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(54) **COPOLYMER, MOLDED BODY, EXTRUDED BODY, AND TRANSFER MOLDED BODY**

(71) Applicant: **DAIKIN INDUSTRIES, LTD.**, Osaka (JP)

(72) Inventors: **Tadaharu ISAKA**, Osaka (JP); **Yumi ZENKE**, Osaka (JP); **Yukari YAMAMOTO**, Osaka (JP); **Hayato TSUDA**, Osaka (JP); **Yasuyuki YAMAGUCHI**, Osaka (JP)

(73) Assignee: **DAIKIN INDUSTRIES, LTD.**, Osaka (JP)

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(57) **ABSTRACT**

There is provided a copolymer containing tetrafluoroethylene unit and perfluoro(propyl vinyl ether) unit, wherein the copolymer has a content of perfluoro(propyl vinyl ether) unit of 4.9 to 7.0% by mass with respect to the whole of the monomer units, a melt flow rate at 372° C. of 0.5 to 1.5 g/10 min, and the number of functional groups of 20 or less per 10^6 main-chain carbon atoms.

COPOLYMER, MOLDED BODY, EXTRUDED BODY, AND TRANSFER MOLDED BODY

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is a Rule 53(b) Continuation of International Application No. PCT/JP2022/003647 filed Jan. 31, 2022, which claims priorities based on Japanese Patent Application No. 2021-031113 filed Feb. 26, 2021 and Japanese Patent Application No. 2021-162080 filed Sep. 30, 2021, the respective disclosures of which are incorporated herein by reference in their entirety.

TECHNICAL FIELD

[0002] The present disclosure relates to a copolymer, a formed article, an extrusion formed article, and a transfer molded article.

BACKGROUND ART

[0003] Patent Document 1 describes an OA device material comprising a tetrafluoroethylene-based copolymer as a component, wherein the tetrafluoroethylene-based copolymer has tetrafluoroethylene unit derived from tetrafluoroethylene and a perfluoro(alkyl vinyl ether) unit derived from perfluoro(alkyl vinyl ether), contains 4.5 to 6.6% by mass of the perfluoro(alkyl vinyl ether) unit with respect to the whole of the monomer units, and contains 20 or less unstable terminal groups per 1×10^6 carbon atoms.

RELATED ART

Patent Document

[0004] Patent Document 1: Japanese Patent Laid-Open No. 2009-042478

SUMMARY

[0005] According to the present disclosure, there is provided a copolymer comprising tetrafluoroethylene unit and perfluoro(propyl vinyl ether) unit, wherein the copolymer has a content of perfluoro(propyl vinyl ether) unit of 4.9 to 7.0% by mass with respect to the whole of the monomer units, a melt flow rate at 372° C. of 0.5 to 1.5 g/10 min, and the number of functional groups of 20 or less per 10^6 main-chain carbon atoms.

Effects

[0006] According to the present disclosure, there can be provided a copolymer that hardly deforms even in a molten state, that is capable of easily providing a thick sheet having a uniform thickness by extrusion forming, and that is capable of providing a formed article which has extremely good transparency, which has a low compression set rate, which has high tensile strength at high temperatures, which has excellent air low permeability, chemical solution low permeability, 110° C. high-temperature rigidity, creep resistance, abrasion resistance and carbon dioxide low permeability, and which hardly makes fluorine ions to dissolve out in a chemical solution such as a hydrogen peroxide solution.

DESCRIPTION OF EMBODIMENTS

[0007] Hereinafter, specific embodiments of the present disclosure will be described in detail, but the present disclosure is not limited to the following embodiments.

[0008] A copolymer of the present disclosure contains tetrafluoroethylene (TFE) unit and perfluoro(propyl vinyl ether) (PPVE) unit.

[0009] The copolymer (PFA) containing TFE unit and PPVE unit is used as a material for forming a thick sheet. While a thick sheet tends to have better tensile strength than a thin sheet, the thicker the sheet, the lower the transparency, and, to form a thick, highly transparent sheet, demand exists for a copolymer having an extremely low haze value. Such a thick sheet is generally produced by extrusion-forming a copolymer using an extrusion forming machine. The copolymer in a molten state discharged from the extrusion forming machine easily deforms due to its own weight before being cooled and solidified, and thus an attempt to produce a thick sheet results in the problem that it is not easy to produce a sheet having a desired thickness. Moreover, such a thick sheet is problematic by being likely to deform or being worn when a load is continuously applied for a long term.

[0010] In Patent Document 1, the QA device material having the above characteristics is described as being a material exhibiting excellent flexibility and toner releasability, having excellent balance between heat resistance and crack resistance, and having excellent melt extrusion moldability. However, the use of this QA device material as a material of a thick sheet is problematic in that a thick sheet having a uniform thickness is not easily obtained and, also, the transparency, abrasion resistance, compression set resistance, and tensile strength at high temperatures of the obtained thick sheet are not sufficient.

[0011] It has been found that by suitably regulating the content of PPVE unit, the melt flow rate (MFR), and the number of functional groups of a copolymer containing TFE unit and PPVE unit, a copolymer can be obtained that hardly deforms even in a molten state, that is capable of easily providing a thick sheet having a uniform thickness by extrusion forming, that has extremely good transparency, that has a low compression set rate, that has high tensile strength at high temperatures, that has excellent air low permeability, chemical solution low permeability, 110° C. high-temperature rigidity, creep resistance, abrasion resistance and carbon dioxide low permeability, and that hardly makes fluorine ions to dissolve out in a chemical solution such as a hydrogen peroxide solution.

[0012] Moreover, by using the copolymer of the present disclosure, a large-diameter pipe having high dimensional accuracy can be produced by extrusion forming. Thus, the copolymer of the present disclosure can be utilized not only as a material for a sheet, but also in a broad range of applications such as a material for a pipe.

[0013] The copolymer of the present disclosure is a melt-fabricable fluororesin. Being melt-fabricable means that a polymer can be melted and processed by using a conventional processing device such as an extruder.

[0014] The content of the PPVE unit of the copolymer is 4.9 to 7.0% by mass with respect to the whole of the monomer units. The content of the PPVE unit of the copolymer is preferably 5.0% by mass or higher, more preferably 5.1% by mass or higher, still more preferably 5.2% by mass or higher, further still more preferably 5.3%

by mass or higher, especially preferably 5.4% by mass or higher, and most preferably 5.5% by mass or higher, and is preferably 6.9% by mass or lower, more preferably 6.8% by mass or lower, still more preferably 6.7% by mass or lower, further still more preferably 6.6% by mass or lower, especially preferably 6.5% by mass or lower, and most preferably 6.4% by mass or lower. Due to that the content of the PPVE unit of the copolymer is in the above range, a copolymer can be obtained that is capable of obtaining a formed article which has extremely good transparency, which has a low compression set rate, which has high tensile strength at high temperatures, and which has excellent air low permeability, chemical solution low permeability, 110° C. high-temperature rigidity, creep resistance, abrasion resistance and carbon dioxide low permeability. An excessively small content of the PPVE unit of the copolymer results in an increased haze value, decreased tensile strength at high temperatures, and poor abrasion resistance.

[0015] The content of the TFE unit of the copolymer is, with respect to the whole of the monomer units, preferably 93.0 to 95.1% by mass, more preferably 93.1% by mass or higher, still more preferably 93.2% by mass or higher, further still more preferably 93.3% by mass or higher, even more preferably 93.4% by mass or higher, especially preferably 93.5% by mass or higher, and most preferably 93.6% by mass or higher, and is more preferably 95.0% by mass or lower, still more preferably 94.9% by mass or lower, further still more preferably 94.8% by mass or lower, even more preferably 94.7% by mass or lower, especially preferably 94.6% by mass or lower, and most preferably 94.5% by mass or lower. Due to that the content of the TFE unit of the copolymer is in the above range, a copolymer can be obtained that is capable of obtaining a formed article which has extremely good transparency, which has a lower compression set rate, which has higher tensile strength at high temperatures, and which has better air low permeability, chemical solution low permeability, 110° C. high-temperature rigidity, creep resistance, abrasion resistance and carbon dioxide low permeability. An excessively large content of the TFE unit of the copolymer possibly results in an increased haze value, decreased tensile strength at high temperatures, and poor abrasion resistance.

[0016] In the present disclosure, the content of each monomer unit in the copolymer is measured by a ^{19}F-NMR method.

[0017] The copolymer can also contain a monomer unit derived from a monomer copolymerizable with TFE and PPVE. In this case, the content of the monomer unit copolymerizable with TFE and PPVE is, with respect to the whole of the monomer units of the copolymer, preferably 0 to 2.1% by mass, more preferably 0.05 to 1.5% by mass, and still more preferably 0.1 to 0.9% by mass.

[0018] The monomers copolymerizable with TFE and PPVE may include hexafluoropropylene (HFP), vinyl monomers represented by $CZ^1Z^2\!=\!CZ^3(CF_2)_nZ^4$ wherein Z^1, Z^2 and Z^3 are identical or different, and represent H or F; Z^4 represents H, F or Cl; and n represents an integer of 2 to 10, perfluoro(alkyl vinyl ether) [PAVE] represented by $CF_2\!=\!CF\!-\!ORf^1$ wherein Rf^1 is a perfluoroalkyl group having 1 to 8 carbon atoms (excluding PPVE), and alkyl perfluorovinyl ether derivatives represented by $CF_2\!=\!CF\!-\!OCH_2\!-\!Rf^1$ wherein Rf^1 represents a perfluoroalkyl group having 1 to 5 carbon atoms. Among these, HFP is preferred.

[0019] The copolymer is preferably at least one selected from the group consisting of a copolymer consisting only of the TFE unit and the PPVE unit, and TFE/HFP/PPVE copolymer, and is more preferably a copolymer consisting only of the TFE unit and the PPVE unit.

[0020] The melt flow rate (MFR) of the copolymer is 0.5 to 1.5 g/10 min. The MFR of the copolymer is preferably 0.6 g/10 min or higher, more preferably 0.7 g/10 min or higher, still more preferably 0.8 g/10 min or higher, and especially preferably 0.9 g/10 min or higher, and is preferably 1.4 g/10 min or lower, more preferably 1.3 g/10 min or lower, and still more preferably 1.1 g/10 min or lower. Due to that the MFR of the copolymer is in the above range, the copolymer hardly deforms even in a molten state, and a thick sheet having a uniform thickness can be easily obtained by extrusion forming. Also, by using such a copolymer, there can be obtained a formed article that has extremely good transparency, that has a low compression set rate, that has high tensile strength at high temperatures, and that has excellent high-temperature rigidity, abrasion resistance, and carbon dioxide low permeability. When the MFR of the copolymer is excessively high, it is difficult to produce a thick sheet having a uniform thickness and, also, the obtained formed article has poor transparency, abrasion resistance, compression set resistance, and tensile strength at high temperatures. When the MFR of the copolymer is excessively low, extrusion pressure during forming is increased, moldability is impaired, and the obtained formed article has poor air permeability, 110° C. high-temperature rigidity, and carbon dioxide low permeability.

[0021] In the present disclosure, the MFR is a value obtained as a mass (g/10 min) of the polymer flowing out from a nozzle having an inner diameter of 2.1 mm and a length of 8 mm per 10 min at 372° C. under a load of 5 kg using a melt indexer, according to ASTM D1238.

[0022] The MFR can be regulated by regulating the kind and amount of a polymerization initiator to be used in polymerization of monomers, the kind and amount of a chain transfer agent, and the like.

[0023] In the present disclosure, the number of functional groups per 10^6 main-chain carbon atoms of the copolymer is 20 or less. The number of functional groups per 10^6 main-chain carbon atoms of the copolymer is preferably 15 or less, more preferably 10 or less, and still more preferably less than 6. Due to that the number of functional groups of the copolymer is in the above range, a formed article can be obtained that has excellent carbon dioxide low permeability, air low permeability, chemical solution low permeability and creep resistance, and that hardly makes fluorine ions to dissolve out in a chemical solution such as a hydrogen peroxide solution.

[0024] For identification of the kind of the functional groups and measurement of the number of the functional groups, infrared spectroscopy can be used.

[0025] The number of the functional groups is measured, specifically, by the following method. First, the copolymer is formed by cold press to prepare a film of 0.25 to 0.30 mm in thickness. The film is analyzed by Fourier transform infrared spectroscopy to obtain an infrared absorption spectrum, and a difference spectrum against a base spectrum that is completely fluorinated and has no functional groups is obtained. From an absorption peak of a specific functional group observed on this difference spectrum, the number N of

the functional group per 1×10^6 carbon atoms in the copolymer is calculated according to the following formula (A).

$$N=I \times K/t \qquad (A)$$

[0026] I: absorbance

[0027] K: correction factor

[0028] t: thickness of film (mm)

[0029] For reference, for some functional groups, the absorption frequency, the molar absorption coefficient and the correction factor are shown in Table 1. Then, the molar absorption coefficients are those determined from FT-IR measurement data of low molecular model compounds.

TABLE 1

Functional Group	Absorption Frequency (cm−1)	Molar Extinction Coefficient (l/cm/mol)	Correction Factor	Model Compound
—COF	1883	600	388	$C_7F_{15}COF$
—COOH free	1815	530	439	$H(CF_2)_6COOH$
—COOH bonded	1779	530	439	$H(CF_2)_6COOH$
—COOCH$_3$	1795	680	342	$C_7F_{15}COOCH_3$
—CONH$_2$	3436	506	460	$C_7H_{15}CONH_2$
—CH$_2$OH$_2$, —OH	3648	104	2236	$C_7H_{15}CH_2OH$
—CF$_2$H	3020	8.8	26485	$H(CF_2CF_2)_3CH_2OH$
—CF═CF$_2$	1795	635	366	CF_2═CF_2

[0030] Absorption frequencies of —CH$_2$CF$_2$H, —CH$_2$COF, —CH$_2$COOH, —CH$_2$COOOCH$_3$ and —CH$_2$CONH$_2$ are lower by a few tens of kaysers (cm^{-1}) than those of —CF$_2$H, —COF, —COOH free and —COOH bonded, —COOCH$_3$ and —CONH$_2$ shown in the Table, respectively.

[0031] For example, the number of the functional group —COF is the total of the number of a functional group determined from an absorption peak having an absorption frequency of 1,883 cm-1 derived from —CF$_2$COF and the number of a functional group determined from an absorption peak having an absorption frequency of 1,840 cm^{-1} derived from —CH$_2$COF.

[0032] The functional groups are ones present on main chain terminals or side chain terminals of the copolymer, and ones present in the main chain or the side chains. The number of the functional groups may be the total of numbers of —CF═CF$_2$, —CF$_2$H, —COF, —COOH, —COOCH$_3$, —CONH$_2$ and —CH$_2$OH.

[0033] The functional groups are introduced to the copolymer by, for example, a chain transfer agent or a polymerization initiator used for production of the copolymer. For example, in the case of using an alcohol as the chain transfer agent, or a peroxide having a structure of —CH$_2$OH as the polymerization initiator, —CH$_2$OH is introduced on the main chain terminals of the copolymer. Alternatively, the functional group is introduced on the side chain terminal of the copolymer by polymerizing a monomer having the functional group.

[0034] By subjecting the copolymer to a fluorination treatment, a copolymer having the number of functional groups within the above range can be obtained. That is, the copolymer of the present disclosure is preferably one which is subjected to the fluorination treatment. Further, the copolymer of the present disclosure preferably has —CF$_3$ terminal groups.

[0035] The melting point of the copolymer is preferably 290 to 310° C. and more preferably 296 to 304° C. Due to that the melting point is in the above range, the copolymer more hardly deforms even in a molten state. Also, a copolymer that gives a formed article having a smaller compression set rate and higher tensile strength at high temperatures can be obtained.

[0036] In the present disclosure, the melting point can be measured by using a differential scanning calorimeter [DSC].

[0037] The copolymer of the present disclosure preferably has a haze value of 4.5% or less, and more preferably 4.0% or less. Due to that the haze value is in the above range, when the fluorine-containing copolymer of the present disclosure is used to obtain a formed article such as a sheet, a pipe, a piping, a joint, a flowmeter housing, a bottle, or a nut, it is easy to observe the inside of the formed article by visual observation, a camera or the like, and thus it is easy to check the flow rate and the residual quantity of the contents. The haze value can be lowered by regulating the content of the PPVE unit and the melt flow rate (MFR) of the copolymer. In the present disclosure, the haze value can be measured according to JIS K 7136.

[0038] In the copolymer of the present disclosure, it is preferable that the compression set rate is 45 to 77% as measured by allowing the copolymer to stand under the condition of a compressibility of 50% at 65° C. for 72 hours. Due to that the compression set rate at 65° C. is in the above range, a formed article can be obtained that hardly deforms or even when a load is continuously applied for a long term.

[0039] In the present disclosure, the compression set rate can be measured according to a method described in ASTM D395 or JIS K6262:2013.

[0040] The copolymer of the present disclosure preferably has a tensile strength at 150° C. of 20.5 MPa or higher. Due to that the tensile strength at 150° C. is in the above range, the obtained formed article can exhibit high durability even at high temperatures and high pressures. The tensile strength at 150° C. can be raised by regulating the content of the PPVE unit and the melt flow rate (MFR) of the copolymer. In the present disclosure, the tensile strength at 150° C. can be measured according to ASTM D638.

[0041] The carbon dioxide permeability coefficient of the copolymer is preferably 2,300 cm^3·mm/(m^2·24 h·atm) or less, and more preferably 2,250 cm^3·mm/(m^2·24 h·atm) or less. Due to that the content of the PPVE unit, the melt flow rate (MFR), and the number of functional groups of the copolymer containing the TFE unit and the PPVE unit are suitably regulated, the copolymer of the present disclosure has excellent carbon dioxide low permeability. Accordingly, for example, the formed article obtained by using the copolymer of the present disclosure can suitably be used as a sealing member for preventing a carbon dioxide refrigerant from leaking.

[0042] In the present disclosure, the carbon dioxide permeability coefficient can be measured under the condition having a test temperature of 70° C. and a test humidity of 0% RH. Specific measurement of the carbon dioxide permeability coefficient can be carried out by a method described in the Examples.

[0043] The air permeability coefficient of the copolymer is preferably 620 cm³·mm/(m²·24 h·atm) or less, and more preferably 600 cm³·mm/(m²·24 h·atm) or less. Due to that the content of the PPVE unit, the melt flow rate (MFR), and the number of functional groups of the copolymer containing the TFE unit and the PPVE unit are suitably regulated, the copolymer of the present disclosure has excellent air low permeability.

[0044] In the present disclosure, the air permeability coefficient can be measured under the condition of a test temperature of 70° C. and a test humidity of 0% RH. Specific measurement of the air permeability coefficient can be carried out by a method described in the Examples.

[0045] The ethyl acetate permeability of the copolymer is preferably 7.8 g·cm/m² or lower, and more preferably 7.2 g·cm/m² or lower. Due to that the content of PPVE unit, the melt flow rate (MFR), and the number of functional groups of the copolymer containing the TFE unit and the PPVE unit are suitably regulated, the copolymer of the present disclosure has excellent ethyl acetate low permeability. That is, by using the copolymer of the present disclosure, a formed article that hardly makes a chemical solution such as ethyl acetate to permeate can be obtained.

[0046] In the present disclosure, the ethyl acetate permeability can be measured under the condition of a temperature of 60° C. and for 45 days. Specific measurement of the ethyl acetate permeability can be carried out by a method described in the Examples.

[0047] The copolymer of the present disclosure can be produced by a polymerization method such as suspension polymerization, solution polymerization, emulsion polymerization or bulk polymerization. The polymerization method is preferably emulsion polymerization or suspension polymerization. In these polymerization methods, conditions such as temperature and pressure, and a polymerization initiator and other additives can suitably be set depending on the formulation and the amount of the copolymer.

[0048] As the polymerization initiator, an oil-soluble radical polymerization initiator, or a water-soluble radical polymerization initiator may be used.

[0049] The oil-soluble radical polymerization initiator may be a known oil-soluble peroxide, and examples thereof typically include:

[0050] dialkyl peroxycarbonates such as di-n-propyl peroxydicarbonate, diisopropyl peroxydicarbonate, di-sec-butyl peroxydicarbonate and di-2-ethoxyethyl peroxydicarbonate;

[0051] peroxyesters such as t-butyl peroxyisobutyrate and t-butyl peroxypivalate;

[0052] dialkyl peroxides such as di-t-butyl peroxide; and

[0053] di[fluoro(or fluorochloro)acyl] peroxides.

[0054] The di[fluoro(or fluorochloro)acyl] peroxides include diacyl peroxides represented by [(RfCOO)—]₂ wherein Rf is a perfluoroalkyl group, an ω-hydroperfluoroalkyl group, or a fluorochloroalkyl group.

[0055] Examples of the di[fluoro(or fluorochloro)acyl] peroxides include di(ω-hydro-dodecafluorohexanoyl) peroxide, di(ω-hydro-tetradecafluoroheptanoyl) peroxide, di((ω-hydrohexadecafluorononanoyl) peroxide, di(perfluoropropionyl) peroxide, di(perfluorobutyryl) peroxide, di(perfluorovaleryl) peroxide, di(perfluorohexanoyl) peroxide, di(perfluoroheptanoyl) peroxide, di(perfluorooctanoyl) peroxide, di(perfluorononanoyl) peroxide, di(ω-chloro-hexafluorobutyryl) peroxide, di(ω-chloro-decafluorohexanoyl) peroxide, di(ω-chloro-tetradecafluorooctanoyl) peroxide, ω-hydrododecafluoroheptanoyl-ω-hydrohexadecafluorononanoyl peroxide, ω-chloro-hexafluorobutyryl-ω-chloro-decafluorohexanoyl peroxide, ω-hydrododecafluoroheptanoyl-perfluorobutyryl peroxide, di(dichloropentafluorobutanoyl) peroxide, di(trichlorooctafluorohexanoyl) peroxide, di(tetrachloroundecafluorooctanoyl) peroxide, di(pentachlorotetradecafluorodecanoyl) peroxide, and di(undecachlorotriacontafluorodocosanoyl) peroxide.

[0056] The water-soluble radical polymerization initiator may be a known water-soluble peroxide, and examples thereof include ammonium salts, potassium salts and sodium salts of persulfuric acid, perboric acid, perchloric acid, perphosphoric acid, percarbonic acid and the like, organic peroxides such as disuccinoyl peroxide and diglutaroyl peroxide, and t-butyl permaleate and t-butyl hydroperoxide. A reductant such as a sulfite salt may be combined with a peroxide and used, and the amount thereof to be used may be 0.1 to 20 times with respect to the peroxide.

[0057] In the polymerization, a surfactant, a chain transfer agent and a solvent may be used, which are conventionally known.

[0058] The surfactant may be a known surfactant, for example, nonionic surfactants, anionic surfactants and cationic surfactants may be used. Among these, fluorine-containing anionic surfactants are preferred, and more preferred are linear or branched fluorine-containing anionic surfactants having 4 to 20 carbon atoms, which may contain an ether bond oxygen (that is, an oxygen atom may be inserted between carbon atoms). The amount of the surfactant to be added (with respect to water in the polymerization) is preferably 50 to 5,000 ppm.

[0059] Examples of the chain transfer agent include hydrocarbons such as ethane, isopentane, n-hexane, and cyclohexane; aromatics such as toluene and xylene; ketones such as acetone; acetate esters such as ethyl acetate and butyl acetate; alcohols such as methanol and ethanol; mercaptans such as methylmercaptan; and halogenated hydrocarbons such as carbon tetrachloride, chloroform, methylene chloride and methyl chloride. The amount of the chain transfer agent to be added may vary depending on the chain transfer constant value of the compound to be used, but is usually in the range of 0.01 to 20% by mass with respect to the solvent in the polymerization.

[0060] The solvent may include water and mixed solvents of water and an alcohol.

[0061] In the suspension polymerization, in addition to water, a fluorinated solvent may be used. The fluorosolvent may include hydrochlorofluoroalkanes such as CH_3CClF_2, CH_3CCl_2F, $CF_3CF_2CCl_2H$ and CF_2ClCF_2CFHCl; chlorofluoroalaknes such as $CF_2ClCFClCF_2CF_3$ and $CF_3CFClCFClCF_3$; hydrofluroalkanes such as $CF_3CFHCFHCF_2CF_2CF_3$, $CF_2HCF_2CF_2CF_2CF_2H$ and $CF_3CF_2CF_2CF_2CF_2CF_2H$; hydrofluoroethers such as $CH_3OC_2F_5$, $CH_3OC_3F_5CF_3CF_2CH_2OCHF_2$, $CF_3CHFCF_2OCH_3$, $CHF_2CF_2OCH_2F$, $(CF_3)_2CHCF_2OCH_3$, $CF_3CF_2CH_2OCH_2CHF_2$ and $CF_3CHFCF_2OCH_2CF_3$; and perfluoroalkanes such as perfluorocyclobutane, $CF_3CF_2CF_2CF_3$, $CF_3CF_2CF_2CF_2CF_3$ and $CF_3CF_2CF_2CF_2CF_2CF_3$, and among these, perfluoroalkanes are preferred. The amount of the fluorosolvent to be used is,

from the viewpoint of suspensibility and the economic efficiency, preferably 10 to 100% by mass with respect to an aqueous medium.

[0062] The polymerization temperature is not limited, and may be 0 to 100° C. The polymerization pressure is suitably set depending on other polymerization conditions to be used such as the kind, the amount, and the vapor pressure of the solvent, and the polymerization temperature, but may usually be 0 to 9.8 MPaG.

[0063] In the case of obtaining an aqueous dispersion containing the copolymer by the polymerization reaction, the copolymer can be recovered by coagulating, washing and drying the copolymer contained in the aqueous dispersion. Then in the case of obtaining the copolymer as a slurry by the polymerization reaction, the copolymer can be recovered by taking out the slurry from a reaction container, and washing and drying the slurry. The copolymer can be recovered in a shape of powder by the drying.

[0064] The copolymer obtained by the polymerization may be formed into pellets. A method of forming into pellets is not limited, and a conventionally known method can be used. Examples thereof include methods of melt extruding the copolymer by using a single-screw extruder, a twin-screw extruder or a tandem extruder and cutting the resultant into a predetermined length to form the copolymer into pellets. The extrusion temperature in the melt extrusion needs to be varied depending on the melt viscosity and the production method of the copolymer, and is preferably the melting point of the copolymer+20° C. to the melting point of the copolymer+140° C. A method of cutting the copolymer is not limited, and a conventionally known method can be adopted such as a strand cut method, a hot cut method, an underwater cut method, or a sheet cut method. Volatile components in the obtained pellets may be removed by heating the pellets (degassing treatment). Alternatively, the obtained pellets may be treated by bringing the pellets into contact with hot water of 30 to 200° C., steam of 100 to 200° C. or hot air of 40 to 200° C.

[0065] Alternatively, the copolymer obtained by the polymerization may be subjected to fluorination treatment. The fluorination treatment can be carried out by bringing the copolymer having been subjected to no fluorination treatment into contact with a fluorine-containing compound. By the fluorination treatment, thermally unstable functional groups of the copolymer, such as —COOH, —COOCH$_3$, —CH$_2$OH, —COF, —CF=CF$_2$ and —CONH$_2$, and thermally relatively stable functional groups thereof, such as —CF$_2$H, can be converted to thermally very stable —CF$_3$. Consequently, the total number (number of functional groups) of —COOH, —COOCH$_3$, —CH$_2$OH, —COF, —CF=CF$_2$, —CONH$_2$ and —CF$_2$H of the copolymer can easily be controlled in the above-mentioned range.

[0066] The fluorine-containing compound is not limited, but includes fluorine radical sources generating fluorine radicals under the fluorination treatment condition. The fluorine radical sources include F$_2$ gas, CoF$_3$, AgF$_2$, UF$_6$, OF$_2$, N$_2$F$_2$, CF$_3$OF, and halogen fluorides (for example, IF$_5$ and ClF$_3$).

[0067] The fluorine radical source such as F$_2$ gas may be, for example, one having a concentration of 100%, but from the viewpoint of safety, the fluorine radical source is preferably mixed with an inert gas and diluted therewith to 5 to 50% by mass, and then used; and it is more preferably to be diluted to 15 to 30% by mass. The inert gas include nitrogen

gas, helium gas and argon gas, but from the viewpoint of the economic efficiency, nitrogen gas is preferred.

[0068] The condition of the fluorination treatment is not limited, and the copolymer in a melted state may be brought into contact with the fluorine-containing compound, but the fluorination treatment can be carried out usually at a temperature of not higher than the melting point of the copolymer, preferably at 20 to 240° C. and more preferably at 100 to 220° C. The fluorination treatment is carried out usually for 1 to 30 hours and preferably 5 to 25 hours. The fluorination treatment is preferred which brings the copolymer having been subjected to no fluorination treatment into contact with fluorine gas (F$_2$ gas).

[0069] A composition may be obtained by mixing the copolymer of the present disclosure and as required, other components. The other components include fillers, plasticizers, processing aids, mold release agents, pigments, flame retarders, lubricants, light stabilizers, weathering stabilizers, electrically conductive agents, antistatic agents, ultraviolet absorbents, antioxidants, foaming agents, perfumes, oils, softening agents and dehydrofluorination agents.

[0070] Examples of the fillers include silica, kaolin, clay, organo clay, talc, mica, alumina, calcium carbonate, calcium terephthalate, titanium oxide, calcium phosphate, calcium fluoride, lithium fluoride, crosslinked polystyrene, potassium titanate, carbon, boron nitride, carbon nanotube and glass fiber. The electrically conductive agents include carbon black. The plasticizers include dioctyl phthalate and pentaerythritol. The processing aids include carnauba wax, sulfone compounds, low molecular weight polyethylene and fluorine-based auxiliary agents. The dehydrofluorination agents include organic oniums and amidines.

[0071] As the above-mentioned other components, other copolymers other than the copolymer may be used. The other polymers include fluororesins other than the copolymer, fluoroelastomer, and non-fluorinated polymers.

[0072] A method of producing the composition includes a method of dry mixing the copolymer and the other components, and a method of previously mixing the copolymer and the other components by a mixer and then melt kneading the mixture by a kneader, melt extruder or the like.

[0073] The copolymer of the present disclosure or the above-mentioned composition can be used as a processing aid, a forming material and the like, and is suitably used as a forming material. There can also be utilized aqueous dispersions, solutions and suspensions of the copolymer of the present disclosure, and the copolymer/solvent-based materials; and these can be used for application of coating materials, encapsulation, impregnation, and casting of films. However, since the copolymer of the present disclosure has the above-mentioned properties, it is preferable to use the copolymer as the forming material.

[0074] Formed articles may be obtained by forming the copolymer of the present disclosure or the above composition.

[0075] A method of forming the copolymer or the composition is not limited, and includes injection molding, extrusion forming, compression molding, blow molding, transfer molding, rotomolding, and rotolining molding. As the forming method, among these, preferable are extrusion forming, compression molding, and transfer molding; more preferable are extrusion forming and transfer molding from the viewpoint of being able to produce formed articles in a high productivity, and still more preferable is extrusion

forming. That is, it is preferable that formed articles are extrusion formed articles, compression molded articles, injection molded articles or transfer molded articles; and from the viewpoint of being able to produce molded articles in a high productivity, being extrusion formed articles or transfer molded articles is more preferable, and being extrusion formed articles is still more preferable. By forming the copolymer of the present disclosure by extrusion forming or transfer molding, a visually attractive formed article can be obtained.

[0076] The formed article containing the copolymer of the present disclosure may be, for example, a nut, a bolt, a joint, a film, a bottle, a gasket, an electric wire coating, a tube, a hose, a pipe, a valve, a sheet, a seal, a packing, a tank, a roller, a container, a cock, a connector, a filter housing, a filter cage, a flow meter, a pump, a wafer carrier, and a wafer box.

[0077] The copolymer of the present disclosure, the above composition and the above formed article can be used, for example, in the following applications.

[0078] Food packaging films, and members for liquid transfer for food production apparatuses, such as lining materials of fluid transfer lines, packings, sealing materials and sheets, used in food production processes;

[0079] chemical stoppers and packaging films for chemicals, and members for chemical solution transfer, such as lining materials of liquid transfer lines, packings, sealing materials and sheets, used in chemical production processes;

[0080] inner surface lining materials of chemical solution tanks and piping of chemical plants and semiconductor factories;

[0081] members for fuel transfer, such as 0 (square) rings, tubes, packings, valve stem materials, hoses and sealing materials, used in fuel systems and peripheral equipment of automobiles, and such as hoses and sealing materials, used in ATs of automobiles;

[0082] members used in engines and peripheral equipment of automobiles, such as flange gaskets of carburetors, shaft seals, valve stem seals, sealing materials and hoses, and other vehicular members such as brake hoses, hoses for air conditioners, hoses for radiators, and electric wire coating materials;

[0083] members for chemical transfer for semiconductor production apparatuses, such as O (square) rings, tubes, packings, valve stem materials, hoses, sealing materials, rolls, gaskets, diaphragms and joints;

[0084] members for coating and inks, such as coating rolls, hoses and tubes, for coating facilities, and containers for inks;

[0085] members for food and beverage transfer, such as tubes, hoses, belts, packings and joints for food and beverage, food packaging materials, and members for glass cooking appliances;

[0086] members for waste liquid transport, such as tubes and hoses for waste transport;

[0087] members for high-temperature liquid transport, such as tubes and hoses for high-temperature liquid transport;

[0088] members for steam piping, such as tubes and hoses for steam piping;

[0089] corrosionproof tapes for piping, such as tapes wound on piping of decks and the like of ships;

[0090] various coating materials, such as electric wire coating materials, optical fiber coating materials, and transparent front side coating materials installed on the light incident side and back side lining materials of photoelectromotive elements of solar cells;

[0091] diaphragms and sliding members such as various types of packings of diaphragm pumps;

[0092] films for agriculture, and weathering covers for various kinds of roof materials, sidewalls and the like;

[0093] interior materials used in the building field, and coating materials for glasses such as non-flammable fireproof safety glasses; and

[0094] lining materials for laminate steel sheets used in the household electric field.

[0095] The fuel transfer members used in fuel systems of automobiles further include fuel hoses, filler hoses, and evap hoses. The above fuel transfer members can also be used as fuel transfer members for gasoline additive-containing fuels, resultant to sour gasoline, resistant to alcohols, and resultant to methyl tertiary butyl ether and amines and the like.

[0096] The above chemical stoppers and packaging films for chemicals have excellent chemical resistance to acids and the like. The above chemical solution transfer members also include corrosion-proof tapes wound on chemical plant pipes.

[0097] The above formed articles also include vehicular radiator tanks, chemical solution tanks, bellows, spacers, rollers and gasoline tanks, waste solution transport containers, high-temperature liquid transport containers and fishery and fish farming tanks.

[0098] The above formed articles further include members used for vehicular bumpers, door trims and instrument panels, food processing apparatuses, cooking devices, water- and oil-repellent glasses, illumination-related apparatuses, display boards and housings of QA devices, electrically illuminated billboards, displays, liquid crystal displays, cell phones, printed circuit boards, electric and electronic components, sundry goods, dust bins, bathtubs, unit baths, ventilating fans, illumination frames and the like.

[0099] Due to that the formed articles containing the copolymer of the present disclosure have extremely good transparency, have a low compression set rate, have high tensile strength at high temperatures, have excellent air low permeability, chemical solution low permeability, 110° C. high-temperature rigidity, creep resistance, abrasion resistance and carbon dioxide low permeability, hardly make fluorine ions to dissolve out in a chemical solution such as a hydrogen peroxide solution, and thus can suitably be utilized as nuts, bolts, joints, packings, valves, cocks, connectors, filter housings, filter cages, flow meters, pumps, or the like. Among these, the formed articles can suitably be utilized as a piping member (in particular, a valve and a joint) used to transfer a chemical solution or as a flowmeter housing having a flow path for a chemical solution in a flowmeter. The piping member and the flowmeter housing of the present disclosure have extremely good transparency, a small compression set rate, and high tensile strength at high temperatures. Accordingly, the piping member and the flowmeter housing of the present disclosure have excellent inside-visibility and, especially in the flowmeter housing, enable the float inside to be easily observed by visual observation, a camera or the like, and are hardly damaged

even when repeatedly receiving stress resulting from starting and stopping the circulation of a chemical solution or changing the flow rate.

[0100] Due to that the formed articles containing the copolymer of the present disclosure have extremely good transparency, have a low compression set rate, have high tensile strength at high temperatures, have excellent air low permeability, chemical solution low permeability, 110° C. high-temperature rigidity, creep resistance, abrasion resistance and carbon dioxide low permeability, hardly make fluorine ions to dissolve out in a chemical solution such as a hydrogen peroxide solution, the formed articles can suitably be utilized as members to be compressed such as gaskets or packings. The members to be compressed of the present disclosure may be gaskets or packings. The gaskets or packings of the present disclosure have extremely good transparency, have a low compression set rate, have high tensile strength at high temperatures, have excellent air low permeability, chemical solution low permeability, 110° C. high-temperature rigidity, creep resistance, abrasion resistance and carbon dioxide low permeability, and hardly make fluorine ions to dissolve out in a chemical solution such as a hydrogen peroxide solution. Also, the members to be compressed of the present disclosure have excellent carbon dioxide low permeability, and thus can suitably be used as a sealing member for preventing a carbon dioxide refrigerant from leaking.

[0101] The members to be compressed of the present disclosure, even when being deformed at a high compression deformation rate, exhibit excellent compression set resistance. The members to be compressed of the present disclosure can be used in a state of being compressed at a compression deformation rate of 10% or higher, and can be used in a state of being compressed at a compression deformation rate of 20% or higher or 25% or higher. By using the members to be compressed of the present disclosure by being deformed at such a high compression deformation rate, a certain rebound resilience can be retained for a long term and the sealing property and the insulating property can be retained for a long term.

[0102] In the case where the members to be compressed are used in a state of being compressed, the compression deformation rate is a compression deformation rate of a portion having the highest compression deformation rate. For example, in the case where a flat member to be compressed is used in a state of being compressed in the thickness direction, the compression deformation rate is that in the thickness direction. Further, for example, in the case where a member to be compressed is used with only some portions of the member in a state of being compressed, the compression deformation rate is that of a portion having the highest compression deformation rate among compression deformation rates of the compressed portions.

[0103] The size and shape of the members to be compressed of the present disclosure may suitably be set according to applications, and are not limited. The shape of the members to be compressed of the present disclosure may be, for example, annular. The members to be compressed of the present disclosure may also have, in plan view, a circular shape, an elliptic shape, a corner-rounded square or the like, and may be a shape having a throughhole in the central portion thereof.

[0104] It is preferable that the members to be compressed of the present disclosure are used as members constituting non-aqueous electrolyte batteries. The members to be compressed of the present disclosure have excellent water vapor low permeability are especially suitable as members used in a state of contacting with a non-aqueous electrolyte in the non-aqueous electrolyte batteries. That is, the members to be compressed of the present disclosure may also be ones having a liquid-contact surface with a non-aqueous electrolyte in the non-aqueous electrolyte batteries.

[0105] The non-aqueous electrolyte batteries are not limited as long as being batteries having a non-aqueous electrolyte, and examples thereof include lithium ion secondary batteries and lithium ion capacitors. Members constituting the non-aqueous electrolyte batteries include sealing members and insulating members.

[0106] For the non-aqueous electrolyte, one or two or more of well-known solvents can be used such as propylene carbonate, ethylene carbonate, butylene carbonate, γ-butyl-lactone, 1,2-dimethoxyethane, 1,2-diethoxyethane, dimethyl carbonate, diethyl carbonate and ethyl methyl carbonate. The non-aqueous electrolyte batteries may further have an electrolyte. The electrolyte is not limited, but may be $LiClO_4$, $LiAsF_6$, $LiPF_6$, $LiBF_4$, $LiCl$, $LiBr$, CH_3SO_3Li, CF_3SO_3Li, cesium carbonate and the like.

[0107] The members to be compressed of the present disclosure can suitably be utilized, for example, as sealing members such as sealing gaskets or sealing packings, and insulating members such as insulating gaskets and insulating packings. The sealing members are members to be used for preventing leakage of a liquid or a gas, or penetration of a liquid or a gas from the outside. The insulating members are members to be used for insulating electricity. The members to be compressed of the present disclosure may be members to be used for the purpose of both of sealing and insulation.

[0108] Due to that the members to be compressed of the present disclosure have a small compression set rate and high tensile strength at high temperatures, the members to be compressed can suitably be used as sealing members for non-aqueous electrolyte batteries or insulating members for non-aqueous electrolyte batteries. For example, in the charge time of batteries such as non-aqueous electrolyte secondary batteries, the temperature of the batteries temporarily may become 40° C. or higher, specially temporarily become 150° C. or higher in some cases. Even when the members to be compressed of the present disclosure are used by being deformed at high temperatures and at a high compression deformation rate in the batteries such as non-aqueous electrolyte secondary batteries, and moreover are brought into contact with non-aqueous electrolytes at high temperatures in non-aqueous electrolyte, a high rebound resilience is not impaired. Therefore, the members to be compressed of the present disclosure, in the case of being used as sealing members, have excellent sealing property and also at high temperatures, retain the sealing property for a long term. Further, the members to be compressed of the present disclosure, due to containing the above copolymer, have excellent insulating property. Therefore, in the case of using the members to be compressed of the present disclosure as insulating members, the members firmly adhere to two or more electrically conductive members and prevent short circuit over a long term.

[0109] The copolymer of the present disclosure can suitably be utilized as a material for forming an electric wire coating.

[0110] The coated electric wire has a core wire, and the coating layer installed on the periphery of the core wire and containing the copolymer of the present disclosure. For example, an extrusion formed article made by melt extruding the copolymer of the present disclosure on a core wire can be made into the coating layer. The coated electric wires are suitable to LAN cables (Ethernet cables), high-frequency transmission cables, flat cables, heat-resistant cables and the like, and among these, suitable to transmission cables such as LAN cables (Ethernet cables) and high-frequency transmission cables.

[0111] As a material for the core wire, for example, a metal conductor material such as copper or aluminum can be used. The core wire is preferably one having a diameter of 0.02 to 3 mm. The diameter of the core wire is more preferably 0.04 mm or larger, still more preferably 0.05 mm or larger and especially preferably 0.1 mm or larger. The diameter of the core wire is more preferably 2 mm or smaller.

[0112] With regard to specific examples of the core wire, for example, AWG (American Wire Gauge)-46 (solid copper wire of 40 μm in diameter), AWG-26 (solid copper wire of 404 μm in diameter), AWG-24 (solid copper wire of 510 μm in diameter), and AWG-22 (solid copper wire of 635 μm in diameter) may be used.

[0113] The coating layer is preferably one having a thickness of 0.1 to 3.0 mm. It is also preferable that the thickness of the coating layer is 2.0 mm or smaller.

[0114] The high-frequency transmission cables include coaxial cables. The coaxial cables generally have a structure configured by laminating an inner conductor, an insulating coating layer, an outer conductor layer and a protective coating layer in order from the core part to the peripheral part. A formed article containing the copolymer of the present disclosure can suitably be utilized as the insulating coating layer containing the copolymer. The thickness of each layer in the above structure is not limited, but is usually: the diameter of the inner conductor is approximately 0.1 to 3 mm; the thickness of the insulating coating layer is approximately 0.3 to 3 mm; the thickness of the outer conductor layer is approximately 0.5 to 10 mm; and the thickness of the protective coating layer is approximately 0.5 to 2 mm.

[0115] Alternatively, the coating layer may be one containing cells, and is preferably one in which cells are homogeneously distributed.

[0116] The average cell size of the cells is not limited, but is, for example, preferably 60 μm or smaller, more preferably 45 μm or smaller, still more preferably 35 μm or smaller, further still more preferably 30 μm or smaller, especially preferably 25 μm or smaller and further especially preferably 23 μm or smaller. Then, the average cell size is preferably 0.1 μm or larger and more preferably 1 μm or larger. The average cell size can be determined by taking an electron microscopic image of an electric wire cross section, calculating the diameter of each cell by image processing and averaging the diameters.

[0117] The foaming ratio of the coating layer may be 20% or higher, and is more preferably 30% or higher, still more preferably 33% or higher and further still more preferably 35% or higher. The upper limit is not limited, but is, for example, 80%. The upper limit of the foaming ratio may be 60%. The foaming ratio is a value determined as ((the specific gravity of an electric wire coating material–the specific gravity of the coating layer)/(the specific gravity of the electric wire coating material)×100. The foaming ratio can suitably be regulated according to applications, for example, by regulation of the amount of a gas, described later, to be injected in an extruder, or by selection of the kind of a gas dissolving.

[0118] Alternatively, the coated electric wire may have another layer between the core wire and the coating layer, and may further have another layer (outer layer) on the periphery of the coating layer. In the case where the coating layer contains cells, the electric wire of the present disclosure may be of a two-layer structure (skin-foam) in which a non-foaming layer is inserted between the core wire and the coating layer, a two-layer structure (foam-skin) in which a non-foaming layer is coated as the outer layer, or a three-layer structure (skin-foam-skin) in which a non-foaming layer is coated as the outer layer of the skin-foam structure. The non-foaming layer is not limited, and may be a resin layer composed of a resin, such as a TFE/HFP-based copolymer, a TFE/PAVE copolymer, a TFE/ethylene-based copolymer, a vinylidene fluoride-based polymer, a polyolefin resin such as polyethylene [PE], or polyvinyl chloride [PVC].

[0119] The coated electric wire can be produced, for example, by using an extruder, heating the copolymer, extruding the copolymer in a molten state on the core wire to thereby form the coating layer.

[0120] In formation of a coating layer, by heating the copolymer and introducing a gas in the copolymer in a molten state, the coating layer containing cells can be formed. As the gas, there can be used, for example, a gas such as chlorodifluoromethane, nitrogen or carbon dioxide, or a mixture thereof. The gas may be introduced as a pressurized gas in the heated copolymer, or may be generated by mingling a chemical foaming agent in the copolymer. The gas dissolves in the copolymer in a molten state.

[0121] The copolymer of the present disclosure can suitably be utilized as a material for products for high-frequency signal transmission.

[0122] The products for high-frequency signal transmission are not limited as long as being products to be used for transmission of high-frequency signals, and include (1) formed boards such as insulating boards for high-frequency circuits, insulating materials for connection parts and printed circuit boards, (2) formed articles such as bases of high-frequency vacuum tubes and antenna covers, and (3) coated electric wires such as coaxial cables and LAN cables. The products for high-frequency signal transmission can suitably be used in devices utilizing microwaves, particularly microwaves of 3 to 30 GHz, in satellite communication devices, cell phone base stations, and the like.

[0123] In the products for high-frequency signal transmission, the copolymer of the present disclosure can suitably be used as an insulator in that the dielectric loss tangent is low.

[0124] As the (1) formed boards, printed wiring boards are preferable in that the good electric property is provided. The printed wiring boards are not limited, but examples thereof include printed wiring boards of electronic circuits for cell phones, various computers, communication devices and the like. As the (2) formed articles, antenna covers are preferable in that the low dielectric loss is low.

[0125] Due to that the copolymer of the present disclosure hardly deforms even in a molten state and can easily provide a thick sheet having a uniform thickness and, moreover, the obtained formed article has extremely good transparency,

hardly deforms at high temperatures, has excellent tensile strength at high temperatures, air low permeability, chemical solution low permeability, 110° C. high-temperature rigidity, creep resistance, abrasion resistance and carbon dioxide low permeability, hardly makes fluorine ions to dissolve out in a chemical solution such as a hydrogen peroxide solution, the copolymer can suitably be utilized as a film or a sheet.

[0126] The film of the present disclosure is useful as a release film. The release films can be produced by forming the copolymer of the present disclosure by melt extrusion, calendering, press molding, casting or the like. From the viewpoint that uniform thin films can be obtained, the release films can be produced by melt extrusion.

[0127] The film of the present disclosure can be applied to the surface of a roll used in OA devices. The copolymer of the present disclosure is formed into required shapes, such as sheets, films or tubes, by extrusion forming, compression molding, press molding or the like, and can be used as surface materials of QA device rolls, OA device belts and the like. A thick sheet and a large pipe can be produced especially by melt extrusion forming.

[0128] The copolymer of the present disclosure hardly deforms even in a molten state, and thus a large-diameter pipe having high dimensional accuracy can be easily obtained by extrusion forming. Moreover, the obtained formed article has extremely good transparency, has a low compression set rate, has high tensile strength at high temperatures, has excellent air low permeability, chemical solution low permeability, 110° C. high-temperature rigidity, creep resistance, abrasion resistance and carbon dioxide low permeability, and hardly makes fluorine ions to dissolve out in a chemical solution such as a hydrogen peroxide solution. Accordingly, the fluorine-containing copolymer of the present disclosure can suitably be utilized for a tube or a pipe. The pipe containing the fluorine-containing copolymer of the present disclosure can be produced in a high productivity even when the diameter thereof is large and even when the thickness thereof is large, also, has a visually attractive shape, has extremely good transparency, has a low compression set rate, has high tensile strength at high temperatures, has excellent air low permeability, chemical solution low permeability, 110° C. high-temperature rigidity, creep resistance, abrasion resistance and carbon dioxide low permeability, and hardly makes fluorine ions to dissolve out in a chemical solution such as a hydrogen peroxide solution.

[0129] Due to that the formed article containing the copolymer of the present disclosure has extremely good transparency, has an excellent low compression set rate, has high tensile strength at high temperatures, has excellent air low permeability, chemical solution low permeability, 110° C. high-temperature rigidity, creep resistance, abrasion resistance and carbon dioxide low permeability, hardly makes fluorine ions to dissolve out in a chemical solution such as a hydrogen peroxide solution, the formed article can suitably be utilized as a bottle. The bottle of the present disclosure enables the contents to be easily viewed, and is hardly damaged during use.

[0130] So far, embodiments have been described, but it is to be understood that various changes and modifications of patterns and details may be made without departing from the subject matter and the scope of the claims.

[0131] According to the present disclosure, there is provided a copolymer comprising tetrafluoroethylene unit and perfluoro(propyl vinyl ether) unit, wherein the copolymer has a content of perfluoro(propyl vinyl ether) unit of 4.9 to 7.0% by mass with respect to the whole of the monomer units, a melt flow rate at 372° C. of 0.5 to 1.5 g/10 min, and the number of functional groups of 20 or less per 10^6 main-chain carbon atoms.

[0132] The copolymer of the present disclosure preferably has a melt flow rate at 372° C. of 0.7 to 1.3 g/10 min.

[0133] According to the present disclosure, an extrusion formed article and a transfer molded article comprising the above copolymer is further provided.

[0134] According to the present disclosure, a coated electric wire having a coating layer comprising the above copolymer is further provided.

[0135] According to the present disclosure, a formed article comprising the above copolymer, wherein the formed article is a sheet or a pipe is further provided.

EXAMPLES

[0136] The embodiments of the present disclosure will now be described by Examples as follows, but the present disclosure is not limited only to these Examples.

[0137] Each numerical value in the Examples was measured by the following methods.

[0138] (Content of Monomer Unit)

[0139] The content of each monomer unit was measured by an NMR analyzer (for example, manufactured by Bruker BioSpin GmbH, AVANCE 300, high-temperature probe).

[0140] (Melt Flow Rate (MFR))

[0141] The polymer was made to flow out from a nozzle having an inner diameter of 2.1 mm and a length of 8 mm at 372° C. under a load of 5 kg by using a Melt Indexer G-01 (manufactured by Toyo Seiki Seisaku-sho, Ltd.) according to ASTM D1238, and the mass (g/10 min) of the polymer flowing out per 10 min was determined.

[0142] (Number of Functional Groups)

[0143] Pellets of the copolymer was formed by cold press into a film of 0.25 to 0.30 mm in thickness. The film was 40 times scanned and analyzed by a Fourier transform infrared spectrometer [FT-IR (Spectrum One, manufactured by PerkinElmer, Inc.)] to obtain an infrared absorption spectrum, and a difference spectrum against a base spectrum that is completely fluorinated and has no functional groups is obtained. From an absorption peak of a specific functional group observed on this difference spectrum, the number N of the functional group per 1×10^6 carbon atoms in the sample was calculated according to the following formula (A).

$$N = I \times K / t \qquad (A)$$

[0144] I: absorbance

[0145] K: correction factor

[0146] t: thickness of film (mm)

[0147] For reference, the absorption frequency, the molar absorption coefficient and the correction factor for the functional groups in the present disclosure are shown in Table 2. The molar absorption coefficients are those determined from FT-IR measurement data of low molecular model compounds.

TABLE 2

Functional Group	Absorption Frequency (cm^{-1})	Molar Extinction Coefficient (l/cm/mol)	Correction Factor	Model Compound
—COF	1883	600	388	C$_7$F$_{15}$COF
—COOH free	1815	530	439	H(CF$_2$)$_6$COOH
—COOH bonded	1779	530	439	H(CF$_2$)$_6$COOH
—COOCH$_3$	1795	680	342	C$_7$F$_{15}$COOCH$_3$
—CONH$_2$	3436	506	460	C$_7$H$_{15}$CONH$_2$
—CH$_2$OH$_2$, —OH	3648	104	2236	C$_7$H$_{15}$CH$_2$OH
—CF$_2$H	3020	8.8	26485	H(CF$_2$CF$_2$)$_3$CH$_2$OH
—CF=CF$_2$	1795	635	366	CF$_2$=CF$_2$

[0148] (Melting Point)

[0149] The polymer was heated, as a first temperature raising step, at a temperature-increasing rate of 10° C./min from 200° C. to 350° C., then cooled at a cooling rate of 10° C./min from 350° C. to 200° C., and then again heated, as second temperature raising step, at a temperature-increasing rate of 10° C./min from 200° C. to 350° C. by using a differential scanning calorimeter (trade name: X-DSC7000, manufactured by Hitachi High-Tech Science Corporation); and the melting point was determined from a melting curve peak observed in the second temperature raising step.

Example 1

[0150] 26.6 L of pure water was charged in a 174 L-volume autoclave; nitrogen replacement was sufficiently carried out; thereafter, 30.4 kg of perfluorocyclobutane and 1.76 kg of perfluoro(propyl vinyl ether) (PPVE) were charged; and the temperature in the system was held at 35° C. and the stirring speed was held at 200 rpm. Then, tetrafluoroethylene (TFE) was introduced under pressure up to 0.58 MPa, and thereafter 0.010 kg of a 50% methanol solution of di-n-propyl peroxydicarbonate was charged to initiate polymerization. Since the pressure in the system decreased along with the progress of the polymerization, TFE was continuously supplied to make the pressure constant, and 0.058 kg of PPVE was added for every 1 kg of TFE supplied and the polymerization was continued for 6 hours. TFE was released to return the pressure in the autoclave to the atmospheric pressure, and thereafter, an obtained reaction product was washed with water and dried to thereby obtain 15 kg of a powder.

[0151] The obtained powder was melt extruded at 360° C. by a screw extruder (trade name: PCM46, manufactured by Ikegai Corp) to thereby obtain pellets of a TFE/PPVE copolymer. The PPVE content of the obtained pellets was measured by the method described above. The results are shown in Table 3.

[0152] The obtained pellets were put in a vacuum vibration-type reactor VVD-30 (manufactured by OKAWARA MFG. CO., LTD.), and heated to 210° C. After vacuumizing, F2 gas diluted to 20% by volume with N$_2$ gas was introduced to the atmospheric pressure. 0.5 hour after the F$_2$ gas introduction, vacuumizing was once carried out and F$_2$ gas was again introduced. Further, 0.5 hour thereafter, vacuumizing was again carried out and F$_2$ gas was again introduced. Thereafter, while the above operation of the F$_2$ gas introduction and the vacuumizing was carried out once every 1 hour, the reaction was carried out at a temperature

of 210° C. for 10 hours. After the reaction was finished, the reactor interior was replaced sufficiently by N$_2$ gas to finish the fluorination reaction. By using the fluorinated pellets, the above physical properties were measured by the methods described above. The results are shown in Table 3.

Example 2

[0153] Fluorinated pellets were obtained as in Example 1, except for changing the charged amount of PPVE to 2.12 kg, adding 0.068 kg of PPVE for every 1 kg of TFE supplied, and changing the polymerization time to 7 hours. The results are shown in Table 3.

Example 3

[0154] 51.8 L of pure water was charged in a 174 L-volume autoclave; nitrogen replacement was sufficiently carried out; thereafter, 40.9 kg of perfluorocyclobutane, 3.01 kg of perfluoro(propyl vinyl ether) (PPVE), and 0.92 kg of methanol were charged; and the temperature in the system was held at 35° C. and the stirring speed was held at 200 rpm. Then, tetrafluoroethylene (TFE) was introduced under pressure up to 0.64 MPa, and thereafter 0.013 kg of a 50% methanol solution of di-n-propyl peroxydicarbonate was charged to initiate polymerization. Since the pressure in the system decreased along with the progress of the polymerization, TFE was continuously supplied to make the pressure constant, and 0.063 kg of PPVE was additionally charged for every 1 kg of TFE supplied. The polymerization was finished at the time when the amount of TFE additionally charged reached 40.9 kg. Unreacted TFE was released to return the pressure in the autoclave to the atmospheric pressure, and thereafter, an obtained reaction product was washed with water and dried to thereby obtain 43.5 kg of a powder.

[0155] By using the obtained powder, the fluorination reaction was carried out as in Example 1 to thereby obtain fluorinated pellets. The results are shown in Table 3.

Comparative Example 1

[0156] 26.6 L of pure water was charged in a 174 L-volume autoclave; nitrogen replacement was sufficiently carried out; thereafter, 30.4 kg of perfluorocyclobutane, 1.32 kg of perfluoro(propyl vinyl ether) (PPVE), and 0.06 kg of methanol were charged; and the temperature in the system was held at 35° C. and the stirring speed was held at 200 rpm. Then, tetrafluoroethylene (TFE) was introduced under pressure up to 0.58 MPa, and thereafter 0.010 kg of a 50% methanol solution of di-n-propyl peroxydicarbonate was charged to initiate polymerization. Since the pressure in the system decreased along with the progress of the polymerization, TFE was continuously supplied to maintain make the pressure constant, and 0.046 kg of PPVE was added for every 1 kg of TFE supplied and the polymerization was continued for 5.5 hours. TFE was released to return the pressure in the autoclave to the atmospheric pressure, and thereafter, an obtained reaction product was washed with water and dried to thereby obtain 15 kg of a powder.

[0157] The obtained powder was melt extruded at 360° C. by a screw extruder (trade name: PCM46, manufactured by Ikegai Corp) to thereby obtain pellets of a TFE/PPVE copolymer. The PPVE content of the obtained pellets was measured by the method described above. The results are shown in Table 3.

[0158] The obtained pellets were put in a vacuum vibration-type reactor VVD-30 (manufactured by OKAWARA MFG. CO., LTD.), and heated to 210° C. After vacuumizing, F2 gas diluted to 20% by volume with N_2 gas was introduced to the atmospheric pressure. 0.5 hour after the F_2 gas introduction, vacuumizing was once carried out and F2 gas was again introduced. Further, 0.5 hour thereafter, vacuumizing was again carried out and F_2 gas was again introduced. Thereafter, while the above operation of the F2 gas introduction and the vacuumizing was carried out once every 1 hour, the reaction was carried out at a temperature of 210° C. for 10 hours. After the reaction was finished, the reactor interior was replaced sufficiently by N_2 gas to finish the fluorination reaction. By using the fluorinated pellets, the above physical properties were measured by the methods described above. The results are shown in Table 3.

Comparative Example 2

[0159] Fluorinated pellets were obtained as in Comparative Example 1, except for changing the charged amount of PPVE to 1.72 kg, changing the charged amount of methanol to 0.08 kg, adding 0.057 kg of PPVE for every 1 kg of TFE supplied, and changing the polymerization time to 6.5 hours. The results are shown in Table 3.

Comparative Example 3

[0160] Fluorinated pellets were obtained as in Comparative Example 1, except for changing the charged amount of PPVE to 2.12 kg, changing the charged amount of methanol to 0.03 kg, adding 0.068 kg of PPVE for every 1 kg of TFE supplied, and changing the polymerization time to 7 hours. The results are shown in Table 3.

Comparative Example 4

[0161] Non-fluorinated pellets were obtained as in Example 1, except for changing the charged amount of PPVE to 2.08 kg, adding 0.067 kg of PPVE for every 1 kg of TFE supplied, and changing the polymerization time to 7 hours. The results are shown in Table 3.

Comparative Example 5

[0162] 51.8 L of pure water was charged in a 174 L-volume autoclave; nitrogen replacement was sufficiently carried out; thereafter, 40.9 kg of perfluorocyclobutane and 3.33 kg of perfluoro(propyl vinyl ether) (PPVE) were charged; and the temperature in the system was held at 35° C. and the stirring speed was held at 200 rpm. Then, tetrafluoroethylene (TFE) was introduced under pressure up to 0.64 MPa, and thereafter 0.004 kg of a 50% methanol solution of di-n-propyl peroxydicarbonate was charged to initiate polymerization. Since the pressure in the system decreased along with the progress of the polymerization, TFE was continuously supplied to make the pressure constant, and 0.068 kg of PPVE was additionally charged for every 1 kg of TFE supplied. The polymerization was finished at the time when the amount of TFE additionally charged reached 40.9 kg. Unreacted TFE was released return the pressure in the autoclave to the atmospheric pressure, and thereafter, an obtained reaction product was washed with water and dried to thereby obtain 41.0 kg of a powder.
[0163] By using the obtained powder, the fluorination reaction was carried out as in Example 1 to thereby obtain fluorinated pellets. The results are shown in Table 3.

TABLE 3

	PPVE content (% by mass)	MFR (g/10 min)	Number of functional groups (groups/C10⁶)	Melting point (° C.)
Example 1	5.5	0.7	<6	301
Example 2	6.4	1.3	<6	298
Example 3	5.9	0.9	<6	301
Comparative Example 1	4.4	1.3	<6	302
Comparative Example 2	5.4	2.3	<6	301
Comparative Example 3	6.4	2.2	<6	298
Comparative Example 4	6.3	1.1	58	299
Comparative Example 5	6.4	0.2	<6	298

[0164] The description "<6" in Table 3 means that the number of functional groups is less than 6.
[0165] Then, by using the obtained pellets, the following properties were evaluated. The results are shown in Table 4.
[0166] (Haze Value)
[0167] By using the pellets and a heat press molding machine, a sheet of approximately 1.0 mm in thickness was prepared. The sheet was immersed in a quartz cell filled with pure water, and the haze value was measured according to JIS K 7136 using a haze meter (trade name: NDH 7000SP, manufactured by NIPPON DENSHOKU INDUSTRIES CO., LTD.).
[0168] (Compression Set Rate (CS))
[0169] The measurement of the compression set rate was carried out according to a method described in ASTM D395 or JIS K6262:2013.
[0170] Approximately 2 g of the pellets was charged in a metal mold (inner diameter: 13 mm, height: 38 mm), and in that state, melted by hot plate press at 370° C. for 30 min, thereafter, water-cooled under a pressure of 0.2 MPa (resin pressure) to thereby prepare a formed article of approximately 8 mm in height. Thereafter, the obtained molded article was cut to prepare a test piece of 13 mm in outer diameter and 6 mm in height. The prepared test piece was compressed to a compression deformation rate of 50% (that is, the test piece of 6 mm in height was compressed to a height of 3 mm) at a normal temperature by using a compression device.
[0171] Then, the compressed test piece being fixed on the compression device was allowed to stand still in an electric furnace at 65° C. for 72 hours. The compression device was taken out from the electric furnace, and cooled to room temperature; thereafter, the test piece was dismounted. The collected test piece was allowed to stand at room temperature for 30 min, and the height of the collected test piece was measured and the compression set rate was determined by the following formula.

Compression set rate $(\%)=(t_0-t_2)/(t_0-t_1)\times100$

[0172] t_0: an original height of the test piece (mm)
[0173] t_1: the height of a spacer (mm)
[0174] t_2: the height of the test piece dismounted from the compression device (mm)
[0175] In the above test, t_0 was 6 mm and t_1 was 3 mm.
[0176] (Tensile Strength (TS) at 150° C.)
[0177] The tensile strength at 150° C. was measured according to ASTM D638.

[0178] A formed article having high tensile strength at 150° C. has excellent pressure resistance.

[0179] (Sheet Formability)

[0180] A φ14 mm extruder (manufactured by Imoto machinery Co., LTD.) and a T die were used to form pellets to prepare a sheet. The extrusion conditions were as follows.

[0181] a) Take-up speed: 0.1 m/min

[0182] b) Roll temperature: 120° C.

[0183] c) Film width: 70 mm

[0184] d) Thickness: 1.00 mm

[0185] e) Extrusion condition:

[0186] Cylinder screw diameter=14 mm, a single-screw extruder of L/D=20

[0187] Set temperature of the extruder: barrel section C-1 (330° C.), barrel section C-2 (350° C.), barrel section C-3 (370° C.), T die section (380° C.)

[0188] The extrusion forming of the copolymer was continued until it became possible to stably extrude the copolymer from the forming machine. Then, the copolymer was extrusion-formed to prepare a sheet of 3 m or longer in length (70 mm in width) so as to be 1.00 mm in thickness. The portion of the film at 2 to 3 m from the edge of the obtained sheet was cut to prepare a test piece (1 m in length, 70 mm in length) to measure a variation in thickness. The thickness was measured at a total of three points, i.e., the central point in the width direction of the edge of the prepared sheet and two points 25 mm away from the central point in the width direction. Moreover, the thickness was measured at a total of nine points, i.e., three central points located at an interval of 25 cm from the central point in the width direction of one end of the sheet toward the other end and two points 25 mm away from each central point in the width direction. Concerning the total 12 measured values, the case where the number of measured values outside the range of 1.00 mm ±10% being 1 or less was regarded as good, and the case where the number of measured values outside the range of 1.00 mm ±10% being 2 or more was regarded as poor.

[0189] (Pipe Formability)

[0190] A pipe 10.0 mm in outer diameter and 1.0 mm in wall thickness was obtained by a φ30-mm extruder (manufactured by Tanabe Plastics Machinery Co., Ltd.). The extrusion conditions were as follows.

[0191] a) Die inner diameter: 25 mm

[0192] b) Mandrel outer diameter: 13 mm

[0193] c) Sizing die inner diameter: 10.5 mm

[0194] d) Take-over speed: 0.4 m/min

[0195] e) Outer diameter: 10.0 mm

[0196] f) Wall thickness: 1.0 mm

[0197] g) Extrusion condition

[0198] Cylinder screw diameter=30 mm, a single screw extruder of L/D=22

[0199] Set temperature of the extruder: barrel section C-1 (350° C.), barrel section C-2 (370° C.), barrel section C-3 (380° C.), head section H-1 (390° C.), die section D-1 (390° C.), die section D-2 (390° C.)

[0200] The obtained pipe was observed and evaluated according to the following criteria. The appearance of the pipe was visually checked.

[0201] Good: good appearance

[0202] Poor: poor appearance, e.g., the cross section is not circular by being flat or having uneven thickness

[0203] (Test of Own Weight Deformation in Melting)

[0204] A formed article of 13 mm in diameter and approximately 6.5 mm in height was prepared by using the pellets and a heat press molding machine. The obtained formed article was cut to prepare a test piece of 6.3 mm in height. The prepared test piece was put in a SUS-made laboratory disk, and heated in an electric furnace at 330° C. for 30 min, and thereafter, the test piece together with the laboratory disk was water cooled. There was measured by slide calibers, the diameter of the surface (bottom surface) of the test piece taken out which surface had contacted with the laboratory disk, and the bottom surface area increase rate was calculated by the following formula.

[0205] Bottom surface area increase rate (%)={the bottom area of the test piece after the heating (mm^2)–the bottom area of the test piece before the heating (mm^2)}/the bottom area of the test piece before the heating (mm^2)×100

[0206] It is meant that the lower the bottom surface area increase rate, the more hardly the formed article deforms by its own weight in melting. The copolymer giving formed articles low in the bottom surface area increase rate is excellent in that even in the case of preparing thick sheets and large pipes by forming the copolymer by extrusion forming, the formed articles in a molten state hardly deform and there can be obtained the formed articles having the desired shapes after being cooled and solidified.

[0207] (Abrasion Test)

[0208] By using the pellets and a heat press molding machine, a sheet-shape test piece of approximately 0.2 mm in thickness was prepared, and a test piece having 10 cm×10 cm was cut out therefrom. The prepared test piece was fixed on a test bench of a Taber abrasion tester (No. 101 Taber type abrasion tester with an option, manufactured by YASUDA SEIKI SEISAKUSHO, LTD.) and the abrasion test was carried out under the conditions of at a load of 500 g, using an abrasion wheel CS-10 (rotationally polished in 20 rotations with an abrasive paper #240) and at a rotation rate of 60 rpm by using the Taber abrasion tester. The weight of the test piece after 1,000 rotations was measured, and the same test piece was further subjected to the test of 10,000 rotations and thereafter, the weight thereof was measured. The abrasion loss was determined by the following formula.

$$\text{Abrasion loss (mg)} = M1 - M2$$

[0209] M1: the weight of the test piece after the 1,000 rotations (mg)

[0210] M2: the weight of the test piece after the 10,000 rotations (mg)

[0211] (Carbon Dioxide Permeability Coefficient)

[0212] By using the pellets and a heat press molding machine, a sheet-shape test piece of approximately 0.1 mm in thickness was prepared. By using the obtained test piece, carbon dioxide permeability was measured with a differential pressure type gas permeation meter (L100-5000 gas permeability meter, manufactured by Systech Illinois) according to the method described in JIS K7126-1:2006. The carbon dioxide permeability value at a permeation area of 50.24 cm^2 at a test temperature of 70° C. at a test humidity of 0% RH was obtained. The obtained carbon dioxide permeability and the test piece thickness were used to calculate the carbon dioxide permeability coefficient from the following equation.

$$\text{Carbon dioxide permeability coefficient (cm}^3 \cdot \text{mm/} (\text{m}^2 \cdot 24 \text{ h} \cdot \text{atm})) = GTR \times d$$

[0213] GTR: carbon dioxide permeability ($cm^3/(m^2 \cdot 24$ $h \cdot atm)$)

[0214] d: test piece thickness (mm)

[0215] (Air Permeability Coefficient)

[0216] By using the pellets and a heat press molding machine, a sheet-shape test piece of approximately 0.1 mm in thickness. Using the obtained test piece, air permeability was measured with a differential pressure type gas permeation meter (L100-5000 gas permeability meter, manufactured by Systech Illinois) according to the method described in JIS K7126-1:2006. The air permeability value at a permeation area of 50.24 cm^2 at a test temperature of 70° C. at a test humidity of 0% RH was obtained. The obtained air permeability and the test piece thickness were used to calculate the air permeability coefficient from the following equation.

$$\text{Air permeability coefficient } (cm^3 \cdot mm/(m^2 \cdot 24 \ h \cdot atm)) = GTR \times d$$

[0217] GTR: air permeability ($cm^3/(m^2 \cdot 24 \ h \cdot atm)$)

[0218] d: test piece thickness (mm)

[0219] (Ethyl Acetate Permeability)

[0220] By using the pellets and a heat press molding machine, a sheet-shape test piece of approximately 0.1 mm in thickness was prepared. 10 g of ethyl acetate was put in a test cup (permeation area: 12.56 cm^2), and the test cup was covered with the sheet-shape test piece; and a PTFE gasket was pinched and fastened to hermetically close the test cup. The sheet-shape test piece was brought into contact with ethyl acetate, and held at a temperature of 60° C. for 45 days, and thereafter, the test cup was taken out and allowed to stand at room temperature for 1 hour, thereafter, the amount of the mass lost was measured. Ethyl acetate permeability ($g \cdot cm/m^2$) was determined by the following formula.

$$\text{Ethyl acetate } (g \cdot cm/m^2) = \text{the amount of the mass lost } (g) \times \text{the thickness of the sheet-shape test piece } (cm)/\text{the permeation area } (m^2)$$

[0221] (Rate of Deflection at 110° C. Under Load)

[0222] By using pellets and a heat press molding machine, a sheet-shape test piece of approximately 4.2 mm in thickness was prepared, and a test piece having 80×10 mm was cut out therefrom and heated in an electric furnace at 100° C. for 20 hours. Except that the obtained test piece was used, a test was carried out according to the method described in JIS K-K 7191-1 with a heat distortion tester (manufactured by YASUDA SEIKI SEISAKUSHO, LTD.) under the condition of a test temperature of 30 to 150° C., a temperature-increasing rate of 120° C./hour, a bending stress of 1.8 MPa, and a flatwise method. The rate of deflection under load was determined by the following formula. A sheet, the rate of deflection at 110° C. under load of which is small, has excellent rigidity at a high temperature of 110° C.

$$\text{Rate of deflection under load } (\%) = a2/a1 \times 100$$

[0223] a1: test piece thickness before the test (mm)

[0224] a2: amount of deflection at 110° C. (mm)

[0225] (Creep Resistance Evaluation)

[0226] Creep resistance was measured according to the method described in ASTM D395 or JIS K6262:2013. By using the pellets and a heat press molding machine, a formed article of 13 mm in outer diameter and 8 mm in height was prepared. The obtained formed article was cut to prepare a test piece of 13 mm in outer diameter and 6 mm in height. The prepared test piece was compressed to a compression deformation rate of 25% at normal temperature by using a compression device. The compressed test piece being fixed on the compression device was allowed to stand still in an electric furnace at 80° C. for 72 hours. The compression device was taken out from the electric furnace, and cooled to room temperature; thereafter, the test piece was dismounted. The collected test piece was allowed to stand at room temperature for 30 min, and the height of the collected test piece was measured and the extent of recovery was determined by the following formula.

$$\text{Extent of recovery } (\%) = (t_2 - t_1)/t_3 \times 100$$

[0227] t_1: the height of the spacer (mm)

[0228] t_2: the height of the test piece dismounted from the compression device (mm)

[0229] t_3: the height after compressive deformation (mm)

[0230] In the above test, t_1 was 4.5 mm and t_3 was 1.5 mm.

[0231] (Hydrogen Peroxide Solution Immersion Test)

[0232] 25 g of pellets was immersed in 50 g of a 3% by weight aqueous hydrogen peroxide solution, heated at 90° C. for 20 hours in an electric furnace, further heated at 121° C. for 1 hour in a sterilizer, and then cooled to room temperature. The pellets were taken out from the aqueous solution, TISAB solution (10) (manufactured by KANTO CHEMICAL CO., INC.) was added to the remaining aqueous solution, and the fluorine ion concentration in the obtained aqueous solution was measured with a fluorine ion meter. From the obtained measured value, the fluorine ion concentration (the amount of fluorine ions dissolving out) per pellet weight was calculated according to the following formula:

$$\text{Amount of fluorine ions dissolving out (mass ppm)} = \text{measured value (mass ppm)} \times \text{amount of aqueous solution (g)/pellet weight (g)}$$

[0233] (Extrusion Pressure)

[0234] The extrusion pressure was measured by using a twin capillary rheometer RHEOGRAPH 25 (manufactured by Goettfert Inc.). There was defined as the extrusion pressure, a pressure value obtained by subjecting, to the Bagley correction, a pressure value in the cylinder after extrusion was carried out by using a main die of 1 mm in inner diameter and 16 in L/D and a sub-die of 1 mm in diameter and lower than 1 in L/D and at a measurement temperature of 390° C., a preheating time after charge of the pellets of 10 min and a shear rate of 20 sec-1 for 10 min. A copolymer low in the extrusion pressure is excellent in formability such as extrudability and injection moldability.

[0235] (Dielectric Loss Tangent)

[0236] By melt forming the pellets, a cylindrical test piece of 2 mm in diameter was prepared. The prepared test piece was set in a cavity resonator for 6 GHz, manufactured by Kanto Electronic Application and Development Inc., and the dielectric loss tangent was measured by a network analyzer, manufactured by Agilent Technologies Inc. By analyzing the measurement result by analysis software "CPMA", manufactured by Kanto Electronic Application and Development Inc., on PC connected to the network analyzer, the dielectric loss tangent (tan δ) at 20° C. at 6 GHz was determined.

TABLE 4

	Haze (%)	Compression value rate (%)	150° C. tensile strength (MPa)	Sheet formability	Pipe formability	Test of deformation by own weight (%)	Abrasion loss (mg)	CO₂ permeability coefficient cm³-mm/(m²·24 h·atm)	Air permeability coefficient cm³-mm/(m²·24 h·atm)	Ethyl acetate permeability (g·cm/m²)	Rate of deflection at 110° C. under load (%)	Creep resistance evaluation Extent of recovery (%)	Hydrogen peroxide solution immersion test of Amount fluorine ions dissolving out (ppm by mass)	Extrusion pressure (kPa)	Dielectric tangent
Example 1	3.8	77	20.5	Good	Good	15.5	8.2	2245	593	7.2	85%	26%	2.3	275	0.00042
Example 2	3.7	77	20.5	Good	Good	28.8	9.2	2262	599	6.9	86%	21%	2.7	179	0.00043
Example 3	3.7	77	20.5	Good	Good	20.0	8.3	2257	596	7.1	86%	24%	2.5	231	0.00043
Comparative Example 1	6.7	77	20.0	—	—	28.8	10.1	1945	510	7.2	78%	32%	1.9	179	0.00040
Comparative Example 2	6.4	78	19.5	—	—	49.4	11.3	1995	527	6.9	79%	24%	2.3	120	0.00041
Comparative Example 3	4.7	78	20.0	—	—	47.4	10.7	2165	573	6.8	84%	20%	2.7	124	0.00043
Comparative Example 4	3.4	78	20.5	—	—	24.4	8.5	2474	651	8.7	86%	19%	11.0	201	0.00057
Comparative Example 5	1.5	77	21.0	—	—	4.0	6.6	2598	699	7.4	94%	25%	2.7	656	0.00044

1. A copolymer, comprising tetrafluoroethylene unit and perfluoro(propyl vinyl ether) unit,

    wherein the copolymer has a content of perfluoro(propyl vinyl ether) unit of 4.9 to 7.0% by mass with respect to the whole of the monomer units,

    a melt flow rate at 372° C. of 0.5 to 1.5 g/10 min, and

    the total number of $-CF{=}CF_2$, $-CF_2H$, $-COF$, $-COOH$, $-COOCH_3$, $-CONH_2$ and $-CH_2OH$ of 20 or less per 10^6 main-chain carbon atoms.

2. The copolymer according to claim 1, wherein the copolymer has a melt flow rate at 372° C. of 0.7 to 1.3 g/10 min.

3. An extrusion formed article, comprising the copolymer according to claim 1.

4. A transfer molded article, comprising the copolymer according to claim 1.

5. A coated electric wire, comprising a coating layer comprising the copolymer according to claim 1.

6. A formed article, comprising the copolymer according to claim 1, wherein the formed article is a sheet or a pipe.

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