 45% by moles of recurring units derived from at least one hydrogenated monomer selected from the group consisting of C₂-C₈ alkenes, preferably from the group consisting of C₂-C₆ alkenes such as ethylene (E), propylene, butylene and hexene and

(b') at least one pendant group of formula (I''-A):



wherein R₄ is a methyl or an ethyl group.

[0082] The polymer (FS-c) typically comprises, preferably consists of:

(a'') organic domains consisting of chains obtainable by the main chain of the polymer (FS) and

(b'') inorganic domains consisting of residues obtainable by hydrolysis

and/or condensation of the pendant groups of formula (I-A):



wherein R_1 is a hydrolysable group and R_2 and R_3 , equal to or different from each other, are independently C_1 - C_4 alkyl groups or hydrolysable groups R_1 .

[0083] The polymer (FS-c) preferably comprises, more preferably consists of:
(a'') organic domains consisting of chains obtainable by the main chain of the polymer (FS) and

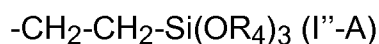
(b'') inorganic domains consisting of residues obtainable by hydrolysis and/or condensation of the pendant groups of formula (I'-A):



wherein R'_1 , R'_2 and R'_3 , equal to or different from each other, are independently hydrolysable groups selected from the group consisting of alkoxy, acyloxy, oxime, epoxy and amine groups, preferably from the group consisting of C_1 - C_6 alkoxy groups, more preferably from the group consisting of C_1 - C_4 alkoxy groups.

[0084] The polymer (FS-c) more preferably comprises, even more preferably consists of:
(a'') organic domains consisting of chains obtainable by the main chain of the polymer (FS) and

(b'') inorganic domains consisting of residues obtainable by hydrolysis and/or condensation of the pendant groups of formula (I''-A):



wherein R_4 is a methyl or an ethyl group.

[0085] The polymer (FS-c) typically has a heat of fusion of less than 15 J/g, as measured by Differential Scanning Calorimetry (DSC), at a heating rate of $10^\circ\text{C}/\text{min}$, according to ASTM D3418.

[0086] The polymer (FS-c) typically has a degree of crosslinking of at least 50% by weight, preferably of at least 65% by weight.

[0087] The polymer (FS-c) typically has a degree of crosslinking of at most 95% by weight, preferably of at most 80% by weight.

[0088] The degree of crosslinking of the polymer (FS-c) may be determined according to techniques generally known in the art.

[0089] Should the disclosure of any patents, patent applications, and publications which are incorporated herein by reference conflict with the description of the present application to the extent that it may render a term unclear, the present description shall take precedence.

[0090] The invention will be now described in more detail with reference to the following examples whose purpose is merely illustrative and not limitative of the scope of the invention.

[0091] **Raw materials**

[0092] Polymer (F-1): ECTFE comprising 59% by moles of chlorotrifluoroethylene (CTFE) and 41% by moles of ethylene (E). The polymer (F-1) has a melting temperature of 180°C, a heat of fusion of 18.6 J/g and a melt flow index of 1 g/10 min (225°C, 2.16 Kg).

[0093] **Determination of the heat of fusion**

Heat of fusion was measured on the polymers by Differential Scanning Calorimetry (DSC), at a heating rate of 10°C/min, according to ASTM D3418 standard procedure.

[0094] **Tensile properties**

[0095] **Determination of the tensile modulus**

Tensile modulus was measured on the polymer films according to ASTM D638 (type V) standard procedure at 23°C.

[0096] **Determination of the strain hardening index (SHI)**

SHI was measured on the polymer films according to the following equation:

$$\text{SHI} = [\sigma (200\% \text{ strain}) - \sigma (100\% \text{ strain})] / [\epsilon (200\% \text{ strain}) - \epsilon (100\% \text{ strain})]$$

wherein σ represents the applied stress on the material and ϵ represents the strain, wherein the stress and the strain were measured according to ASTM D638 (type V) standard procedure.

The higher the value of the SHI, the higher the elastic behaviour of the polymer film under a specific temperature.

[0097] **Hot set test**

Hot set test was carried out according to IEC 60811-2-1 standard procedure by measuring the elongation of the polymer films at 200°C

under the action of a tensile load of 0.20 N/mm² and its recovery after removal of the load. A dumbbell of specified shape and size was suspended from a vertical frame inside a hot air oven with the load suspended from its lower end.

The elongation of the test specimen after 15 minutes under the above conditions and its subsequent recovery after removal of the load represent a measure of the degree of crosslinking of the polymer film.

[0098] Example 1: Manufacture of a silane-crosslinkable fluoropolymer [polymer (FS-1)]

A composition comprising the polymer (F-1) in the form of pellets, vinyl trimethoxy silane and an organic initiator was processed in molten phase by extrusion in a single screw extruder equipped with 5 temperature zones thereby providing the polymer (FS-1) in the form of pellets.

Processing set points were set as in Table 1 hereinbelow:

Table 1

Z1	Z2	Screw	Z1	Head	Kg/h
200°C	240°C	130°C	240°C	190°C	12

[0099] Example 2: Manufacture of a silane-crosslinked fluoropolymer [polymer (FS-c1)]

A composition comprising the polymer (FS-1) in the form of pellets and 5% by weight, based on the weight of the polymer (FS-1), of dioctyltin dilaurate as crosslinking catalyst was processed in molten phase by extrusion using a single screw extruder thereby providing a film comprising the polymer (FS-c1). The single screw extruder was equipped with a conventional barrier screw (L/D = 25) and a flat die having a wideness of 20 mm and a die gap of 1.3 mm.

Processing set points were set as in Table 2 hereinbelow:

Table 2

T1	T2	T2	Head	Die	Screw speed	Absorption	Line speed
165°C	175°C	175°C	190°C	210°C	10.8	4.1 A	2.1 m/min

					rpm		
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[0100] **Comparative Example 1**

The polymer (F-1) was provided in the form of pellets and then processed in molten phase by extrusion using a twin screw extruder thereby providing a film. The twin screw extruder was equipped with a conventional three zone screw (L/D = 25) and a flat die having a wideness of 20 mm and a die gap of 1 mm.

Processing set points were set as in Table 3 hereinbelow:

Table 3

T1	T2	T2	Head	Die	Screw speed	Absorption	Line speed
170°C	190°C	210°C	220°C	230°C	9.5 rpm	4.4 A	1.3 m/min

[0101] The results set forth in Table 4 hereinbelow have shown that extruded articles obtained from the polymer (FS-c) according to the invention such as the film comprising the polymer (FS-c1) according to Example 2 advantageously exhibited a lower tensile modulus, a higher thermal rating and a higher elongation at break as compared with the film obtained from the uncrosslinked polymer (F-1) according to Comparative Example 1.

Table 4

Run	Tensile modulus	SHI	Hot set test
Ex. 2	836	12.4 (23°C) 1.12 (150°C) 0.87 (175°C) 0.77 (200°C)	Elongation: 35% Residual elongation: -10%
C. Ex. 1	1092	10.2 (23°C) 0 (150°C) 0 (175°C) 0 (200°C)	Elongation: broken Residual elongation: broken

[0102] Also, the polymer (FS-c) according to the invention advantageously had a lower heat of fusion as compared with the uncrosslinked polymer (F). In particular, the polymer (FS-c1) according to Example 2 had a heat of

fusion of 12.5 J/g.

Claims

1. A process for the manufacture of a silane-crosslinkable fluoropolymer [polymer (FS)], said process comprising processing in molten phase a composition [composition (F)] comprising:
(A) at least one fluoropolymer [polymer (F)] comprising recurring units derived from:
(a) chlorotrifluoroethylene (CTFE) and
(b) at least one hydrogenated monomer selected from the group consisting of C₂-C₈ alkenes,
(B) at least one vinyl silane compound of formula (I):
$$\text{CH}_2=\text{CH}-\text{SiR}_1\text{R}_2\text{R}_3 \text{ (I)}$$
wherein R₁ is a hydrolysable group and R₂ and R₃, equal to or different from each other, are independently C₁-C₄ alkyl groups or hydrolysable groups R₁ and
(C) at least one organic initiator.
2. The process according to claim 1, wherein the polymer (F) comprises recurring units derived from:
(a) chlorotrifluoroethylene (CTFE) and
(b) at least one hydrogenated monomer selected from the group consisting of C₂-C₈ alkenes, preferably from the group consisting of C₂-C₆ alkenes such as ethylene (E), propylene, butylene and hexene.
3. The process according to claim 1 or 2, wherein the polymer (F) comprises:
(a) from 50% to 70% by moles, preferably from 55% to 65% by moles of recurring units derived from chlorotrifluoroethylene (CTFE) and
(b) from 30% to 50% by moles, preferably from 35% to 45% by moles of recurring units derived from at least one hydrogenated monomer selected from the group consisting of C₂-C₈ alkenes, preferably from the group consisting of C₂-C₆ alkenes such as ethylene (E), propylene, butylene and hexene.
4. The process according to any one of claims 1 to 3, wherein the vinyl silane compound is of formula (I'):
$$\text{CH}_2=\text{CH}_2-\text{SiR}'_1\text{R}'_2\text{R}'_3 \text{ (I')}$$
wherein R'₁, R'₂ and R'₃, equal to or different from each other, are independently hydrolysable groups selected from the group consisting of

alkoxy, acyloxy, oxime, epoxy and amine groups, preferably from the group consisting of C₁-C₆ alkoxy groups, more preferably from the group consisting of C₁-C₄ alkoxy groups.

5. The process according to any one of claims 1 to 4, wherein the organic initiator is selected from the group consisting of organic peroxides, peresters and diazo compounds.
6. The process according to any one of claims 1 to 5, said process comprising:
 - (i) processing in molten phase by melt extrusion the composition (F) thereby providing an extruded article comprising at least one polymer (FS) and
 - (ii) pelletizing the extruded article provided in step (i) thereby providing a polymer (FS) in the form of pellets.
7. A silane-crosslinkable fluoropolymer [polymer (FS)] obtainable from the process according to any one of claims 1 to 6.
8. The polymer (FS) according to claim 7, said polymer (FS) comprising, preferably consisting of:
 - (a') at least one main chain comprising recurring units derived from chlorotrifluoroethylene (CTFE) and from at least one hydrogenated monomer selected from the group consisting of C₂-C₈ alkenes and
 - (b') at least one pendant group of formula (I-A):
$$-\text{CH}_2-\text{CH}_2-\text{SiR}_1\text{R}_2\text{R}_3 \text{ (I-A)}$$
wherein R₁ is a hydrolysable group and R₂ and R₃, equal to or different from each other, are independently C₁-C₄ alkyl groups or hydrolysable groups R₁.
9. A process for the manufacture of a silane-crosslinked fluoropolymer [polymer (FS-c)], said process comprising:
 - (i') processing in molten phase by melt extrusion a composition [composition (FS)] comprising:
 - (A') at least one polymer (FS) according to claim 7 or 8 and
 - (B') optionally, at least one crosslinking catalystthereby providing an extruded article comprising at least one polymer (FS) and
 - (ii') contacting the extruded article provided in step (i') with water or atmosphere having a water vapour content of more than 0.001% v/v.
10. The process according to claim 9, wherein the crosslinking catalyst is selected from the group consisting of metal carboxylates, organometallic compounds,

organic or inorganic bases and organic or inorganic acids.

11. The process according to claim 9 or 10, wherein the composition (FS) further comprises at least one crosslinking promoter.
12. A silane-crosslinked fluoropolymer [polymer (FS-c)] obtainable from the process according to any one of claims 9 to 11.
13. The polymer (FS-c) according to claim 12, said polymer (FS-c) comprising, preferably consisting of:
 - (a'') organic domains consisting of chains obtainable by the main chain of the polymer (FS) according to claim 7 or 8 and
 - (b'') inorganic domains consisting of residues obtainable by hydrolysis and/or condensation of the pendant groups of formula (I-A):
$$-\text{CH}_2-\text{CH}_2-\text{SiR}_1\text{R}_2\text{R}_3 \text{ (I-A)}$$
wherein R_1 is a hydrolysable group and R_2 and R_3 , equal to or different from each other, are independently C_1 - C_4 alkyl groups or hydrolysable groups R_1 .
14. A cable comprising at least one layer comprising at least one polymer (FS) according to claim 7 or 8 and/or at least one polymer (FS-c) according to claim 12 or 13.
15. A tube comprising at least one layer comprising at least one polymer (FS) according to claim 7 or 8 and/or at least one polymer (FS-c) according to claim 12 or 13.
16. A film comprising at least one layer comprising at least one polymer (FS) according to claim 7 or 8 and/or at least one polymer (FS-c) according to claim 12 or 13.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2015/067552

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08F214/24 C08F259/08
ADD.

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)
C08F

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 practicable, 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	EP 0 650 987 A1 (ASAHI GLASS CO LTD [JP]) 3 May 1995 (1995-05-03) example 3 claims 1-3,6-7 column 6, lines 25-42 -----	1-16
A	EP 0 761 757 A1 (ASAHI GLASS CO LTD [JP]) 12 March 1997 (1997-03-12) claims 1,4,7-10 examples 58-72 -----	1-16
A	JP 2000 129585 A (CHUO HATSUJO KK; ASAHI GLASS CO LTD) 9 May 2000 (2000-05-09) example 1 ----- -/-	1-16



Further documents are listed in the continuation of Box C.



See patent family annex.

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INTERNATIONAL SEARCH REPORT

International application No

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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