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(54) Title: FLUOROPOLYMERS, FLUOROPOLYMER COMPOSITIONS AND FLUOROPOLYMER DISPERSIONS

(57) Abstract: A tetrafluoroethene copolymer having a melting point of from about 240°C to 325°C, a melt flow index (MFI at 372°C and 5 kg load) of 0.5-80 grams / 10 minutes and having at least 70% by weight of units derived from tetrafluoroethene and further comprising units derived from at least one perfluorinated alkyl allyl ether (PAAE) comonomer corresponding to the general formula: $CF_2=CF-CF_2-O-Rf$ (I) where Rf is a perfluorinated alkyl residue having from 1 to 10 carbon atoms and wherein the alkyl chain of the residue may be interrupted once or more than once by an oxygen atom and further, optionally, comprising units derived from perfluoromethyl vinyl ether (PMVE), perfluoroethyl vinyl ether (PEVE) and a combination thereof and wherein the content of units derived PAAEs and, optionally, PMVE, PEVE or a combination thereof, is at least 1.0 % by weight.

WO 2019/161153 A1

FLUOROPOLYMERS, FLUOROPOLYMER COMPOSITIONS AND FLUOROPOLYMER DISPERSIONS

Field

The present disclosure relates to fluoropolymers and fluoropolymer compositions, to methods of making them and to their applications.

Background

Fluorinated polymers with a high content of TFE and thus high melting points and low melt-flow indexes are typically prepared by aqueous emulsion polymerization, i.e., a radical polymerization carried out in an aqueous phase in the presence of an emulsifier. A perfluorinated alkanoic acid, in particular perfluorooctanoic acid, has been widely used in the industry as preferred emulsifier. Due to the poor biodegradation of perfluorooctanoic acid there is a need to avoid or reduce its use. Polymerizations without adding any perfluoroalkanoic acids have been developed, for example polymerizations using more biodegradable alternative fluorinated emulsifiers as described for example in US Patent No 7,671,112.

However, perfluorinated alkanoic acids, in particular those having from 6 to 12 carbon atoms, have been found in copolymers of tetrafluoroethene (TFE) and perfluorinated vinylethers (PAVEs), in particular perfluoro propyl vinyl ether (PPVE) and higher chain homologues of PPVE even if no such perfluorinated alkanoic acids had been used in the production of the polymers. It is believed that these perfluorinated alkanoic acids may be formed as side products during the polymerization when such perfluorinated vinyl ethers are used as comonomers. Perfluorinated propyl vinyl ethers are commonly used as comonomers in the production of fluoropolymers to provide melt-processable thermoplastic polymers for making shaped articles which great chemical inertness and high service temperatures or to provide shear stable fluoropolymer dispersions, for example to make coating compositions.

Therefore, there is a need to provide high-melting TFE-based copolymers and TFE-based copolymer dispersions without creating any perfluorinated alkanoic acids, in particular those with C_8 to C_{13} alkyl chains, or creating these compounds at very low amounts only. In addition, the resulting polymers advantageously have good mechanical properties, in particular mechanical properties that allow for coatings and making shaped articles.

Summary

In one aspect there is provided a tetrafluoroethene copolymer having a melting point of from about 240°C to 325°C, a melt flow index (MFI at 372°C and 5 kg load) of 0.5-80 grams / 10 minutes and having at least 70% by weight of units derived from tetrafluoroethene and further having units derived from at least one perfluorinated allyl ether (PAAE) comonomer corresponding to the general formula:

$$CF_2=CF-CF_2-O-Rf \qquad (I)$$

where Rf is a perfluorinated alkyl residue having from 1 to 10 carbon atoms and wherein the alkyl chain of the residue may be interrupted once or more than once by an oxygen atom and wherein the polymer, optionally, further comprises units derived from perfluoromethyl vinyl ether (PMVE), perfluoroethyl vinyl ether (PEVE) and a combination thereof, and wherein the total content of units derived from PAAEs, and, optionally derived from PMVE, PEVE, is at least 1.0 % by weight, preferably at least 1.5% by weight.

In another aspect there is provided a composition comprising the tetrafluoroethene copolymer.

In yet another aspect there is provided a method for producing the tetrafluoroethene copolymer comprising copolymerizing tetrafluoroethene, the one or more PAAE, and the optional PMVE, PEVE or a combination thereof, through aqueous emulsion polymerization without adding any perfluorinated alkanoic acid emulsifiers.

In a further aspect there is provided a shaped article comprising the tetrafluoroethene copolymer.

In yet another aspect there is provided a coating containing the tetrafluoroethene copolymer.

In a further aspect there is provided a method of making the coating.

In another aspect there is provided a method of making a blend comprising the tetrafluoroethene copolymer and one or more fluoroelastomer, the method comprises (i) providing an aqueous dispersion comprising the tetrafluoroethene copolymer, (ii) providing an aqueous dispersion comprising the one or more fluoroelastomer, (iii) combining at least a part of the dispersion of (i) with at least a part of the dispersion of (ii).

Detailed Description

In this application terms such as “a” or “an” are meant to encompass “one or more” and are used interchangeably with the term “at least one”.

Any numerical ranges of amounts of ingredients or parameters describing physical/mechanical properties are inclusive of their end points and non-integral values between the endpoints unless stated otherwise (e.g. 1 to 5 includes 1, 1.5, 2, 2.75, 3.80, 4, 5 etc.).

Unless noted otherwise, all parts and percentages are by weight and are based on the total weight of the respective composition, which is 100% by weight. The amounts of all ingredients of that composition add up to 100% by weight. Percentages by weight are also indicated herein as “% wt”, or “weight %”. Likewise percentages indicated to be by mole are based on the total molar composition, which is 100% by mole. The molar percentages of all ingredients of that composition add up to 100% by mole.

In case the description refers to standards like DIN, ASTM, ISO etc and in case the year that standard was issued is not indicated, the version that was in force in 2017 is referred to. In case no version was in force in 2017 anymore, for example the standard has expired, the version in force at the date closest to 2017 is referred to.

The tetrafluoroethene-based polymers of the present disclosure comprise units derived from tetrafluoroethene (TFE), and at least one perfluorinated alkyl or alkoxy allyl ether (PAAE). Such TFE-based polymers can be provided that are essentially free of perfluorinated alkanoic acids. The polymers can form shear-stable aqueous dispersions. To improve the mechanical or other properties of the polymers and their preparation, the polymers preferably contain additionally repeating units derived from perfluoromethyl vinyl ether (PMVE; $CF_2=CF-O-CF_3$), perfluoroethyl vinyl ether (PEVE; $CF_2=CF-O-C_2F_5$) and a combination thereof. It has been found that fluoropolymers according to the present disclosure can easily removed from molds when heat-pressed without leaving residues and metal and also blends of the fluoropolymers according to the present disclosures with inorganic fillers, for example carbon fillers like graphite can be easily removed from the molds after heat-pressing. It has also been found that the polymers according to the present disclosure may be compatible with fluoroelastomers to provide blends with fluoroelastomers.

The polymers are TFE-based and comprise at least 70% by weight, or at least 75 % by weight, preferably at least 85% by weight and more preferably at least 94 % by weight of (comonomer) units derived from TFE (based on the weight of the polymer which corresponds to 100% by weight).

The TFE-based polymers further contain units derived from one or more than one perfluorinated alkyl allyl or alkoxy allyl ether (PAAE) as described below and unites derived from one or more than one perfluorinated alkyl vinyl ether as described below.

PAAEs

The TFE-based polymers further comprise units derived from one or more than one perfluorinated alkyl allyl or alkoxy allyl ether (PAAE's). Suitable PAAEs include unsaturated ethers according to the general formula:

$$CF_2=CF-CF_2-ORf \qquad (I).$$

In formula (I) Rf represents a linear or branched, cyclic or acyclic perfluorinated alkyl or alkoxy residue. Rf may contain up to 10 carbon atoms, i.e., 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10 carbon atoms. Preferably Rf contains up to 8, more preferably up to 6 carbon atoms and most preferably 3 or 4 carbon atoms. The alkyl residue may contain one or more than one catenary oxygen atom, in which case the allyl ethers are also referred to as alkoxy allyl ethers.

Examples of Rf with one or more than one catenary oxygen atoms include but are not limited to residues containing one or more of the following units and combinations thereof: $-(CF_2O)-$, $-(CF_2CF_2-O)-$, $(-O-CF_2)-$, $-(O-CF_2CF_2)-$, $-CF(CF_3)-$, $-CF(CF_2CF_3)-$, $-O-CF(CF_3)-$, $-O-CF(CF_2CF_3)-$, $-CF(CF_3)-O-$, $-CF(CF_2CF_3)-O-$. Further examples of Rf include but are not limited to:

$-(CF_2)_{r1}-O-C_3F_7,$

$-(CF_2)_{r2}-O-C_2F_5,$

$-(CF_2)_{r3}-O-CF_3,$

$-(CF_2-O)_{s1}-C_3F_7$,
$-(CF_2-O)_{s2}-C_2F_5$,
$-(CF_2-O)_{s3}-CF_3$,
$-(CF_2CF_2-O)_{t1}-C_3F_7$,
$-(CF_2CF_2-O)_{t2}-C_2F_5$,
$-(CF_2CF_2-O)_{t3}-CF_3$,

wherein r1 and s1 represent 1, 2, 3, 4, or 5, r2 and s2 represent 1, 2, 3, 4, 5 or 6, r3 and s3 represent 1, 2, 3, 4, 5, 6 or 7; t1 represents 1 or 2; t2 and t3 represent 1, 2 or 3.

Specific examples of PAAE comonomers further include
$F_2C=CF-CF_2-O-(CF_2)_3-(OCF_2)_2-F$,
$F_2C=CF-CF_2-O-CF_2-(OCF_2)_3-CF_3$,
$F_2C=CF-CF_2-O-CF_2-(OCF_2)_4-CF_3$,
$F_2C=CF-CF_2-O-(CF_2O)_2-OCF_3$,
$F_2C=CF-CF_2-O-(CF_2O)_3-OCF_3$,
$F_2C=CF-CF_2-O-(CF_2O)_4-OCF_3$.

In a particular embodiment Rf is a perfluorinated alkyl, preferably a perfluorinated alkyl selected from perfluoromethyl ($-CF_3$), perfluoroethyl ($-C_2F_5$), perfluoropropyl ($-C_3F_7$), and perfluorobutyl ($-C_4F_9$). Preferrably Rf is selected from $-C_3F_7$ or $-C_4F_9$ and preferably is linear. Most preferred PAAE is $CF_2=CF-CF_2-O-CF_2-CF_2-CF_3$ (MA-3), i.e. Rf is
$-CF_2CF_2CF_3$.

PAAEs as described above are either commercially available, for example from Anles Ltd. St. Peterburg, Russia or can be prepared according to methods described in U.S. Pat. No. 4,349,650 (Krespan) or by modifications thereof or by methods known to the skilled person.

Instead of using a single PAAE comonomer also a combination of different PAAE comonomers may be used.

Perfluorinated alkyl vinyl ethers

Preferably, the TFE-based polymers further comprise units derived from one or more than one perfluorinated alkyl vinyl ether (PAVE) selected from perfluoro methyl vinyl ether (PMVE; $CF_2=CF-O-CF_3$) and perfluoro ethyl vinyl ether (PEVE; $CF_2=CF-O-CF_2-CF_3$) and a combination thereof.

Co-polymerizable optional comonomers

The copolymers of the present disclosure may contain, optionally, units derived from further co-polymerizable comonomers, they are referred to herein as “co-polymerizable optional comonomers”. Such comonomers may be fluorinated or non-fluorinated but preferably are fluorinated, chlorinated or chlorinated and fluorinated. These copolymerizable optional comonomers preferably contain an alpha-olefinic functionality, i.e. a $CX_1X_2=CX_3$- group wherein X_1,X_2 and X_3 are independently from each other F, Cl or H with the proviso that at least one is H or F. Preferably all of X_1, X_2 and X_3 are F. The optional comonomers include other perfluorinated alpha-olefins such as hexafluoropropene (HFP), or partially fluorinated alpha olefins such as vinylidenefluoride, vinylfluoride, or F and Cl containing olefins such as chlorotrifluoroethene, or non-fluorinated alpha olefins such as ethane or propene. Also vinyl ethers other than PMVE and PEVE may be used, however, such other vinyl ethers may cause the formation of perfluorinated alkanoic acids during the polymerization reaction. Such vinyl ethers may preferably only be used in low amounts or only for short polymerization periods and, preferably, are avoided, i.e. the polymer according to the present disclosure is free of units derived from perfluorinated vinyl ethers other than PEVE and PMVE.

The optional comonomers also include “functional comonomers”. Functional comonomers, contain additional functional groups. Such functional groups include a second or third alpha-olefinic group or more additional unsaturations, for example to introduce branching sites (“branching modifiers”). Other functional groups include polar end groups (“polarity modifiers”). Polarity modifiers include olefins having polar groups for example acid groups or protected acid groups as additional functional groups. To improve shear stability polarity modifiers may be used as functional monomers. Polarity modifiers may introduce end groups and the end groups may help to stabilize the dispersion, or in combination with appropriate emulsifiers. Polarity modifiers include comonomers with an alpha-olefinic functionality and at least one functional group, preferably an acid group such as an -COOX or an $-SO_2X$ group wherein X may be a hydrogen proton or a metal or ammonium cation. Examples of polarity modifiers include but are not limited to olefin monomers independently represented by formula $CF_2=CF(CF_2)_a-(OC_bF_{2b})_c-(O)_d-(C_eF_{2e})-SO_2X$, and $CF_2=CF(CF_2)_a-(OC_bF_{2b})_c-(O)_d-(C_eF_{2e})-COOX$ wherein a is 0 or 1, each b is independently from 1 to 4, c is 0 to 4, d is 0 or 1, e is 1 to 6, and X is as defined above. In some embodiments, b is 1 to 3, 1 to 2, or 1. In some embodiments, c is 0, 1, or 2; 1 or 2; or 0 or 1. In some embodiments, e is 1 to 4, 1 to 3, or 1 to 2. In some embodiments, c is 0, d is 1, and e is 1 to 4. In some embodiments, a is 0, OC_bF_{2b} is $OCF_2CF(CF_3)$, c is 1 or 2, d is 1, and e is 1 to 4. In some embodiments, a is 1, b is 1, c is 0 to 4, d is 1, e is 1 to 4. C_eF_{2e} may be linear or branched. In some embodiments, C_eF_{2e} can be written as $(CF_2)_e$, which refers to a linear perfluoroalkylene group. When c is 2, the b in the two C_bF_{2b} groups may be independently selected. However, within a C_bF_{2b} group, a person skilled in the art would understand that b is not independently selected. Examples of suitable olefin monomers represented by formula $CF_2=CF(CF_2)_a-(OC_bF_{2b})_c-(O)_d-(C_eF_{2e})-SO_2X$ include $CF_2=CF-CF_2-SO_2X$, $CF_2=CF-O-CF_2-CF_2-SO_2X$, $CF_2=CF-CF_2-O-CF_2-CF_2-SO_2X$, $CF_2=CF-O-(CF_2)_4-SO_2X$, $CF_2=CF-CF_2-O-(CF_2)_4-SO_2X$, and $CF_2=CF-O-CF_2-CF(CF_3)-O-CF_2-CF_2-SO_2X$. $CF_2=CF(CF_2)_a-(OC_bF_{2b})_c-(O)_d-(C_eF_{2e})-CO_2X$ include $CF_2=CF-CF_2-CO_2X$, $CF_2=CF-O-CF_2-CF_2-CO_2X$, $CF_2=CF-CF_2-O-CF_2-CF_2-CO_2X$, $CF_2=CF-O-(CF_2)_4-CO_2X$, $CF_2=CF-CF_2-O-(CF_2)_4-CO_2X$, and $CF_2=CF-O-CF_2-CF(CF_3)-O-CF_2-CF_2-CO_2X$. Certain of these olefin monomers are commercially available. Others may be prepared by known methods. See, for example, U.S. Pat. Nos. 3,282,875 (Connolly), 3,718,627 (Grot), 4,267,364 (Grot), and 4,273,729 (Krespan). To achieve a range from 0 to 200 $-SO_2X$ groups per 10^6 carbon atoms, the amount of $CF_2=CF-O-CF_2-CF(CF_3)-O-CF_2-CF_2-SO_2X$, for example, is typically less than 0.18 weight percent (wt. %), based on the total weight of the monomers incorporated into the copolymer. Such functional comonomers are preferably added into the polymerization at the final stages of the polymerization, preferably during the last 10%, more preferably during the last 5% of the reaction time, analogue to the polymerization as described in EP 1,533,325 B1.

Polymer Properties

The polymers according to the present disclosure are essentially free of perfluorinated alkanoic acids, in particular C_6 to C_{12} acids, i.e. acids according to formula (II) below and their salts. "Essentially free" refers to total and combined amounts of the respective ingredients of less than 500 ppb, preferably less than 200 ppb and more preferably less than 100 ppb. Therefore, the polymers according to the present disclosure contain C_6 to C_{12} acids of less than 500 ppb, preferably less than 200 ppb and more preferably less than 100 ppb. It is believed that the polymers are also essentially free of perfluoroalkanoic acids having from 2 to 16 carbon atoms. In one embodiment the polymers contain a total amount of C_9 to C_{14} perfluorinated alkanoic acids of less than 100 ppb, preferably less than 50 ppb (based on the weight of the polymer), for example from 2 to 20 ppb (based on the weight of the polymer). In one embodiment, the polymers contain less than 50 ppb, preferably less than 45 ppb, for example between 5 and 40 ppb (based on polymer) of perfluorooctanoic acid (C_8-acid) or its salts. The fluorinated acid content of the polymers is determined by extraction of the polymer sample with methanol and is therefore also referred to herein as "extractable acid content". Typically, 1 g of freeze-dried polymer sample is treated with 3 ml of methanol for 16h @ 250 rpm stirring speed at a temperature of 50°C). The supernatant is analysed for acid content by mass spectrometry.

An advantage of the polymers according to the present disclosure is that compositions, for example aqueous dispersions, containing such fluoropolymers can be prepared that are also essentially free of any perfluorinated alkanoic acids, in particular, essentially free of such acids with 6 to 12 carbon atoms. When referred to as perfluorinated alkanoic acids, the term is meant to include the free acids and also their salts. "Essentially free" in this context refers to total and combined amounts of perfluorinated C_6 to C_{12} acids of less than 500 ppb, preferably less than 200 ppb and more preferably less than 100 ppb (the amounts are based on polymer content (solid content) of the dispersion. It is believed that the polymers dispersions are also essentially free of perfluoroalkanoic acids having from 2 to 16 carbon atoms. The polymer dispersions may contain a total amount of C_9 to C_{14} perfluorinated alkanoic acids of less than 100 ppb, preferably less than 50 ppb (based on the weight of the polymer), for example from 2 to 20 ppb (based on the weight of the polymer (solid content)). The dispersions also contain less than 50 ppb, preferably less than 45 ppb, for example between 5 and 40 ppb (based on polymer (solid content)) of perfluorooctanoic acid or its salts. These amounts of acids/salts apply to raw dispersions, for example to dispersions with a fluoropolymer content (solid content) of from about 10 to 40% by weight, as well as to upconcentrated dispersions, for example dispersions with a polymer content of from 50 to 70% by weight.

Perfluorinated alkanoic acids can be represented by the general formula

$$F_3C\text{-}(CF_2)n\text{-}COOM \quad (II)$$

wherein n is an integer. For example if n is 4, the resulting acid is a C_6 acid. Typically n is an integer of from 1 to 14, preferably from (and including) 4 to 10. M is H in case of the free acid or a cation, for example a metal cation or an ammonium cation in case the acid is present as a salt. In case of perfluorooctanoic acid, n is 6 to give a total amount of carbon atoms of 8 ("C_8-acid").

Despite having low amount of acids, the polymers according to the present disclosure still have good mechanical properties and can be used to make shaped articles or can be used for coatings or impregnating substrates. To make shaped articles, the polymers are separated from their dispersions as will be described below. To make coatings, the polymers are typically upconcentrated to increase the polymer content in the dispersion as will be described in greater detail below.

The TFE-based copolymers of the present disclosure typically have a melting point of from about 240°C to about 325°C. In one embodiment the copolymers are high melting. They may have a melting point of from 265°C to 325°C and preferably a melting point of at least 286°C, for example a melting point within the range of from 286°C up to 316°C.

The TFE-based copolymers of the present disclosure are melt-processable. They typically have a melt flow index (MFI) at a temperature of 372°C and a 5 kg load of from about 0.5 to 80 grams per 10 minutes, preferably from about 1.0 gram / 10 minutes to 50 grams / 10 minutes, more preferably from 1.1 g / 10 min to 35 g/ 10 mins.

The TFE-based copolymers preferably have a tensile strength of at least 17 MPa, for example between 21 and 60 MPa. The TFE-based copolymers preferably have an elongation at break of at least 230% (length/length), in some embodiments between 250 and 400%. The TFE-based copolymers may have a flexural modulus of at least 520, in some embodiments between 520 and 600 MPa (ASTM D 790; injection molded bars, 127 mm by 12.7 mm by 3.2 mm, 23°C). The polymers typically may have a specific gravity (DIN EN ISO 12086) of from 2.11 to 2.17 g/cm^3. The copolymer typically may have a hardness (shore D; DIN EN ISO 868) of from 40 to 80, preferably 50 to 70.

The TFE-based copolymers with the above properties may be prepared using the comonomer described herein in the appropriate amounts. Preferably, the copolymers are perfluorinated, which means they are free or essentially free of units derived from any partially or non-fluorinated comonomers. The tetrafluoroethene-based copolymers according to the present disclosure typically contain units derived from the one or more PAAE comonomers in an amount of from about of 0.5 % by weight to about 6 % by weight based on the weight of the polymer, preferably from about 1.5 to 4.0 % by weight. The weight ratio of units derived from PAAE to units derived from the optional PMVE, PEVE or the combination thereof may be from 1 : 10 to 10 :1, preferably from 1 : 5 to 5 : 1. Typically, the TFE-based copolymer has from 75 to 99 % by weight units derived from tetrafluoroethene and from 0.1 to 6% by weight of units derived from the at least one PAAE as described above and from 0.1 to 6 % by weight and, optionally, units derived from PMVE, PEVE or a combination, preferably up to 6 % by weight. Preferably the TFE-based copolymer further comprises from 0 up to 4.4% by weight of units derived from PMVE, PEVE or a combination thereof, with PMVE being preferred. The TFE-copolymer according to the present disclosure may have from 0 up to 8% by weight of units derived from one or more co-polymerizable comonomers as described above, preferably HFP and/or one or more functional comomers (polarity modifiers for creating polar end groups). Preferably, the total amount of PAAE comonomers and PMVE and/or PEVE, if present, is at least 1.1 % by weight, preferably at least 1.5 % by weight. The total amount of units of the polymer, i.e. the total weight of the polymer gives 100.0% by weight. Preferably the PAAE comonomers comprise MA-3.

Preferably, the TFE-based copolymers contain from 90 to 98 % by weight of units derived from TFE and from 1.5 to 10% of units derived from one or more PAAE and from PMVE and from 0 – 5% of units derived from one or more perfluorinated optional comonomers with the total amount of units corresponding to 100% weight.

In one embodiment the TFE-based copolymer of the present disclosure comprises from 94 to 99 % by weight units derived from tetrafluoroethene and from 1 to 5% by weight of units derived from the at least one PAAE and from 0.5 % up to 5 % by weight, preferably up to 4.4% by weight of units derived from PMVE and from 0 to 5% by weight, preferably from 0 to 1.5% by weight, of one or more co-polymerizable optional comonomer, wherein the total amount of units is 100% by weight.

In one embodiment the TFE-based copolymer of the present disclosure comprises from 94 to 99 % by weight units derived from tetrafluoroethene and from 1 to 5% by weight of units derived from the at least one PAAE and from 0.5 % up to 5 % by weight, preferably up to 4.4% by weight of units derived from PMVE, PEVE and a combination thereof, and from 0 to 5% by weight, preferably from 0 to 1.5% by weight, of one or more co-polymerizable optional comonomer, wherein the total amount of units is 100% by weight.

Methods of preparing the polymers

The tetrafluoroethene copolymers described herein may be prepared by emulsion or suspension polymerization in an aqueous phase. In case of emulsion polymerization an emulsifier is used. In case of a suspension polymerization no emulsifier is used. Emulsion polymerization is preferred as it results in stable dispersions of small polymer particles. TFE is copolymerized in the presence of initiators and the comonomers described above. The comonomers are used in effective amounts to produce a copolymer with the properties described herein. Effective amounts include the amounts described above and below and exemplified herein.

Typically, fluorinated emulsifiers are employed in the aqueous emulsion polymerization, however, the polymerization is carried out without adding any perfluorinated alkanoic acids, i.e., compounds according to the formula (II) above, and in particular the polymerization is carried out without adding perfluorinated octanoic acid.

Alternative fluorinated emulsifiers or non-fluorinated emulsifiers may be used instead. When used, a fluorinated alternative emulsifier is typically used in an amount of 0.01% by weight to 1% by weight based on solids (polymer content) to be achieved. Suitable alternative fluorinated emulsifiers include those that correspond to the general formula:

$$[R_f\text{-O-L-COO}^-]_i X_i^+ \qquad \text{(III)}$$

wherein L represents a linear or branched or cyclic partially or fully fluorinated alkylene group or an aliphatic hydrocarbon group, R_f represents a linear or branched, partially or fully fluorinated aliphatic group or a linear or branched partially or fully fluorinated group interrupted once or more than once by an ether oxygen atom, X_i^+ represents a cation having the valence i and i is 1, 2 and 3. In case the emulsifier contains partially fluorinated aliphatic groups it is referred to as a partially fluorinated emulsifier. Preferably, the molecular weight of the emulsifier is less than 1,500 g/mole. Specific examples are described in, for example, US Patent No. 7,671,112. Exemplary emulsifiers include: $CF_3CF_2OCF_2CF_2OCF_2COOH$, $CHF_2(CF_2)_5COOH$, $CF_3(CF_2)_6COOH$, $CF_3O(CF_2)_3OCF(CF_3)COOH$, $CF_3CF_2CH_2OCF_2CH_2OCF_2COOH$, $CF_3O(CF_2)_3OCHFCF_2COOH$, $CF_3O(CF_2)_3OCF_2COOH$, $CF_3(CF_2)_3(CH_2CF_2)_2CF_2CF_2CF_2COOH$, $CF_3(CF_2)_2CH_2(CF_2)_2COOH$, $CF_3(CF_2)_2COOH$, $CF_3(CF_2)_2(OCF(CF_3)CF_2)OCF(CF_3)COOH$, $CF_3(CF_2)_2(OCF_2CF_2)_4OCF(CF_3)COOH$, $CF_3CF_2O(CF_2CF_2O)_3CF_2COOH$, and their salts.

In one embodiment, the molecular weight of the emulsifier, preferably a partially fluorinated emulsifier, is less than 1500, 1000, or even 500 grams/mole.

In order to further improve the stability of the aqueous emulsion, it may be preferred to add one or more emulsifiers during or after the polymerization.

The emulsifier may be added as a microemulsion with a fluorinated liquid, such as described in U.S. Publ. No. 2008/0015304 (Hintzer et al.), WO Publ. No. 2008/073251 (Hintzer et al.), and EP Pat. No. 1245596 (Kaulbach et al.).

Instead of using alternative emulsifiers also the use of non-fluorinated emulsifiers is contemplated. They may be useful when polymers with low melting points or high MFI's are being produced. Examples for polymerizations of fluoropolymers with non-fluorinated emulsifiers are described, for example, in U.S. patent application No. US 2007/0149733.

The aqueous emulsion polymerization may be initiated with a free radical initiator or a redox-type initiator. Any of the known or suitable initiators for initiating an aqueous emulsion polymerization of TFE can be used. Suitable initiators include organic as well as inorganic initiators. Exemplary inorganic initiators include: ammonium-, alkali- or earth alkali salts of persulfates, permanganic or manganic acids, with potassium permanganate preferred. A persulfate initiator, e.g., ammonium persulfate (APS), may be used on its own or may be used in combination with a reducing agent. The reducing agent typically reduces the half-life time of the persulfate initiator. Additionally, a metal salt catalyst such as for example copper, iron, or silver salts may be added.

The amount of the polymerization initiator may suitably be selected, but it is usually from 2 to 600 ppm, based on the mass of water used in the polymerization. The amount of the polymerization initiator can be used to adjust the MFI of the tetrafluoroethene copolymers. If small amounts of initiator are used a low MFI may be obtained. The MFI can also, or additionally, be adjusted by using a chain-transfer agent. Typical chain-transfer agents include ethane, propane, butane, alcohols such as ethanol or methanol or ethers like but not limited to dimethyl ether, tertiary butyl ether, methyl tertiary butyl ether. The amount and the type of perfluorinated comonomer may also influence the melting point of the resulting polymer.

The aqueous emulsion polymerization system may further comprise auxiliaries, such as buffers because some initiators are most effective within certain pH ranges, and complex-formers. It is preferred to keep the amount of auxiliaries as low as possible to ensure a higher colloidal stability of the polymer latex.

The polymerization is preferably carried out by polymerizing TFE and the comonomers simultaneously. Typically, the reaction vessel is charged with the ingredients and the reaction is started by activating the initiator. In one embodiment the TFE and the comonomers are then continuously fed into the reaction vessel after the reaction has started. They may be fed continuously or discontinuously, at a constant TFE : comonomer ratio or at a changing TFE : comonomer ratios.

In another embodiment, a seeded polymerization may be used to produce the tetrafluoroethene copolymers. If the composition of the seed particles is different from the polymers that are formed on the seed particles a core-shell polymer is formed. That is, the polymerization is initiated in the presence of small particles of fluoropolymer, typically small PTFE particles that have been homopolymerized with TFE or produced by copolymerizing TFE with one or more perfluorinated comonomers as described above. These seed particles typically have an average diameter of between 50 and 100 nm or 50 and 150 nm (nanometers). Such seed particles may be produced, for example, in a separate aqueous emulsion polymerization. They may be used in an amount of 20 to 50% by weight based on the weight of water in the aqueous emulsion polymerization. Accordingly, the thus produced particles will comprise a core of a homopolymer of TFE or a copolymer of TFE and an outer shell comprising either a homopolymer of TFE, or a copolymer of TFE. The polymer may also have one or more intermediate shells if the polymer compositions are varied accordingly. The use of seed particles may allow a better control over the resulting particle size and the ability to vary the amount of TFE in the core or shell. Such polymerization of TFE using seed particles is described, for example, in U.S. Pat. No. 4,391,940 (Kuhls et al.) or in WO03/059992 A1.

The aqueous emulsion polymerization, whether done with or without seed particles, will preferably be conducted at a temperature of at least 65°C, preferably at least 70°C. Lower temperatures may not allow to introduce sufficient amounts of PAAE into the polymer to reach the required comonomer content. Upper temperatures may typically include temperatures of 80°C, 90ºC, 100ºC, 110ºC, 120ºC, or even 150ºC.

The polymerization will preferably be conducted at a pressure of at least 0.3, 1.0, 1.5, 1.75, 2.0, or even 2.5 MPa (megaPascals); at most 2.25, 2.5, 3.0, 3.5, 3.75, 4.0, or even 4.5 MPa.

The aqueous emulsion polymerization usually is carried out until the concentration of the polymer particles in the aqueous emulsion is at least 15, 20, 25, or even 30 % by weight (also referred to as “solid content”). To further increase the shear stability of the fluoropolymer dispersion small amounts of comonomers, for example HFP or other perfluorinated comonomers may be added towards the final stage of the polymerization, as described, for example, in EP 1,533,325 B1. Instead of non-function comonomers like HFP or other alpha olefinic perfluorinated comonomers, also functional comonomers as described above (polarity modifiers) may be added towards the final stages of the polymerization analogue to the methods described in EP 1,533,325 B1, typically during the last 10, preferably the last 5 % of the polymerization reaction.

In the resulting dispersion, the average particle size of the polymer particles (i.e., primary particles) is at least 50, 100, or even 150 nm; at most 250, 275, 300, or even 350 nm. These raw dispersions may be subjected to upconcentration to provide fluoropolymer dispersions that may be used, for example, for coating or impregnating substrates.

Fluoropolymer Dispersions

In one embodiment of the present disclosure, the fluoropolymers described herein are provided in the form of an aqueous dispersion. In one embodiment, the dispersion is a raw dispersion, for example a reaction mixture. Such dispersions typically have a fluoropolymer content (solid content) of from about 10 to 35% by weight. Such dispersions are typically free of non-fluorinated anionic, cationic and particularly non-ionic surfactants, in particular of the non-ionic surfactant described below.

In another embodiment of the present disclosure the fluoropolymers described herein are provided as upconcentrated dispersions. For example, the aqueous fluoropolymer dispersions may have a copolymer content of at least 45 % by weight, for example, between 50 and 70 % by weight, or between 46 and 66% by weight (based on the total weight of the dispersion).

Such dispersions may be obtained from the raw dispersions by upconcentration, for example using ultrafiltration as described, for example in US 4,369,266 or by thermal decantation (as described for example in US 3,037,953) or by electrodecantation.

Since, the amounts of perfluorinated acids in the raw and upconcentrated dispersions is already very low, there is no need to subject the dispersions to a treatment to remove them but such a treatment is not detrimental. However, after the conclusion of the polymerization reaction, the dispersions may be treated by anion exchange to remove the alternative fluorinated emulsifiers as described above, if desired. Methods of removing the emulsifiers from the dispersions by anion-exchange and addition of non-ionic emulsifiers are disclosed for example in EP 1 155 055 B1, by addition of polyelectrolytes are disclosed in WO2007/142888 or by addition of non-ionic stabilizers such as polyvinyl alcohols, polyvinyl esters and the like. Typically, dispersions subjected to a treatment of reducing the amount of the alternative fluorinated emulsifiers contain a reduced amount thereof, such as for example amounts of from about 1 to about 500 ppm (or 2 to 200 ppm) based on the total weight of the dispersion. Reducing the amount of the alternative fluorinated emulsifiers can be carried out for an individual dispersion or for combined dispersion, e.g. bimodal or multimodal dispersions or other blends of dispersions, for example fluoroelastomer dispersions.

Salts or ionic emulsifiers may be added to the dispersion to adjust their properties, in particular when the dispersions are used for coating applications, for example to adjust the viscosity, shelf-life or the wettability of the dispersions. For example, the level of conductivity may be adjusted by adding an anionic non-fluorinated surfactant to the dispersion as disclosed in WO 03/020836. Adding cationic emulsifiers to the dispersions is also possible, as described for example in WO 2006/069101. Typical anionic non-fluorinated surfactants that may be used include surfactants that have an acid group, in particular a sulfonic or carboxylic acid group. For example, the dispersions may have a viscosity (20°C) of 5 to 20 MPas, preferably 7-18 MPas (DIN ISO 3219).

Non-fluorinated non-ionic surfactants may also be present in the dispersion, typically for increasing the shear stability of the dispersion. They may be added merely for that purpose or they may be present because they were added, for example, during the work-up proceedings, for example, during the ion-exchange process or upconcentration process. The aqueous dispersions provided herein may have a shear stability of at least 2 minutes, preferably at least 5 minutes.

Examples of non-ionic surfactants can be selected from the group of alkyl aryl polyethoxy alcohols (although not preferred), polyoxyalkylene alkyl ether surfactants, and alkoxylated acetylenic diols, preferably ethoxylated acetylenic diols, and mixtures of such surfactants.

In particular embodiments, the non-ionic surfactant or mixture of non-ionic surfactants corresponds to the general formula:

$$R_1O\text{-}X\text{-}R_3 \qquad \text{(IV)}$$

wherein R_1 represents a linear or branched aliphatic or aromatic hydrocarbon group that may contain one or more catenary oxygen atoms and having at least 8 carbon atoms, preferably 8 to 18 carbon atoms. In a preferred embodiment, the residue R_1 corresponds to a residue (R')(R'')HC- wherein R' and R'' are the same or different, linear, branched or cyclic alkyl groups. R_3 represents hydrogen or a C_1-C_3 alkyl group. X represents a plurality of ethoxy units that can also contain one or more propoxy unit. For example, X may represent - $[CH_2CH_2O]_n$-$[R_2O]_m$-R_3. R_2 represents an alkylene having 3 carbon atoms, n has a value of 0 to 40, m has a value of 0 to 40 and the sum of n+m is at least 2 and the distribution of $[CH_2CH_2O]$ and $[R_2O]$ units may be interchangeable and at random. When the above general formula represents a mixture, n and m will represent the average amount of the respective groups. Also, when the above formula represents a mixture, the indicated amount of carbon atoms in the aliphatic group R_1 may be an average number representing the average length of the hydrocarbon group in the surfactant mixture. Commercially available non-ionic surfactants or mixtures of non-ionic surfactants include those available from Clariant GmbH under the trade designation GENAPOL such as GENAPOL X-080 and GENAPOL

PF 40. Further suitable non-ionic surfactants that are commercially available include those of the trade designation Tergitol TMN 6, Tergitol TMN 100X and Tergitol TMN 10 from Dow Chemical Company. Ethoxylated amines and amine oxides may also be used as emulsifiers.

Other examples of non-ionic surfactants include sugar surfactants, such as glycoside surfactants as described, for example, in WO2011/014715 A2 (Zipplies et al).

Another class of non-ionic surfactants includes polysorbates. Polysorbates include ethoxylated, propoxylated or alkoxylated sorbitans and may further contain linear cyclic or branched alkyl residues, such as but not limted to fatty alcohol or fatty acid residues. Useful polysorbates include those available under the trade designation Polysorbate 20, Polysorbate 40, Polysorbate 60 and Polysorbate 80. Polysorbate 20, is a laurate ester of sorbitol and its anhydrides having approximately twenty moles of ethylene oxide for each mole of sorbitol and sorbitol anhydrides. Polysorbate 40 is a palmitate ester of sorbitol and its anhydrides having approximately twenty moles of ethylene oxide for each mole of sorbitol and sorbitol anhydrides. Polysorbate 60 is a mixture of stearate and palmitate esters of sorbitol and its anhydrides having approximately twenty moles of ethylene oxide for each mole of sorbitol and sorbitol anhydrides.

Typically, the dispersions may contain from about 1 to 12 % by weight based on the weight of the dispersion of one or more non-ionic surfactants.

Polyelectrolytes, such as polyanionic compounds (for example polyanionic poly acrylates) may also be added to the dispersion in addition or instead of the surfactants described above.

The dispersions may further contain ingredients that may be beneficial when coating or impregnating the dispersion on a substrate, such as adhesion promoters, friction reducing agents, pigments and the like. Optional components include, for example, buffering agents and oxidizing agents as may be required or desired for the various applications.

The dispersions comprising the copolymers according to the present disclosure can be used to produce coatings or coating compositions for coating various substrates such as metals, or non-metals, for example polymer substrates and include fluoropolymer substrates. They may also be used to coat fabrics, such as, for example, glass fiber-based fabrics. Such fabrics may be used as architectural fabrics. Generally, the fluoropolymer dispersions may be blended with further components typically used to produce a final coating composition. Such further components may be dissolved or dispersed in an organic solvent such as toluene, xylene and the like. Typical components that are used in a final coating composition include polymers such as polyamide imides, polyimides or polyarylene sulphides or inorganic carbides, such as silicium carbide, and metal oxides. They are typically employed as heat resistant adhesion promoters or primers. Still further ingredients such as pigments and mica particles may be added as well to obtain the final coating composition. The fluoropolymer dispersions typically represent about 10 to 80% by weight of the final composition. Details on coating compositions for metal coatings and components used therein have been described in e.g. WO 02/78862, WO 94/14904, EP 1 016 466 A1, DE 2 714 593 A1, EP 0 329 154 A1, WO 0044576, and US 3,489,595.

The polymer dispersion can also be used to prepare dispersions with bimodal, and multimodal particle-size distributions for example by mixing different dispersions, for example by mixing with one or more other dispersions, for example PTFE dispersions. These combined dispersions may have a wide particle size distribution, such as, for example, particle sizes ranging from 20 nm to 1000 nm as disclosed in e.g. US 5,576,381, EP 0 990 009 B1 and EP 969 055 A1. Multi-modal fluoropolymer particle dispersions may present advantageous properties in coatings, such as better adhesion to the substrate and denser film formation.

The fluoropolymer dispersions may be used, for example, to laminate, coat and/or impregnate a substrate. The substrate or the treated surface thereof may be an inorganic or organic material. The substrate may be, for example a fiber, a fabric, a granule or a layer. Typical substrates include organic or inorganic fibers, preferably glass fibers, organic or inorganic fabrics, granules (such as polymer beads) and layers containing one or more organic polymers, including, for example, fluoropolymers. The fabrics may be woven or non-woven fabrics. The substrate may also be a metal or an article containing a metal surface or a fluoropolymer surface or layer, such as but not limited to PTFE surface or layers. In a preferred embodiment, the copolymers are used as additives for PTFE dispersions for providing coatings, for example anti-corrosive or low friction coatings of metal surfaces.

Coatings may be obtained with copolymers described herein having a critical film forming thickness of at least 5 µm. The coatings may have a transmittance of at least 55%, preferably greater than 60%, for example between 65% and 80%.

The dispersions when used to coat a substrate may provide coatings having a critical film forming thickness (CFT) of at least 5 µm. The dispersions may be provided typically at a pH between 9 and 11 but another pH may be adjusted if desired.

Solids:

The fluoropolymers may also be used for melt processing and are processed as solids. For melt processing and making shaped articles the tetrafluoroethene copolymers are used in dry form and therefore have to be separated from the dispersion. The tetrafluoroethene copolymers described herein may be collected by deliberately coagulating them from the aqueous dispersions by methods known in the art. In one embodiment, the aqueous emulsion is stirred at high shear rates to deliberately coagulate the polymers. Other salt-free methods include the addition of mineral acids. If salt content is not a problem salts can be added as coagulating agents, such as for example, chloride salts or ammonium carbonate. Agglomerating agents such as hydrocarbons like toluenes, xylenes and the like may be added to increase the particle sizes and to form agglomerates. Agglomeration may lead to particles (secondary particles) having sizes of from about 0.5 to 1.5 mm, which may also be average sizes (median). Drying of the coagulated and/or agglomerated polymer particles can be carried out at temperatures of, for example, from 100 °C to 300 °C. Particle sizes of coagulated particles can be determined by electron microscopy. The average particle sizes can be expressed as number average by standard particle size determination software. The particle sizes may be further increased by melt-pelletizing. The melt pellets may have a particle size (longest diameter) of from at least 2, typically from about 2 to about 10 mm.

The coagulated fluoropolymers or melt pellets may be subjected to a fluorination treatment as known in the art to remove thermally unstable end groups. Unstable end groups include -$CONH_2$, - COF and –COOH groups. Fluorination may be conducted so as to reduce the total number of those end groups to less than 100 or less than 50 per 10^6 carbon atoms in the polymer backbone. Suitable fluorination methods are described for example in US 4,743,658 or DE 195 47 909 A1. The amount of end groups can be determined by IR spectroscopy as described for example in EP 226 668 A1. Another advantage of the present disclosure is that the polymers obtained by the polymerization have predominantly – COOH end groups and low amounts of –COF end groups. This allows easier and more effective fluorination because –COOH end groups convert more readily than –COF end groups. End groups are often removed for increasing the thermal stability of the fluoropolymers but also for reducing adhesion to metal substrates, such as molds, when making shaped articles by a heat-pressure treatment. However, another advantage of the polymers according to the present is that an expansive post.fluorination treatment is not needed for reducing adhesion to mold surface upon heat-pressure treatment. Fluoropolymers according to the present disclosure can be easily removed from molds after heat-pressure treatment.

For making shaped articles the tetrafluoroethene copolymers may be brought to the melt (optionally after having been pelletized) and may then be processed from the melt to shaped articles, for example, by injection molding, blow molding, melt extruding, melt spinning, transfer-molding and the like. Additives may be added before or during the melt processing. Such articles include, for example, fibers, films, O-rings, containers, tubes, inner linings of hoses or containers or outer linings of wire, cables, components of pumps, housings and the like. The copolymers typically show good demolding properties, i.e. they can be easily removed from the processing equipment, e.g. molds.

Easy demolding has not only been observed for the fluoropolymers according to the present disclosure but also for compositions containing them, in particular for dry blends or solid compositions of particles, for example filler compositions and elastomer blends described below.

Blends with one or more fillers:

The TFE-copolymers according to the present disclosure may be used for making filler compositions. Typically, such filler compositions contain the fluoropolymers according to the present disclosure as a binder material. The content of fluoropolymer in such composition is typically rather lower, for example from about 5 to 35% by weight or from about 8 to 25% by weight, typically between and including 10 to 20% by weight (based on the total weight of the composition). Fillers typically include inorganic fillers, preferably carbon-fillers, i.e. fillers containing only carbon or predominantly carbon, preferably more than 50% by weight of carbon. Carbon-based fillers include, for example, but are not limited to graphite, coal, carbon black, soot, carbon fibers and combinations thereof. Typical filler compositions contain from about 5 to 35% by weight of one or more fluoropolymer according to the present disclosure and from 95 to 65 percent of carbon-based fillers and from 0 to 35% by weight of one or more other optional ingredients with the proviso that the total amount of ingredients is 100% by weight.

Filler compositions may be used to make, for example, heat-exchangers, electrodes, bipolar plates or a component thereof. A Bipolar plate is a multi-functional component within a fuel cell. It connects and separates the individual fuel cells in series to form a fuel cell stack with required voltage, aids uniform distribution of fuel gas and oxygen over the active surface area of the membrane-electrode assemblies (MEA) of a fuel cell. A bipolar plate conducts electrical current from the anode of one cell to the cathode of the next, facilitates water management within the cell, supports thin membrane and electrodes and clamping forces for the stack assembly, among other things. Essentially the bipolar plates are the electrically-conducting plates which join together the anode of one cell to the cathode of another.

Blends with one or more fluoroelastomer:

The TFE-copolymers can also be used to prepare blends with one or more fluoroelastomer, for example by mixing a TFE-copolymer dispersion with a fluoroelastomer dispersion. Such blends may be a solid composition of particles, including powders, but may also be in the form of pastes or other forms. These combined dispersions may have a wide or a narrow particle size distribution, such as, for example, particle sizes ranging from 20 nm to 1000 nm, depending on the choice of the dispersions to be mixed. The combined dispersions can be used to make coatings as described above. The combined dispersions may also be used to make solid blends (dry blends), by coagulating, isolating, washing and drying the polymer particles using methods as described herein for making solids. These dry blends may be particularly useful for making articles, in particular for processing semiconductors or articles containing semiconductors. In such applications, it may be useful to provide materials that are not only free of metal cations but also do not leak acids or acidic residues. Articles made from the dry blends may contain the blends but the blends usually are no longer in the form of dry compositions of particles.

In commercial blends the fluoroelastomer provides the elastic properties required for sealing or valve applications but they are expensive. Therefore, chemically inert fillers, for example tetrafluoroethene homopolymers (PTFE) are used as fillers in commercial blends with fluoroelastomer. Methods of providing fluoroelastomers that have low amounts of metal cations are known in the art, and basically include avoiding the use of metal salts, using ultrapure materials and may use chemically inert polymer reactor linings to avoid metal contamination by abrasion from reactor vessels. Methods are also available for producing fluoroelastomers without using fluorinated emulsifier acids. Compositions from the preparation of fluoroleastomers containing units derived from vinyl ethers can be treated by anion exchange processes or dispersions (or coagulates) can be treated with organic solvents and water to remove residual fluorinated acids. In the latter case the combined dispersions of TFE-based copolymers according to the present disclosure and the fluoroelastomers may be coagulated, for example by adding one or more mineral acid and subjected to a treatment with a composition containing one or more organic solvents and subsequent washing and drying. Alternatively, dry blends may be prepared by mixing solid particles of the fluoropolymers. It has been found that the TFE-copolymers of the present disclosure are more compatible with fluoroelastomer in such blends than, for example, PTFE. When preparing such blends and measuring the crystallization temperature of the blend, the crystallization temperature of the blends is lower than the crystallization temperature of the unblended thermoplastic polymer, typically lower by 10 to 20°C. This is an indication that the materials are more compatible with each other and that a new thermoplastic-elastomer phase has been formed in the blends. It is believed that such greater compatibility will lead to more stable or resistant products.

Fluoroelastomers suitable in such blends preferably are curable. Preferably they have a glass transition temperature (Tg) of less than 30°C, preferably less than 20°C. The fluoroelastomers may typically have a Mooney viscosity (ML 1+10 at 121°C) of from about 2 to about 150, for example from 10 to 100, or from 20 to 70. The curable fluoropolymers may typically have an onset of cure (Ts2) of less than 1 minute at 180°C.

The fluoroelastomers for making such blends include partially fluorinated elastomers and perfluorinated elastomers. Partially fluorinated elastomers typically contain units derived from TFE and VDF (vinylidene fluoride). Perfluorinated elastomers typically include units derived from TFE and/or one or PAAE or perfluorinated vinyl ether, for example, PMVE. In one embodiment the elastomer contains also units derived from HFP. Typical compositions of a perfluorinated elastomer comprises from 44-62 wt.% units derived from TFE and from 38-56 wt.% of units derived from PMVE and from 0-10% wt. units derived from cure site monomers containing bromine, iodine and/or nitrile functionalities and from 0-10% wt. of units derived from other comonomers or modifiers with the amount of ingredients being selected such that the total amount is 100% by weight.

Typical compositions of a partially fluorinated elastomer comprise from about 22-30 wt.% of units derived from TFE, 30-38 wt.% of units derived from VDF, 34-42 wt.% of units derived from hexafluoropropene (HFP) and from 0-10% wt. of units derived from cure-site monomors containing bromine, iodine and/or nitrile functionalities, and from 0-10% wt. of other comonomers or modifiers with the amount of ingredients being selected such that the total amount is 100% wt.

In a particular embodiment the fluoroelastomer contains from 5-30 mol% of TFE, 15-25 mol% of HFP, 50 to 80 ml% of VDF. In another embodiment the fluoropolymer contains from 5 to 20 mol% of TFE, 55 to 80 mol% of VDF and 15 to 25 mol % of PAVE or PAAE. Specific examples include a fluoropolymer containing 25 mol % TFE, 53 mol % VDF and 22 mol % HFP. Such elastomers may have a Tg of less than -1°C and a Mooney viscosity (ML 1+10 at 121°C) of between 1 and 100, for example 20 to 70. Such fluoropolymers have a nominal fluorine content of between 64 and 70 wt%.

The fluoroelastomers may contain units derived from one or more modifier. Modifiers include perfluorinated bisolefinic ethers. These ethers may modify the polymer architecture by generating branches in the polymer backbone. Therefore, these bisolefinic ethers are also referred to herein as “modifiers”. Suitable perfluorinated bisolefinic ethers include those represented by the general formula:

$CF_2=CF-(CF_2)_n-O-(Rf)-O-(CF_2)_m-CF=CF_2$

wherein n and m are independent from each other either 1 or 0 and wherein Rf represents a perfluorinated linear or branched, cyclic or acyclic aliphatic or aromatic hydrocarbon residue that may be interrupted by one or more oxygen atoms and comprising up to 30 carbon atoms. Preferably, the modifiers are used and present in low amounts, for example in lower amounts than any of the comonomers described above. More preferably, the modifiers are present in amounts of greater than 0 and up to about 1.4 %, for example from about 0.1% to about 1.2 or from about 0.3% to about 0.8% by weight based on the total weight of fluoropolymer.

The fluoroelastomer may also contain one or more cure-sites. Suitable cure-sites include iodine, bromine and nitrile groups and combinations thereof. They can be introduced into the molecule by using chain-transfer agents or cure-site monomers. Examples of cure-site comonomers include for instance:

(a) bromo- or iodo- (per)fluoroalkyl-(per)fluorovinylethers, for example including those having the formula:

$ZRf\text{-}O\text{-}CX{=}CX_2$

wherein each X may be the same or different and represents H or F, Z is Br or I, Rf is a C1-C12 (per)fluoroalkylene, optionally containing chlorine and/or ether oxygen atoms. Suitable examples include $ZCF_2\text{-}O\text{-}CF{=}CF_2$, $ZCF_2CF_2\text{-}O\text{-}CF{=}CF_2$, $ZCF_2CF_2CF_2\text{-}O\text{-}CF{=}CF_2$, $CF_3CFZCF_2\text{-}O\text{-}CF{=}CF_2$ or $ZCF_2CF_2\text{–}O\text{-}CF_2CF_2CF_2\text{-}O\text{-}CF{=}CF_2$ wherein Z represents Br of I; and

(b) bromo- or iodo perfluoroolefins such as those having the formula:

$Z'\text{-}(Rf)r\text{-}CX{=}CX_2$

wherein each X independently represents H or F, Z' is Br or I, Rf is a C_1-C_{12} perfluoroalkylene, optionally containing chlorine atoms and r is 0 or 1; and

(c) non-fluorinated bromo and iodo-olefins such as vinyl bromide, vinyl iodide, 4-bromo- 1-butene and 4-iodo-1-butene.

Examples of nitrile containing monomers that may be used correspond to the following formulae: $CF_2{=}CF\text{-}CF_2\text{-}O\text{-}Rf\text{-}CN$; $CF_2{=}CFO(CF_2)_rCN$; $CF_2{=}CFO[CF_2CF(CF_3)O]_p(CF_2)_vOCF(CF_3)CN$; $CF_2{=}CF[OCF_2CF(CF_3)]_kO(CF_2)_uCN$ wherein, r represents an integer of 2 to 12; p represents an integer of 0 to 4; k represents 1 or 2; v represents an integer of 0 to 6; u represents an integer of 1 to 6, Rf is a perfluoroalkylene or a bivalent perfluoroether group. Specific examples of nitrile containing fluorinated monomers include perfluoro (8-cyano-5-methyl-3,6-dioxa-1-octene), $CF_2{=}CFO(CF_2)_5CN$, and $CF_2{=}CFO(CF_2)_3OCF(CF_3)CN$.

To further enhance the bonding between the fluoroelastomer matrix, in particular a perfluoroelastomer matrix, the TFE-copolymer can be modified with Br-, I- and/or CN-containing comonomers, e.g. BTFE, iodine-/nitrile-containing olefins (vinyl/allyl ethers) to have iodine, bromine or nitrile end or side groups. The cure site monomers described herein can be used for this purpose. For this purpose, the cure-site monomers are used preferably during end of the polymerization reaction, for example during the last 5 – 10 % of the polymerization process; the overall content of cure site monomers or its units is typically less than 1 % by weight based on the weight the TFE-copolymer. During a cross-linking reaction the thermoplastic material can be bonded further to the fluoroelastomer material.

The dry blends may typically contain the one or more fluoroelastomer in an amount of from about 10 % up to about 90 % by weight based on the total weight of the blend which is 100% by weight. The blend may contain the fluorothermoplastic polymers in an amount from about 90 % by weight up to 10 % by weight based on the total weight of the blend which 100 % by weight. In one embodiment the blends are solid particles. Preferably, the blend has a total extractable amount of perfluorinated C_6-C_{12} alkanoic carboxylic acids or its salts of less than 500 ppb based on the amount of the copolymer. Preferably, the blends have a total amount of perfluorooctanoic acid or its salts of less than 50 ppb, preferably less than 25 ppb (based on total fluoropolymer content).

In one embodiment, the blend is an aqueous dispersion. Such dispersion may contain from about 10 to 80% by weight of water and from 10% to 90% by weight of fluoroelastomers and from 10 to 90% by weight of fluorothermoplastic polymer and wherein the amounts are selected such that the total weight of the dispersion is 100% by weight. The weight ratio of TFE-copolymer to fluoroelastomer may be from 1 : 9 to 9 : 1. Preferably, the dispersion has a total extractable amount of perfluorinated C_6-C_{12} alkanoic carboxylic acids or its salts of less than 500 ppb based on the total amount of the fluoropolymers. Preferably, the blends have a total amount of perfluorooctanoic acid or its salts of less than 50 ppb, preferably less than 25 ppb based on the total amount of fluoropolymers.

Preferably, in the dispersion the fluoroelastomer and thermoplastic fluoropolymer have a particle size of from about 50 – 300 nm, preferably from 80 – 250 nm. The average particle size of the fluoroelastomer may be smaller, greater or the same as the average particle size of the thermoplastic fluoropolymer.

Advantages and embodiments of this invention are further illustrated by way of examples, without, however, intending to limit the disclosure to these examples. The disclosure can be practised with other materials, ranges and embodiments within the scope of the claims.

Methods:

Melt flow index:

The melt flow index (MFI), reported in g/10 min, was measured according to DIN EN ISO 1133-1:2012 03 at a support weight of 5.0 kg. The MFI was obtained with a standardized extrusion die of 2.1 mm diameter and a length of 8.0 mm. Unless otherwise noted, a temperature of 372°C was applied.

Tensile properties:

Tensile strength and elongation at break were determined at 23 °C following DIN EN ISO 527-1. Tests were performed with 2 mm thick test specimens according to DIN EN ISO 12086-2:2006-05 and with a testing speed of 50 mm/min. The results of measurements with five test specimen were averaged.

Melting peaks:

Melting peaks of the fluororesins were determined in accordance with DIN EN ISO 11357-3:2013-04 using a Mettler-Toledo DSC 2 under nitrogen flow and heating and cooling rates of 10°C/min. The indicated melting points relate to the melting peak maximum of the second heating run.

Particle size determination:

The latex particle size determination can be conducted by means of dynamic light scattering with a *Malvern Zetasizer 1000 HSA* in accordance to DIN ISO 13321:2004 10.

Particle sizes of solid composition of particles (not of dispersions as above) can be determined by optical microscopy and using particle size software or imaging. If particles are not regular or spherical the largest dimension is chosen as diameter of the particle. Average particle sizes of solid compositions is the median.

Content of perfluorinated alkanoic acids (extractable acids):

The polymer latex was freezed dried to remove the water after spiking with a surrogate recovery standard (SRS) $^{13}C_4$-PFOA (perfluorooctanoic acid having 4 of its carbon atoms replaced by ^{13}C isotopes; commercially available from Campro Scientific GmbH, Berlin, Germany) at a concentration of 25 ppb based on solid content of the dispersion. 1 g of the freeze-dried polymer material was treated with 3 ml methanol in a vial for 16 h @ 250 rpm stirring speed and a temperature of 50°C) to extract perfluorinated alkanoic acids. The mixture was centrifuged (~10 min @ 4400 rpm) and an aliquot of the supernatant was transferred into a 2ml autosampler vial.

The extract was analyzed for perfluorocarboxylic acids with reversed phase HPLC coupled with a triple quadrupole mass spectrometer (e.g. Agilent 6460 or ABSciex API 4000 QQQ-MS) in negative Multiple Reaction Mode (MRM) using analyte typical transitions, e.g. m/z 413 -> 369 for PFOA. The HPLC (Agilent 1200 or 1260) was equipped with an Agilent C18 column (Zorbax Eclipse XDB-C18 4.6x50mm 1.8 µm) and run in gradient mode with high purity water and methanol @ 50°C, both solvents were LC-MS grade and modified with 10 mmol ammonium acetate (gradient 15% MeOH -> 100% MeOH). The analytes were quantified using equivalent or similar isotope labelled internal standards (e.g. $^{13}C_8$-PFOA as internal standard for PFOA, available from Campro Scientific GmbH, Berlin, Germany) in a calibration range of 0.5 – 200 ng/ml analyte in methanolic extract, resulting in a lower level of quantification (LLOQ) related to polymer of 1.5 ppb and an upper limit of quantification (ULOQ) of 600 ppb. Analytes with concentrations higher than ULOQ were diluted with methanol into the calibration range and the analysis was repeated.

For a most effective extraction of fluorinated acids from solid polymer samples, the particle size of the polymer sample should be less than 250 µm. Samples with larger particles should be ground under mild conditions (e.g. by cryo milling) before the extraction. Solid samples, for example coagulated polymer, were washed 6 times with water (each washing step was carried out with at least 100 times of the volume of the samples, and then dried for 6 hours at 115°C at reduced pressure (200 mbar) to remove the water).

Solid Content:

The solid content (fluoropolymer content) of the dispersions can be determined gravimetrically according to ISO 12086. A correction for non-volatile inorganic salts is not carried out. The solid content of the polymer dispersions is taken as polymer content.

Vinyl and allyl ether comonomer content:

Thin films of approximately 0.1 mm thickness were prepared by moulding the polymer at 350 °C using a heated plate press. These films were then scanned in nitrogen atmosphere using a Nicolet DX 510 FT-IR spectrometer. The OMNIC software (ThermoFisher Scientific, Waltham, Mass.) was used for data analysis. Herein the $CF_2=CF\text{-}CF_2\text{-}O\text{-}CF_2\text{-}CF_2\text{-}CF_3$ (MA-3) content, reported in units of weight%, was determined from an infrared band at 999 1/cm and was calculated as 1.24 × the ratio (factor determined by means of solid-state NMR) of the 999 1/cm absorbance to the absorbance of the reference peak located at 2365 1/cm. The $CF_2=CF\text{-}O\text{-}CF_3$ (PMVE) content, reported in units of weight%, was determined from an infrared band at 889 1/cm and was calculated as 11.2 × the ratio of the 889 1/cm absorbance to the absorbance of the reference peak located at 2365 1/cm. The $CF_2=CF\text{-}O\text{-}CF_2\text{-}CF_2\text{-}CF_3$ (PPVE) content, reported in units of weight%, was determined from an infrared band at 993 1/cm and was calculated as 0.95 × the ratio of the 993 1/cm absorbance to the absorbance of the reference peak located at 2365 1/cm.

Shear stability:

150 g dispersion, thermostated to 20°C, were put in a 250 ml standard glass beaker of an inner diameter of 65 mm. The agitation head (S 25 N - 25 G) of an Ultra Turrax T25, supplied by Janke & Kunkel, was immersed in the center of the beaker such that the end of the head was 7 mm above the beaker bottom. The Ultra Turrax was switched on at a revolution speed of 8000 rpm. Agitation rendered the surface of the dispersion "turbulent" or "wavy". After 10 to 20 sec, 2.0 g xylene were added dropwise within less than 10 sec to the agitated dispersion. Time measurement started with the addition of xylene and was stopped when the surface of the agitated dispersion no longer showed visible turbulence. The surface "freezes" or smoothes due to coagulation. Coagulation was accompanied by a characteristic change of sound of the Ultra Turrax. In case that the "surface freezing" could not be observed clearly due to foam formation the time measurement was stopped with the onset of the change of sound. Reported shear stability values in the examples are the average of 5 measurements.

Specific gravity:

The protocol of DIN EN ISO 12086 can be followed.

Transmission/transmittance:

The transmission can be measured according to ASTM D 1003 using a direct reading haze meter, (the transparency meter "haze-gard plus", from BYK-Gardner GmbH, Geretsried, Germany, serial number 111156). Samples can be prepared as follows: The dispersion is precipitated by adding 1 litre of dispersion into a 2L beaker and mixing it with 20 ml of concentrated hydrochloric acid at a stirring speed of 800 rpm and agglomerated by adding 10 ml of gasoline (Shellsol 80-110). The precipitate is washed with distilled water and dried in a rotary evaporator at 90°C at reduced pressure. The dried agglomerates are then dried further in a vacuum oven at 210°C for 16 h. 10 g of the precipitate are sieved through a 2 mm sieve and then compressed in a 4-stations press (350 bar, 5 min holding time) into a sheet having a diameter of 80 mm. This sheet is sintered as follows: heating from room temperature to 290 °C at the maximum heating rate. Then the sample is heated from 290 °C to 380 °C at a heating rate of 120 °C per hour and holding the temperature of 380 °C for 30 min before cooling the sample down to a temperature of 294 °C at a cooling rate of 60 °C per hour after which the oven is switched off and the samples were allowed to reach room temperature. The haze meter indicates transmission values (in per cent) of the samples.

Critical film thickness (CTF):

A 200ml ml beaker was filled with the dispersion. Foam, if present, was removed by a pipette. A degreased aluminum test plate (200mm x 40mm x 1 mm; degreasing by rinsing with acetone), was immersed into the dispersion for 10 seconds and then hung at a plate holder at an angle of 20° and dried at ambient conditions for 5 minutes. The test sample was then put in an oven kept at 380°C for 10 minutes. The aluminum plate was then taken out of the oven and allowed to cool down at ambient conditions to reach room temperature. The plate was then examined by an optical microscope (100 x magnification) for the formation of cracks. The thickness of the layer formed on the aluminum plate was determined (using a MiniTest 3100 from ElektroPhysik Dr. Steingroever GmbH& Co. KG, Cologne, Germany). The procedure was repeated until cracks were visible. The thickness of the layer before cracks have appeared is determined as critical film thickness. The results reported were the average from two measurements.

Glass transition temperature (Tg):

The Tg can be measured by differential scanning calometry, for example using a TA Instruments Q200 modulated DSC (heating rate from -150°C to 50°C at 2-3°C / minute; modulation amplitude of +/- 1°C per minute during 60 seconds).

Mooney viscosity:

Mooney viscosities can be determined in accordance with ASTM D1646 - 07(2012), 1 minute pre-heat and a 10 minute test at 121°C (ML 1+10 @ 121°C).

Examples

Example 1 (TFE/MA-3 copolymer)

A polymerization kettle with a total volume of 48 L equipped with an impeller agitator system was charged with 28 L deionized water and 670 g of a 30 mass% aqueous solution of ammonium 4,8-dioxa-3-H-perfluorononanoate (CF_3-O-$(CF_2)_3$-O-CFH-CF_2-$COONH_4$, prepared as described in "Preparation of Compound 11" in U.S. Pat. No. 7,671,112). The oxygen-free kettle was then heated up to 90 °C and the agitation system was set to 230 rpm. The kettle was charged with 40 mbar ethane and 100 g MA-3. Then the reactor was pressurized with 365 g TFE to 6 bar absolute reaction pressure. The polymerization was initiated by the addition of 2 g ammonium peroxydisulfate (APS). As the reaction started, the reaction temperature of 90 °C was maintained and the reaction pressure of 6 bar absolute was maintained by feeding TFE and MA-3 into the gas phase with monomer mole fractions of $x_{TFE} = 0.9924$ and $x_{MA-3} = 0.0076$. During the polymerization period a 0.5 mass% aqueous solution of APS was added to the kettle at constant rate of 135 g/h. When a total feed of 6 kg TFE was reached in 240 min, the feed of the monomers was interrupted by closing the monomer valves. Then the reactor was vented and flushed with N_2 in four cycles. The so-obtained 35 kg polymer dispersion, having a solid content of 17.5 mass% and latex particles with 183 nm in diameter according to dynamic light scattering, was removed at the bottom of the reactor. After the polymerization was completed a sample was freeze-coagulated at -18 °C in a refrigerator overnight. After defrosting, the so-obtained agglomerate was washed five times with deionized water under vigorous agitation and then dried in an oven at 130 °C for 12 hours. The polymer showed a melting point of 312 °C, an MFI of 10 g/10 min, an MA-3 content of 1.9 mass%, a tensile strength of 23.9 MPa (23 °C), and an elongation at break of 369 % (23 °C).

The dispersion was upconcentrated by thermal treatment (evaporation) to reach a solid content of about 50% by weight. 5.0 % weight of non-fluorinated non-ionic surfactants were added. The shear stability of the dispersion was determined to be 228 s. The content of perfluorinated alkanoic acids is given in Table 1.

Example 2 (TFE/MA-3 copolymer, HFP addition)

A copolymer was prepared in the same manner as in Example 1 except that after feeding 5.6 kg of TFE the feeding of MA-3 was stopped and 2 g APS were added. Subsequently 60 g of HFP were added. After 270 min of polymerization time 35.5 kg of polymer dispersion was obtained with a solid content of 17.6 mass% and latex particles with 184 nm in diameter. The polymer showed a melting point of 312 °C, an MFI of 12.5 g/10 min, and an MA-3 content of 2.0 mass%.

The raw dispersion was upconcentrated as described in example 1. The shear stability of the dispersion was determined to be 278 s. The content of perfluorinated alkanoic acids is given in Table 1.

Example 3 (TFE/MA-3 copolymer with MV4S addition)

A copolymer was prepared in the same manner as in Ex 1 except that after feeding 5.6 kg of TFE the feeding of MA-3 was stopped and 2 g APS were added. Subsequently 32 g of an aqueous emulsion of perfluoro(5-oxahept-6-ene-1-sulfonyl fluoride) ($CF_2=CF-O-(CF_2)_4-SO_2F$; MV4S) (50 mass%) and ammonium-4,8-dioxa-3-H-perfluorononanoate (0.25 mass%) were added. After 240 min of polymerization time 35 kg of polymer dispersion was obtained with a solid content of 17.7 mass% and latex particles with 181 nm in diameter.

The polymer showed a melting point of 312 °C, an MFI of 9.6 g/10 min, and an MA-3 content of 2.0 mass%.

The raw dispersion was upconcentrated as described in example 1. The shear stability of the dispersion was determined to be more than 60 min. The content of perfluorinated alkanoic acids is given in Table 1.

Comparative Example 1 (TFE/PMVE copolymer)

The copolymer of Comparative Example 1 was prepared using a method similar to the one of Example 1. However, the kettle was heated up to 70 °C before charging with 140 mbar ethane and 57 g PMVE. Then the reactor was pressurized with 640 g TFE to 8.7 bar absolute reaction pressure. The polymerization was initiated by the addition of 7 g ammonium peroxydisulfate (APS). A polymerization temperature of 70 °C and a reaction pressure of 8.7 bar were used. The monomer feed mole fractions were adjusted to $x_{\mathrm{TFE}} = 0.985$ and $x_{\mathrm{PMVE}} = 0.015$. During the polymerization no APS was added to the kettle. When a total feed of 12.2 kg TFE was reached in 270 min, the feed of the monomers was interrupted by closing the monomer valves. The so-obtained 43 kg polymer dispersion, having a solid content of 29.5 mass% and latex particles with 150 nm in diameter according to dynamic light scattering, was removed at the bottom of the reactor. The polymer showed a melting point of 309 °C, an MFI of 16 g/10 min, and a PMVE content of 2.5 mass%. Because the material was very brittle, the required test specimen for tensile tests could not be prepared. The raw dispersion was upconcentrated as described in example 1. The shear stability of the dispersion was determined to be 284 s. The content of perfluorinated alkanoic acids is given in Table 1.

Comparative Example 2 (TFE/PPVE copolymer)

The copolymer of Comparative Example 2 was prepared using a method similar to the one of Example 1. However, only 390 g of a 30 mass% aqueous solution of ammonium 4,8-dioxa-3-H-perfluorononanoate was used. Additionally, the kettle was heated up to 70 °C before charging with 110 mbar ethane and 90 g PPVE-1. Then the reactor was pressurized with 1100 g TFE to 8.7 bar absolute reaction pressure. The polymerization was initiated by the addition of 1.7 g ammonium peroxydisulfate (APS). A polymerization temperature of 70 °C and a reaction pressure of 8.7 bar were used. The monomer feed mole fractions were adjusted to $x_{\mathrm{TFE}} = 0.985$ and $x_{\mathrm{PPVE\text{-}1}} = 0.015$. During the polymerization no APS was added to the kettle. When a total feed of 12.2 kg TFE was reached in 260 min, the feed of the monomers was interrupted by closing the monomer valves. The so-obtained 43 kg polymer dispersion, having a solid content of 29.4 mass% and latex particles with 153 nm in diameter according to dynamic light scattering, was removed at the bottom of the reactor. The polymer showed a melting point of 310 °C, an MFI of 9.3 g/10 min, a PPVE-1 content of 3.3 mass%, a tensile strength of 27.4 MPa (23 °C), and an elongation at break of 366 % (23 °C).

The raw dispersion was upconcentrated as described in example 1. The shear stability of the dispersion was determined to be 970 s. The content of perfluorinated alkanoic acids is given in Table 1.

Example 4

TFE/MA-3/PMVE copolymer

The copolymer of Example 4 was prepared using a method similar to the one of Example 1. However, the kettle was charged with 13 mbar ethane, 87 g MA-3, and 29 g PMVE. Then the reactor was pressurized with 560 g TFE to 8.7 bar absolute reaction pressure. The polymerization was initiated by the addition of 3.7 g ammonium peroxydisulfate (APS). A reaction pressure of 8.7 bar was used. The monomer feed mole fractions were adjusted to $x_{\mathrm{TFE}} = 0.988$, $x_{\mathrm{MA\text{-}3}} = 0.004$, and $x_{\mathrm{PMVE}} = 0.008$. During the polymerization period a 0.5 mass% aqueous solution of APS was added to the kettle at constant rate of 100 g/h. When a total feed of 5.9 kg TFE was reached in 210 min, the feed of the monomers was interrupted by closing the monomer valves. The so-obtained 37 kg polymer dispersion, having a solid content of 17.0 mass% and latex particles with 146 nm in diameter according to dynamic light scattering, was removed at the bottom of the reactor. The polymer showed a melting point of 306 °C, an MFI of 2.0 g/10 min, an MA-3 content of 1.3 mass%, a PMVE content of 0.9 mass%, a tensile strength of 32.0 MPa (23 °C), and an elongation at break of 372 % (23 °C).

The raw dispersion was upconcentrated as described in example 1. The shear stability of the dispersion was determined to be 106 s. The content of perfluorinated alkanoic acids is given in Table 1.

Table 1: Content of perfluorinated alkanoic acids in ppb relative to solid content of the dispersion (based on polymer weight).

Example	C_9	C_{10}	C_{11}	C_{12}	Sum C_9–C_{12}
Ex 1	1.9	< 1.4	< 1.4	< 1.4	< 6.1
Ex 2	< 13.0	< 13.0	< 13.0	< 13.0	< 52.0
Ex 3	< 13.0	< 13.0	32.8	< 13.0	< 71.8
Comp Ex 1	3.0	3.8	2.4	< 1.4	< 10.6
Comp Ex 2	6729.0	177.1	6033.0	148.2	13087.3
Ex 4	< 13.2	< 13.2	< 13.2	< 13.2	< 52.8

The amount of perfluorinated octanoic acid (C_8) was 40 ppb for examples 1 to 3, 10 ppb for example 4 and 700 ppb for comparative example 2. The metal content of the compositions was less than 10 ppm for each of the following metals: alkaline metals, alkaline earth metals, Al, Fe, Cr, Ni, Co, Mn, Zn.

Example 4A

An aqueous dispersion comprising a TFE/MA-3/PMVE polymer according to the present disclosure was prepared similar to the process described in example 4 but with an HFP addition towards the end of the reaction similar to the process described in example 2. The dispersion was subjected to a shear stability test and showed a shear stability of more than 8 minutes.

Comparative Example 3 (PFE Blend with PTFE)

An aqueous perfluoroelastomer (PFE) latex (solid content 29.7 w%, particle size 80 nm, repeating units of TFE and PMVE and having nitrile cure sites; pH 2,4) obtained by aqueous polymerization with alternative fluorinated emulsifier was blended with an aqueous PTFE dispersion having a particle size of 220 nm to give a PFE to PTFE blend of 80% to 20% in respect to the mass fraction. The dispersion was coagulated into HNO_3 solution (5wt.%), washed with deionized water and oven dried at 115° for 16 h. The melting point of the dry blend was 330°C and the crystallization temperature was 317°C. The crystallization temperature of the blend was not shifted from that of the original PTFE.

Example 5 (PFE blend with thermoplastic fluoropolymer according to the invention)

The an aqueous fluoroelastomer (PFE) latex of comparative example 3 was blended with a 30 wt.% aqueous latex of a perfluorinated thermoplastic fluoropolymer according to the present disclosure (TFE copolymerized with MA-3 having an MFI of 3 (372°C/5kg) and a melting point of 306°C) to achieve a ratio of 80/20 by weight of elastomer to thermoplastic. The dispersion was coagulated into HNO_3 solution (5wt.%), washed with deionized water and oven dried at 115° for 16 h. The melting point of the dry blend was 302°C and the crystallization temperature was 265°C. The crystallization temperature of the blend was 18°C lower compared to the crystallization temperature the original perfluorinated thermoplastic fluoropolymer. This indicates greater homogeneity of the blend. The same trend of lower crystallization temperature of the blend compared to the original thermoplastic component was observed when using a TFE copolymer according to the present disclosure containing units derived from MA-3 and PMVE.

Example 6 (Blend of thermoplastic fluoropolymer with filler)

Graphite was added to a fluoropolymer dispersion prepared analogue to example 4 to which graphite was added to give a ratio of graphite to fluoropolymer (TFE-MA-3,PMVE) in a weight ratio of about graphite to fluoropolymer of about 4 : 2. The resulting mixture was filtered off and dried to remove the water. The resulting powder mixture was then heat pressed (between two steel plate (each plate of 100 mm width x 100 mm length, thickness about 4 mm; heating from room temperature to 300°C at 100 kbar pressure within 15 minutes and keeping at 300°C and 100 kbar for 3 minutes. After cooling down to room temperature the mixture was pressed into a homogeneous sheet that could be easily removed from the steel plates without leaving any on the steel plates.

Comparative example 4

Example 6 was repeated but instead copolymer of TFE with PPVE was used. A sheet was formed that could not be removed easily from the steel plate. The surface of the sheet was uneven because part of the compressed mixture stuck to the steel plate.

Example 7 (press sintering of fluoropolymers)

A TFE-MA-3-PMVE polymer according to the present disclosure was prepared analogue to example 4 and dried. The resulting powder was press-sintered in a sintering press covered with a protective aluminum sheet. The powder was press-sintered into a disk having a thickness of about 2mm by heating to from 40°C to 360°C within 180°C and keeping the press at 360°C for min at a pressure of 50 bar and cooling down to room temperature within 15 minutes. The disk could be easily removed from the press and the protective aluminum sheet. The example was repeated with a PFA (a TFE-PPVE copolymer). The resulting disk stuck to the aluminum sheet.

List of particular, illustrative embodiments

The following list is provided to illustrate the present disclosure by some particular embodiments without any intention to limit the present disclosure to the embodiments provided in this list.

First illustrative embodiment: A tetrafluoroethene copolymer having a melting point of from about 240°C to 325°C, a melt flow index (MFI at 372°C and 5 kg load) of 0.5-80 grams / 10 minutes and having at least 70% by weight of units derived from tetrafluoroethene and further having units derived from at least one perfluorinated allyl ether (PAAE) comonomer corresponding to the general formula:

$$CF_2=CF-CF_2-O-Rf \qquad (I)$$

where Rf is a perfluorinated alkyl residue having from 1 to 10 carbon atoms and wherein the alkyl chain of the residue may be interrupted once or more than once by an oxygen atom and wherein the polymer, optionally, further comprises units derived from perfluoromethyl vinyl ether (PMVE), perfluoroethyl vinyl ether (PEVE) and a combination thereof, and wherein the total content of units derived from and PAAEs, and, optionally derived from PMVE, PEVE, is at least 1.0 % by weight, preferably at least 1.5% by weight.

Second illustrative embodiment: The tetrafluoroethene copolymer of the first embodiment having a melting point between 265°C and 325°C, a melt flow index between 1 and 80 g / 10 mins and further comprising at least 90% by weight of units derived from TFE and further having a tensile strength of at least 17 MPa and an elongation at break of at least 230%.

Third illustrative embodiment: The tetrafluoroethene copolymer of either one of the first or the second embodiment comprising at least 90% by weight, preferably at least 95% by weight, and wherein the polymer comprises a PAAE according to formula (I) with Rf selected from the group consisting of:

perfluoromethyl (-CF_3), perfluoroethyl (-C_2F_5), perfluoropropyl (-C_3F_7) and perfluorobutyl (C_4F_9), preferably -C_2F_5, -C_3F_7 or -C_4F_9.

Fourth illustrative embodiment: The tetrafluoroethene copolymer of any one of the preceding illustrative embodiments wherein the copolymer comprises a PAAE selected from CF_2=CF-CF_2-O-CF_2-CF_2-CF_3 (MA-3).

Fifth illustrative embodiment: The tetrafluoroethene copolymer of any one of the preceding illustrative embodiments having a melting point between 240°C and 280°C, a melt flow index between 0.8 and 80 g / 10 mins and further comprising repeating units derived from hexafluoropropene.

Sixth illustrative embodiment: The tetrafluoroethene copolymer of any one of the preceding illustrative embodiments comprising from about 75 % by weight to about 99 % by weight, preferably up to 98,5 % by weight, of units derived from tetrafluoroethene and from 0.1 to 6% by weight of units derived from the at least one PAAE as described above and from 0% by weight up to 6 % by weight of units derived from PMVE, PEVE or a combination thereof and from 0% by weight up to 8% by weight of units derived HFP wherein the total weight of the polymer gives 100 % by weight.

Seventh illustrative embodiment: The tetrafluoroethene copolymer of any one of the preceding illustrative embodiments having less than 50 ppb of perfluorinated octanoic acid (C_8-acid) or its salts.

Eighth illustrative embodiment: The tetrafluoroethene copolymer of any one of the preceding illustrative embodiments having a total amount of perfluorinated alkanoic C_9-C_{12} acids or their salts of less than 300 ppb.

Ninth illustrative embodiment: A composition comprising the tetrafluoroethene copolymer of any one of the preceding illustrative embodiments.

Tenth illustrative embodiment: A composition of the tetrafluoroethene copolymer of any one of the preceding illustrative embodiments, preferably, wherein the composition has a total content of perfluorinated alkanoic C_9-C_{12} acids or their salts of less than 300 ppb, or wherein the composition contains less than 50 ppb of perfluorinated octanoic acid or its salts (based on the total fluoropolymer content of the composition) or both.

Eleventh illustrative embodiment: A composition comprising the fluoropolymer of any one of the preceding illustrative embodiments or the composition according to the ninth or tenth embodiment further comprising one or more fluoroelastomers.

Twelfth illustrative embodiment: The composition of any one of the ninth to the eleventh illustrative embodiments wherein the composition is an aqueous dispersion.

Thirteenth illustrative embodiment: The composition of the twelfth illustrative embodiment wherein the aqueous dispersion further comprises one or more fluorinated surfactants corresponding to the general formula

$$[R_f\text{-O-L-COO}^-]_i X^{i+} \qquad \text{(III)}$$

wherein L represents a linear, branched or cyclic, partially or fully fluorinated alkylene group or an aliphatic hydrocarbon group, R_f represents a partially or fully fluorinated aliphatic group or a partially or fully fluorinated aliphatic group interrupted once or more than once with an oxygen ether atom, X^{i+} represents a cation having the valence i and i is 1, 2 or 3.

Fourteenth illustrative embodiment: The composition of either the twelfth or the thirteenth illustrative embodiment further comprising one or more non-fluorinated, non-ionic emulsifiers.

Fifteenth illustrative embodiment: The composition of the eleventh illustrative embodiment wherein, preferably, the composition is a solid composition of particles.

Sixteenth illustrative embodiment: The composition of any one of the ninth to the eleventh illustrative embodiment wherein the composition comprises one or more carbon-based filler.

Seventeenth illustrative embodiment: The composition of any one of the ninth to the eleventh illustrative embodiment wherein the composition comprises from 5 to 35% by eight of fluoropolymer and from 20 to 90 % by weight of one or more carbon-based filler and from 0 to 50% by weight of one or more optional ingredients with the proviso that the total amount of the ingredients is 100% by weight.

Eighteenth illustrative embodiment: A method for producing a tetrafluoroethene copolymer according to any one of the first to the eighth illustrative embodiments comprising copolymerizing tetrafluoroethene, the one or more PAAE, and the optional PMVE, PEVE or a combination thereof, through aqueous emulsion polymerization without adding any perfluorinated alkanoic acid emulsifier.

Nineteenth illustrative embodiment: A shaped article comprising a tetrafluoroethene copolymer of any one of the first to the eighth illustrative embodiment.

Twentieth illustrative embodiment: The article of the nineteenth illustrative embodiment wherein the article is selected from the group consisting of tubes, hoses, cables, pumps, valves, wafers, containers,lids. electrodes, bipolar plates, heat-exchangers or a component thereof.

Twenty-first illustrative embodiment: A coating containing the tetrafluoroethene copolymer of any one of the first to the eighth illustrative embodiment.

Twenty-second illustrative embodiment: A method of making a coating comprising providing a composition comprising the composition according to any one of the twelfth to the fourteenth illustrative embodiment and applying the composition to a substrate and removing water.

Twenty-third illustrative embodiment: A method of making a blend comprising a tetrafluoroethene copolymer according to any one of the first to the eighth illustrative embodiments and one or more fluoroelastomer, the method comprises (i) providing an aqueous dispersion comprising the tetrafluoroethene copolymer, (ii) providing an aqueous dispersion comprising the one or more fluoroelastomer, (iii) combining at least a part of the dispersion of (i) with at least a part of the dispersion of (ii).

Claims

1. A tetrafluoroethene copolymer having a melting point of from about 240°C to 325°C, a melt flow index (MFI at 372°C and 5 kg load) of 0.5-80 grams / 10 minutes and having at least 70% by weight of units derived from tetrafluoroethene and further having units derived from at least one perfluorinated allyl ether (PAAE) comonomer corresponding to the general formula:

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

where Rf is a perfluorinated alkyl residue having from 1 to 10 carbon atoms and wherein the alkyl chain of the residue may be interrupted once or more than once by an oxygen atom and wherein the polymer, optionally, further comprises units derived from perfluoromethyl vinyl ether (PMVE), perfluoroethyl vinyl ether (PEVE) and a combination thereof, and wherein the total content of units derived PAAEs and, optionally, derived from PMVE, PEVE, is at least 1.0 % by weight, preferably at least 1.5% by weight.

2. The tetrafluoroethene copolymer of claim 1 having a melting point between 265°C and 325°C, a melt flow index between 1 and 80 g / 10 mins and further comprising at least 90% by weight of units derived from TFE and further having a tensile strength of at least 17 MPa and an elongation at break of at least 230%.

3. The tetrafluoroethene copolymer of claim 1 having a melting point between 265°C and 325°C, a melt flow index between 1 and 80 g / 10 mins and further comprising at least 90% by weight, preferably at least 95% by weight, of units derived from TFE and further having a tensile strength of at least 17 MPa and an elongation at break of at least 230% and wherein the polymer comprises a PAAE with Rf selected from the group consisting of: perfluoromethyl ($-CF_3$), perfluoroethyl ($-C_2F_5$), perfluoropropyl ($-C_3F_7$) and perfluorobutyl (C_4F_9), preferably $-C_2F_5$, $-C_3F_7$ or $-C_4F_9$.

4. The tetrafluoroethene copolymer of claim 1 wherein the polymer comprises a PAAE selected from $CF_2{=}CF\text{-}CF_2\text{-}O\text{-}CF_2\text{-}CF_2\text{-}CF_3$ (MA-3).

5. The tetrafluoroethene copolymer of claim 1 having a melting point between 240°C and 280°C, a melt flow index between 0.8 and 80 g / 10 mins and further comprising repeating units derived from hexafluoropropene.

6. The tetrafluoroethene copolymer of claim 1 comprising from about 75 % by weight to about 99 % by weight, preferably up to 98.5 % by weight, of units derived from tetrafluoroethene and from 0.1 to 6% by weight of units derived from the at least one or more PAAE and from 0% by weight up to 6 % by weight of units derived from PMVE, PEVE or a combination thereof and from 0% by

weight up to 8% by weight of units derived HFP wherein the total weight of the polymer gives 100 % by weight.

7. The tetrafluoroethene copolymer of claim 1 containing less than 50 ppb of perfluorinated octanoic acid or its salts.

8. The tetrafluoroethene copolymer of claim 1 having a total amount of perfluorinated alkanoic C_9-C_{12} acids or their salts of less than 300 ppb.

9. A composition comprising the tetrafluoroethene copolymer of claim 1.

10. The composition of claim 9 wherein the composition has a total content of perfluorinated alkanoic C_9-C_{12} acids or their salts of less than 300 ppb (based on the fluoropolymer content of the composition) or the composition contains less than 50 ppb of perfluorinated octanoic acid or its salts or both.

11. The composition of claim 9 further comprising one or more elastomers.

12. The composition of claim 9 being an aqueous dispersion.

13. The composition of claim 9 being an aqueous dispersion further comprising one or more fluorinated surfactants corresponding to the general formula

$$[R_f\text{-O-L-COO}^-]_i X^{i+} \qquad \text{(III)}$$

wherein L represents a linear, branched or cyclic, partially or fully fluorinated alkylene group or an aliphatic hydrocarbon group, R_f represents a partially or fully fluorinated aliphatic group or a partially or fully fluorinated aliphatic group interrupted once or more than once with an oxygen ether atom, X^{i+} represents a cation having the valence i and i is 1, 2 or 3.

14. The composition of 9 being an aqueous dispersion and further comprising one or more non-fluorinated, non-ionic emulsifiers.

15. The composition of claim 9 wherein the composition comprises one or more fluorinated elastomer and wherein, preferably, the composition is a solid composition of particles.

16. The composition of claim 9 wherein the composition comprises one or more carbon-based filler.

17. The composition of claim 9 wherein the composition comprises from 5 to 35% by eight of fluoropolymer and from 20 to 90 % by weight of one or more carbon-based filler and from 0 to 50% by weight of one or more optional ingredients with the proviso that the total amount of the ingredients is 100% by weight.

18. A method for producing a tetrafluoroethene copolymer of claim 1 comprising copolymerizing tetrafluoroethene, the one or more PAAE, and the optional PMVE, PEVE or a combination thereof, through aqueous emulsion polymerization without adding any perfluorinated alkanoic acid emulsifiers.

19. A shaped article comprising a tetrafluoroethene copolymer according to claim 1.

20. The article of claim 19 selected from the group consisting of tubes, hoses, cables, pumps, valves, wafers, containers, lids, electrodes, heat-exchangers, bipolar plates and components thereof.

21. A coating containing the tetrafluoroethene copolymer of claim 1.

22. Method of making a coating comprising providing a composition comprising the dispersion according to claim 12 and applying the composition to a substrate and removing the water.

23. Method of making a blend comprising the tetrafluoroethene copolymer according to claim 1 and one or more fluoroelastomer, the method comprises (i) providing an aqueous dispersion comprising the tetrafluoroethene copolymer, (ii) providing an aqueous dispersion comprising the one or more fluoroelastomer, (iii) combining at least a part of the dispersion of (i) with at least a part of the dispersion of (ii).

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2019/018142

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☒ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2019/018142

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09D127/18 C08F214/26 C08F2/24 C08J5/00 C08L27/18
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08F C09D C08J C09J C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2016/130904 A1 (3M INNOVATIVE PROPERTIES CO [US]) 18 August 2016 (2016-08-18)	1-10,12, 13,15,18
Y	example 1	11,14, 16,17, 19-23

Y	US 2007/015864 A1 (HINTZER KLAUS [DE] ET AL) 18 January 2007 (2007-01-18) cited in the application example 1	11,14, 16,17, 19-23

L	WO 2018/034839 A1 (3M INNOVATIVE PROPERTIES CO [US]) 22 February 2018 (2018-02-22) examples	1-10,12, 13,15,18

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search 23 May 2019	Date of mailing of the international search report 04/06/2019
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Parry, Julian

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2019/018142

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WO 2018034839 A1	22-02-2018	CN 109563206 A	02-04-2019
		WO 2018034839 A1	22-02-2018

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-23(partially)

   The subject matter of claims 1-23 (in part)

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2. claims: 1-23(partially)

   The subject matter of claims 1-23 (in part)
