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(54) **Titre : COMPOSITES DE PERFLUOROELASTOMERE D'UNE GRANDE PURETE ET PROCEDE DE PRODUCTION DE CES COMPOSITES**

(54) **Title: HIGH PURITY PERFLUOROELASTOMER COMPOSITES AND A PROCESS TO PRODUCE THE SAME**

(57) **Abrégé/Abstract:**

High purity perfluoroelastomer composites and processes for producing the same are provided. High purity composites may be formed from compositions comprising a crosslinkable fluoroelastomer terpolymer of TFE, PAVE, and CNVE, and functionalized PTFE, which may be crosslinked to form crosslinked composites having low metal content and low compression set. Emulsion mixtures for forming the high purity composites are also provided.



ABSTRACT OF THE DISCLOSURE

High purity perfluoroelastomer composites and processes for producing the same are provided. High purity composites may be formed from compositions comprising a crosslinkable fluoroelastomer terpolymer of TFE, PAVE, and CNVE, and functionalized PTFE, which may be crosslinked to form crosslinked composites having low metal content and low compression set. Emulsion mixtures for forming the high purity composites are also provided.

High Purity Perfluoroelastomer Composites and
a Process to Produce the Same ✓

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BACKGROUND OF THE INVENTION

Perfluoroelastomers have achieved outstanding commercial success and are used in a wide variety of applications in which severe environments are encountered, in particular those end uses where
10 exposure to high temperatures and aggressive chemicals occurs. For example, these polymers are often used in seals for aircraft engines, in semiconductor manufacturing equipment, in oil-well drilling devices, and in sealing elements for industrial equipment used at high temperatures.

The outstanding properties of perfluoroelastomers are largely
15 attributable to the stability and inertness of the copolymerized perfluorinated monomer units that make up the major portion of the polymer backbones in these compositions. Such monomers include tetrafluoroethylene (TFE) and perfluoro(alkyl vinyl) ethers (PAVE). In order to develop elastomeric properties fully, perfluoroelastomers are
20 typically crosslinked, i.e. vulcanized. To this end, a small percentage of cure site monomer is copolymerized with the perfluorinated monomer units. Cure site monomers containing at least one nitrile group, for example perfluoro-8-cyano-5-methyl-3,6-dioxa-1-octene, are especially preferred. Such compositions are described, for example, in U.S.
25 Patents 4,281,092; 4,394,489; 5,789,489; and 5,789,509.

The polymerization processes of perfluoroelastomers are most typically done in the presence of a perfluoro carboxylic acid salt or fluorinated sulfonic acid salt. If the salt contains a metal ion, it contaminates the formed polymer. If the salt is a non-metal, usually the
30 resulting pH of the polymerization media is acidic leading to corrosion of polymerization vessel or downstream lines and vessels, and subsequent contamination of the resulting polymer. Further, coagulation of the emulsion or dispersion is usually accomplished by use of magnesium, barium, or other metallic salts resulting in two distinct problems. First,
35 they add metallic contamination to the elastomeric crumb and second, the metallic salts of the perfluoro carboxylic acids become much more difficult to remove from the crumb.

The prior art further teaches compounding the perfluoroelastomer, for example, on a roll mill, Banbury[®] mixer, extruder, or the like. In the step, crosslinking catalysts or other additives may be mixed with the perfluoroelastomer crumb in the melt to facilitate sufficient crosslinking
5 as may be required by the application. For example, one goal may be to attain sufficient crosslinking to achieve good high temperature compression set resistance. Compounding may actually result in the addition of metallic and/or other contaminants by the direct addition via additives; additionally high temperature melt compounding often results
10 in metal contamination by corrosion of the compounding equipment and exposure to environmental contamination. If organic crosslinking agents are used, the resulting articles are usually brown due to thermal decomposition of the agents.

Perfluoroelastomer articles such as seals, O-rings, and valve
15 packings are often highly filled with carbon black or metallic fillers for reinforcement rendering them opaque and providing an additional source of contamination. When exposed to plasmas in end uses such as semiconductor manufacturing, the polymeric component of these articles is etched away, leaving the fillers as undesirable particle contaminants.
20 Furthermore, as the polymer decomposes any fillers such as metals, metal oxides or metal salts originally contained in articles may be released.

Recent patents of Saito *et al.* and Coughlin and Wang (U.S. Pat. No. 5,565,512, and WO 02/48200) have discussed the value of
25 producing clear and pure perfluoroelastomer parts with low metal ion contamination. Market forces that are driving the move to clear, clean perfluoroelastomer parts include both the semi conductor industry and the pharmaceutical industry which desires extremely low concentrations of metals. In addition, the pharmaceutical and biotechnology industries
30 desire overall purity and elimination of certain perfluoro carboxylic acids which accumulate in the body is highly desirable. For example, some companies manufacturing fluoropolymer resins or parts have established limits of perfluoro octanoic acid (PFOA), the acid form of ammonium perfluoro octanoate (APFO) which is a common surfactant used in
35 fluoromonomer emulsion polymerization.

However, the need for crosslinkable perfluoroelastomers and crosslinked parts that have a low metallic ion contamination and a low perfluoro carboxylic concentration has not been met with the usual

processes of forming these. Therefore, one embodiment of the present invention is a method for producing perfluoroelastomer compositions having low metallic ion contamination and low perfluoro carboxylic concentration.

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SUMMARY OF THE INVENTION

This invention relates to crosslinkable perfluoroelastomers and cured perfluoroelastomer articles having low metallic ion concentration and a low concentration of residual fluorosurfactant, and inventive processes for making the same. In the absence of additives, transparent articles having high purity are produced by the methods of the present invention.

In one embodiment, methods of the present invention minimize contamination in part by minimizing corrosion that results from conventional polymerization processes performed in the presence of perfluorocarboxylic acid salt by using a non-metallic buffer and/or corrosion resistant vessel and/or lines. Corrosion resistant materials useful in the present invention include high Ni alloys, for example, Inconel[®] or Hastelloy[®] alloys. Processes of present invention may also solve the problem of contamination encountered by coagulation of the emulsion or dispersion using metallic salts. For example, by using nitric acid (HNO₃) or ammonium salts like (NH₄)₂CO₃ and NH₄NO₃ as coagulants, metallic contamination can be minimized or eliminated. Known methods for curing elastomeric resin may result in contamination by using compounding steps that add metallic and/or other contaminants, or by corrosion of the compounding equipment, or exposure to environmental contamination. It has been unexpectedly discovered that perfluoroelastomeric uncrosslinked gum, having a low concentration of perfluoro carboxylic acids or salt containing perfluoro cyano vinyl ether crosslink sites, such as 8-CNVE, can be cured in the mold at about 250°C, or greater than 250°C, without a compounding step and without the addition of any other chemicals.

Combining these inventive steps results in the production of crosslinked perfluoro elastomer parts having metallic ion contamination more than a factor of 100 or a factor of 1000 lower than currently known. For example, in one embodiment of the present invention crosslinked perfluoroelastomeric parts are produced having less than about 3 parts

per million (ppm) or more preferably, less than about 0.5 ppm metallic ion. The concentration of perfluoro carboxylic acid also may be less than about 2 ppm, or less than about 1 ppm. Advantageously, crosslinked parts of the present invention may have compression set values
 5 measuring less than or equal to about 35% at about 200°C. Preferred crosslinked parts are transparent and colorless.

DESCRIPTION OF THE FIGURES

10 Figure 1. Curing kinetics of samples according to Example 2 obtained at 250°C.
 Figure 2. Curing kinetics of samples according to Example 4 obtained at 250°C.

DETAILED DESCRIPTION OF THE INVENTION

In one embodiment, the present invention is directed to a composition comprising a crosslinkable perfluoroelastomer terpolymer consisting essentially of TFE, PAVE and a cure site monomer having at
 20 least one nitrile-containing group; thus, the crosslinkable composition forms a crosslinked terpolymer without additional materials such as crosslinking agents and the like. The present invention is further directed to methods of making the crosslinkable terpolymer, methods of crosslinking the terpolymer in the absence of a crosslinking agent, and
 25 articles made therefrom.

In one embodiment, perfluoroelastomers of the present invention may comprise crosslinkable terpolymers polymerized from monomer units consisting essentially of TFE, PAVE, and perfluorocyano vinyl ether. In one embodiment the PAVE monomer is perfluoromethylvinyl
 30 ether (PMVE), however, other suitable perfluorinated vinyl ethers may also be selected from monomers, or mixtures of monomers, of the formula



where Rf' and Rf'' are different linear or branched perfluoroalkylene groups of 2-6 carbon atoms, m and n are independently 0-10, and Rf is a
 35 perfluoroalkyl group of 1-6 carbon atoms.

Another class of perfluorovinyl ethers for use in the present invention includes compositions of the formula



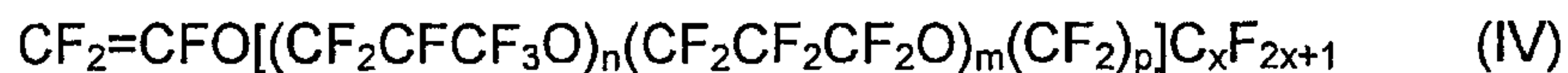
where X is F or CF_3 , n is 0-5, and Rf is a perfluoroalkyl group of 1-6 carbon atoms.

A further class of perfluorovinyl ethers includes those ethers wherein n is 0 or 1 and Rf contains 1-3 carbon atoms. Examples of such perfluorinated ethers include PMVE, perfluoroethyl vinyl ether (PEVE) and perfluoropropyl vinyl ether (PPVE). Other useful monomers include compounds of the formula



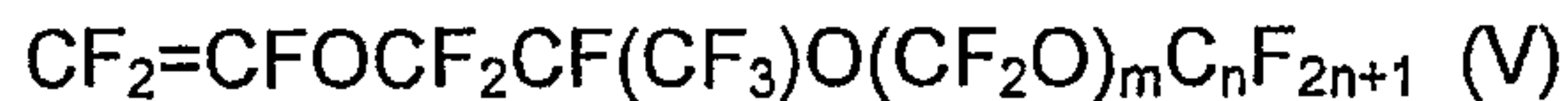
where Rf is a perfluoroalkyl group having 1-6 carbon atoms, m=0 or 1, n=0-5, and Z=F or CF_3 . Preferred members of this class are those in which Rf is C_3F_7 , m=0, and n=1.

Additional perfluorovinyl ether monomers for use in the present invention may include compounds of the formula



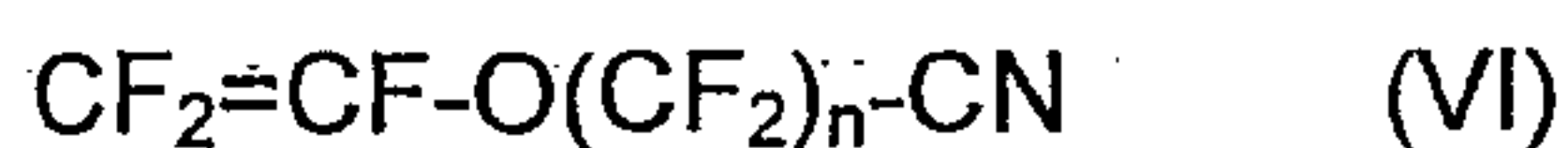
where m and n independently = 1-10, p=0-3, and x=1-5. Preferred members of this class include compounds where n = 0-1, m=0-1, and x = 1.

Another example of a useful perfluorovinyl ether includes



where n=1-5, m=1-3, and where, preferably, n=1.

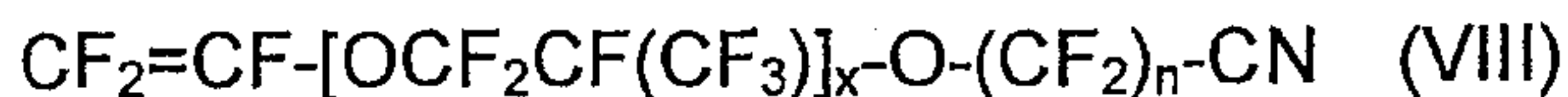
Crosslinkable terpolymers of the present invention have cure site monomers containing at least one nitrile group. In one embodiment, the monomers include fluorinated olefins containing at least one nitrile group, and in another embodiment, the monomers comprise nitrile-containing fluorinated vinyl ethers, including those having the following formulae.



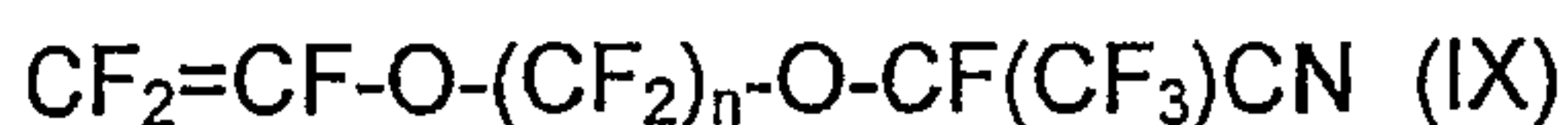
where n=2-12, preferably 2-6;



where n=0-4, preferably 0-2;



where x=1-2, and n=1-4; and



where n=2-4. Particularly preferred cure site monomers are perfluorinated polyethers having a nitrile group and a trifluorovinyl ether

group, including perfluoro(8-cyano-5-methyl-3,6-dioxa-1-octene),
 $\text{CF}_2=\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{CN}$ (X).

Preferred perfluoroelastomer compositions of the present invention are comprised of a crosslinkable terpolymer consisting essentially of units of TFE, PAVE and cure site units having at least one nitrile-containing group, where in one embodiment PAVE is PMVE and further, wherein 8- perfluorocyano vinyl ether (8-CNVE) is the nitrile-containing cure site monomer. The crosslinkable terpolymer may be polymerized from the above monomers by known methods including those described in WO 02/060968 to Coggio et al., and further, methods as described in detail in the examples presented below. In one embodiment, crosslinkable perfluoroelastomer terpolymers consist essentially of approximately from 38 to 81.7 mole percent TFE, 18 to 58 mole percent PAVE, and 0.3 to 4 mole percent of a nitrile-containing cure site monomer. Other crosslinkable terpolymers of the present invention consist essentially of about 47 to 80 mole percent TFE, 19 to 50 mole percent PAVE, and 1 to 3 mole percent nitrile-containing cure site monomer.

After polymerization to form crosslinkable terpolymers of the present invention, the gum may be further processed with a finishing step as described in Example 1 below which may facilitate the elimination of some contaminants.

In one embodiment, the highly pure crosslinkable terpolymers have low metal ion content (or metal contamination), as well as low fluorosurfactant concentration. The metal content of the crosslinkable terpolymer is less than 200 ppm, and preferably less than 3000 parts per billion (ppb), also preferred less than about 2000 ppb, further preferred less than about 1000 ppb, more preferably less than about 500, and most preferably less than about 200 ppb when measured according to the methods described herein for determining metal content. The metal content of preferred crosslinked terpolymer is also less than 200 ppm, preferably less than 3000 ppb, more preferably less than about 2000 ppb, further preferred less than about 1000 ppb or less than about 500 ppb when measured according to the methods described herein for determining metal content. In one embodiment, the fluorosurfactant concentration is preferably less than 2 ppm for one or both of the uncrosslinked and crosslinked terpolymer, when measured according to

the methods described herein. Preferably, the concentration of perfluoro carboxylic acid may be less than about 2 ppm, and less than 1 ppm.

Uncrosslinked and crosslinked terpolymers may have a fluoro sulfonic acid concentration of less than about 2 ppm, or less than 1 ppm. APFO concentrations of uncrosslinked and crosslinked compositions may be less than 2 ppm or in a further embodiment less than 1 ppm.

The present invention is further directed to a process for making highly pure crosslinked perfluoroelastomeric articles. One embodiment of the present invention comprises a method comprising heating a composition comprising a crosslinkable terpolymer consisting essentially of TFE, PAVE, and nitrile-containing cure-site monomer units, to form highly pure crosslinked composition to which no crosslinking agents have been added. One method comprises:

1) forming a composition comprising a crosslinkable

perfluoroelastomeric terpolymer of the present invention consisting essentially of a) TFE, b) PAVE, and c) nitrile-containing cure site monomer;

2) shaping the crosslinkable perfluoroelastomeric terpolymer composition;

3) heating said shaped perfluoroelastomeric terpolymer composition, and

4) crosslinking the perfluoroelastomer terpolymer by heating, wherein the process is performed without adding or, in the absence of, a crosslinking agent.

The method of the present invention may include shaping by molding or other fabrication techniques by means that do not introduce significant metallic contamination.

In one embodiment, the method comprises heating and crosslinking the terpolymer having units with nitrile-containing cure sites in the absence of, or without the addition of, one or more crosslinking agents, until sufficient crosslinking is achieved. Crosslinking agents including coagents, catalysts, and the like (such as peroxides, isocyanurates, ammonia-generating compounds, and bisamidoxime) that are typically used for curing crosslinkable polymers, impart contaminants, and are not necessary for crosslinking terpolymers using the novel methods of the present invention. The exclusion of these crosslinking agents from the method of the present invention results in crosslinked compositions having higher purity than achieved by currently

known methods. Preferred crosslinked perfluoroelastomers are translucent or transparent after heating.

In one embodiment, the method comprises heating and crosslinking shaped perfluoroelastomer to greater than or equal to about 5 250°C in the absence, or without the addition of crosslinking agents or additives, until sufficient crosslinking is achieved; in a further embodiment, the method comprises heating to greater than or equal to about 300°C, in the absence of, or without the addition of, crosslinking agents. Heating and crosslinking are maintained at temperatures and for 10 times sufficient to cure the terpolymer to a desired level. In a further embodiment, the heating and crosslinking are continued for times and temperatures necessary to obtain a specific compression set. For example, the method comprises heating and crosslinking until a crosslinked terpolymer or shaped article is formed having a compression 15 set of less than or equal to about 50% when tested at about 200°C according to the method described herein. In other embodiments the method comprises heating and crosslinking until a crosslinked terpolymer or shaped article has a compression set of less than or equal to about 40%, less than or equal to about 35%, less than or equal to 20 about 30%, or less than or equal to about 10% when tested at about 200°C according to the method used herein, and described below. A crosslinkable terpolymer composition may be heated, for example, for about 30 minutes or greater, or for about 60 minutes or greater, at a temperature of greater than about 250°C or greater than or equal to 25 about 300°C, to achieve these properties. Preferred crosslinked compositions of the present invention have a compression set less than or equal to about 40%, and more preferably less than or equal to about 35%, when tested at about 200°C according to the method described herein.

30 For use in evaluating the crosslinked compositions, compression set is measured according to ASTM D 395-01 Method B, at approximately 25% deflection, for about 70 hours in air. Articles are taken off from the testing device and reheated to the testing temperature for one (1) hour and measured.

35 Articles made from the perfluoroelastomer terpolymer of the present invention are useful in applications requiring higher purity than can be obtained by currently known methods. A few uses of articles formed from compositions of the present invention include gaskets such

as o-rings, tubes, diaphragms, seals and the like. Crosslinkable terpolymers of the present invention may be shaped and cured directly into usable articles.

In a further embodiment of the present invention the crosslinkable terpolymers may be blended with other materials, such as an additive or filler, to impart or enhance desired properties, or, further, other monomer or polymer compositions. Thus, in one embodiment a blend is formed comprising a composition comprising a crosslinkable fluoroelastomer terpolymer consisting essentially of TFE, PAVE and CNVE, and from about 1-20 wt%, based on the composite weight of at least one additional material selected from fillers and additives, which may be added prior to shaping or forming the composite into an article. For example, one such composite of the present invention is formed having a filler comprising SiO₂, and preferably, where PAVE comprises PMVE, PEVE, or PPVE and CNVE comprises 8-CNVE. Crosslinkable fluoroelastomer terpolymer composites may have a metal content of less than about 3000 ppb, less than about 2000 ppb, less than 1000 ppb, less than 500 ppb, or less than 200 ppb. Preferred composites, when crosslinked, have a compression set of less than 50%, less than 40% or less than 30%, when tested at 200°C.

In one other embodiment of the present invention, composites are formed from a blend comprising 1) a composition comprising a crosslinkable terpolymer consisting essentially of TFE, PAVE, and nitrile-containing cure site monomer units, such as the terpolymers of the present invention described above, and 2) functionalized polytetrafluoroethylene (PTFE). At least one additional material selected from fillers and additives may be added. Composites of functionalized PTFE and crosslinkable fluoroelastomer terpolymers also may have a metal content of less than about 3000 ppb, less than about 2000 ppb, less than 1000 ppb, less than 500 ppb, or less than 200 ppb. Preferred composites, when crosslinked, have a compression set of less than 50%, less than 40% or less than 30%, when tested at 150°C.

The blends may be formed from an emulsion mixture of the crosslinkable terpolymers. In one embodiment, an emulsion mixture comprises an emulsion of a composition comprising a crosslinkable perfluoroelastomer terpolymer consisting essentially of units of TFE, PAVE, and perfluorocyclo vinyl ether (CNVE), and a dispersion of at least one additional material selected from fillers and additives. In one

embodiment the emulsion of the composition comprising the terpolymer is a microemulsion, and the at least one additional material comprises a dispersion of silica. Preferred terpolymers comprise units of PMVE, PPVE, or PEVE, and 8-CNVE. Methods for forming the emulsions are taught, for example, in the detailed examples herein.

In one other embodiment, an emulsion mixture comprises an emulsion of i) an emulsion comprising the crosslinkable perfluoroelastomer terpolymers of the present invention consisting essentially of units of TFE, PAVE, and CNVE, and ii) a PTFE polymer comprising 0.1-3 mol% perfluorocyano vinyl ether. Preferred terpolymers comprise units of PMVE, PPVE, or PEVE, and 8-CNVE. Methods for forming the emulsions are taught, for example, in the detailed examples herein. Microemulsions and nanoemulsions of functionalized PTFE having particle sizes of less than about 100 nm are preferred. A nano emulsion comprising PTFE polymer functionalized with perfluorocyano vinyl ether, most preferably 8-cyano vinyl ether, and having a particle size of from about 10 nm to 100 nm is preferred.

The emulsion mixtures of the present invention may be coagulated to form the blends. For example, one blend of the present invention comprising functionalized PTFE and crosslinkable perfluoroelastomer terpolymer is coagulated to form a functionalized PTFE-filled crosslinkable perfluoroelastomer terpolymer blend, as described herein. The functionalized PTFE may be present in an amount of about 1 to 20 wt% of a dried composite resulting from the emulsion mixture, and the crosslinkable perfluoroelastomer terpolymer in an amount of about 80-99 wt% of a dried composite resulting from the emulsion mixture. The functionalized PTFE-filled crosslinkable terpolymer blend may be crosslinked according to the methods described herein, including heating and crosslinking the blend in the absence of any crosslinking agent, to form a cured functionalized PTFE-filled polymer having properties such as a desired level of crosslinking, compression set and purity values as described previously herein.

The blends may further comprise at least one additional material such as fillers and additives to impart specifically desired properties to the composite. The at least one additional material comprises about 1 to 20 wt % of the composite, and in one embodiment it is added as a dispersion to an emulsion mixture. In one embodiment silica is added as a dispersion to the microemulsions or the emulsion mixture. In one

embodiment, it is desired to add at least one additional material to a functionalized PTFE-filled terpolymer blend prior to shaping, heating and crosslinking the article.

Articles made from the functionalized PTFE-filled terpolymer
5 include, gaskets such as o-rings, and the like.

Test Methods

APFO Analysis

10 The methanolic HCl derivitization method is used to change the APFO form from the salt or carboxylic acid into its methylester derivative. This form is easily analyzed via Gas Chromatography (GC).

The APFO in about 1 g polymer is extracted and derivitized into 10 ml Methanolic HCl (Part # 33050-U, Supelco) over two hours at 55°C.
15 The derivative mixture is then combined with 20 ml of half saturated NaCl/aqueous solution (98+%, Sigma Aldrich) and 10 ml n-Hexane (99+%, Sigma Aldrich). The derivative is extracted into the Hexane layer, which is then removed for GC analysis.

The GC analysis is performed splitless using a non-polar column
20 and an Electron Capture Detector (Examples 2, 3 and 4) or Flame Ionization Detector (Examples 5, 6 and 7).

EXAMPLES

25 Example 1

An aqueous emulsion containing 10 g 8-CNVE [$\text{CF}_2=\text{CF}-\text{O}-(\text{CF}_2)_3-\text{O}-\text{CF}(\text{CF}_3)-\text{CN}$], 135 g deionized (DI) water and 5 g 20 wt% ammonium perfluorooctanoate (APFO) aqueous solution was prepared by using an Omini Mixer Homogenizer (Omini International Cö.) for 5 minutes. This
30 solution is designated as "stock solution A".

Approximately 1500 g DI water, 300 g 20 wt% APFO aqueous solution and 16 g 8-CNVE were charged into an oxygen-free 4-liter reactor. Then, 190 g TFE and 300 g PMVE were added into the reactor. The reactor was then heated to 70°C under 2285 KPa and the
35 polymerization reaction was initiated by feeding 202 g ammonium persulfate (APS) aqueous solution (2 g APS dissolved in 200 g DI water) within 2 minutes. As the reaction pressure decreased to 1800 KPa, 105 g stock solution A with 120 g DI water and 20 g TFE were charged into

the reactor within 3 minutes. Then, 150.5 g APS solution (0.5 g APS dissolved in 150 DI water) was fed into the reactor within 1 minute. As the reaction pressure decreased to 1600 KPa, 45 g stock solution A with 150 g DI water and 20 g TFE were charged into the reactor within 1
5 minute. Then, 150.5 g APS solution (0.5 g APS dissolved in 150 g DI water) was added into the reactor within 1 minute. The polymerization reaction was stopped after 221 minutes from the initiation of the reaction under 518 KPa. The reactor was cooled and the residual gas was purged. The emulsion latex containing 16.9 wt% solids was obtained.

10

Finishing Process 1

Approximately 10 ml nitric acid (minimum 65%, semiconductor grade, Riedel-deHaen) was introduced into 200 ml of the emulsion latex (prepared substantially according to Example 1) in a polypropylene (PP)
15 beaker with stirring at room temperature. The liquids were decanted and then the precipitated solids were immersed in 200 ml methanol (semiconductor grade, Riedel-deHaen) at room temperature. After 24 hours, the methanol was decanted and the polymer was washed with 200 ml methanol (semiconductor grade, Riedel-deHaen). The polymer
20 was dried at 120°C for 12 hours in a convection oven.

Finishing Process 2:

The procedure is the same as the above, but the nitric acid used was an ACS reagent grade (70%, Aldrich) and the methanol used was a
25 PRA grade (99.9%, Aldrich).

The 2 dried polymer samples were analyzed by Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS) for 16 metal elements. Table 1 lists the metal ion levels in the polymers.

Solid-state ^{19}F NMR was carried out to characterize the
30 composition of the polymer. This polymer sample contained 62.4 mol% TFE, 36.6 mol% PMVE and 1.0 mol% 8-CNVE.

Example 2

An aqueous solution containing 10 g 8-CNVE [$\text{CF}_2=\text{CF}-\text{O}-(\text{CF}_2)_3-\text{O}-\text{CF}(\text{CF}_3)-\text{CN}$], 136 g DI water and 4 g of 20 wt% APFO aqueous solution
35 was prepared by using an Omini Mixer Homogenizer for 5 minutes. This solution is designated as "stock solution B".

Approximately 1500 g DI water, 300 g 20 wt% APFO aqueous solution and 16 g 8-CNVE were charged into an oxygen-free 4-liter reactor. Then, 190 g TFE and 320 g PMVE were added into the reactor. The reactor was then heated to 70°C under 2347 KPa and the
5 polymerization reaction was initiated by feeding 200.5 g APS aqueous solution (0.5 g APS dissolved in 200 g DI water) within 1 minute. As the reaction pressure decreased to 1900 KPa, 105 g stock solution B with 120 g DI water and 20 g TFE were charged into the reactor within 2 minutes. As the reaction pressure decreased to 1700 KPa, 45 g stock
10 solution B with 150 g DI water and 20 g TFE were charged into the reactor within 2 minutes. The polymerization reaction was stopped after 367 minutes from the initiation of the reaction under 600 KPa. The reactor was cooled and the residual gas was purged. The emulsion latex containing 18.2 wt% solids was obtained.

15 Approximately 400 ml of the emulsion latex was coagulated at room temperature with 20 ml nitric acid (70%, ACS reagent, Aldrich) in a PP beaker. The liquids were decanted and then the precipitated material was immersed in 400 ml methanol (99.9%, PRA grade, Aldrich) for 24 hours at room temperature. Then, the methanol was decanted and the
20 material was washed with 400 ml methanol (99.9%, PRA grade, Aldrich). The methanol was decanted and the washed material was dried at 70°C for 48 hours in a convection oven.

The APFO residual detected from the polymer was 0.3 ppm. Solid-state ^{19}F NMR showed it had 61.7 mol% TFE, 37.3 mol% PMVE
25 and 1.0 mol% 8-CNVE.

An ARES rheometer (Rheometrics) was used to monitor the curing process. Disks having an 8 mm diameter and about a 0.8 mm thickness were molded from the polymer at 100°C for 2 minutes. A disk was placed between two 8 mm diameter parallel plates at 60°C for 100
30 seconds and then heated to a setting curing temperature from a starting temperature of 60°C at a heating rate of 80°C/min. Curing was carried out at a frequency of 10 rad/second, a strain of 0.1% and a setting temperature in air. Torque and $\text{Tan}\delta = G''/G'$ were monitored with time, where G' is the storage shear modulus and G'' the loss shear modulus. Its
35 curing curve is shown in Figure 1.

The crumb polymer was molded into AS-568A K214 (Aerospace Standard O-ring size) O-rings at 300°C and 1727 psi for 1 hour and then

were postcured in air at 300°C for 24 hours. The O-rings made were transparent.

Compression set was measured on O-rings largely based on ASTM D 395-01 Method B. However, the ASTM method does not have a quantitative time or temperature scale as to how soon or at what temperature the tested specimens should be taken off from the testing device. Different compression set values can be obtained when tested specimens are taken off from the testing device at different temperatures. To avoid this issue, tested specimens taken off from the testing device were reheated to the testing temperature for 1 hour, and then measured according to ASTM D 395-01, i.e., cooling for 30 minutes, etc. The compression set value is given in Table 3.

Example 3

An aqueous solution containing 10 g 8-CNVE [$\text{CF}_2=\text{CF}-\text{O}-(\text{CF}_2)_3-\text{O}-\text{CF}(\text{CF}_3)-\text{CN}$], 480 g DI water and 10 g 20 wt% APFO aqueous solution was prepared by using an Omini Mixer Homogenizer for 5 minutes. This solution is designated as "stock solution C".

Approximately 1500 g DI water, 300 g 20 wt% APFO aqueous solution and 16 g 8-CNVE were charged into an oxygen-free 4-liter reactor. Then, 260 g TFE and 300 g PMVE were added into the reactor. The reactor was then heated to 70°C under 2584 KPa and the polymerization reaction was initiated by feeding 200.2 g APS aqueous solution (0.2 g APS dissolved in 200 g DI water) within 1 minute. Then, stock solution C was fed into the reactor as follows:

Time after reaction initiation (in minutes)	Stock solution C added (in grams)
2	60
16	60
28	60
40	60
51	50
61	60
72	60
83	80
98	10

As the reaction pressure decreased to 2120 KPa, 20 g TFE was charged into the reactor within 1 minute. Another 20 g TFE was added into the reactor within 1 minute as the reaction pressure decreased to 1920 KPa. The polymerization reaction was stopped after 219 minutes
5 from the initiation of the reaction under 1200 KPa. The reactor was cooled and the residual gas was purged. The emulsion latex containing 15.9 wt% solids was obtained.

The coagulation process was substantially the same as the first finishing process as shown in Example 1. The polymer was dried at
10 70°C for 48 hours in a convection oven.

The dried polymer sample was analyzed by ICP-MS for 16 metal elements. Table 1 lists the metal ion levels in the polymer.

The APFO residual detected from the polymer was 1.2 ppm. This polymer had 74.9 mol% TFE, 24.2 mol% PMVE and 0.9 mol% 8-CNVE,
15 as determined by solid-state ¹⁹F NMR.

The crumb polymer was molded into AS-568A K214 O-rings, heating at 300°C and 1658 psi for 5 minutes, and then was postcured in air at 250°C for 24 hours. The O-rings made were transparent. The compression set value is given in Table 3. The crumb polymer was also
20 molded and cured into 1 mm thick films between Kapton® films under the same molding, heating and postcuring condition. The purity of the crosslinked film is shown in Table 1.

Example 4

25 Approximately 1800 g DI water and 180 g 20 wt% APFO aqueous solution were charged into an oxygen-free 4-liter reactor. Then, 3.6 g 8-CNVE [CF₂=CF-O-(CF₂)₅-CN], 76 g PMVE and 62.8 g TFE were added into the reactor.

The reactor was heated to 60°C, and then the mixture of TFE with
30 PMVE (55/45, wt/wt) was charged into the reactor until the pressure increased to 920 KPa. Then 200 ml aqueous solution containing 6 g APS and 4 g 25 wt% ammonium sulfite was added into the reactor to initiate the polymerization reaction.

Once the initiation reaction started, 8-CNVE was continuously
35 charged into the reactor at a rate of 0.143 g/min, and the mixture of TFE with PMVE (55/45 wt/wt) was also continuously supplied to the reactor to maintain the reaction pressure at 930-950 KPa.

After 440 minutes from the start of the reaction initiation, the supply of 8-CNVE and the mixture of TFE with PMVE was then stopped. The reactor was kept in that state for another hour. Then reactor was cooled and the residual gas was purged. The emulsion latex containing
5 27.5 wt% solids was obtained.

The coagulation process is the same as the first finishing process as shown in Example 1. The polymer was dried at 70°C for 48 hours in a convection oven.

The dried polymer sample was analyzed by ICP-MS for 16 metal
10 elements. Table 1 lists the metal ion levels in the polymer.

The APFO residual detected from the polymer was 0.8 ppm. Solid-state ^{19}F NMR was carried out to characterize the composition of the polymer. This polymer sample contained 69.6 mol% TFE, 29.2 mol% PMVE and 1.2 mol% 8-CNVE.

15 An ARES rheometer (Rheometrics) was used to monitor the curing process. Disks having an 8 mm diameter and about a 0.8 mm thickness were molded from the polymer at 100°C for 2 minutes. A disk was placed between two 8 mm diameter parallel plates. Curing was carried out at a frequency of 10 rad/second, a strain of 0.5% and heating
20 at about 250°C in air. Torque and $\text{Tan}\delta = G''/G'$ were monitored with time. Its curing curve is shown in Figure 2.

The crumb polymer was molded into AS-568A K214 O-rings heating at 250°C and 1727 psi for 30 min and then was postcured in air at 90 °C for 4 hours, 204°C for 24 hours and 288°C for 24 hours. The O-
25 rings made were transparent. The compression set value is given in Table 3. The crumb polymer was also molded into 1 mm thick films between Kapton® films under the same molding and postcuring condition. The purity of the crosslinked film is shown in Table 1.

30 Example 5

An aqueous solution containing 5 g 8-CNVE [$\text{CF}_2=\text{CF}-\text{O}-(\text{CF}_2)_3-\text{O}-\text{CF}(\text{CF}_3)-\text{CN}$], 490 g DI water and 10 g 20 wt% APFO aqueous solution was prepared by using an Omini Mixer Homogenizer for 5 minutes. This solution is designated as "stock solution E".

35 Approximately 1500 g DI water, 300 g 20 wt% APFO aqueous solution and 8 g 8-CNVE were charged into an oxygen-free 4-liter reactor. Then, 190 g TFE and 300 g PMVE were added into the reactor. The reactor was then heated to 70°C under 2258 KPa and the

polymerization reaction was initiated by feeding 200.5 g APS aqueous solution (0.5 g APS dissolved in 200 g DI water) within 1 minute. Then, stock solution E was fed into the reactor as follows:

5

Time after reaction initiation (in minutes)	Stock solution E added (in grams)
3	100
12	115
23	65
29	90
38	80
43	50

As the reaction pressure decreased to 1800 KPa, 20 g TFE was charged into the reactor within 1 minute. Another 20 g TFE was added into the reactor within 1 minute as the reaction pressure decreased to 1600 KPa. The polymerization reaction was stopped after 198 minutes from the initiation of the reaction under 600 KPa. The reactor was cooled and the residual gas was purged. The emulsion latex collected containing 17.3 wt% solids was obtained. The polymer had 49.6 wt% TFE, 48.5 wt% PMVE and 1.9 wt% 8-CNVE determined by FTIR.

Fumed silica (1.73 g) (R812, Degussa) was dispersed in 50 ml 2-propanol (IPA) (99.8%, PR grade, Aldrich). This fumed silica IPA dispersion was then introduced into 100 g of the polymer emulsion with stirring at room temperature. This mixture was coagulated with 5 ml nitric acid (70%, ACS reagent, Aldrich). The liquids were decanted and then the precipitated material was immersed in 100 ml methanol (99.9%, PRA grade, Aldrich) for 24 hours at room temperature. Then, the methanol was decanted and the material was washed with 100 ml methanol. The methanol was decanted and the washed material was dried at 70°C for 48 hours in a convection oven.

The dried polymer sample was analyzed by ICP-MS for 16 metal elements. Table 2 lists the metal ion levels in the polymer. The APFO residual detected in the dried silica-filled polymer was less than 2 ppm.

The silica-filled polymer was molded into AS-568A K214 O-rings heating at 250°C and 1727 psi for 30 minutes and then was post cured in air at 250°C for 24 hours. The compression set value is given in Table 3.

Example 6

Preparation of TFE-PMVE-8CNVE terpolymer emulsion:

- 5 An aqueous solution containing 20 g 8-CNVE [$\text{CF}_2=\text{CF}-\text{O}-(\text{CF}_2)_3-\text{O}-\text{CF}(\text{CF}_3)-\text{CN}$], 490 g DI water and 11 g 20 wt% APFO aqueous solution was prepared by using an Omini Mixer Homogenizer for 5 minutes. This solution is designated as "stock solution F".

- 10 Approximately 1500 g DI water, 300 g 20 wt% APFO aqueous solution and 32 g 8-CNVE were charged into an oxygen-free 4-liter reactor. Then, 190 g TFE and 300 g PMVE were added into the reactor. The reactor was then heated to 70°C under 2250 KPa and the polymerization reaction was initiated by feeding 200.5 g APS aqueous solution (0.5 g APS dissolved in 200 g DI water) within 2 minutes. Then,
15 stock solution F was fed into the reactor as follows:

Time after reaction initiation (in minutes)	Stock solution F added (in grams)
2	70
14	70
26	70
39	45
53	50
102	105
128	90

- 20 As the reaction pressure decreased to 1800 KPa, 20 g TFE was charged into the reactor within 1 minute. Another 20 g TFE was added into the reactor within 1 minute as the reaction pressure decreased to 1600 KPa. The polymerization reaction was stopped after 465 minutes from the initiation of the reaction under 730 KPa. The reactor was cooled and the residual gas was purged. The emulsion latex containing
25 17.4 wt% solids was obtained. The polymer had 58.7 mol% TFE, 38.2 mol% PMVE and 3.1 mol% 8-CNVE, as determined by solid-state ^{19}F NMR.

Preparation of 8-CNVE functionalized nano PTFE emulsion:

Approximately 1700 g DI water, 300 g 20 wt% APFO aqueous solution, 45 g hexafluorobenzene (HFB) and 3.5 g 8-CNVE [CF₂=CF-O-(CF₂)₃-O-CF(CF₃)-CN] were charged into an oxygen-free 4-liter reactor. Then, 130 g TFE was added into the reactor. The reactor was then heated to 70°C under 1200 KPa and the polymerization reaction was initiated by feeding 200.5 g APS aqueous solution (0.5 g APS dissolved in 200 g DI water) within 3 minutes. About 820 g TFE was fed into the reactor to keep a constant pressure of 1200 KPa within 322 minutes. The reactor was cooled and the residual gas was purged. A nano emulsion latex containing 24.2 wt% solids was obtained. The average size of PTFE particles was 19.4 nm in diameter measured by dynamic light scattering (90 Plus, Brookhaven Instruments). The polymer had 99.9 mol% TFE and 0.1 mol% 8-CNVE, as determined by solid-state ¹⁹F NMR.

Approximately 100 g of the terpolymer emulsion was mixed with 14.4 g of the nano PTFE emulsion. The emulsion mixture was coagulated with 5 ml nitric acid (70%, ACS reagent, Aldrich). The liquids were decanted and then the precipitated material was immersed in 100 ml methanol (99.9%, PRA grade, Aldrich) for 24 hours at room temperature. Then, the methanol was decanted and the material was washed with 100 ml methanol. The methanol was decanted and the washed material was dried at 70°C for 48 hours in a convection oven forming a functionalized nano PTFE-filled polymer composite. The APFO residual detected in the dried polymer was less than 2 ppm.

The functionalized nano PTFE-filled polymer was molded into AS-568A K214 O-rings heating at 300°C and 1727 psi for 30 minutes and then postcured in air at 250°C for 24 hours. The O-rings made were transparent. The compression set value is given in Table 3.

Example 7

Preparation of 8-CNVE functionalized nano PTFE emulsion:

Approximately 1700 g DI water, 300 g 20 wt% APFO aqueous solution, 45 g HFB and 7 g 8-CNVE [CF₂=CF-O-(CF₂)₃-O-CF(CF₃)-CN] were charged into an oxygen-free 4-liter reactor. Then, 120 g TFE was added into the reactor. The reactor was then heated to 70°C under 12

bar and the polymerization reaction was initiated by feeding 200.5 g APS aqueous solution (0.5 g APS dissolved in 200 g DI water) within 3 minutes. 760 g TFE was fed into the reactor to keep a constant pressure of 12 bars within 447 minutes. The reactor was cooled and the residual
5 gas was purged. The emulsion latex containing 26.8 wt% solids was obtained. The average size of the PTFE particles was 24.3 nm in diameter determined by dynamic light scattering. The polymer had 99.8 mol% TFE and 0.2 mol% 8-CNVE, as determined by solid-state ^{19}F NMR.

10 Approximately 100 g of the terpolymer emulsion made in Example 6 was mixed with 13 g of the nano PTFE emulsion. The emulsion mixture was coagulated with 5 ml nitric acid (70%, ACS reagent, Aldrich). The liquids were decanted and then the precipitated material was immersed in 100 ml methanol (99.9%, PRA grade, Aldrich) for 24 hours
15 at room temperature. Then, the methanol was decanted and the material was washed with 100 ml methanol. The methanol was decanted and the washed material was dried at 70°C for 48 hours in a convection oven.

The dried polymer sample was analyzed by ICP-MS for 16 metal
20 elements. Table 2 lists the metal ion levels in the polymer. The APFO residual detected in the resulting dried functionalized nano PTFE-filled polymer was less than 2 ppm.

The functionalized nano PTFE-filled polymer was molded into AS-568A K214 O-rings heating at 300°C and 1727 psi for 30 minutes, and
25 then postcured in air at 250 °C for 24 hours. The O-rings made were transparent. The compression set value is given in Table 3.

Table 1. Metal ions detected in the crosslinkable polymers and the crosslinked parts.

Metal Ions	Ex. 1 ⁽¹⁾ Level Detected (ppb)	Ex. 1 ⁽²⁾ Level Detected (ppb)	Ex. 3 ⁽³⁾ Level Detected (ppb)	Ex. 3 ⁽⁴⁾ Level Detected (ppb)	Ex. 4 ⁽⁵⁾ Level Detected (ppb)	Ex. 4 ⁽⁶⁾ Level Detected (ppb)
Al	1	< 1	< 1	12	1	8
Ba	< 1	< 1	1	1	< 1	< 1
Ca	37	15	50	100	20	70
Cr	6	< 5	< 5	< 5	< 5	13
Cu	< 5	< 5	< 5	< 5	< 5	< 5
Fe	17	10	< 10	< 10	< 10	30
Pb	< 1	< 1	< 1	< 1	< 1	< 1
Li	1	3	< 1	< 1	< 1	< 1
Mg	1	1	18	29	12	23
Mn	1	1	2	3	< 1	2
Ni	36	37	16	14	27	33
K	11	< 10	< 10	< 10	< 10	10
Na	70	8	22	26	9	200
Sr	< 1	< 1	< 1	< 1	< 1	< 1
Ti	< 10	< 10	< 10	< 10	< 10	< 10
Zn	< 10	< 10	< 10	< 10	< 10	< 10

5

- (1) The polymer obtained by finishing process 2.
 (2) The polymer obtained by finishing process 1.
 (3) The crumb polymer.
 (4) The crosslinked film.
 (5) The crumb polymer.
 (6) The crosslinked film.

10

Table 2.
Metal ions detected in the crosslinkable polymer composites.

Metal Ions	Ex. 5 Level Detected (ppb)	Ex. 7 Level Detected (ppb)
Al	8	4
Ba	4	3
Ca	< 10	20
Cr	< 5	< 5
Cu	24	9
Fe	60	50
Pb	< 1	< 1
Li	< 1	< 1
Mg	< 1	3
Mn	1	2
Ni	5	11
K	< 10	< 10
Na	< 5	< 5
Sr	< 1	< 1
Ti	< 10	< 10
Zn	< 10	< 10

5

Table 3.

Compression set values.

	Compression set, %*
Example 2	65 ⁽¹⁾
Example 3	35 ⁽¹⁾
Example 4	7 ⁽¹⁾
Example 5	31 ⁽²⁾
Example 6	33 ⁽³⁾
Example 7	39 ⁽³⁾

10 *25% deflection, 70 hours, in air; ⁽¹⁾ 204 °C; ⁽²⁾ 200 °C; ⁽³⁾ 150 °C

We claim:

1. A crosslinkable composite comprising
 - i) a composition comprising a crosslinkable fluoroelastomer terpolymer consisting essentially of tetrafluoroethylene (TFE), perfluoroalkyl vinyl ether (PAVE) and perfluorocyano vinyl ether (CNVE), and
 - ii) a functionalized polytetrafluoroethylene (PTFE),wherein the crosslinkable composite has less than 3000 ppb metal content, and is crosslinked in the absence of a crosslinking agent, coagent, or catalyst.
2. The composite of claim 1, wherein the composition further comprises SiO₂.
3. The composite of claim 1, wherein the composite, when crosslinked, has a compression set of less than 40% when tested at 150°C.
4. The composite of claim 1, wherein the composite, when crosslinked has a compression set of less than 30% when tested at 150°C.
5. The composite of claim 1 wherein the crosslinkable fluoroelastomer terpolymer comprises 8-perfluorocyano vinyl ether (8-CNVE).
6. The composite of claim 1, wherein the crosslinkable terpolymer has a metal content of less than 2000 ppb.
7. The composite of claim 1, wherein the crosslinkable terpolymer has a metal content of less than 1000 ppb.
8. The composite of claim 1, wherein the crosslinkable terpolymer has a

metal content of less than 500 ppb.

9. The composite of claim 1, wherein the crosslinkable terpolymer has a metal content of less than 200 ppb.

10. The composite of claim 1, wherein the composite has a metal content of less than 2000 ppb.

11. The composite of claim 1, wherein the composite has a metal content of less than 1000 ppb.

12. The composite of claim 1, wherein the composite has a metal content of less than 500 ppb.

13. The composite of claim 1, wherein the crosslinkable terpolymer has a metal content of less than 200 ppb.

14. The composite of claim 1, wherein the composite has an ammonium perfluorooctanoate (APFO) concentration of less than 2 ppm.

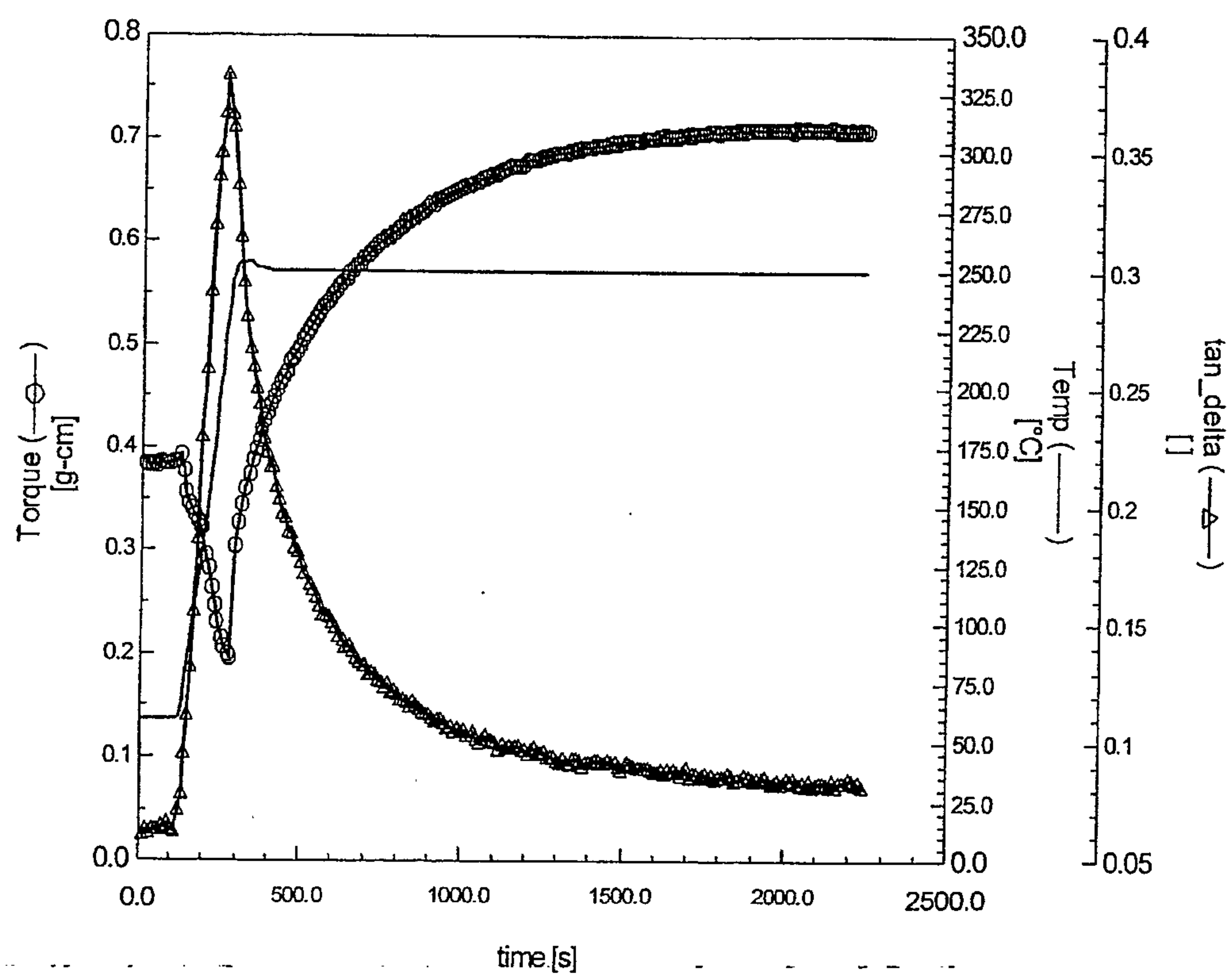
15. The crosslinkable composite of claim 1, further comprising at least one additional material selected from fillers and additives.

16. The crosslinkable composite of claim 1, wherein the composite, when crosslinked, has a compression set of less than 50% when tested at 150°C.

17. The composite of claim 15, wherein the at least one additional material is 1 to 20 wt % of the composite.

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Figure 1. Curing kinetics obtained at 250 °C (Example 2)



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Figure 2. Curing kinetics obtained at 250 °C (Example 4)

