DESCRIPTION

Title of the Invention: METHOD FOR PRODUCING REGENERATED PERFLUORO(CO)POLYMER AND METHOD FOR PRODUCING REGENERATED MATERIAL

Technical Field

[0001]

The present invention relates to a method for producing a regenerated perfluoro(co)polymer and a method for producing a regenerated material.

Background Art

[0002]

Conventionally, a sealing material has been widely used in various applications, and among these applications, one example of applications in which a sealing material is most heavily loaded is a sealing material used in, for example, a semiconductor manufacturing apparatus.

[0003]

For such a sealing material, a crosslinkable fluoroelastomer such as a fluoroelastomer (FKM) or a perfluoroelastomer (FFKM) is used because a sealing material excellent in plasma resistance and radical resistance can be obtained, and in particular, FFKM is used, for example, when

high temperature or severe chemicals are used.

[0004]

The sealing material made of a crosslinkable fluoroelastomer as described above is generally used as a sealing material formed by using an elastomer composition obtained by blending additives such as a crosslinking agent and a crosslinking aid into the crosslinkable fluoroelastomer, and molding and crosslinking the elastomer composition.

[0005]

The sealing material, like a general molded product, may require a treatment of, for example, a scrap (flash) or a defective product generated during molding, or a used molded product. However, the crosslinked fluoroelastomer has conventionally been discarded by, for example, landfilling as its excellent properties paradoxically obstruct, for example, a chemical treatment, and its incineration produces a corrosive decomposition product, making thermal recycling also not easy.

[0006]

However, in recent years, with the growing awareness of, for example, environmental protection through, for example, reduction of landfill volume, and effective utilization of resources, there has been a demand for the

development of a method for reusing a crosslinked fluoroelastomer that has conventionally been discarded.

[0007]

As a method for reusing such a crosslinked fluoroelastomer, for example, Patent Literature 1 discloses a method for decrosslinking a crosslinked fluorine-containing polymer in a supercritical fluid or a subcritical fluid of a compound having active hydrogen.

Patent Literature 2 discloses a method for subjecting a vulcanized fluororubber to a heat treatment in air.

Citation List

Patent Literature

[0008]

Patent Literature 1: JP 2007-63334 A

Patent Literature 2: JP S61-69805 A

Summary of Invention

Technical Problem

[0009]

However, the method described in Patent Literature 1, in which a supercritical fluid or a subcritical fluid is used, does not lend itself to easy processing and cannot be readily implemented in practice, and therefore there has been

room for improvement.

Further, as a result of intensive studies conducted by the present inventors, it was found that the method described in Patent Literature 2 does not sufficiently cause devulcanization of the vulcanized fluororubber (regeneration of a crosslinking site), and that the heat treatment causes, for example, decomposition of the vulcanized fluororubber, resulting in a large mass reduction rate of the fluororubber before and after the heat treatment.

[0010]

The present invention has been made in view of the above, and an object of the present invention is to provide a method for producing a regenerated perfluoro(co)polymer, which is a method for producing a regenerated perfluoro(co)polymer in which a crosslinking site of a crosslinked perfluoro(co)polymer obtained by crosslinking is regenerated, and is capable of sufficiently regenerating the crosslinking site by a simple method while suppressing mass reduction of the perfluoro(co)polymer upon regeneration of the crosslinking site.

Solution to Problem

[0011]

As a result of intensive studies to solve the above

problems, the present inventors have found that the above problems can be solved according to the following configuration examples, and has completed the present invention.

The configuration examples of the present invention are as follows.

[0012]

[1] A method for producing a regenerated perfluoro(co)polymer, the method including a step of subjecting a crosslinked perfluoro(co)polymer obtained by crosslinking a perfluoro(co)polymer having a crosslinking site to a heat treatment in an inert gas atmosphere to regenerate the crosslinking site.

[0013]

[2] The method for producing a regenerated perfluoro(co)polymer according to [1], in which the crosslinking site is a nitrile group.

[0014]

[3] The method for producing a regenerated perfluoro(co)polymer according to [1] or [2], in which the inert gas is at least one type selected from nitrogen gas, argon gas, and helium gas.

[0015]

[4] The method for producing a regenerated

perfluoro(co)polymer according to any one of [1] to [3], in which the perfluoro(co)polymer having a crosslinking site is a (co)polymer that does not contain a carbon-hydrogen bond in a main chain of the (co)polymer.

[0016]

[5] A method for producing a regenerated material, the method including a step of crosslinking a regenerated material-forming material containing a regenerated perfluoro(co)polymer obtained by the method for producing a regenerated perfluoro(co)polymer according to any one of [1] to [4].

[0017]

[6] The method for producing a regenerated material according to [5], in which the regenerated material-forming material further contains a crosslinking agent.

[0018]

[7] The method for producing a regenerated material according to [5] or [6], in which the regenerated material-forming material further contains an uncrosslinked perfluoro(co)polymer.

[0019]

[8] The method for producing a regenerated material according to [7], in which a content of the regenerated perfluoro(co)polymer in the regenerated material-forming

material is 0.5 parts by mass or more with respect to 100 parts by mass of the uncrosslinked perfluoro(co)polymer.

[0020]

[9] The method for producing a regenerated material according to any one of [5] to [8], in which the regenerated material is a sealing material.

Advantageous Effects of Invention

[0021]

According to the present invention, when a crosslinking site of a crosslinked perfluoro(co)polymer obtained by crosslinking is regenerated, the crosslinking site of the crosslinked perfluoro(co)polymer can be sufficiently regenerated by a simple method while suppressing mass reduction of the perfluoro(co)polymer upon regeneration of the crosslinking site.

As described above, since the crosslinking site of the crosslinked perfluoro(co)polymer can be sufficiently regenerated while suppressing mass reduction, a molded body (regenerated material) having physical properties (hardness, tensile strength, elongation at break, compression set, and plasma resistance) comparable to those obtained when using a virgin product (uncrosslinked perfluoro(co)polymer) can be formed even when using the resulting regenerated

perfluoro(co)polymer.

Thus, the regenerated material can be suitably used as, for example, a sealing material for a semiconductor manufacturing apparatus and a sealing material for a plasma processing apparatus.

Description of Embodiments

[0022]

<<Method for producing regenerated perfluoro(co)polymer>>

A method for producing a regenerated perfluoro(co)polymer (hereinafter also referred to as "present regenerated product") according to the present invention (hereinafter also referred to as "present regenerated product production method") includes a step of subjecting a crosslinked perfluoro(co)polymer (hereinafter also referred to as "material to be regenerated") obtained by crosslinking a perfluoro(co)polymer having a crosslinking site to a heat treatment in an inert gas atmosphere to regenerate the crosslinking site.

[0023]

Whether or not the crosslinking site has been regenerated in the material to be regenerated can be determined by, for example, measuring the amount of the

crosslinking site in the material to be regenerated and the amount of the crosslinking site in the obtained regenerated product using FT-IR.

The present regenerated product production method is desirably a method by which, when the content of the crosslinking site in the material to be regenerated is taken as 100%, the content of the crosslinking site in the resulting regenerated product is preferably 150% or more, and more preferably 200% or more, from the viewpoint that, for example, a regenerated material having desired physical properties can be easily formed using the obtained regenerated product.

The content of the crosslinking site can be measured using FT-IR, specifically, by the method described in the following examples.

[0024]

In addition, the present regenerated product production method is desirably a method by which, the mass reduction rate due to the heat treatment, specifically, the mass reduction rate represented by the following formula (1) is preferably 2% or less, and more preferably 1% or less, from the viewpoint that, for example, a regenerated material having desired physical properties can be easily formed using the obtained regenerated product.

Mass reduction rate (%) = [(mass of material to be regenerated - mass of present regenerated product)/mass of material to be regenerated] × 100 (1)

[0025]

<Material to be regenerated>

The material to be regenerated is a crosslinked perfluoro(co)polymer obtained by crosslinking a perfluoro(co)polymer having a crosslinking site (hereinafter also referred to as "uncrosslinked perfluoro(co)polymer"), and examples thereof include a crosslinked perfluoro(co)polymer contained in, for example, an (unused) molded body such as a sealing material formed using a conventional uncrosslinked perfluoro(co)polymer (virgin product), a scrap (flash) or a defective product generated during the production of such a molded body, and a used molded body.

Examples of the used molded body include not only a used molded body used in a semiconductor manufacturing apparatus, but also a used molded body used in, for example, a chemical plant, and various industrial machinery.

In the present regenerated product production method, as the raw material to be subjected to a heat treatment, the crosslinked perfluoro(co)polymer itself may be used, or the (unused) molded body, the scrap (flash) or defective product,

or the used molded body may be used.

[0026]

The crosslinked perfluoro(co)polymer in the material to be regenerated is a crosslinked body obtained by crosslinking the following uncrosslinked perfluoro(co)polymer (virgin product) by a conventionally known method.

Examples of the conventionally known method include crosslinking using a crosslinking agent, and the crosslinking agent may be appropriately selected according to the uncrosslinked perfluoro(co)polymer to be used, and examples thereof include a peroxide-based crosslinking agent, a bisphenol-based crosslinking agent, a triazine-based crosslinking agent, an oxazole-based crosslinking agent, an imidazole-based crosslinking agent, a thiazole-based crosslinking agent, an amidoxime-based crosslinking agent, and an amidrazone-based crosslinking agent. That is, examples of the material to be regenerated include a crosslinked perfluoro(co)polymer having at least one type of crosslinked structure selected from crosslinked structures derived from such crosslinking agents and intermediate structures upon formation of such crosslinked structures (example: an amidine structure upon formation of an oxazole structure).

The degree of crosslinking in the material to be

regenerated is not particularly limited as long as it is comparable to the degree of crosslinking when a molded body such as a sealing material is formed.

[0027]

[Uncrosslinked perfluoro(co)polymer]

The uncrosslinked perfluoro(co)polymer is a perfluoro(co)polymer having a crosslinking site before crosslinking, and can also be referred to as “virgin product”.

The uncrosslinked perfluoro(co)polymer is preferably a perfluoroelastomer (FFKM).

The FFKM is not particularly limited, but is preferably a polymer that does not contain a hydrogen atom (carbon-hydrogen bond) in a main chain of the polymer (exclusive of the terminal), and specific examples thereof include a tetrafluoroethylene (TFE)-perfluorovinyl ether-based copolymer having a crosslinking site, and a copolymer that contains a TFE-derived structural unit and a perfluorovinyl ether-derived structural unit, and further contains a crosslinking site-containing monomer-derived structural unit as necessary is preferred.

[0028]

Preferred examples of the perfluorovinyl ether include perfluoro(alkyl vinyl ether) and perfluoro(alkoxyalkyl vinyl

ether).

[0029]

Examples of the perfluoro(alkyl vinyl ether) include a compound whose alkyl group has, for example, 1 to 10 carbon atoms, specific examples thereof include perfluoro(methyl vinyl ether), perfluoro(ethyl vinyl ether), and perfluoro(propyl vinyl ether), and perfluoro(methyl vinyl ether) is preferred.

[0030]

Examples of the perfluoro(alkoxyalkyl vinyl ether) include a compound whose group bonded to a vinyl ether group (CF_2=CFO-) has 3 to 15 carbon atoms, and specific examples thereof include the following compounds.

CF_2=$CFOCF_2CF(CF_3)OC_nF_{2n+1}$

CF_2=$CFO(CF_2)_3OC_nF_{2n+1}$

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

CF_2=$CFO(CF_2)_2OC_nF_{2n+1}$

In these formulae, each n is independently, for example, 1 to 5, and m is, for example, 1 to 3.

[0031]

The crosslinking site means a crosslinkable site, and examples thereof include a nitrile group, a halogen atom (examples: I and Br), and a perfluorophenyl group, and among these, a nitrile group is preferred from the viewpoint that,

for example, the effect of the present invention is further exhibited.

[0032]

Examples of a crosslinking site monomer having a nitrile group as the crosslinking site include a nitrile group-containing perfluorovinyl ether, and specific examples thereof include the following compounds.

$CF_2=CFO(CF_2)_nOCF(CF_3)CN$ (n is, for example, 2 to 4)

$CF_2=CFO(CF_2)_nCN$ (n is, for example, 2 to 12)

$CF_2=CFO[CF_2CF(CF_3)O]_m(CF_2)_nCN$ (n is, for example, 1 to 4, and m is, for example, 1 to 5)

$CF_2=CFO[CF_2CF(CF_3)O]_nCF_2CF(CF_3)CN$ (n is, for example, 0 to 4)

$CF_2=CF(CF_2)_nCN$ (n is, for example, an integer of 1 to 8)

$CF_2=CFCF_2(OCF_2)_nCN$ (n is, for example, an integer of 0 to 5)

$CF_2=CFCF_2(OCF(CF_3)CF_2)_m$-CN (m is, for example, an integer of 0 to 5, and n is, for example, an integer of 0 to 5)

$CF_2=CF(OCF_2CF(CF_3))_mO(CF_2)_n$-CN (m is, for example, an integer of 0 to 5, and n is, for example, an integer of 1 to 8)

$CF_2=CF(OCF_2CF(CF_3))_m$-CN (m is, for example, an integer

of 1 to 5)

$CF_2=CFOCF_2(CF(CF_3)OCF_2)_nCF(-CN)CF_3$ (n is, for example, an integer of 1 to 4)

$CF_2=CFO(CF_2)_nOCF(CF_3)$-CN (n is, for example, an integer of 2 to 5)

$CF_2=CF(OCF_2CF(CF_3))_nOCF_2CF(CF_3)$-CN (n is, for example, an integer of 1 to 2)

$CF_2=CFO(CF_2CF(CF_3)O)_m(CF_2)_n$-CN (m is, for example, an integer of 0 to 5, and n is, for example, an integer of 1 to 3)

$CF_2=CFO(CF_2CF(CF_3)O)_mCF_2CF(CF_3)$-CN (m is an integer of 0 or more)

$CF_2=CFOCF(CF_3)CF_2O(CF_2)_n$-CN (n is an integer of 1 or more)

$CF_2=CFOCF_2OCF_2CF(CF_3)OCF_2$-CN

[0033]

Examples of the crosslinking site-containing monomer having a halogen atom as the crosslinking site include halogen group-containing perfluorovinyl ether, and specific examples thereof include compounds obtained by replacing the nitrile group with a halogen atom in the specific examples of the nitrile group-containing perfluorovinyl ether. Examples of the crosslinking site-containing monomer having a halogen atom include compounds described in WO 2009/119409 A, JP

2002-97329 A, and JP 2008-56739 A.

[0034]

In FFKM, the content of the TFE-derived structural unit is preferably 50.0 to 79.9 mol%, the content of the perfluorovinyl ether-derived structural unit is preferably 20.0 to 46.9 mol%, and the content of the crosslinking site-containing monomer-derived structural unit is preferably 0.1 to 2.0 mol%.

[0035]

<Heat treatment conditions and others>

The heat treatment in the present regenerated product production method is characterized by being performed in an inert gas atmosphere.

By performing the heat treatment in an inert gas atmosphere, when a regenerated product is obtained from a material to be regenerated, for example, decomposition of the material to be regenerated can be suppressed, mass reduction can be suppressed, and the present regenerated product having a large regeneration amount of the crosslinking site can be easily obtained.

[0036]

Specific examples of the inert gas include nitrogen gas, argon gas, and helium gas, and among these, nitrogen gas is preferred.

As the inert gas, one type may be used or two or more types may be used.

The inert gas is preferably a gas containing no oxygen or a gas containing a small amount of oxygen from the viewpoint that, for example, the effect of the present invention is further exhibited.

The gas containing a small amount of oxygen is desirably a gas in which the content of oxygen is preferably less than 5 vol%, more preferably 3 vol% or less, and still more preferably 1 vol% or less with respect to the entire gas because thermal decomposition of the material to be regenerated easily proceeds when the content of oxygen is large.

[0037]

The temperature and time during the heat treatment are not particularly limited as long as the temperature and time are such that the crosslinking site is regenerated in the material to be regenerated.

The temperature during the heat treatment is usually a temperature higher than the temperature upon crosslinking of the uncrosslinked perfluoro(co)polymer (virgin product) by a conventionally known method, and is preferably 300 to 400°C, more preferably 320 to 390°C, and still more preferably 350 to 380°C.

The time during the heat treatment depends on the heat treatment temperature, but is preferably 30 minutes to 5 hours, and more preferably 1 to 3 hours.

The pressure during the heat treatment is not particularly limited, but it is preferred to perform the heat treatment under normal pressure.

[0038]

<<Method for producing regenerated material>>

A method for producing a regenerated material according to the present invention (hereinafter also referred to as "present regenerated material production method") includes a step of crosslinking a regenerated material-forming material containing the present regenerated product obtained by the present regenerated product production method.

In the present regenerated material production method, by using a regenerated product obtained by performing a heat treatment in an inert gas atmosphere, a regenerated material having particularly excellent plasma resistance can be formed as compared with, for example, a case of using a regenerated product obtained by performing a heat treatment in air.

[0039]

<Regenerated material-forming material>

The regenerated material-forming material is not

particularly limited as long as it contains the present regenerated product, and may be a material substantially composed only of the present regenerated product, but may contain other conventionally known components that have conventionally been blended in a molded body such as a sealing material as necessary.

Examples of the other components include: an uncrosslinked perfluoro(co)polymer (virgin product); a crosslinking agent; a crosslinking aid; an ethylenically unsaturated bond-containing compound; a reactive organosilicon compound having two or more hydrosilyl groups in the molecule; perfluoropolyether; a non-adhesive agent such as fluorine oil; a catalyst; a polyol-based compound; a (co)polymer other than the perfluoro(co)polymer (example: fluororesin); an acid acceptor such as magnesium oxide or calcium hydroxide; an organic pigment such as an anthraquinone-based pigment, a perylene-based pigment, or a dioxazine-based pigment; a processing aid; a vulcanization accelerator; an anti-aging agent; an antioxidant; an inorganic filler; and an organic filler.

As each of the other components, only one type may be used or two or more types may be used.

[0040]

[Present regenerated product]

The present regenerated product used in the regenerated material-forming material may be of one type or two or more types.

In consideration of the balance between the viewpoint of the environmental protection and the effective utilization of resources and the viewpoint that a regenerated material having desired physical properties can be easily formed, the amount of the present regenerated product used is preferably 0.5 to 60 mass%, more preferably 1 to 50 mass%, and still more preferably 10 to 40 mass% with respect to 100 mass% of the regenerated material-forming material.

When an uncrosslinked perfluoro(co)polymer is used in the regenerated material-forming material, the amount of the present regenerated product used is preferably 0.5 parts by mass or more, more preferably 0.5 to 90 parts by mass, still more preferably 1 to 80 parts by mass, and particularly preferably 10 to 70 parts by mass with respect to 100 parts by mass of the uncrosslinked perfluoro(co)polymer from the viewpoint that, for example, a regenerated material having desired physical properties can be easily formed.

[0041]

[Uncrosslinked perfluoro(co)polymer]

As the regenerated material-forming material, an uncrosslinked perfluoro(co)polymer (virgin product) is

preferably used from the viewpoint that, for example, a regenerated material-forming material excellent in molding processability can be easily obtained, and a regenerated material having desired physical properties (hardness, tensile strength, elongation at break, compression set, and plasma resistance) can be easily formed.

Examples of the uncrosslinked perfluoro(co)polymer include (co)polymers similar to the uncrosslinked perfluoro(co)polymer described in the above-mentioned section of material to be regenerated.

As the uncrosslinked perfluoro(co)polymer, a perfluoro(co)polymer having a crosslinking site different from the crosslinking site contained in the present regenerated product used for the regenerated material-forming material may be used, but it is preferred to use a perfluoro(co)polymer having a similar crosslinking site to the crosslinking site contained in the present regenerated product used for the regenerated material-forming material.

[0042]

When an uncrosslinked perfluoro(co)polymer is used in the regenerated material-forming material, the amount of the uncrosslinked perfluoro(co)polymer used is preferably 40 to 99.5 mass%, more preferably 50 to 99 mass%, and still more preferably 50 to 90 mass% with respect to 100 mass% of the

regenerated material-forming material from the viewpoint that, for example, a regenerated material having desired physical properties can be easily formed.

[0043]

[Crosslinking agent]

The regenerated material-forming material can be crosslinked without using a crosslinking agent, but it is preferred to use a crosslinking agent appropriate to the type of the present regenerated product used or the uncrosslinked perfluoro(co)polymer for the regenerated material-forming material from the viewpoint that, for example, a regenerated material which is sufficiently crosslinked and is excellent in balance among hardness, tensile strength, elongation at break, and tensile stress at 100% elongation (100% Mo) can be easily formed.

[0044]

As the crosslinking agent, for example, a conventionally known crosslinking agent such as a crosslinking agent described in JP 5278312 B2 can be used without particular limitation, and specific examples thereof include a peroxide-based crosslinking agent, a bisphenol-based crosslinking agent, a triazine-based crosslinking agent, an oxazole-based crosslinking agent, an imidazole-based crosslinking agent, a thiazole-based crosslinking

agent, an amidoxime-based crosslinking agent, and an amidrazone-based crosslinking agent.

[0045]

Examples of the peroxide-based crosslinking agent include 2,5-dimethyl-2,5-di(t-butylperoxy)hexane, dicumyl peroxide, 2,4-dichlorobenzoyl peroxide, di-t-butyl peroxide, t-butyldicumyl peroxide, benzoyl peroxide, 2,5-dimethyl-2,5-(t-butylperoxy)hexyne-3, 2,5-dimethyl-2,5-di(benzoylperoxy)hexane, α,α'-bis(t-butylperoxy-m-isopropyl)benzene, t-butylperoxy isopropyl carbonate, di-(4-t-butylcyclohexyl) peroxydicarbonate, p-chlorobenzoyl peroxide, t-butylperoxy-2-ethylhexanoate, t-butyl peroxybenzoate, 1,1-bis(t-butylperoxy)-3,5,5-trimethylcyclohexane, 2,5-dimethylhexane-2,5-dihydroperoxide, α,α-bis(t-butylperoxy)-p-diisopropylbenzene, t-butyl peroxybenzene, and t-butyl peroxymaleic acid.

[0046]

Examples of the bisphenol-based crosslinking agent include bisphenol AF and bisphenol S.

[0047]

Examples of the triazine-based crosslinking agent include 2,4,6-trimercapto-1,3,5-triazine, 2-hexylamino-4,6-dimercaptotriazine, 2-diethylamino-4,6-dimercaptotriazine, 2-cyclohexylamino-4,6-dimercaptotriazine, 2-dibutylamino-4,6-

dimercaptotriazine, 2-anilino-4,6-dimercaptotriazine, and 2-phenylamino-4,6-dimercaptotriazine.

In addition, the triazine crosslinking agent may be a compound that can serve as a catalyst for forming a triazine ring only with a nitrile group contained in the present regenerated product or an uncrosslinked perfluoro(co)polymer as with an organotin compound such as tetraphenyltin or triphenyltin.

[0048]

Examples of the oxazole-based crosslinking agent include 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane (BOAP), 4,4'-sulfonylbis(2-aminophenol), and 9,9-bis(3-amino-4-hydroxyphenyl)fluorene.

[0049]

Examples of the imidazole crosslinking agent include 2,2-bis(3,4-diaminophenyl)hexafluoropropane, 2,2-bis[3-amino-4-(N-methylamino)phenyl]hexafluoropropane, 2,2-bis[3-amino-4-(N-ethylamino)phenyl]hexafluoropropane, 2,2-bis[3-amino-4-(N-propylamino)phenyl]hexafluoropropane, 2,2-bis[3-amino-4-(N-phenylamino)phenyl]hexafluoropropane, 2,2-bis[3-amino-4-(N-perfluorophenylamino)phenyl]hexafluoropropane, and 2,2-bis[3-amino-4-(N-benzylamino)phenyl]hexafluoropropane.

[0050]

Examples of the thiazole-based crosslinking agent

include 2-mercaptobenzothiazole and dibenzothiazyl disulfide.

[0051]

When a crosslinking agent is used for the regenerated material-forming material, the amount of the crosslinking agent used is preferably 0.2 to 4 parts by mass, and more preferably 0.2 to 2.5 parts by mass with respect to 100 parts by mass of the total of the present regenerated product and the uncrosslinked perfluoro(co)polymer, from the viewpoint that, for example, the crosslinking reaction sufficiently proceeds, and a regenerated material excellent in balance among hardness, tensile strength, elongation at break, and 100% Mo can be easily formed.

[0052]

[Crosslinking aid]

In the regenerated material-forming material, the crosslinking agent may be used alone, but in the case of using the crosslinking agent such as the peroxide-based crosslinking agent, it is preferred to use a crosslinking aid. As the crosslinking aid, a known crosslinking aid may be selected depending on the type of crosslinking agent.

[0053]

Examples of the crosslinking aid to be used in the case of using a peroxide-based crosslinking agent include compounds capable of radically co-crosslinking

(polyfunctional monomers) such as triallyl isocyanurate; triallyl cyanurate; trimethallyl isocyanurate; triallyl formal; triallyl trimellitate; N,N'-m-phenylenebismaleimide; dipropargyl terephthalate; diallyl phthalate; tetraallyl terephthalamide; and polyfunctional (meth)acrylates, for example, ethylene glycol di(meth)acrylate and trimethylolpropane tri(meth)acrylate: metal salts of higher carboxylic acids: polyhydric alcohol (meth)acrylates: and (meth)acrylic acid metal salts.

Among them, triallyl isocyanurate is preferred from the viewpoints of, for example, excellent reactivity and being capable of easily obtaining a sealing material having excellent heat resistance, high hardness, and high modulus.

[0054]

When a crosslinking aid is used for the regenerated material-forming material, the amount of the crosslinking aid used is preferably 0.5 parts by mass or more, and preferably 10 parts by mass or less, more preferably 7 parts by mass or less, and still more preferably 6 parts by mass or less with respect to 100 parts by mass of the total of the present regenerated product and the uncrosslinked perfluoro(co)polymer from the viewpoint that, for example, the crosslinking reaction sufficiently proceeds, and a sealing material excellent in balance among hardness, tensile

strength, elongation at break, and 100% Mo can be easily formed.

[0055]

When a crosslinking agent and a crosslinking aid are used for the regenerated material-forming material, the mass ratio of the content of the crosslinking aid to the content of the crosslinking agent in the regenerated material-forming material (the content of the crosslinking aid/the content of the crosslinking agent) is preferably 1 or more, more preferably 2 or more, and preferably 30 or less, more preferably 20 or less from the viewpoint that, for example, the crosslinking agent can be reacted without excess or deficiency, and a regenerated material exhibiting desired physical properties can be easily formed.

[0056]

[Ethylenically unsaturated bond-containing compound]

Examples of the ethylenically unsaturated bond-containing compound include compounds described in, for example, WO 2022/065054 A, JP 2003-183402 A, and JP H11-116684 A.

[0057]

[Reactive organosilicon compound]

Examples of the reactive organosilicon compound include compounds which are similar to the organosilicon

compounds described in, for example, JP 2003-183402 A and JP H11-116684 A.

[0058]

[Catalyst]

Examples of the catalyst include catalysts which are similar to the catalysts described in, for example, JP 2003-183402 A and JP H 11-116684 A.

[0059]

[Organic pigment]

Examples of the organic pigment include organic pigments which are similar to the organic pigments described in, for example, WO 2016/043100 A, JP 4720501 B2, WO 2004/094527 A, and JP 5278312 B2.

[0060]

[Filler]

Examples of the inorganic filler include particulate (powdery) inorganic materials of, for example, carbon black, silica, barium sulfate, titanium oxide, and aluminum oxide.

Examples of the organic filler include particulate (powdery) organic materials of, for example, fluororesins such as PTFE, PFA, FEP, ETFE, and PVDF, polyethylene, polyimide, polyamideimide, polyetherimide, polyether ether ketone, polyether ketone, a silicone resin, and a melamine resin.

[0061]

[Method for preparing regenerated material-forming material]

The regenerated material-forming material can be prepared by mixing (kneading) the present regenerated product and the above-mentioned other components as necessary.

When the present regenerated product and the above-mentioned other components are mixed, the mixing order thereof is not particularly limited. These may be sequentially mixed (kneaded) in any order, or may be mixed (kneaded) all at once, but it is preferred that these are sequentially mixed (kneaded) such that the respective components are uniform.

[0062]

When performing the mixing (kneading), a conventionally known mixing (kneading) machine can be used, and examples thereof include an open roll, a Banbury mixer, a biaxial roll, and a kneader.

Further, when performing the mixing (kneading), the mixing (kneading) may be performed under heating or cooling as necessary depending on a mixing (kneading) machine.

[0063]

<Step of crosslinking regenerated material-forming material>

The present regenerated material production method is not particularly limited as long as it includes the step of crosslinking the regenerated material-forming material.

[0064]

When a regenerated material is formed from the regenerated material-forming material, it is preferred to perform a sheeting step from the viewpoint of, for example, improving the efficiency of the molding operation and reducing the defect rate. This sheeting step is usually performed using, for example, a roll, and is usually also a step of preliminarily molding the regenerated material-forming material into a sheet.

[0065]

The sheet obtained in the sheeting step is preferably preliminarily molded into a desired regenerated material shape before the crosslinking step.

In this preliminary molding, a desired regenerated material shape may be directly formed from the sheet obtained in the sheeting step, or the sheet obtained in the sheeting step may be formed into, for example, a rope shape (also synonymous with, for example, a ribbon shape or a noodle shape) by, for example, cutting or extrusion molding, and then the obtained rope-shaped product may be formed into a desired regenerated material shape.

[0066]

The crosslinking step more preferably includes a primary crosslinking step and a secondary crosslinking step.

The crosslinking step is preferably performed using a preliminarily molded body having a desired regenerated material shape that is obtained by the preliminary molding.

[0067]

The primary crosslinking step is preferably a step of heating and pressurizing the preliminarily molded body having a desired regenerated material shape that is obtained by the preliminary molding, and specific examples thereof include a step of casting the preliminarily molded body into a mold, followed by crosslinking at a temperature of, for example, 150 to 200°C for, for example, about 5 minutes to 1 hour under a pressure of about 2 to 15 MPa by, for example, a heat press.

[0068]

The secondary crosslinking step is preferably a step of heating the molded body obtained in the primary crosslinking step, and specific examples thereof include a step of heating the molded body at a temperature of, for example, 150 to 300°C for about 1 to 48 hours, more preferably about 3 to 24 hours using various ovens, preferably a vacuum oven, under normal pressure to reduced

pressure.

By this secondary crosslinking step, crosslinking can be promoted, or even if an unreacted component remains after the primary crosslinking step, the unreacted component can be decomposed and volatilized, and a regenerated material with less generation of release gas can be formed.

[0069]

In the present regenerated material production method, a step of performing irradiation with radiation (step of irradiating with radiation) may be performed after the crosslinking step from the viewpoint that, for example, a crack that may occur in the regenerated material, for example, in a plasma atmosphere can be more easily suppressed. The regenerated material obtained through the step of irradiation with radiation can be considered as a radiation-treated product.

[0070]

The radiation used for irradiation in the step of irradiation with radiation is not particularly limited, and examples thereof include an X-ray, a gamma ray, an electron beam, a proton beam, a neutron beam, a heavy particle beam, an alpha ray, and a beta ray, and among these, a gamma ray and an electron beam are preferred.

The radiation used for the irradiation may be of one

type alone or two or more types.

[0071]

Upon irradiation with radiation, it is desirable to perform irradiation with radiation so that the absorbed dose is preferably 1 to 120 kGy and more preferably 20 to 100 kGy. When irradiation with radiation is performed at such a dose, it is possible to reduce unreacted components that can be particles or released gas, and it is possible to easily form a regenerated material excellent in, for example, plasma resistance and crack resistance without excessively reducing the molecular weights of the present regenerated product and the uncrosslinked perfluoro(co)polymer.

The step of irradiation with radiation may be performed in two or more stages with the conditions changed.

[0072]

Upon irradiation with radiation, the irradiation may be performed in air. However, when oxygen is present during irradiation with radiation, the crosslinking reaction may be inhibited, and the mechanical strength of the obtained regenerated material may be reduced or the surface of the obtained regenerated material may become sticky. Thus, the step of irradiation with radiation is preferably performed in an atmosphere of an inert gas such as nitrogen or argon.

[0073]

<Regenerated material>

The regenerated material obtained by the present regenerated material production method is not particularly limited, but can be used as, for example, a gasket or a packing for various members, and especially can be suitably used as a sealing material for a semiconductor manufacturing apparatus or a sealing material for a plasma processing apparatus, and particularly as a sealing material for a drive unit including a gate valve used for an opening of a plasma processing chamber unit.

The regenerated material is preferably a sealing material, and examples of the sealing material include an O-ring, a square-ring, a gasket, a packing, an oil seal, a bearing seal, and a lip seal.

The regenerated material has, for example, a shape that may be appropriately selected according to the intended use.

[0074]

The semiconductor manufacturing apparatus is not particularly limited to an apparatus for manufacturing a semiconductor, and broadly includes all manufacturing apparatus used in the semiconductor field requiring a high degree of cleanliness, such as an apparatus for manufacturing, for example, a liquid crystal panel, or a

plasma panel, and specific examples thereof include an apparatus described in, for example, JP 5278312 B2.

[0075]

The IRHD of the regenerated material measured based on JIS K 6253-2:2012 is preferably 45 or more, and more preferably 50 or more.

The tensile strength of the regenerated material measured by the method described in the following examples is preferably 7 MPa or more, and more preferably 8 MPa or more.

The elongation at break of the regenerated material measured by the method described in the following examples is preferably 120% or more, and more preferably 130% or more.

The mass reduction rate of the regenerated material measured by the method described in the following examples is preferably 5% or less, more preferably 3% or less, and the lower limit thereof is not particularly limited, but is, for example, 0%.

Examples

[0076]

Next, the present invention will be described in more detail with reference to examples, but the present invention is not limited thereto.

[0077]

<Crosslinked perfluoro(co)polymer (material to be regenerated)>

The crosslinked perfluoro(co)polymer (material to be regenerated) used in the following examples and comparative examples is as follows.

· "Crosslinked perfluoro(co)polymer-1": A molded body (O-ring) (corresponding to an unused or used molded body) produced by kneading 100 parts by mass of a perfluoroelastomer (PFE 131T [manufactured by 3M Company], a perfluoro(co)polymer in which a crosslinking site is a nitrile group) and 0.5 parts by mass of an oxazole-based crosslinking agent (BOAP, 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane, manufactured by Tokyo Chemical Industry Co., Ltd.) with an open roll, then filling an O-ring-shaped mold with the resulting massive elastomer composition, and performing press-molding at 180°C for 30 minutes under a pressure of 5 MPa using a compression vacuum press (primary crosslinking), and subsequently heating the press-molded sheet in an oven at 250°C for 24 hours (secondary crosslinking).

· "Crosslinked perfluoro(co)polymer-2": A molded body (O-ring) (corresponding to an unused or used molded body) produced by kneading 100 parts by mass of a perfluoroelastomer (Tecnoflon PFR94 [manufactured by Solvay

S.A.], a perfluoro(co)polymer in which a crosslinking site is a halogen atom), 1 part by mass of TAIC (triallyl isocyanurate manufactured by Mitsubishi Chemical Corporation), and 0.5 parts by mass of PERHEXA 25B (manufactured by NOF Corporation) with an open roll, then filling an O-ring-shaped mold with the resulting massive elastomer composition, and performing press-molding at 170°C for 10 minutes under a pressure of 5 MPa using a compression vacuum press (primary crosslinking), and subsequently heating the press-molded sheet in an oven at 200°C for 4 hours (secondary crosslinking).

[0078]

[Example 1]

The crosslinked perfluoro(co)polymer-1 (material to be regenerated) was placed in KDF-75Plus manufactured by Yamato Scientific Co., Ltd. and subjected to a heat treatment at 380°C and 1 atm for 1 hour in a nitrogen atmosphere to obtain a regenerated perfluoro(co)polymer-1 (regenerated product).

[0079]

[Example 2]

A regenerated perfluoro(co)polymer-2 (regenerated product) was obtained in the same manner as in Example 1 except that the crosslinked perfluoro(co)polymer-2 (material to be regenerated) was used instead of the crosslinked

perfluoro(co)polymer-1.

[0080]

[Example 3]

The crosslinked perfluoro(co)polymer-1 (material to be regenerated) was placed in KDF-75Plus manufactured by Yamato Scientific Co., Ltd. and subjected to a heat treatment at 370°C and 1 atm for 1 hour in a helium gas atmosphere to obtain a regenerated perfluoro(co)polymer-3 (regenerated product).

[0081]

[Example 4]

The crosslinked perfluoro(co)polymer-1 (material to be regenerated) was placed in KDF-75Plus manufactured by Yamato Scientific Co., Ltd. and subjected to a heat treatment at 370°C and 1 atm for 1 hour in an argon gas atmosphere to obtain a regenerated perfluoro(co)polymer-4 (regenerated product).

[0082]

[Comparative Example 1]

The crosslinked perfluoro(co)polymer-1 (material to be regenerated) was placed in KDF-75Plus manufactured by Yamato Scientific Co., Ltd. and subjected to a heat treatment at 380°C and 1 atm for 1 hour in air to obtain a regenerated perfluoro(co)polymer-c1 (regenerated product).

[0083]

[Comparative Example 2]

A regenerated perfluoro(co)polymer-c2 (regenerated product) was obtained in the same manner as in Comparative Example 1 except that the crosslinked perfluoro(co)polymer-2 (material to be regenerated) was used instead of the crosslinked perfluoro(co)polymer-1.

[0084]

<Content of crosslinking site>

The content of the crosslinking site in each of the crosslinked perfluoro(co)polymer (material to be regenerated) and the regenerated perfluoro(co)polymer (regenerated product) was measured using FT-IR (HYPERION 3000, manufactured by Bruker Corporation) under the conditions of a resolution of 4 cm^{-1}, a scan number of 32, a transmission method, and a measurement range of 400 to 4000 cm^{-1}. The results are shown in Table 1.

Specifically, the content of the crosslinking site (nitrile group) was defined as a value obtained by dividing the maximum intensity when a baseline was drawn by connecting the intensities at 2230-2290 cm^{-1} by the intensity at 2500 cm^{-1} when a baseline was drawn by connecting the intensities at 2200-2700 cm^{-1}. However, when the calculation result (content of crosslinking site (nitrile group)) was less than 0.01, the

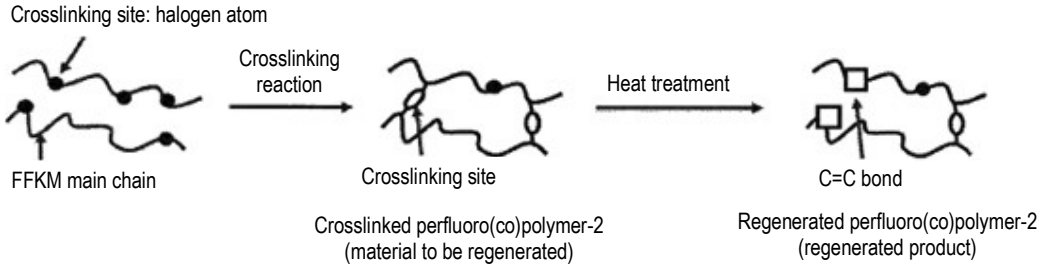
content of the crosslinking site (nitrile group) was taken to be 0.01.

[0085]

In the column of Example 2 in Table 1 below, the content of the crosslinking site is indicated as "-"; however, in Example 2, it is considered that sufficient regeneration of the crosslinking site (C=C bond) on the right side of the following formula has occurred.

[0086]

[Chem. 1]



[0087]

<Mass reduction rate>

The mass of the crosslinked perfluoro(co)polymer (material to be regenerated) before the heat treatment used in the above examples or comparative examples was measured, and the mass of the obtained regenerated perfluoro(co)polymer (regenerated product) was measured.

The mass reduction rate (%) was determined by the following formula. The results are shown in Table 1.

Mass reduction rate (%) = [(mass of material to be regenerated - mass of regenerated product)/mass of material to be regenerated] × 100

[0088]

[Table 1]

		Example 1	Example 2	Example 3	Example 4	Comparative Example 1	Comparative Example 2
Heat treatment atmosphere		Nitrogen	Nitrogen	Helium	Argon	Air	Air
Content of crosslinking site	Material to be regenerated	0.1	-	0.1	0.1	0.1	-
	Regenerated product	0.35	-	0.28	0.36	0.22	-
Mass reduction rate (%)		0.6	0.9	0.5	0.4	2.3	2.4

[0089]

<Uncrosslinked perfluoro(co)polymer (virgin product)>

The uncrosslinked perfluoro(co)polymer (virgin product) used in the following examples and comparative examples is as follows.

· "Uncrosslinked perfluoro(co)polymer-1": PFE 131T (manufactured by 3M Company)

· "Uncrosslinked perfluoro(co)polymer-2": Tecnoflon PFR94 (manufactured by Solvay S.A.)

[0090]

[Example 5]

A massive elastomer composition was obtained by kneading 60 parts by mass of the uncrosslinked perfluoro(co)polymer-1 (virgin product), 40 parts by mass of

the regenerated perfluoro(co)polymer-1 (regenerated product), and 0.5 parts by mass of an oxazole-based crosslinking agent (BOAP, 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane, manufactured by Tokyo Chemical Industry Co., Ltd.) with an open roll.

A molded body (O-ring) was obtained by filling an O-ring-shaped mold with the obtained massive elastomer composition, followed by press-molding at 180°C for 30 minutes under a pressure of 5 MPa using a compression vacuum press (primary crosslinking), and then heating the press-molded sheet at 250°C for 24 hours in an oven (secondary crosslinking).

[0091]

[Comparative Examples 3 and 4]

A molded body was obtained in the same manner as in Example 5 except that the (co)polymers of the types and amounts (numerical values: parts by mass) shown in Table 2 were used as the uncrosslinked perfluoro(co)polymer and the regenerated perfluoro(co)polymer in Example 5.

[0092]

[Example 6]

A massive elastomer composition was obtained by kneading 60 parts by mass of the uncrosslinked perfluoro(co)polymer-2 (virgin product), 40 parts by mass of

the regenerated perfluoro(co)polymer-2 (regenerated product), 10 parts by mass of PTFE particles (Lubron L5 (manufactured by Daikin Industries, Ltd.)), 0.5 parts by mass of PERHEXA 25B (manufactured by NOF CORPORATION), and 1 part by mass of TAIC (triallyl isocyanurate, manufactured by Mitsubishi Chemical Corporation) with an open roll.

A molded body (O-ring) was obtained by filling an O-ring-shaped mold with the obtained massive elastomer composition, followed by press-molding at 170°C for 10 minutes under a pressure of 5 MPa using a compression vacuum press (primary crosslinking), and then heating the press-molded sheet at 200°C for 4 hours in an oven (secondary crosslinking).

[0093]

[Comparative Examples 5 and 6]

A molded body was obtained in the same manner as in Example 6 except that the (co)polymers of the types and amounts (numerical values: parts by mass) shown in Table 2 were used as the uncrosslinked perfluoro(co)polymer and the regenerated perfluoro(co)polymer in Example 6.

[0094]

<IRHD>

According to JIS K 6253-2:2012, the hardness of the obtained molded body was measured at 23°C by an IRHD hardness

tester. The results are shown in Table 2.

[0095]

<Tensile strength and elongation at break>

The obtained molded body (O-ring) was pulled at 500 mm/min, and the tensile strength and the elongation at break were measured at 23°C using a Shopper type tensile tester. The results are shown in Table 2.

[0096]

<Compression set>

The compression set of the sealing material was determined in accordance with JIS K 6262:2013.

The obtained molded body was held at 200°C for 72 hours at a compression rate of 25%, then the pressure was released, and the molded body was allowed to cool at a standard temperature in a test chamber for 30 minutes, and then the thickness of the molded body was measured.

Further, the obtained molded body was held at 260°C for 72 hours at a compression rate of 20%, then the pressure was released, and the molded body was allowed to cool at a standard temperature in a testing room for 30 minutes, and then the thickness of the molded body was measured.

The compression set rate (CS) was calculated based on the following formula. The results are shown in Table 2.

Compression set rate (%) = {(h0 - h1)/(h0 - h2)} × 100

[h0: thickness (mm) of molded body before compression, h1: thickness (mm) of molded body after cooling for 30 minutes, h2: thickness (height) of spacer (mm)]

[0097]

<Mass reduction rate (plasma resistance)>

The obtained molded body was measured for the plasma resistance (mass reduction rate). Specifically, measurement was performed as follows. The results are shown in Table 2.

A fluorine radical exposure test was performed in which the obtained molded body (O-ring) was exposed to fluorine radicals generated from NF_3 by remote plasma under the following conditions. The mass of the molded body (O-ring) was measured before and after the test, and the mass reduction rate was determined by the following formula to evaluate the plasma resistance. It can be said that the smaller the mass reduction rate is, the better the plasma resistance is.

Mass reduction rate (%) = {(mass before test - mass after test)/(mass before test)} × 100

[0098]

(Conditions)

· Plasma source: remote plasma source

· Plasma output: 5000 W

· Gas flow rate: NF_3; 1.5 SLM, Argon; 1.5 SLM

· Vacuum degree: 7 torr

· Test temperature: 250°C

· Test time: 5 hours

[0099]

[Table 2]

	Example 5	Comparative Example 3	Comparative Example 4	Example 6	Comparative Example 5	Comparative Example 6
Uncrosslinked perfluoro(co)polymer-1	60	60	100			
Uncrosslinked perfluoro(co)polymer-2				60	60	100
Regenerated perfluoro(co)polymer-1	40					
Regenerated perfluoro(co)polymer-c1		40				
Regenerated perfluoro(co)polymer-2				40		
Regenerated perfluoro(co)polymer-c2					40	
IRHD	51	51	52	64	63	60
Tensile strength (MPa)	8.6	8.2	10.4	8.6	10.6	8.8
Elongation at break (%)	187	203	185	195	225	205
CS (%) at compression of 25%, 200°C × 72 h	2	3	2	41	46	41
CS (%) at compression of 20%, 260°C × 72 h	7	9	10	104	104	101
Mass reduction rate (%)	0.11	0.17	0.11	0.48	0.61	0.45

[0100]

In Example 5, it was possible to obtain a molded body having an IRHD and an elongation at break similar to those in Comparative Example 4 using only a virgin product, and it was possible to obtain a molded body having a smaller compression set and exhibiting superior plasma resistance (smaller mass reduction rate) as compared with Comparative Example 3.

In Example 6, it was possible to obtain a molded body having an IRHD and a tensile strength similar to those in Comparative Example 6 using only a virgin product, and it was possible to obtain a molded body having a smaller compression

set when held at 200°C for 72 hours at a compression rate of 25%, and exhibiting superior plasma resistance (smaller mass reduction rate) as compared with Comparative Example 5.

CLAIMS

[Claim 1]

A method for producing a regenerated perfluoro(co)polymer, the method comprising a step of subjecting a crosslinked perfluoro(co)polymer obtained by crosslinking a perfluoro(co)polymer having a crosslinking site to a heat treatment in an inert gas atmosphere to regenerate the crosslinking site.

[Claim 2]

The method for producing a regenerated perfluoro(co)polymer according to claim 1, wherein the crosslinking site is a nitrile group.

[Claim 3]

The method for producing a regenerated perfluoro(co)polymer according to claim 1, wherein the inert gas is at least one type selected from nitrogen gas, argon gas, and helium gas.

[Claim 4]

The method for producing a regenerated perfluoro(co)polymer according to claim 1, wherein the perfluoro(co)polymer having a crosslinking site is a (co)polymer that does not contain a carbon-hydrogen bond in a main chain of the (co)polymer.

[Claim 5]

A method for producing a regenerated material, the method comprising a step of crosslinking a regenerated material-forming material containing a regenerated perfluoro(co)polymer obtained by the method for producing a regenerated perfluoro(co)polymer according to any one of claims 1 to 4.

[Claim 6]

The method for producing a regenerated material according to claim 5, wherein the regenerated material-forming material further comprises a crosslinking agent.

[Claim 7]

The method for producing a regenerated material according to claim 5, wherein the regenerated material-forming material further comprises an uncrosslinked perfluoro(co)polymer.

[Claim 8]

The method for producing a regenerated material according to claim 7, wherein a content of the regenerated perfluoro(co)polymer in the regenerated material-forming material is 0.5 parts by mass or more with respect to 100 parts by mass of the uncrosslinked perfluoro(co)polymer.

[Claim 9]

The method for producing a regenerated material

according to claim 5, wherein the regenerated material is a sealing material.