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- (54) **Title:** BIMODAL DIELECTRIC NANOPARTICLES AND NANOCOMPOSITES

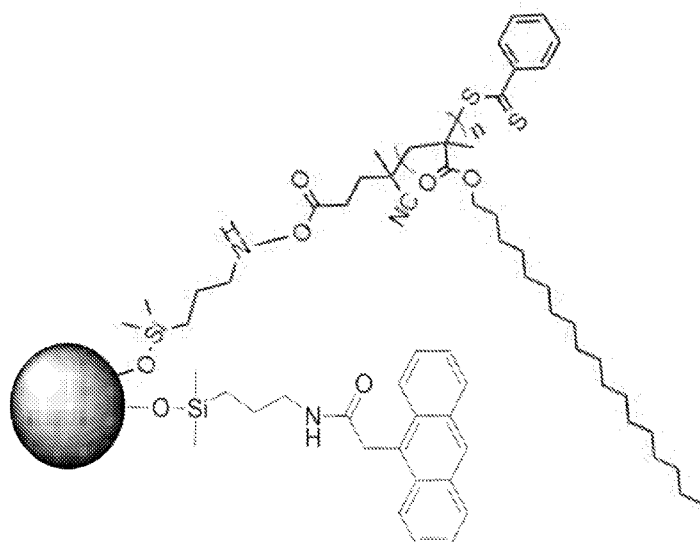


FIG. 14

(57) **Abstract:** The present invention relates to a bimodal dielectric nanoparticle comprising a nanoparticle having a core modified with a population of functional short ligands and with a population of matrix compatible long ligands. The short ligand comprises an electroactive molecule, and the long ligand comprises a polymer that is compatible with a matrix of the nanoparticle and that extends beyond the short ligand in relation to the nanoparticle core. The present invention also relates to a dielectric nanocomposite comprising a plurality of bimodal dielectric nanoparticles of the present disclosure and a matrix compatible with the bimodal dielectric nanoparticle. The present invention further relates to methods of making the bimodal dielectric nanoparticles and the dielectric nanocomposites of the present disclosure.



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GW, KM, ML, MR, NE, SN, TD, TG).

BIMODAL DIELECTRIC NANOPARTICLES AND NANOCOMPOSITES**CROSS-REFERENCE TO RELATED APPLICATIONS**

- 5 **[0001]** This application claims priority benefit of U.S. Provisional Patent Application Serial No. 61/883,387, filed September 27, 2013, the disclosure of which is hereby incorporated by reference herein in its entirety.

FIELD OF THE INVENTION

- 10 **[0002]** The present invention relates to nanoparticles that have been modified with a bimodal population of surface ligands (bimodal dielectric nanoparticles) and dielectric nanocomposites containing a plurality of the bimodal dielectric nanoparticles. The present invention also relates to methods of making the bimodal dielectric nanoparticles and the dielectric nanocomposites of the present disclosure. The present invention further relates to
- 15 the use of the bimodal dielectric nanoparticles and the dielectric nanocomposites in various electrical applications, as well as to electrical devices, materials, and components comprising the bimodal dielectric nanoparticles and dielectric nanocomposites of the present disclosure.

BACKGROUND OF THE INVENTION

- 20 **[0003]** Nanodielectrics, or dielectric polymer nanocomposites, can exhibit significant improvements in endurance strength and dielectric breakdown strength compared to the unfilled polymer (T. Tanaka, G. Montanari and R. Mulhaupt, "Polymer nanocomposites as dielectrics and electrical insulation-perspectives for processing technologies, material characterization and future applications", IEEE Trans. Dielectr. Electr. Insul., vol. 11, pp.
- 25 763-784, 2004; M. Roy, J. Nelson, R. MacCrone, L. Schadler, C. Reed, R. Keefe and W. Zenger, "Polymer nanocomposite dielectrics - The role of the interface", IEEE Trans. Dielectr. Electr. Insul., vol. 12, pp. 629-643, 2005; M. Takala, H. Ranta, P. Nevalainen, P. Pakonen, J. Pelto, M. Karttunen, S. Virtanen, V. Koivu, M. Pettersson, B. Sonnerud and K. Kannus, "Dielectric properties and partial discharge endurance of polypropylene-silica
- 30 nanocomposite", IEEE Trans. Dielectr. Electr. Insul., vol. 17, pp. 1259-1267, 2010; and R. C. Smith, J. K. Nelson and L. S. Schadler, "Electrical behavior of particle filled polymer nanocomposites", Physical Properties of Polymer Nanocomposites, 3rd ed., S. J. Tjong and Y.-M. Mai, Eds. Cambridge, UK, Woodhead Publishing, 2010). There are experimental results suggesting that in addition to controlling the dispersion of particles, controlling the relative
- 35 polar or nonpolar nature of the particle surface will allow for property optimization (C. A. Grabowski, S. P. Fillery, N. M. Westing, C. Chi, J. S. Meth, M. F. Durstock and R. A. Vaia,

“Dielectric breakdown in silica-amorphous polymer nanocomposite films: The Role of the polymer matrix”, *ACS Appl. Mater. Interfaces*, vol5, pp. 5486-5492, 2013).

[0004] In addition, directly bonding the particle to the polymer matrix has been shown to prevent conductive percolation across particle surfaces resulting in reduced interfacial polarization within the composite and increased dielectric breakdown strength (T.P. Schuman, S. Siddabattuni, O. Cox, F. Dogan, "Improved dielectric breakdown strength of covalently-bonded interface polymer-particle nanocomposites", *Composite Interfaces*, vol 17, pp. 719-731, 2010). Furthermore, significant reduction in leakage currents and dielectric losses and improvement in dielectric breakdown strengths have resulted when phenyl rings with electron-withdrawing functional groups were grafted to the particle surface (S.Siddabattuni, T.P. Schuman, F. Dogan, "Dielectric properties of polymer-particle nanocomposites influenced by electronic nature of filler surfaces", *ACS Appl. Mater. Interfaces*, vol 5, pp. 1917–1927, 2013). The challenge in this prior work is that the nanoparticle dispersion was intrinsically linked to the modification of the nanoparticles with surface ligands. Nanofiller dispersion is also well known to impact dielectric properties. Therefore, it would be beneficial to independently control the dielectric properties of the nanoparticle/matrix interface and the nanoparticle dispersion.

[0005] The present invention is directed to overcoming these and other deficiencies in the art.

SUMMARY OF THE INVENTION

[0006] The present invention relates to a bimodal dielectric nanoparticle comprising a nanoparticle having a core modified with a population of functional short ligands and with a population of matrix compatible long ligands. The short ligand comprises an electroactive molecule, and the long ligand comprises a polymer that is chemically compatible with a matrix and that extends beyond the short ligand in relation to the nanoparticle core.

[0007] The present invention also relates to a dielectric nanocomposite comprising a plurality of bimodal dielectric nanoparticles of the present disclosure and a matrix compatible with the bimodal dielectric nanoparticle.

[0008] The present invention further relates to a method of making a bimodal dielectric nanoparticle of the present disclosure. This method involves (i) providing a nanoparticle having a core and (ii) grafting a population of functional short ligands and a population of matrix compatible long ligands onto the core of the nanoparticle, thereby yielding a bimodal dielectric nanoparticle. The short ligand comprises an electroactive

molecule, and the long ligand comprises a polymer that is compatible with a matrix of the nanoparticle and that extends beyond the short ligand in relation to the nanoparticle core.

[0009] The present invention also relates to a method of making a dielectric nanocomposite. This method involves (i) providing a plurality of bimodal dielectric nanoparticles of the present disclosure; and (ii) dispersing the plurality of bimodal dielectric nanoparticles in a matrix to form a dielectric nanocomposite.

[0010] The present invention further relates to the use of the bimodal dielectric nanoparticles and the dielectric nanocomposites in various electrical applications, as well as to electrical devices, materials, and components comprising the bimodal dielectric nanoparticles and dielectric nanocomposites of the present disclosure.

[0011] Therefore, the present invention also relates to a composition for use in electrical applications, where the composition comprises bimodal dielectric nanoparticles or dielectric nanocomposites of the present disclosure.

[0012] In one aspect, the present disclosure provides a new dielectric polymer-matrix nanocomposite and novel techniques for preparing the dielectric nanocomposite. In various embodiments, the dielectric nanocomposite exhibits improved dielectric breakdown strengths and customizable dielectric constants that allow for improved operation and operating lifetime in insulating and capacitive applications. The dielectric nanocomposite of the present disclosure utilizes low filler loadings, allowing for the use of existing polymer processing techniques. Additionally, the method for making the dielectric nanocomposite of the present disclosure can be used without the need for expensive elements and compounds. For example, the methods enable the ability to achieve various dielectric property increases without needing to use rare earth elements.

[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 drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] For the purpose of illustrating aspects of the present invention, there are depicted in the drawings certain embodiments of the invention. However, the invention is not limited to the precise arrangements and instrumentalities of the embodiments depicted in the drawings. Further, as provided, like reference numerals contained in the drawings are meant to identify similar or identical elements.

[0015] Figure 1 is a schematic illustrating a surface modification process of silica to afford bimodal brush grafted core functionalized nanoparticles.

[0016] Figures 2A-2C are schematics showing the chemical structure of entities attached to azide linker at silica core by click reaction: FIG. 2A: alkyne terminated oligothiophene. FIG. 2B: ethynylferrocene. FIG. 2C: alkyne terminated PGMA.

[0017] Figure 3 is a graph showing 2 and 3-parameter Weibull fits plotted with breakdown data from neat epoxy.

[0018] Figures 4A-4B are graphs showing: (i) IR spectra of bare, monomodal and bimodal particles (FIG. 4A) where the peak at 840 is characteristic of SiO_2 ; and (ii) the area of interest: arrows show disappearing $\text{N}=\text{N}=\text{N}$ vibration at 2110 cm^{-1} and intense $\text{C}=\text{O}$ peak at 1736 cm^{-1} in bimodal particles (FIG. 4B). Note that the "PGMA-thio" and "PGMA-oligothiophene" refer to the same filler system.

[0019] Figure 5 is a schematic representation of one embodiment of a bimodal brush grafted core functionalized silica nanoparticle. The short brush is oligothiophene and long brush is PGMA.

[0020] Figure 6 is a photograph illustrating transparency of composites from block samples made for TEM analysis. From left: 1 wt% bare silica, 2 wt% silica-PGMA, 2 wt% silica-PGMA-oligothiophene and 2 wt% silica-PGMA-ferrocene in epoxy.

[0021] Figures 7A-7D are TEM images of epoxy composites with: (i) 1 wt% bare silica (FIG. 7A); (ii) 2 wt% silica-PGMA (FIG. 7B); (iii) 2 wt% silica-PGMA-oligothiophene (FIG. 7C); and (iv) 2 wt% silica-PGMA-ferrocene (FIG. 7D).

[0022] Figure 8 is a graph illustrating a 3-Parameter Weibull Plot of breakdown data for neat epoxy and the 2 wt% composites.

[0023] Figures 9A-9B are graphs showing (i) real component of permittivity (FIG. 9A) and (ii) the loss component (FIG. 9B) as a function of frequency for neat epoxy, bare silica filled composite and for composites which have an electroactive layer and epoxy compatible polymer layer on the filler particle core.

[0024] Figure 10 is a graph showing Weibull fits of breakdown data for neat epoxy, and epoxy filled with 2 wt% of silica of the composites listed in Table 2.

[0025] Figures 11A-11B are graphs illustrating space charge measured at various times during polarization (FIG. 11A) and depolarization (FIG. 11B) of neat epoxy. The anode is the bottom electrode and the cathode is the top electrode.

[0026] Figure 12 is a graph illustrating the decay space charge density of various samples, each at a 2% loading. Refer to Table 2 for sample specifications. Dotted lines are fitted to the slopes of the decay curves, one for each trap distribution.

[0027] Figure 13 is a graph illustrating thermally stimulated depolarization current data from a neat epoxy sample and a bimodal anthracene composite polarized at 15 kV/mm. Peaks are labeled corresponding to Table 5.

[0028] Figure 14 is a schematic for a modified silica nanoparticle filler of one embodiment of the present disclosure. The schematic shows the silica particle (in grey) with attached poly stearyl methacrylate (PSMA) long chains (top) and the attached anthracene functional groups (bottom).

[0029] Figure 15 is a graph illustrating improvements in dielectric breakdown strength in a system according to the one shown in Figure 14, which includes a modified silica nanoparticle filler that can be used in a matrix such as a polypropylene matrix.

DETAILED DESCRIPTION OF THE INVENTION

[0030] The present invention generally relates to bimodal dielectric nanoparticles and dielectric nanocomposites containing a plurality of the bimodal dielectric nanoparticles. The present invention also relates to methods of making the bimodal dielectric nanoparticles and the dielectric nanocomposites of the present disclosure. The present invention further relates to the use of the bimodal dielectric nanoparticles and the dielectric nanocomposites in various electrical applications, as well as to electrical devices, materials, and components comprising the bimodal dielectric nanoparticles and dielectric nanocomposites of the present disclosure.

[0031] In one aspect, the present invention relates to a bimodal dielectric nanoparticle comprising a nanoparticle having a core modified with a population of functional short ligands and with a population of matrix compatible long ligands. The short ligand comprises an electroactive molecule, and the long ligand comprises a polymer that is compatible with a matrix of the intended composite and that extends beyond the short ligand in relation to the nanoparticle core.

[0032] The bimodal dielectric nanoparticle of the present disclosure is advantageous over the existing technology, in that the electroactive molecule is effective to improve a dielectric characteristic of the nanoparticle by altering the dielectric properties of the interface and maintaining good nanoparticle dispersion. Thus, in accordance with one aspect, the bimodal nanoparticles are advantageous over the existing art because they allow for one to independently tune the dielectric properties of the interface and the nanoparticle dispersion. Without meaning to limit the scope of the present disclosure, in certain embodiments, the improved dielectric characteristics of the bimodal dielectric nanoparticle of the present disclosure can include, without limitation, dielectric breakdown strength (DBS), endurance strength, dielectric constant, dielectric loss, non-linear dielectric response, complex

permittivity, and conductivity. Without meaning to limit the scope of the present disclosure, “good nanoparticle dispersion” can refer to a nanoparticle dispersion having a preponderance of agglomerates smaller than about 200 nanometers in diameter.

[0033] The bimodal dielectric nanoparticle can comprise various nanoparticles. In one embodiment, the nanoparticle can include, without limitation, an inorganic nanoparticle. Suitable inorganic nanoparticles can include, without limitation, silica, alumina, titania, indium tin oxide, CdSe, zirconia, ZnO, MgO, CuO, AgO, barium titanate, and the like, or mixtures thereof.

[0034] The bimodal dielectric nanoparticle can be used with various matrices. Any matrix suitable for use with the bimodal dielectric nanoparticle of the present disclosure is contemplated herein. In various embodiments, a suitable matrix can include, without limitation, epoxy, polypropylene, silicone, polyethylene, polyamide, polyimide, polyethyleneterephthalate, and polyetherimide, or mixtures thereof.

[0035] In accordance with embodiments of the present disclosure, the electroactive molecule of the bimodal dielectric nanoparticle can be directly grafted to the nanoparticle or indirectly grafted to the nanoparticle by a linking polymer chain. In a particular embodiment, the linking polymer chain can be a short polymer chain. Regardless of the length of the linking polymer chain, in certain embodiments, the electroactive molecule can be a functional group of the linking polymer chain (e.g., of the short polymer chain), and more specifically can be a side group of the linking polymer chain (e.g., the short polymer chain).

[0036] In particular embodiments, the electroactive molecule can include, without limitation, a metallocene, a substituted or unsubstituted cyclic or polycyclic aromatic hydrocarbon, and functional derivatives thereof. In these embodiments, the electroactive molecule can further include an electron donating group and/or an electron withdrawing group. Examples of certain electron donating or electron withdrawing groups can include, without limitation, amine groups, nitro groups, etc.

[0037] In certain embodiments, the electroactive molecule can include, without limitation, an oligothiophene compound, an oligoaniline compound, ferrocene, benzene, pentacene, anthracene, naphthalene, and the like, or functional derivatives thereof.

[0038] In certain embodiments, the matrix compatible polymer of the bimodal dielectric nanoparticle of the present disclosure can include, without limitation, poly(glycidyl methacrylate) (PGMA), poly stearyl methacrylate (PSMA), epoxy, polypropylene, silicone, polyethylene, polyamide, polyimide, polyethyleneterephthalate, polyetherimide, polymethylmethacrylate, polystyrene, polyacrylate, and derivatives thereof.

[0039] As discussed herein, the bimodal dielectric nanoparticle of the present disclosure includes a population of functional short ligands and a population of matrix compatible long ligands (e.g., long ligands that are chemically compatible with the matrix). In certain embodiments, the short and long ligands are directly or indirectly covalently grafted onto the core of the nanoparticle.

[0040] In various embodiments, the short ligands are grafted to the nanoparticle core at a high density and the long ligands are grafted to the nanoparticle core at a low density relative to that of the short ligands. More particularly, in certain embodiments, the high density of the short ligands ranges from about 0.1 to about 1.0 ligand chain per square nanometer (nm^2), and the low density of the long ligands ranges from about 0.02 to about 0.2 ligand chain per square nanometer (nm^2).

[0041] The present invention further relates to a method of making a bimodal dielectric nanoparticle of the present disclosure. This method involves (i) providing a nanoparticle having a core and (ii) grafting a population of functional short ligands and a population of matrix compatible long ligands onto the core of the nanoparticle, thereby yielding a bimodal dielectric nanoparticle. The short ligand comprises an electroactive molecule, and the long ligand comprises a polymer that is compatible with a matrix of the nanoparticle and that extends beyond the short ligand in relation to the nanoparticle core.

[0042] In one embodiment of this method, the population of functional short ligands is grafted onto the nanoparticle core prior to the grafting on of the population of long ligands. Suitable techniques and materials for grafting the ligands onto the nanoparticle are known in the relevant art.

[0043] The various nanoparticles, matrices, electroactive molecules, matrix compatible polymers, short ligands, and long ligands as described above in reference to the bimodal dielectric nanoparticles of the present disclosure are also useful in the method of making the bimodal dielectric nanoparticles.

[0044] According to one embodiment of this method, the short and long ligands can be directly or indirectly grafted onto the core of the nanoparticle at various densities. In certain embodiments, the short ligands are grafted onto the core at a high density while the long ligands are grafted onto the core at a low density relative to the density of the short ligands. In particular embodiments, in accordance with this method, the short ligands ranges from about 0.1 to about 1.0 ligand chain per square nanometer (nm^2), and wherein the low density of the long ligands ranges from about 0.02 to about 0.2 ligand chain per square nanometer (nm^2).

[0045] The present invention also relates to a dielectric nanocomposite comprising a plurality of bimodal dielectric nanoparticles of the present disclosure and a matrix compatible with the bimodal dielectric nanoparticle.

[0046] The various nanoparticles, matrices, electroactive molecules, matrix compatible polymers, short ligands, and long ligands as described above in reference to the bimodal dielectric nanoparticles of the present disclosure are contemplated for the dielectric nanocomposite of the present disclosure.

[0047] In certain embodiments of the dielectric nanocomposite of the present disclosure, the bimodal dielectric nanoparticles are dispersed in the matrix.

[0048] In particular embodiments, the bimodal dielectric nanoparticles form agglomerations having an average size that is less than about 200 nanometers (nm).

[0049] The electroactive molecule of the bimodal dielectric nanoparticle provides electroactive functionality to the dielectric nanocomposite. In certain embodiments, the dielectric nanocomposite has improved dielectric breakdown strength (DBS) compared to a nanocomposite having the same nanoparticle core but not the same population of short and long ligands.

[0050] The present invention also relates to a method of making a dielectric nanocomposite. This method involves (i) providing a plurality of bimodal dielectric nanoparticles of the present disclosure; and (ii) dispersing the plurality of bimodal dielectric nanoparticles in a matrix to form a dielectric nanocomposite.

[0051] The various nanoparticles, matrices, electroactive molecules, matrix compatible polymers, short ligands, and long ligands as described above in reference to the bimodal dielectric nanoparticles of the present disclosure are also useful in the method of making the dielectric nanocomposites of the present disclosure.

[0052] In a particular embodiment of this method, the bimodal dielectric nanoparticles are made by a process comprising: (i) providing the plurality a nanoparticles having a core; and (ii) grafting a population of functional short ligands and a population of matrix compatible long ligands onto the core of the nanoparticle, thereby yielding the plurality of bimodal dielectric nanoparticles, where the short ligand comprises an electroactive molecule, and where the long ligand comprises a polymer that is compatible with a matrix of the nanoparticle and that extends beyond the short ligand in relation to the nanoparticle core.

[0053] In one embodiment of this method of making the dielectric nanocomposite of the present disclosure, the population of functional short ligands is grafted onto the nanoparticle core prior to the grafting on of the population of long ligands. Suitable

techniques and materials for grafting the ligands onto the nanoparticle are known in the relevant art.

[0054] As provided herein, the bimodal dielectric nanoparticles and the dielectric nanocomposites of the present disclosure have dielectric properties and electric strength that are suitable for use as devices, materials, and/or components in a variety of electrical applications. Thus, in another aspect, the present invention further relates to the use of the bimodal dielectric nanoparticles and the dielectric nanocomposites in various electrical applications, as well as to electrical devices, materials, and components comprising the bimodal dielectric nanoparticles and dielectric nanocomposites of the present disclosure.

[0055] Without intending to limit the scope of the present disclosure, the bimodal dielectric nanoparticles and the dielectric nanocomposites of the present disclosure can be used in electrical applications that include, without limitation, the following: high voltage alternating current (HVAC) and high voltage direct current (HVDC) capacitor films; HVAC and HVDC cable insulation; motor/machine insulation; and impregnation media of a porous matrix comprising at least one of the following: paper, cellulose, glass or mica. Any such impregnated but dry insulation systems containing the bimodal dielectric nanoparticles or dielectric nanocomposites of the present disclosure can be used in dry bushings or machine stator bars.

[0056] Thus, according to one aspect, the present invention also relates to a composition for use in electrical applications, where the composition comprises bimodal dielectric nanoparticles or dielectric nanocomposites of the present disclosure.

[0057] In various embodiments, the composition comprises an electrical device, material, or component selected from the group consisting of high voltage alternating current (HVAC) capacitor films, high voltage direct current (HVDC) capacitor films, HVAC cable insulation, HVDC cable insulation, motor/machine insulation, and impregnation media of a porous matrix, where the porous matrix comprises at least one of paper, cellulose, glass, or mica. Any compositions such as impregnated but dry insulation systems can be used in dry bushings, machine stator bars, and the like.

EXAMPLES

[0058] The following examples are intended to illustrate particular embodiments of the present invention, but are by no means intended to limit the scope of the present invention.

EXAMPLE 1**Dielectric Breakdown Strength of Epoxy Bimodal-Polymer-Brush-Grafted Core Functionalized Silica Nanocomposites**

[0059] The central goal of dielectric nanocomposite design is to create a large
5 interfacial area between the matrix polymer and nanofillers and to use it to tailor the properties of the composite. The interface can create sites for trapping charge carriers leading to increased dielectric breakdown strength (DBS). Nanoparticles with a bimodal population of covalently anchored molecules were created using ligand engineering. Electrically active short molecules (oligothiophene or ferrocene) and matrix compatible long
10 poly(glycidyl methacrylate) (PGMA) chains comprise the bimodal brush. The dielectric breakdown strength was evaluated from recessed samples and dielectric spectroscopy was used to study the dielectric constant and loss as a function of frequency. The dielectric breakdown strength and permittivity increased considerably with only 2 wt% filler loading while the dielectric loss remained comparable to the reference epoxy.

15 [0060] Although the large interfacial area is a key component in improving the breakdown strength, it also presents a challenge: nanoscale fillers tend to agglomerate, reducing the impact of the filler. A brush of polymer chains tethered to the filler particles can be used to overcome this challenge. By using matrix compatible polymer brushes the particles can be chemically compatibilized with the matrix (S. Milner, "Polymer brushes",
20 Science, vol. 251, pp. 905-914, FEB 22, 1991; A. C. Balazs, T. Emrick and T. P. Russell, "Nanoparticle polymer composites: where two small worlds meet," Science, vol. 314, pp. 1107-1110, November 17, 2006) and dispersed, retaining their surface-to-volume ratio. Especially beneficial is a bimodal brush geometry: one population of high graft density short functional molecules and the other of low graft density long matrix compatible chains. This
25 design allows particles to disperse even if the short brush is incompatible with the matrix (D. Maillard, S. K. Kumar, A. Rungta, B. C. Benicewicz and R. E. Prud'homme, "Polymer-grafted-nanoparticle surfactants," Nano Lett., vol. 11, pp. 4569-4573, NOV, 2011).

[0061] There are two methods for producing these brushes: the "grafting to" approach where chains are polymerized and subsequently attached to the surface (K. Yang, X. Huang,
30 L. Xie, C. Wu, P. Jiang and T. Tanaka, "Core-shell structured polystyrene/BaTiO₃ hybrid nanodielectrics prepared by in situ RAFT polymerization: A route to high dielectric constant and low loss materials with weak frequency dependence", Macromol. Rapid Commun., vol. 33, pp. 1921-1926, NOV 23, 2012), and a "grafting from" approach, during which polymerization takes place from a site on the surface of the particle. The latter has the

advantage of achieving high graft densities because steric hindrance does not inhibit the attachment of additional chains.

[0062] The “grafting to” approach however, is quick and easy to scale up and provides more flexibility in the chemistry of the attached molecule. “Grafting to” lacks control over graft density (B. Zhao and W. Brittain, "Polymer brushes: surface-immobilized macromolecules", *Prog. Polym. Sci.*, vol. 25, pp. 677-710, JUN, 2000) but good dispersion of particles has been observed using this approach (G. D. Smith and D. Bedrov, "Dispersing nanoparticles in a polymer matrix: are long, dense polymer tethers really necessary?" *Langmuir*, vol. 25, pp. 11239-11243, 2009) and a parametric phase diagram has been experimentally validated to predict the dispersion of bimodal-polymer-brush “grafted to” nanoparticles (Y. Li, P. Tao, A. Vishwanath, B. C. Benicewicz, and L. S. Schadler, "Bimodal surface ligand engineering: The key to tunable nanocomposites," *Langmuir*, 29, 1211-1220, 2013).

[0063] “Grafting to” can be done using “click” chemistry. This type of reaction proceeds rapidly to completion and also tends to be highly selective for a single product (H. Kolb, M. Finn and K. Sharpless, "Click chemistry: Diverse chemical function from a few good reactions", *Angewandte Chemie-International Edition*, vol. 40, pp. 2004, 2001). This approach has been used for functionalization of silica (T. Lummerstorfer and H. Hoffmann, "Click chemistry on surfaces: 1,3-dipolar cycloaddition reactions of azide-terminated monolayers on silica", *J Phys Chem B*, vol. 108, pp. 3963-3966, 2004; Y. Wang, J. Chen, J. Xiang, H. Li, Y. Shen, X. Gao and Y. Liang, "Synthesis and characterization of end-functional polymers on silica nanoparticles via a combination of atom transfer radical polymerization and click chemistry", *React Funct Polym*, vol. 69, pp. 393-399, 2009; R. Ranjan and W. J. Brittain, "Combination of living radical polymerization and click chemistry for surface modification", *Macromolecules*, vol. 40, pp. 6217-6223, 2007; D. E. Achatz, F. J. Heiligt, X. Li, M. Link and O. S. Wolfbeis, "Colloidal silica nanoparticles for use in click chemistry-based conjugations and fluorescent affinity assays", *Sensors and Actuators B-Chemical*, vol. 150, pp. 211-219, 2010) and also used as way to make “matrix free” silica polymer composite by using alkyne and azide modified polymer brushes on silica (B. I. Dach, H. R. Rengifo, N. J. Turro and J. T. Koberstein, "Cross-linked "matrix-free" nanocomposites from reactive polymer-silica hybrid nanoparticles", *Macromolecules*, vol. 43, pp. 6549-6552, 2010).

[0064] Polyglycidylmethacrylate (PGMA) has been “grafted to” TiO₂ nanoparticles and mixed into an epoxy matrix resulting in a composite with high refractive index and transparency (P. Tao, Y. Li, A. Rungta, A. Viswanath, J. Gao, B. C. Benicewicz, R. W.

Siegel and L. S. Schadler, "TiO₂nanocomposites with high refractive index and transparency", *Journal of Materials Chemistry*, vol. 21, pp. 18623-18629, 2011).

Additionally, it has been shown to have minimal effects on the crosslinking density of epoxy composites as a whole when grafted to silica nanoparticles (J. Gao, Juntao Li, Brian C.

- 5 Benicewicz, S. Zhao, H. Hillborg, and L.S. Schadler, "The mechanical properties of epoxy composites filled with rubbery copolymer grafted SiO₂", *Polymers* 4 (1) 187–210, 2012).

[0065] Electroactive molecules have been attached to polymers grafted to a silica particle surface and the electroactivity of the molecules has been retained (Y. Li and B. C. Benicewicz, "Functionalization of silica nanoparticles via the combination of surface-initiated
10 RAFT polymerization and click reactions", *Macromolecules*, vol. 41, pp. 7986-7992, 2008).

Electron acceptors like oligothiophene and ferrocene can be attached using click chemistry (S. Potratz, A. Misra and P. Bäuerle, "Thiophene-based Donor–Acceptor Co-oligomers by Copper-catalyzed 1,3-dipolar Cycloaddition", *Beilstein J. Org. Chem.*, vol. 8, pp. 683, 2012; V. Ganesh, V. S. Sudhir, T. Kundu and S. Chandrasekaran, "10 Years of click chemistry:
15 synthesis and applications of ferrocene-derived triazoles", *Chemistry-an Asian Journal*, vol. 6, pp. 2670-2694, 4, 2011).

[0066] This example concentrates on the synthesis and dielectric properties of epoxy matrix nanocomposites with silica nanoparticles modified with a short ligand: oligothiophene or ferrocene to control the electrical properties and a long epoxy compatible ligand (PGMA)
20 that ensures optimal dispersion.

EXPERIMENTAL

The Interface:

- [0067] Silica particles were modified using copper(I)-catalyzed Huisgen 1,3-dipolar
25 cycloaddition of azides and terminal alkynes, known as [3+2] cycloaddition (CuAAC) reaction (R. Huisgen, *Angewandte Chemie*, vol. 75, pp. 604, 1963). Alkyne-terminated PGMA was received as a solution in tetrahydrofuran (THF) and synthesized as reported previously (P. Tao, Y. Li, A. Rungta, A. Viswanath, J. Gao, B. C. Benicewicz, R. W. Siegel and L. S. Schadler, "TiO₂nanocomposites with high refractive index and transparency",
30 *Journal of Materials Chemistry*, vol. 21, pp. 18623-18629, 2011). Alkyne functionalized oligothiophene was synthesized as follows: [2,2':5',2''-Terthiophene]-5-ethanol was prepared as outlined in the literature (W. Li, Y. Yamamoto, T. Fukushima, A. Saeiki, S. Seki, S. Tagawa, H. Masunga, S. Sasaki, M. Takata and T. Aida, "Amphiphilic molecular design as a rational strategy for tailoring bicontinuous electron donor and acceptor arrays:
35 Photoconductive liquid crystalline oligothiophene-C₆₀ dyads", *J. Am. Chem. Soc.*, vol.130,

pp. 8886-8887, 2008). To 50 ml of dry dichloromethane (DCM) [2,2':5',2''-Terthiophene]-5-ethanol (0.47 g, 1.6 mmol), 5-hexynoic acid (0.20g, 1.8 mmol) and 4-dimethylaminopyridine (16 mg, 0.13 mmol) were added. The solution was then cooled to 0°C and flushed with nitrogen before adding N,N'-dicyclohexylcarbodiimide (0.33 g, 1.6 mmol) in 10 ml of DCM drop wise over 30 min. The solution was allowed to warm to room temperature and react overnight. The resulting salts were filtered and the solvent removed under reduced pressure leaving a dark yellow solid. The resultant solid was then subjected to column chromatography (SiO₂, CHCl₃) yielding a bright yellow solid (0.54 g, 1.4 mmol) with 87% yield.

[0068] Nissan® MEK-ST colloidal silica was functionalized with 3-(Chloropropyl)trimethoxysilane (Sigma Aldrich) in order to be able to click polymers and oligomers to the core; previously reported reaction conditions were used (C. Li, J. Han, C. Y. Ryu and B. Benicewicz, "A versatile method to prepare RAFT agent anchored substrates and the preparation of PMMA grafted nanoparticles", *Macromolecules*, vol. 39, pp. 3175-3183, 2006).

[0069] Special care should be taken to minimize the possible explosion in the preparation and handling of the azide compound.

[0070] To give azide functionality to the silane linker; 3-(Chloropropyl)trimethoxysilane functionalized silica particles (0.59 g, 3 mmol) and sodium azide (Sigma Aldrich) (0.3 g, 5.52 mmol) were added into a 100 ml round bottom flask in dimethyl formamide (DMF) and refluxed at 100°C in an oil bath for 4 hours. After the reaction, the particles were precipitated with deionized water and excess sodium azide was washed with deionized water three times. The particles were dissolved in THF to form a clear solution. An aliquot for thermo gravimetric analysis (TGA) was taken and the concentration was determined (mg/ml).

[0071] To attach polymers and oligomers, 0.8g functionalized particles; azide (1 equiv), 0.04g ethynylferrocene or 0.08g alkyne terminated oligothiophene (1 equiv) and 0.2g alkyne terminated PGMA(1:10 equiv) and N,N,N',N'',N''' Pentamethyldiethylene-triamine (PMDTA) (Acros) 40µl (0.5 equiv) were added to 40 ml of THF. The mixture was degassed by bubbling argon gas for 5 minutes to get rid of oxygen before adding 14 mg CuBr (0.5 equiv). Cu(I)Br (99.999%, Aldrich) was purified with glacial acetic acid and washed with ethanol before use. The mixture was degassed by bubbling argon gas for an additional 5 minutes, and stirred for 24 hrs. Particles were precipitated using deionized water and centrifugation (4000 x g 10min) and re-suspended in THF. This step was done twice to wash away any free functional molecule and catalyst. All solvents used were A.C.S reagent grade.

Success of the bimodal-polymer-grafted core functionalized silica was verified with TGA, transmission infrared spectroscopy (IR) and UV-vis spectroscopy. The complete reaction scheme is shown in Figure 1 and the ligands attached by click reaction are shown in Figure 2.

[0072] To create a monomodal silica PGMA reference samples “grafting from”

5 synthesis known as surface-initiated reversible addition-fragmentation chain transfer (RAFT) polymerization was used. Details of this synthesis are shown in Example 2.

The Dielectric Composite:

[0073] Particles were mixed with Huntsman Araldite GY 2600; a bisphenol-A based
10 epoxy resin using a Hauschild high shear mixer (FlackTek). Solvent residue was evaporated in vacuum. Loading of silica was determined via TGA, and the resin was diluted and combined with aliphatic amine based Huntsman Aradur 956-2 hardener to achieve the appropriate final composite loading. The composite resin and hardener mixture was likewise mixed in a high shear mixer and then cast into the appropriate shapes. Recessed samples (I.
15 Ball, Proceedings of the IEE-part I, general, 84–86,1951;R. Fava, Proceedings of the Institution of Electrical Engineers;vol. 112,819,1965) were used for breakdown tests, disks were created for dielectric spectroscopy, and microtome samples were created and processed for transmission electron microscope (TEM) analysis.

[0074] The dispersion of the filler was determined from TEM images that were
20 converted to binary format. The free-space length, L_f between particles was calculated using MATLAB© to quantitatively characterize nanocomposite dispersion. A statistically large number of squares of prescribed size are placed in random locations on the binary image. The number of particles within each box is counted. L_f is chosen as the characteristic square size that corresponds to a length for which the mode of the boxes contains no particles. It is an
25 excellent parameter for properties that depend on the amount of modified polymer. It is not a magnitude that defines a unique dispersion, but rather corresponds to the unaffected polymer domains in the composite (H. S. Khare and D. L. Burris, "A quantitative method for measuring nanocomposite dispersion," Polymer, vol. 51, pp. 719-729, FEB 5, 2010).

[0075] The AC dielectric breakdown strength (DBS) was measured for all the
30 composite samples using a recessed geometry. Breakdown results were fitted with a two-parameter and a three-parameter Weibull distribution, whose cumulative distribution function is given by

$$F(x) = 1 - \exp \left\{ - \left(\frac{x - t}{\alpha} \right)^\beta \right\} \quad (1)$$

where $F(x)$ gives the probability of breakdown at a certain electric field strength x . The scale parameter α is related to the field strength at 63.2% probability of breakdown. The shape parameter, β , describes the shape of the distribution with higher values of β corresponding to narrower spreads of data. The location parameter, t , is used to better fit data which displays a downturn at low fields. This downturn is seen across all samples and composite formulations in this work. The two-parameter Weibull distribution is equivalent to a three-parameter Weibull with a t of zero. Both distributions are commonly used in empirical failure analysis (R.B. Abernethy, J.E. Breneman, C.H. Medlin, and G.L. Reinman, "Weibull Analysis Handbook". West Palm Beach, Florida.1983) and the use of a non-zero location parameter is recommended for this type of deviation from a two-parameter Weibull by IEEE standard 930 (*IEEE Guide for the Statistical Analysis of Electrical Insulation Breakdown Data*, 930, 2004). Figure 3 shows a comparison between the two-parameter and the three-parameter Weibull distribution. It is visually apparent that the two-parameter distribution does not adequately fit the data at low fields. A comparison of the two fits can be seen in Figure 3. The three-parameter Weibull distribution gives a coefficient of determination, R^2 , of 0.9809. The R^2 value given by the two-parameter Weibull is 0.8746. An improvement in the fit is to be expected due to the extra free parameter. Nonetheless, it is appealing that the three-parameter Weibull does fit the data well, including in the low field region. One possible explanation for the deviation from a two-parameter Weibull is the pre-test sample inspection which rejects obviously flawed samples. Removal of samples that are expected to fail at low fields is likely to skew the low field part of the data.

[0076] Dielectric spectroscopy was used to study the dielectric constant and loss as a function of frequency.

RESULTS

The Interface:

[0077] From infrared spectroscopy(IR), the presence of PGMA can be confirmed from the C=O vibration at 1736 cm^{-1} and a reduction in the characteristic peak of the azide group at 2110 cm^{-1} . When PGMA chains alone are attached, the azide peak does not disappear, indicating that not all the azide has reacted, as the chains are too large to fill all the places available and graft density is thus limited by steric hindrance. When a short molecule (oligothiophene or ferrocene) is also used, the azide peak at 2110 cm^{-1} disappears indicating efficient attachment of the short molecule. The strongest C=O signal is seen from particles that have only PGMA. The peak from $850\text{--}750\text{ cm}^{-1}$ is characteristic of SiO_2 .

Theoligothiophene modified particles result in a more intense C=O peak than the ferrocene modified particles (Figure 4).

[0078] Ferrocene is known to be very reactive in “click” reactions (V. Ganesh, V. S. Sudhir, T. Kundu and S. Chandrasekaran, "10 Years of click chemistry: synthesis and applications of ferrocene-derived triazoles", Chemistry-an Asian Journal, vol. 6, pp. 2670-2694, 4, 2011) and it is possible that in a one-pot synthesis it will react much faster than longer PGMA and occupy most of the available positions. The presence of the electroactive molecule was verified by UV-vis spectroscopy. Oligothiophene absorbs at a wavelength 360 nm and ferrocene at 440 nm. Attachment of PGMA to the particle core was verified as a strong peak in the derivative of weight change versus temperature above 400°C using TGA. This degradation peak differs from degradation of unattached PGMA that shows a strong peak below 400°C.

[0079] The particles contain two populations of chains: one electroactive population forms a functional layer surrounding the core of the particle and the long polymer forms an epoxy compatible outer layer (Figure 5).

The Dielectric Composite:

[0080] Simple visual inspection of composites with core functionalized silica and bare silica shows that grafted PGMA alone can help to disperse the silica in the epoxy and the transparency stays at a similar level for all the bimodal composites, though the ferrocene bimodal composite is slightly opaque (Figure 6).

[0081] Representative TEM images from composites are shown in Figure 7. In composites containing bare silica, some of the silica particles are agglomerated, so the concentration of particles at the nano-scale was low. On the contrary the monomodal and bimodal particles dispersed efficiently. There is still a smaller number of individual ferrocene modified particles than oligothiophene modified particles at the same loading. This indicates that the ferrocene modified particles had larger agglomerates (Figures 7C and 7D). This is likely due to an inadequate amount of PGMA on the ferrocene modified nanoparticles as indicated by the low intensity C=O peak in the IR spectra (Figure 4). Thus further optimization may be possible by reducing the amount of grafted ferrocene to leave room for the PGMA during the one-pot synthesis.

[0082] Figure 8 displays breakdown data from a composites with 2 wt% oligothiophene and PGMA modified bimodal silica and 2 wt% ferrocene and PGMA modified bimodal nanoparticles compared to composites with 2 wt% PGMA modified silica in epoxy and neat epoxy data. Note that the horizontal scale in this plot is not adjusted for the

location parameter, as multiple curves are shown. This leads to the curved tails in the plot which are otherwise comparable in the same manner as a two parameter Weibull plot.

Significant increases in the DBS were observed, represented by the 63.2% parameter calculated from α from the Weibull distribution plus the location parameter, t . Two weight percent silica grafted with PGMA and oligothiophene provided an increase in the 63.2% characteristic DBS of greater than 40%. The free-space length L_f and 63.2% DBS with shape factor are shown in Table 1. An unexpectedly large location parameter is required for the three-parameter Weibull fit. This warrants future investigation. Comparison between the bare silica and the PGMA modified silica shows a significant improvement in DBS corresponding to a large decrease in L_f without the addition of electroactive molecules.

[0083] In addition, it is also clear that the electroactive short molecules have a significant impact on DBS. The 2 wt% PGMA modified particle composites have the same L_f as the 2 wt% oligothiophene and PGMA modified particle composites, but the DBS increases substantially with the addition of the oligothiophene short brush. This indicates that the electroactivity of the molecules on the surface of the silica is an important factor in the improving the DBS. From the viewpoint of eventual practical application, it is perhaps also important to observe from Figure 8 that the enhanced DBS for the functionalized formulations is also retained at low breakdown probabilities.

Table 1

<i>Sample</i>	<i>L_f</i>	<i>3-parameter</i>					<i>2-Parameter</i>	
	$\pm 10nm$	63%	$\pm$	α	β	t	α	β
neat epoxy	NA	185	22	66	1.4	119	187	4.2
1 wt% bare SiO ₂	900	182	29	83	1.6	99	192	4.4
2 wt% SiO ₂ -PGMA	250	213	24	84	1.4	129	228	3.7
2 wt% SiO ₂ -PGMA-ferro	550	235	35	112	1.4	124	252	3.4
2 wt% SiO ₂ -PGMA-thio	250	266	24	134	1.9	132	277	4.3

[0084] The free-space length, L_f ; 63.2% characteristic DBS and its 95% confidence interval derived from the 3-parameter Weibull; the scale factor, α , shape factor, β ; and location, t from the 3-parameter and 2-parameter Weibull fits for each composite

[0085] Figure 9 displays the real and imaginary components of the dielectric constant as a function of frequency for representative composites. Dielectric permittivity increases in the bimodal composite that contains oligothiophene. Losses stay at a low level for all other composites but the 2 wt% silica-PGMA-ferrocene composites; which had fewer particles

dispersed at the nano-scale and larger Lf than the other polymer grafted silica composites with same loading (Table 1, Figure 6). The larger Lf indicates that some of the filler is agglomerated. The interfacial polarization of these inclusions could be responsible for the increase in low frequency losses for this particular composite (M. Roy, J. Nelson, R.

MacCrone, L. Schadler, C. Reed, R. Keefe and W. Zenger, "Polymer nanocomposite dielectrics - The role of the interface", IEEE Trans. Dielectr. Electr. Insul., vol. 12, pp. 629-643, 2005). All composites filled with matrix compatibilized silica do not exhibit any significant shift in the peaks in the imaginary permittivity, though a shift to lower frequency is seen in the bare silica composite.

DISCUSSION

[0086] The data indicates that the electroactivity of the short molecules on the silica surface are largely responsible for the improvements in DBS. Even when good dispersion is achieved with PGMA modified silica filler, the small improvement in DBS reveals the silica filler alone is not responsible for the larger improvements seen in the bimodal filler composites. Ferrocene and PGMA bimodal composites with higher free space length than monomodal PGMA brush composites displayed higher DBS. This reveals that the electroactive short brush can overcome the effects of dispersion in some cases. Polar molecules and substituents with greater inductive coefficients, which describe the polarity of the molecule, have been correlated to greater enhancement in DBS (S.Siddabattuni, T.P. Schuman, F. Dogan, "Dielectric properties of polymer-particle nanocomposites influenced by electronic nature of filler surfaces", ACS Appl. Mater. Interfaces, vol 5, pp. 1917–1927, 2013). Nevertheless more data from composites with a wide range of short brush molecules is needed to test this hypothesis, two general observations may be drawn. First, the improvement seen in DBS when comparing the unmodified silica composites to the monomodal PGMA brush composite is due to the improvement in dispersion (see Table 1). The increase in loading from 1 wt% to 2 wt% is not sufficient to explain the reduction in free space length seen when comparing the bare silica composite to the PGMA grafted silica composite. The PGMA brush is not expected to alter the behavior of the matrix epoxy due to its similar chemistry. This lends support to the model of charge carrier trapping at the particle surface, as in chemically similar systems, the only explanation for improvements in DBS is the decreased interparticle distance. Some changes are seen in both DBS and permittivity with monomodal PGMA modified particle composite systems. This may be attributed to minor changes in local crosslink density as well as the presence of the silica-polymer interface. PGMA is known to have a higher density of epoxide groups than the epoxy matrix,

but otherwise shares very similar chemistry, and thus is unlikely to be responsible for any large change in composite properties. Second, when comparing the short brush populations of the bimodal composites, the improvements seen in DBS correlate with the reduction potential of the short brush molecules. The reduction potential is a measure of the voltage required in an electrochemical cell to cause a particular chemical species to gain electrons. Ferrocene exhibits a reduction potential of 0.4 V (R.R. Gagne, C.A. Koval, and G.C. Lisensky. "Ferrocene as an internal standard for electrochemical measurements." *Inorganic Chemistry*, vol. 12, pp. 2854–2855, 1980) while oligothiophene displays a reduction potential between 0.8 V-0.9 V (M.B. Camarada, P. Jaque, F. R. Díaz, and M. A. del Valle, "Oxidation potential of thiophene oligomers: Theoretical and experimental approach." *Journal of Polymer Science Part B: Polymer Physics*, vol. 49 (24), pp. 1723–1733, 2011). This indicates that oligothiophene on the silica surface may trap charge carriers in the composite. Ultimately, the size of the electroactive molecules will also need to be considered; as larger molecules could also enhance these effects due to the increased volume they influence.

[0087] These results demonstrate that surface modification using electroactive groups is effective at manipulating the dielectric properties of nanocomposites. The dispersion is enhanced with bimodal brush modified nanoparticles and dielectric properties improve considerably. The DBS exhibits a substantial increase over the unfilled epoxy and bare silica filled epoxy. Oligothiophene molecules located at the surface of the filler particles are additionally effective at increasing the real permittivity while maintaining low imaginary permittivity at power frequencies. This is attributed to polarization mechanisms associated with the delocalized electrons in the oligothiophene molecules. These improvements, tested in AC conditions, are the largest seen to the knowledge of the authors.

CONCLUSION

[0088] A new synthetic approach was used to afford well dispersed silica particles with an electroactive brush on the surface of the silica nanofiller. The long, epoxy compatible PGMA brush ensured good dispersion and allowed study of the effect of the electroactive layer on the breakdown strength. The DBS increased considerably in the bimodal brush particle composites. Bimodal brush nanoparticles with functional short brush molecules and matrix compatible long brush molecules have the capability to increase dielectric breakdown strength of the nanocomposite while adjusting the permittivity. The results shown in this paper are a first step towards filler surface modification allow for tailoring of the dielectric properties of the nanocomposite while offering control over dispersion of the nanoparticles. Factors upon which the DBS enhancement depends are the quality of the dispersion and

loading, characterized by the free space length; and the electronic character, i.e. reduction potential, of the short brush. Further investigation is required to determine quantitatively the relative importance of these factors.

5

EXAMPLE 2

Synthesis of Monomodal Silica-PGMA Particles

- [0089] As indicated in Example 1, to create a monomodal silica PGMA, reference samples “grafting from” synthesis known as surface-initiated reversible addition-fragmentation chain transfer (RAFT) polymerization was used. Details of this synthesis are provided in this example.
- [0090] Colloidal silica Nissan® MEK-ST (10 g) was added to a 100 ml round bottom flask with 3-ethoxydimethylsilyl-1-propanamine (30 mg, 0.19 mmol). The solution was diluted to 50ml with THF and stirred for 4 h at 70°C under N₂ atmosphere. The solution was then allowed to cool to room temperature before adding 1-azido-3-ethoxydimethylsilyl-propane (0.25 g, 1.3 mmol). The solution was left to stir overnight at 70°C under N₂ protection. Next the particles were precipitated in a large amount of hexanes and centrifuged at 3,000 rpm for 5 minutes, the supernatant was discarded, and the particles were dispersed back into THF. This was repeated 3 times, and upon the final wash the particles were dispersed into 30 ml of THF for subsequent use. Then 78 mg of activated 4-cyanopentanoic acid dithiobenzoate (CPDB) was prepared as reported previously and was anchored to the particle surface as described before (C. Li, J. Han, C. Y. Ryu and B. Benicewicz, "A versatile method to prepare RAFT agent anchored substrates and the preparation of PMMA grafted nanoparticles", *Macromolecules*, vol. 39, pp. 3175-3183, 2006).
- [0091] CPDB anchored silica nanoparticles (3 g) with glycidyl methacrylate (8.23 g, 57.9 mmol), azobisisobutyronitrile (AIBN) (1.9 mg, 13.4 μmol), and dry THF (10ml) were added to a 50 ml Schlenk tube. The particles were dispersed into the solution via sonication for 1 min. and subsequently degassed by 4 sequential freeze pump thaw cycles. The flask was then placed into an oil bath at 60°C for 4 h. The resultant polymer grafted particles were then precipitated into a large amount of hexanes and centrifuged at 3,000 rpm for 5 min. and the particles were dispersed back into THF. This was repeated 3 times.

EXAMPLE 3

**Enhanced Charge Trapping in Bimodal Brush Functionalized
Silica-Epoxy Nanocomposite Dielectrics**

[0092] This example details the processing, and investigates the dielectric properties, of surface ligand engineered epoxy nanocomposites. They display significant improvements in dielectric breakdown strength (DBS). Thermally stimulated depolarization current (TSDC) measurements and pulsed electroacoustic analysis (PEA) results are used to investigate space charge evolution and trapping. These techniques reveal the potential underlying phenomena behind the DBS enhancement.

[0093] It is commonly accepted that nanocomposite dielectrics can display improved dielectric breakdown strength (DBS) (M. Roy, J. K. Nelson, R. K. MacCrone, L. S. Schadler, C. W. Reed, R. Keefe, and W. Zenger, "Polymer nanocomposite dielectrics - the role of the interface," *IEEE Trans. Dielectr. Electr. Insul.*, vol. 12, no. 4, pp. 629–643, Aug. 2005). However, the mechanisms remain elusive (C. Green and A. Vaughan, "Nanodielectrics-How Much Do We Really Understand?," *Electr. Insul. Mag. IEEE*, 2008), though the novel properties can be traced back to electronic activity of the filler-matrix interface (M. Roy, J. K. Nelson, R. K. MacCrone, L. S. Schadler, C. W. Reed, R. Keefe, and W. Zenger, "Polymer nanocomposite dielectrics - the role of the interface," *IEEE Trans. Dielectr. Electr. Insul.*, vol. 12, no. 4, pp. 629–643, Aug. 2005). Interestingly, varying the electronic character of the interface with electron-accepting and donating functional groups to create a highly polar surface has been shown to significantly affect the DBS of the composite (S. Siddabattuni, T. P. Schuman, and F. Dogan, "Dielectric properties of polymer-particle nanocomposites influenced by electronic nature of filler surfaces.," *ACS Appl. Mater. Interfaces*, vol. 5, no. 6, pp. 1917–27, Mar. 2013).

[0094] The high specific surface area of nanofillers creates both an opportunity to effect change in bulk composite properties, but also presents a problem in avoiding agglomeration. Interfacial energy drives agglomeration. Energy penalties are largely due to mismatch in surface energies between filler and matrix and may be addressed with brushes of matrix compatible polymer chains covalently grafted to the filler surface (A. Balazs, T. Emrick, and T. Russell, "Nanoparticle polymer composites: where two small worlds meet," *Science*, vol. 314, no. 5802, pp. 1107–1110, 2006). A solution is to adopt two populations of surface ligands: one of dense short chains for enthalpic shielding and one of long, disperse chains to suppress autophobic dewetting. This has been shown to be effective with short molecules of chemistry dissimilar to the matrix (D. Maillard, S. K. Kumar, A. Rungta, B. C. Benicewicz, and R. E. Prud'homme, "Polymer-grafted-nanoparticle surfactants.," *Nano Lett.*,

vol. 11, no. 11, pp. 4569–73, Nov. 2011), opening up an opportunity to introduce electrical functionality onto the surface of the particle without hindering the mixing properties of the composite. The applicability of this functional bimodal brush technique in improving DBS in epoxy/silica nanocomposites has been demonstrated (S. Virtanen, T. M. Krentz, J. K. Nelson, L. S. Schadler, M. Bell, B. C. Benicewicz, H. Hillborg, and S. Zhao, “Dielectric Breakdown Strength of Epoxy Bimodal-Polymer-Brush-Grafted Core Functionalized Silica Nanocomposites,” *IEEE Trans. Dielectr. Electr. Insul.*, vol. 21, no. 2, pp. 563–570, 2014). In these studies, TSDC and PEA measurements are used to investigate the effect of ligand engineered filler particles on trapped charge and the evolution of space charge in the composite.

EXPERIMENTAL METHODS

A. Chemistry:

1. Mercaptothiazoline Activated Anthracene

[0095] 2-(Anthracen-9-yl)acetic acid was prepared as described previously (J. R. Shah, P. D. Mosier, B. L. Roth, G. E. Kellogg, and R. B. Westkaemper, “Synthesis, structure-affinity relationships, and modeling of AMDA analogs at 5-HT_{2A} and H₁ receptors: structural factors contributing to selectivity,” *Bioorg. Med. Chem.*, vol. 17, no. 18, pp. 6496–504, Sep. 2009). 2-(Anthracen-9-yl)acetic acid (1.00 g, 4.2 mmol) was dissolved into 30ml dichloromethane along with 2-mercaptothiazoline (0.56 g, 4.7 mmol), and 4-dimethylaminopyridine (50 mg, 0.4 mmol). The solution was cooled to 0°C and flushed with N₂ for 20 minutes. N,N'-dicyclohexylcarbodiimide (0.87 g, 4.2 mmol) was dissolved into a minimal amount of dichloromethane and added dropwise to the anthracene acetic acid solution. The solution was allowed to warm to room temperature and stir over night. The solids were then removed via vacuum filtration and solvent was removed under reduced pressure. The crude product was then purified via column chromatography (SiO₂, 7:3, dichloromethane:hexane) leaving the product as a yellow powder (0.62 g) with 43% final yield.

2. Anthracene Coated Particles

[0096] A suspension (10 g) of 30 wt % colloidal silica in methylethyl ketone was added to a 100 ml round bottom flask with 3-ethoxydimethylsilyl-1-propanamine (90 mg, 0.56 mmol). The solution was diluted to 50ml with tetrahydrofuran (THF) and stirred for 4 hours at 70 °C under N₂ atmosphere. Next the particles were precipitated in a large amount of hexane and centrifuged at 3,000 RPM for 5 minutes, the supernatant was discarded, and the

particles were dispersed back into THF. This was repeated 3 times. Then the particles were dispersed into 30ml of THF for subsequent use. The resultant particle solution was cooled to 0 °C and flushed with N₂ before adding mercaptothiazoline activated anthracene (0.23 g, 0.68 mmol) in THF dropwise via syringe. The solution was then allowed to warm to room temperature and stir overnight. The anthracene coated particles were then precipitated into a large amount of 1:1 hexane:THF solution and centrifuged at 3,000 RPM for 5 minutes, the supernatant was discarded, and the particles were dispersed back into THF. This was repeated 3 times; then the particles were dispersed into 30 ml of THF for subsequent use.

3. Anthracene + CPDB Coated Particles

[0097] Activated 4-cyanopentanoic acid dithiobenzoate (CPDB) was prepared as described previously (C. Li, J. Han, C. Y. Ryu, and B. C. Benicewicz, "A Versatile Method To Prepare RAFT Agent Anchored Substrates and the Preparation of PMMA Grafted Nanoparticles," *Macromolecules*, vol. 39, no. 9, pp. 3175–3183, May 2006). The anthracene-coated particles described above were dispersed into 50 ml THF along with 3-ethoxydimethylsilyl-1-propanamine. The solution was stirred at 70 °C for 4 hours. After cooling to room temperature, the anthracene + amine coated particles were precipitated into a large amount of hexane and centrifuged at 3,000 RPM for 5 minutes, the supernatant was discarded, and the particles were dispersed back into THF. This was repeated 3 times. The particles were then dissolved into 50 ml THF. The resultant particle solution was cooled to 0 °C and flushed with N₂ for 20 min before adding a solution of activated CPDB (61 mg, 0.16 mmol) in THF dropwise via syringe. The solution was allowed to warm to room temperature and stir overnight. The anthracene + CPDB coated particles were then precipitated into a large amount of hexane and centrifuged at 3,000 RPM for 5 minutes, the supernatant was discarded, and the particles were dispersed back into THF. This was repeated 3 times; then the particles were then dried in vacuum.

4. PGMA + Anthracene Particles

[0098] CPDB + anthracene anchored silica nanoparticles (1 g) with glycidial methacrylate (1.4 g, 9.8 mmol), azobisisobutyronitrile (AIBN) (0.3 mg, 2.0 µmol), and dry THF (3ml) were added to a 25 ml Schlenk tube. The particles were dispersed into the solution via sonication for 1 minute, and subsequently degassed by 4 sequential freeze pump thaw cycles. The flask was then placed into an oil bath at 60 °C for 4 hours. The resultant polymer grafted particles were then isolated by centrifugation at 20,000 RPM for 1 hour. The

supernatant was discarded and the particles were dispersed into THF. This washing process was repeated 3 times.

B. Sample Preparation:

5 [0099] Nanoparticles as modified in Table 2 in solution were mixed with Huntsman Araldite GY 2600; a bisphenol-A based epoxy resin using a Hauschild high shear mixer. Solvent was then evaporated in vacuum. Silica loading was measured with thermo gravimetric analysis (TGA), whereupon the composite resin was diluted to achieve the desired loading and mixed with aliphatic amine based Huntsman Aradur 956-2 using the same high shear mixer and cast into samples. A formulation was also made with free 9- anthracenemethanol in epoxy at a 0.1 wt% loading. Recessed samples for breakdown tests and flat samples for TSDC and PEA were prepared as described in the literature (S. Virtanen, T. M. Krentz, J. K. Nelson, L. S. Schadler, M. Bell, B. C. Benicewicz, H. Hillborg, and S. Zhao, "Dielectric Breakdown Strength of Epoxy Bimodal-Polymer-Brush-Grafted Core Functionalized Silica Nanocomposites," *IEEE Trans. Dielectr. Electr. Insul.*, vol. 21, no. 2, pp. 563–570, 2014).

Table 2
Sample Specifications

Sample Name	Short Brush/graft density	PGMA M_w /graft density
Colloidal Silica	NA	NA
Monomodal PGMA	NA	17k/0.15 nm ⁻²
Bimodal Anthracene	Anthracene/0.28 nm ⁻²	Short Chains/0.11 nm ⁻²

C. Pulsed Electro-Acoustic (PEA) Test:

[00100] The PEA test used an aluminum bottom electrode and a carbon black loaded semi-conductive polymer upper electrode. Transformer grade silicone fluid was used between the sample and the electrode to reduce the acoustic attenuation. The probe pulse used had a width of 10 ns, a repetition frequency of 140 Hz and amplitude of 300 V. A dc voltage of -20 kV (electric field = 60 kV/mm) was applied to samples via the top electrode for 1 hour at room temperature and the depolarization charge profile was measured immediately after voltage removal for 1 hour.

D. Thermally Stimulated Depolarization Current (TSDC):

[00101] TSDC tests were carried out on flat samples identical to those used for PEA tests. The samples were heated to 120 °C and polarized at 15 kV/mm for 20 minutes. They

were then quenched with liquid nitrogen. Surface charges were removed with a 5 minute short-circuit, and the sample was shorted across a sensitive current meter while the temperature was ramped at 0.5 °C/min.

5

RESULTS & DISCUSSION

A. DBS:

[00102] The distribution of breakdown strength values for the tested composites are shown in Fig. 10. Of note are the progressive improvements seen in the DBS, (Table 3). Filler modified with a monomodal brush (PGMA) for matrix compatibility shows a small improvement, while anthracene and PGMA bimodally modified fillers (Anth) show greater improvements up to 27% over the neat polymer.

10

Table 3
Weibull Fit Parameters

Sample	Weibull Fit Parameters		
	<i>Shape</i>	<i>Scale (kV/mm)</i>	<i>95% confidence interval (kV/mm)</i>
Neat Epoxy	4.3	198	21
Colloidal Silica	4.4	192	22
Monomodal PGMA	3.7	228	25
Bimodal Anthracene	4.4	246	20
Free Anthracene	3.5	164	22

15

B. PEA:

[00103] The space charge profile of neat epoxy during polarization is shown in Fig. 11. The displacement of the peak front indicates the presence of injected charges of the same polarity as the electrode. Most injected charge was trapped in the vicinity of the electrode without traveling into the bulk, in agreement with previous results (L. Dissado, V. Griseri, W. Peasgood, E. S. Cooper, K. Fukunaga, and J. Fothergill, "Decay of space charge in a glassy epoxy resin following voltage removal," *IEEE Trans. Dielectr. Electr. Insul.*, vol. 13, no. 4, pp. 903–916, 2006). Little difference was observed for each sample in the space charge profile under field due to the strong influence of the image charges and limited spatial resolution of the test system.

20

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[00104] The depolarization space charge profile confirmed that the injected charges were trapped near the electrode (Fig. 11). The signal from the cathode is less accurate due to the attenuation and dispersion of the acoustic wave, so we concentrated our analysis on the decay of the homocharge peak close to the anode, where the acoustic signal is collected. The space charge decay profiles are plotted in Fig. 12. The space charge density was obtained by

30

integrating the homocharge peak next to the anode. The detrapping model proposed by Dissado (L. Dissado, V. Griseri, W. Peasgood, E. S. Cooper, K. Fukunaga, and J. Fothergill, “Decay of space charge in a glassy epoxy resin following voltage removal,” *IEEE Trans. Dielectr. Electr. Insul.*, vol. 13, no. 4, pp. 903–916, 2006) (eqns 1-3) was applied, wherein a square distribution of traps was assumed and the charge density was found to be logarithmically proportional to the decay rate.

$$\rho(t) = \rho(0), \quad t < [\nu \exp(-\Delta_{\min}/kT)]^{-1} \quad (1)$$

$$\rho(t) \approx [\rho(0)kT/(\Delta_{\max}-\Delta_{\min})](a - \ln(t)),$$

$$[\nu \exp(-\Delta_{\min}/kT)]^{-1} < t < [\nu \exp(-\Delta_{\max}/kT)]^{-1} \quad (2)$$

$$\rho(t) = 0, \quad t > [\nu \exp(-\Delta_{\max}/kT)]^{-1} \quad (3)$$

[00105] Here ν is the attempt to escape frequency; $\rho(t)$ is the space charge density at time t ; $\Delta_{\max}$ and $\Delta_{\min}$ represents the maximum and minimum trap depth respectively; and a is the time independent factor. A plateau can be clearly seen for monomodal PGMA and bimodal anthracene samples, implying the existence of deep traps. Therefore two square distributions of traps were used to better capture the decay (shown as two lines in Fig. 12). The minimum trap depth was taken as 0.79 eV for all samples, calculated from the minimum observable relaxation time of 5 seconds. The maximum trap depths were calculated from the longest relaxation times taken from the intercept value on the time axis for each fitted line respectively. The occupation percent for each distribution is calculated from the total charge and decay associated with each distribution. The results are summarized in Table 4. The introduction of silica nanoparticles increased the maximum trap depth for holes by 0.10 eV while the anthracene modified silica nanoparticles increased the depth by 0.22 eV.

Table 4

PEA Trap Depth Fitting Results

Sample		Neat epoxy		Monomodal PGMA		Bimodal Anthracene	
Trap Depth (eV)	min	0.79	0.92	0.79	0.91	0.79	0.91
	max	0.92	1.04	0.91	1.14	0.91	1.26
Occupation%		63%	37%	85%	15%	71%	29%

C. TSDC:

[00106] TSDC data was collected from unfilled epoxy samples and from samples filled with silica nanoparticles bimodally modified with PGMA and anthracene. The data, seen in Fig. 13, demonstrates an additional peak at low temperatures, as well as a shift in the location of the intrinsic neat epoxy low temperature peak. The appearance of a new peak is attributed to the introduction of a uniform population of traps related to the anthracene modified filler. The shift to higher temperatures of the low temperature intrinsic peak is likewise attributed to enhanced trapping of charge due to the filler, which slows the decay of charge, as seen in the PEA results. The values of the activation energy for these peaks were calculated per the Bucci-Fieschi theory, and can be seen in Table 5.

Table 5
TSDC Trap Depth Fitting Results

		Neat epoxy	Bimodal Anthracene
Trap Depth of Peak (eV)	1	NA	1.5
	2	0.35	0.43
	3	0.51	0.68

[00107] The DBS results demonstrate the efficacy of a ligand engineered filler with a high graft density of functional molecules and a low graft density of a matrix compatible polymer brush. Additionally, the nanofiller's role in spatially controlling the functional molecule is critical, as the epoxy with free anthracene displays a significant decrease in DBS compared to the neat epoxy, while anthracene grafted to the nanofiller surface significantly improved DBS. We attribute this to the traps associated with the anthracene. When evenly distributed as free molecules, they may increase hopping conduction and thus reduce the DBS. Conversely, when they are localized at isolated particle surfaces, their trapping behavior reduces the mobility of space charge, increasing the DBS. This theory is supported by the trap population analysis obtained from space charge decay results in the PEA tests. Detectable increases in deeper traps are attributed to the nanoparticle filler, and significantly enhanced by surface modification of the filler with anthracene. TSDC results corroborate this theory, revealing increases in trap depth similar to those seen in the PEA, as well as revealing a new type of trap in the composite.

CONCLUSIONS

[00108] Surface modification of nanofiller particles can significantly increase DBS, and these increases are correlated with increases in the number, depth, and occupancy of deeper traps. These traps are associated with the filler surface ligands, but the ligand molecules by themselves are not sufficient to generate the improvements in DBS. Thus, both the surface chemistry of the filler, and the inhomogeneous physical distribution of traps are central to the properties seen in these composites. Ongoing work will expand these studies to reveal the most important functional molecule properties that lead to the improvements in DBS and investigate their applicability across other material systems.

EXAMPLE 4

Modified Silica Filler with a Conceptually Similar Surface Chemistry to a Matrix

[00109] In various embodiments, the present invention contemplates the use of modified silica fillers that can be used with various matrices. One particular embodiment of a suitable modified silica filler for use in the present disclosure is shown in Figure 14. In various embodiments, the modified silica filler shown in Figure 14 can be used in a matrix having a similar surface chemistry, such as a polypropylene matrix. More particularly, the schematic shown in Figure 14 is of a modified silica nanoparticle filler of one embodiment of the present disclosure, with the silica particle being shown in grey with a poly stearyl methacrylate (PSMA) long chain (top) and anthracene functional group short chain (bottom) attached to the silica particle.

[00110] Figure 15 provides data demonstrating that a silica filler with conceptually identical filler, a combination of long matrix-compatible polymer chains and short functional groups, also generates property improvements (~28% increase) in a polypropylene matrix. In particular, Figure 15 provides breakdown field (kV/mm) data for a neat PP peak (illustrated as a line with circles), a 2% PSMA-Silica (0.06ch/nm) (illustrated as a line with squares), and a 2% PSMA + Anthracene-Silica (illustrated with a line with diamonds). Additionally, comparison to the same filler particles with only the matrix-compatible long chains demonstrates the importance of the small functional groups.

[00111] All references cited herein are incorporated herein by reference in their entirety and for all purposes to the same extent as if each individual publication, patent or patent application was specifically and individually indicated to be incorporated by reference in its entirety for all purposes.

[00112] Citation of a reference herein shall not be construed as an admission that such reference is prior art to the present invention. All references cited herein are hereby incorporated by reference in their entirety.

[00113] Although preferred embodiments have been depicted and described in detail
5 herein, it will be apparent to those skilled in the relevant art that various modifications, additions, substitutions, and the like can be made without departing from the spirit of the invention and these are therefore considered to be within the scope of the invention as defined in the claims which follow.

WHAT IS CLAIMED IS:

1. A bimodal dielectric nanoparticle comprising:
a nanoparticle having a core modified with a population of functional short
ligands and with a population of matrix compatible long ligands,
5 wherein the short ligand comprises an electroactive molecule, and
wherein the long ligand comprises a polymer that is compatible with a matrix
of the nanoparticle and that extends beyond the short ligand in relation to the nanoparticle
core.

10 2. The bimodal dielectric nanoparticle according to claim 1, wherein the
nanoparticle comprises an inorganic nanoparticle.

3. The bimodal dielectric nanoparticle according to claim 2, wherein the
inorganic nanoparticle is selected from the group consisting of silica, alumina, titania, indium
15 tin oxide, CdSe, zirconia, ZnO, MgO, CuO, AgO, and barium titanate, or mixtures thereof.

4. The bimodal dielectric nanoparticle according to claim 1, wherein the
matrix is selected from the group consisting of epoxy, polypropylene, silicone, polyethylene,
polyamide, polyimide, polyethyleneterephthalate, and polyetherimide, or mixtures thereof.

20 5. The bimodal dielectric nanoparticle according to claim 1, wherein the
electroactive molecule is directly grafted to the nanoparticle or is indirectly grafted to the
nanoparticle by a linking polymer chain.

25 6. The bimodal dielectric nanoparticle according to claim 5, wherein the
electroactive molecule is selected from the group consisting of a metallocene, a substituted or
unsubstituted cyclic or polycyclic aromatic hydrocarbon, and functional derivatives thereof,
and wherein the electroactive molecule can further include an electron donating group and/or
an electron withdrawing group.

30 7. The bimodal dielectric nanoparticle according to claim 5, wherein the
electroactive molecule is selected from the group consisting of an oligothiophene compound,
an oligoaniline compound, ferrocene, benzene, pentacene, anthracene, naphthalene, and
functional derivatives thereof.

8. The bimodal dielectric nanoparticle according to claim 1, wherein the electroactive molecule is effective to improve a dielectric characteristic of the nanoparticle.

9. The bimodal dielectric nanoparticle according to claim 8, wherein the dielectric characteristic is selected from the group consisting of dielectric breakdown strength (DBS), endurance strength, dielectric constant, dielectric loss, non-linear dielectric response, complex permittivity, and conductivity.

10. The bimodal dielectric nanoparticle according to claim 1, wherein the matrix compatible polymer is selected from the group consisting of poly(glycidyl methacrylate) (PGMA), poly stearyl methacrylate (PSMA), epoxy, polypropylene, silicone, polyethylene, polyamide, polyimide, polyethyleneterephthalate, polyetherimide, polymethylmethacrylate, polystyrene, polyacrylate, and derivatives thereof.

11. The bimodal dielectric nanoparticle according to claim 1, wherein the short and long ligands are directly or indirectly covalently grafted onto the core of the nanoparticle.

12. The bimodal dielectric nanoparticle according to claim 1, wherein the short ligands are grafted to the nanoparticle core at a high density and the long ligands are grafted to the nanoparticle core at a low density relative to that of the short ligands.

13. The bimodal dielectric nanoparticle according to claim 12, wherein the high density of the short ligands ranges from about 0.1 to about 1.0 ligand chain per square nanometer (nm^2), and wherein the low density of the long ligands ranges from about 0.02 to about 0.2 ligand chain per square nanometer (nm^2).

14. A dielectric nanocomposite comprising:
a plurality of bimodal dielectric nanoparticles according to any one of claims 1-13; and
a matrix compatible with the bimodal dielectric nanoparticles.

15. The dielectric nanocomposite according to claim 14, wherein the bimodal dielectric nanoparticles are dispersed in the matrix.

16. The dielectric nanocomposite according to claim 15, wherein the bimodal dielectric nanoparticles form agglomerations having an average size that is less than about 200 nanometers (nm).

5 17. The dielectric nanocomposite according to claim 14, wherein the electroactive molecule of the bimodal dielectric nanoparticle provides electroactive functionality to the dielectric nanocomposite.

10 18. The dielectric nanocomposite according to claim 14, wherein the dielectric nanocomposite has improved dielectric breakdown strength (DBS) compared to a nanocomposite having the same nanoparticle core but not the same population of short and long ligands.

15 19. A method of making a bimodal dielectric nanoparticle, said method comprising the steps of:

providing a nanoparticle having a core; and

grafting a population of functional short ligands and a population of matrix compatible long ligands onto the core of the nanoparticle, thereby yielding a bimodal dielectric nanoparticle,

20 wherein the short ligand comprises an electroactive molecule, and

wherein the long ligand comprises a polymer that is compatible with a matrix of the nanoparticle and that extends beyond the short ligand in relation to the nanoparticle core.

25 20. The method according to claim 19, wherein the population of functional short ligands is grafted onto the nanoparticle core prior to the grafting on of the population of long ligands.

30 21. The method according to claim 19, wherein the nanoparticle comprises an inorganic nanoparticle.

22. The method according to claim 21, wherein the inorganic nanoparticle is selected from the group consisting of silica, alumina, titania, indium tin oxide, CdSe, zirconia, ZnO, MgO, CuO, AgO, and barium titanate, or mixtures thereof.

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23. The method according to claim 21, wherein the matrix is selected from the group consisting of epoxy, polypropylene, silicone, polyethylene, polyamide, polyimide, polyethyleneterephthalate, and polyetherimide, or mixtures thereof.

5 24. The method according to claim 19, wherein the electroactive molecule is directly grafted to the nanoparticle or is indirectly grafted to the nanoparticle by a linking polymer chain.

10 25. The method according to claim 24, wherein the electroactive molecule is selected from the group consisting of a metallocene, a substituted or unsubstituted cyclic or polycyclic aromatic hydrocarbon, and functional derivatives thereof, wherein the electroactive molecule can further include an electron donating group and/or an electron withdrawing group.

15 26. The method according to claim 24, wherein the electroactive molecule is selected from the group consisting of an oligothiophene compound, an oligoaniline compound, ferrocene, benzene, pentacene, anthracene, naphthalene, and functional derivatives thereof.

20 27. The method according to claim 19, wherein the electroactive molecule is effective to improve a dielectric characteristic of the nanoparticle.

25 28. The method according to claim 27, wherein the dielectric characteristic is selected from the group consisting of dielectric breakdown strength (DBS), endurance strength, dielectric constant, dielectric loss, non-linear dielectric response, complex permittivity, and conductivity.

30 29. The method according to claim 19, wherein the matrix compatible polymer is selected from the group consisting of poly(glycidyl methacrylate) (PGMA), poly stearyl methacrylate (PSMA), epoxy, polypropylene, silicone, polyethylene, polyamide, polyimide, polyethyleneterephthalate, polyetherimide, polymethylmethacrylate, polystyrene, polyacrylate, and derivatives thereof.

35 30. The method according to claim 19, wherein the short and long ligands are directly or indirectly covalently grafted onto the core of the nanoparticle.

31. The method according to claim 19, wherein the short ligands are grafted to the nanoparticle core at a high density and the long ligands are grafted to the nanoparticle core at a low density relative to that of the short ligands.

5

32. The method according to claim 31, wherein the high density of the short ligands ranges from about 0.1 to about 1.0 ligand chain per square nanometer (nm^2), and wherein the low density of the long ligands ranges from about 0.02 to about 0.2 ligand chain per square nanometer (nm^2).

10

33. A method of making a dielectric nanocomposite, said method comprising the steps of:

providing a plurality of bimodal dielectric nanoparticles according to any one of claims 1-13; and

15

dispersing the plurality of bimodal dielectric nanoparticles in a matrix to form a dielectric nanocomposite.

34. The method according to claim 33, wherein the bimodal dielectric nanoparticles are made by a process comprising:

20

providing the plurality a nanoparticles having a core; and

grafting a population of functional short ligands and a population of matrix compatible long ligands onto the core of the nanoparticle, thereby yielding the plurality of bimodal dielectric nanoparticles,

wherein the short ligand comprises an electroactive molecule, and

25

wherein the long ligand comprises a polymer that is compatible with a matrix of the nanoparticle and that extends beyond the short ligand in relation to the nanoparticle core.

35. The method according to claim 34, wherein the population of functional short ligands is grafted onto the nanoparticle core prior to the grafting on of the population of long ligands.

30

36. A composition for use in electrical applications, said composition comprising a bimodal dielectric nanoparticle according to any one of claims 1-13 or a dielectric nanocomposite according to any one of claims 14-18.

5 37. The composition according to claim 36, wherein the composition comprises an electrical device, material, or component selected from the group consisting of high voltage alternating current (HVAC) capacitor films, high voltage direct current (HVDC) capacitor films, HVAC cable insulation, HVDC cable insulation, motor/machine insulation, and impregnation media of a porous matrix, said porous matrix comprising at least one of
10 paper, cellulose, glass, or mica.

38. The composition according to claim 37, wherein the composition is used in dry bushings or machine stator bars.

15

Surface functionalized Silica
(10-15 nm)

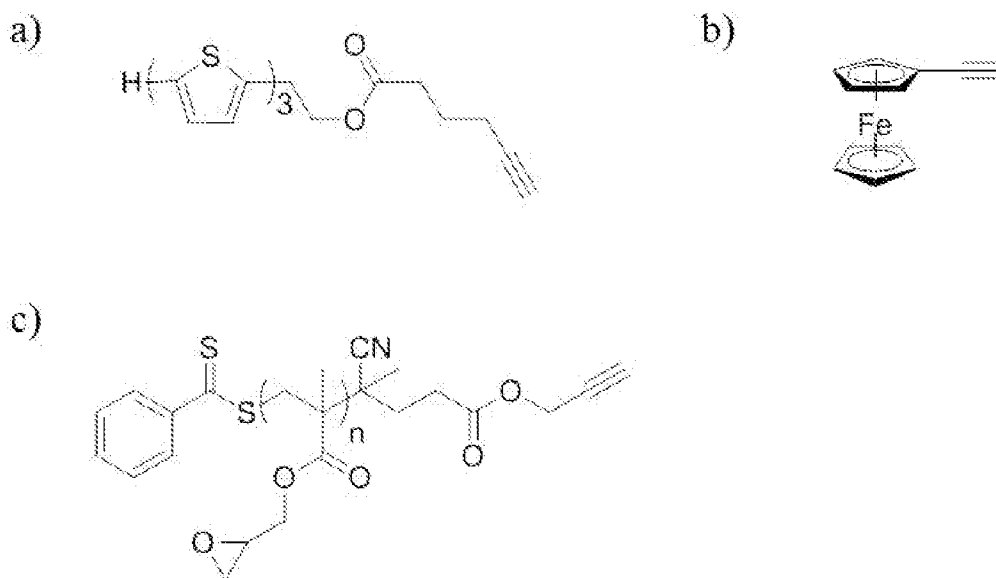
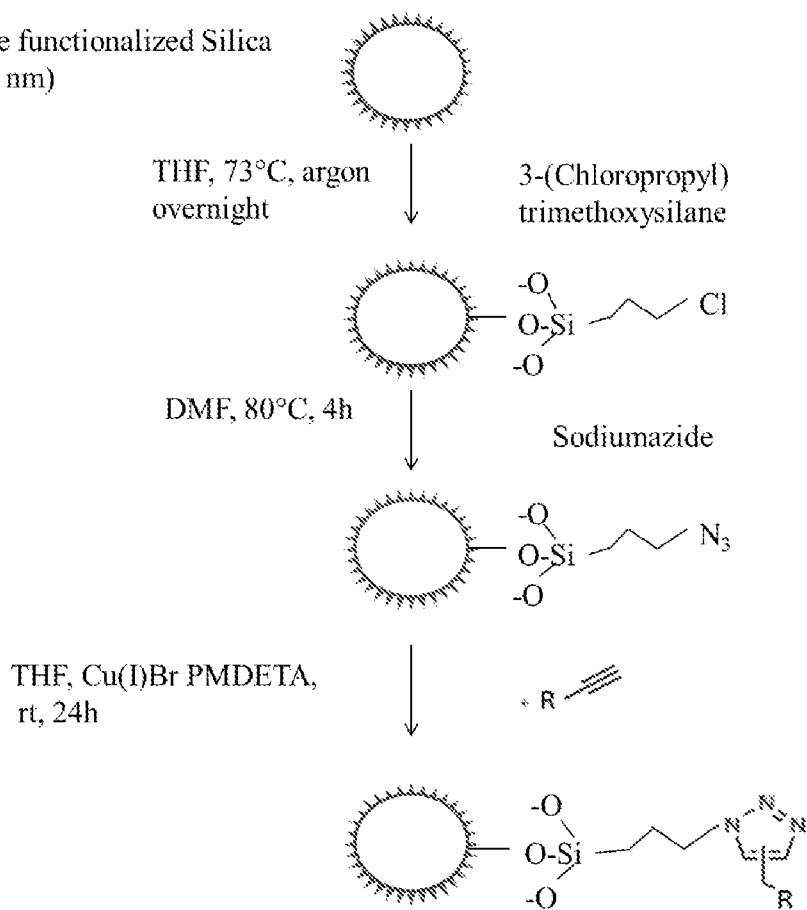


FIG. 2

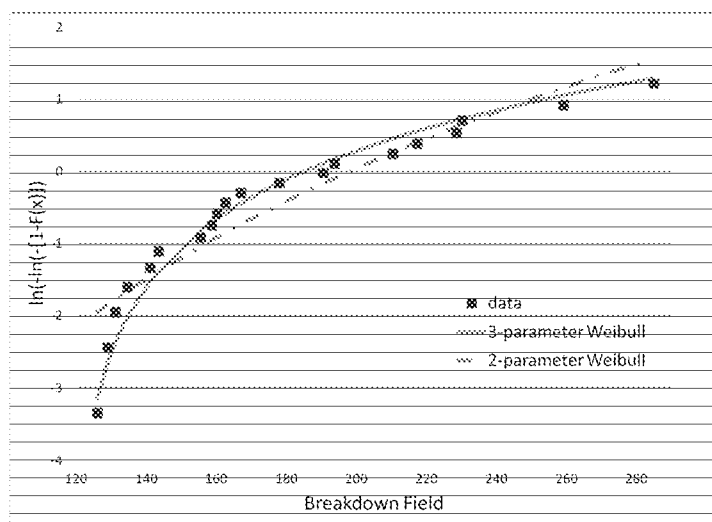


FIG. 3

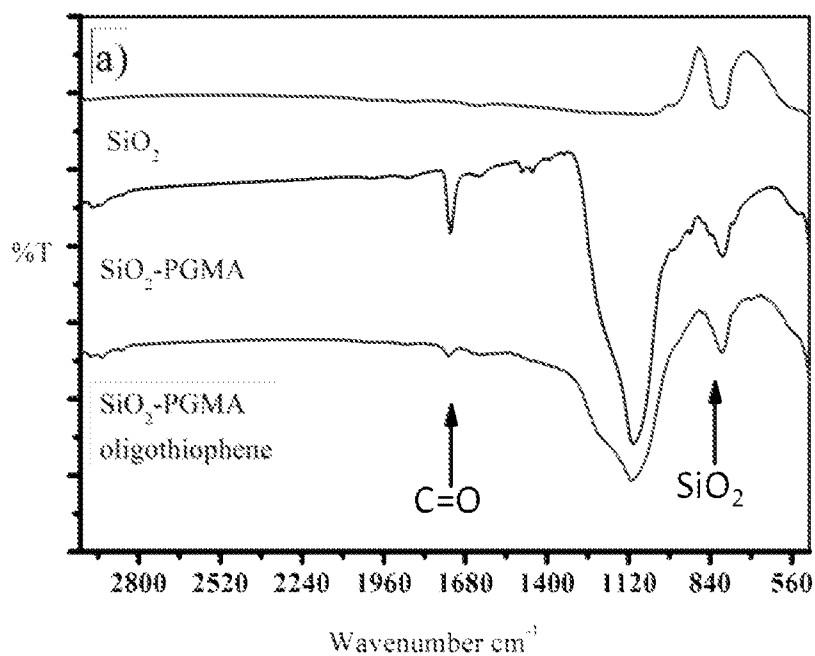


FIG. 4A

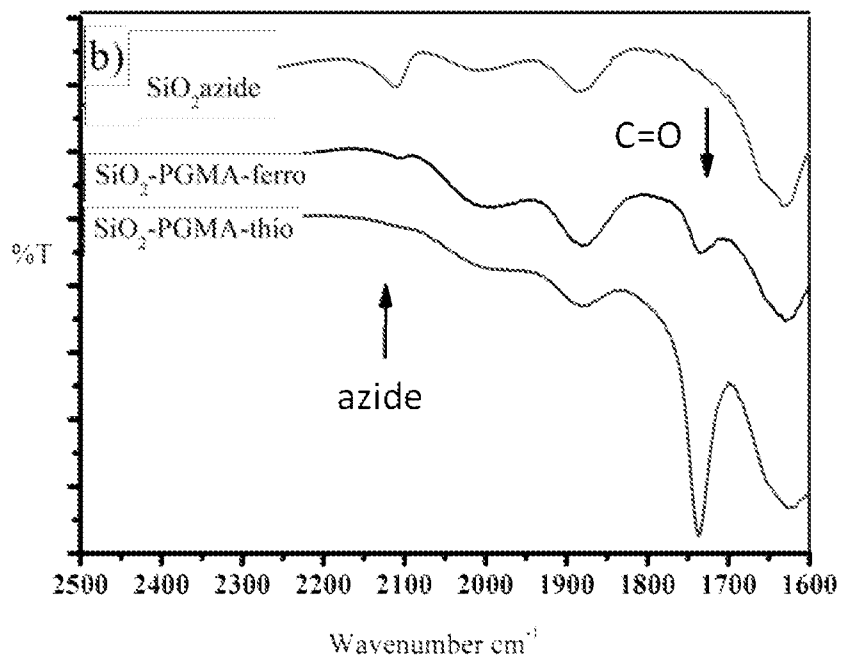


FIG. 4B

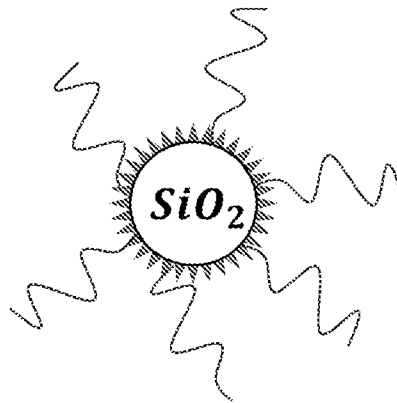
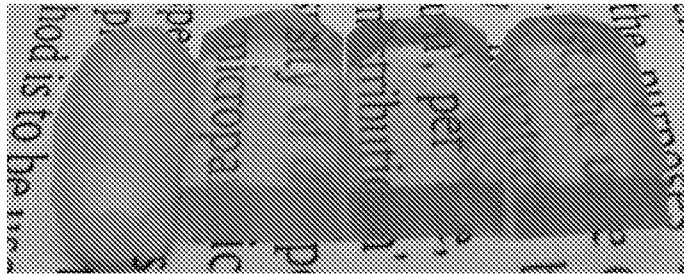
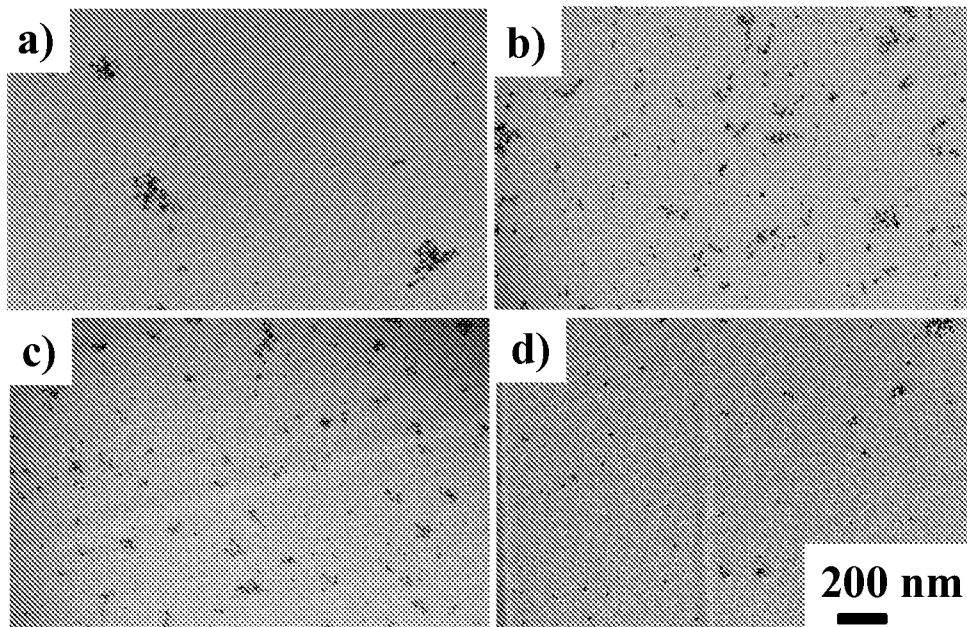
**FIG. 5****FIG. 6****FIG. 7**

FIG. 8

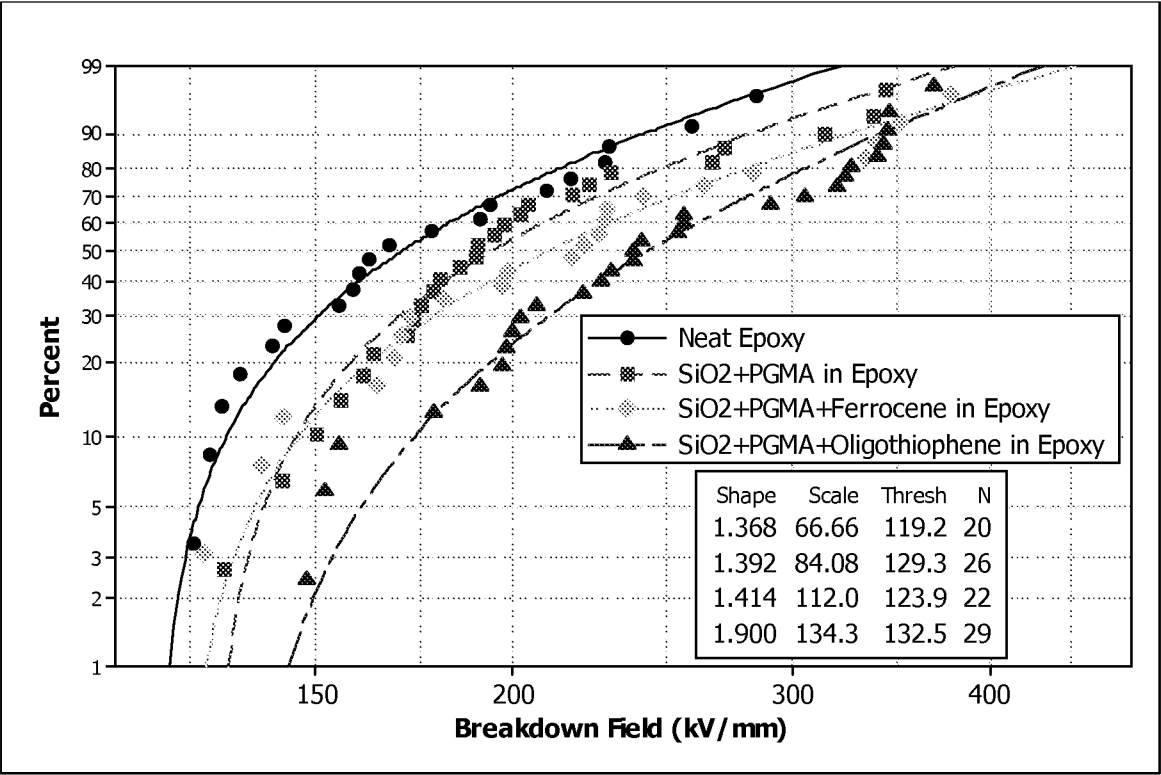


FIG. 9A

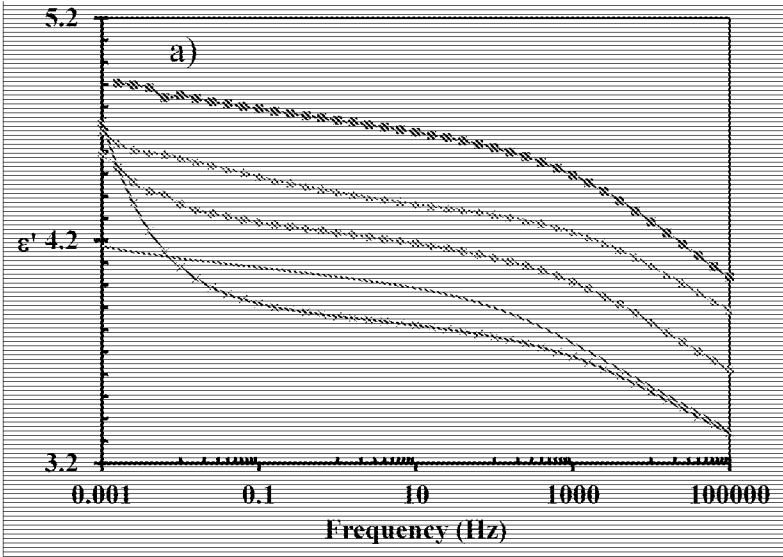
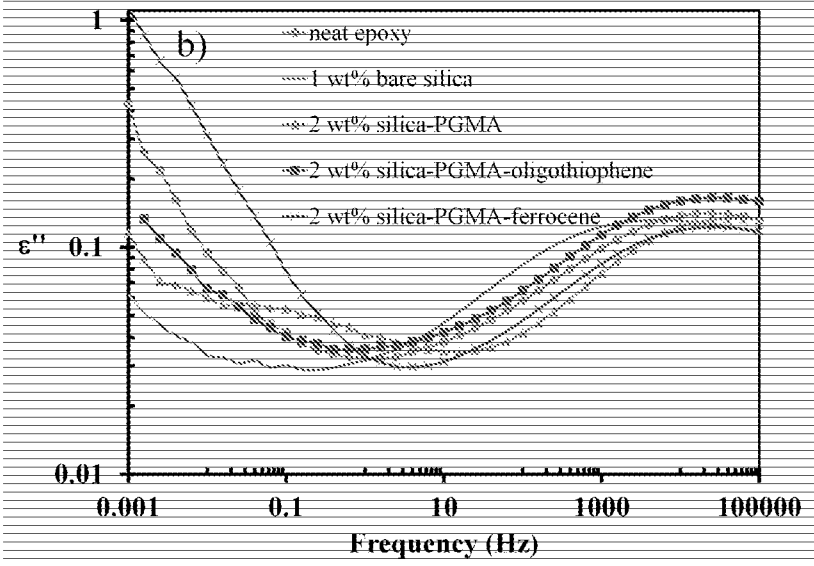


FIG. 9B



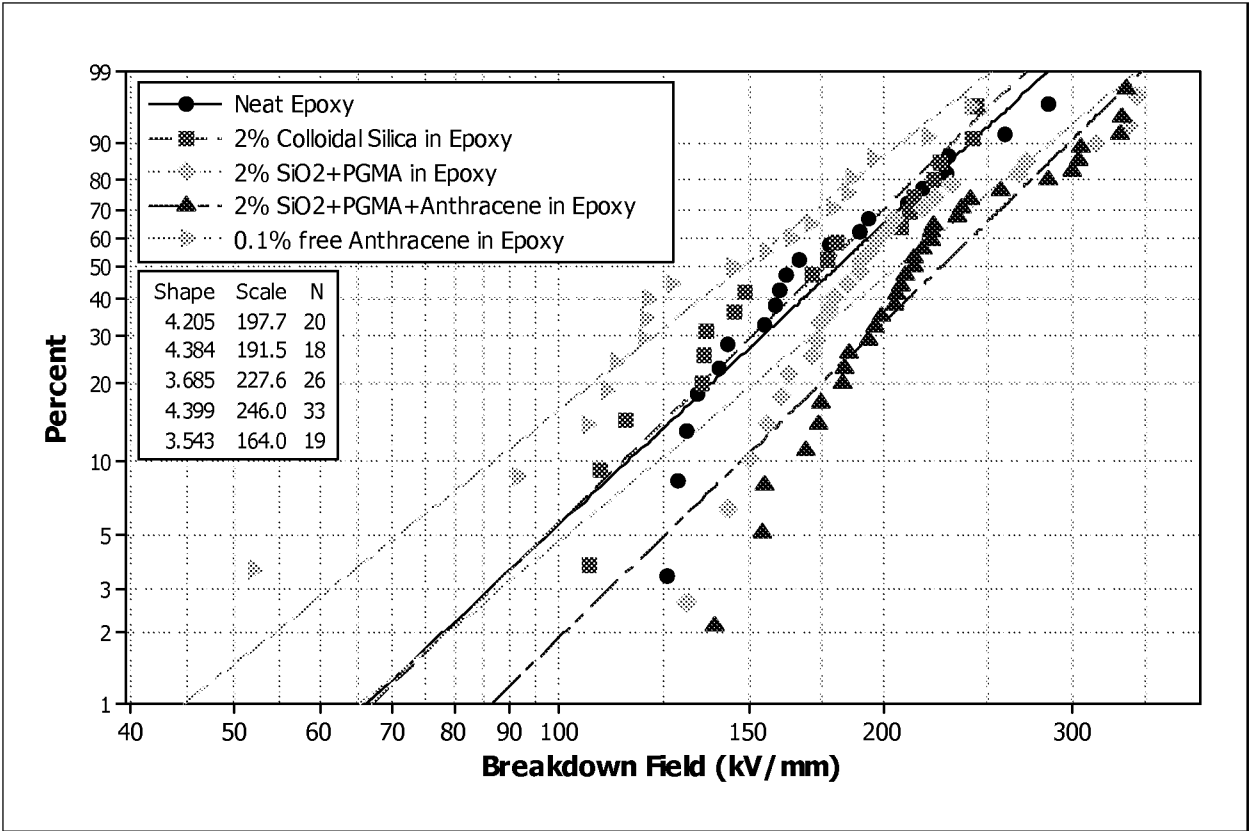


FIG. 10

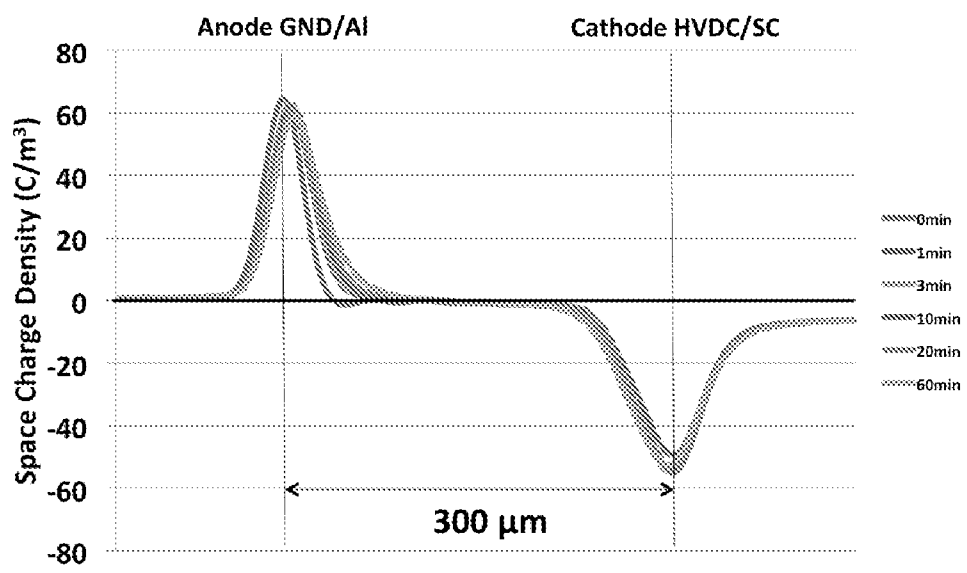
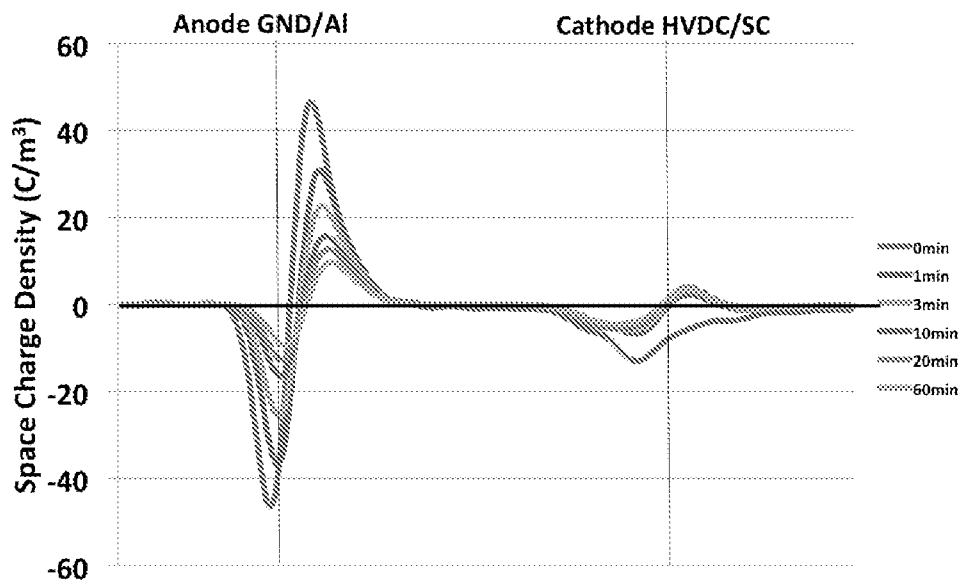
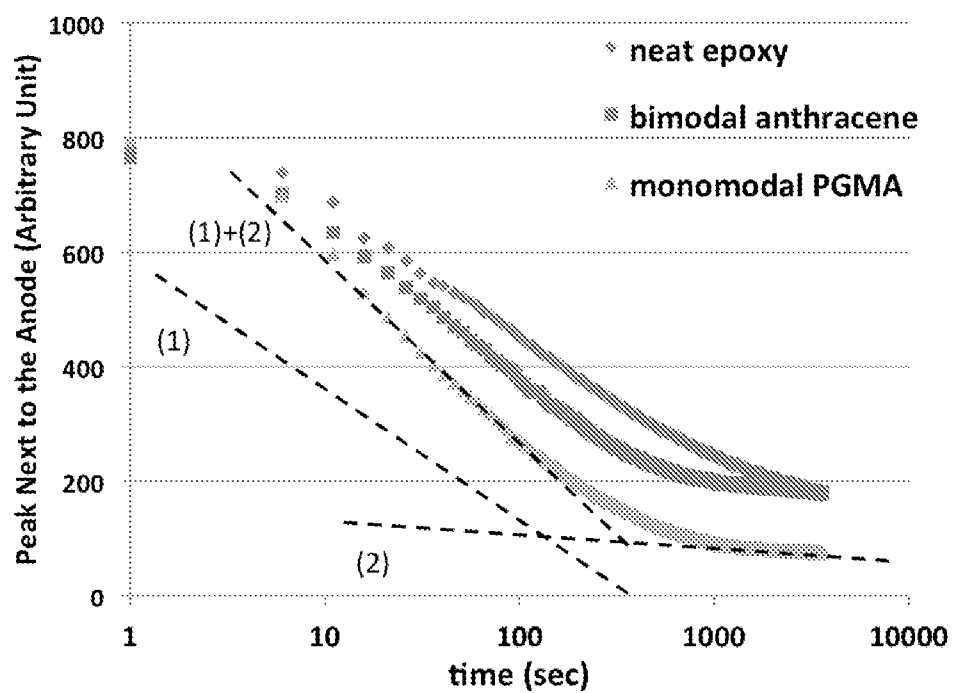
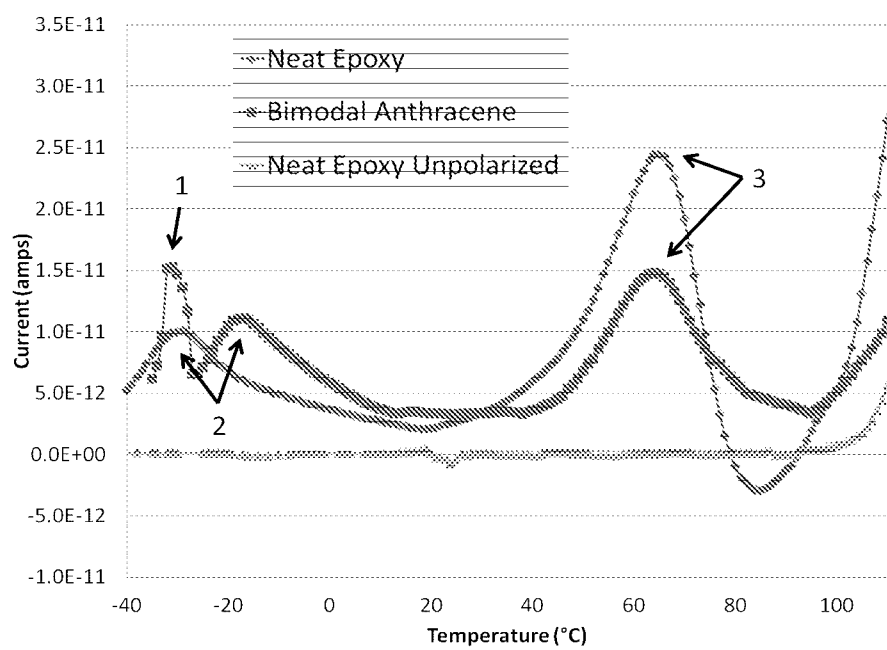
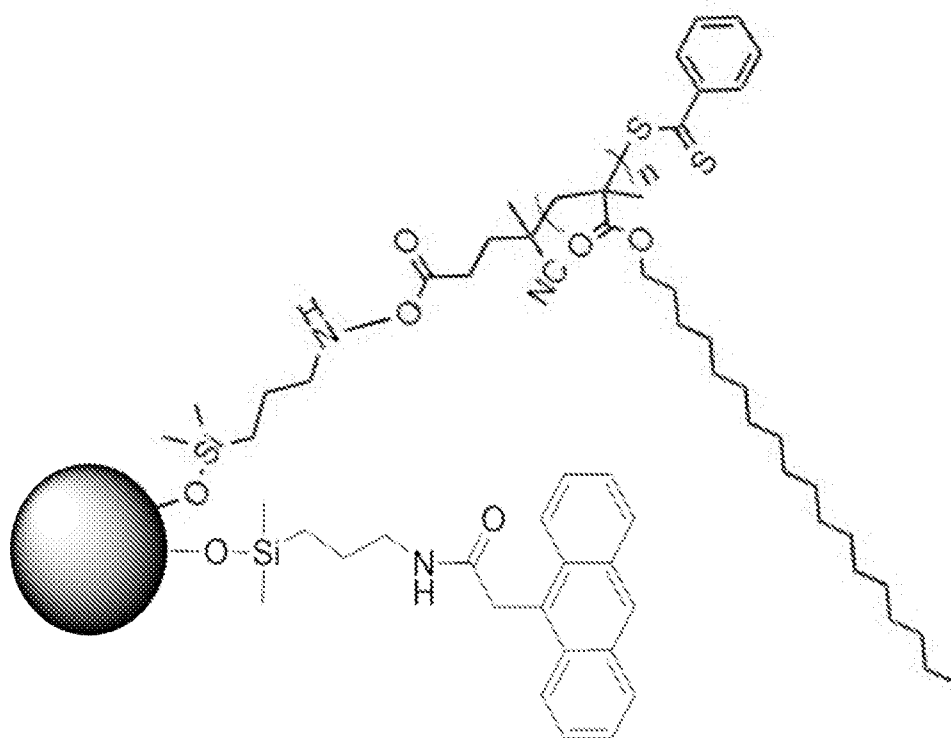


FIG. 11A

**FIG. 11B****FIG. 12**

**FIG. 13****FIG. 14**

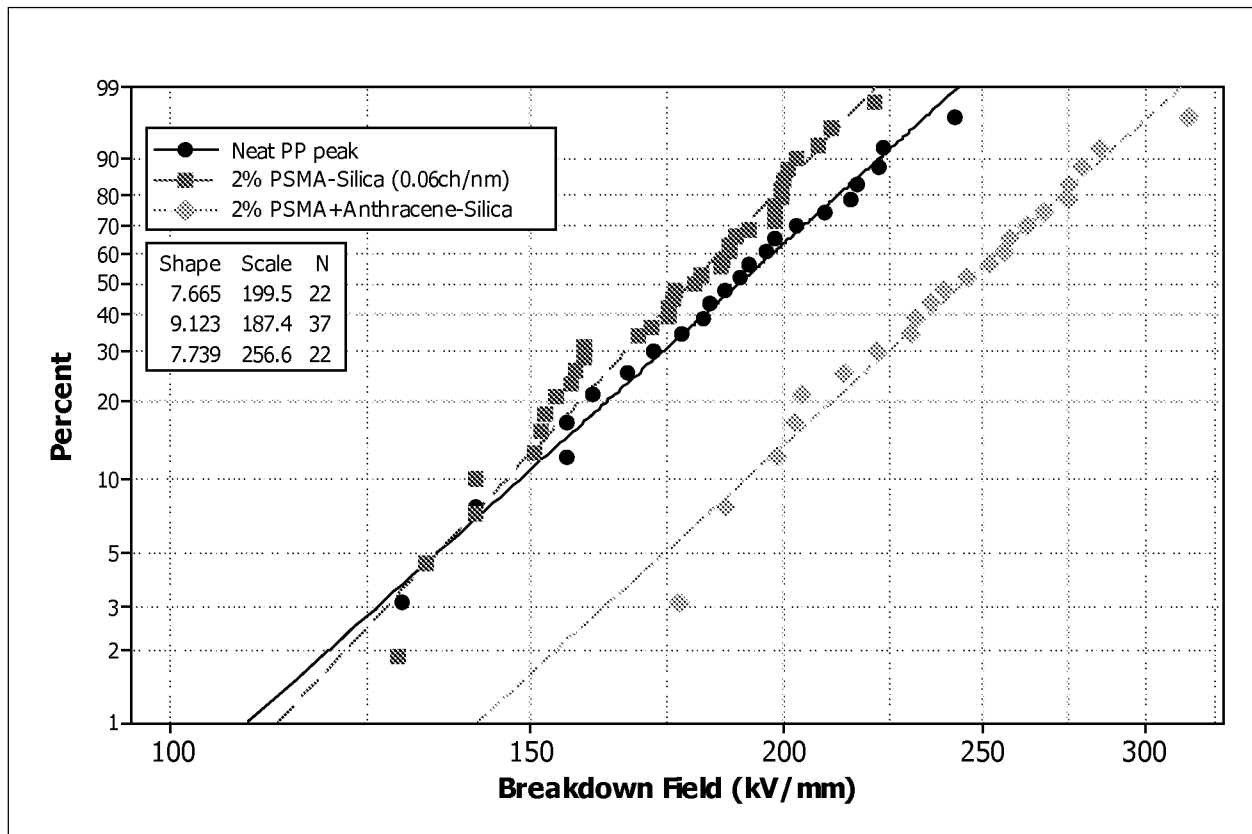


FIG. 15

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US14/58095

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - B82Y 30/00; B82B 1/00 (2014.01)

CPC - B82Y 30/00; C08K 7/00, 7/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC(8) - B82Y 30/00; B82B 1/00 (2014.01)

CPC - B82Y 30/00; C08K 7/00, 7/04, 7/18; USPC - 977/700, 773, 778, 810

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

MicroPatent (US-G, US-A, EP-A, EP-B, WO, JP-bib, DE-C,B, DE-A, DE-T, DE-U, GB-A, FR-A); ProQuest; IEEE; Google Scholar; nanoparticle, bimodal, dielectric, polymer, metallocene, ferrocene, anthracene

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2013/0041112 A1 (BENICEWICZ, BC et al.) 14 February 2013; figures 1, 3; paragraphs [0020]-[0026], [0036], [0049], [0055]-[0056], [0076], [0108]-[0110], [0115]-[0117]	1-35
Y	CHEN, W et al. Photoluminescence and conductivity studies of anthracene-functionalized ruthenium nanoparticles. Nanoscale. 15 April 2011. Vol. 3. pages 2294-2300; abstract; pages 2294-2298	1-35
Y	US 8,518,473 B2 (TAO, P et al.) 27 August 2013; column 4, lines 23-61; column 5, lines 13-19	4, 14/4, 15/14/4, 16/15/14/1-12, 17/14/4, 18/14/4, 23, 33/4, 34/33/4, 35/34/33/4
Y	KUMAR, SK et al. Nanocomposites with Polymer Grafted Nanoparticles. Macromolecules. 23 April 2013. Vol. 49. pages 3199-3214; abstract; pages 3201-3202	13, 14/13, 15/14/13, 16/15/14/13, 17/14/13, 18/14/13, 32, 33/13, 34/33/13, 35/34/33/13

☐ Further documents are listed in the continuation of Box C.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

26 November 2014 (26.11.2014)

Date of mailing of the international search report

11 DEC 2014

Name and mailing address of the ISA/US

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P.O. Box 1450, Alexandria, Virginia 22313-1450
Facsimile No. 571-273-3201

Authorized officer:

Shane Thomas

PCT Helpdesk: 571-272-4300
PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US14/58095

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 36-38
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.