apparatuses. The filler may be a carbon filler, such as carbon black, graphitized carbon or graphite. The filler may be in the form of a particle or fiber, wherein the particle size is preferably not more than 5 microns.

[00013] U.S. Patent No. 9,725,582 B2 provides a fluororesin composition for a molded product that has good tensile strength. The fluororesin composition includes a fluororesin and a fluorinated nanodiamond present in an amount of 0.001 to 5% mass based on the fluororesin. The fluorinated nanodiamond is described as a powder having an average particle size of 0.001 to 1 micron.

[0014] International Patent Publication No. WO 2016/104604 A1 describes a fluorine-containing elastomer composition used to form molded articles having improved chemical-resistance, solvent-resistance, and heat-resistance. The sealing material also demonstrates improved plasma-resistance and can be used in the working chamber of a semiconductor manufacturing apparatus. The composition includes a fluorine-containing elastomer with 0.0001-4 mass parts fullerene with respect to 100 mass parts of the fluorine-containing elastomer.

[0015] U.S. Patent No. 9,512,302 B2 provides a fluoropolymer coating with improved tribological properties. In one aspect, the invention relates to a slurry composition of a fluoropolymer and nanodiamond particles having specific properties. The nanodiamond particles may be in single or agglomerated form, and the particle size is preferably between 0.008 microns and 0.030 microns. The concentration of the nanodiamond in the slurry is at most 5% by weight.

[0016] While as noted above, there have been attempts in the prior art to integrate a highly plasma-resistant carbon-based filler into fluoroelastomers and perfluoroelastomers, as such materials lack the strength of a resin, the use of a high-strength particle such as a nanodiamond has been taught as being unfavorable when the particle size increases due to defect rates, which are typically associated with particulation or other factors and are also not believed to provide strength without loss of good elastomeric properties in such materials. Thus, there remains a need in the art to achieve such adequate physical properties or to improve them while retaining elastomeric sealing properties and improving the resistance to harsh plasma environments.

BRIEF SUMMARY

[0017] The disclosure herein includes a curable fluorine-containing elastomer composition comprising at least one curable fluoropolymer comprising at least one fluorinated monomer, and at least one fluorine-containing cure site monomer comprising at

least one cure site; and microdiamond particles having an average particle size of greater than 0.10 micron to about 100 microns.

[0017a] In one aspect of the present disclosure, there is provided a curable fluorine-containing elastomer composition comprising

at least one curable fluoropolymer comprising at least one fluorinated monomer, and at least one fluorine-containing cure site monomer comprising at least one cure site; and

microdiamond particles having an average particle size of greater than 0.10 micron to about 100 microns.

[0017b] In another aspect of the present disclosure, there is provided a cured fluorine-containing elastomer formed by curing the curable fluorine-containing composition disclosed herein.

[0017c] In a further aspect of the present disclosure, there is provided a molded article formed by heat curing and shaping a composition disclosed herein.

[0017d] In another aspect of the present disclosure, there is provided a method for forming a fluoroelastomeric article with reduced particulation, comprising:

preparing a curable fluorine-containing elastomer composition comprising at least one curable fluoropolymer comprising at least one fluorinated monomer, and at least one fluorine-containing cure site monomer comprising at least one cure site;

adding into the curable fluorine-containing elastomer composition microdiamond particles having an average particle size of greater than 0.10 microns to about 100 microns; and

curing the curable fluorine-containing elastomer composition to form the fluoroelastomeric article, wherein the fluoroelastomeric article has reduced particulation in comparison to a second fluoroelastomeric article having the same fluorine-containing elastomer composition but that does not include the microdiamond particles, when the fluoroelastomeric article and the second fluoroelastomeric article are exposed to at least one of a fluorine-based plasma, an oxygen-based plasma, a hydrogen-based plasma, and combinations thereof.

[0017e] In a further aspect of the present disclosure, there is provided a method of forming an fluoroelastomeric article having reduced compression set, comprising:

preparing a curable fluorine-containing elastomer composition comprising at least one first curable fluoropolymer comprising at least one fluorinated monomer, and at least one fluorine-containing cure site monomer comprising at least one cure site;

adding into the curable fluorine-containing elastomer composition microdiamond particles having an average particle size of greater than 0.10 microns to 100 microns;

and curing the curable fluorine-containing elastomer composition to form the fluoroelastomeric article, wherein the fluoroelastomeric article has a compression set value

at 250°C/70 hours/25% deflection that is reduced in comparison to an second fluoroelastomeric article formed of the same curable fluorine-containing elastomer composition, but that does not include the microdiamond particles.

[0017f] In another aspect of the present disclosure, there is provided a method of forming an fluoroelastomeric article having a reduced sticking force, comprising:

preparing a curable fluorine-containing elastomer composition comprising at least one first curable fluoropolymer comprising at least one fluorinated monomer, and at least one fluorine-containing cure site monomer comprising at least one cure site;

adding into the curable fluorine-containing elastomer composition microdiamond particles having an average particle size of greater than 0.10 microns to 100 microns;

and curing the curable fluorine-containing elastomer composition to form the fluoroelastomeric article, wherein the fluoroelastomeric article has a sticking force that is reduced in comparison to a second fluoroelastomeric article formed of the same curable fluorine-containing elastomer composition as the curable fluorine-containing elastomer, but that does not include the microdiamond particles.

[0017g] In a further aspect of the present disclosure, there is provided a method for forming a fluoroelastomeric article with reduced particulation, comprising:

preparing a curable fluorine-containing elastomer composition comprising at least one curable fluoropolymer comprising at least one fluorinated monomer, and at least one fluorine-containing cure site monomer comprising at least one cure site; and at least one curative;

adding into the curable fluorine-containing elastomer composition microdiamond particles having an average particle size of greater than 0.10 microns to about 100 microns; and

curing the curable fluorine-containing elastomer composition to form the fluoroelastomeric article, wherein the fluoroelastomeric article is capable of being used in service temperatures of at least about 350°C.

[0018] In one example, the microdiamond particles may have an average particle size of greater than 0.1 micron to about 10 microns, or may have an average particle size of about greater than 0.1 micron to about 5 microns. The average particle size of the microdiamonds may also be about 0.20 micron to about 2 microns, or may be about 0.25 micron to about 1 micron. In further examples, the microdiamond particles may have an average particle size of about 0.25 micron to about 0.5 micron. The microdiamond particles may have a shape selected from spherical particles, fibers or flasks. The microdiamond particles may be natural and/or synthetic microdiamond particles. The particles may be present in an agglomerated or aggregate form.

[0019] In one example, the composition comprises about 0.1 to about 100 parts of microdiamond particles per 100 parts by weight of the at least one curable fluoropolymer, and preferably comprises about 1 to about 50 parts of microdiamond particles per 100 parts by weight of the at least one curable fluoropolymer. More preferably, the composition comprises about 2 parts to about 20 parts per 100 parts by weight of the at least one curable fluoropolymer.

[0020] The at least one curable fluoropolymer may be a curable perfluoropolymer, wherein the at least one fluorinated monomer is tetrafluoroethylene and the perfluoropolymer may further comprise a perfluoroalkylvinyl ether monomer, and the at least one fluorine-containing cure site monomer may be a perfluorinated cure site monomer.

[0021] In another example, the at least one curable fluoropolymer may be a curable perfluoropolymer, the at least one fluorinated monomer may be tetrafluoroethylene, the curable perfluoropolymer may further comprise a perfluoroalkylvinyl ether monomer, and the curable perfluoropolymer may comprise fluoroplastic particles therein.

[0022] In each of the examples of the composition noted above, the composition may also comprise at least one curative that may be incorporated a curative into the fluorine-containing elastomer composition before curing the composition. In one example, the at least one curative may be a peroxide cure system.

[0023] The curable fluoropolymer may also be a first perfluoropolymer, wherein the at least one fluorinated monomer is tetrafluoroethylene and the perfluoropolymer further comprises a perfluoroalkylvinyl ether monomer, and wherein there are at least two of the fluorine-containing cure site monomers, each having at least one cure site and the composition includes two or more curatives, one of which may be a peroxide cure system. In such an example, the curable fluorine-containing elastomer composition may

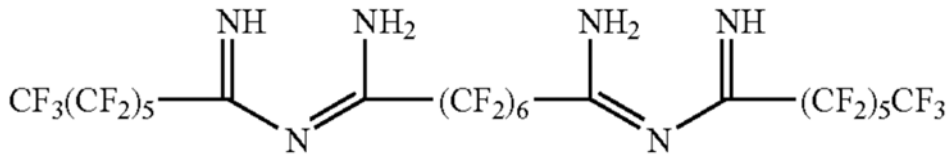
comprise a blend of such a curable perfluoropolymer with a second curable perfluoropolymer comprising tetrafluoroethylene, a second perfluoroalkylvinyl ether monomer and a perfluorinated cure site monomer, and wherein the second perfluoropolymer comprises fluoroplastic particles therein, and may also comprise at least two curatives, one of which may be a peroxide cure system.

[0024] In such an blended fluoropolymer example, a range of a ratio of a weight percent of first curable perfluoropolymer to a weight of the second curable perfluoropolymer may be about 5:95 to about 95:5, about 20:80 to about 80:20, about 40:60 to about 60:40 or about 50:50.

[0025] Also in such an example, the at least two cure site monomers of the first curable perfluoropolymer may each be present in an amount of about 0.1 to about 10 mole percent in the first curable perfluoropolymer and the at least one cure site monomer of the second curable perfluoropolymer may be present in an amount of about 0.1 to about 10 mole percent in the second curable perfluoropolymer. Further, the cure sites in at least two cure site monomers in the first curable perfluoropolymer may be nitrogen-containing cure sites. In such a case, the first curable perfluoropolymer may comprise a first cure site monomer comprising a primary cyano cure site and a second cure site monomer comprising a secondary cyano cure site.

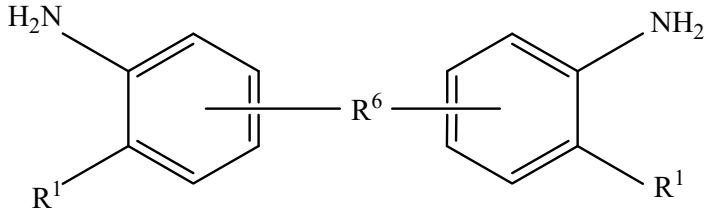
[0026] In the blended example, the at least one cure site in each of the at least two cure site monomers in the first curable perfluoropolymer may be selected from the group consisting of cyano, carboxyl, carbonyl, alkoxycarbonyl, and combinations thereof.

[0027] In the method noted above, the method may also comprise incorporating at least one curative into the fluorine-containing elastomer composition before curing the composition, and in a preferred example including at least two curatives. Further, the at least two curatives may be present in the blended composition in a total amount of about 0.2 to about 10 parts by weight per 100 parts by weight of the curable perfluoropolymers in the composition. In such an example further, each of the at least two curatives may be present in the composition in an amount of about 0.1 part to about 6 parts by weight per 100 parts by weight of the curable perfluoropolymers. In a further blended example, the at least two curatives may comprise a first curative that is present in the composition in an amount of about 0.5 part to about 4 parts by weight per 100 parts by weight of the curable perfluoropolymers, and a second curative that is present in the composition in an amount of about 0.3 part to about 2 parts by weight per 100 parts by weight of the curable perfluoropolymers. In one example, the first curative is



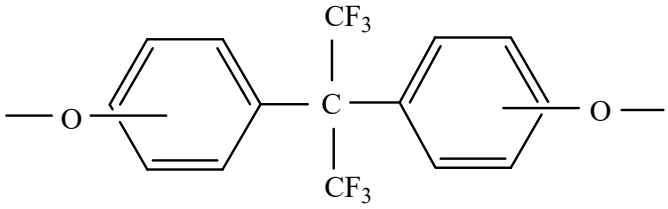
(XII)

and the second curative is



(VIII)

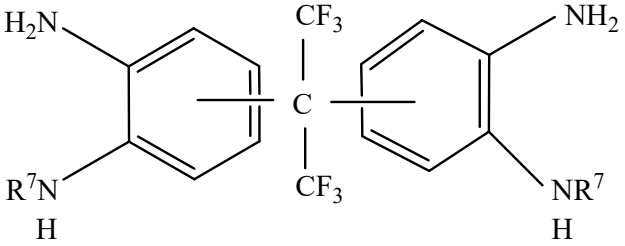
wherein each R^1 is independently $-NH_2$, $-NHR_2$, -OH or -SH; R^2 is a monovalent organic group; and wherein R^6 is $-SO_2$, -O-, -CO-, an alkylene group of 1 to about 6 carbon atoms, a perfluoroalkylene group of 1 to about 10 carbon atoms, a single bond or a group as shown in Formula (IX):



(IX)

.

[0028] In a further example, the second curative is a compound according to formula (X):



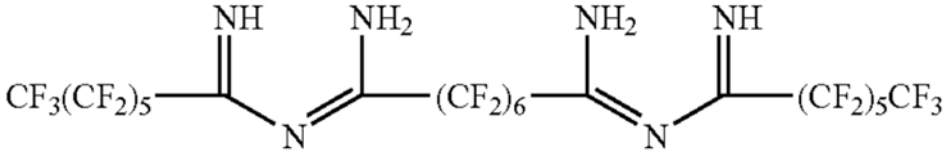
(X)

wherein R^7 is independently selected from hydrogen, an alkyl group of 1 to about 10 carbon atoms; a partially fluorinated or perfluorinated alkyl group of 1 to 10 carbon atoms; a phenyl group; a benzyl group; or a fluorinated or partially fluorinated phenyl group; a fluorinated or partially fluorinated benzyl group; or a phenyl or an alkyl group having a function group or groups that is a lower alkyl or perfluoroalkyl group.

[0029] In another preferred example, the second curative may be bisaminophenol or a salt thereof.

[0030] The second curable perfluoropolymer may also comprise a cure site monomer having a cure site selected from the group consisting of halogen, nitrogen-containing groups, carboxyl, alkoxycarbonyl and combinations thereof.

[0031] In another preferred example, at least two curatives are selected from the group consisting of:



(XII),

bisaminophenol and combinations thereof.

[0032] In a further preferred example, he first curative may be a compound according to claim (XII) and the second curative may be bisaminophenol.

[0033] In one example of the present disclosure of the curable fluorine-containing elastomer composition, the composition may comprise a second curable fluoropolymer comprising tetrafluoroethylene and at least one second fluorine-containing monomer, one of which is a cure site monomer comprising at least one second cure site.

[0034] In such an example, the first curable fluoropolymer and/or the second curable fluoropolymer may be a perfluoropolymer, and the first curable fluoropolymer and the second curable fluoropolymer are preferably different.

[0035] The present disclosure further includes a cured fluorine-containing elastomer formed by curing the curable fluorine-containing compositions noted above.

[0036] The present disclosure also includes a molded article formed by heat curing and shaping a compositions noted above.

[0037] The present disclosure further includes a method for forming a fluoroelastomeric article with reduced particulation, comprising: preparing a curable fluorine-containing elastomer composition comprising at least one curable fluoropolymer comprising at least one fluorinated monomer and at least one fluorine-containing cure site monomer comprising at least one cure site; adding into the curable fluorine-containing elastomer composition microdiamond particles having an average particle size of greater than 0.10 microns to about 100 microns; and curing the curable fluorine-containing elastomer composition to form the fluoroelastomeric article, wherein the fluoroelastomeric article has reduced particulation in comparison to a second fluoroelastomeric article having the same fluorine-containing elastomer composition but that does not include the microdiamond particles, when the fluoroelastomeric article and the second fluoroelastomeric article are exposed to a

fluorine-based plasma, an oxygen-based plasma, a hydrogen-based plasma, and combinations thereof.

[0038] In such a method, the curable fluorine-containing elastomer composition may further include at least one filler and the method may further comprise adding the microdiamond particles into the fluorine-containing elastomer composition while adding the at least one filler to the at least one first curable fluoropolymer.

[0039] In the method noted above, the at least one curable fluoropolymer may be a perfluoropolymer, the fluorinated monomer may be tetrafluoroethylene, the at least one fluorine-containing cure site monomer may be a perfluorinated cure site monomer and the perfluoropolymer may further comprise a perfluoroalkyl vinyl ether.

[0040] In the method noted above, the method may also comprise incorporating a curative into the fluorine-containing elastomer composition before curing the composition.

[0041] In the method, the fluoroelastomeric article preferably also has a compression set value at 250°C/70 hours/25% deflection that is reduced in comparison to the second fluoroelastomeric article. In such an example, the curable fluorine-containing elastomer composition used to form the second fluoroelastomeric article may further comprise a carbon black filler.

[0042] In the method, the fluoroelastomeric article preferably also has a reduced sticking force in comparison to the second fluoroelastomeric article. In such an example, the curable fluorine-containing elastomer composition used to form the second fluoroelastomeric article may further comprise a carbon black filler.

[0043] In the method, the fluoroelastomeric article preferably further has improved resistance to a fluorine-based plasma, an oxygen-based plasma, a hydrogen-based plasma, and combinations thereof in comparison to the second fluoroelastomeric article.

[0044] In the method, the fluoroelastomeric article preferably further has improved physical properties in comparison to the second fluoroelastomeric article.

[0045] In the method, the compression set value of the fluoroelastomeric article at 350°C/70 hours/18% deflection is preferably also reduced in comparison to the second fluoroelastomeric article. In such an example, the curable fluorine-containing elastomer composition used to form the second fluoroelastomeric article may further comprise a carbon black filler.

[0046] The present disclosure also includes a method of forming an fluoroelastomeric article having reduced compression set, comprising: preparing a curable fluorine-containing elastomer composition comprising at least one first curable fluoropolymer comprising at least one fluorinated monomer, and at least one fluorine-containing cure site monomer

comprising at least one cure site; adding into the curable fluorine-containing elastomer composition microdiamond particles having an average particle size of greater than 0.10 microns to 100 microns; and curing the curable fluorine-containing elastomer composition to form the fluoroelastomeric article, wherein the fluoroelastomeric article has a compression set value at 250°C/70 hours/25% deflection that is reduced in comparison to an second fluoroelastomeric article formed of the same curable fluorine-containing elastomer composition, but that does not include the microdiamond particles.

[0047] In such a method the at least one curable fluoropolymer may be a perfluoropolymer, the fluorinated monomer is tetrafluoroethylene, the at least one fluorine-containing cure site monomer may be a perfluorinated cure site monomer and the perfluoropolymer may further comprise a perfluoroalkyl vinyl ether.

[0048] In the method noted above, the method may also comprise incorporating a curative into the fluorine-containing elastomer composition before curing the composition.

[0049] In the method, the fluoroelastomeric article preferably also has reduced particulation in comparison to the second fluoroelastomeric article when the fluoroelastomeric article and the second fluoroelastomeric article are exposed to a fluorine-based plasma, an oxygen-based plasma, a hydrogen-based plasma, and combinations thereof. In such an example of the method, the curable fluorine-containing elastomer composition used to form the second fluoroelastomeric article further comprises a carbon black filler.

[0050] In the method, the fluoroelastomeric article preferably also has a reduced sticking force in comparison to the second fluoroelastomeric article. In such an example, the curable fluorine-containing elastomer composition used to form the second fluoroelastomeric article may further comprise a carbon black filler.

[0051] In the method, the fluoroelastomeric article preferably also has improved resistance to a fluorine-based plasma, an oxygen-based plasma, a hydrogen-based plasma, and combinations thereof in comparison to the second fluoroelastomeric article.

[0052] In the method, the fluoroelastomeric article preferably also has improved physical properties in comparison to the second fluoroelastomeric article.

[0053] In the method, the compression set value of the fluoroelastomeric article at 350°C/70 hours/18% deflection is preferably also reduced in comparison to the second fluoroelastomeric article. In such an example of the method, the curable fluorine-containing elastomer composition used to form the second fluoroelastomeric article may further comprise a carbon black filler.

[0054] The present disclosure also includes a method of forming an fluoroelastomeric article having a reduced sticking force, comprising: preparing a curable fluorine-containing elastomer composition comprising at least one first curable fluoropolymer comprising at least one fluorinated monomer, and at least one fluorine-containing cure site monomer comprising at least one cure site; adding into the curable fluorine-containing elastomer composition microdiamond particles having an average particle size of greater than 0.10 microns to 100 microns; and curing the curable fluorine-containing elastomer composition to form the fluoroelastomeric article, wherein the fluoroelastomeric article has a sticking force that is reduced in comparison to a second fluoroelastomeric article formed of the same curable fluorine-containing elastomer composition as the curable fluorine-containing elastomer, but that does not include the microdiamond particles.

[0055] In the method, the at least one curable fluoropolymer may be a perfluoropolymer, the fluorinated monomer may be tetrafluoroethylene, the at least one fluorine-containing cure site monomer may be a perfluorinated cure site monomer and the perfluoropolymer may further comprises a perfluoroalkyl vinyl ether.

[0056] In the method noted above, the method may also comprise incorporating a curative into the fluorine-containing elastomer composition before curing the composition.

[0057] In the method, the fluoroelastomeric article preferably also has a compression set value at 250°C/70 hours/25% deflection that is reduced in comparison to the second fluoroelastomeric article. In such an example, the curable fluorine-containing elastomer composition used to form the second fluoroelastomeric article may further comprise a carbon black filler.

[0058] In the method, the fluoroelastomeric article preferably also has reduced particulation in comparison to the second fluoroelastomeric article when the fluoroelastomeric article and the second fluoroelastomeric article are exposed to a fluorine-based plasma, an oxygen-based plasma, a hydrogen-based plasma, and combinations thereof. In such an example of the method, the curable fluorine-containing elastomer composition used to form the second fluoroelastomeric article may further comprise a carbon black filler.

[0059] In the method, the fluoroelastomeric article preferably also has improved resistance to a fluorine-based plasma, an oxygen-based plasma, a hydrogen-based plasma, and combinations thereof in comparison to the second fluoroelastomeric article.

[0060] In the method, the fluoroelastomeric article preferably also has improved physical properties in comparison to the second fluoroelastomeric article.

[0061] In the method, the compression set value of the fluoroelastomeric article at 350°C/70 hours/18% deflection is preferably reduced in comparison to the second fluoroelastomeric

article. In such an example, the curable fluorine-containing elastomer composition used to form the second fluoroelastomeric article may further comprise a carbon black filler.

[0062] The present disclosure further includes a method for forming a fluoroelastomeric article with reduced particulation, comprising: preparing a curable fluorine-containing elastomer composition comprising at least one curable fluoropolymer comprising at least one fluorinated monomer, and at least one fluorine-containing cure site monomer comprising at least one cure site; adding into the curable fluorine-containing elastomer composition microdiamond particles having an average particle size of greater than 0.10 microns to about 100 microns; and curing the curable fluorine-containing elastomer composition to form the fluoroelastomeric article, wherein the fluoroelastomeric article is capable of being used in service temperatures of at least about 350°C.

[0063] In the method noted above, the method may also comprise incorporating a curative into the fluorine-containing elastomer composition before curing the composition.

[0064] In the method, the fluoroelastomeric article may be a perfluoroelastomeric article. In the method, the fluoroelastomeric article preferably has a compression set value at 350°C/70 hours/18% deflection that is reduced in comparison to a second fluoroelastomeric article formed of the same curable fluorine-containing elastomer composition, but that does not include the microdiamond particles. In such an example, the curable fluorine-containing elastomer composition used to form the second fluoroelastomeric article further comprises a carbon black filler.

DETAILED DESCRIPTION OF THE INVENTION

[0065] As noted in the Background Section, the prior art indicates that use of diamond nanoparticles with sizes greater than 0.1 micron would cause high defect rates which are typically associated with particulation. Applicants have surprisingly found that use of particles of microdiamond larger than 0.1 micron provide lower particulation than known competitive, plasma-resistant compositions. Further, in preferred embodiments herein, such fillers unexpectedly also lead to reduced compression set values, even at high temperatures, reduced sticking force, enhanced resistance to fluorine-based plasma, oxygen-based plasma, hydrogen-based plasma, and combinations thereof, and improved physical properties, and in further preferred embodiments allows for use in high service temperatures with reduction of compression set.

The curable fluorine-containing elastomer composition includes at least one curable fluoropolymer comprising tetrafluoroethylene, and at least one fluorine-containing