



US 20070116976A1

(19) **United States**

(12) **Patent Application Publication** (10) **Pub. No.: US 2007/0116976 A1**

Tan et al. (43) **Pub. Date: May 24, 2007**

(54) **NANOPARTICLE ENHANCED THERMOPLASTIC DIELECTRICS, METHODS OF MANUFACTURE THEREOF, AND ARTICLES COMPRISING THE SAME**

(76) Inventors: **Qi Tan**, Rexford, NY (US); **Yang Cao**, Niskayuna, NY (US); **Patricia Chapman Irwin**, Altamont, NY (US)

Correspondence Address:
**GENERAL ELECTRIC COMPANY
GLOBAL RESEARCH
PATENT DOCKET RM. BLDG. K1-4A59
NISKAYUNA, NY 12309 (US)**

(21) Appl. No.: **11/286,097**

(22) Filed: **Nov. 23, 2005**

Publication Classification

(51) **Int. Cl.**
B22F 5/00 (2006.01)

(52) **U.S. Cl.** **428/546; 977/700**

(57) **ABSTRACT**

Disclosed herein is a nanocomposite composition comprising a polymeric composition; wherein the polymeric composition comprises thermoplastic polymers; and nanoparticles, wherein the nanoparticles have an average largest dimension of less than or equal to about 500 nanometers; and wherein the nanocomposite composition has a higher dielectric constant than the polymeric composition without the nanoparticles. Disclosed herein too is a method comprising blending a thermoplastic polymer with nanoparticles to form a nanocomposite composition; wherein the nanoparticles have an average largest dimension of less than or equal to about 500 nanometers; and molding the nanocomposite composition. Disclosed herein too is a method comprising blending a thermoplastic polymer with nanoparticles to form a nanocomposite composition; wherein the nanoparticles have an average largest dimension of less than or equal to about 500 nanometers; and casting the nanocomposite composition on a substrate.

FIG. 1

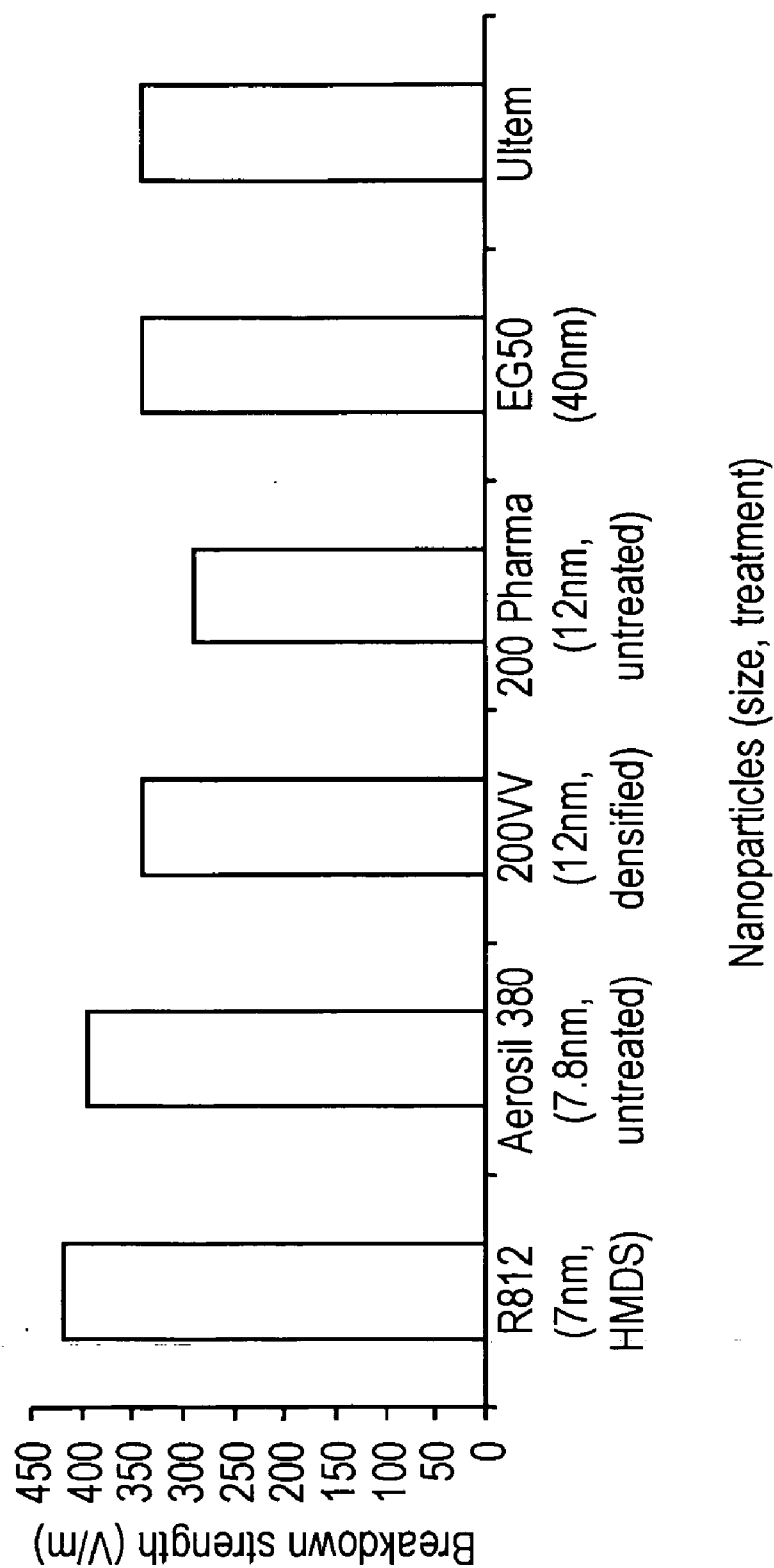


FIG. 2

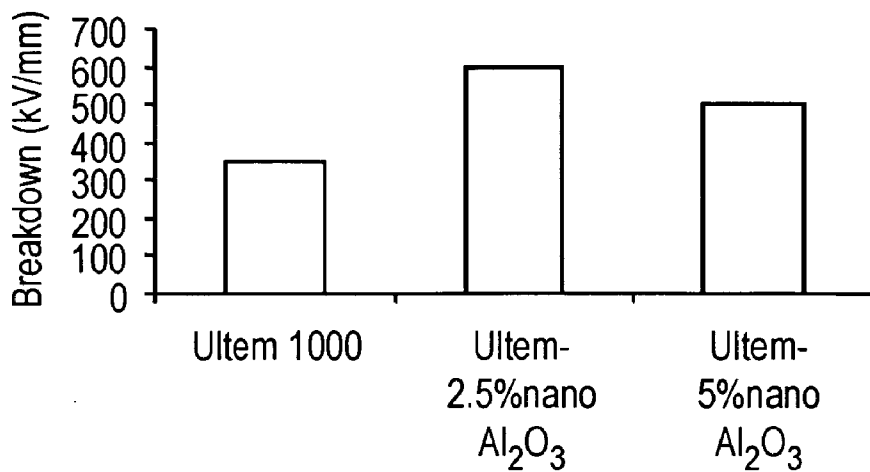


FIG. 3

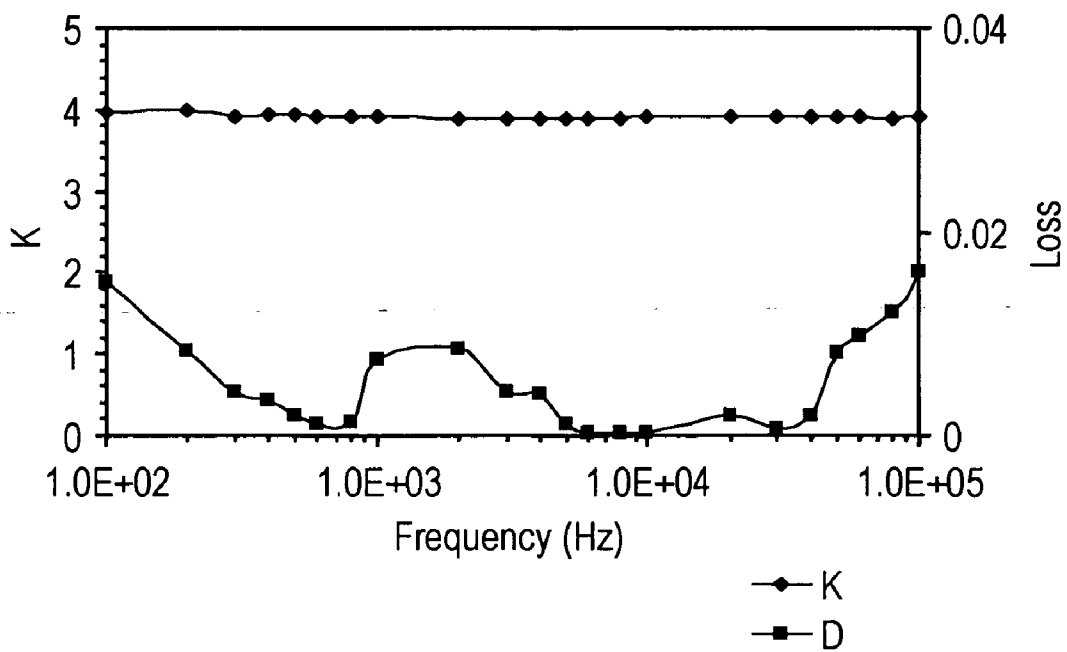
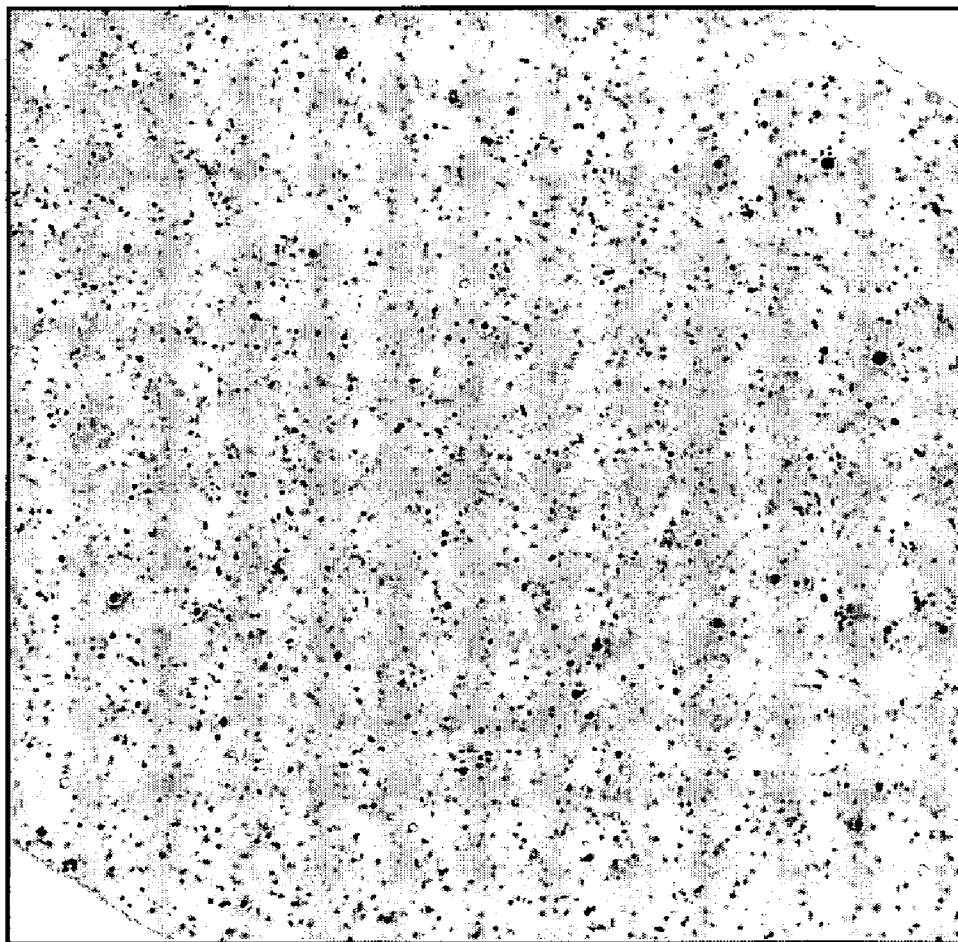


FIG. 4



Schum05-1611A.002.tif

2 microns

ULTEM film 5 Al₂O₃

HV = 100kV

Print Mag: 11400x @7 in.

Direct Mag: 5800x

Microscopist: E. Olsen

GE GLOBAL RESEARCH

NANOPARTICLE ENHANCED THERMOPLASTIC DIELECTRICS, METHODS OF MANUFACTURE THEREOF, AND ARTICLES COMPRISING THE SAME

BACKGROUND

[0001] This disclosure relates to nanoparticle enhanced thermoplastic dielectrics, methods of manufacture thereof, and articles comprising the same.

[0002] It is desirable in commercial applications, such as spark plug caps for automobiles, to have a high breakdown voltage and corona resistance. Corona resistance is achieved by using large volume fractions of fillers. This reduces mechanical properties such as impact strength and ductility in the spark plug cap.

[0003] It is also desirable for energy storage devices, such as DC-link capacitors, that are utilized in high energy density power conversion applications to withstand the high voltage and high temperature environments of electrical devices such as motors and generators. It is therefore desirable for such storage devices to display a high breakdown voltage and corona resistance.

[0004] In the electronics industry as well as in the automotive industry, there is a need for new polymeric compositions with high dielectric constants and high breakdown strength as well as good mechanical strength. It is therefore desirable to have a composition that combines improved impact strength with effective corona resistance.

SUMMARY

[0005] Disclosed herein is a nanocomposite composition comprising a polymeric composition; wherein the polymeric composition comprises thermoplastic polymers; and nanoparticles, wherein the nanoparticles have an average largest dimension of less than or equal to about 500 nanometers; and wherein the nanocomposite composition has a higher dielectric constant than the polymeric composition without the nanoparticles.

[0006] Disclosed herein too is a nanocomposite composition comprising a polymeric composition; wherein the polymeric composition comprises polyetherimide, fluorenyl polyester (FPE), polyvinylidene fluoride, polyvinylidene fluoride-trifluoroethylene, polyvinylidene-tetrafluoroethylene copolymers, polyvinylidene trifluoroethylene hexafluoropropylene copolymers, polyvinylidene hexafluoropropylene copolymers, epoxy, polypropylene, polyester, polyimide, polyarylate, polyphenylsulfone, polystyrene, polyethersulfone, polyamideimide, polyurethane, polycarbonate, polyetheretherketone, silicone, or a combination comprising at least one of the foregoing; and nanoparticles of a size and an amount effective to produce an impact strength of greater than or equal to about 5 kilojoules per square meter, a Class A surface finish and a breakdown strength of at least 300 V/micrometer.

[0007] Disclosed herein too is a method comprising blending a thermoplastic polymer with nanoparticles to form a nanocomposite composition; wherein the nanoparticles have an average largest dimension of less than or equal to about 500 nanometers; and molding the nanocomposite composition.

[0008] Disclosed herein too is a method comprising blending a thermoplastic polymer with nanoparticles to form a nanocomposite composition; wherein the nanoparticles have an average largest dimension of less than or equal to about 500 nanometers; and casting the nanocomposite composition on a substrate.

DESCRIPTION OF FIGURES

[0009] FIG. 1 represents a bar graph of the change in breakdown strength of a nanocomposite composition when various silica nanoparticles were incorporated into a polymeric composition;

[0010] FIG. 2 represents a bar graph of the change in breakdown strength of a nanocomposite composition when various weight percents of alumina nanoparticles were incorporated into a polymeric composition;

[0011] FIG. 3 represents a graph of the increase in dielectric constant when alumina nanoparticles were incorporated into a polymeric composition; and

[0012] FIG. 4 is a scanning electron micrograph illustrating the dispersion of alumina nanoparticles within a polymeric composition.

DETAILED DESCRIPTION

[0013] It is to be noted that the terms “first,” “second,” and the like as used herein do not denote any order, quantity, or importance, but rather are used to distinguish one element from another. The terms “a” and “an” do not denote a limitation of quantity, but rather denote the presence of at least one of the referenced item. The modifier “about” used in connection with a quantity is inclusive of the stated value and has the meaning dictated by the context (e.g., includes the degree of error associated with measurement of the particular quantity). It is to be noted that all ranges disclosed within this specification are inclusive and are independently combinable.

[0014] Disclosed herein are nanocomposite compositions comprising a polymeric composition and nanoparticles. In one embodiment, the nanoparticles are inorganic oxides. The nanocomposite composition has a dielectric constant, breakdown voltage, energy density, corona resistance, and mechanical properties such as impact strength, tensile strength and ductility that are superior to a composition without the nanoparticles. The nanocomposite composition also has impact strength that is superior to a composition that comprises a polymeric composition and particles whose sizes are in the micrometer range instead of in the nanometer range. In one embodiment, the nanocomposite composition has a dielectric constant that is greater than that of the polymeric composition alone or greater than the composition that comprises a polymeric composition and particles whose sizes are in the micrometer range. The nanocomposite composition has a breakdown voltage of greater than or equal to about 300 V/micrometer. The nanocomposite composition advantageously has an energy density of about 1 J/cm³ to about 10 J/cm³. The nanocomposite composition has improved properties over the polymeric compositions without the nanoparticles. These improved properties include a higher dielectric constant, improved breakdown strength and corona resistance, improved impact strength, tensile strength and ductility, as well as improved ease of processing and a Class A surface finish.

[0015] The polymeric composition comprises thermoplastic polymers. In one embodiment, the polymeric composition comprises thermoplastic polymers that have a high glass transition temperature of greater than or equal to about 100° C. In one embodiment, the inorganic oxide nanoparticles comprise silica. In another embodiment, the inorganic oxide nanoparticles comprise metal oxides such as alumina, ceria, titanate, zirconia, niobium pentoxide, tantalum pentoxide, or the like, or a combination comprising at least one of the foregoing. In one embodiment, the inorganic oxide nanoparticles have particle sizes of less than or equal to about ten nanometers. In another embodiment, the inorganic oxide nanoparticles have particle sizes of greater than or equal to about ten nanometers. In another embodiment, the inorganic oxide nanoparticles are surface treated to enhance dispersion within the polymeric composition. For example, the surface treatment comprises coating the inorganic oxide nanoparticles with an organic material such as a silane. In one embodiment, the inorganic oxide nanoparticles and the polymeric composition are combined with one another by blending, such as solution blending, melt blending, or the like, or a combination comprising at least one of the foregoing.

[0016] The polymeric composition used in the nanocomposite compositions may be selected from a wide variety of thermoplastic polymers blends of thermoplastic polymers, or blends of thermoplastic polymers with thermosetting polymers. The polymeric composition can comprise a homopolymer, a copolymer such as a star block copolymer, a graft copolymer, an alternating block copolymer or a random copolymer, ionomer, dendrimer, or a combination comprising at least one of the foregoing. The polymeric composition may also be a blend of polymers, copolymers, terpolymers, or the like, or a combination comprising at least one of the foregoing.

[0017] Examples of thermoplastic polymers that can be used in the polymeric composition include polyacetals, polyacrylics, polycarbonates, polyalkyds, polystyrenes, polyolefins, polyesters, polyamides, polyaramides, polyamideimides, polyarylates, polyurethanes, epoxies, phenolics, silicones, polyarylsulfones, polyethersulfones, polyphenylene sulfides, polysulfones, polyimides, polyetherimides, polytetrafluoroethylenes, polyetherketones, polyether etherketones, polyether ketone ketones, polybenzoxazoles, polyoxadiazoles, polybenzothiazinophenothiazines, polybenzothiazoles, polypyrazinoquinoxalines, polypyromellitimides, polyquinoxalines, polybenzimidazoles, polyoxindoles, polyoxoisindolines, polydioxoisindolines, polytriazines, polypyridazines, polypiperazines, polypyridines, polypiperidines, polytriazoles, polypyrazoles, polycarbonates, polyoxabicyclononanes, polydibenzofurans, polyphthalides, polyacetals, polyanhydrides, polyvinyl ethers, polyvinyl thioethers, polyvinyl alcohols, polyvinyl ketones, polyvinyl halides, polyvinyl nitriles, polyvinyl esters, polysulfonates, polysulfides, polythioesters, polysulfones, polysulfonamides, polyureas, polyphosphazenes, polysilazanes, polypropylenes, polyethylenes, polyethylene terephthalates, polyvinylidene fluorides, polysiloxanes, or the like, or a combination comprising at least one of the foregoing thermoplastic polymers.

[0018] Exemplary thermoplastic polymers include polyetherimide, fluorenyl polyester (FPE), polyvinylidene fluoride, polyvinylidene fluoride-trifluoroethylene P(VDF-

TrFE), polyvinylidene-tetrafluoroethylene copolymers P(VDF-TFE), polyvinylidene trifluoroethylene hexafluoropropylene copolymers P(VDF-TFE-HFE) and polyvinylidene hexafluoropropylene copolymers P(VDF-HFE), epoxy, polypropylene, polyester, polyimide, polyarylate, polyphenylsulfone, polystyrene, polyethersulfone, polyamideimide, polyurethane, polycarbonate, polyetheretherketone, silicone, or the like, or a combination comprising at least one of the foregoing. Exemplary polymers are ULTEM®, a polyetherimide, or SILTEM®, a polyetherimide-polysiloxane copolymer, both commercially available from General Electric Plastics (GE Plastics).

[0019] Examples of blends of thermoplastic polymers include acrylonitrile-butadiene-styrene/nylon, polycarbonate/acrylonitrile-butadiene-styrene, polyphenylene ether/polystyrene, polyphenylene ether/polyamide, polycarbonate/polyester, polyphenylene ether/polyolefin, or the like, or a combination comprising at least one of the foregoing.

[0020] In another embodiment, thermosetting polymers can be blended with the thermoplastic polymers for use in the nanocomposite composition. Examples of thermosetting polymers are resins of epoxy/amine, epoxy/anhydride, isocyanate/amine, isocyanate/alcohol, unsaturated polyesters, vinyl esters, unsaturated polyester and vinyl ester blends, unsaturated polyester/urethane hybrid resins, polyurethaneureas, reactive dicyclopentadiene (DCPD) resin, reactive polyamides, or the like, or a combination comprising at least one of the foregoing. An exemplary thermosetting polymer is thermosetting NORYL® (TSN NORYL®), a polyphenylene ether, commercially available from GE Plastics.

[0021] In one embodiment, suitable thermosetting polymers include thermosetting polymers that can be made from an energy activatable thermosetting pre-polymer composition. Examples include polyurethanes such as urethane polyesters, silicone polymers, phenolic polymers, amino polymers, epoxy polymers, bismaleimides, polyimides, and furan polymers. The energy activatable thermosetting pre-polymer component can comprise a polymer precursor and a curing agent. The polymer precursor can be heat activatable, eliminating the need for a catalyst. The curing agent selected will not only determine the type of energy source needed to form the thermosetting polymer, but may also influence the resulting properties of the thermosetting polymer. Examples of curing agents include aliphatic amines, aromatic amines, acid anhydrides, or the like, or a combination comprising at least one of the foregoing. The energy activatable thermosetting pre-polymer composition may include a solvent or processing aid to lower the viscosity of the composition for ease of extrusion including higher throughputs and lower temperatures. The solvent could help retard the crosslinking reaction and could partially or totally evaporate during or after polymerization.

[0022] As noted above, it is desirable for the thermoplastic polymers to have a glass transition temperature of greater than or equal to about 150° C. In one embodiment, it is desirable for the thermoplastic polymers to have a glass transition temperature of greater than or equal to about 175° C. In another embodiment, it is desirable for the thermoplastic polymers to have a glass transition temperature of greater than or equal to about 200° C. In yet another embodiment, it is desirable for the thermoplastic polymers to have a glass transition temperature of greater than or equal

to about 225° C. In yet another embodiment, it is desirable for the thermoplastic polymers to have a glass transition temperature of greater than or equal to about 250° C.

[0023] In one embodiment, the polymeric composition is used in an amount of about 5 to about 99.999 wt % of the total weight of the nanocomposite composition. In another embodiment, the polymeric composition is used in an amount of about 10 wt % to about 99.99 wt % of the total weight of the nanocomposite composition. In another embodiment, the polymeric composition is used in an amount of about 30 wt % to about 99.5 wt % of the total weight of the nanocomposite composition. In another embodiment, the polymeric composition is used in an amount of about 50 wt % to about 99.3 wt % of the total weight of the nanocomposite composition.

[0024] As noted above, the nanoparticles comprise inorganic oxides. Examples of inorganic oxides include calcium oxide, silicon dioxide, or the like, or a combination comprising at least one of the foregoing. In one embodiment, the nanoparticles comprise metal oxides such as metal oxides of alkali earth metals, alkaline earth metals, transition metals, metalloids, poor metals, or the like, or a combination comprising at least one of the foregoing. In another embodiment, the nanosized metal oxides comprise perovskites and perovskite derivatives such as barium titanate, barium strontium titanate, and strontium-doped lanthanum manganate. In another embodiment, the nanosized metal oxides comprise a composition with a high dielectric constant such as calcium copper titanate ($\text{CaCu}_3\text{Ti}_4\text{O}_{12}$), cadmium copper titanate ($\text{CdCu}_3\text{Ti}_4\text{O}_{12}$), $\text{Ca}_{1-x}\text{La}_x\text{MnO}_3$, and (Li, Ti) doped NiO, or the like, or a combination comprising at least one of the foregoing. Suitable examples of metal oxides are, cerium oxide, magnesium oxide, titanium oxide, zinc oxide, silicon oxide (e.g., silica and/or fumed silica), copper oxide, aluminum oxide (e.g., alumina and/or fumed alumina), or the like, or a combination comprising at least one of the foregoing metal oxides.

[0025] Examples of nanoparticles comprising inorganic oxides include aluminum oxide, calcium oxide, cerium oxide, copper oxide, magnesium oxide, niobium oxide, silicon oxide, tantalum oxide, titanium oxide, yttrium oxide, zinc oxide, and zirconium oxide.

[0026] Commercially available examples of nanosized inorganic oxides are NANOACTIVE™ calcium oxide, NANOACTIVE™ calcium oxide plus, NANOACTIVE™ cerium oxide, NANOACTIVE™ magnesium oxide, NANOACTIVE™ magnesium oxide plus, NANOACTIVE™ titanium oxide, NANOACTIVE™ zinc oxide, NANOACTIVE™ silicon oxide, NANOACTIVE™ copper oxide, NANOACTIVE™ aluminum oxide, NANOACTIVE™ aluminum oxide plus, all commercially available from NanoScale Materials Incorporated.

[0027] As noted above, the nanoparticles are particles that have one dimension in the nanometer range (10^{-9} meter range). In one embodiment, the nanoparticles can have particle sizes of less than or equal to about ten nanometers. In another embodiment, the nanoparticles have particle sizes of greater than or equal to about ten nanometers. In one embodiment, the nanoparticles can be surface treated to facilitate bonding with the polymeric composition. In another embodiment, the nanoparticles having particle sizes of less than or equal to about ten nanometers are not surface

treated. It is generally desirable for the nanoparticles having particle sizes greater than or equal to about ten nanometers to be surface treated. In one embodiment, the surface treatment comprises coating the nanoparticles with a silane-coupling agent. Examples of suitable silane-coupling agents include tetramethylchlorosilane, hexadimethylenedisilazane, gamma-aminopropoxysilane, or the like, or a combination comprising at least one of the foregoing silane coupling agents. The silane-coupling agents generally enhance compatibility of the nanoparticles with the polymeric composition and improve dispersion of the nanoparticles within the polymeric composition.

[0028] In another embodiment, the nanoparticles can be surface treated by coating with a polymer or a monomer such as, for example, surface coating in-situ, spray drying a dispersion of nanoparticle and polymer solution, co-polymerization on the nanoparticle surface, and melt spinning followed by milling. In the case of surface coating in-situ, the nanoparticles are suspended in a solvent, such as, for example demineralized water and the suspension's pH is measured. The pH can be adjusted and stabilized with small addition of acid (e.g., acetic acid or dilute nitric acid) or base (e.g., ammonium hydroxide or dilute sodium hydroxide). The pH adjustment produces a charged state on the surface of the nanoparticle. Once a desired pH has been achieved, a coating material (for example, a polymer or other appropriate precursor) with opposite charge is introduced into the solvent. The coating material is coupled around the nanoparticle to provide a coating layer around the nanoparticle. Once the coating layer has formed, the nanoparticle is removed from the solvent by drying, filtration, centrifugation, or another method appropriate for solid-liquid separation. This technique of coating a nanoparticle with another material using surface charge can be used for a variety of nanocomposite compositions.

[0029] When a solvent is used to apply a coating, as in the in-situ surface coating method described above, the polymeric composition can also be dissolved in the solvent before or during coating, and the final nanocomposite composition formed by removing the solvent.

[0030] As noted above, the nanoparticles have at least one dimension in the nanometer range. It is generally desirable for the nanoparticles to have an average largest dimension that is less than or equal to about 500 nm. The dimension may be a diameter, edge of a face, length, or the like. The nanoparticles may have shapes whose dimensionalities are defined by integers, e.g., the nanoparticles are either 1, 2 or 3-dimensional in shape. They may also have shapes whose dimensionalities are not defined by integers (e.g., they may exist in the form of fractals). The nanoparticles may exist in the form of spheres, flakes, fibers, whiskers, or the like, or a combination comprising at least one of the foregoing forms. These nanoparticles may have cross-sectional geometries that may be circular, ellipsoidal, triangular, rectangular, polygonal, or a combination comprising at least one of the foregoing geometries. The nanoparticles, as commercially available, may exist in the form of aggregates or agglomerates prior to incorporation into the polymeric composition or even after incorporation into the polymeric composition. An aggregate comprises more than one nanoparticle in physical contact with one another, while an agglomerate comprises more than one aggregate in physical contact with one another.

[0031] Regardless of the exact size, shape and composition of the nanoparticles, they may be dispersed into the polymeric composition at loadings of about 0.0001 to about 50 wt % of the total weight of the nanocomposite composition when desired. In one embodiment, the nanoparticles are present in an amount of greater than or equal to about 1 wt % of the total weight of the nanocomposite composition. In another embodiment, the nanoparticles are present in an amount of greater than or equal to about 1.5 wt % of the total weight of the nanocomposite composition. In another embodiment, the nanoparticles are present in an amount of greater than or equal to about 2 wt % of the total weight of the nanocomposite composition. In one embodiment, the nanoparticles are present in an amount of less than or equal to 40 wt % of the total weight of the nanocomposite composition. In another embodiment, the nanoparticles are present in an amount of less than or equal to about 30 wt % of the total weight of the nanocomposite composition. In another embodiment, the nanoparticles are present in an amount of less than or equal to about 25 wt % of the total weight of the nanocomposite composition.

[0032] The polymeric composition together with the nanoparticles and any other optionally desired fillers may generally be processed in several different ways such as, but not limited to melt blending, solution blending, or the like, or a combination comprising at least one of the foregoing methods of blending. Melt blending of the composition involves the use of shear force, extensional force, compressive force, ultrasonic energy, electromagnetic energy, thermal energy or a combination comprising at least one of the foregoing forces or forms of energy and is conducted in processing equipment wherein the aforementioned forces are exerted by a single screw, multiple screws, intermeshing co-rotating or counter rotating screws, non-intermeshing co-rotating or counter rotating screws, reciprocating screws, screws with pins, barrels with pins, rolls, rams, helical rotors, or a combination comprising at least one of the foregoing.

[0033] Melt blending involving the aforementioned forces may be conducted in machines such as, but not limited to, single or multiple screw extruders, Buss kneader, Henschel, helicones, Ross mixer, Banbury, roll mills, molding machines such as injection molding machines, vacuum forming machines, blow molding machine, or then like, or a combination comprising at least one of the foregoing machines. It is generally desirable during melt or solution blending of the composition to impart a specific energy of about 0.01 to about 10 kilowatt-hour/kilogram (kwhr/kg) of the composition. Within this range, a specific energy of greater than or equal to about 0.05, preferably greater than or equal to about 0.08, and more preferably greater than or equal to about 0.09 kwhr/kg is generally desirable for blending the composition. Also desirable is an amount of specific energy less than or equal to about 9, preferably less than or equal to about 8, and more preferably less than or equal to about 7 kwhr/kg for blending the nanocomposite composition.

[0034] In one embodiment, the polymeric composition in powder form, pellet form, sheet form, or the like, may be first dry blended with the nanoparticles and other optional fillers if desired in a Henschel or a roll mill, prior to being fed into a melt blending device such as an extruder or Buss kneader. In another embodiment, the nanoparticles are introduced into the melt blending device in the form of a

masterbatch. In such a process, the masterbatch may be introduced into the melt blending device downstream of the polymeric composition.

[0035] When a masterbatch is used, the nanoparticles may be present in the masterbatch in an amount of about 1 to about 50 wt %, of the total weight of the masterbatch. In one embodiment, the nanoparticles are used in an amount of greater than or equal to about 1.5 wt % of the total weight of the masterbatch. In another embodiment, the nanoparticles are used in an amount of greater than or equal to about 2wt %, of the total weight of the masterbatch. In another embodiment, the nanoparticles are used in an amount of greater than or equal to about 2.5 wt %, of the total weight of the masterbatch. In one embodiment, the nanoparticles are used in an amount of less than or equal to about 30 wt %, of the total weight of the masterbatch. In another embodiment, the nanoparticles are used in an amount of less than or equal to about 10 wt %, of the total weight of the masterbatch. In another embodiment, the nanoparticles are used in an amount of less than or equal to about 5 wt %, of the total weight of the masterbatch. Examples of polymeric compositions that may be used in masterbatches are polypropylene, polyetherimides, polyamides, polyesters, or the like, or a combination comprising at least one of the foregoing polymeric compositions.

[0036] In another embodiment relating to the use of masterbatches in polymeric blends, it is sometimes desirable to have the masterbatch comprising a polymeric composition that is the same as the polymeric composition that forms the continuous phase of the nanocomposite composition. In yet another embodiment relating to the use of masterbatches in polymeric blends, it may be desirable to have the masterbatch comprising a polymeric composition that is different in chemistry from other the polymers that are used in the nanocomposite composition. In this case, the polymeric composition of the masterbatch will form the continuous phase in the blend.

[0037] The nanocomposite composition comprising the polymeric composition and the nanoparticles may be subject to multiple blending and forming steps if desirable. For example, the nanocomposite composition may first be extruded and formed into pellets. The pellets may then be fed into a molding machine where it may be formed into other desirable shapes. Alternatively, the nanocomposite composition emanating from a single melt blender may be formed into sheets or strands and subjected to post-extrusion processes such as annealing, uniaxial or biaxial orientation.

[0038] Solution blending may also be used to manufacture the nanocomposite composition. The solution blending may also use additional energy such as shear, compression, ultrasonic vibration, or the like to promote homogenization of the nanoparticles with the polymeric composition. In one embodiment, a polymeric composition suspended in a fluid may be introduced into an ultrasonic sonicator along with the nanoparticles. The mixture may be solution blended by sonication for a time period effective to disperse the nanoparticles within the polymeric composition. The polymeric composition along with the nanoparticles may then be dried, extruded and molded if desired. It is generally desirable for the fluid to swell the polymeric composition during the process of sonication. Swelling the polymeric composition generally improves the ability of the nanoparticles to

impregnate the polymeric composition during the solution blending process and consequently improves dispersion.

[0039] In another embodiment related to solution blending, the nanoparticles are sonicated together with polymeric composition precursors. Polymeric composition precursors are generally monomers, dimers, trimers, or the like, which can be reacted into polymeric compositions. A fluid such as a solvent may optionally be introduced into the sonicator with the nanoparticles and the polymeric composition precursor. The time period for the sonication is generally an amount effective to promote encapsulation of the nanoparticles by the polymeric composition precursor. After the encapsulation, the polymeric composition precursor is then polymerized to form a polymeric composition within which is dispersed the nanoparticles.

[0040] Suitable examples of monomers that may be used to facilitate this method of encapsulation and dispersion are those used in the synthesis of thermoplastic polymers such as, but not limited to polyacetals, polyacrylics, polycarbonates, polystyrenes, polyesters, polyamides, polyamideimides, polyarylates, polyurethanes, polyarylsulfones, polyethersulfones, polyarylene sulfides, polyvinyl chlorides, polysulfones, polyetherimides, polytetrafluoroethylenes, polyetherketones, polyether etherketones, or the like, or a combination comprising at least one of the foregoing. In one embodiment, the mixture of polymeric composition, polymeric composition precursor, fluid and/or the nanoparticles is sonicated for a period of about 1 minute to about 24 hours. In another embodiment, the mixture is sonicated for a period of greater than or equal to about 5 minutes. In another embodiment, the mixture is sonicated for a period of greater than or equal to about 10 minutes. In another embodiment, the mixture is sonicated for a period of greater than or equal to about 15 minutes. In one embodiment, the mixture is sonicated for a period of less than or equal to about 15 hours. In another embodiment, the mixture is sonicated for a period of less than or equal to about 10 hours. In another embodiment, the mixture is sonicated for a period of and more preferably less than or equal to about 5 hours.

[0041] Solvents may optionally be used in the solution blending of the nanocomposite composition. The solvent may be used as a viscosity modifier, or to facilitate the dispersion and/or suspension of nanoparticles. Liquid aprotic polar solvents such as propylene carbonate, ethylene carbonate, butyrolactone, acetonitrile, benzonitrile, nitromethane, nitrobenzene, sulfolane, dimethylformamide, N-methylpyrrolidone, or the like, or a combination comprising at least one of the foregoing solvents may be used. Polar protic solvents such as water, methanol, acetonitrile, nitromethane, ethanol, propanol, isopropanol, butanol, or the like, or a combination comprising at least one of the foregoing polar protic solvents may be used. Other non-polar solvents such as benzene, toluene, methylene chloride, carbon tetrachloride, hexane, diethyl ether, tetrahydrofuran, or the like, or a combination comprising at least one of the foregoing solvents may also be used if desired. Co-solvents comprising at least one aprotic polar solvent and at least one non-polar solvent may also be used. In one embodiment, the solvent is xylene or N-methylpyrrolidone.

[0042] If a solvent is used, it may be utilized in an amount of about 1 to about 50 wt %, of the total weight of the nanocomposite composition. In one embodiment, if a sol-

vent is used, it may be utilized in an amount of about 3 to about 30 wt %, of the total weight of the nanocomposite composition. In yet another embodiment, if a solvent is used, it may be utilized in an amount of about 5 to about 20 wt %, of the total weight of the nanocomposite composition. It is generally desirable to evaporate the solvent before, during and/or after the blending of the nanocomposite composition.

[0043] After solution blending, the solution comprising the desired composition can be cast, spin cast, dip coated, spray painted, brush painted and/or electrostatically spray painted onto a desired substrate. The solution is then dried leaving behind the composition on the surface. In another embodiment, the solution comprising the desired composition may be spun, compression molded, injection molded or blow molded to form an article comprising the composition.

[0044] Blending can be assisted using various secondary species such as dispersants, binders, modifiers, detergents, and additives. Secondary species may also be added to enhance one to more of the properties of the nanocomposite composition. Blending can also be assisted by pre-coating the nanoparticles with a thin layer of the polymeric composition or with a phase that is compatible with the polymeric composition, such as, for example a silane layer.

[0045] A nanocomposite composition comprising a polymeric composition and nanoparticles has advantages over the polymeric composition alone or other commercially available compositions that comprise a polymeric composition and particles having particle sizes in the micrometer range. In one embodiment, the nanocomposite composition has a dielectric constant that is at least 50% greater than a composition comprising polymeric composition alone. In another embodiment, the nanocomposite composition has a dielectric constant that is at least 75% greater than the polymeric composition alone. In another embodiment, the nanocomposite composition has a dielectric constant that is at least 100% greater than the polymeric composition alone.

[0046] The nanocomposite composition also has a breakdown voltage that is advantageously greater than the polymeric composition alone or other commercially available compositions that comprise a polymeric composition and particles having particle sizes in the micrometer range. In one embodiment, the nanocomposite composition has a breakdown voltage that is at least 300 Volts/micrometer (V/micrometer). The breakdown is generally determined in terms of the thickness of the nanocomposite composition. In another embodiment, the nanocomposite composition has a breakdown voltage that is at least 400 V/micrometer. In another embodiment, the nanocomposite composition has a breakdown voltage that is at least 500V/micrometer.

[0047] The nanocomposite composition also has a corona resistance that is advantageously greater than the polymeric composition alone or other commercially available compositions that comprise a polymeric composition and particles having particle sizes in the micrometer range. In one embodiment, the nanocomposite composition has a corona resistance that is resistant to a current of about 1000 volts to 5000 volts applied for about 200 hours to about 2000 hours. In another embodiment, the nanocomposite composition has a corona resistance that is resistant to a current of about 1000 volts to 5000 volts applied for about 250 hours to about 1000 hours. In yet another embodiment, the nanocomposite com-

position has a corona resistance that is resistant to a current of about 1000 volts to 5000 volts applied for about 500 hours to about 900 hours.

[0048] In another embodiment, the nanocomposite composition also has an impact strength of greater than or equal to about 5 kilojoules per square meter (kJ/m^2). In another embodiment, the nanocomposite composition has an impact strength of greater than or equal to about $10 \text{ kJ}/\text{m}^2$. In another embodiment, the nanocomposite composition has an impact strength of greater than or equal to about $15 \text{ kJ}/\text{m}^2$. In another embodiment, the nanocomposite composition has an impact strength of greater than or equal to about $20 \text{ kJ}/\text{m}^2$.

[0049] In yet another embodiment, the nanocomposite composition also has a Class A surface finish when molded. Molded articles can be manufactured by injection molding, blow molding, compression molding, or the like, or a combination comprising at least one of the foregoing.

[0050] The nanocomposite composition can advantageously be used in spark plug caps, capacitors, defibrillators, or other articles.

[0051] The following examples, which are meant to be exemplary, not limiting, illustrate compositions and methods of manufacturing of some of the various embodiments of the nanocomposite compositions and the methods of manufacture described herein.

EXAMPLES

Example 1

[0052] Example 1 illustrates the effect on breakdown strength when various silica nanoparticles are incorporated into a polymeric composition. The polymeric composition is ULTEM® commercially available from General Electric Advanced Materials. The silica nanoparticles are AEROSIL® particles commercially available from Degussa. The particles ranged in size from 7 nanometers to 40 nanometers. The silica nanoparticles tested were hexamethyldisilazane (HDMZ) treated AEROSIL® R 812, untreated AEROSIL® 380, densified AEROSIL® 200 W, untreated AEROSIL® 200 Pharma, and untreated AEROSIL® EG 50.

[0053] The particle sizes are shown in the Table 1.

TABLE 1

Particle Identification	Particle size (nanometers)
hexamethyldisilazane (HDMZ) treated AEROSIL® R 812	7
untreated AEROSIL® 380	7.8
densified AEROSIL® 200 W	12
untreated AEROSIL® 200 Pharma	12
untreated AEROSIL® EG 50	40

[0054] 25 grams of ULTEM® was first dissolved in 153 grams of n-methyl pyrrolidone (NMP) solvent to form an ULTEM® solution. The silica nanoparticles were added in an amount of about 5 wt %, based on the total weight of the ULTEM® as well as the nanoparticles. The ULTEM® solution containing the nanoparticles was then cast under a clean hood. The solution was dried until films were formed. The nanocomposite composition films were subjected to breakdown strength tests by applying an electric field at a

increasing rate of 500 volts per second. The results are shown in the FIG. 1. From the FIG. 1 it may be seen that the smaller particles having a particle size of less than or equal to about 10 nanometers were found to increase the breakdown strength. Surface treated silica nanoparticles facilitate the development of a higher breakdown strength. The coarser particles do not display a tendency to increase the breakdown strength. From the FIG. 1, it may be seen that the dielectric constant can increase by an amount of about 33% by decreasing the size of the particles from micrometer sized particles to nanoparticles.

Example 2

[0055] Example 2 illustrates the effect on breakdown strength when various weight percents of alumina nanoparticles are incorporated into a polymeric composition. The alumina nanoparticles were 40 nanometers in size and incorporated into ULTEM® at 2.5 wt % and 5 wt % as detailed in the Example 1. The results are shown as a bar graph in FIG. 2. From the FIG. 2, it can be seen that the incorporation of the nanoparticles increases the dielectric strength by a factor of at least about 60%.

Example 3

[0056] Example 3 illustrates the increase in the dielectric constant when alumina nanoparticles are incorporated into a polymeric composition. The alumina nanoparticles were 40 nanometers in size and incorporated into ULTEM® at 5 wt % in a manner similar to that described in the Example 1. The results are shown as a graph in FIG. 3. Dielectric constant as a function of frequency of measurement was measured at room temperature using a HP4285A LCR dielectric spectrometer manufactured by Hewlett Packard. From the FIG. 3 it can be seen that the dielectric constant for the nanocomposite is about 4, which is 25% increase as compared to that of ULTEM®, which has a dielectric constant (K) of about 3.15.

[0057] FIG. 4 is a scanning electron micrograph of the dispersed alumina nanoparticles at 5800× magnification.

[0058] From the above examples it may be seen that the breakdown strength of the nanocomposite composition is increased by at least 50% over a polymeric composition that does not contain the nanoparticles. In one embodiment, the breakdown strength of the nanocomposite composition is increased by at least 100% over a polymeric composition that does not contain the nanoparticles. In another embodiment, the breakdown strength of the nanocomposite composition is increased by at least 150% over a polymeric composition that does not contain the nanoparticles.

[0059] In one exemplary embodiment, the nanocomposite composition can have an impact strength of greater than or equal to about $10 \text{ kJ}/\text{m}^2$, a Class A surface finish and a breakdown strength of at least 300 V/micrometer.

[0060] In another exemplary embodiment, the nanocomposite composition can have an impact strength of greater than or equal to about $10 \text{ kJ}/\text{m}^2$, a Class A surface finish and a corona resistance of about 1000 volts to 5000 volts applied for about 200 hours to about 2000 hours.

[0061] While the invention has been described with reference to exemplary embodiments, it will be understood by those skilled in the art that various changes may be made and

equivalents may be substituted for elements thereof without departing from the scope of the invention. In addition, many modifications may be made to adapt a particular situation or material to the teachings of the invention without departing from the essential scope thereof. Therefore, it is intended that the invention not be limited to the particular embodiment disclosed as the best mode contemplated for carrying out this invention, but that the invention will include all embodiments falling within the scope of the appended claims.

What is claimed is:

1. A nanocomposite composition comprising:
 - a polymeric composition; wherein the polymeric composition comprises a thermoplastic polymer; and
 - nanoparticles, wherein the nanoparticles have an average largest dimension of less than or equal to about 500 nanometers; and wherein the nanocomposite composition has a higher dielectric constant than the polymeric composition without the nanoparticles.
2. The nanocomposite composition of claim 1 wherein the nanocomposite composition has a dielectric constant that is about 50% greater than the polymeric composition without nanoparticles.
3. The nanocomposite composition of claim 1 wherein the nanocomposite composition has an energy density that is greater than the polymeric composition without the nanoparticles.
4. The nanocomposite composition of claim 1 wherein the nanocomposite composition has an energy density that is about 1 Joule/cubic centimeter to about 10 Joules/cubic centimeter.
5. The nanocomposite composition of claim 1, wherein the polymeric composition further comprises a thermosetting polymer.
6. The nanocomposite composition of claim 1, wherein the thermoplastic polymeric composition has a glass transition temperature of greater than or equal to about 100° C.
7. The nanocomposite composition of claim 1, wherein the polymeric composition comprises thermoplastic polymers, and wherein the thermoplastic polymers are polyurethanes, polyacrylics, polycarbonates polystyrenes, polyesters, polyamides, polyamideimides, polyarylates, polyarylsulfones, polyethersulfones, polyphenylene sulfides, polysulfones, polyimides, polyetherimides, polytetrafluoroethylenes, polyetherketones, polyether etherketones, polyether ketone ketones, polybenzoxazoles, polyoxadiazoles, polyacetals, polyvinyl ethers, polyvinyl thioethers, polyvinyl alcohols, polyvinyl ketones, polyvinyl halides, polyvinyl nitriles, polyvinyl esters, polysulfonates, polysulfides, polythioesters, polysulfones, polysulfonamides, polyureas, polyphosphazenes, polysilazanes, or a combination comprising at least one of the foregoing thermoplastic polymers.
8. The nanocomposite composition of claim 1, wherein nanoparticles having a particle size of greater than or equal to about 10 nanometers are treated with a silane coupling agent.
9. The nanocomposite composition of claim 1, having an energy density of about 1 Joule per cubic centimeter to about 10 Joules per cubic centimeters.
10. The nanocomposite composition of claim 1, wherein the thermoplastic polymer is a polyetherimide.

11. The nanocomposite composition of claim 1, wherein the nanoparticles comprise inorganic oxides, and wherein the inorganic oxide comprises aluminum oxide, magnesium oxide, calcium oxide, cerium oxide, copper oxide, silicon oxide, tantalum oxide, titanium oxide, niobium oxide, yttrium oxide, zinc oxide, zirconium oxide, perovskites and perovskite derivatives, barium titanate, barium strontium titanate, strontium-doped lanthanum manganate, calcium copper titanate, cadmium copper titanate, compounds having the formula $\text{Ca}_{1-x}\text{La}_x\text{MnO}_3$, lithium, titanium doped nickel oxide, or a combination comprising at least one of the foregoing inorganic oxides.

12. The nanocomposite composition of claim 1, having a breakdown strength of at least 300 V/micrometer, an energy density of about 1 Joule per cubic centimeter to about 10 Joules per cubic centimeter and a corona resistance of about 1000 volts to 5000 volts applied for about 200 hours to about 2000 hours.

13. The nanocomposite composition of claim 1, having an impact strength of greater than or equal to about 10 kilojoules per square meter, a Class A surface finish and a breakdown strength of at least 300 V/micrometer.

14. The nanocomposite composition of claim 1, having an impact strength of greater than or equal to about 10 kilojoules per square meter, a Class A surface finish and a corona resistance of about 1000 volts to 5000 volts applied for about 200 hours to about 2000 hours.

15. A nanocomposite composition comprising:

- a polymeric composition; wherein the polymeric composition comprises polyetherimide, fluorenyl polyester (FPE), polyvinylidene fluoride, polyvinylidene fluoride-trifluoroethylene, polyvinylidene-tetrafluoroethylene copolymers, polyvinylidene trifluoroethylene hexafluoropropylene copolymers, polyvinylidene hexafluoropropylene copolymers, epoxy, polypropylene, polyester, polyimide, polyarylate, polyphenylsulfone, polystyrene, polyethersulfone, polyamideimide, polyurethane, polycarbonate, polyetheretherketone, silicone; and

- nanoparticles of a size and an amount effective to produce an impact strength of greater than or equal to about 5 kilojoules per square meter, a Class A surface finish and a breakdown strength of at least 300 V/micrometer.

16. The nanocomposite composition of claim 15, having an impact strength of greater than or equal to about 10 kilojoules per square meter and a corona resistance of about 1000 volts to 5000 volts applied for about 200 hours to about 2000 hours

17. A method comprising:

- blending a thermoplastic polymer with nanoparticles to form a nanocomposite composition; wherein the nanoparticles have an average largest dimension of less than or equal to about 500 nanometers; and

- molding the nanocomposite composition.

18. The method of claim 17, wherein the blending comprises melt blending, solution blending, or a combination comprising at least one of the foregoing methods.

19. The method of claim 17, wherein the blending is conducted in a twin screw extruder.

20. An article comprising the nanocomposite composition of claim 1.

21. The article of claim 20, wherein the article is a capacitor or a component for a spark plug.

22. An article manufactured by the method of claim 17.

23. The article of claim 22, wherein the article is a capacitor or a component for a spark plug.

24. A method comprising:

blending a thermoplastic polymer with nanoparticles to form a nanocomposite composition; wherein the nano-

particles have an average largest dimension of less than or equal to about 500 nanometers; and

casting the nanocomposite composition on a substrate.

25. The method of claim 24, wherein the casting comprises spin casting, spray painting, electrostatic spray painting, dip coating, or a combination comprising at least one of the foregoing methods of casting.

26. An article manufactured by the method of claim 24.

* * * * *