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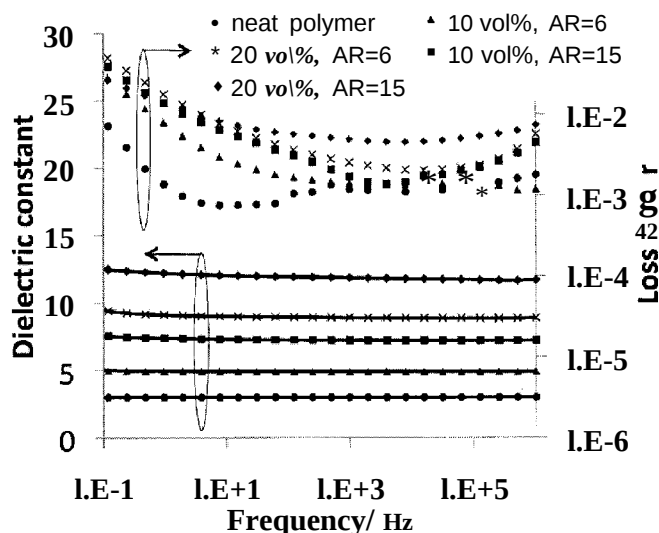
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(54) Title: HIGH DIELECTRIC CONSTANT CERAMIC FILLER PARTICLES, COMPOSITES AND METHODS FOR MAKING SAME



(a)

(57) Abstract: The present invention includes a method for preparing high dielectric constant ceramic filler particles, the method including the steps of providing a ceramic sol-gel mixed with a polymer, forming filler particles from said mixture, and heating said filler particles in order to obtain high dielectric constant perovskite structures. Also within the scope of the invention are polymer composites including the high dielectric constant ceramic filler particles and methods of making the same.

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HIGH DIELECTRIC CONSTANT CERAMIC FILLER PARTICLES, COMPOSITES AND METHODS FOR MAKING SAME

Cross-Reference to Related Applications

[0001] This application claims priority under 35 U.S.C. § 119 to U.S. Provisional Application No. 61/399,221, filed July 8, 2010, which is herein incorporated by reference in its entirety.

Technical Field

[0001] The present invention generally relates to particle filled polymer and more particularly to high dielectric constant ceramic filled polymer composites.

Background Information

[0002] Spherical ferroelectric ceramic fillers have been used to increase the dielectric constant of polymer composites because of their high dielectric constant and low dielectric loss. The ability of spherical particles to increase the dielectric constant is small at low volume fractions according to the rule of mixtures. Thus, in order to reach a significant dielectric constant improvement, high volume fractions of fillers (40%-80%) have been used. However, at high filler concentration, the mechanical strength and the adhesion properties of polymers are sacrificed. Similarly, while higher volume fractions lead to increased dielectric constant, they also lead to a reduction in electrical breakdown strength.

[0003] Composites with high aspect ratio ceramic fillers exhibit higher dielectric constant at lower loading, thereby potentially maintaining the mechanical properties and dielectric breakdown strength. High aspect ratio fillers, however, have not been studied as extensively as their spherical counterparts because of challenges in manufacturing high aspect ratio ferroelectric fillers. There is a need for high aspect ratio, high dielectric constant ceramic fillers that will allow for polymer composites with increased dielectric constant with little to no loss of mechanical stability.

SUMMARY OF THE INVENTION

[0004] In one aspect, the invention includes a method for preparing high dielectric constant ceramic filler particles, the method including the steps of providing ceramic/polymer filler particles with an aspect ratio greater than 2, heating the ceramic/polymer filler particles to a temperature of at least 400°C for at least 10 hours to form ceramic filler particles, calcinating the ceramic filler particles at time and temperature conditions sufficient to obtain calcinated high

dielectric ceramic filler particles containing between 50% and 100% high dielectric constant perovskite structures, and cooling these calcinated high dielectric constant filler particles. These high dielectric constant filler particles have a relative dielectric constant of greater than 80.

[0005] In a second aspect, the invention includes a method for preparing a high dielectric constant polymer composite material, the method including the steps of providing a ceramic sol-gel, mixing the ceramic sol-gel with a compatible polymer to form a mixture, forming ceramic/polymer filler particles with an aspect ratio greater than 2 from the mixture, heating the ceramic/polymer filler particles to a temperature of at least 400°C for at least 10 hours to form ceramic filler particles, calcinating the ceramic filler particles at time and temperature conditions sufficient to obtain calcinated high dielectric constant ceramic filler particles containing between 50% and 100% high dielectric constant perovskite structures, cooling these calcinated high dielectric constant ceramic filler particles, and dispersing these cooled calcinated high dielectric constant ceramic filler particles into a polymer matrix. In some embodiments, the filler particle-containing polymer matrix may be cross linked.

[0006] In a third aspect, the invention includes a high dielectric constant ceramic filler particle, wherein the filler particle contains between 50% and 100% high dielectric constant perovskite structures, has a relative dielectric constant of greater than 80, and is less than 2 microns at its smallest cross-section.

[0007] In a fourth aspect, the invention includes a high dielectric constant polymer composite material, wherein the composite material contains a) a high dielectric constant ceramic filler particle having its smallest cross-section less than 2 microns and aspect ratio between 2 and 100, and contains between 50% and 100% perovskite structures; and b) a matrix polymer.

[0008] In a fifth aspect, the invention includes a high dielectric constant polymer composite material obtainable by the processes described herein.

[0009] In a sixth aspect, the invention includes an electric field control device for grading an electric field at an interruption of the insulation layer arranged around the conductor in a medium or high-voltage cable, and the device contains a high dielectric constant polymer composite of the invention.

[0010] In a seventh aspect, the invention relates to a use of a high dielectric constant polymer composite of the invention for grading an electric field in a cable termination or a cable joint.

[0011] In an eighth aspect, the invention relates to a use of a high dielectric constant polymer composite of the invention as a component of an electrical insulator.

[0012] In a ninth aspect, the invention relates to a use of a high dielectric constant polymer composite of the invention as a component of an electrical machine.

[0013] These and other objects, features and advantages of this invention will become apparent from the following detailed description of the various aspects of the invention taken in conjunction with the accompanying examples.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] FIG. 1 shows a graph illustrating X-ray diffraction patterns of calcinated filler particles according to the invention.

[0015] FIG. 2 shows SEM images of calcinated filler particles after different heat treatments, according to the invention.

[0016] FIG. 3 presents a graph showing a) Dielectric spectroscopy of polymer composite materials of the invention and b) Experimental data compared to Maxwell-Garnett rule of mixtures for different aspect ratios.

[0017] FIG. 4 depicts dielectric spectroscopy of composites of the invention.

[0018] FIG. 5 shows a graph of dielectric constants of composites of the invention.

DETAILED DESCRIPTION OF THE INVENTION

[0019] High dielectric constant ceramic fillers have been widely used to increase the dielectric constant of composites. However, the ability of traditional spherical particles to increase the dielectric constant is limited at low volume fraction (as described by the rule of mixtures), and high concentration of spherical fillers usually leads to undesirable mechanical properties. In this invention, high aspect ratio filler particles are used to increase the effective dielectric constant of polymer composites without an increase in dielectric loss over the pure matrix. These ceramic filler particles possess both high dielectric constant and high aspect ratio, which in combination can better increase the dielectric constant of the polymer composite. Moreover, by tailoring the dimension and microstructure of fibers, controllable dielectric/mechanical properties can be obtained. By mixing these filler particles with different

polymers, the technique can be potentially used in various electric applications. This allows the creation of high dielectric constant, low loss materials with excellent mechanical properties.

[0020] The present invention provides for ceramic filler particles, polymer composites, and methods of making ceramic filler particles and polymer composites. The following description is intended to provide examples of the invention and to explain how various aspects of the invention relate to each other. However, it is important to note that the scope of the invention is fully set out in the claims and this description should not be read as limiting those claims.

[0021] In one aspect, the invention includes a method for preparing high dielectric constant ceramic filler particles. The first step of the method includes providing ceramic/polymer filler particles with an aspect ratio greater than 2. This can be accomplished by providing a ceramic sol-gel and mixing it with a compatible polymer to form a mixture.

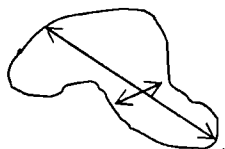
[0022] The ceramic sol-gel may be pure metal oxide or it may be modified, such as by doping, or by adding other ingredients. In some embodiments of the invention, the ceramic material includes at least one ferroelectric ceramic. In other embodiments, the ceramic material includes, but is not limited to, BaTiO₃, BaSrTiCh, PbTiO₃, PbZrO₃, SrTiO₃, and other ferroelectric ceramics, or mixtures thereof. In some embodiments, the ceramic material includes at least BaTiC[^]. Additionally, it is advantageous that the ceramic sol-gel allow possess characteristics that allow for mixing with a compatible polymer to form filler particles of the ceramic sol-gel/polymer mixture (e.g., viscosity).

[0023] The term "compatible" as used herein (i.e., for "compatible polymer") means that the ceramic sol-gel can be mixed with the polymer in such as way as to 1) minimize or avoid chemical reaction between the ceramic and the polymer, and 2) provide a viscosity that permits filler particle formation of the ceramic sol-gel/polymer mixture. Additionally, the polymer must be able to be substantially removed from the ceramic filler particles by heating. For instance, the heating may occur at 400°C for 10 hours. In some embodiments of the invention, the compatible polymer is a polar polymer, preferably a polar, water-soluble polymer. In some embodiments of the invention, the compatible polymer is polyvinylpyrrolidone (PVP).

[0024] The aspect ratio is defined as the ratio between the largest cross-section of a filler particle and the smallest cross-section of the same filler particle. For instance, a sphere, no matter its dimensions, would by definition have an aspect ratio of 1 (because all cross-section measurements are the same). A fiber, on the other hand, could have a very large aspect ratio if the smallest cross-section (its diameter) is much smaller than its largest cross-section (its length).

The ceramic/polymer filler particles of the invention may have any shape that allows the aspect ratio to be greater than 2. This includes, but is not limited to, fibers, plates, needles, flakes, rods, chips, whiskers, etc. or mixtures of any of these.

[0025] In some embodiments of the invention, the smallest cross-section is less than 2 microns. In these instances, then, if the smallest cross-section of a filler particle is 1.5 microns, then the largest (e.g., longest) cross-section must be at least 3 microns. This is true whether the shape is relatively uniform, as with a fiber, or of irregular shape, as illustrated below:



[0026] In some embodiments of the invention, the diameter of a filler particle is between 100 nm and 10 microns. In other embodiments, the diameter of a filler particle is between 100 nm and 2 microns. In still other embodiments, the diameter of a filler particle is between 100 nm and 1 micron. In yet other embodiments, the diameter of a filler particle is between 200 nm and 800 nm. In other embodiments, the diameter of a filler particle is between 300 nm and 600 nm. For the purpose of this application, "diameter" is defined as the length of a straight line through the center of an object.

[0027] In some embodiments of the invention, the ceramic/polymer filler particles are fibers wherein the smallest cross-section is less than 2 microns. A fiber is defined as a filler particle substantially in the shape of a rod or cylinder, as exemplified in Figure 2. The aspect ratio of a fiber of the invention must be greater than 2.

[0028] In some embodiments of the invention, the filler particle aspect ratio is greater than 2. In other embodiments, the aspect ratio is between 2 and 100. In other embodiments, the aspect ratio is between 2 and 60. In yet other embodiments, the aspect ratio is between 2 and 15. In other embodiments, the aspect ratio is between 3 and 15. In still other embodiments, the aspect ratio is greater than 5, e.g. between 5 and 100. In still other embodiments, the aspect ratio is greater than 10, e.g. between 10 and 100.

[0029] The ceramic sol-gel/polymer mixture can then be formed into ceramic/polymer filler particles. Filler particle production methods include any application-appropriate method that results in a filler particle with the desired aspect ratio. For instance, in some embodiments of the invention, methods for filler particle production include, but are not limited to, electrospinning,

force spinning, blow spinning, and any other filler particle production method or their combinations. In some embodiments of the invention, forming the ceramic/polymer mixture to produce filler particles is accomplished by electrospinning.

[0030] After forming the ceramic sol-gel/polymer mixture into ceramic/polymer filler particles by one or more of the foregoing methods, substantially all of the polymer is removed from the ceramic/polymer filler particles to form ceramic filler particles. For instance, the particles may be subjected to heat treatment at time and temperature conditions sufficient to remove substantially all of the polymer. As an example, the temperature can be from 200°C to any temperature that is higher than the degradation temperature of the sacrificial polymer, yet does not cause sintering. The heat treatment time will typically be a minimum of one hour. One non-limiting example includes the use of a temperature of at least 400°C for at least 10 hours. The person of skill will recognize that conditions necessary to substantially remove all of the polymer will be related to the type of polymer used.

[0031] These ceramic filler particles are then calcinated at time and temperature conditions sufficient to obtain between 50% and 100% high dielectric constant perovskite, and especially tetragonal, structures. In some embodiments of the invention, calcinating the ceramic filler particles is accomplished at a temperature of 950-1050°C for a time of approximately two hours. In some of these embodiments, the calcination temperature ramping rate is at least 200°C/minute. In other embodiments of the invention, calcinating the ceramic filler particles occurs at a temperature of 1150-1250°C for approximately five minutes. In some of these embodiments, the calcination temperature ramping rate is at least 2000°C/minute. This relatively high heating rate facilitates the preparation of the desired high dielectric constant ceramic filler particles while still maintaining the filler particle morphology. Higher aspect ratio filler particles were found to increase the composite dielectric constant by more than a factor of two, compared to corresponding shorter fibers or spherical particles, and this increase in composite dielectric constant was accompanied by a very moderate increase of the loss factor.

[0032] The presence of the perovskite structures, and especially tetragonal structures, results in the cooled, calcinated filler particles having a relative dielectric constant greater than 80. Clearly, it is desired that the calcination conditions are such that the filler particle morphology is maintained; for instance, the conditions should not be so harsh as to cause sintering. The calcinated high dielectric constant filler particles are then cooled.

[0033] In another embodiment, the invention includes a method for preparing a high dielectric constant polymer composite material. This method includes providing ceramic filler particles, as described above. The high dielectric constant ceramic filler particles are then dispersed in a polymer matrix. The polymer matrix may be selected from a large range of polymers. Blends of two or more polymers may be suitable in some cases. In some embodiments of the invention, suitable polymers include, but are not limited to, elastomeric materials (silicone, EPDM, etc.); thermoplastic polymers (polyethylene or polypropylene, etc.) thermoplastic elastomers; thermosetting materials (epoxy resins, etc.); or a combination of such materials, including co-polymers (for example a combination of polyisobutylene and amorphous polypropylene).

[0034] In some embodiments, it may be advantageous to employ a cross-linker in the preparation of the polymer matrices. Application-appropriate cross-linkers will be known by a person of skill in the art. Non-limiting examples of crosslinkers include methylhydrosiloxane-dimethylsiloxane copolymers for addition curing silicone rubbers, as well as peroxide-curing silicone rubbers.

[0035] A variety of methods of dispersing the ceramic filler particles in the polymer matrix are within the scope of the invention. Non-limiting examples include 1) dissolving the matrix polymer and ceramic filler particles in a solvent and precipitating them from that solvent or casting the solution and evaporating the solvent; 2) mixing the ceramic filler particles in a melt (thermoplastic) and then allowing the mixture to cool and harden; 3) mixing the ceramic filler particles in an oligomer and then chemically crosslinking them (for example, in an epoxy or a silicone); and 4) dispersing the ceramic filler particles in the polymer matrix while the matrix is still a monomer and then polymerizing the monomer to form a thermoplastic or a cross-linked polymer.

[0036] In some embodiments, the invention includes a method for preparing a high dielectric constant polymer composite material by providing a barium titanate sol-gel and mixing it with a compatible polymer to form a mixture. In some embodiments, the compatible polymer is PVP. This mixture is then subjected to electrospinning to produce barium titanate/polymer fibers. In some embodiments, the smallest cross-section of said barium titanate/polymer fiber is less than 1 micron. The barium titanate/polymer fibers are then heated to a temperature of at least 400°C for at least 10 hours to remove substantially all of the polymer to form barium titanate fibers. In some embodiments of the invention, the barium titanate/polymer fibers are heated to 450-500°C for about 12 hours. The barium titanate fibers are then calcinated at time and temperature

conditions sufficient to obtain high dielectric constant perovskite structure. In some embodiments of the invention, it is advantageous to produce barium titanate fibers having >50% tetragonal perovskite crystal structure. In some embodiments, the barium titanate fibers are calcinated for five minutes at 1200°C at a ramping rate of 2000°C/minute. The calcinated fibers are then cooled. In some embodiments, the calcinated fibers are cooled to room temperature. The cooled fibers are then dispersed into a polymer matrix. In some embodiments, the polymer matrix is silicone rubber. If desired, the silicone rubber is then cross-linked. In some embodiments, the length of the cooled calcinated fibers is decreased just before or during the dispersion of the fibers into a polymer matrix.

[0037] By changing the parameters used in heat treatment process (e.g., calcination temperature, ramping rate and treating time), the filler particle morphology, microstructure and crystal structure, as well as the dielectric constant of the filler particles, can be controlled. It has been found that the dielectric constant of the composites was higher than traditional spherical particle-filled ones, and that the increase in dielectric loss over the pure matrix was low.

[0038] The length of the calcinated high dielectric constant ceramic filler particles may be changed before or during the mixing process. For instance, higher (i.e., longer) aspect ratio composites may be obtained by direct mixing of the calcinated filler particles with the precursor resin. Medium aspect ratio filler particle composites may be prepared by, for instance, adding alumina balls during the mixing process to break the filler particles. Calcinated filler particles can also be crushed, for instance, in a mortar and pestle, to obtain low aspect ratios. In some embodiments of the invention, the filler particle aspect ratio is greater than 2. In other embodiments, the aspect ratio is between 2 and 1000. In other embodiments, the aspect ratio is between 2 and 100. In still other embodiments, the aspect ratio is between 2 and 30. In yet other embodiments, the aspect ratio is between 2 and 15. In other embodiments, the aspect ratio is between 3 and 15. In still other embodiments, the aspect ratio is greater than 5, e.g. between 5 and 1000. In yet other embodiments, the aspect ratio is greater than 5, e.g. between 5 and 100. In still other embodiments, the aspect ratio is greater than 10, e.g. between 10 and 1000. In yet other embodiments, the aspect ratio is greater than 10, e.g. between 10 and 100.

[0039] In some embodiments of the invention, the high dielectric constant ceramic filler particles comprise from about 1 to about 50 percent by volume of the high dielectric constant polymer composite material. In other embodiments, the filler particles comprise from about 1 to about 30 percent by volume of the high dielectric constant polymer composite material. In other embodiments, the filler particles comprise from about 5 to about 30 percent by volume of the

high dielectric constant polymer composite material. In other embodiments, the filler particles comprise from about 1 to about 20 percent by volume of the high dielectric constant polymer composite material. In other embodiments, the filler particles comprise from about 5 to about 20 percent by volume of the high dielectric constant polymer composite material. In other embodiments, the filler particles comprise from about 10 to about 50 percent by volume of the high dielectric constant polymer composite material. In other embodiments, the filler particles comprise from about 10 to about 30 percent by volume of the high dielectric constant polymer composite material. In other embodiments, the filler particles comprise from about 10 to about 20 percent by volume of the high dielectric constant polymer composite material. In other embodiments, the filler particles comprise from about 5 to about 15 percent by volume of the high dielectric constant polymer composite material.

[0040] In some embodiments of the invention, graphene platelets (GPLs) with high aspect ratio in two dimensions may be dispersed into the polymer matrix. These graphene platelets are 1-10 micrometers in in-plane dimensions and are comprised of approximately three to four graphene sheets within each platelet. In some embodiments, the total graphene platelet thickness is less than 2 nm. In other embodiments, the total graphene platelet thickness is less than 1 nm. In some embodiments, the graphene platelets are dispersed at a concentration of 0.1 vol% to 1 vol%. In other embodiments, the graphene platelets are dispersed at a concentration of 0.1 vol% to 0.5 vol%. In still other embodiments, the graphene platelets are dispersed at a concentration of 0.5 vol% to 1 vol%. In still other embodiments, the graphene platelets are dispersed at a concentration of 0.25 vol% to 0.75 vol%. One example is described below under Example 3.

[0041] In another embodiment, the invention relates to a high dielectric constant ceramic filler particle. This filler particle contains between 50% and 100% high dielectric constant perovskite structures, has a relative dielectric constant of greater than 80, has its smallest cross-section less than 2 microns, and has an aspect ratio greater than 2.

[0042] In another embodiment, the invention relates to a high dielectric constant polymer composite material. This material includes a high dielectric constant ceramic filler particle and a matrix polymer. The high dielectric constant ceramic filler particle has a smallest cross-section less than 2 microns and an aspect ratio between 2 and 100. The filler particle contains between 50% and 100% perovskite structures. In some embodiments, these filler particles comprise from 5 to 50 percent by volume of the high dielectric constant polymer composite material. In some embodiments, the high dielectric constant polymer composite material includes barium titanate filler particles in a cross-linked silicone rubber matrix.

[0043] In some embodiments, the invention relates to high dielectric constant polymer composite material obtainable by the processes described herein.

[0044] The presence of perovskite structure is indicative of high dielectric constant in the ferroelectric ceramic filler particle. While cubic, orthorhombic, tetragonal or trigonal structure exist in many perovskite structures, generally in the high temperature sintering process, the cubic perovskite structure changes to other perovskite structures, which have a high dielectric constant. The heat treatment parameters of the invention allow the ceramic filler particles to develop high dielectric constant. High temperature calcination allows one to obtain the tetragonal structure (with high dielectric constant), while limiting the calcination time to avoid sintering of the filler particles.

[0045] Although not all ceramic filler particles must have tetragonal structure in order to have a high dielectric constant, BaTiC[^] filler particles, for instance, do possess a high dielectric constant when they are in tetragonal structure. The XRD graph in Figure 1b demonstrates that almost all the BaTiO₃ is in tetragonal form, shown by the complete splitting of the (200) peak.

[0046] Ceramic filler particles according to this aspect of the invention may be used in a variety of applications, including the polymer composite materials in the present description. In such applications, the amount of ceramic filler particle present in a given embodiment of the invention, relative to the amount of polymeric matrix present, can vary as desired in an application-specific manner. A non-limiting example of amounts of ceramic filler particle typically present in various embodiments of the invention is a range where the ceramic filler particle loading fraction is between about 5 percent and about 50 percent.

[0047] According to various aspects of the present invention, the use of different loading fractions of ceramic filler particles to affect one or more properties of the polymer composite is contemplated. As an example, by tailoring the dimension and microstructure of the filler particles, controllable dielectric and mechanical properties can be obtained. Loading fractions of about 5% to 50% by volume of ceramic filler particles in a polymer matrix material may be used to affect the dielectric properties of the material. Specifically, in certain embodiments, increasing the loading fraction of ceramic filler particles may result in a progressively higher dielectric constant than the polymer matrix alone would have.

[0048] It is also contemplated as within the scope of the present invention that ceramic filler particles may be modified differently in order to tailor the effect of a particular loading fraction on the dielectric and mechanical properties of the polymer composite material, allowing for a

desired modification of the dielectric and/or mechanical properties of the polymer composite material relative to the polymeric matrix material alone. For example, depending upon the specific modification to a particular ceramic filler particle, a 40% loading fraction may result in a polymer composite according to aspects of the present invention having a different dielectric and mechanical properties than the polymer matrix material alone. An example of this is shown in the table below:

[0049] Table. Dielectric constant and loss factor (in parenthesis) of silicone rubber containing 10 or 20 vol.% BaTiO₃ fibers with different aspect ratios. The dielectric constant and loss factor for the neat silicone rubber are 3.02 and 0.0008, respectively. Measurements performed at ambient temperature at 60 Hz.

Fiber aspect ratio	10 vol%	20 vol%
15	7.3 (0.0036)	12.0 (0.0060)
6	4.9 (0.0018)	9.0 (0.0042)
3	4.5 (0.0008)	6.5 (0.0011)

[0050] Tuning of the dielectric constant by varying the ceramic filler particles and modifications thereof, and/or by varying the loading fraction of the ceramic filler particles, is one example of how the present invention may be used to create desirable polymer composite materials. Potential applications of tuning of the dielectric constant of a material include: electric field control devices, grading an electric field in a cable termination, grading an electric field in a cable joint, as a component of an electrical insulator (including bushings), and as a component of an electrical machine, among others.

[0051] Compared to the spherical filler composites, the improvement of effective dielectric constant for high aspect ratio filler composites is much more significant at low volume fraction. FIGURE 3a demonstrates this phenomenon for BaTiO₃ fiber/ silicone rubber composites.

EXAMPLES

[0052] Explained herein are embodiments of the invention describing fabrication of high dielectric constant polymer composite materials. The invention may, however, be embodied in many different forms and should not be construed as being limited to the exemplary embodiments set forth herein; rather, these embodiments are provided so that this disclosure will be thorough and complete, and will convey the concept of the invention to those skilled in the art.

Example 1:

[0053] BaTiO₃ fibers were prepared by electrospinning of a mixture consisting BaTiO₃ sol-gel and poly(vinyl pyrrolidone) (PVP, MW=1,300,000) solution. 5 mM barium acetate (Ba(CH₃COO)₂) was dissolved in 3 ml of acetic acid. Then under constant stirring, 5 mM titanium isopropoxide ((CH₃)₂CHO⁻Ti⁺) was added into solution. After that, a solution consisting of 0.2 g poly(vinyl pyrrolidone) and 3 ml ethanol was added into the mixture. A clear pale yellow precursor was obtained by stirring the mixture.

[0054] The precursor was then loaded into a syringe for electrospinning. The electrospinning process is well known to a person of skill. Briefly, a positive voltage (16 kV) was applied on the needle tip of syringe, and an aluminum foil was grounded as counter electrode. The distance between needle tip and counter electrode was 23 cm, and the precursor was fed at a constant rate (31 μl/min) by a syringe pump. When the high voltage was applied, the liquid at the needle tip was charged and stretched by electrostatic repulsion force to form a "Taylor cone". Because of the high viscosity, a fiber was ejected from the tip, elongated in the air and deposited on the grounded electrode. The synthesized BaTiO₃/PVP fiber had a diameter less than 1 μm. The surface of the fiber was smooth and the diameter was uniform along the fiber.

[0055] The synthesized BaTiO₃/PVP fibers were then subjected to heat treatment to remove PVP polymer, and to obtain the desired perovskite crystal structure. Representative SEM pictures of synthesized BaTiO₃/PVP fibers are shown in Figure 2, and those calcinated at 1000 °C are shown in Figure 2b. After calcination at 1000 °C for 2 hours, the fiber diameter was reduced to 300nm with all the PVP removed and BaTiO₃ grains were observed at the fiber surface. Fiber morphology, microstructure and crystal structure can be changed when different heat treatment parameters (calcination temperature, ramping rate and treating time) are applied.

[0056] After calcinations above 800 °C, crystal structure was developed from amorphous BaTiO₃ as illustrated in Figure 1. From the (200) peak shape at around 45 °, influence of heating rate on crystal structure was shown. By using high heating rate, grain growth process was much more favored than nucleation process, and larger grains were developed. At the mean time, more tetragonal structure appeared characterized by the splitting of (200) peak, as shown. The tetragonal phase was predicted to have higher dielectric constant than cubic phase.

[0057] After calcination, BaTiO₃ fibers were mixed into a polymer matrix (in this case, silicone rubber) by shear mixing and subsequently crosslinked. Dispersion of the fibers in the polymer is

generally good. Dielectric spectroscopy showed an increase of dielectric constant from 3 to 5.6 at 9.74 vol% of fibers. The increase of loss factor was small (from 0.001 to 0.0046 at 60Hz).

Example 2

[0058] BaTiO_3 fibers were prepared by electrospinning a BaTiO_3 sol-gel and poly(vinyl pyrrolidone) precursor. The experimental details of the electrospinning can be found in the literature [J Yuh, J Nino, and W Sigmund, Materials Letters **59**, 3645-3647 (2005)]. The synthesized BaTiO_3 /PVP fibers had a diameter less than 1 μm . The surface was smooth and the diameter was uniform along the fiber. A special high temperature treatment was developed to obtain large grains of tetragonal phase BaTiO_3 , which possess a high dielectric constant, while avoiding sintering of the fibers. The fibers were annealed at 500 °C for 12 hours to remove the solvent and the PVP polymer, and then calcinated at higher temperatures to obtain the perovskite crystal structure. The calcinated BaTiO_3 fibers were mixed with Sylgard 184 silicone rubber using a FlackTek Speed Mixer, then the uniform mixture was cured.

[0059] Long fiber (AR = 15) composites were obtained by direct mixing of the calcinated fibers with the precursor resin. Medium length (AR = 6) fiber composites were prepared by adding alumina balls during the mixing process to break the fibers. Calcinated fibers were also crushed in a mortar and pestle to obtain low aspect ratio fibers (AR = 3). The fiber aspect ratios were calculated from SEM images. The adhesion between the fibers and the silicone rubber matrix was good, as shown by a lack of debonding.

[0060] The volume fraction of fillers was calculated from the weight fraction measured by a TA Instruments Q50 thermogravimetric analyzer. The dielectric spectroscopy was tested in a Novocontrol alpha high resolution dielectric/impedance analyzer. AC breakdown tests were carried out at room temperature Dow Corning 561 silicone transformer fluid at a frequency of 60 Hz, with a voltage ramp rate of 200 V s⁻¹. X-ray diffraction (XRD) 2 θ scans were performed on a Bruker D8 Discover X-ray diffractometer. The morphology of the fibers was investigated using a Carl Zeiss Supra scanning electron microscope (SEM).

[0061] After the heat treatment, the final crystal structure of BaTiO_3 fibers depended on the heating rate, as well as the calcination temperature and time. **Fig. 1a** shows XRD patterns that illustrate the effect of calcination temperature on the crystal structure of the BaTiO_3 fibers. After calcination at a temperature above 800 °C, the XRD pattern is consistent with the XRD data of BaTiO_3 in the literature. Above 900 °C, the impurity phase (mainly BaCO_3) was removed as

indicated by the absence of peaks below $2\Theta = 30^\circ$. The influence of the heating rate in the calcinations process on the BaTiO_3 crystal structure is shown in **Fig. 1b**. A low heating rate ($10^\circ\text{C min}^{-1}$) resulted in a symmetric (200) peak confirming the cubic symmetry. The cubic crystal structure is facilitated by the smaller grain size (see **Fig. 2b-c**). At a heating rate of $200^\circ\text{C min}^{-1}$ the asymmetric peak shape indicates the appearance of a tetragonal crystal phase, evidenced by a (002) peak, even though the cubic phase is still dominant. A very fast heating rate ($2000^\circ\text{C min}^{-1}$) resulted in a complete splitting of the (200) and (002) peaks. This indicates that most of the crystals are tetragonal phase.

[0062] Figure 2 shows SEM images of BaTiO_3 fibers after different heat treatments: a) ramping rate: 2000°C/min (thermally shocked), calcinated during 5 min at 1200°C ; b) ramping rate: 200°C/min , calcinated during 120 min at 1000°C ; c) ramping rate: 10°C/min , calcinated during 120 min at 1000°C ; d) fractured surface silicone rubber containing 1.6 vol. % BaTiO_3 fibers (AR = 15).

[0063] Higher heating rate resulted in larger grains, as shown in **Fig. 2a-c**, as a result of the maximized crystal growth rate compared to the nucleation rate. Correspondingly when a low heating rate was used, the diffusion process was inhibited during the crystal formation, resulting small grains with pores among them as shown in **Fig. 2c**. If an annealing temperature higher than 500°C was used prior to the calcination, smaller grains were obtained after the same calcinations process, due to the initiation of nucleation during the annealing process. Meanwhile, the crystal structure of BaTiO_3 is related to the grain size. The tetragonal phase BaTiO_3 has high dielectric constant, which typically exists at grain sizes larger than 100nm . At the grain boundary or free surface, BaTiO_3 tends to be in the low dielectric constant cubic phase due to a lack of constraint compared to the "ferroelectric core" in bulk. To optimize the formation of the high dielectric constant tetragonal phase while maintaining the fiber morphology, a rapid heating rate ($2000^\circ\text{C min}^{-1}$) in combination with a short calcination step (5 min at 1200°C) was required. After the heat treatment, a polycrystalline bamboo-like structure was obtained as shown in **Fig. 2a**.

[0064] Dielectric spectroscopy (**Fig. 3a**) shows an increased dielectric constant for the BaTiO_3 fiber/silicone rubber composites. The real relative dielectric constant ϵ' is flat in the tested frequency range, indicating the absence of conduction effects. Both the dielectric constant and loss factor increase with fiber aspect ratio and filler volume fraction, which is consistent with the rule of mixtures. The dielectric constant increased from 3 to 6.5 for the composites filled with 20 vol% of the lowest aspect ratio fibers (AR=3). The relative dielectric constant increase over the neat polymer is comparable to that of the composites filled with spherical or irregular BaTiO_3

particles reported in the literature. Meanwhile, the high aspect ratio fiber (AR=15) significantly increased the composite dielectric constant to 12. The loss factor of all the tested composites is below 0.006, only an order of magnitude higher than that of the neat polymer. Figure 3b shows experimental data compared to Maxwell-Garnett rule of mixtures for different aspect ratios.

[0065] To summarize, a high heating rate was found to be the key to preparing the desired tetragonal phase of BaTiO₃ while still maintaining the fiber morphology. Higher aspect ratio BaTiO₃ fibers were found to increase the composite dielectric constant by more than a factor of two, compared to corresponding shorter fibers or spherical particles, in combination with a very moderate increase of the loss factor.

Example 3: Ceramic Fibers and Graphene Platelets

A. Preparation of BaTiO₃ Fibers

[0066] BaTiO₃ fibers were prepared by electrospinning a mixture that consisted of BaTiO₃ sol-gel and poly(vinyl pyrrolidone) (PVP, M_w = 1,300,000) solution [11]. A positive voltage (16 kV) was applied on the needle tip of a syringe, and an aluminum foil was grounded as the counter electrode. The distance between the needle tip and the counter electrode was 25 cm, and the precursor was fed at a constant rate (30 μl/min) by a syringe pump.

[0067] Synthesized BaTiO₃/PVP fibers were subjected to a heat treatment to remove the PVP polymer, and to obtain the desired perovskite crystal structure. Fibers were annealed in an oven at 500 °C for 12 hours to remove the residual solvent and most of the PVP. They were then calcinated at 1200 °C to crystallize. In the heat treatment process, a fast heating rate of over 2000 °C/min was achieved by inserting the sample into a preheated oven. The fibers were then cooled down to room temperature in air. A scanning electron microscope (SEM) image of prepared BaTiO₃ fibers is shown in **Fig. 2a**.

B. Preparation of Graphene Platelets (GPLs)

[0068] The GPLs were obtained by the one-step thermal exfoliation and reduction of graphite oxide. In this method, graphite oxide is subjected to a thermal shock (rapid heating rate of about 2000° C/min) which exfoliates and reduces the graphite oxide into GPLs. The GPLs are several micrometers in in-plane dimensions and are comprised of 3-4 graphene sheets within each platelet. The total platelet thickness is less than 2 nm.

C. Preparation of Composites

[0069] Sylgard 184 (Dow Corning), consisting of poly(dimethyl siloxane) (PDMS) and a reinforcing silica filler was used as polymer matrix. The calcinated **BaTiCb** fibers were directly mixed into the precursor Sylgard 184A using a FlackTek Speed Mixer at 3000 rpm for 10 minutes. Composites were then prepared by carefully mixing the precursors Sylgard 184A (containing the fibers) and Sylgard 184B (crosslinker) at a ratio of 10:1 by mass, followed by curing in a mold at 150 °C for 12 hours. Planar samples with a diameter of 3.2 cm and a thickness of around 300 μm were obtained. Prepared samples were dried in an oven at 120 °C for 12 hours prior to any dielectric testing to remove any trapped moisture. Good dispersion of the **BaTiO₃** fibers and the graphene platelets in the polymer matrix was observed.

D. Characterization

[0070] Thermogravimetric analysis (TGA) was carried out to determine the weight fraction of fibers in the composites, using a TA Instruments Q50 thermogravimetric analyzer. Parameters from the literature and the manufacturer datasheet (**BaTiCb** density = 6.02 g/cm³, PDMS density = 1.03 g/cm³) were used to calculate the filler volume fraction. The composite samples were tested in a Novocontrol alpha high resolution dielectric/impedance analyzer for dielectric spectroscopy at room temperature. A frequency range from 10⁻¹ to 10⁶ Hz was utilized. The morphology of the fibers was investigated using a Carl Zeiss Supra scanning electron microscope. The electric flux density-electric field (D-E) measurement was taken in an ambient of dielectric mineral oil at 20 °C following the ASTM standard D3487.

E. Results

[0071] **Dielectric Spectroscopy:** The dielectric constant and dissipation factor of composites filled with GPLs was measured. Both the dielectric constant and dissipation factor have a large increase at a small volume fraction of GPLs. The sheet morphology and high aspect ratio of GPLs lead to a low percolation threshold of less than 0.01 in volume fraction. The large dissipation factor above percolation threshold is caused by the leakage current. Without being held to any one theory, the high dielectric constant can be explained by percolation theory, which describes the critical behavior of composites when the volume fraction of conductive fillers approaches the percolation threshold. However, a large dissipation factor is usually not desired in electrical applications. A GPL volume fraction of 0.0043 was chosen for the three-phase composite preparation. At this loading, the dielectric constant is improved with only a moderate increase of the dissipation factor. The GPLs prepared by the thermal shock method have a small thickness, and thus can reach percolation at a lower volume fraction.

[0072] The dielectric spectroscopy of several representative composites is shown in **Fig. 4**. The real relative dielectric constant ϵ' is flat in the tested frequency range, indicating the absence of conduction effects. The relative dielectric constant increase over the neat polymer is significantly larger than that of the composites filled with spherical or irregular BaTiO₃ particles reported in the literature. For example, the dielectric constant of 20 vol% BaTiO₃ fiber filled composites is 400% of the neat polymer, and the same volume fraction of spherical BaTiO₃ particle only increases the dielectric constant to about 200%. This difference agrees with the prediction from the rule of mixtures. The increase in dielectric constant of the composites is summarized in **Fig. 5**. By adding 0.43 vol% of GPLs into the BaTiO₃ fiber/PDMS composites, the dielectric constant was further increased to 13.7 and 18.6 for 10 vol% and 20 vol% BaTiO₃ fiber composites, respectively. The frequency for these dielectric spectroscopy tests was 60 Hz.

[0073] The dissipation factor of the composites is shown in **Fig. 4b**. The largest dissipation factor of all the composites is about one order of magnitude higher than that in the neat PDMS. Generally the dielectric loss increases with the volume fraction of fibers and the GPLs. Adding 0.43 vol% of GPLs into the BaTiO₃ fiber composites increases the dissipation factor, but is not higher than the pure GPL/PDMS composites. By combining the two types of fillers, the three-phase composite shows a larger dielectric constant than either of the two-phase composites without a further increase in loss factor. By using high aspect ratio ceramic fillers to increase the dielectric constant of the base matrix, the dielectric constant of the final composites is further improved.

[0074] D-E Measurement: The high voltage behavior of materials was investigated through D-E measurements. Both BaTiO₃ fiber composites and three-phase composites were tested under several field conditions below the breakdown strength of materials.

[0075] The relative permittivity was calculated using an approach found in the literature [J. Robertson and D. Hall, *Journal of Physics D: Applied Physics*, vol. 41, Jun. 2008, p. 15407]. The real dielectric constant for composites is listed in Table II. From the literature, ferroelectric ceramics such as barium titanate usually exhibit a nonlinear dielectric constant. Depending on the microstructure and crystal morphology, the dielectric constant of barium titanate can either increase or decrease with increasing field strength. In our result, however, the dielectric constant remains unchanged at elevated electrical field.

TABLE II

REAL RELATIVE PERMITTIVITY OF COMPOSITES AT ELEVATED FIELD

Ac field (kV/mm)	20 vol% BaTiO ₃ fibers	20 vol% BaTiO ₃ fibers +0.43 vol% GPLs
Low field ^a	12	18.6
2	11.9	17.5
5	11.7	18.1
7.5	11.8	-

^a The value of low field dielectric constant is from the dielectric spectroscopy

[0076] Two types of high aspect ratio fillers, BaTiO₃ fibers and GPLs, were mixed with PDMS to make composites. The dielectric spectroscopy showed that the high aspect ratio BaTiO₃ fibers can better increase the dielectric constant of composites than their spherical counterparts while maintaining a moderate dissipation factor. The GPLs alone can also increase the dielectric constant at a very low filler volume fraction. However, the loss increased dramatically when reaching the percolation threshold. By combining those two fillers and avoiding the percolation of GPLs, the highest dielectric constant was reached without further increase in the dissipation factor. The D-E measurement showed a linear dielectric constant at high voltage.

[0077] While several aspects of the present invention have been described and depicted herein, alternative aspects may be effected by those skilled in the art to accomplish the same objectives. Accordingly, it is intended to cover all such alternative aspects as fall within the true spirit and scope of the invention.

CLAIMS

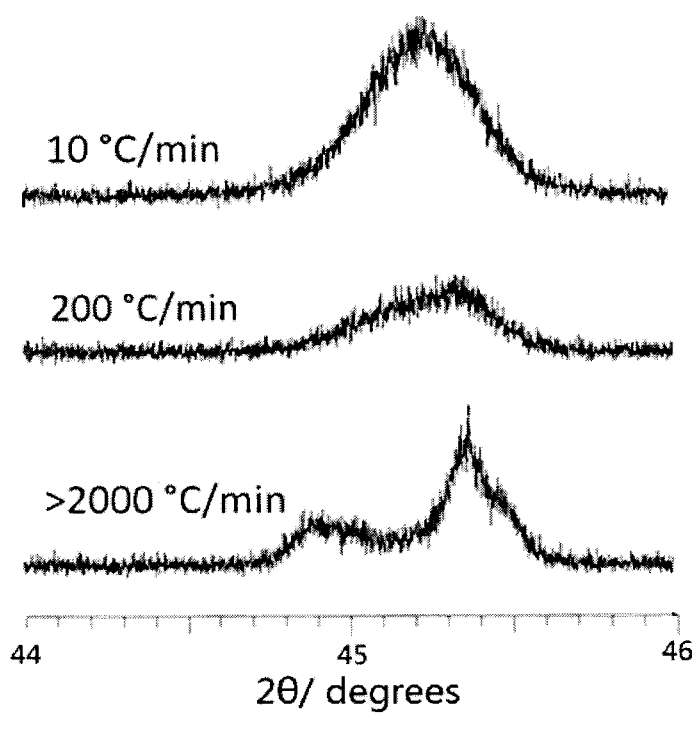
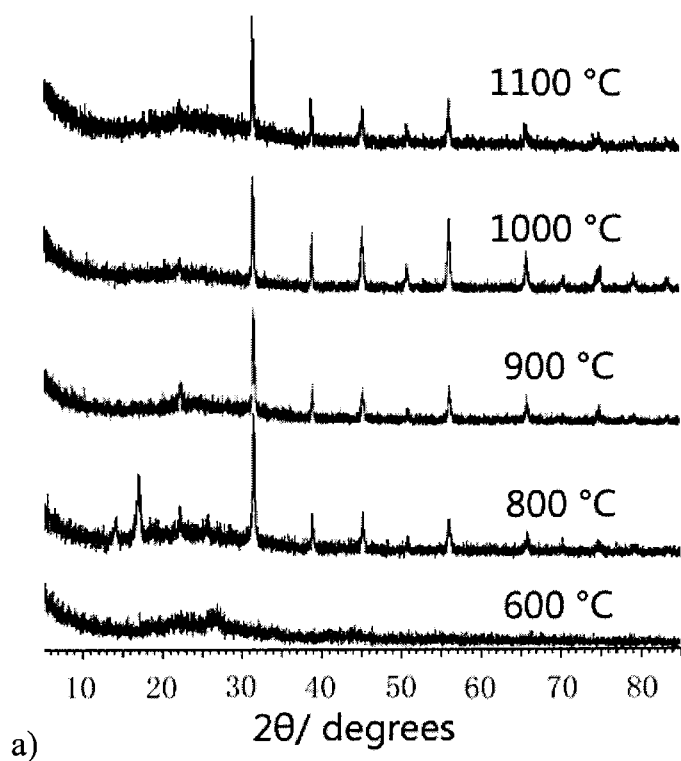
1. A method for preparing high dielectric constant ceramic filler particles, said method comprising
 - a. providing ceramic/polymer filler particles with an aspect ratio greater than 2;
 - b. heating said ceramic/polymer filler particles to a temperature of at least 400°C for at least 10 hours to form ceramic filler particles;
 - c. calcinating said ceramic filler particles at time and temperature conditions sufficient to obtain calcinated high dielectric ceramic filler particles containing between 50% and 100% high dielectric constant perovskite structures; and
 - d. cooling said calcinated high dielectric constant filler particles;wherein said high dielectric constant filler particles have a relative dielectric constant of greater than 80.
2. The method of claim 1, wherein said providing said ceramic/polymer filler particles with an aspect ratio greater than 2 is accomplished by
 - a. Providing a ceramic sol-gel;
 - b. Mixing said ceramic sol-gel with a compatible polymer to form a mixture;
 - c. Forming said mixture to produce ceramic/polymer filler particles.
3. A method for preparing a high dielectric constant polymer composite material, said method comprising
 - a. providing a ceramic sol-gel;
 - b. mixing said ceramic sol-gel with a compatible polymer to form a mixture;
 - c. forming said mixture to produce ceramic/polymer filler particles with an aspect ratio greater than 2;
 - d. heating said ceramic/polymer filler particles to a temperature of at least 400°C for at least 10 hours to form ceramic filler particles;
 - e. calcinating said ceramic filler particles at time and temperature conditions sufficient to obtain calcinated high dielectric constant ceramic filler particles containing between 50% and 100% high dielectric constant perovskite structures;
 - f. cooling said calcinated high dielectric constant ceramic filler particles;
 - g. dispersing said cooled calcinated high dielectric constant ceramic filler particles into a polymer matrix; and
 - h. optionally crosslinking said filler particle-containing polymer matrix.
4. The method of any one of claims 1 to 3, wherein the ceramic comprises at least one ferroelectric ceramic.
5. The method of claim 4, wherein the at least one ferroelectric ceramic is selected from BaTiO₃, BaSrTiCb, PbTiO₃, PbZrO₃ and SrTiO₃.
6. The method of claim 5, wherein the ceramic comprises BaTiO₃.

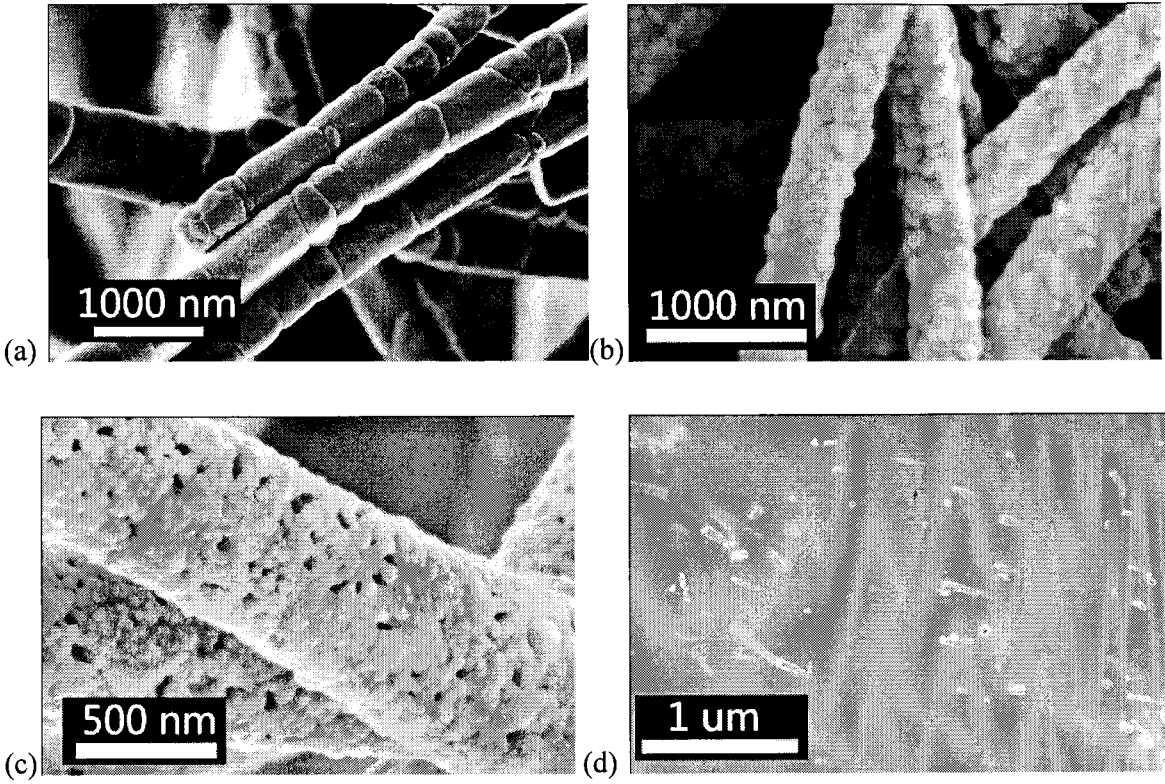
7. The method of claim 2 or claim 3, wherein said forming said mixture to produce ceramic/polymer filler particles is accomplished by a method selected from at least one of electrospinning, force spinning and blow spinning.
8. The method of claim 7, wherein said forming said mixture to produce ceramic/polymer filler particles is accomplished by electrospinning.
9. The method of any one of claims 1 to 3, wherein said calcinating said ceramic filler particles is accomplished at a temperature of 950-1050°C for a time of approximately two hours.
10. The method of claim 9, wherein the calcination temperature ramping rate is at least 200°C/minute.
11. The method of any one of claims 1 to 3, wherein said calcination occurs at a temperature of 1150-1250°C for approximately five minutes.
12. The method of claim 11, wherein the calcination temperature ramping rate is at least 2000°C/minute.
13. The method of claim 3, wherein the matrix polymer is selected from an elastomeric material, a thermoplastic polymer, a thermoplastic elastomer, and a thermosetting material.
14. The method of claim 13, wherein the matrix polymer is selected from silicone, EPDM, polyethylene, polypropylene, polyisobutylene, amorphous polypropylene, an epoxy resin, and combinations thereof.
15. The method of any of claims 1 to 3, wherein the compatible polymer is PVP.
16. The method of any one of the above claims, wherein the smallest cross-section of said ceramic/polymer filler particle is less than 2 microns.
17. The method of claim 16, wherein said ceramic/polymer filler particle is a fiber having its smallest cross-section less than 2 microns.
18. A method for preparing a high dielectric constant polymer composite material according to claim 3, said method comprising
 - a. providing a barium titanate sol-gel;
 - b. mixing said barium titanate sol-gel with a compatible polymer to form a mixture;
 - c. electrospinning said mixture to produce barium titanate/polymer fibers;
 - d. heating said barium titanate/polymer fibers to a temperature of at least 400°C for at least 10 hours to form barium titanate fibers;
 - e. calcinating said barium titanate fibers at time and temperature conditions sufficient to obtain high dielectric constant perovskite structure;

- f. cooling said calcinated fibers;
 - g. dispersing said cooled calcinated fibers into a polymer matrix; and
 - h. optionally crosslinking said fiber-containing polymer matrix.
19. The method of claim 18, wherein said method comprises:
- a. providing a barium titanate sol-gel;
 - b. mixing said barium titanate sol-gel with compatible polymer to form a mixture, wherein said compatible polymer is polyvinyl pyrrolidone);
 - c. electrospinning said mixture to produce barium titanate/PVP fibers;
 - d. heating said barium titanate/PVP fibers to a temperature of 450-500°C for about 12 hours to form barium titanate fibers;
 - e. calcinating said barium titanate fibers for five minutes at 1200°C at a ramping rate of 2000°C/minute;
 - f. cooling said calcinated fibers to room temperature;
 - g. dispersing said cooled calcinated fibers into a polymer matrix, wherein said polymer matrix is a silicone rubber; and
 - h. crosslinking said fiber-containing polymer matrix.
20. The method of claim 18 or claim 19, wherein the smallest cross-section of said barium titanate/polymer fiber is less than 1 micron.
21. The method of any one of claims 3, 18 or 19 further comprising decreasing the length of the cooled calcinated filler particles or fibers just before or during the dispersion of said filler particles or fibers into a polymer matrix.
22. The method of any one of claims 3, 18 or 19, wherein said method additionally comprises dispersing graphene platelets with high aspect ratio in two dimensions into the polymer matrix.
23. The method according to claim 28, wherein said graphene platelets are dispersed at a concentration of 0.1 vol% to 1 vol%.
24. A high dielectric constant ceramic filler particle, wherein
- a. said filler particle contains between 50% and 100% high dielectric constant perovskite structures;
 - b. said filler particle has a relative dielectric constant of greater than 80;
 - c. the smallest cross-section of said filler particle is less than 2 microns; and
 - d. said filler particle has an aspect ratio greater than 2.
25. A high dielectric constant ceramic filler particle according to claim 24, wherein said filler particle comprises at least one ferroelectric ceramic.
26. A high dielectric constant ceramic filler particle according to claim 25, wherein the at least one ferroelectric ceramic is selected from BaTiO₃, BaSrTiO₃, PbTiO₃, PbZrO₃ and SrTiO₃.

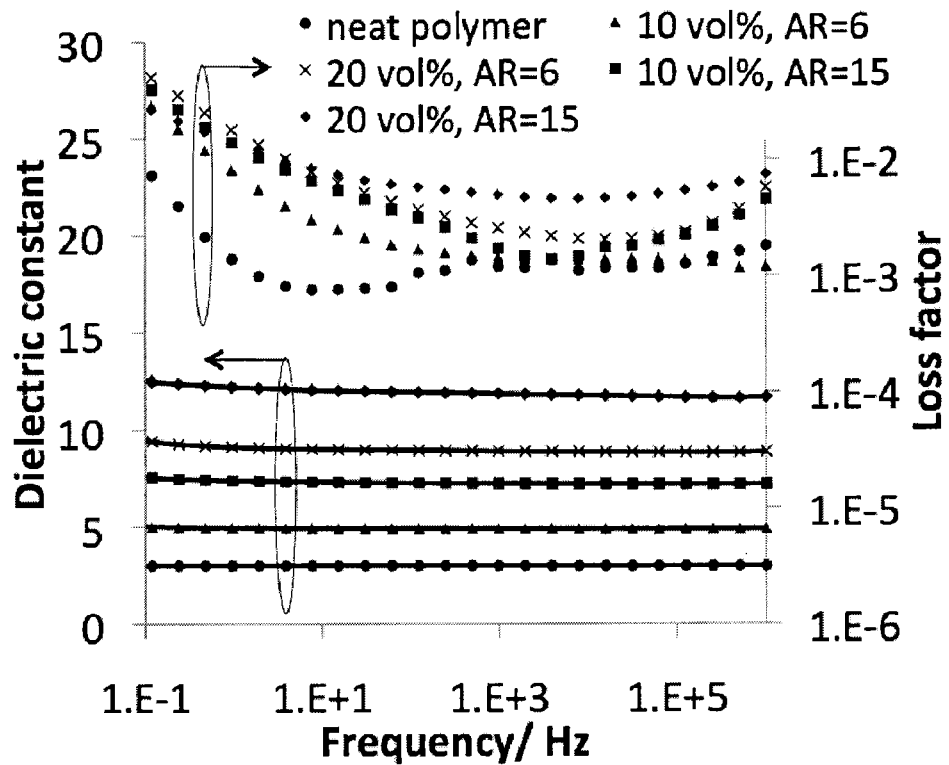
27. A high dielectric constant ceramic filler particle according to claim 26, wherein the ceramic comprises BaTiO_3 .
28. A high dielectric constant ceramic filler particle according to claim 24, wherein said filler particle is a fiber with an aspect ratio between 2 and 100.
29. A high dielectric constant ceramic filler particle according to claim 28, wherein said filler particle is a fiber with an aspect ratio between 2 and 60.
30. A high dielectric constant ceramic filler particle according to claim 29, wherein said filler particle is a fiber with an aspect ratio between 2 and 30.
31. A high dielectric constant ceramic filler particle according to claim 30, wherein said filler particle is a fiber with an aspect ratio between 2 and 15.
32. A high dielectric constant polymer composite material, said material comprising
 - a. a high dielectric constant ceramic filler particle, wherein the smallest cross-section of said filler particle is less than 2 microns and the aspect ratio is between 2 and 100, said filler particle containing between 50% and 100% perovskite structures; and
 - b. a matrix polymer.
33. A high dielectric constant polymer composite material according to claim 32 wherein said filler particles comprise from 5 to 50 percent by volume of said high dielectric constant polymer composite material.
34. A high dielectric constant ceramic filler particle according to claim 32 or 33, wherein said filler particle comprises at least one ferroelectric ceramic.
35. A high dielectric constant ceramic filler particle according to claim 34, wherein the at least one ferroelectric ceramic is selected from BaTiO_3 , BaSrTiO_3 , PbTiO_3 , PbZrO_3 and SrTiO_3 .
36. A high dielectric constant ceramic filler particle according to claim 35, wherein the ceramic comprises $\text{BaTi}(\frac{3}{4})$.
37. A high dielectric constant ceramic filler particle according to claim 32, wherein said filler particle is a fiber with an aspect ratio between 2 and 60.
38. A high dielectric constant ceramic filler particle according to claim 37, wherein said filler particle is a fiber with an aspect ratio between 2 and 30.
39. A high dielectric constant ceramic filler particle according to claim 38, wherein said filler particle is a fiber with an aspect ratio between 2 and 15.

40. A high dielectric constant polymer composite material according to any one of claims 32-33 wherein said matrix polymer is selected from silicone, EPDM, polyethylene, polypropylene, polyisobutylene, amorphous polypropylene, an epoxy resin, and combinations thereof.
41. A high dielectric constant polymer composite material according to claim 32 comprising barium titanate filler particles in a cross-linked silicone rubber matrix.
42. A high dielectric constant polymer composite material obtainable by the process of any of claims 3 or 18-23.
43. An electric field control device for grading an electric field at an interruption of the insulation layer arranged around the conductor in a medium or high-voltage cable, wherein the device comprises a high dielectric constant polymer composite material according to any one of claims 32-41 .
44. An electric field control device according to claim 43, wherein the high dielectric constant polymer composite material is arranged circumferentially around the interruption of the insulation and in contact with the conductor of the cable and with the grounded screen of the cable.
45. Use of a high dielectric constant polymer composite material according to any one of claims 32-41 for grading an electric field in a cable termination or a cable joint.
46. Use of a high dielectric constant polymer composite material according to any one of claims 32-41 as a component of an electrical insulator.
47. Use of a high dielectric constant polymer composite material according to claim 46 as a component of a bushing.
48. Use of a high dielectric constant polymer composite material according to any one of claims 32-41 as a component of an electrical machine.

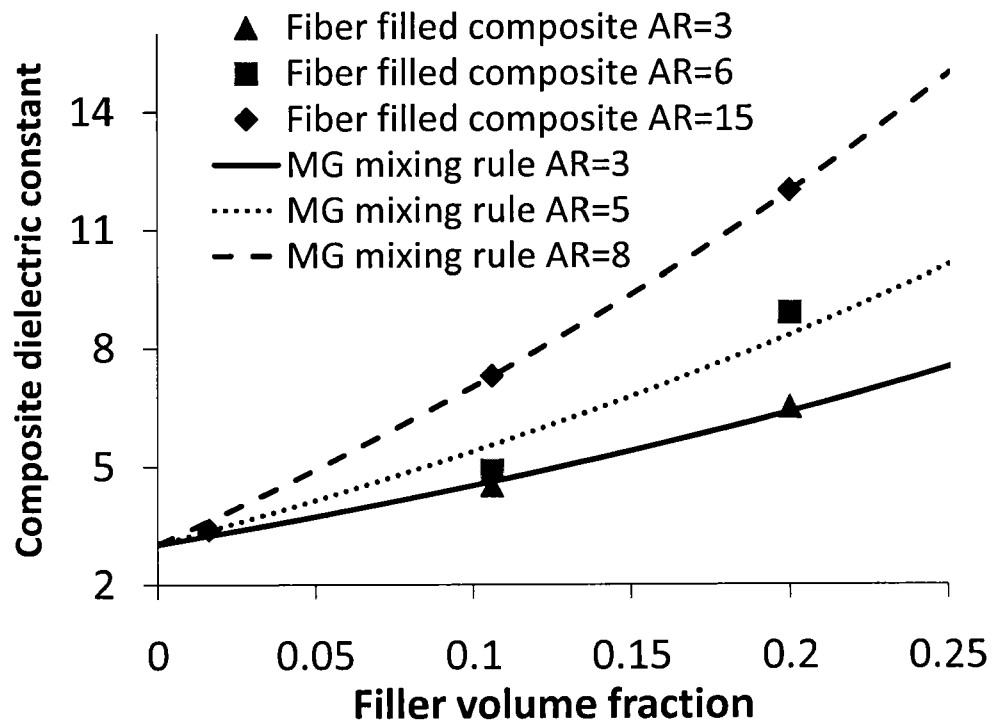
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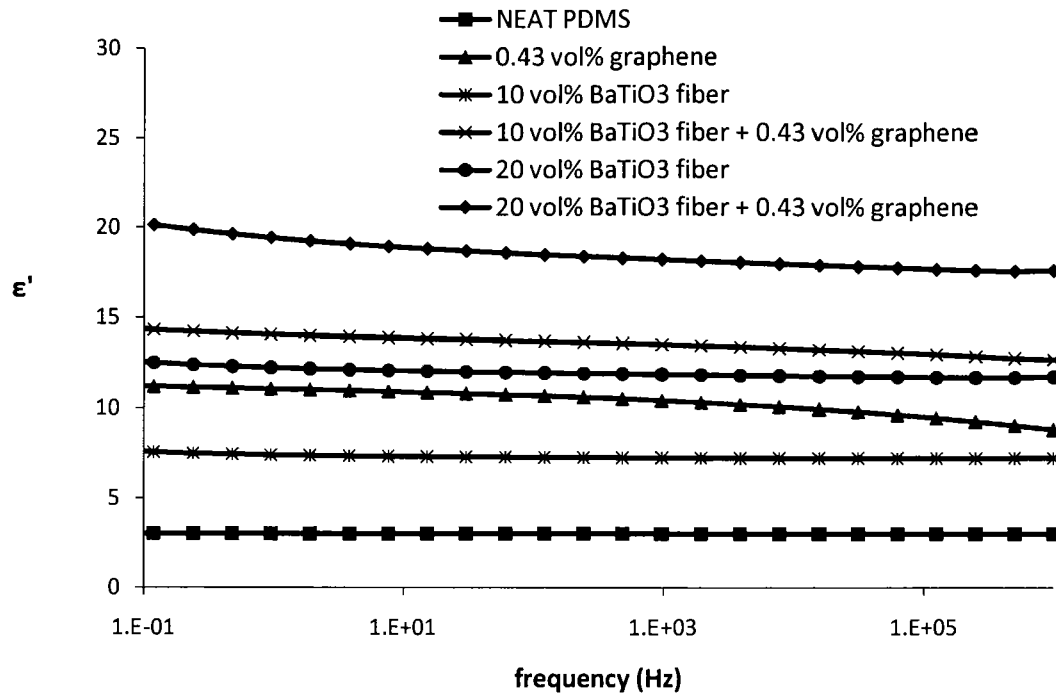


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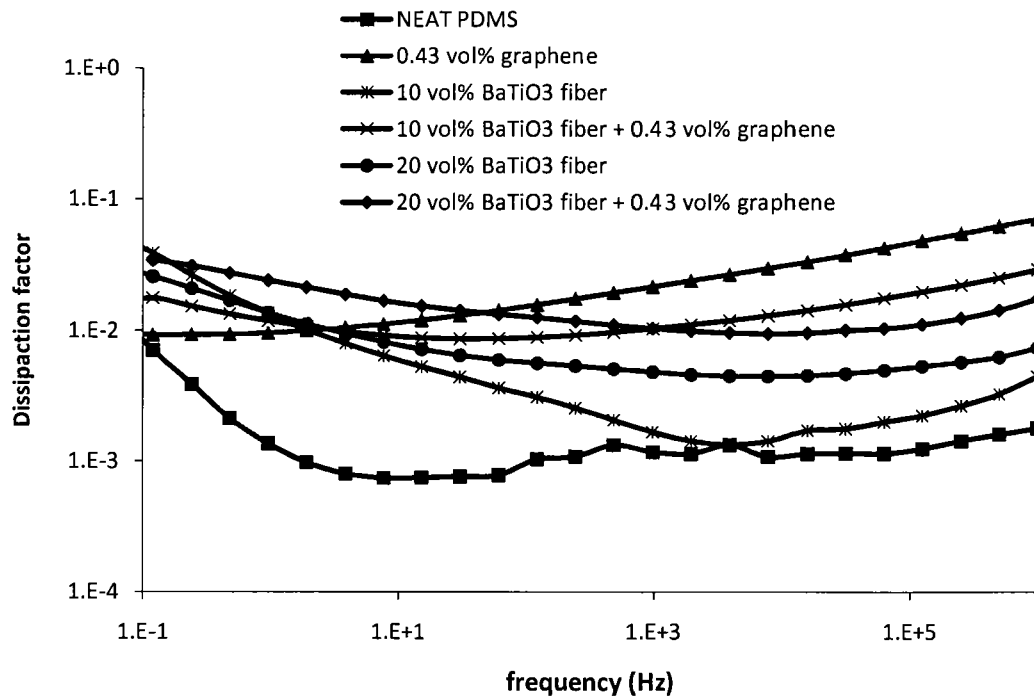
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