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(54) **MELT-FLOWABLE FLUOROPOLYMER COMPRISING REPEATING UNITS ARISING FROM TETRAFLUOROETHYLENE AND A HYDROCARBON MONOMER HAVING A FUNCTIONAL GROUP AND A POLYMERIZABLE CARBON-CARBON DOUBLE BOND**

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(57) **ABSTRACT**

Disclosed is a melt-flowable fluoropolymer comprising repeating units arising from (a) tetrafluoroethylene and (b) a monomer having at least one functional group and a polymerizable carbon-carbon double bond, wherein the sum of the weight percent of (a) and (b) comprises at least about 99 weight percent of all repeating units comprising the melt-flowable fluoropolymer.

**MELT-FLOWABLE FLUOROPOLYMER
COMPRISING REPEATING UNITS ARISING
FROM TETRAFLUOROETHYLENE AND A
HYDROCARBON MONOMER HAVING A
FUNCTIONAL GROUP AND A
POLYMERIZABLE CARBON-CARBON
DOUBLE BOND**

FIELD OF THE DISCLOSURE

[0001] This disclosure relates in general to melt-flowable fluoropolymers comprising repeating units arising from tetrafluoroethylene and a hydrocarbon monomer having a functional group and a polymerizable carbon-carbon double bond.

BACKGROUND

[0002] Fluorine containing polymers are important commercial products due to their low surface energy and high thermal and chemical resistance. Tetrafluoroethylene homopolymers (PTFE) find commercial use in gaskets, bearings, tape, electrical insulation, and liners for pipes, valves and reactors. However, the low surface energy of PTFE leads to poor adhesion to substrates.

[0003] Certain functional groups are known to modify the adhesive properties of partially fluorinated polymers. Incorporation of such groups during polymerization of partially fluorinated polymers without significantly sacrificing desirable polymer properties has been met with limited success to date. Monomers containing functional groups may not copolymerize with fluorinated monomers or may cause other undesirable effects in a copolymerization. Incorporation of monomers containing functional groups can adversely affect the thermal stability or chemical resistance of the resulting polymer.

[0004] The art is silent as to melt-flowable PTFE homopolymers having groups that allow for adhesion to substrates while retaining the desirable polymer properties of chemical resistance and thermal stability.

SUMMARY

[0005] A melt-flowable fluoropolymer is taught herein containing functional groups that allow for adhesion of the fluoropolymer to substrates while retaining its chemical resistance and thermal stability.

[0006] Described herein is a melt-flowable fluoropolymer comprising repeating units arising from: (a) tetrafluoroethylene; and (b) a monomer having at least one functional group and a polymerizable carbon-carbon double bond; wherein the sum of the weight percent of (a) and (b) comprises at least about 99 weight percent of all repeating units comprising the melt-flowable fluoropolymer.

[0007] In an embodiment, the melt-flowable fluoropolymer has about 0.001 to about 1 weight percent of repeating units arising from the monomer having at least one functional group and a polymerizable carbon-carbon double bond. In another embodiment, the functional group is at least one selected from the group consisting of amine, amide, carboxyl, hydroxyl, phosphonate, sulfonate, nitrile, boronate and epoxide. In another embodiment, the functional group is a dicarboxylic acid anhydride group.

[0008] In another embodiment, the melt-flowable fluoropolymer further comprises about 1 weight percent or less of repeating units arising from a fluoromonomer other than tetra-

rafluoroethylene. In another embodiment, the fluoromonomer other than tetrafluoroethylene is at least one selected from the group consisting of chlorotrifluoroethylene (CTFE), hexafluoropropylene (HFP), perfluoro-2,2-dimethyl-1,3-dioxole (PDD), perfluoro-2-methylene-4-methyl-1,3-dioxolane (PMD), perfluoro(methyl vinyl ether) (PMVE), perfluoro(ethyl vinyl ether) (PEVE), perfluoro(propyl vinyl ether) (PPVE), and perfluoro(butyl vinyl ether) (PBVE).

[0009] The foregoing general description and the following detailed description are exemplary and explanatory only and are not restrictive of the invention, as defined in the appended claims.

DETAILED DESCRIPTION

[0010] Embodiments described above are merely exemplary and not limiting. After reading this specification, skilled artisans appreciate that other aspects and embodiments are possible without departing from the scope of the invention.

[0011] Other features and benefits of any one or more of the embodiments will be apparent from the following detailed description, and from the claims. The detailed description addresses:

- [0012]** 1. Definitions and Clarification of Terms;
- [0013]** 2. FG-Fluoropolymer;
- [0014]** 3. Hydrocarbon monomer having a functional group and a Polymerizable Carbon-Carbon Double Bond (FG);
- [0015]** 4. Fluoromonomer other than Tetrafluoroethylene (Modifier);
- [0016]** 5. FG-Fluoropolymer Melting Point and Melt Flow Rate; and
- [0017]** 6. Process for the Manufacture of the FG-Fluoropolymer, and Examples.

1. Definitions and Clarification of Terms

[0018] Before addressing further details of these embodiments, some terms are defined or clarified.

[0019] By “melt-flowable” is meant that the fluoropolymer has a melt flow rate (MFR) that is measurable by ASTM D 1238-94a and is obtained by direct polymerization under the process disclosed herein that prevents very long fluoropolymer chains from forming.

[0020] As used herein, the terms “comprises,” “comprising,” “includes,” “including,” “has,” “having” or any other variation thereof, are intended to cover a non-exclusive inclusion. For example, a process, method, article, or apparatus that comprises a list of elements is not necessarily limited to only those elements but may include other elements not expressly listed or inherent to such process, method, article, or apparatus. Further, unless expressly stated to the contrary, “or” refers to an inclusive or and not to an exclusive or. For example, a condition A or B is satisfied by any one of the following: A is true (or present) and B is false (or not present), A is false (or not present) and B is true (or present), and both A and B are true (or present).

[0021] Also, use of “a” or “an” are employed to describe elements and components described herein. This is done merely for convenience and to give a general sense of the scope of the invention. This description should be read to include one or at least one and the singular also includes the plural unless it is obvious that it is meant otherwise.

[0022] Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly

understood by one of ordinary skill in the art to which the claims belong. Although methods and materials similar or equivalent to those described herein can be used in the practice or testing of the embodiments disclosed, suitable methods and materials are described below. All publications, patent applications, patents, and other references mentioned herein are incorporated by reference in their entirety, unless a particular passage is cited. In case of conflict, the present specification, including definitions, will control. In addition, the materials, methods, and examples are illustrative only and not intended to be limiting.

[0023] To the extent not described herein, many details regarding specific materials and processing acts are conventional and may be found in textbooks and other sources within the fluoropolymer art.

2. FG-Fluoropolymer

[0024] Described herein is a melt-flowable fluoropolymer comprising repeating units arising from: (a) tetrafluoroethylene; and (b) a monomer having at least one functional group and a polymerizable carbon-carbon double bond; wherein the sum of the weight percent of (a) and (b) comprises at least about 99 weight percent of all repeating units comprising the melt-flowable fluoropolymer. Such fluoropolymer is alternately referred to herein as "FG-fluoropolymer."

[0025] The claimed FG-fluoropolymer has been discovered to have a sufficient concentration of functional groups that results in adhesion of the FG-fluoropolymer to substrates such as metals, inorganics and functional group containing polymers, such as polyamides. Surprisingly, this concentration of functional groups does not lead to a decrease in the desirable fluoropolymer properties, such as chemical resistance and thermal stability.

[0026] FG-fluoropolymer can be adhered to such substrates by known methods, such as thermal lamination.

[0027] FG-fluoropolymer cannot be fabricated by the typical melt fabrication methods of extrusion and injection molding, which involve both shear and melt flow. Instead, FG-fluoropolymer can be fabricated by known non-melt flow operations such as paste extrusion of a PTFE/organic lubricant mixture at a temperature typically between 15° C. and 150° C., followed by sintering to coalesce the FG-fluoropolymer particles into a molded article.

3. Hydrocarbon Monomer Having a Functional Group and a Polymerizable Carbon-Carbon Double Bond (FG)

[0028] 3.1. Constitution of the Functional Group Monomer

[0029] The present melt-flowable fluoropolymer has repeating units arising from a monomer having at least one functional group and a polymerizable carbon-carbon double bond. Monomer having at least one functional group and a polymerizable carbon-carbon double bond is alternately referred to herein as "functional group monomer" or "FG". The polymerizable carbon-carbon double bond functions to allow repeating units arising from the functional group monomer to be incorporated into the fluoropolymer carbon-carbon chain backbone arising from polymerized units of tetrafluoroethylene. The functional group serves to increase the adhesion of a fluoropolymer to a given substrate with which it is in contact over the amount of adhesion that such a substrate and fluoropolymer not containing FG would otherwise exhibit. This results, for example, in adhesion between a layer of

FG-fluoropolymer and a layer of polyamide. Polyamide and fluoropolymer containing no FG normally have no adhesion of one to the other.

[0030] Functional group monomer generally includes compounds having a functional group and a polymerizable carbon-carbon double bond that meet the aforementioned functional criteria. In another embodiment, all monovalent atoms in the functional group monomer are hydrogen. In another embodiment, functional group monomer comprises the elements carbon, hydrogen and oxygen. In another embodiment, functional group monomer comprises the elements of carbon, hydrogen and oxygen and further comprises elements selected from the group consisting of nitrogen, phosphorus, sulfur and boron. In another embodiment, functional groups comprise at least one selected from the group consisting of amine, amide, carboxyl, hydroxyl, phosphonate, sulfonate, nitrile, boronate and epoxide.

[0031] In another embodiment, FG contains a carboxyl group ($-\text{C}(=\text{O})\text{O}-$) and a polymerizable carbon-carbon double bond. In another embodiment, FG contains a dicarboxylic acid anhydride group ($-\text{C}(=\text{O})\text{OC}(=\text{O})-$) and a polymerizable double bond. In another embodiment, FG contains a dicarboxylic acid group capable of forming a cyclic dicarboxylic acid anhydride and a polymerizable carbon-carbon double bond. In another embodiment, FG contains a 1,2- or 1,3-dicarboxylic acid group and a polymerizable carbon-carbon double bond. In another embodiment, FG includes C_4 to C_{10} dicarboxylic acids and dicarboxylic acid anhydrides containing a polymerizable carbon-carbon double bond. FG containing a carboxyl group include, for example: maleic anhydride, maleic acid, fumaric acid, itaconic anhydride, itaconic acid, citraconic anhydride, citraconic acid, mesaconic acid, 5-norbornene-2,3-dicarboxylic anhydride and 5-norbornene-2,3-dicarboxylic acid.

[0032] In another embodiment, FG contains an amine group and a polymerizable carbon-carbon double bond. Examples include aminoethyl acrylate, dimethylaminoethyl methacrylate, dimethylaminoethyl acrylate, aminoethyl vinyl ether, dimethylaminoethyl vinyl ether and vinyl aminoacetate.

[0033] In another embodiment, FG contains an amide group and a polymerizable carbon-carbon double bond. Examples include N-methyl-N-vinyl acetamide, acrylamide and N-vinylformamide.

[0034] In another embodiment, FG contains an hydroxyl group and a polymerizable carbon-carbon double bond. Examples include 2-hydroxyethyl vinyl ether and omega-hydroxybutyl vinyl ether.

[0035] In another embodiment, FG contains a phosphonate group and a polymerizable carbon-carbon double bond. An example is diethylvinyl phosphonate.

[0036] In another embodiment, FG contains a sulfonate group and a polymerizable carbon-carbon double bond. An example is ammonium vinyl sulfonate.

[0037] In another embodiment, FG contains a nitrile group and a polymerizable carbon-carbon double bond. An example is acrylonitrile.

[0038] In another embodiment, FG contains a boronate group and a polymerizable carbon-carbon double bond. Examples include vinyl boronic acid dibutyl ester, 4-vinyl phenyl boronic acid and 4-bentenyl boronic acid.

[0039] In another embodiment, FG contains an epoxide group and a polymerizable carbon-carbon double bond. An example is allyl glycidal ether (AGE).

[0040] 3.2. Amount of Repeating Units Arising from Functional Group Monomer in the FG-Fluoropolymer

[0041] In an embodiment, FG-perfluoropolymer comprises about 0.001 to about 1 weight percent of repeating units arising from FG. In another embodiment, FG-perfluoropolymer comprises about 0.001 to about 0.5 weight percent of repeating units arising from FG. In another embodiment, FG-perfluoropolymer comprises about 0.001 to about 0.3 weight percent of repeating units arising from FG. In another embodiment, FG-perfluoropolymer comprises about 0.001 to about 0.1 weight percent of repeating units arising from FG. In another embodiment, FG-perfluoropolymer comprises about 0.001 to about 0.01 weight percent of repeating units arising from FG. The weight percent of repeating units arising from FG referred to here is relative to the sum of the weight of repeating units arising from FG, tetrafluoroethylene, and any perfluoromonomer other than tetrafluoroethylene (modifier) in the FG-perfluoropolymer.

4. Fluoromonomer Other Than Tetrafluoroethylene (MODIFIER)

[0042] 4.1. Constitution of the Modifier

[0043] In an embodiment, the present melt-flowable fluoropolymer comprises repeating units arising from a fluoromonomer other than tetrafluoroethylene. Fluoromonomer other than tetrafluoroethylene (also referred to herein as "modifier") comprises compounds containing the elements carbon and fluorine and carbon-carbon unsaturation. In another embodiment, all monovalent atoms bonded to carbon in the modifier are fluorine. In another embodiment, the modifier further contains heteroatoms selected from the group consisting of oxygen, sulfur and nitrogen.

[0044] In another embodiment, modifiers of utility include perfluoroalkenes and perfluorinated vinyl ethers having 2 to 8 carbon atoms. In another embodiment, perfluorinated vinyl ethers are represented by the formula $CF_2=CFOR$ or $CF_2=CFOR'OR$, wherein R is perfluorinated linear or branched alkyl groups containing 1 to 5 carbon atoms, and R' is perfluorinated linear or branched alkylene groups containing 1 to 5 carbon atoms. In another embodiment, R groups contain 1 to 4 carbon atoms. In another embodiment, R' groups contain 2 to 4 carbon atoms.

[0045] Modifier includes, for example: hexafluoropropylene (HFP), perfluoro-2,2-dimethyl-1,3-dioxole (PDD), perfluoro-2-methylene-4-methyl-1,3-dioxolane (PMD) and perfluoro(alkyl vinyl ethers) (PAVE) such as perfluoro(methyl vinyl ether) (PMVE), perfluoro(ethyl vinyl ether) (PEVE), perfluoro(propyl vinyl ether) (PPVE), and perfluoro(butyl vinyl ether) (PBVE).

[0046] 4.2. Amount of Repeating Units Arising from the Modifier in the FG-Fluoropolymer

[0047] FG-fluoropolymer comprises about 1 weight percent or less of repeating units arising from the modifier.

[0048] In another embodiment, FG-fluoropolymer comprises about 0.001 to about 1 weight percent of repeating units arising from the modifier. In another embodiment, FG-fluoropolymer comprises about 0.001 to about 0.5 weight percent of repeating units arising from the modifier. In another embodiment, FG-fluoropolymer comprises about 0.001 to about 0.3 weight percent of repeating units arising from the modifier. In another embodiment, FG-fluoropolymer comprises about 0.001 to about 0.1 weight percent of repeating units arising from the modifier. In another embodiment, FG-

fluoropolymer comprises about 0.001 to about 0.01 weight percent of repeating units arising from the modifier.

[0049] The weight percent of repeating units arising from the modifier referred to above is relative to the sum of the weight of repeating units arising from FG, tetrafluoroethylene and the modifier.

5. FG-Fluoropolymer Melting Point and Melt Flow Rate

[0050] FG-fluoropolymer melting point can be determined by ASTM method D 4591-01, "Standard Test Method for Determining Temperatures and Heats of Transitions of Fluoropolymers by Differential Scanning calorimetry."

[0051] In another embodiment the melting point of the FG-fluoropolymer is below about 265° C. In another embodiment the melting point of the FG-fluoropolymer is below about 260° C. In another embodiment the melting point of the FG-fluoropolymer is below about 250° C. In another embodiment the melting point of the FG-fluoropolymer is below about 240° C. In another embodiment the melting point of the FG-fluoropolymer is below about 230° C. In another embodiment the melting point of the FG-fluoropolymer is below about 225° C. In another embodiment the melting point of the FG-fluoropolymer is below about 220° C.

[0052] FG-fluoropolymer melt flow rate (MFR) can be determined by ASTM method D1238-04c. FG-fluoropolymer can be produced having a desired MFR for a given utility.

[0053] In one embodiment, MFR of FG-fluoropolymer produced by the present process is about 1 to about 400 g/10 minutes. In another embodiment, MFR of FG-fluoropolymer produced by the present process is about 10 to about 300 g/10 minutes. In another embodiment, MFR of FG-fluoropolymer produced by the present process is about 1 to about 100 g/10 minutes. In another embodiment, MFR of FG-fluoropolymer produced by the present process is about 20 to about 90 g/10 minutes. In another embodiment, MFR of FG-fluoropolymer produced by the present process is about 1 to about 50 g/10 minutes. In another embodiment, MFR of FG-fluoropolymer produced by the present process is about 5 to about 40 g/10 minutes. In another embodiment, MFR of FG-fluoropolymer produced by the present process is about 10 to about 30 g/10 minutes. In another embodiment, MFR of FG-fluoropolymer produced by the present process is about 15 to about 30 g/10 minute. In another embodiment, MFR of FG-fluoropolymer produced by the present process is about 20 to about 30 g/10 minutes.

6. Process for the Manufacture of the FG-Fluoropolymer

[0054] The present FG-fluoropolymer can be manufactured by an aqueous polymerization process, comprising:

[0055] (A) combining water, tetrafluoroethylene and at least one chain transfer agent to form a reaction mixture;

[0056] (B) initiating polymerization of the tetrafluoroethylene;

[0057] (C) polymerizing a portion of the tetrafluoroethylene to form particles of polymerized tetrafluoroethylene in the reaction mixture;

[0058] (D) adding to the reaction mixture a hydrocarbon monomer having a functional group and a polymerizable carbon-carbon double bond (FG); and

[0059] (E) polymerizing the tetrafluoroethylene and the FG in the presence of the particles of polymerized tetrafluoroethylene to form the FG-fluoropolymer.

[0060] 6.1. Combining Water, Tetrafluoroethylene and Chain Transfer Agent to Form a Reaction Mixture (A)

[0061] The process involves (A) combining water, tetrafluoroethylene and at least one chain transfer agent to form a reaction mixture.

[0062] 6.1.1. Surfactant

[0063] In an embodiment, surfactant is further added to the reaction mixture and the reaction mixture comprises an aqueous dispersion. Surfactants generally suitable for use in dispersion polymerization of tetrafluoroethylene copolymers are of utility. Surfactants include, for example, ammonium perfluorooctanoate, ammonium perfluorononanoate, and perfluoroalkyl ethane sulfonic acids and salts thereof.

[0064] 6.1.2 Chain Transfer Agent

[0065] A chain transfer agent (CTA) is further added to the reaction mixture. A wide range of compounds can be used as CTA, including, for example, hydrogen-containing compounds such as molecular hydrogen, lower alkanes, and lower alkanes substituted with halogen atoms. The chain transfer activity of such compounds when used in this process can result in FG-perfluoropolymer having $-\text{CF}_2\text{H}$ end groups. The CTA can contribute other end groups, depending on the identity of the CTA. Example CTAs include methane, ethane, and substituted hydrocarbons such as methyl chloride, methylene chloride, chloroform, and carbon tetrachloride. The amount of CTA used to achieve desired molecular weight will depend, for given polymerization conditions, on the amount of initiator used and on the chain transfer efficiency of the chosen CTA.

[0066] Chain transfer efficiency can vary substantially from compound to compound, and varies with temperature. The amount of CTA needed to obtain a desired polymerization result can be determined by one of ordinary skill in this field without undue experimentation.

[0067] 6.2. Initiating Polymerization of the Tetrafluoroethylene (B)

[0068] The process involves (B) initiating polymerization of the tetrafluoroethylene.

[0069] Following (A), in which water, tetrafluoroethylene and CTA are combined to form a reaction mixture, the reaction mixture is optionally heated to a chosen temperature and then agitation is started. Initiator is then added at a desired rate to initiate polymerization of the tetrafluoroethylene.

[0070] Tetrafluoroethylene addition is started and controlled according to the scheme chosen to regulate the polymerization. An initiator, which can be the same as or different from the first initiator used, is usually added over the total period of polymerization.

[0071] In another embodiment, additional CTA is added over the total period of polymerization.

[0072] 6.2.1 Initiator

[0073] Initiators of utility in the process are those commonly employed in emulsion (dispersion) polymerization of tetrafluoroethylene homopolymers. For example, water-soluble free-radical initiators such as ammonium persulfate (APS), potassium persulfate (KPS), or disuccinic acid peroxide, or redox systems such as those based on potassium permanganate. The amount of initiator used depends on the amount of chain-transfer agent (CTA) used. For APS and KPS for which initiation efficiency approaches 100% at high temperature (e.g., 100° C.), the amount of initiator, relative to the amount of FG-perfluoropolymer formed, is generally less than 1.5 mol/mol, desirably no more than 1.0 mol/mol, and preferably no more than 0.45 mol/mol. When the initiator has

lower initiation efficiency, such as APS or KPS at lower temperature, these initiator amounts refer to the proportion of polymer molecules initiated (made) by the initiator. Both situations can be described in terms of effective initiator amount per mole of polymer made.

[0074] 6.2.2 Temperature

[0075] In the embodiment where the aqueous polymerization process comprises aqueous dispersion polymerization, a broad range of temperatures are of utility. Because of heat transfer considerations and the use of thermally activated initiators, higher temperatures are advantageous, such as temperatures in the range of about 50-100° C. In another embodiment, temperatures in the range 70-90° C. are used. Surfactants used in emulsion polymerization appear to be less effective at temperatures above 103-108° C. as there is a tendency to lose dispersion stability.

[0076] 6.2.3. Pressure

[0077] Any workable pressure can be used in the polymerization process. High pressure offers an advantage over low pressure in increased reaction rate. However, the polymerization of tetrafluoroethylene is highly exothermic, so high reaction rate increases the heat that must be removed or accommodated as temperature increases. Pressures that can be used are also determined by equipment design and by safety concerns in the handling of tetrafluoroethylene. In another embodiment, pressures in the range of about 0.3-7 MPa are used. In another embodiment, pressures in the range 0.7-3.5 MPa are used. While it is common to maintain constant pressure in the reactor, in another embodiment, pressure can be varied.

[0078] 6.3. Polymerizing a Portion of the Tetrafluoroethylene to Form Particles of Polymerized Tetrafluoroethylene (C)

[0079] The process involves a step of (C) polymerizing a portion of the tetrafluoroethylene to form particles of polymerized tetrafluoroethylene in the reaction mixture. In (C), polymerizing a portion of the tetrafluoroethylene means an amount of tetrafluoroethylene less than the total amount combined with water and CTA in (A) to form the reaction mixture.

[0080] In another embodiment, to determine that a portion of the tetrafluoroethylene has polymerized and formed particles of polymerized tetrafluoroethylene in the reaction mixture, the total pressure within the vessel containing the reaction mixture is monitored. A tetrafluoroethylene pressure drop following initiation (B) indicates that polymerization of tetrafluoroethylene has begun and particles of polymerized tetrafluoroethylene have been formed (i.e., kickoff). In another embodiment, the pressure drop is at least about 35 KPa (5 psi). In another embodiment, the pressure drop is at least about 70 KPa (10 psi). In another embodiment, proof that polymerization of a portion of the tetrafluoroethylene has been achieved is that the reactor continues to consume tetrafluoroethylene, observed for example by the activation of a tetrafluoroethylene feed valve attached by a feedback control loop.

[0081] In another embodiment, the pressure drop represents about a 0.1 weight percent solids polymerized tetrafluoroethylene based on the water phase of the reaction mixture. Below such a solids level it is uncertain whether the polymerization has established itself enough to avoid being quenched by (D) addition to the reaction mixture of FG. In another embodiment, (C) polymerizing a portion of the tetrafluoroethylene to form particles of polymerized tetrafluoroethylene is carried out until about 2 weight percent solids polymer has been formed based on the water phase of the reaction mixture.

This represents a small portion of the final batch size, typically less than about 5 percent of the total polymer to be made. Waiting until higher levels of polymer has been formed in (C) does not give additional benefit to establishing the polymerization, and might begin to make the reaction mixture unnecessarily non-homogeneous.

[0082] In a suspension or granular PTFE type polymerization embodiment, the about 0.1 to about 2 weight percent solids polymerized tetrafluoroethylene is in the form of small irregular spongy polymer particles of indeterminate size and shape, non-water wetted, and floating on the surface of the reaction mixture where they are available for direct polymer-vapor space polymerization. As the polymerization proceeds, more polymer particles are formed and the ones already in existence become larger. The size and shape of the polymer particles depend on the details of the polymerization. In another embodiment, suspension polymerization particles formed early in the batch have the size and shape of popped popcorn that has been rolled and crushed by hand. In another embodiment, suspension polymerization particles formed early in the batch have the size and shape of shredded coconut from the grocery store. In another embodiment, suspension polymerization particles formed early in the batch have the appearance and texture of powdered sugar.

[0083] In a dispersion polymerization embodiment, wherein surfactant is further added to the reaction mixture and the reaction mixture comprises a colloiddally stable aqueous dispersion, the about 0.1 to about 2 weight percent polymerized tetrafluoroethylene is in the form of the initial particles made during initiation of polymerization. After tetrafluoroethylene pressure drop following initiation, the presence of the colloiddally stable particles inhibits formation of more particles by sweeping the aqueous reaction mixture phase of colloiddally unstable precursor particles before the precursors have a chance to grow large enough to become colloiddally stable themselves.

[0084] In another embodiment of this step of (C) polymerizing a portion of the tetrafluoroethylene to form particles of polymerized fluoromonomer, there are about 10^{12} particles of polymerized tetrafluoroethylene per gram of water in the reaction mixture. With fewer particles than that, the particles can undesirably become too large at too low a percent solids to be colloiddally stable, resulting in coagulum problems. The value of 10^{12} particles per gram of water in the reaction mixture is calculated for a polymerization with RDPS of 400 nm at 10% solids as a lower limit of industrial practicality. In another embodiment, particles have an RDPS of 300 nm or less at 20% solids or greater.

[0085] 6.3.1. Regulating the Rate of Polymerization

[0086] There are several alternatives for regulating the rate of polymerization. It is common with most alternatives first to precharge at least a portion of the modifier, if used, and then to add tetrafluoroethylene to the desired total pressure. Additional tetrafluoroethylene is then added after initiation and polymerization kickoff to maintain a chosen pressure, and additional modifier can be added, also. The tetrafluoroethylene can be added at a constant rate, with agitator speed changed as necessary to increase or decrease actual polymerization rate and thus to maintain constant total pressure. In a variant of this alternative, pressure can be varied to maintain constant reaction rate at constant tetrafluoroethylene feed rate and constant agitator speed. Alternatively, the total pressure and the agitator speed can both be held constant, with tetrafluoroethylene added as necessary to maintain the pressure

constant. A third alternative is to carry out the polymerization in stages with variable agitator speed, but with steadily increasing tetrafluoroethylene feed rate. When modifiers are added during the reaction, it is convenient to inject them at a fixed rate. In another embodiment, the rate of modifier addition is uniform during a given phase of polymerization. However, one skilled in the art will appreciate that a wide variety of modifier addition programs can be employed. Thus, for example, a series of discrete modifier additions can be used such as discrete additions can be made in equal or varying amounts, and at equal or varying intervals. Other non-uniform programs for addition of the modifier can be used.

[0087] 6.4. Adding to the Reaction Mixture a Hydrocarbon Monomer Having a Functional Group and a Polymerizable Carbon-Carbon Double Bond (D)

[0088] The total pressure above the reaction mixture is monitored. A pressure drop of at least about 35 KPa (5 psi), generally at least about 70 KPa (10 psi), occurring after initiation indicates that polymerization of tetrafluoroethylene has begun and particles of polymerized tetrafluoroethylene are being formed.

[0089] Following the pressure drop indicating that polymerization of tetrafluoroethylene has begun and particles of polymerized tetrafluoroethylene have formed, hydrocarbon monomer having a functional group and a polymerizable carbon-carbon double bond (functional group monomer, or FG) is added to the reaction mixture. In another embodiment, FG is added to the reaction mixture in one aliquot. In another embodiment, FG is added to the reaction mixture continuously or periodically over the total period of polymerization.

[0090] Addition of FG to the polymerization aqueous reaction mixture following the pressure drop indicating that polymerization of tetrafluoroethylene has begun and particles of polymerized tetrafluoroethylene are being formed, has been discovered to lead to productive and controllable incorporation in the fluoropolymer carbon-carbon backbone of repeating units arising from FG.

[0091] Precharging FG to the polymerization aqueous reaction mixture has been discovered to not lead to productive incorporation in the fluoropolymer carbon-carbon backbone of repeating units arising from FG.

[0092] 6.4.1. pH of the Reaction Mixture

[0093] In another embodiment, FG contains a carboxyl group capable of forming a carboxylic acid and/or a carboxylic acid anhydride, and the pH of the reaction mixture measured at 25° C. is less than or equal to the pK_a of the carboxylic acid of the FG during (C) polymerization of the tetrafluoroethylene to form particles of polymerized tetrafluoroethylene and (D) the addition of FG to the reaction mixture.

[0094] In another embodiment of the process, FG contains a cyclic dicarboxylic acid anhydride and/or a dicarboxylic acid capable of forming a cyclic dicarboxylic acid anhydride, and the pH of the reaction mixture measured at 25° C. is less than or equal to the pK_{a1} of the dicarboxylic acid of the FG during (C) polymerization of the tetrafluoroethylene to form particles of polymerized tetrafluoroethylene and (D) the addition of FG to the reaction mixture.

[0095] Controlling the pH of the aqueous polymerization process reaction mixture has been discovered to lead to productive incorporation in the fluoropolymer carbon-carbon backbone of repeating units arising from FG. Without wishing to be bound by theory, it is believed that controlling the pH of the aqueous polymerization process reaction mixture

results in a sufficient concentration of FG being present in the phase of the reaction mixture containing reactive fluoropolymer chain radicals.

[0096] In another embodiment of the described process, a strong acid is further added to the reaction mixture for the purpose of controlling the pH of the reaction mixture measured at 25° C. at less than or equal to the pK_a of the carboxylic acid of the FG during (C) polymerization of the tetrafluoroethylene to form particles of polymerized tetrafluoroethylene and (D) the addition of FG to the reaction mixture. Strong acids of utility include any that will not impede the polymerization process, including inorganic or mineral acids (e.g., nitric acid) and organic acids (e.g., oxalic acid). In another embodiment, strong acid comprises those acids with a pK_a of about 1 or less.

[0097] In another embodiment of the described process, an acidic buffer is further added to the reaction mixture for the purpose of controlling the pH of the reaction mixture measured at 25° C. at less than or equal to the pK_a of the carboxylic acid of the FG during (C) polymerization of the tetrafluoroethylene to form particles of polymerized tetrafluoroethylene and (D) the addition of FG to the reaction mixture. Acidic buffers of utility include any that will not impede the polymerization process, for example, phosphate buffer.

[0098] For the purpose of these comparisons of reaction mixture pH with pK_a (or pK_{a1}) of the carboxylic acid, pH is measured at 25° C.

EXAMPLES

[0099] The concepts described herein will be further described in the following examples, which do not limit the scope of the invention described in the claims.

Example 1

[0100] A cylindrical, horizontal, water-jacketed, paddle-stirred, stainless steel reactor having a length to diameter ratio of about 1.5 and a water capacity of 1 gallons (3.8 L) was charged with 1800 mL of demineralized water, 1.0 g of oxalic acid, 25 mL of a 30 wt % solution of ammonium perfluorohexylethylsulfonate surfactant in water and 0.5 g of Krytox® 157 FSL perfluoropolymer carboxylic acid. With the reactor paddle agitated at 150 rpm, the reactor was heated to 25° C., and evacuated and purged three times with tetrafluoroethylene (TFE). The reactor was then charged to 27 inches Hg (95 KPa). The reactor temperature then was increased to 90° C. After the temperature had become steady at 90° C., TFE was added to the reactor to achieve a final pressure of 250 psig (1.83 MPa). Then 9 mL of freshly prepared aqueous initiator solution containing 1.0 wt % ammonium persulfate (APS) was charged to the reactor. After polymerization had begun as indicated by a 10 psi (70 KPa) drop in reactor pressure (kick-off), additional TFE was added to the reactor at a rate of 2.1 pound (0.95 kg)/110 minutes, and initiator solution was injected at 1 mL/min for 70 minutes. After 0.1 pound (45 g) of TFE had been fed after kickoff, an aqueous solution of 0.1 wt mesaconic acid was started at 1 mL/minute and continued for the remainder of the batch. After 2.1 pounds (0.95 kg) of TFE had been injected over a reaction period of 110 minutes, the reaction was terminated. At the end of the reaction period, the TFE and mesaconic acid solution feeds were stopped, and the reactor was slowly vented. After venting to nearly atmospheric pressure, the reactor was purged with nitrogen to

remove residual monomer, and the dispersion was discharged from the reactor. After coagulation, the polymer was isolated by filtering and then drying in a 150° C. convection air oven. The melt-flowable fluoropolymer isolated had a mesaconic acid content of 0.011 wt %. Note that not all of the activities described above in the general description or the examples are required, that a portion of a specific activity may not be required, and that one or more further activities may be performed in addition to those described. Still further, the order in which activities are listed are not necessarily the order in which they are performed.

[0101] In the foregoing specification, the concepts have been described with reference to specific embodiments. However, one of ordinary skill in the art appreciates that various modifications and changes can be made without departing from the scope of the invention as set forth in the claims below. Accordingly, the specification is to be regarded in an illustrative rather than a restrictive sense, and all such modifications are intended to be included within the scope of invention.

[0102] Benefits, other advantages, and solutions to problems have been described above with regard to specific embodiments. However, the benefits, advantages, solutions to problems, and any feature(s) that may cause any benefit, advantage, or solution to occur or become more pronounced are not to be construed as a critical, required, or essential feature of any or all the claims.

[0103] It is to be appreciated that certain features are, for clarity, described herein in the context of separate embodiments, may also be provided in combination in a single embodiment. Conversely, various features that are, for brevity, described in the context of a single embodiment, may also be provided separately or in any subcombination. Further, reference to values stated in ranges include each and every value within that range.

What is claimed is:

1. A melt-flowable fluoropolymer comprising repeating units arising from:
 - (a) tetrafluoroethylene; and
 - (b) a hydrocarbon monomer having at least one functional group and a polymerizable carbon-carbon double bond; wherein the sum of the weight percent of said (a) and said (b) comprises at least about 99 weight percent of all repeating units comprising said melt-flowable fluoropolymer, and wherein the amount of said repeating units arising from said (b) is about 0.001 to about 1 weight percent.
2. The melt-flowable fluoropolymer of claim 1, wherein said at least one functional group is at least one selected from the group consisting of amine, amide, carboxyl, hydroxyl, phosphonate, sulfonate, nitrile, boronate and epoxide.
3. The melt-flowable fluoropolymer of claim 1, wherein said at least one functional group is a dicarboxylic acid anhydride.
4. The melt-flowable fluoropolymer of claim 1, wherein said at least one functional group is a dicarboxylic acid.
5. The melt-flowable fluoropolymer of claim 1, further comprising about 1 weight percent or less of repeating units arising from a fluoromonomer other than tetrafluoroethylene.
6. The melt-flowable fluoropolymer of claim 5, wherein said fluoromonomer other than tetrafluoroethylene is at least one selected from the group consisting of chlorotrifluoroethylene, hexafluoropropylene, perfluoro-2,2-dimethyl-1,3-dioxole, perfluoro-2-methylene-4-methyl-1,3-dioxolane, per-

fluoro(methyl vinyl ether), perfluoro(ethyl vinyl ether), perfluoro(propyl vinyl ether) and perfluoro(butyl vinyl ether).

7. The melt-flowable fluoropolymer of claim 1, wherein the amount of said repeating units arising from said (b) is about 0.001 to about 0.5 weight percent.

8. The melt-flowable fluoropolymer of claim 1, wherein the amount of said repeating units arising from said (b) is about 0.001 to about 0.3 weight percent.

9. The melt-flowable fluoropolymer of claim 1, wherein the amount of said repeating units arising from said (b) is about 0.001 to about 0.1 weight percent.

10. The melt-flowable fluoropolymer of claim 1, wherein the amount of said repeating units arising from said (b) is about 0.001 to about 0.01 weight percent.

11. The melt-flowable fluoropolymer of claim 1, wherein said hydrocarbon monomer has at least one amine functional group and a polymerizable carbon-carbon bond.

12. The melt-flowable fluoropolymer of claim 1, wherein said hydrocarbon monomer has at least one amide functional group and a polymerizable carbon-carbon double bond.

13. The melt-flowable fluoropolymer of claim 1, wherein said hydrocarbon monomer has at least one phosphonate functional group and a polymerizable carbon-carbon double bond.

14. The melt-flowable fluoropolymer of claim 1, wherein said hydrocarbon monomer has at least one boronate functional group and a polymerizable carbon-carbon double bond.

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