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(54) Titre : COPOLYMERE DE CHLOROTRIFLUOROETHYLENE/PERFLUORO (ALKYLVINYLETHER)
(54) Title: CHLOROTRIFLUOROETHYLENE/PERFLUORO (ALKYL VINYL ETHER) COPOLYMER

(57) Abrégé/Abstract:
The present invention provides a copolymer comprising chlorotrifluoroethylene and 0.01 to 1% by mole of perfluoro(alkyl vinyl ether) of the formula: R_f-O-CF=CF_2 (I) wherein R_f is a C_3-C_6 perfluoroalkyl group. The copolymer has a melt flow rate of 0.01 to 200 x 10^{-3} cc/sec., good mechanical strength and a sufficiently high melting point. The copolymer of the present invention is suitable for molding into tubes and films for a variety of uses.

ABSTRACT

The present invention provides a copolymer comprising chlorotrifluoroethylene and 0.01 to 1% by mole of perfluoro(alkyl vinyl ether) of the formula:

$$R_f\text{-}O\text{-}CF=CF_2 \qquad (I)$$

wherein R_f is a C_3-C_6 perfluoroalkyl group. The copolymer has a melt flow rate of 0.01 to 200 x 10^{-3} cc/sec., good mechanical strength and a sufficiently high melting point. The copolymer of the present invention is suitable for molding into tubes and films for a variety of uses.

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CHLOROTRIFLUOROETHYLENE/PERFLUORO(ALKYL VINYL ETHER) COPOLYMER

The present invention relates to a chlorotrifluoroethylene/perfluoro(alkyl vinyl ether) copolymer. In particular, the present invention relates to a chlorotrifluoroethylene/perfluoro(alkyl vinyl ether) copolymer which contains the perfluoro(alkyl vinyl ether) in a specific amount and has a specific melt flow rate.

Since polychlorotrifluoroethylene is a fluororesin having good moisture-proof properties, transparency and mechanical strength, it is widely used in various areas. For example, it can be molded into a pipe form and used as a level gauge, or it can be used as a moisture-proof film.

Since polychlorotrifluoroethylene is very easily crystallized, it loses its transparency or becomes brittle as time passes. However, crystallization of polychlorotrifluoroethylene is prevented by copolymerization with vinylidene fluoride. In this case, when the amount of vinylidene fluoride is too small, crystallization is not prevented, while when the amount of vinylidene fluoride is too large, the melting point of such a copolymer decreases or mechanical strength of the copolymer deteriorates greatly.

An object of the present invention is to provide a copolymer of chlorotrifluoroethylene which does not suffer from a decrease in melting point or a deterioration of mechanical strength, and can prevent crystallization advantageously.

According to the present invention, there is provided a copolymer which comprises chlorotrifluoroethylene and 0.01 to 1% by mole of perfluoro(alkyl vinyl ether) of the formula:

$$R_f\text{-}O\text{-}CF=CF_2 \qquad (I)$$

wherein R_f is a C_3-C_6 perfluoroalkyl group, and has a melt flow rate of 0.01 to 200 x 10^{-3} cc/sec.

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The perfluoro(alkyl vinyl ether) to be copolymerized with chlorotrifluoroethylene according to the present invention is an ether of the formula (I). The perfluoroalkyl group R_f of the formula (I) has 3 to 6 carbon atoms and may optionally have at least one substituent. Specific examples of the perfluoroalkyl group include a perfluoropropyl group, a perfluorobutyl group, a perfluoro(propoxypropyl) group, and the like. From the viewpoint of ease of availability and cost, perfluoro(propyl vinyl ether) is preferred.

The content of the perfluoro(alkyl vinyl ether) (I) in the copolymer is from 0.01 to 1% by mole.

When the content of the perfluoro(alkyl vinyl ether) is increased, the crystallization of the copolymer can be effectively prevented but the melting point of the polymer decreases and the copolymer becomes soft such that the mechanical strength deteriorates. Preferably, the content of perfluoro(alkyl vinyl ether) is from 0.05 to 0.5% by mole.

When the content of perfluoro(alkyl vinyl ether) exceeds 1% by mole, the polymerization rate is decreased to 50% or less of a homopolymerization rate of chlorotrifluoroethylene. Such a low polymerization rate is uneconomical, or at such a low polymerization rate, the degree of polymerization may not be increased.

The copolymer of the present invention may be prepared by a conventional method. In general, the copolymerization is carried out in an autoclave equipped with a stirrer. Preferably, an aqueous suspension polymerization is employed. In this case, the weight ratio of water to chlorotrifluoroethylene is from 1/10 to 10/1. Polymerization temperature is from 0 to 100°C, preferably from 5 to 30°C. Polymerization pressure is determined by the vapour pressure of chlorotrifluoroethylene and in turn the polymerization temperature.

The weight of the perfluoro(alkyl vinyl ether) (I) to be copolymerized depends on the type of perfluoro(alkyl vinyl ether) (I). The method of addition of the perfluoro(alkyl

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vinyl ether) (I) is not critical, and all of the perfluoro(alkyl vinyl ether) (I) may be added to the reaction system in an initial stage or may be added portionwise or continuously.

As a polymerization initiator, an organic peroxide is preferably used. Among the organic peroxides, to improve heat stability of the produced copolymer, organic peroxides of the following formulas are preferably used:

$$[Cl(CF_2CFCl)_m\text{-}CF_2COO]_2$$

wherein m is an integer of 1 to 5, and

$$[X(CF_2CF_2)_nCOO]_2$$

wherein n is an integer of 1 to 5, and X is a hydrogen atom, a fluorine atom or a chlorine atom.

In the present invention, the composition and properties of the copolymer are measured as follows:

Content of perfluoro(alkyl vinyl ether)

The content of the perfluoro(alkyl vinyl ether) is measured by ^{19}F FT-NMR of a solution of the copolymer in benzotrifluoride. Thus, the content of the perfluoro(alkyl vinyl ether) is calculated from a ratio of an integrated strength of the peak assigned to the side chain perfluoro(alkyl ether) groups to those of other peaks from the ^{19}F NMR spectrum.

Melt flow rate

Using a KOKA-Type flow tester, melt flow rate is measured by extruding a melt of the copolymer from a nozzle having a diameter of 1 mm and a length of 1 mm under a load of 100 kg/cm^2 at 230°C.

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Bending crack test

From a sheet which is molded with a heat press and has a thickness of 1 mm, a sample having a length of 60 mm and a width of 8 mm is cut out and heated in an electric furnace at 100°C for one hour to prepare a test sample. Each sample is bent by a bending modulus tester with increments in the bending angle of 10 degrees, and an angle at which the sample is first whitened on bending is measured as a whitening start angle. The larger whitening start angle means better suppression of crystallization.

The present invention will be illustrated by the following Examples, in which "parts" are by weight, but is not to be limited to them.

Example 1

Preparation of a chlorotrifluoroethylene polymer modified with 0.05% by mole of perfluoro(propyl vinyl ether)

In a jacketed polymerization reactor equipped with a stirrer with a capacity of 4000 parts of water were added, deionized deaerated water (1000 parts) and sodium hydrogencarbonate (0.75 part). After replacing the interior atmosphere with pure nitrogen gas, the nitrogen gas was evacuated under reduced pressure. Then, chlorotrifluoro-ethylene (1000 parts), perfluoro(propyl vinyl ether) (10 parts) and carbon tetrachloride (10 parts) were injected under pressure. After adjusting the interior temperature to 20°C, stirring was started. To the stirred mixture, a solution of $[Cl(CF_2CFCl)_2-CF_2COO]_2$ in trichlorotrifluoroethane (0.3 g/ml) (13 parts) was added as a polymerization initiator. After 24 hours of polymerization, unreacted chlorotrifluoroethylene was purged, and the resulting copolymer was recovered, washed with warm water and dried to yield a powdery copolymer (370 parts).

The composition and properties of the copolymer are shown in the Table.

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Example 2

Preparation of a chlorotrifluoroethylene polymer modified with 0.5% by mole of perfluoro(propyl vinyl ether)

In the same manner as in Example 1, but charging 107 parts of perfluoro(propyl vinyl ether) and no carbon tetrachloride, polymerization was carried out to yield a powdery copolymer (240 parts).

The composition and properties of the copolymer are shown in the Table.

Comparative Example 1

Preparation of a chlorotrifluoroethylene polymer modified with 1.1% by mole of perfluoro(propyl vinyl ether)

In the same manner as in Example 1, but charging 244 parts of perfluoro(propyl vinyl ether) and no carbon tetrachloride, polymerization was carried out to yield a powdery copolymer (120 parts).

The composition and properties of the copolymer are shown in the Table.

Comparative Example 2

Preparation of a chlorotrifluoroethylene polymer modified with 4.0% by mole of vinylidene fluoride

In a jacketed polymerization reactor equipped with a stirrer with a capacity of 4000 parts of water, were added deionized deaerated water (1000 parts) and sodium hydrogencarbonate (0.75 part). After replacing the interior atmosphere with pure nitrogen gas, the nitrogen gas was evacuated under reduced pressure. Then, chlorotrifluoroethylene (1000 parts), vinylidene fluoride (16 parts) and carbon tetrachloride (8 parts) were injected under pressure. After adjusting the interior temperature to 20°C, stirring was started. To the stirred mixture, a solution of $[Cl(CF_2CFCl)_2CF_2COO]_2$ in trichlorotrifluoroethane (the same concentration as in Example 1) (10 parts) was added as a polymerization initiator. During polymerization, vinylidene fluoride (10 parts) was additionally added over 48 hours to make the gas

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composition in the reactor constant, and after 24 hours from the start of the polymerization, the same solution of $[Cl(CF_2CFCl)_2\text{-}CF_2COO]_2$ in trichlorotrifluoroethane as above (10 parts) was added. The total polymerization time was 48 hours. Thereafter, unreacted chlorotrifluoroethylene was purged, and the resulting copolymer was recovered, washed with warm water and dried to yield a powdery copolymer (580 parts).

The composition and properties of the copolymer are shown in the Table.

Comparative Example 3

Preparation of a homopolymer of chlorotrifluoroethylene

In a jacketed polymerization reactor equipped with a stirrer with a capacity of 4000 parts of water, were added deionized deaerated water (1000 parts) and sodium hydrogencarbonate (0.75 part). After replacing the interior atmosphere with pure nitrogen gas, the nitrogen gas was evacuated under reduced pressure. Then, chlorotrifluoroethylene (1000 parts) was injected under pressure. After adjusting the interior temperature to 20°C, stirring was started. To the stirred mixture, a solution of $[Cl(CF_2CFCl)_2\text{-}CF_2COO]_2$ in trichlorotrifluoroethane (the same concentration as in Example 1) (3 parts) was added as a polymerization initiator. After 24 hours from the start of the polymerization, the same solution of $[Cl(CF_2CFCl)_2\text{-}CF_2COO]_2$ in trichlorotrifluoroethane as above (1.5 parts) was added. The total polymerization time was 42 hours. Thereafter, unreacted chlorotrifluoroethylene was purged, and a resulting copolymer was recovered, washed with warm water and dried to obtain a powdery copolymer (460 parts).

The composition and properties of the copolymer are shown in the Table.

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Table

Example No.	Modifier (mol %)	Melt flow rate ($\times 10^{-3}$ cc/sec.)	Melting point (°C)	Heat of fusion (cal/g)	Crystallization temp.	Tensile properties*) YS (kg/cm^2)	TS (kg/cm^2)	EL (%)	Whitening start angle (°)
1	Perfluoro-(propyl vinyl ether) (0.05)	27.6	213.5	5.22	174.0	424.7	257.2	49.5	60
2	+ (0.5)	2.65	201.0	3.04	164.0	389.4	262.3	61.5	90
Comp. 1	+ (1.1)	27.6	189.5	2.45	146.0	368.2	269.2	139.8	90
Comp. 2	Vinylidene fluoride (4.0)	59.0	193.5	4.61	153.0	367.8	219.7	64.2	60
Comp. 3	---	39.4	213.5	4.81	178.5	441.7	274.7	72.5	40

Note; *) YS; Yield Stress
TS; Tensile strength
EL; Elongation

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CLAIMS:

1. A copolymer which comprises chlorotrifluoroethylene and 0.01 to 1% by mole of perfluoro(alkyl vinyl ether) of the formula:

$$R_f\text{-}O\text{-}CF=CF_2 \qquad (I)$$

wherein R_f is a C_3-C_6 perfluoroalkyl group, and has a melt flow rate of 0.01 to 200 x 10^{-3} cc/sec.

2. A copolymer according to claim 1, wherein the content of said perfluoro(alkyl vinyl ether) is 0.05 to 0.5% by mole.

3. A copolymer according to claim 1, wherein said perfluoro(alkyl vinyl ether) is perfluoro(propyl vinyl ether).