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DESCRIPTION

TECHNICAL FIELD

[0001] The present invention relates to flexible pipes.

BACKGROUND ART

[0002] Pipes used in offshore oil fields include risers (pipes for pumping up crude oil), umbilicals (integration of pipes for supplying chemicals for crude oil viscosity reduction for the purpose of controlling the pumping, power cables, and others), flow lines (pipes for transporting pumped crude oil which extend on the sea floor), and the like. They have various structures, and known pipes include metal-made pipes and metal/resin hybrid pipes. In order to achieve weight reduction, use of metal-made pipes tends to be reduced and metal/resin hybrid pipes are becoming the mainstream. Since oil drilling sites become much deeper and the temperature of crude oil pumped therefrom rises, resins used for these pipes need to have better mechanical strength and chemical resistance at high temperatures (resistance to high-temperature crude oil, resistance to acidic gas, such as hydrogen sulfide, contained in crude oil at high temperatures, resistance to chemicals such as methanol, CO₂, and hydrogen chloride injected so as to reduce the crude oil viscosity at high temperatures), and lower permeability at high temperatures. Thus, there is a demand for materials which can take the place of polyamide (the operating temperature range is up to 90°C) and polyvinylidene fluoride (the operating temperature range is up to 130°C) which have been used for the pipes.

[0003] Patent Literature 1 discloses as a material suitable for flexible pipes a fluororesin which is a copolymer containing copolymerized units of tetrafluoroethylene, vinylidene fluoride, and an ethylenic unsaturated monomer excluding tetrafluoroethylene and vinylidene fluoride, and has a specific storage elastic modulus.

[0004] Patent Literature 2 discloses a flexible, unbonded pipe useful for the transportation of gases and crude oils comprising a polymer layer and a film layer exhibiting high flexibility and low gas permeability. Said polymer layer has a thickness preferably comprised between 4 and 25 mm and is made of copolymers or terpolymers comprising two or more different members selected from the group consisting of vinylidene fluoride, trifluoroethylene, chlorotrifluoroethylene, tetrafluoroethylene, hexafluoropropene, and hexafluoroethylene.

CITATION LIST

- Patent Literature

[0005]

Patent Literature 1: WO 2010/110129

Patent Literature 2: US 2012/232798

SUMMARY OF INVENTION**- Technical Problem**

[0006] Flexible pipes are exposed to gas generated from an oil reservoir and gas such as CO₂ injected so as to push out crude oil from the oil reservoir during pumping of the crude oil. Thus, resin pipes constituting flexible pipes need to exhibit high barrier performance in order to prevent these gases (fluids) from leaking out of the resin pipes. Since currently the sites of oil fields become deeper and thus the temperature and pressure in the environment of pumping up crude oil become higher, there is a demand for further improvement of the barrier performance of resin pipes. One method of achieving this demand is to thicken the resin pipes. However, as the thickness of a resin pipe increases, blisters are more likely to occur due to gas dissolved in the resin in a high-temperature and high-pressure environment.

[0007] Thus, flexible pipes need to include a resin pipe which is less likely to cause blisters even if it has a greater thickness.

[0008] The present invention is developed in view of the above state of the art, and aims to provide a flexible pipe having excellent blister resistance in a high-temperature and high-pressure environment even though including a thick resin pipe.

- Solution to Problem

[0009] The present invention relates to a flexible pipe including a resin pipe having a thickness of greater than 5 mm, the resin pipe being formed from a resin having a CO₂ permeability coefficient $P(\text{CO}_2)$ of $20 \times 10^{-9} \text{ cm}^3 \cdot \text{cm} / \text{cm}^2 \cdot \text{s} \cdot \text{cmHg}$ or lower at 150°C; a CH₄ permeability coefficient $P(\text{CH}_4)$ of $10 \times 10^{-9} \text{ cm}^3 \cdot \text{cm} / \text{cm}^2 \cdot \text{s} \cdot \text{cmHg}$ or lower at 150°C; a ratio $D(\text{CO}_2)/S(\text{CO}_2)$ between a CO₂ diffusion coefficient $D(\text{CO}_2)$ and a CO₂ solubility coefficient $S(\text{CO}_2)$ of $3 \times 10^{-5} \text{ Pa} \cdot \text{m}^2/\text{s}$ or higher at 150°C; and a ratio $D(\text{CH}_4)/S(\text{CH}_4)$ between a CH₄ diffusion coefficient $D(\text{CH}_4)$ and a CH₄ solubility coefficient $S(\text{CH}_4)$ of higher than $15 \times 10^{-5} \text{ Pa} \cdot \text{m}^2/\text{s}$ at 150°C.

[0010] The resin preferably does not break in Izod impact testing at -40°C.

[0011] The resin is preferably a fluororesin or polyether ether ketone.

[0012] The flexible pipe of the present invention is preferably a riser pipe or a flow line.

- Advantageous Effects of Invention

[0013] The flexible pipe of the present invention has excellent blister resistance in a high-temperature and high-pressure environment even though including a thick resin pipe.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] Fig. 1 is a schematic view of one example of the structure of a flexible pipe.

DESCRIPTION OF EMBODIMENTS

[0015] The present invention will be specifically described hereinbelow.

[0016] The present invention relates to a flexible pipe including a resin pipe having a thickness of greater than 5 mm. The resin pipe is formed from a resin having a CO₂ permeability coefficient $P(\text{CO}_2)$ of $20 \times 10^{-9} \text{ cm}^3 \cdot \text{cm} / \text{cm}^2 \cdot \text{s} \cdot \text{cmHg}$ or lower at 150°C, a CH₄ permeability coefficient $P(\text{CH}_4)$ of $10 \times 10^{-9} \text{ cm}^3 \cdot \text{cm} / \text{cm}^2 \cdot \text{s} \cdot \text{cmHg}$ or lower at 150°C, a ratio $D(\text{CO}_2)/S(\text{CO}_2)$ between a CO₂ diffusion coefficient $D(\text{CO}_2)$ and a CO₂ solubility coefficient $S(\text{CO}_2)$ of $3 \times 10^{-5} \text{ Pa} \cdot \text{m}^2/\text{s}$ or higher at 150°C, and a ratio $D(\text{CH}_4)/S(\text{CH}_4)$ between a CH₄ diffusion coefficient $D(\text{CH}_4)$ and a CH₄ solubility coefficient $S(\text{CH}_4)$ of higher than $15 \times 10^{-5} \text{ Pa} \cdot \text{m}^2/\text{s}$ at 150°C.

[0017] The flexible pipe of the present invention has excellent blister resistance in a high-temperature and high-pressure environment even though including a thick resin pipe having a thickness of greater than 5 mm. The high temperature herein means 100°C or higher, preferably 130°C or higher, more preferably 150°C or higher. The upper limit thereof may be 200°C, for example. The high pressure herein means 70 MPa or higher, preferably 100 MPa or higher, more preferably 130 MPa or higher, still more preferably 150 MPa or higher. The upper limit thereof may be 350 MPa, for example. The flexible pipe of the present invention can exhibit excellently low permeability and excellent blister resistance even in a pumping environment at a pressure as high as 10 kpsi (about 70 MPa) or higher, 15 kpsi (about 105 MPa) or higher, or 20 kpsi (about 140 MPa) or higher.

[0018] The resin pipe of the flexible pipe of the present invention has a thickness of greater than 5 mm. The resin pipe having a thickness within the above range has excellent barrier performance in a high-temperature and high-pressure environment. Thus, the resin pipe can prevent various fluids (gases) flowing through the flexible pipe from leaking out of the resin pipe in a high-temperature

and high-pressure environment. The thickness means the thickness in the radial direction of the resin pipe.

[0019] The thickness is preferably 6 mm or greater, more preferably 8 mm or greater, still more preferably 10 mm or greater. In view of the blister resistance, the flexibility, and the economic efficiency, the thickness is preferably 50 mm or smaller, more preferably 15 mm or smaller.

[0020] The resin pipe is a pipe formed from a resin. The resin constituting the resin pipe has a CO₂ (carbon dioxide) permeability coefficient $P(\text{CO}_2)$ of $20 \times 10^{-9} \text{ cm}^3 \cdot \text{cm} / \text{cm}^2 \cdot \text{s} \cdot \text{cmHg}$ or lower at 150°C. This allows the resin pipe to exhibit excellent CO₂ barrier performance in a high-temperature environment. The permeability coefficient $P(\text{CO}_2)$ is more preferably $15 \times 10^{-9} \text{ cm}^3 \cdot \text{cm} / \text{cm}^2 \cdot \text{s} \cdot \text{cmHg}$ or lower, still more preferably $13 \times 10^{-9} \text{ cm}^3 \cdot \text{cm} / \text{cm}^2 \cdot \text{s} \cdot \text{cmHg}$ or lower. The lower limit thereof may be $0.1 \times 10^{-9} \text{ cm}^3 \cdot \text{cm} / \text{cm}^2 \cdot \text{s} \cdot \text{cmHg}$.

[0021] The resin has a CH₄ (methane) permeability coefficient $P(\text{CH}_4)$ of $10 \times 10^{-9} \text{ cm}^3 \cdot \text{cm} / \text{cm}^2 \cdot \text{s} \cdot \text{cmHg}$ or lower at 150°C. This allows the resin pipe to exhibit excellent CH₄ barrier performance in a high-temperature environment. The permeability coefficient $P(\text{CH}_4)$ is more preferably $5 \times 10^{-9} \text{ cm}^3 \cdot \text{cm} / \text{cm}^2 \cdot \text{s} \cdot \text{cmHg}$ or lower, still more preferably $3 \times 10^{-9} \text{ cm}^3 \cdot \text{cm} / \text{cm}^2 \cdot \text{s} \cdot \text{cmHg}$ or lower. The lower limit thereof may be $0.1 \times 10^{-9} \text{ cm}^3 \cdot \text{cm} / \text{cm}^2 \cdot \text{s} \cdot \text{cmHg}$.

[0022] The permeability coefficients $P(\text{CO}_2)$ and $P(\text{CH}_4)$ can be determined by photoacoustic detection.

[0023] The resin has a ratio $D(\text{CO}_2)/S(\text{CO}_2)$ between a CO₂ diffusion coefficient $D(\text{CO}_2)$ and a CO₂ solubility coefficient $S(\text{CO}_2)$ of $3 \times 10^{-5} \text{ Pa} \cdot \text{m}^2/\text{s}$ or higher at 150°C. The resin pipe formed from a resin having a ratio $D(\text{CO}_2)/S(\text{CO}_2)$ within the above range has excellent blister resistance in a high-temperature and high-pressure environment even though having a large thickness. As a result, the flexible pipe of the present invention including this resin pipe has excellent durability in a high-temperature and high-pressure environment.

[0024] The ratio $D(\text{CO}_2)/S(\text{CO}_2)$ may be $3.0 \times 10^{-5} \text{ Pa} \cdot \text{m}^2/\text{s}$ or higher, preferably $5 \times 10^{-5} \text{ Pa} \cdot \text{m}^2/\text{s}$ or higher, most preferably $10 \times 10^{-5} \text{ Pa} \cdot \text{m}^2/\text{s}$ or higher. The upper limit thereof may be $100 \times 10^{-5} \text{ Pa} \cdot \text{m}^2/\text{s}$.

[0025] The resin has a ratio $D(\text{CH}_4)/S(\text{CH}_4)$ between a CH₄ diffusion coefficient $D(\text{CH}_4)$ and a CH₄ solubility coefficient $S(\text{CH}_4)$ of higher than $15 \times 10^{-5} \text{ Pa} \cdot \text{m}^2/\text{s}$ at 150°C. The resin pipe formed from a resin having a ratio $D(\text{CH}_4)/S(\text{CH}_4)$ within the above range has excellent blister resistance in a high-temperature and high-pressure environment even though having a large thickness. As a result, the flexible pipe of the present invention including this resin pipe has excellent durability in a high-temperature and high-pressure environment.

[0026] The ratio $D(\text{CH}_4)/S(\text{CH}_4)$ is preferably $40 \times 10^{-5} \text{ Pa} \cdot \text{m}^2/\text{s}$ or higher, more preferably $45 \times 10^{-5} \text{ Pa} \cdot \text{m}^2/\text{s}$ or higher, most preferably $50 \times 10^{-5} \text{ Pa} \cdot \text{m}^2/\text{s}$ or higher. The upper limit thereof may be $500 \times 10^{-5} \text{ Pa} \cdot \text{m}^2/\text{s}$.

[0027] The diffusion coefficients $D(\text{CO}_2)$ and $D(\text{CH}_4)$ can be determined by photoacoustic detection.

[0028] The solubility coefficients $S(\text{CO}_2)$ and $S(\text{CH}_4)$ can be determined by photoacoustic detection.

[0029] The resin preferably has no glass transition temperature or, if the resin has a glass transition temperature, the glass transition temperature is preferably 0°C to 220°C . The resin pipe formed from a resin having no glass transition temperature or a glass transition temperature within the above range has excellent blister resistance in a high-temperature and high-pressure environment. If the resin has a glass transition temperature, the glass transition temperature is more preferably 10°C to 210°C , still more preferably 30°C to 200°C .

[0030] The glass transition temperature is determined by dynamic mechanical analysis using DVA-220 (IT Keisoku Seigyo K.K.). The temperature at a $\tan\delta$ peak determined at a temperature-increasing rate of $2^\circ\text{C}/\text{min}$ and a frequency of 10 Hz is defined as the glass transition temperature.

[0031] The resin preferably has a brittleness temperature of 0°C or lower. The brittleness temperature is more preferably -20°C or lower, still more preferably -40°C or lower, most preferably -60°C or lower.

[0032] The brittleness temperature is a value determined using a brittle point temperature tester model S (Toyo Seiki Seisaku-sho, Ltd.) in conformity with ASTM D746.

[0033] The resin preferably has a melting point of 180°C to 400°C . The resin pipe formed from a resin having a melting point within the above range has excellent blister resistance in a high-temperature and high-pressure environment. The melting point is more preferably 200°C to 350°C , still more preferably 200°C to 290°C .

[0034] The melting point is determined by thermal analysis at a temperature-increasing rate of $10^\circ\text{C}/\text{min}$ using a differential scanning calorimeter RDC220 (Seiko Instruments Inc.) in conformity with ASTM D-4591. The temperature corresponding to the peak of the resulting endothermic curve is defined as the melting point.

[0035] The resin preferably has a melt flow rate (MFR) of 0.1 to 50 g/10 min. The resin pipe formed from a resin having a MFR within the above range has excellent blister resistance in a high-temperature and high-pressure environment. The MFR is more preferably 0.2 to 30 g/10 min, still more preferably 0.3 to 10 g/10 min.

[0036] The MFR can be determined using a melt indexer (Toyo Seiki Seisaku-sho, Ltd.) in conformity with ASTM D3307-01. The MFR can be determined as the mass (g/10 min) of a polymer flowed out of a nozzle (inner diameter: 2 mm, length: 8 mm) per 10 minutes at a load of 5 kg and a

temperature of 297°C in the case of copolymers containing copolymerized units of tetrafluoroethylene, vinylidene fluoride, and an ethylenic unsaturated monomer to be mentioned later, 380°C to 430°C in the case of polyether ether ketone, or a temperature higher than the melting point by 50°C in the case of any other resin.

[0037] The resin preferably has excellent impact resistance at low temperature. In other words, the resin preferably does not break in Izod impact testing at room temperature. The resin more preferably does not break in Izod impact testing at 0°C, still more preferably does not break in Izod impact testing at -20°C, particularly preferably does not break in Izod impact testing at -40°C.

[0038] In the Izod impact testing, the notched Izod impact strength is determined using U-F impact tester (Ueshima Seisakusho Co., Ltd.) in conformity with ASTM D256. The phrase "not break in Izod impact testing" herein means that a resin specimen is not divided into two or more fractions.

[0039] The resin may be fluororesin, polyether ether ketone (PEEK), polyimide, polyether ketone, polyether ketone ketone, polyether ketone ether ketone ketone, or any mixture thereof. In order to achieve excellent creep resistance at high temperature, fluororesin, polyether ether ketone (PEEK), and a mixture of fluororesin and PEEK are preferred. In order to achieve excellent impact resistance at low temperature, excellent crack resistance at high pressure, and excellent blister resistance in a high-temperature and high-pressure environment, fluororesin and a mixture of fluororesin and PEEK are more preferred.

[0040] In order to easily control the permeability coefficient and the diffusion coefficient/solubility coefficient ratio within the above ranges and to improve the blister resistance in a high-temperature and high-pressure environment, the fluororesin is preferably a copolymer containing copolymerized units of tetrafluoroethylene, vinylidene fluoride, and an ethylenic unsaturated monomer excluding tetrafluoroethylene and vinylidene fluoride.

[0041] The ethylenic unsaturated monomer may be any monomer copolymerizable with tetrafluoroethylene and vinylidene fluoride. Still, it is preferably at least one selected from the group consisting of ethylenic unsaturated monomers represented by either of the following formulas (1) and (2) :

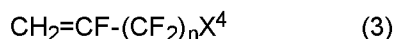


wherein X^1 , X^2 , X^3 , and X^4 may be the same as or different from each other, and are each H, F, or Cl; n is an integer of 0 to 8, excluding tetrafluoroethylene and vinylidene fluoride,

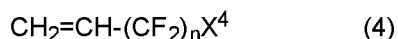


wherein R^1 is a C1-C3 alkyl group or a C1-C3 fluoroalkyl group.

[0042] The ethylenic unsaturated monomer represented by the formula (1) is preferably at least one selected from the group consisting of $\text{CF}_2=\text{CFCl}$, $\text{CF}_2=\text{CFCF}_3$, those represented by the following formula (3):



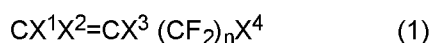
(wherein X^4 and n are defined in the same manner as mentioned above), and those represented by the following formula (4):



(wherein X^4 and n are defined in the same manner as mentioned above), more preferably at least one selected from the group consisting of $\text{CF}_2=\text{CFCl}$, $\text{CH}_2=\text{CFCF}_3$, $\text{CH}_2=\text{CH}-\text{C}_4\text{F}_9$, $\text{CH}_2=\text{CH}-\text{C}_6\text{F}_{13}$, $\text{CH}_2=\text{CF}-\text{C}_3\text{F}_6\text{H}$, and $\text{CF}_2=\text{CFCF}_3$, still more preferably at least one selected from the group consisting of $\text{CF}_2=\text{CFCl}$ and $\text{CH}_2=\text{CFCF}_3$.

[0043] The ethylenic unsaturated monomer represented by the formula (2) is preferably at least one selected from the group consisting of $\text{CF}_2=\text{CF}-\text{OCF}_3$, $\text{CF}_2=\text{CF}-\text{OCF}_2\text{CF}_3$, and $\text{CF}_2=\text{CF}-\text{OCF}_2\text{CF}_2\text{CF}_3$.

[0044] The fluororesin is preferably a copolymer containing 55.0 to 90.0 mol% of a copolymerized unit of tetrafluoroethylene, 5.0 to 44.9 mol% of a copolymerized unit of vinylidene fluoride, and 0.1 to 10.0 mol% of a copolymerized unit of the ethylenic unsaturated monomer represented by the formula (1) :



wherein X^1 , X^2 , X^3 , and X^4 may be the same as or different from each other, and are each H, F, or Cl; n is an integer of 0 to 8, excluding tetrafluoroethylene and vinylidene fluoride.

[0045] The fluororesin is more preferably a copolymer containing 55.0 to 85.0 mol% of a copolymerized unit of tetrafluoroethylene, 10.0 to 44.9 mol% of a copolymerized unit of vinylidene fluoride, and 0.1 to 5.0 mol% of a copolymerized unit of the ethylenic unsaturated monomer represented by the formula (1).

[0046] The fluororesin is still more preferably a copolymer containing 55.0 to 85.0 mol% of a copolymerized unit of tetrafluoroethylene, 13.0 to 44.9 mol% of a copolymerized unit of vinylidene fluoride, and 0.1 to 2.0 mol% of a copolymerized unit of the ethylenic unsaturated monomer represented by the formula (1).

[0047] In order to improve the mechanical strength of the fluororesin at high temperature, as well as to achieve excellently low permeability of the fluororesin, the ethylenic unsaturated monomer represented by the formula (1) is preferably at least one monomer selected from the group consisting of $\text{CH}_2=\text{CH}-\text{C}_4\text{F}_9$, $\text{CH}_2=\text{CH}-\text{C}_6\text{F}_{13}$, and $\text{CH}_2=\text{CF}-\text{C}_3\text{F}_6\text{H}$. More preferably, the ethylenic

unsaturated monomer represented by the formula (1) is at least one monomer selected from the group consisting of $\text{CH}_2=\text{CH}-\text{C}_4\text{F}_9$, $\text{CH}_2=\text{CH}-\text{C}_6\text{F}_{13}$, and $\text{CH}_2=\text{CF}-\text{C}_3\text{F}_6\text{H}$ and the fluororesin is a copolymer containing

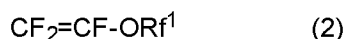
55.0 to 80.0 mol% of a copolymerized unit of tetrafluoroethylene,
19.5 to 44.9 mol% of a copolymerized unit of vinylidene fluoride, and
0.1 to 0.6 mol% of a copolymerized unit of the ethylenic unsaturated monomer represented by the formula (1).

[0048] The fluororesin may be a copolymer containing 58.0 to 85.0 mol% of a copolymerized unit of tetrafluoroethylene,

10.0 to 41.9 mol% of a copolymerized unit of vinylidene fluoride, and
0.1 to 5.0 mol% of a copolymerized unit of the ethylenic unsaturated monomer represented by the formula (1).

[0049] The fluororesin is also preferably a copolymer containing

55.0 to 90.0 mol% of a copolymerized unit of tetrafluoroethylene,
9.2 to 44.2 mol% of a copolymerized unit of vinylidene fluoride, and
0.1 to 0.8 mol% of a copolymerized unit of the ethylenic unsaturated monomer represented by the formula (2) :



wherein R^1 is a C1-C3 alkyl group or a C1-C3 fluoroalkyl group.

[0050] The fluororesin is more preferably a copolymer containing

58.0 to 85.0 mol% of a copolymerized unit of tetrafluoroethylene,
14.5 to 39.9 mol% of a copolymerized unit of vinylidene fluoride, and
0.1 to 0.5 mol% of a copolymerized unit of the ethylenic unsaturated monomer represented by the formula (2) .

[0051] The fluororesin is also preferably a copolymer containing

55.0 to 90.0 mol% of a copolymerized unit of tetrafluoroethylene,
5.0 to 44.8 mol% of a copolymerized unit of vinylidene fluoride,
0.1 to 10.0 mol% of a copolymerized unit of the ethylenic unsaturated monomer represented by the formula (1), and
0.1 to 0.8 mol% of a copolymerized unit of the ethylenic unsaturated monomer represented by the formula (2).

[0052] The fluororesin is more preferably a copolymer containing

55.0 to 85.0 mol% of a copolymerized unit of tetrafluoroethylene,
9.5 to 44.8 mol% of a copolymerized unit of vinylidene fluoride,
0.1 to 5.0 mol% of a copolymerized unit of the ethylenic unsaturated monomer represented by the formula (1), and
0.1 to 0.5 mol% of a copolymerized unit of the ethylenic unsaturated monomer represented by the formula (2).

[0053] The fluoro-resin is still more preferably a copolymer containing 55.0 to 80.0 mol% of a copolymerized unit of tetrafluoroethylene, 19.8 to 44.8 mol% of a copolymerized unit of vinylidene fluoride, 0.1 to 2.0 mol% of a copolymerized unit of the ethylenic unsaturated monomer represented by the formula (1), and 0.1 to 0.3 mol% of a copolymerized unit of the ethylenic unsaturated monomer represented by the formula (2). The fluoro-resin having this composition has particularly excellently low permeability.

[0054] The fluoro-resin may be a copolymer containing 58.0 to 85.0 mol% of a copolymerized unit of tetrafluoroethylene, 9.5 to 39.8 mol% of a copolymerized unit of vinylidene fluoride, 0.1 to 5.0 mol% of a copolymerized unit of the ethylenic unsaturated monomer represented by the formula (1), and 0.1 to 0.5 mol% of a copolymerized unit of the ethylenic unsaturated monomer represented by the formula (2).

[0055] The fluoro-resin in which the amounts of the respective monomers are within the above ranges has better mechanical strength, better chemical resistance, and lower permeability at high temperature than conventionally known copolymers containing tetrafluoroethylene, vinylidene fluoride, and a third component. The low permeability at high temperature means, for example, low permeability to methane, hydrogen sulfide, CO₂, methanol, hydrochloric acid, and others.

[0056] The amounts of the respective monomers of the copolymer can be calculated by appropriately combining NMR and elemental analysis in accordance with the types of the monomers.

[0057] The fluoro-resin preferably has a pyrolysis starting temperature (1 mass% reduction temperature) of 360°C or higher. The lower limit is more preferably 370°C. The upper limit of the pyrolysis starting temperature may be, for example, 410°C as long as it is within the above range.

[0058] The pyrolysis starting temperature is the temperature at which 1 mass% of a fluoro-resin subjected to a heating test is decomposed, and is a value obtained by determining the temperature at which the mass of the fluoro-resin subjected to the heating test is reduced by 1 mass% using a thermogravimetry-differential thermal analyzer (TG-DTA).

[0059] The fluoro-resin may be produced by polymerization such as solution polymerization, bulk polymerization, emulsion polymerization, or suspension polymerization. For industrially easy production, the fluoro-resin is preferably produced by emulsion polymerization or suspension polymerization.

[0060] In the above polymerization, a polymerization initiator, a surfactant, a chain-transfer agent, and a solvent may be used, and each may be conventionally known one.

[0061] The polymerization initiator may be an oil-soluble radical polymerization initiator or a water-soluble radical initiator.

[0062] The oil-soluble radical polymerization initiator may be a known oil-soluble peroxide. Typical examples thereof include dialkyl peroxydicarbonates such as diisopropyl peroxydicarbonate, di-n-propyl peroxydicarbonate, and di-sec-butyl peroxydicarbonate; peroxy esters such as t-butyl peroxyisobutyrate and t-butyl peroxyphenylacetate; dialkyl peroxides such as di-t-butyl peroxide, as well as di(perfluoro)acyl (or di(fluorochloro)acyl) peroxides such as di(ω -hydro-dodecafluoroheptanoyl)peroxide, di(ω -hydro-tetradecafluoroheptanoyl)peroxide, di(ω -hydro-hexadecafluorononanoyl) peroxide, di(perfluorobutyl)peroxide, di(perfluorovaleryl)peroxide, di(perfluorohexanoyl)peroxide, di(perfluoroheptanoyl)peroxide, di(perfluorooctanoyl)peroxide, di(perfluorononanoyl)peroxide, di(ω -chloro-hexafluorobutyl)peroxide, di(ω -chloro-decafluorohexanoyl)peroxide, di(ω -chloro-tetradecafluorooctanoyl)peroxide, ω -hydro-dodecafluoroheptanoyl- ω -hydrohexadecafluorononanoyl-peroxide, ω -chloro-hexafluorobutyl- ω -chloro-decafluorohexanoyl-peroxide, ω -hydrododecafluoroheptanoyl-perfluorobutyl-peroxide, di(dichloropentafluorobutanoyl)peroxide, di(trichlorooctafluorohexanoyl)peroxide, di(tetrachloroundecafluorooctanoyl)peroxide, di(pentachlorotetradecafluorodecanoyl)peroxide, and di(undecachlorodotriacontafuorodocosanoyl)peroxide.

[0063] The water-soluble radical polymerization initiator may be a known water-soluble peroxide, and examples thereof include ammonium salts, potassium salts, sodium salts, t-butyl permaleate, and t-butyl hydroperoxide of persulfuric acid, perboric acid, perchloric acid, perphosphoric acid, or percarbonic acid. Any reducing agent such as a sulfite or a sulfurous acid salt may be used in combination with a peroxide, and the amount thereof may be 0.1 to 20 times the amount of the peroxide.

[0064] The surfactant may be a known surfactant, and examples thereof include nonionic surfactants, anionic surfactants, and cationic surfactants. Preferred are fluorine-containing anionic surfactants, and more preferred are C₄-C₂₀ linear or branched fluorine-containing anionic surfactants optionally containing etheric oxygen (in other words, an oxygen atom may be present between carbon atoms). The amount thereof (relative to the water where the polymerization occurs) is preferably 50 to 5000 ppm.

[0065] Examples of the chain-transfer agent include hydrocarbons such as ethane, isopentane, n-hexane, and cyclohexane; aromatic substances such as toluene and xylene; ketones such as acetone; acetates such as ethyl acetate and butyl acetate; alcohols such as methanol and ethanol; mercaptans such as methyl mercaptan; and halogenated hydrocarbons such as carbon tetrachloride, chloroform, methylene chloride, and methyl chloride. The amount thereof may vary in accordance with the chain transfer constant of the compound, and is usually 0.01 to 20 mass% relative to the polymerization solvent.

[0066] Examples of the solvent include water and solvent mixtures of water and an alcohol.

[0067] In suspension polymerization, a fluorine-based solvent may be used in addition to water. Examples of the fluorine-based solvent include hydrochlorofluoroalkanes such as CH₃CClF₂, CH₃CCl₂F, CF₃CF₂CCl₂H, and CF₂ClCF₂CFHCl; chlorofluoroalkanes such as CF₂ClCFClCF₂CF₃ and CF₃CFClCFClCF₃; and perfluoroalkanes such as perfluorocyclobutane, CF₃CF₂CF₂CF₃, CF₃CF₂CF₂CF₂CF₃, and CF₃CF₂CF₂CF₂CF₂CF₃. Preferred are perfluoroalkanes. In view of the suspension performance and economic efficiency, the amount of the fluorine-based solvent is

preferably 10 to 100 mass% relative to the aqueous medium.

[0068] The polymerization temperature may be any temperature, and may be 0°C to 100°C. The polymerization pressure is appropriately determined in accordance with other polymerization conditions, such as the type and amount of a solvent, the vapor pressure, and the polymerization temperature. It may usually be 0 to 9.8 MPaG.

[0069] The resin may be mixed with any additive such as a filler, a plasticizer, a processing aid, a release agent, a pigment, a flame retardant, a lubricant, a photostabilizer, a weather resistance stabilizer, a conductive agent, an antistatic, an ultraviolet absorber, an antioxidant, a foaming agent, a perfume, an oil, a softening agent, and a dehydrofluorinating agent, before molding. Examples of the filler include polytetrafluoroethylene, mica, silica, talc, celite, clay, titanium oxide, and barium sulfate. Examples of the conductive agent include carbon black. Examples of the plasticizer include dioctyl phthalate and pentaerythritol. Examples of the processing aid include carnauba wax, sulfone compounds, low molecular weight polyethylene, and fluorine-based aids. Examples of the dehydrofluorinating agent include organic onium and amidines.

[0070] The resin pipe may be produced by, for example, extrusion-molding the resin.

[0071] One embodiment of the flexible pipe of the present invention is shown in Fig. 1. Still, the flexible pipe of the present invention is not limited thereto.

[0072] A pipe (fluid barrier layer) 2 corresponds to the resin pipe in the present invention, and prevents a resource flowing through the flexible pipe from leaking out of the pipe. The resin pipe has excellently low permeability in a high-temperature and high-pressure environment. Thus, even when corrosive gas, such as hydrogen sulfide or carbon dioxide, at high temperature and high pressure flows through the pipe, the layers outside the pipe 2 are less likely to be attacked by such corrosive gas. The resin pipe also has excellent blister resistance in a high-temperature and high-pressure environment. Thus, even when exposed to methane, carbon dioxide, or hydrogen at high temperature and high pressure, the pipe 2 is less likely to suffer blisters. When high-temperature and high-pressure fluid flows through a pipe, the materials constituting the pipe 2 may thrust into a reinforcing layer 3, deform, or suffer cracking. In contrast, the flexible pipe of the present invention including the above resin pipe can overcome these problems.

[0073] A body (carcass) 1 is disposed inside the pipe 2, and it can withstand a high pressure to maintain the pipe shape even when the flexible pipe is applied to deep-sea uses. A reinforcing layer 3 and a reinforcing layer 5 made of metal are disposed around the pipe 2, and a friction-resistant layer 4 for preventing friction is disposed between the reinforcing layer 3 and the reinforcing layer 5. The reinforcing layers 3 and 5 act to prevent burst of the flexible pipe due to the pressure of a resource flowing through the pipe. These reinforcing layers may be made of metal. If the reinforcing layers 3 and 5 have different structures, the pipe can withstand stresses applied in different directions. In order to prevent damages on the pipe 2 which may be generated by contact with the metal reinforcing layers, a thermoplastic resin layer may be disposed between the pipe 2 and the body 1 or reinforcing layer 3. The thermoplastic resin layer may be formed from the same material as the pipe 2, or may be formed from a different material. An outer layer resin 6 is disposed around the reinforcing layer 5, and has a function of partitioning the inside and outside of the flexible pipe.

The outer layer resin 6 may be formed from polyethylene or polyamide.

[0074] The flexible pipe of the present invention can be suitably used as a riser pipe or a flow line for transporting a resource from the sea floor to the surface of the sea in an offshore oil or gas field. Examples of the resource include fluids such as crude oil, petroleum gas, and natural gas.

[0075] Use of the flexible pipe in an environment at 100°C or higher and 70 MPa or higher is also one aspect of the present invention. The flexible pipe can be used in an environment at 130°C or higher and in an environment at 100 MPa or higher, 130 MPa or higher, or 150 MPa or higher.

EXAMPLES

[0076] Next, the present invention is described referring to, but not limited to, examples.

[0077] The parameters in the examples were determined by the following methods.

Monomer composition (fluororesin)

[0078] The monomer composition was determined by ¹⁹F-NMR using a nuclear magnetic resonance device AC300 (Bruker-Biospin) with a measurement temperature set to the polymer melting point + 20°C, optionally in combination with elemental analysis as appropriate in accordance with the integral values of the respective peaks and the types of the monomers.

Glass transition temperature

[0079] The glass transition temperature was determined by dynamic mechanical analysis using DVA-220 (IT Keisoku Seigyo K.K.). The temperature at a tanδ peak determined at a temperature-increasing rate of 2°C/min and a frequency of 10 Hz was defined as the glass transition temperature.

Melting point

[0080] The melting point was determined by thermal analysis at a temperature-increasing rate of 10°C/min using a differential scanning calorimeter RDC220 (Seiko Instruments Inc.) in conformity with ASTM D-4591. The temperature corresponding to the peak of the resulting endothermic curve is defined as the melting point.

Melt flow rate (MFR)

[0081] The MFR was determined as the mass (g/10 min) of a polymer flowed out of a nozzle (inner diameter: 2 mm, length: 8 mm) per 10 minutes at a load of 5 kg and a temperature of 297°C using a melt indexer (Toyo Seiki Seisaku-sho, Ltd.) in conformity with ASTM D3307-01.

Pyrolysis starting temperature (1 mass% reduction temperature)

[0082] The temperature at which the mass of the fluororesin subjected to the heating test was reduced by 1 mass% using a thermogravimetry-differential thermal analyzer (TG-DTA) was defined as the pyrolysis starting temperature.

Permeability coefficient, diffusion coefficient, and solubility coefficient

[0083] The permeability coefficient, diffusion coefficient, and solubility coefficient were determined by photoacoustic detection using WaSul-Perm system (Hilase) with N₂ flow at the detection side and test gas flow at the test gas side.

Blister resistance test (RGD test)

[0084] A predetermined gas is charged into a pressure-resistant container up to a predetermined pressure. The system was warmed up to a predetermined temperature and a sample was immersed therein for one week, and then decompressed at 70 bar/min. The system was again pressurized and warmed, and the sample was immersed therein for 24 hours, and then decompressed at 70 bar/min. The cycle of pressurization, warming, and decompression was repeated 20 times, and the sample was checked for blisters and slits.

Izod impact testing

[0085] The notched Izod impact strength at a thickness of 12.7 ± 2 mm was determined using a U-F impact tester (Ueshima Seisakusho Co., Ltd.) in conformity with ASTM D256.

Example 1

[0086] A fluororesin A (copolymer of tetrafluoroethylene/vinylidene fluoride/ethylenic unsaturated monomer, MRF: 2.0 g/10 min, melting point: 217°C, Izod impact testing: not break at -40°C, T_g: absence, 1 mass% reduction temperature: 386°C) was used. The permeability coefficients (P), diffusion coefficients (D), solubility coefficients (S), and diffusion coefficient (D)/solubility coefficient (S) ratios were as shown in Table 1. The permeability coefficients (P), diffusion coefficients (D), and solubility coefficients (S) were determined by the aforementioned photoacoustic detection using a 1-mm-thick sample obtained by press-molding the fluororesin A with a 300°C heat press.

[Table 1]

		Permeability coefficient (P) ($10^{-9} \text{ cm}^3 \cdot \text{cm} / \text{cm}^2 \cdot \text{s} \cdot \text{cmHg}$)		Diffusion coefficient (D) ($10^{-12} \text{ m}^2/\text{s}$)		Solubility coefficient (S) (10^{-7} 1/Pa)		Diffusion coefficient (D)/Solubility coefficient (S) ($10^{-5} \text{ Pa} \cdot \text{m}^2/\text{s}$)	
Gas		CO ₂	CH ₄	CO ₂	CH ₄	CO ₂	CH ₄	CO ₂	CH ₄
Temperature (°C)	50	2.19	0.05	9.2	5.7	179.0	6.92	0.05	0.82
	100	4.08	0.42	78.6	61.4	39.0	5.13	2.02	11.97
	150	12.78	2.39	317.0	303.0	30.3	5.93	10.46	51.10

[0087] The fluororesin A was extrusion-molded into a pipe sample having an outer diameter of 90 mm and a thickness of 6 mm under the conditions as shown in Table 2. This pipe was cut into a sample A having a size of 2.5 cm × 5 cm.

(RGD testing)

[0088] The sample A was put into a pressure-resistant container. The pressure and the temperature were increased up to 15 kpsi and 130°C with 100% CO₂ gas. The system was maintained for one week until it reached an equilibrium state, and then decompressed at 70 bar/min. The cycle of pressurization, warming, and decompression was repeated 20 times in accordance with the aforementioned method. No blisters or slits were observed on the sample A after the test.

[Table 2]

Molding conditions						
Cylinder temperature (°C)	C1	C2	C3	C4	adapter	D1
	280	290	300	310	320	330
Screw rotational speed	80 rpm					
Sizing die tank temperature	25°C					
Line speed	0.2 m/min					

Comparative Example 1

[0089] A PVDF resin (MRF: 2.5 to 4.0 g/10 min, melting point: 170°C, Izod impact testing: broke at -40°C (Izod impact strength: 27.2 kg·cm/cm²), Tg: -40°C, 1 mass% reduction temperature: 383°C) was used. The permeability coefficients (P), diffusion coefficients (D), solubility coefficients (S), and diffusion coefficient (D)/solubility coefficient (S) ratios were as shown in Table 3. The permeability coefficients (P), diffusion coefficients (D), and solubility coefficients (S) were determined by the

aforementioned photoacoustic detection using a 1-mm-thick sample obtained by press-molding the PVDF resin with a 240°C heat press.

[Table 3]

		Permeability coefficient (P) ($10^{-9} \text{ cm}^3 \cdot \text{cm} / \text{cm}^2 \cdot \text{s} \cdot \text{cmHg}$)		Diffusion coefficient (D) ($10^{-12} \text{ m}^2/\text{s}$)		Solubility coefficient (S) (10^{-7} 1/Pa)		Diffusion coefficient (D) /Solubility coefficient (S) ($10^{-5} \text{ Pa} \cdot \text{m}^2/\text{s}$)	
Gas		CO ₂	CH ₄	CO ₂	CH ₄	CO ₂	CH ₄	CO ₂	CH ₄
Temperature (°C)	50	1.13	0.01	2.49	1.56	342.00	6.53	0.01	0.24
	100	2.77	0.21	33.10	31.00	62.90	4.99	0.53	6.21
	150	13.30	1.88	164.00	230.00	61.00	6.15	2.69	37.40

[0090] The PVDF resin was extrusion-molded into a pipe sample having an outer diameter of 90 mm and a thickness of 6 mm under the conditions as shown in Table 4. This pipe was cut into a sample B having a size of 2.5 cm × 5 cm.

(RGD testing)

[0091] The sample B was put into a pressure-resistant container. The pressure and the temperature were increased up to 15 kpsi and 130°C with 100% CO₂ gas. The system was maintained for one week until it reached an equilibrium state, and then decompressed at 70 bar/min. The cycle of pressurization, warming, and decompression was repeated 20 times in accordance with the aforementioned method. Many blisters and slits were observed on the sample B after the test.

[Table 4]

Molding conditions						
Cylinder temperature (°C)	C1	C2	C3	C4	adapter	D1
	220	230	240	250	260	270
Screw rotational speed	70 rpm					
Sizing die tank temperature	25°C					
Line speed	0.2 m/min					

REFERENCE SIGNS LIST

[0092]

- 1: Body (carcass)
- 2: Pipe (fluid barrier layer)
- 3: Reinforcing layer
- 4: Friction-resistant layer
- 5: Reinforcing layer
- 6: Outer layer resin

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- [WO2010110129A \[0005\]](#)
- [US2012232798A \[0005\]](#)

FLEKSIBELT RØR**Patentkrav**

- Krav 1. Fleksibelt rør, der omfatter
 et harpiksrør med en tykkelse på mere end 5 mm,
 hvor harpiksrøret er dannet ud fra en harpiks med en CO₂-
permeabilitetskoefficient $P(\text{CO}_2)$ på $20 \times 10^{-9} \text{ cm}^3 \cdot \text{cm}/\text{cm}^2 \cdot \text{s} \cdot \text{cmHg}$ eller mindre ved
150 °C; en CH₄-permeabilitetskoefficient $P(\text{CH}_4)$ på $10 \times 10^{-9} \text{ cm}^3 \cdot \text{cm}/\text{cm}^2 \cdot \text{s} \cdot \text{cmHg}$
eller mindre ved 150 °C; et $D(\text{CO}_2)/S(\text{CO}_2)$ -forhold mellem en CO₂-diffusionskoefficient
 $D(\text{CO}_2)$ og en CO₂-opløselighedskoefficient $S(\text{CO}_2)$ på $3 \times 10^{-5} \text{ Pa} \cdot \text{m}^2/\text{s}$ eller mere ved
150 °C; og et $D(\text{CH}_4)/S(\text{CH}_4)$ -forhold mellem en CH₄-diffusionskoefficient $D(\text{CH}_4)$ og en
CH₄-opløselighedskoefficient $S(\text{CH}_4)$ på mere end $15 \times 10^{-5} \text{ Pa} \cdot \text{m}^2/\text{s}$ ved 150 °C,
hvor $P(\text{CO}_2)$, $P(\text{CH}_4)$, $D(\text{CO}_2)$, $D(\text{CH}_4)$, $S(\text{CO}_2)$ og $S(\text{CH}_4)$ bestemmes ved fotoakustisk
detektering under anvendelse af et Hilase WaSul-Perm-system med N₂-strøm på
detekteringssiden og testgasstrøm på testgassiden.
- Krav 2. Fleksibelt rør ifølge krav 1,
 hvor harpiksen ikke brækker ved Izod-slagprøvning ved -40 °C,
 hvor Izod-kærslagstyrken ved Izod-slagprøvningen bestemmes under anvendelse af
 en U-F-slagtester fra Ueshima Seisakusho Co., Ltd. i overensstemmelse med ASTM
 D256.
- Krav 3. Fleksibelt rør ifølge krav 1 eller 2,
 hvor harpiksen er en fluorharpiks eller polyetheretherketon.
- Krav 4. Anvendelse af det fleksible rør ifølge krav 1, 2 eller 3 som et stigrør eller en
 flowledning.

DRAWINGS

FIG.1

