(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
12 January 2017 (12.01.2017)

WIPO | PCT

(10) International Publication Number
WO 2017/005280 A1

(51) International Patent Classification:
H01B 3/44 (2006.01) ***C08L 23/04*** (2006.01)

(21) International Application Number:
PCT/EP2015/065216

(22) International Filing Date:
3 July 2015 (03.07.2015)

(25) Filing Language: English

(26) Publication Language: English

(71) Applicant: **ABB TECHNOLOGY LTD** [CH/CH]; Affolternstrasse 44, CH-8050 Zürich (CH).

(72) Inventors: **HO, Chau-Hon**; Unterfeldstrasse 6, CH-4332 Stein (CH). **SCHEEL, Saskia**; Neuhofstrasse 14a, CH-5600 Lenzburg (CH). **PETERSSON, Linnea**; Vargbogatan 5E, S-723 34 Västerås (SE). **KÄSELAU, Sven**; Bürgerweide 52, 20535 Hamburg (DE). **LUINSTRA, Gerrit**; Grillenweg 13, 22523 Hamburg (DE).

(74) Agent: **AXELL, Kristina**; ABB AB, Intellecutual Property, Ingenjör Bååths Gata 11, 721 83 Västerås (SE).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— *of inventorship (Rule 4.17(iv))*

Published:

— *with international search report (Art. 21(3))*

(54) Title: NEXT LEVEL NANOCOMPOSITES FOR ELECTRICAL INSULATION

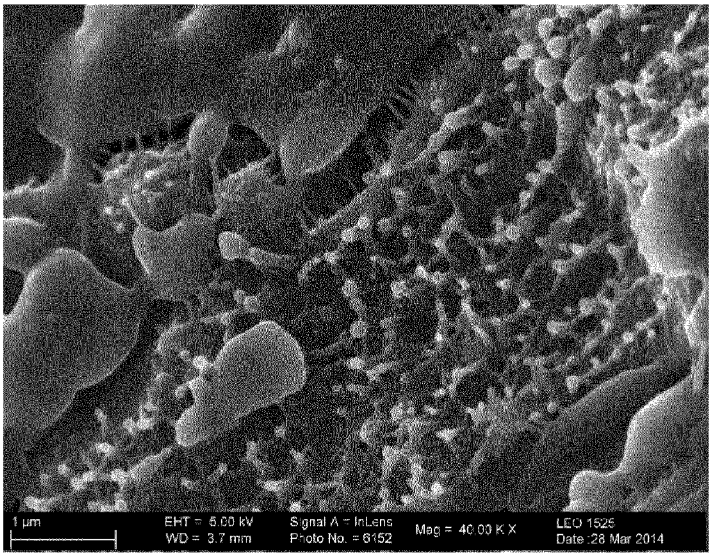

Fig. 1

(57) Abstract: The present invention refers to an electrical insulation composition for insulating an electrical device, and to a method for producing the same. The present invention also refers to an electrical insulation material comprising the electrical insulation composition, and to a dielectric film comprising the electrical insulation material. The present invention further refers to the use of the electrical insulation material or the dielectric film in the preparation of electrical devices, such as a capacitor. The present invention also refers to the use of spherical-type modified nanoparticles having a core-shell structure for increasing the dielectric breakdown strength of an electrical insulation material. Moreover, the present invention refers to a cable for low and/or medium and/or high voltage power transmission or distribution comprising a conductor surrounded by the electrical insulation material or the dielectric film. Also, the present invention is concerned with a capacitor comprising the electrical insulation material or the dielectric film as dielectric and to an electrical device comprising the electrical insulation material or the dielectric film.

NEXT LEVEL NANOCOMPOSITES FOR ELECTRICAL INSULATION

FIELD OF INVENTION

[001] The present invention refers to an electrical insulation composition for insulating an electrical device, and to a method for producing the same. The present invention also refers to an electrical insulation material comprising the electrical insulation composition, and to a dielectric film comprising the electrical insulation material. The present invention further refers to the use of the electrical insulation material or the dielectric film in the preparation of electric devices, such as a capacitor. The present invention also refers to the use of spherical-type modified nanoparticles having a core-shell structure for increasing the dielectric breakdown strength of an electrical insulation material. Moreover, the present invention refers to a cable for low and/or medium and/or high voltage power transmission or distribution comprising a conductor surrounded by the electrical insulation material or the dielectric film. Also, the present invention is concerned with a capacitor comprising the electrical insulation material or the dielectric film as dielectric, and to an electrical device comprising the electrical insulation material or the dielectric film.

STATE OF THE ART

[002] The addition of inorganic nanofillers to thermoplastic polymers in order to obtain nanocomposites is a known method for improving the properties of polymers used as electrical insulation materials, e.g. for reducing the electrical conductivity thereof. Typically, these nanocomposites are prepared by conventional methods such as melt blending, solution mixing or direct nanoparticle synthesis (sol-gel process involving a soluble precursor).

[003] The conventional methods for preparing nanocomposites have several drawbacks. For instance, in all of them, the high viscosity of plastic and the chemical incompatibility between the nanofillers and the polymer matrix usually result in aggregates of the nanoparticle in the composite material. This is detrimental to the

mechanical and, especially to the electrical properties of the final polymer insulation material. For instance, nanoparticle aggregation may result in lower tensile strength and lower dielectric breakdown strength leading to a higher probability of failure. The introduction of surfactants may lead to a reduction of the number and change the size or type of agglomerates, however such additional chemicals (which are usually volatile and able to migrate) may again negatively influence the electrical properties. In addition, when using solution mixing or direct nanoparticle synthesis, an excessive amount of chemical solvents is required, and therefore, these methods are neither cost-effective nor environmentally acceptable.

[004] In view of the above, there is a need for next level nanocomposites, i.e. thermoplastic resins with nanoparticles useful as electrical insulation materials and having improved electrical properties, e.g. improved dielectric breakdown strength, as well as for a method for producing the same.

BRIEF DESCRIPTION OF THE INVENTION

[005] As a result of intensive studies conducted taking the above described problems into consideration, the present inventors were surprised to find that by blending distinct modified nanoparticles into a polyolefin, an electrical insulation composition (i.e. a nanocomposite) is provided which shows no particle aggregation within the polymer matrix. More specifically, a uniform nanoparticle distribution of more or less individually dispersed nanoparticles within the polymer matrix is observed which provides several advantages over those nanocomposites which have been produced by conventional methods such as melt blending, solution mixing or direct nanoparticle synthesis.

[006] For instance, the electrical insulation composition according to the present invention, having such a uniform particle distribution, is particularly useful for producing electrical insulation materials having high dielectric breakdown strength and low conductivity while at the same time having good mechanical properties. By blending the electrical insulation composition according to the present invention with another polyolefin, an electrical insulation material is obtained having improved AC and DC dielectric breakdown strength by up to 34% (for AC dielectric breakdown strength)

compared to an electrical insulation material composed of a conventional nanocomposite blended within a polyolefin. This is highly beneficial for the development of more robust insulation systems such as cable insulations and capacitor dielectrics.

[007] This highly beneficial increase in dielectric breakdown strength of electrical insulation materials according to the present invention is particularly owed to the fact that the nanoparticles are blended together with an olefin and a catalyst system under conditions of an in-situ olefin polymerization. Although not limited by this presumption, it is envisioned that the electrical insulation capability of the composite is increased in a very particular way by a better dispersion of the nanoparticles in the polymer matrix, and by the properties of the modified nanoparticles. More specifically, the nanoparticles used are modified such that they have a core shell structure (core shell morphology) wherein the shell comprises a co-catalyst system for an in-situ polymerization of olefins. In other words, the shell of the modified nanoparticles defined herein does not only represent a coating composition which - in the final electrical insulation composition - may have a smaller dielectric constant than the neat nanoparticle as it would be obtained by synthesis or simply by coating the nanoparticle via conventional processes such as chemical vapor deposition (CVD), atomic layer deposition (ALD), expanding thermal plasma (ETP) or the like. In fact, the shell of the modified nanoparticles used within the present invention comprises a chemically active co-catalyst system for a polymerization of olefins. This co-catalytic functionality of the nanoparticle shell may provide several benefits. It may be presumed that by adding a catalyst for in-situ polymerization (such as a metallocene catalyst) to these co-catalytic functionalized nanoparticles (e.g. in a solvent), the catalyst will link to the co-catalyst, thereby forming a reactive catalytic olefin polymerization system on the nanoparticles' surface. As a consequence, olefin monomers can polymerize directly on the surface of the nanoparticles. This may prevent the formation of particle agglomerates and leads to a highly homogeneous particle distribution within the electrical insulation composition as well to a pronounced interface and a binding situation between the nanoparticles and the polymer matrix (polyolefin). Without being bound to theory, the highly homogeneous particle distribution would be owed to the fact that, in principle, the polymerization starts on each nanoparticle surface (comprising the catalytic system) by the interaction of a specific number of monomers with the catalytic system (consisting of

co-catalyst and catalyst) positioned on the nanoparticle surface. Thereby, the polymerization propagates in all directions from the surface of each modified nanoparticle acting as an autonomous polymerization reactor. In other words, the modified nanoparticles of the present invention are completely integrated in the polymerization process instead of only being passively present.

[008] A high degree of matrix homogeneity and a specific binding situation between the nanoparticles and the polymer matrix improves the reliability of electrical devices made of the electrical insulation composition having the distinct modified nanoparticles dispersed therein. This enables the production of designs with smaller dimensions of electrical devices as well as higher operation ratings due to a higher withstand of the insulation material towards electrical fields. Moreover, since the olefin monomer polymerizes directly on the surface of the particles, complex mixing procedures between polymers and particles are largely avoided, and thus, air contamination (caused by conventional mixing) is obviated so that health and safety with regards to work environment is improved. Overall, the shell of the modified nanoparticles combines several benefits by only using one component (i.e. the co-catalyst) in the sense that it leads to a binding between the particles and the polymer matrix, provides a homogeneous particle distribution and results in an increase in catalytic activity.

[009] By contrast, blending conventional nanofillers (which do not exhibit a co-catalyst surrounding the particle core) with (already prepared, commercially available) polymers results in the challenge that these nanofillers have to be uniformly dispersed within the polymer matrix (being in the form of a polymer powder or pellets) in order to avoid the formation of concentration gradients and local field variations / enhancement within the matrix leading to early dielectric breakdown of the final electrical insulation material. A time-consuming and cost-intensive mixing process is the consequence, together with an increased health and safety risk due to possible air contamination caused by these nanofillers during the mixing process. In spite of highly sophisticated mixing processes, there is still a significant risk of the formation of nanofiller agglomerates within the polymer matrix resulting in undesired concentration gradients, less uniform nanofiller distribution, and finally in early dielectric breakdown and inferior mechanical properties,

such as a decreased elongation at break. This is particular true when nanofillers are prepared or not stored properly, or are stored for a long time. Thus, blending nanofillers with polyolefins by conventional mixing processes does not result in nanocomposites having such a high degree of homogeneity as is the case for the electrical insulation compositions of the present invention.

[0010] Moreover, when blending conventional nanofillers (which do not exhibit a co-catalyst surrounding the particle core) with monomers, in principle, the polymerization reaction of the monomers can be induced whether or not nanoparticles are present. At best, these nanoparticles do not influence the polymerization negatively. In other words, in contrast to the specific nanoparticles used in the present invention, these conventional nanofillers are not integrated in the polymerization process, and thus play an ill-defined role during polymerization, and the results of the preparation may vary with respect to dispersion of the particles and the electrical properties of the composites prepared therefrom.

[0011] Above all, by using conventional nanofillers (without a co-catalyst surrounding the particle core), often one or more additional surface treatments are required in order to facilitate bonding or adhesion with the polymeric material. For instance, nanofillers can be coated with silane-coupling agents in order to enhance compatibility of the nanofillers with the polymeric material and to improve dispersion of the nanofillers within the polymeric material. Such surface treatments imply an additional cost-intensive process step and do not lead to such a close entanglement between the nanofillers and the polymer matrix since polymerization of the monomers does not take place directly on the surface of nanofillers. Moreover, these surface treatments may also have a negative effect on the electrical losses of the material and may deteriorate the mechanical properties thereof.

[0012] The present invention is defined in the claims. The present invention refers to an electrical insulation composition for insulating an electrical device, comprising
- a (at least one) polyolefin, and
- spherical-type modified nanoparticles dispersed within the polyolefin,

wherein the spherical-type modified nanoparticles have a core-shell structure, and wherein the shell has a total content of at least one of a metal and a metalloid of 0.01 wt% to 10 wt%, based on the total weight of the spherical-type modified nanoparticle.

[0013] The present invention further refers to a method for producing an electrical insulation composition, comprising the steps of:

i) providing spherical-type modified nanoparticles having a core-shell structure,

ii) adding at least one olefin monomer to the spherical-type modified nanoparticles, and

iii) adding at least one catalyst to start (and perform) an in-situ polymerization of the olefin monomer onto the spherical-type modified nanoparticles to obtain a composite, wherein the shell of the spherical-type modified nanoparticles acts as a co-catalyst for the in-situ polymerization.

[0014] The present invention further refers to an electrical insulation material, comprising 1 wt% to 95 wt% of the electrical insulation composition as defined herein dispersed in 5 wt% to 99 wt% of a polyolefin, based on the total weight of the electrical insulation material.

[0015] The present invention further refers to a dielectric film comprising the electrical insulation material according to the present invention.

[0016] The present invention further refers to the use of the electrical insulation material or the dielectric film according to the present invention in the preparation of electrical devices, such as a capacitor.

[0017] The present invention further refers to the use of spherical-type modified nanoparticles having a core-shell structure for increasing the dielectric breakdown strength of an electrical insulation material. The electrical insulation material can comprise at least one polyolefin formed by in-situ polymerization. The shell of the modified nanoparticles can comprise a co-catalyst for the in-situ polymerization.

[0018] The present invention further refers to the use of the electrical insulation material or the dielectric film according to the present invention for electrically insulating electrical components such as cables, capacitors, bushings and transformers.

[0019] The present invention further refers to a cable for low and/or medium and/or high voltage power transmission or distribution comprising a conductor surrounded by the electrical insulation material or the dielectric film according to the present invention.

[0020] The present invention further refers to a capacitor comprising the electrical insulation material or the dielectric film according to the present invention as dielectric.

[0021] The present invention further refers to an electrical device comprising the electrical insulation material or the dielectric film according to the present invention.

[0022] Further embodiments, aspects, advantages and features of the present invention are described in the dependent claims, the description and the accompanying drawings.

[0023] In the following, if not otherwise defined, “wt%” (% by weight) refers to the total weight of the respective entity (e.g. the total weight of the electrical insulation composition or the total weight of electrical insulation material). Furthermore, if not otherwise stated, all measurements were carried out at room temperature.

BRIEF DESCRIPTION OF THE DRAWINGS

[0024] The details will be described in the following with reference to **Figs. 1** to **8**.

[0025] **Fig. 1:** SEM analysis on a cryo-break pressed surface of LLDPE-MgO (in-situ) with 5 % nanofiller.

[0026] **Fig. 2:** SEM analysis on a cryo-break pressed surface of LLDPE-MgO (extruded) with 5 % nanofiller.

[0027] **Fig. 3:** SEM analysis on a cryo-break pressed surface of LLDPE-$Mg(OH)_2$ (in-situ) with 5 % nanofiller.

[0028] **Fig. 4:** SEM analysis on a cryo-break pressed surface of LLDPE-$Mg(OH)_2$ (extruded) with 5 % nanofiller.

[0029] **Fig. 5:** AFM analysis on a surface of a microtome section from a pressed sample of LLDPE without nanofiller.

[0030] **Fig. 6:** AFM analysis on a surface of a microtome section from a pressed sample of LLDPE-MgO (in-situ).

[0031] **Fig. 7:** AFM analysis on a surface of a microtome section from a pressed sample of LLDPE-$Mg(OH)_2$ (in-situ).

[0032] **Fig. 8:** Example of a cable structure according to the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0033] Reference will now be made in detail to various embodiments and aspects of the invention. Each embodiment and each aspect is provided by way of explanation and is not meant as a limitation. For example, features illustrated or described as part of one embodiment or aspect can be used on or in conjunction with any other embodiment or aspect to yield yet a further embodiment or aspect. It is intended that the present disclosure includes any such combinations and variations.

[0034] According to an embodiment, the invention relates to an electrical insulation composition for insulating an electrical device, comprising
- a (at least one) polyolefin, and
- spherical-type modified nanoparticles dispersed within the polyolefin,

wherein the spherical-type modified nanoparticles have a core-shell structure,
and
wherein the shell has a total concentration of at least one of a metal and a metalloid of 0.01 wt% to 10 wt%, based on the total weight of the spherical-type modified nanoparticle.

[0035] According to an aspect, the electrical insulation composition comprises no particle aggregates, determined via visual inspection, polarized microscopy, atomic force microscopy (AFM), transmission electron microscopy (TEM), scanning electron microscopy (SEM), or a combination of one or more of these techniques. For the purpose of this application, particle agglomerates determined via the above-mentioned techniques are understood to be clusters of particles having an average grain size of greater than 5 μm. Preferably, particle agglomerates determined via the above-mentioned techniques are, at maximum, composed of ten modified individual nanoparticles. Thus, an electrical insulation composition comprising no particle agglomerates determined via the above-mentioned techniques is actually an electrical insulation composition which does not comprise particle agglomerates having an average grain size of greater than 5 μm and/or being composed of no more than ten modified individual nanoparticles. In other words, the electrical insulation composition comprises more or less individually dispersed modified nanoparticles which are homogeneously dispersed in the polymer matrix of the electrical insulation composition. Applying the above-mentioned techniques shows that the electrical insulation composition shows no particle aggregation throughout the whole electrical insulation composition. For instance, in Figs. 1 and 3 (referring to the SEM analysis of exemplary electrical insulation compositions according to the present invention), no nanoparticle agglomeration on a length scale of > 1 μm can be observed while in Figs. 2 and 4 (referring to the SEM analysis of exemplary conventional extruded electrical insulation compositions), agglomeration is observed on a length scale of > 1 μm. Fig. 5 shows a LLDPE without nanofillers (Blank 3, see Table 1). Fig. 6 shows single nanoparticles in PE matrix of an exemplary electrical insulation composition according to the present invention, i.e. LLDPE-MgO-1 %). In Fig. 7, nanoparticles of up to 300 nm are detected (in an exemplary electrical insulation composition according to the present invention, i.e. LLDPE-$Mg(OH)_2$-1 %) which are probably not agglomerates.

[0036] According to an aspect, the electrical insulation composition can comprise the (at least one) polyolefin in a concentration of 90 wt% to 99.9 wt%, preferably 92 wt% to 99.8 wt%, more preferably 94 wt% to 99.5 wt%, based on the total weight of the electrical insulation composition.

[0037] According to an aspect, the electrical insulation composition can comprise the spherical-type modified nanoparticles in a concentration of 0.1 wt% to 10 wt%, preferably 0.2 wt% to 8 wt%, more preferably 0.3 wt% to 7 wt%, even more preferably 0.5 wt% to 6 wt%, based on the total weight of the electrical insulation composition.

[0038] Examples of polyolefins that can be used in the electrical insulation composition include polyethylene (PE), polypropylene (PP), polymethylpentene (PMP), polybutene-1 (PB-1), copolymers of polyethylene and polypropylene, ethylene propylene diene rubber (EPDM), polystyrene (PS), or a combination comprising at least two of the foregoing polyolefins. Particularly preferred polyolefins that can be used in the electrical insulation composition include polyethylene (PE) and polypropylene (PP).

[0039] Examples of polyethylenes (PE) that can be used in the electrical insulation composition include high density polyethylene (HDPE) having a density of between 0.94 g/cm^3 und 0.97 g/cm^3, low density polyethylene (LDPE) having a density of between 0.915 g/cm^3 und 0.935 g/cm^3, linear low density polyethylene (LLDPE) having a density of between 0.87 g/cm^3 und 0.94 g/cm^3, high molecular weight polyethylene (HMWPE) having an average molar mass of 500-1000 kg/mol, and ultra high molecular weight polyethylene (UHMWPE) having an average molar mass of up to 6000 kg/mol and a density of between 0.93–0.94 g/cm^3. A particularly preferred polyethylene (PE) that can be used in the electrical insulation composition is a linear low density polyethylene (LLDPE) having a density of between 0.87 g/cm^3 und 0.94 g/cm^3.

[0040] Examples of polypropylenes (PP) that can be used in the electrical insulation composition include isotactic polypropylene (i-PP) and syndiotactic polypropylene (s-PP). A particularly preferred isotactic polypropylene (i-PP) that can be used in the electrical insulation composition has an isotacticity of greater than 90% mmmm-pentads.

[0041] Apart from the polyolefins described above, the electrical insulation composition according to the present invention comprises spherical-type modified nanoparticles.

[0042] For the purpose of this application, “nanoparticles” are understood to be particles having an average grain size within the range of 1 nm to 1000 nm, more preferably within the range of 10 nm to 500 nm, most preferably within the range of 20 nm to 400 nm. The average grain size can be determined via SEM, TEM, particle analyzer or DLS. Preferably, the average grain size can be determined by TEM. In particular, the average grain size can be determined by taking TEM images and evaluating the grain sizes. The term “nanoparticle” refers to a particle having no surface modification. In other words, a “nanoparticle” is understood to be the “neat”, “naked” particle which is not modified on its surface after its preparation. By contrast, a “modified nanoparticle” is understood to be a nanoparticle which has undergone surface modification(s). For instance, a “modified nanoparticle” can be a nanoparticle which – upon surface treatment – bears specific functional groups on its surface. A “modified nanoparticle” can also be a nanoparticle which – upon surface treatment – bears a coating layer on its surface. In case the modified nanoparticle has a “core-shell structure” the “core” corresponds to the “naked” nanoparticle while the “shell” corresponds to the coating layer.

[0043] For the purpose of this application, a “spherical-type” modified nanoparticle is understood as a particle having an aspect ratio, defined as a function of the smallest diameter d_{min} and the largest diameter d_{max} orthogonal to it: $A_R = d_{min}/d_{max}$ which is preferably from 0.3 to 1, more preferably from 0.4 to 1, most preferably from 0.5 to 1. Preferably, in the “spherical-type” modified nanoparticle, the largest possible ideal sphere which can be inserted in the modified nanoparticle while being completely filled with modified nanoparticle material has a volume which correspond to at least 40 vol%, preferably at least 60 vol% of the total modified nanoparticle volume. Also preferably, the “spherical-type” modified nanoparticle according to the present invention fulfills the following equation:

$$d_1:d_2 \text{ is at least 1.0 and at most 5.0, when } d_1 \geq d_2.$$

where d_1 is the distance between any point on the surface of the modified nanoparticle (i.e. any point on the surface of the shell) and the center of gravity of the particle, and d_2 is the distance between any other point on the surface of the modified nanoparticle (i.e.

any other point on the surface of the shell) and the center of gravity of the particle. More preferably, the expression “spherical-type” means that the modified nanoparticles have a shape approximating that of a sphere. In other words, the modified nanoparticles are nearly orbicular in shape and have a cross-sectional geometry that is essentially circular. Although not excluded, this does not necessarily mean that the modified nanoparticles used in the electrical insulation composition have the shape of a perfect sphere or ball. More likely, the shape of the modified nanoparticles can exhibit a certain deviation from a sphere as long as the skilled person considers the shape as being similar to a sphere or as an approximation of a sphere, and is different from needles or tubes, like e.g. carbon nanotubes or Halloysites aluminum silicate, as used e.g. in DE 10 2012 221 584 A1. The approximate spherical-type shape of the modified nanoparticles is of high relevance for electrical applications. Using spherical-type modified nanoparticles having an aspect ratio outside the above-mentioned range, e.g. nanoparticles having the shape of needles or tubes would lead to an accumulation of charge at the particle tips, which is not desirable for electrical applications. Thus, while needle-like or tubular modified nanoparticles may be suitable for mechanical properties of polymers, e.g. in the automobile industry, they are not particular suitable for electrical applications, such as for those described in the present application.

[0044] According to an aspect, the spherical-type modified nanoparticles are dispersed within the polyolefin. Preferably, the spherical-type modified nanoparticles are distributed in the polyolefin matrix in an essentially homogenous way. This means that the amount of spherical-type modified nanoparticles in an arbitrary space of 10 μm^3 within the electrical insulation composition is essentially constant.

[0045] The modified nanoparticles used in the electrical insulation composition according to the invention have a core-shell structure. The core may exist in the form of spheres, flakes, whiskers, or shapes approximating these forms. Preferably, the core exists in the form of spheres. The core may have a cross-sectional geometry that may be circular, ellipsoidal, triangular, rectangular, polygonal, or a combination comprising at least two of the foregoing geometries. In a particular aspect, the core may have a shape approximating that of a sphere. In other words, the core has a spherical-type shape as defined above. The average grain size of the core corresponds to that of the nanoparticles as defined above.

[0046] According to an aspect, the core of the modified nanoparticles used in the electrical insulation composition according to the present invention can comprise an inorganic material. According to another aspect, the core of the modified nanoparticles used in the electrical insulation composition according to the present invention can consist of an inorganic material. Examples of the inorganic material that can be comprised in the core include metal nitride, metal oxide (also in form of stoichiometric dimetal oxides), metal hydroxide, metalloid oxide, layered metalloid, carbides, silicides, phosphides, sulfides, selenides, or a combination comprising at least two of the foregoing compounds. For the purpose of this application, metals are elements that are - in the periodic table of elements - in the area to the left of and below a line from boron to astatine. For the purpose of this application, metalloids are elements selected from borum (B), silicon (Si), arsenic (As), tellurium (Te) and germanium (Ge).

[0047] Suitable metal nitrides of the core include AlN, BN or a combination thereof.

[0048] Suitable metal oxides of the core include MgO, CaO, Al_2O_3, WO_3, CuO, CoO, TiO_2, $TiBaO_3$, Sb_2O_3, ZnO, CdO, BaO, Fe_2O_3, $CaCO_3$, or a combination comprising at least two of the foregoing metal oxides.

[0049] Suitable metal hydroxides of the core include $Mg(OH)_2$, $Ca(OH)_2$, $Al(OH)_3$, $Ba(OH)_2$, or a combination comprising at least two of the foregoing metal hydroxides.

[0050] Suitable metalloid oxides of the core include SiO_2, B_2O_3, GeO_2, or a combination comprising at least two of the foregoing metalloid oxides.

[0051] A suitable layered metalloid of the core includes clay.

[0052] In a particular preferred aspect, the core comprises MgO. In a further particular preferred aspect, the core comprises $Mg(OH)_2$. In a still further particular preferred aspect, the core comprises SiO_2. In a still further particular preferred aspect, the core comprises clay.

[0053] According to an aspect, the shell of the modified nanoparticles used in the electrical insulation composition according to the present invention can comprise an inorganic material. According to another aspect, the shell of the modified nanoparticles used in the electrical insulation composition according to the present invention can consist of an inorganic material. Examples of the inorganic material that can be comprised in the shell include at least one metal oxide, at least one metalloid oxide, or a combination of at least one metal oxide and at least one metalloid oxide.

[0054] Suitable metal oxides of the shell include MgO, Al_2O_3, ZnO, TiO_2, $BaTiO_3$, or a combination comprising at least two of the foregoing metal oxides. In a particular preferred aspect, the shell comprises MgO. In a further particular preferred aspect, the shell comprises Al_2O_3. In a still further particular preferred aspect, the shell comprises MgO and Al_2O_3.

[0055] Suitable metalloid oxides of the shell include SiO_2, B_2O_3, GeO_2, or a combination comprising at least two of the foregoing metalloid oxides.

[0056] According to an aspect, the shell can comprise the same inorganic material as the core of the modified nanoparticles. For instance, the shell comprises MgO (and optionally another metal oxide such as Al_2O_3) while the core also comprises MgO. Such a specific shell composition results in both a high catalytic activity and a high dielectric breakdown strength.

[0057] According to an aspect, the shell of the modified nanoparticles used in the electrical insulation composition according to the present invention has a total concentration of at least one of a metal and a metalloid of 0.01 wt% to 10 wt%, preferably 0.1 wt% to 8 wt%, more preferably 0.5 wt% to 5 wt%, based on the total weight of the spherical-type modified nanoparticle. For instance, in case where the shell comprises Al_2O_3, the concentration of Al is 0.01 wt% to 10 wt%, preferably 0.1 wt% to 8 wt%, more preferably 0.5 wt% to 5 wt%, based on the total weight of the spherical-type modified nanoparticle. In case where the shell comprises MgO and Al_2O_3, the concentration of Mg and Al is 0.01 wt% to 10 wt%, preferably 0.1 wt% to 8 wt%, more preferably 0.5 wt% to 5 wt%, based on the total weight of the spherical-type modified nanoparticle. The total concentration of the at least one of a metal and/or a metalloid in the shell can be measured by TGA analysis, i.e. by determining the increase in weight of the original nanoparticles after removing all of the polymer by thermolysis. EDX measurements or elementary analysis can be used to determine the composition of the shell and the concentrations of metal and/or metalloid.

[0058] According to a further aspect, the shell of the modified nanoparticles used in the electrical insulation composition according to the present invention has a total concentration of at least one of a metal and a metalloid of 0.01 wt% to 5 wt%, preferably 0.02 wt% to 3 wt%, more preferably 0.03 wt% to 1 wt%, based on the total weight of the electrical insulation composition.

[0059] Suitable metals of the shell include Al (aluminum), Mg (magnesium), Zn (zinc), Ti (titanium), or a combination comprising at least two of the foregoing metals.

[0060] Suitable metalloids of the shell include B (boron), Si (silicon), or a combination thereof.

[0061] A balanced metal/metalloid concentration in the shell of the modified nanoparticles is highly important for the electrical properties of an electrical insulation material comprising these modified nanoparticles. On the one hand, using a higher metal/metalloid concentration in the shell (obtained from using a higher co-catalyst concentration in the method for producing the modified nanoparticles) will lead to a better dispersion of the nanoparticles in the polymer matrix and to a higher catalytic activity for the in-situ polymerization. On the other hand, using a concentration of the metal/metalloid in the shell that is too high will lead to an increase in the conductivity of the final electrical insulation material, thereby reducing its dielectric breakdown strength. This may be owed to the fact that a too high concentration of metal/metalloids in the nanoparticle shell may result in a multitude of free metal species (ions) that cannot be bound in the shell and thus can migrate into the polymer matrix leading to a higher conductivity thereof. The present inventors found that the above-outlined concentration range of metal/metalloid in the shell is well balanced and provides good nanoparticle dispersion in the polymer matrix, a sufficiently high catalytic activity, and improved dielectric breakdown strength in the final electrical insulation material.

[0062] According to an aspect, the shell can have a thickness of 1 nm to 50 nm, preferably 2 nm to 40 nm, more preferably 5 nm to 20 nm. A thicker shell will most likely lead to reduced dielectric breakdown strength due to a higher total amount of metal/metalloid in the shell while a thinner shell will lead to a decrease in catalytic activity and a decreased homogeneity of particle distribution in the polymer matrix.

[0063] The shell of the modified nanoparticles used in the electrical insulation composition according to the present invention can be formed on the core (i.e. on the nanoparticle) in a method described in more detail below.

[0064] According to an embodiment, the invention also relates to a method for producing an electrical insulation composition, comprising the steps of:

i) providing spherical-type modified nanoparticles having a core-shell structure,

ii) adding at least one olefin monomer to the spherical-type modified nanoparticles, and

iii) adding at least one catalyst to start and perform in-situ polymerization of the at least one olefin monomer onto the spherical-type modified nanoparticles to obtain a composite, wherein the shell of the spherical-type modified nanoparticles acts as a co-catalyst for the in-situ polymerization.

[0065] According to an aspect, the spherical-type modified nanoparticles having a core-shell structure provided in step i) are produced as follows.

[0066] Neat nanoparticles as defined above are added to (dispersed in) a solvent to obtain a mixture (of solvent and nanoparticle). Optionally, these nanoparticles can be dried in a preliminary calcination step for 10 hours to 30 hours at 60°C to 400°C. Solvents that can be used for dispersing the nanoparticles can include liquid aromatic compounds. Examples of such liquid aromatic compounds include benzene, toluene, xylene, methyl styrene, ethylbenzene, liquid alkanes such as pentane, hexane, heptane, octane, or a combination comprising at least two of the foregoing compounds. Among these, it is preferable to use toluene as the solvent.

[0067] After having added the nanoparticles to the solvent, at least one co-catalyst for the in-situ polymerization performed in step iii) is added to the mixture. This means that one, two, three or more co-catalysts can be added to the solvent at the same time, or alternatively, one after another. Preferably, only one co-catalyst is added to the solvent. Also preferably, two co-catalysts can be added to the solvent one after another. In a preferred aspect, at least one of the two co-catalysts added comprises the same metal/metalloid as the core of the nanoparticle. This helps to provide both a high catalytic activity in step iii) and a high dielectric breakdown strength in the final electrical insulation material.

[0068] For the purpose of this application, a “co-catalyst” is understood to be a compound that activates the catalytic action of a catalyst.

[0069] Examples of co-catalysts that can be used for the in-situ polymerization include aluminum alkyl, zinc alkyl, magnesium alkyl, borate, or a combination comprising at least two of the foregoing.

[0070] Suitable aluminum alkyls include methylaluminoxane (MAO), trimethyl aluminum, triethyl aluminum, tributyl aluminum, triisobutyl aluminum hydride, ethyl aluminum sesquichloride, or a combination comprising at least two of the foregoing. Among these, it is preferable to use methylaluminoxan as co-catalyst.

[0071] Suitable zinc alkyls include dimethyl zinc, diethyl zinc, dibutyl zinc, diisobutyl zinc, or a combination comprising at least two of the foregoing. Among these, it is preferable to use diethyl zinc as co-catalyst.

[0072] Suitable magnesium alkyls include dimethyl magnesium, diethyl magnesium, dibutyl magnesium, diisobutyl magnesium, butyl octyl magnesium or a combination comprising at least two of the foregoing. Among these, it is preferable to use dibutyl magnesium as co-catalyst.

[0073] Suitable borates include Mg_2B_2O, $Na_2B_4O_7$, $CaAlB_3O_7$, $NaBO_2$, $Li_6B_4O_9$, $Ca_3(BO_3)_2$, or a combination comprising at least two of the foregoing. Among these, it is preferable to use Mg_2B_2O as co-catalyst.

[0074] According to an aspect, the at least one co-catalyst can be added to the nanoparticle/solvent dispersion in a weight ratio of co-catalyst:nanoparticle of 0.2:100 to 20:100, preferably 0.5:100 to 10:100, more preferably 1:100 to 8:100. The weight ratio between the at least one co-catalyst and the nanoparticle is highly important since it determines the final metal/metalloid concentration in the shell of the nanoparticles thereby laying the foundation for the electric properties of the final electrical insulation material (as details above).

[0075] The addition of the at least one co-catalyst to the solvent leads to the modification of the nanoparticle surface, thereby forming the shell around the nanoparticle core leading to the benefits as discussed in detail above.

[0076] After step i), step ii) is performed by adding at least one olefin monomer to the spherical-type modified nanoparticles (which are preferably dispersed in the solvent).

[0077] Examples of olefin monomers that can be used in step ii) include alkenes such as ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 1-octene, cyclohexene, cyclooctene, 1,3-butadiene, 4-methyl-1-pentene, styrene, norborene, isoprene, or a combination comprising at least two of the foregoing monomers. Particularly preferred olefins that can be used in in step ii) include ethylene and propylene.

[0078] According to an aspect, the at least one olefin monomer is added to the dispersion by saturating the solvent with the at least one olefin monomer, preferably at a pressure of between 0.5 and 5 bar, more preferably at 2 bar.

[0079] In step iii), at least one catalyst is added to start in-situ polymerization of the at least one olefin monomer onto the spherical-type modified nanoparticles to obtain a composite. Thereby, the shell of the spherical-type modified nanoparticles acts as a co-catalyst for the in-situ polymerization as explained in detail above.

[0080] Suitable catalysts (or precatalysts) that can be added in step iii) include metal salts or metal complexes. Preferred catalysts that can be used in step iii) include Ziegler-Natta, Phillips catalysts, constrained geometry complex catalysts, and Brookhart-Gibson catalysts, or a combination comprising at least two of the foregoing. In other words, preferred catalysts that can be used in step iii) lead to Ziegler-Natta or Phillips type of catalyst systems, are constrained geometry complex catalysts, and Brookhart-Gibson catalysts, or a combination comprising at least two of the foregoing. Suitable Ziegler-Natta catalysts include Ti-based heterogeneous precatalysts, metallocene catalysts, and non-metallocene catalysts. Suitable Phillips precatalysts include all Cr based compounds. In principle, these catalysts (or precatalysts) are metal compounds that will form olefin polymerization catalyst systems by interaction with the coated shell. These would comprise transition metal halogenides or alkoxides or oxo complexes, or any precursor known to those skilled in the art to form heterogenous (co)polymerization catalysts (as could be found in Handbook of Transition Metal Polymerization Catalysts (ISBN: 9780470137987)), or, metal complexes like titanocenes, zirconocenes, hafnocenes or e.g. complexes mentioned in H.-H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger and R. *Waymouth,* Angew. Chem. 1995, *107*, 1255; *Angew. Chem. Int. Ed. Engl.* 1995, *34*, 1143, or S. D. Ittel, L. K. Johnson, and M. *Brookhart*, *Chem. Rev.*, 100, 1169 (2000), or for example so called FI Catalysts (Iwashita, Akihiko; Makio, Haruyuki; Fujita, Terunori, Catalysis by Metal Complexes (2011), 36 (Olefin Upgrading Catalysis by Nitrogen-Based Metal Complexes II), 1-38). The resulting catalyst systems are probably of heterogeneous nature or are immobilized homogenous metal centers with ancillary ligands. Particularly preferred catalysts that can be used in step iii) include metallocene catalysts, and preferably include metallocene catalysts having Zr as central metal atom.

[0081] According to an aspect, the method for producing an electrical insulation composition further comprises step iv) drying the composite obtained in step iii). Step iv) is preferably performed for 1 hour to 48 hours, more preferably for 6 hours to 32 hours in an oven under vacuum at 20°C to 90°C, preferably at 30°C to 70°C.

[0082] The above described method allows the formation of pronounced interface and a strong entanglement of filler and polymer matrix. Furthermore, high loadings of the modified nanoparticles (> 5 wt%) can be achieved in the electrical insulation composition which is usually difficult with melt extrusion or solution blending – especially if “agglomeration-free” is required. This makes the method highly attractive and cost-efficient for manufacturing highly loaded masterbatches that can be later diluted with neat polyolefins via conventional melt extrusion in order to obtain electrical insulation materials. By performing the method using modified nanoparticles according to the present invention, an electrical insulation composition can be manufactured that is free from agglomerations and exhibits a strong bond between nanoparticles and the polymer matrix, thereby lowering the risk of early electrical and mechanical breakdown. In contrast to conventional melt blending processes, the technology applied in the present invention enables the formation of “next level” nanocomposites without any particle agglomeration – which is highly beneficial for production stability and avoiding premature product failure (e.g. by dielectric breakdown).

[0083] According to an embodiment, the invention also relates to an electrical insulation material, comprising 1 wt% to 95 wt% of the electrical insulation composition (as defined above) dispersed in 5 wt% to 99 wt% of an (additional) polyolefin, based on the total weight of the electrical insulation material.

[0084] According to an aspect, the electrical insulation material can comprise the electrical insulation composition in a concentration of 1 wt% to 95 wt%, preferably 5 wt% to 80 wt%, more preferably 10 wt% to 50 wt%, based on the total weight of the electrical insulation material.

[0085] According to an aspect, the electrical insulation material can comprise the (additional) polyolefin in a concentration of 5 wt% to 99 wt%, preferably 20 wt% to 95 wt%, more preferably 50 wt% to 90 wt%, based on the total weight of the electrical insulation material.

[0086] According to an aspect, the electrical insulation material can comprise the spherical-type modified nanoparticles in a concentration of 0.1 wt% to 7wt%, preferably 0.2 wt% to 4 wt%, more preferably 0.5 wt% to 3 wt%, based on the total weight of the electrical insulation material.

[0087] Examples of (additional) polyolefins that can be used in the electrical insulation material include homo and copolymers of polyethylene (PE), polypropylene (PP), polymethylpentene (PMP), polybutene-1 (PB-1), ethylene propylene diene rubber (EPDM), polystyrene (PS), or a combination comprising at least two of the foregoing polyolefins. Particularly preferred polyolefins that can be used in the electrical insulation material include (co)polyethylenes (PEs) and (co)polypropylenes (PPs).

[0088] Examples of polyethylenes (PE) that can be used in the electrical insulation material include high density polyethylene (HDPE) having a density of between 0.94 g/cm^3 und 0.97 g/cm^3, low density polyethylene (LDPE) having a density of between 0.915 g/cm^3 und 0.935 g/cm^3, linear low density polyethylene (LLDPE) having a density of between 0.87 g/cm^3 und 0.94 g/cm^3, high molecular weight polyethylene (HMWPE) having an average molar mass of 500-1000 kg/mol, and ultra high molecular weight polyethylene (UHMWPE) having an average molar mass of up to 6000 kg/mol and a density of between 0.93–0.94 g/cm^3. A particularly preferred polyethylene (PE) that can be used in the electrical insulation material is a linear low density polyethylene (LDPE) having a density of between 0.915 g/cm^3 und 0.935 g/cm^3.

[0089] For producing the electrical insulation material, the electrical insulation composition as described herein is mixed with the additional polyolefin. Sufficient mixing is important for avoiding the formation of precipitation in the final electrical insulation material. According to a preferred aspect, mixing the electrical insulation composition with the (additional) polyolefin is performed with a mixer, on small scale e.g. propeller mixer, an ultrasonic device or a shaker, preferably with a propeller mixer. The mixture obtained is subsequently extruded, preferably in a double screw extruder (on small scale e.g. “Rheomex PTW 24/40-MC OS”). Preferably, the core temperature for extrusion is from 100°C to 300°C, more preferably from 150°C to 250°C. The electrical insulation material obtained shows improved AC and/or DC dielectric breakdown strength by up to 34% compared to an electrical insulation material composed of a conventional nanocomposite blended within a polyolefin (see particularly Tables 4 and 6). AC dielectric breakdown strength (60 Hz) can be measured using a Bauer DTA 100 equipment on 45x45x1 mm^3 specimens in with Nytro 10XN oil with a voltage raise of 2 kV/s. Specimens are placed among brass spherical electrodes with 12.5 mm diameter in the sample cell. DC dielectric breakdown strength can be determined on 0.5 mm thick plates and measured in transformer oil using a 300 kV digital HVDC source with a voltage ramping rate of 2 kV/s.

[0090] According to an embodiment, the invention further relates to a dielectric film comprising the electrical insulation material of the present invention.

[0091] According to an aspect, the dielectric film is in a form of a non-oriented or partially oriented film comprising the electrical insulation material, or a biaxially oriented film comprising the electrical insulation material. According to a particular aspect, the dielectric film is in a form of a non-oriented or partially oriented polypropylene film or a biaxially oriented polypropylene film. According to another particular aspect, the dielectric film is in a form of a non-oriented or partially oriented polyethylene film or a biaxially oriented polyethylene film.

[0092] Preferably, the biaxially oriented film comprising the electrical insulation material has a drawing ratio in machine direction of greater than 1.5, and more preferably greater than 3.0; and the biaxially oriented film comprising the electrical insulation material has a drawing ratio in transverse direction of greater than 1.5 and more preferably greater than 3.0. Further preferably, the biaxially oriented polypropylene film or the biaxially oriented polyethylene film has a drawing ratio in machine direction of greater than 1.5 and more preferably greater than 3.0. Preferably, the biaxially oriented polypropylene film or the biaxially oriented polyethylene film has a drawing ratio in transverse direction of greater than 1.5 and more preferably greater than 3.0. Preferably, the biaxially oriented film comprising the electrical insulation material has a dielectric strength of at least 200 V/µm. Preferably, the biaxially oriented polypropylene film has a dielectric strength of at least 400 V/µm,_preferably at least 500 V/µm, and most preferably at least 550 V/µm. Preferably, the biaxially oriented polyethylene film has a dielectric strength of at least 200 V/µm,_preferably at least 250 V/µm, and most preferably at least 300 V/µm.

[0093] According to a further aspect, the dielectric film (preferably in the form of a non biaxially drawn film) has a dielectric strength of at least 200 V/μm, and preferably at least 250 V/μm.

[0094] According to an embodiment, the invention further relates to the use of the electrical insulation material or the dielectric film described herein in the preparation of (di)electric devices, such as a capacitor.

[0095] According to an embodiment, the invention further relates to the use of the spherical-type modified nanoparticles having a core-shell structure (described herein) wherein the shell of the modified nanoparticles comprises a co-catalyst for the in-situ polymerization for increasing the dielectric breakdown strength of an electrical insulation material which comprises at least one polyolefin formed by in-situ polymerization. Preferably, the spherical-type modified nanoparticles are those nanoparticles provided in step i) of the above-described method for producing an electrical insulation composition.

[0096] According to an embodiment, the invention further relates to a cable for (direct alternating current (AC) or current (DC)) low and/or medium and/or high voltage power transmission or distribution.

[0097] According to an aspect, said inventive cable preferably comprises a conductor surrounded by the electrical insulation material or the dielectric film according to the present invention, and is optionally surrounded by a conductive and/or a semi-conductive layer located between the conductor and the inner surface of the electrical insulation material or the dielectric film, and is further optionally surrounded by a jacketing layer covering the outer surface of the electrical insulation material or the dielectric film characterized in that the cable insulation exhibits a value of dielectric loss of less than 10^{-2}, preferably less than 10^{-3}, and more preferably of less than 10^{-4}, determined by ASTM D150 und ASTM D2520.

[0098] According to another aspect, at least one of the following features (a_1) to (a_3) is met for said inventive cable:

a_1) a conductive layer is located between the conductor and the inner surface of the electrical insulation material or the dielectric film,
(a_2) a semi-conductive layer is present in the cable,
(a_3) a jacketing layer covers at least one of the conductive layer, electrical insulation material or dielectric film, and/or semi-conductive layer.

[0099] An example of a cable according to the present invention is shown in Fig. 8 having the following structure (from the center moving outwards):

- a stranded multi-wire conductor 10;
- a first extruded conductive or semi-conductive shield 11 disposed around and outside the conductor 10 and inside a conductor insulation 12;
- an extruded conductor insulation 12 with an extruded electrical insulation material according to the present invention;
- a second extruded semi-conductive shield 13 disposed outside the conductor insulation 12;
- a metallic screen 14 ;
- an outer jacketing layer 15 arranged outside the metallic screen 14.

[00100] Another example of a cable according to the present invention comprises (from the center moving outwards) a stranded multi-wire conductor, a first extruded conductive or semi-conductive shield 11 disposed around and outside the conductor 10 and inside a conductor insulation 12, an extruded conductor insulation 12 with an extruded electrical insulation material according to the present invention, a second extruded semi-conductive shield 13 disposed outside the conductor insulation 12, a metallic screen 14; an outer jacketing layer 15 arranged outside the metallic screen 14.

[00101] According to an embodiment, the invention further relates to a capacitor comprising the electrical insulation material or the dielectric film of the present invention as dielectric.

[00102] According to an embodiment, the invention further relates to an electrical device comprising the electrical insulation material or the dielectric film of the present invention.

[00103] According to an embodiment, the invention also relates to the use of the electrical insulation material or the dielectric film (as described herein) for electrical components, preferably cables, capacitors, bushings transformers, switches, sensors, converters and cable end seals.

[00104] Preferred uses of the electrical insulation material according to the present invention are in low and/or medium and/or high-voltage insulations for indoor and outdoor use, e.g. in insulators for gas insulated switch gear, support insulators, current and voltage transformers and sensors, bushings, as impregnating resins, for outdoor insulators associated with high-voltage lines, in long-rods, in composite and cap-type insulators, and also in base insulators in the medium-voltage sector, in the production of insulators associated with outdoor power switches, in measuring transducers, in lead-throughs, and in overvoltage protectors, in switchgear constructions, in power switches, dry-type transformers and electrical machines, in coating materials for transistors and other semiconductor elements.

[00105] The present invention shall be described in more detail in the following Examples.

[00106] 1. Preparation of electrical insulation materials

[00107] 1.1 Method for producing an electrical insulation composition according to the present invention:

[00108] Preparation of polyethylene masterbatch

[00109] All polymerization reactions were performed in a 10L stainless steel reactor. MgO was added to the reactor and heated for 18h under a vacuum at 80°C. After cooling down to reaction temperature, 3.5 L of dry toluene was added to the reactor. The required

amounts of dibutyl magnesium and 80 mL 1-octene were subsequently added to the suspension. After stirring for 15 min at 170 rpm, the co-catalyst MAO was injected to the suspension. Next the toluene was saturated with ethylene at a partial pressure of 2 bar. The reaction was started after 45 min by injecting a catalyst solution in toluene. The reaction was terminated after 30 min by degassing the system and quenching by the addition of 50 mL ethanol. The reaction mixture was filtered and the residue washed with water and ethanol. Finally, the product was dried for one day in an oven operated under a vacuum at 40°C.

[00110] Preparation of polypropylene masterbatch

[00111] Polymerization reactions were performed in a 10L stainless steel reactor. MgO was added to the reactor and heated for 18 h under a vacuum at 80°C. After cooling down to reaction temperature, 3.5 L of dry toluene was added to the reactor. DBM was subsequently added to the suspension. After stirring for 15 min at 170 rpm, the co-catalyst MAO was injected to the suspension. The mixture was saturated with propylene at a partial pressure of 2 bar. The reaction was started after 45 min by introducing a catalyst solution in toluene with a syringe. The reaction was terminated after 30 min by degassing the system and quenching by the addition of 50 mL ethanol. The reaction mixture was filtered and the residue washed with water and ethanol. The product was dried for one day in an oven operated under a vacuum at 40°C.

[00112] 1.2 Conventional method for producing an electrical insulation composition

[00113] Conventional masterbatch

[00114] A conventional melt blending process was performed for comparison: Extrusion experiments with commercial LLDPE were performed in a “Polylab 16” double screw extruder. The core temperature for extrusion was about 220°C. A composite with 5 wt% nanofiller was obtained from 950 g polymer and 50 g nanoparticles (premixed). The obtained composite was dried overnight in an oven operated under a vacuum at 50°C. After drying the composite was extruded again at the same parameters.

[00115] 1.3 Method for producing electrical insulation materials (by dilution of masterbatches into LDPE):

[00116] Extrusion experiments with commercial LDPE were performed in a double screw extruder “Rheomex PTW 24/40-MC OS”. The core temperature for extrusion was about 200°C. LDPE granules were mixed with the masterbatches produced under items 1.1 and 1.2 above.

[00117] **2. Components**

[00118] In Table 1 below, the components used for preparing exemplary electrical insulation compositions and electrical insulation materials are shown.

[00119] Table 1:

Pure materials	
Blank 1	LDPE from Borealis
Blank 2	LLDPE-C6 from Sabic
Blank 3	LLDPE In-house LLDPE with no filler produced at Uni Hamburg
MgO	MgO nanofiller 20-100 nm from IOLITEC NANOMATERIALS
$Mg(OH)_2$	Mg(OH)2 nanofiller 50-200 nm from US Research Nanomaterials Inc.

[00120] **3. Masterbatches**

[00121] In Table 2 below, exemplary electrical insulation compositions are shown (polyethylene masterbatches).

[00122] Table 2:

Masterbatches produced according to the present invention
In-situ polymerized masterbatch with 95 wt-% LLDPE and 5 wt% MgO (5 wt% modified nanoparticle)
In-situ polymerized masterbatch with 95 wt-% LLDPE and 5 wt% $Mg(OH)_2$ (5 wt% modified nanoparticle)

Masterbatches produced via conventional melt compounding
Extruded masterbatch with 95 wt-% LLDPE (Blank 2) and 5 wt% MgO (5 wt% nanoparticle)
Extruded masterbatch with 95 wt-% LLDPE (Blank 2) and 5 wt% $Mg(OH)_2$ (5 wt% nanoparticle)

[00123] **4. Electrical insulation materials**

[00124] In Table 3 below, exemplary electrical insulation materials are shown (based on polyethylene masterbatches).

[00125] Table 3:

Electrical insulation materials	
Reference 1	Diluted reference with 80 parts Blank 1 (LDPE) and 20 parts Blank 3 (In-house LLDPE)
Reference 2	Diluted reference with 60 parts Blank 1 (LDPE) and 40 parts Blank 3 (In-house LLDPE)
PE-MgO-1% (in-situ)	Diluted sample of 80 parts LDPE and 20 parts LLDPE-MgO (in-situ) Final MgO content (final modified nanoparticle content): 1 wt%
PE-MgO-2% (in-situ)	Diluted sample of 60 parts LDPE and 40 parts LLDPE-MgO (in-situ) Final MgO content (final modified nanoparticle content): 2 wt%
PE-$Mg(OH)_2$-1% (in-situ)	Diluted sample of 80 parts LDPE and 20 parts LLDPE-$Mg(OH)_2$ (in-situ) Final $Mg(OH)_2$ content (final modified nanoparticle content): 1 wt%
PE-$Mg(OH)_2$-2% (in-situ)	Diluted sample of 60 parts LDPE and 40 parts LLDPE-$Mg(OH)_2$ (in-situ) Final $Mg(OH)_2$ content (final modified nanoparticle content): 2 wt%
PE-MgO-1% (extruded)	Diluted sample of 80 parts LDPE and 20 parts LLDPE-MgO (extruded) Final MgO content (final nanoparticle content): 1 wt%
PE-MgO-2% (extruded)	Diluted sample of 60 parts LDPE and 40 parts LLDPE-MgO (extruded) Final MgO content (final nanoparticle content): 2 wt%
PE-$Mg(OH)_2$-1% (extruded)	Diluted sample of 80 parts LDPE and 20 parts LLDPE-$Mg(OH)_2$ (extruded) Final $Mg(OH)_2$ content (final nanoparticle content): 1 wt%

PE-$Mg(OH)_2$-2% (extruded)	Diluted sample of 60 parts LDPE and 40 parts LLDPE-$Mg(OH)_2$ (extruded) Final $Mg(OH)_2$ content (final nanoparticle content): 2 wt%

[00126] **5. Measurements**

[00127] DC conductivity (I-V measurement) was determined for each sample at 70°C and 20 kV/mm on 1 mm thick plates for 100 hours.

[00128] AC dielectric breakdown strength (60 Hz) was measured for each sample using a Bauer DTA 100 equipment on 45x45x1 mm^3 specimens in Nytro 10XN oil with a voltage raise of 2 kV/s. Specimens were placed among brass spherical electrodes with 12.5 mm diameter in the sample cell.

[00129] DC dielectric breakdown strength was determined for each sample on 0.5 mm thick plates and measured in transformer oil using a 300 kV digital HVDC source with a voltage ramping rate of 2 kV/s.

[00130] **6. Results**

[00131] In the following tables, the results for the above-outlined measurements are given:

[00132] Table 4 below shows the scale parameters α of different samples referring to AC dielectric breakdown strength. For a better overview, the relative improvement in relation to the reference sample (Reference 1) (% [α]) is shown as well.

[00133] Table 4:

Sample	**AC breakdown strength α**	**Δ α**
Reference 1 (no filler)	56 kV/mm	
PE-MgO-1% (in-situ)	72 kV/mm	+29 %
PE-MgO-1% (extruded)	56 kV/mm	0

PE-$Mg(OH)_2$-1% (in-situ)	79 kV/mm	+41 %
PE-$Mg(OH)_2$-1% (extruded)	61 kV/mm	+9
Reference 2 (no filler)	56 kV/mm	
PE-MgO-2% (in-situ)	69 kV/mm	+23 %
PE-MgO-2% (extruded)	57 kV/mm	+2 %
PE-$Mg(OH)_2$-2% (in-situ)	75 kV/mm	+34 %
PE-$Mg(OH)_2$-2% (extruded)	56 kV/mm	+9

[00134] Table 5 below shows the DC conductivity of different samples.

[00135] Table 5:

Sample	**DC conductivity**
Reference 1 (no filler)	30 fS/m
PE-MgO-1% (in-situ)	3.4 fS/m
PE-MgO-1% (extruded)	8.2 fS/m
PE-$Mg(OH)_2$-1% (in-situ)	4.6 fS/m
PE-$Mg(OH)_2$-1% (extruded)	20 fS/m
Reference 2 (no filler)	30 fS/m
PE-MgO-2% (in-situ)	1.9 fS/m
PE-MgO-2% (extruded)	5.2 fS/m
PE-$Mg(OH)_2$-2% (in-situ)	3.8 fS/m
PE-$Mg(OH)_2$-2% (extruded)	16.7 fS/m

[00136] Table 6 below shows the scale parameters α of different samples referring to DC dielectric breakdown strength.

[00137] Table 6:

Sample	**DC breakdown strength** ”standard average”	**STD** (standard average)

Reference 1 (no filler)	252 kV/mm	24
PE-MgO-1% (in-situ)	345 kV/mm	78
PE-$Mg(OH)_2$-2% (in-situ)	333 kV/mm	50

WHAT IS CLAIMED IS:

1. Electrical insulation composition for insulating an electrical device, comprising
   - a polyolefin, and
   - spherical-type modified nanoparticles dispersed within the polyolefin,

   wherein the spherical-type modified nanoparticles have a core-shell structure, and wherein the shell has a total content of at least one of a metal and a metalloid of 0.01 wt% to 10 wt%, based on the total weight of the spherical-type modified nanoparticle.

2. Electrical insulation composition according to claim 1, wherein the electrical insulation composition comprises no particle agglomerates, determined via visual inspection, polarized microscopy, atomic force microscopy (AFM), transmission electron microscopy (TEM) and scanning electron microscopy (SEM).

3. Electrical insulation composition according to any one of the preceding claims, wherein the core of the spherical-type modified nanoparticles comprises an inorganic material.

4. Electrical insulation composition according to claim 3, wherein the inorganic material is selected from the group consisting of metal nitride, metal oxide, metal hydroxide, metalloid oxide, layered metalloid, and any combination thereof.

5. Electrical insulation composition according to claim 1, wherein aluminum, magnesium, zinc, or any combination thereof is used as the metal and boron, silicon or a combination thereof is used as the metalloid.

6. Electrical insulation composition according to any one of the preceding claims, wherein the polyolefin is selected from the group consisting of polyethylene (PE), polypropylene (PP), polymethylpentene (PMP), polybutene-1 (PB-1), and any combination thereof.

7. Method for producing an electrical insulation composition, comprising the steps of:
   i) providing spherical-type modified nanoparticles having a core-shell structure,
   ii) adding at least one olefin monomer to the spherical-type modified nanoparticles, and
   iii) adding at least one catalyst to start and perform an in-situ polymerization of the at least one olefin monomer onto the spherical-type modified nanoparticles to obtain a composite, wherein the shell of the spherical-type modified nanoparticles acts as a co-catalyst for the in-situ polymerization.

8. Method according to claim 7, wherein in step i), providing spherical-type modified nanoparticles having a core-shell structure comprises adding nanoparticles to a solvent in order to obtain a mixture, and further adding at least one co-catalyst for the in-situ polymerization to the mixture.

9. Method according to claim 8, wherein in step i), the at least one co-catalyst is added to the mixture in a weight ratio of co-catalyst:nanoparticle of 0.2:100 to 20:100.

10. Method according to claims 8 or 9, wherein the at least one co-catalyst is selected from the group consisting of aluminum alkyl, zinc alkyl, magnesium alkyl and borate.

11. Method according to any one of claims 7-10, wherein the catalyst is selected from the group consisting of metal salts or metal complexes.

12. Electrical insulation material, comprising 1 wt% to 95 wt% of the electrical insulation composition according to any one of claims 1-6 dispersed in 5 wt% to

99 wt% of a polyolefin, based on the total weight of the electrical insulation material.

13. A dielectric film comprising the electrical insulation material according to claim 12.

14. The dielectric film according to claim 13, which is in a form of a non-oriented or partially oriented film comprising the electrical insulation material, or a biaxially oriented film comprising the electrical insulation material.

15. The dielectric film according to claim 13, which has a dielectric strength of at least 200 V/μm.

16. The dielectric film according to claim 14, wherein the biaxially oriented film has a drawing ratio in machine direction of greater than 1.5, and more preferably greater than 3.0; and the biaxially oriented film has a drawing ratio in transverse direction of greater than 1.5 and more preferably greater than 3.0.

17. The dielectric film according to claim 14, wherein the biaxially oriented film has a dielectric strength of at least 200 V/μm.

18. Use of the electrical insulation material according to claim 12 or the dielectric film according to any one of claims 13-17 in the preparation of electrical devices, such as a capacitor.

19. Use of spherical-type modified nanoparticles having a core-shell structure for increasing the dielectric breakdown strength of an electrical insulation material comprising at least one polyolefin formed by in-situ polymerization, wherein the shell of the modified nanoparticles comprises a co-catalyst for the in-situ polymerization.

20. Use of the electrical insulation material according to claim 12 or the dielectric film according to claims 13-17 for electrically insulating electrical components, such as cables, capacitors, bushings and transformers.

21. Cable for low and/or medium and/or high voltage power transmission or distribution comprising a conductor surrounded by the electrical insulation material according to claim 12 or the dielectric film according to claims 13-17.

22. Cable according to claim 21, wherein at least one of the following features (a_1) to (a_3) is met:
a_1) a conductive layer is located between the conductor and the inner surface of the electrical insulation material or the dielectric film,
(a_2) a semi-conductive layer is present in the cable,
(a_3) a jacketing layer covers at least one of the conductive layer, electrical insulation material or dielectric film, and/or semi-conductive layer.

23. Capacitor comprising the electrical insulation material according to claim 12 or the dielectric film according to claims 13-17 as dielectric.

24. Electrical device comprising the electrical insulation material according to claim 12 or the dielectric film according to claims 13-17.

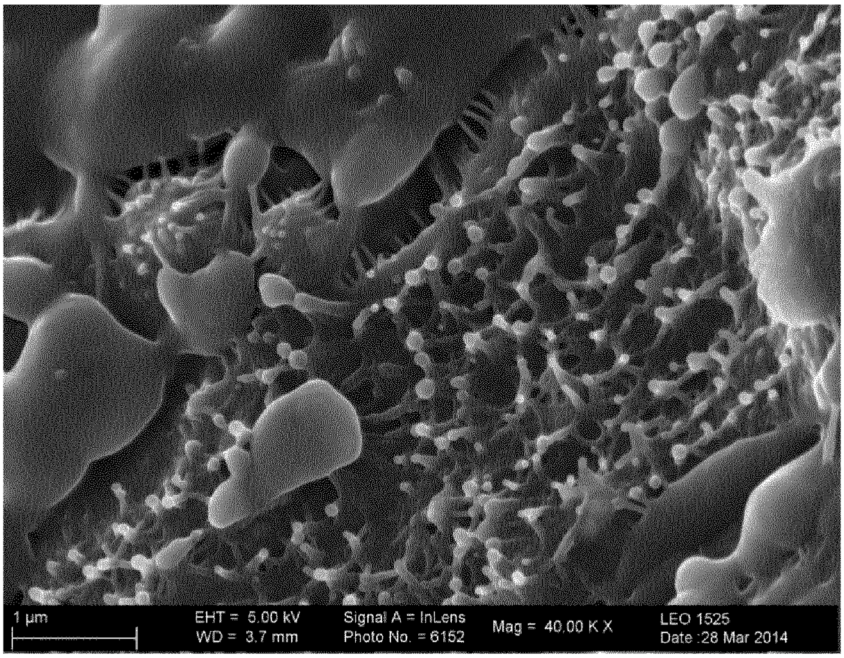
1 µm
EHT = 5.00 kV
WD = 3.7 mm
Signal A = InLens
Photo No. = 6152
Mag = 40.00 K X
LEO 1525
Date :28 Mar 2014

Fig. 1

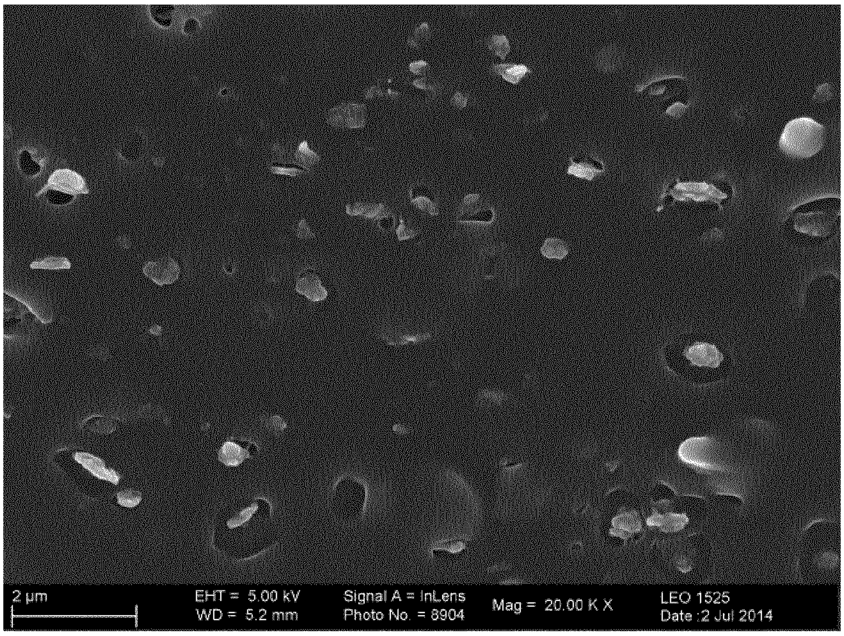
2 µm
EHT = 5.00 kV
WD = 5.2 mm
Signal A = InLens
Photo No. = 8904
Mag = 20.00 K X
LEO 1525
Date :2 Jul 2014

Fig. 2

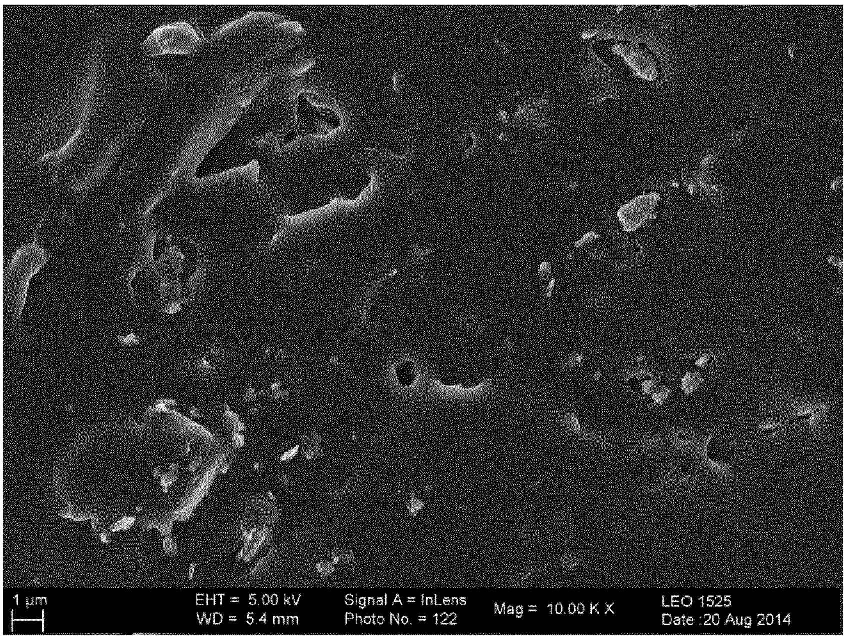
1 μm
EHT = 5.00 kV
WD = 5.4 mm
Signal A = InLens
Photo No. = 122
Mag = 10.00 K X
LEO 1525
Date :20 Aug 2014

Fig. 3

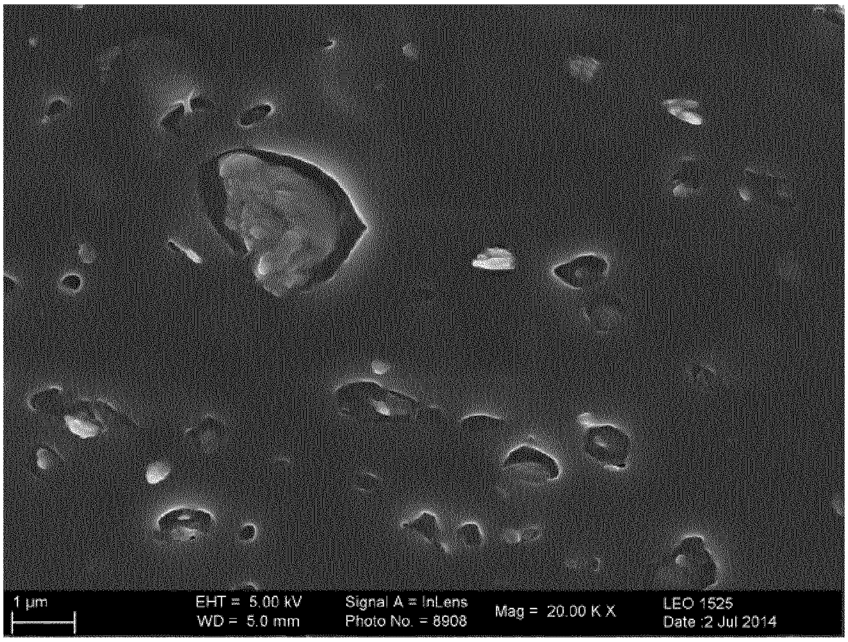
1 µm
EHT = 5.00 kV
WD = 5.0 mm
Signal A = InLens
Photo No. = 8908
Mag = 20.00 K X
LEO 1525
Date :2 Jul 2014

Fig. 4

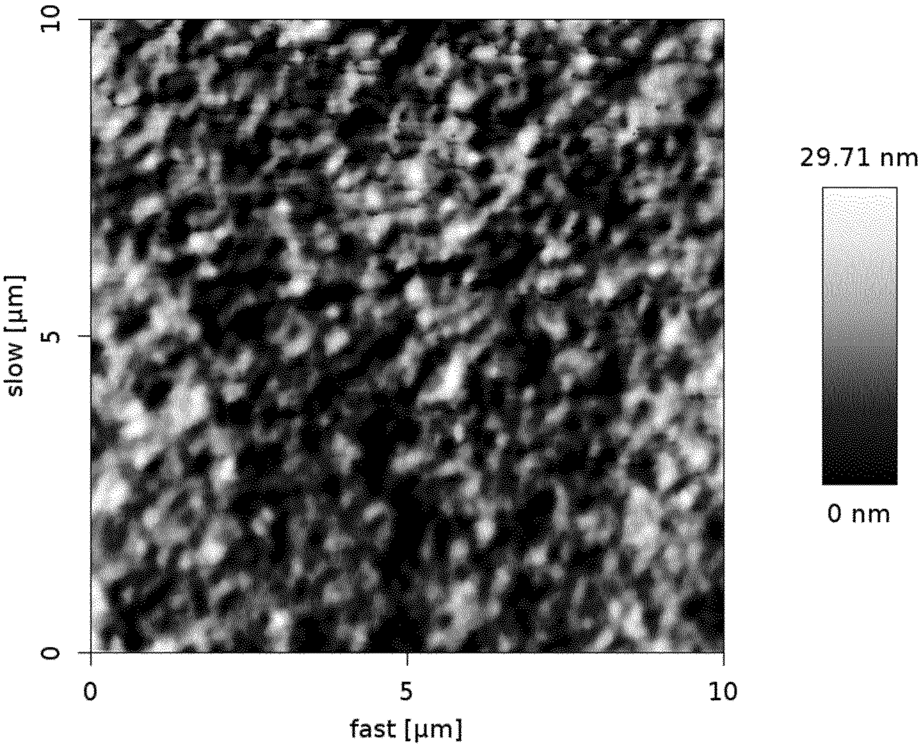

Fig. 5

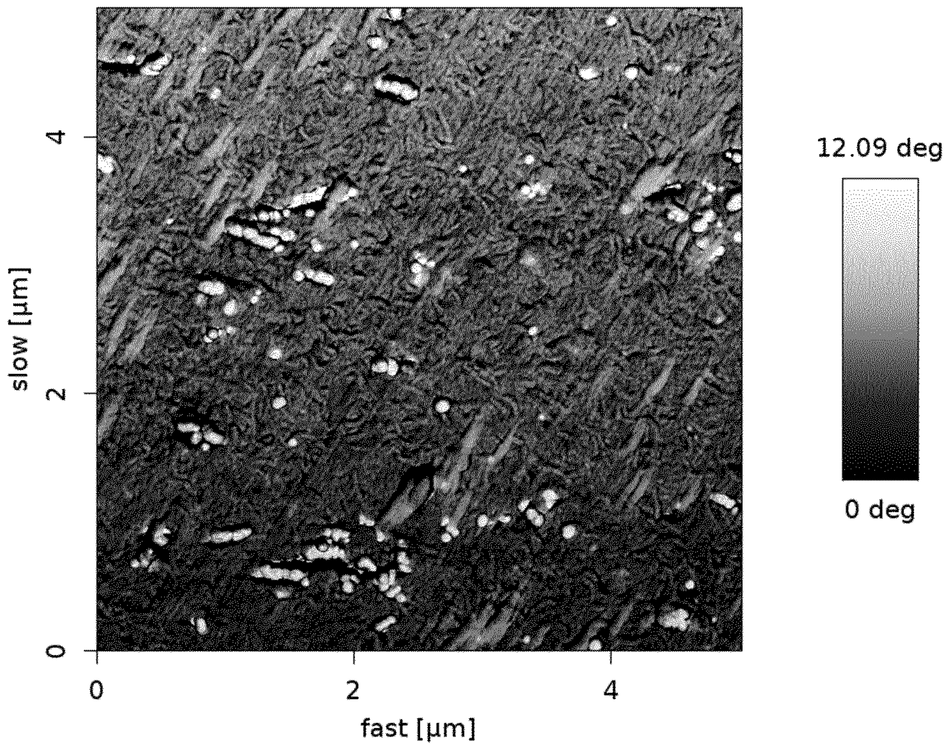

Fig. 6

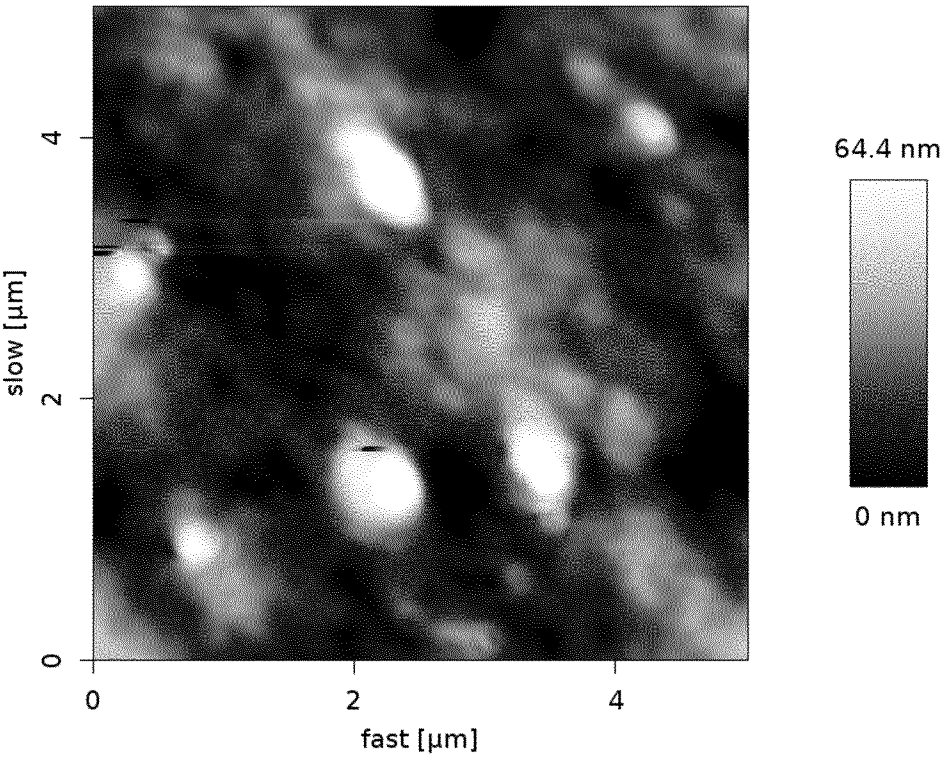

Fig. 7

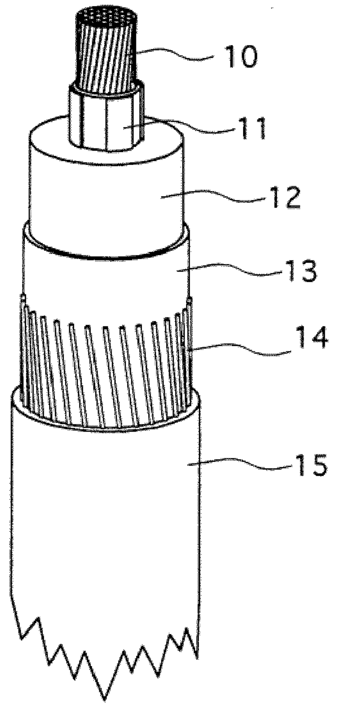

Fig. 8

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2015/065216

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01B3/44 C08L23/04
ADD.

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)
H01B C08L C08K

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)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Week 201040 Thomson Scientific, London, GB; AN 2010-D86885 XP002755341, & CN 101 677 033 A (SHENZHEN ADVANCED TECHNOLOGY RES INST) 24 March 2010 (2010-03-24) abstract -----	1-6, 12-24
X	DATABASE WPI Week 201429 Thomson Scientific, London, GB; AN 2014-E33834 XP002755342, & CN 103 497 394 A (UNIV XIAN JIAOTONG) 8 January 2014 (2014-01-08) abstract ----- -/--	1-24

☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* 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 10 March 2016	Date of mailing of the international search report 21/03/2016
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Marsitzky, Dirk

1

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2015/065216

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	EP 1 656 682 B1 (RENSSELAER POLYTECH INST [US]) 16 September 2015 (2015-09-16) paragraph [0001] - paragraph [0025] -----	1-24
X	EP 2 230 272 A2 (GEN ELECTRIC [US]) 22 September 2010 (2010-09-22) paragraph [0002] - paragraph [0036]; examples 1-2 -----	1-24

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2015/065216

Patent document cited in search report		Publication date	Patent family member(s)			Publication date
CN 101677033	A	24-03-2010	NONE			
CN 103497394	A	08-01-2014	NONE			
EP 1656682	B1	16-09-2015	CN	1902716	A	24-01-2007
			EP	1656682	A2	17-05-2006
			JP	4772676	B2	14-09-2011
			JP	2007503101	A	15-02-2007
			US	2007199729	A1	30-08-2007
			WO	2005036563	A2	21-04-2005
EP 2230272	A2	22-09-2010	CA	2696380	A1	17-09-2010
			EP	2230272	A2	22-09-2010
			JP	2010215909	A	30-09-2010
			US	2010240804	A1	23-09-2010