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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
11 January 2007 (11.01.2007)

PCT

(10) International Publication Number
WO 2007/003513 A1

(51) International Patent Classification:
C08J 3/00 (2006.01) *A61L 31/14* (2006.01)
A61L 27/56 (2006.01)

(21) International Application Number:
PCT/EP2006/063443

(22) International Filing Date: 22 June 2006 (22.06.2006)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/696,470 1 July 2005 (01.07.2005) US

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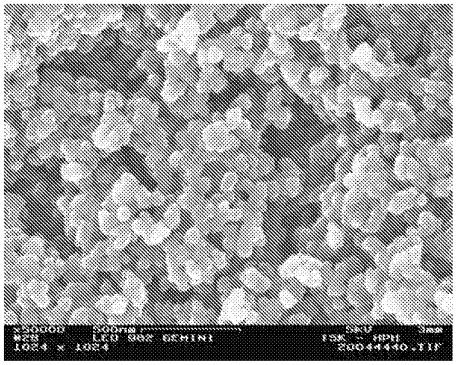
(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SY, 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, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: PROCESS FOR THE PRODUCTION OF POROUS RETICULATED COMPOSITE MATERIALS



(57) Abstract: The present invention relates to porous reticulated composite materials and methods for the production thereof. Particularly, the present invention relates to a process for the production of porous composite materials comprising the steps of providing a mixture capable of flowing, comprising at least one inorganic and/or organic reticulating agent; at least one matrix material selected from polymers or polymer mixtures; and solidifying the liquid mixture.

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Process for the Production of Porous Reticulated Composite Materials

Field Of The Invention

The present invention relates to porous reticulated composite materials and methods for the production thereof. Particularly, the present invention relates to a process for the production of porous composite materials comprising the steps of providing a mixture capable of flowing, comprising at least one inorganic and/or organic reticulating agent; at least one matrix material selected from polymers or polymer mixtures; and solidifying the liquid mixture.

Background of the Invention

Porous materials can be important in different application fields in industry, for example for membranes for filtration and separation of fluid mixtures, in sensors, electrodes, dielectric materials in microelectronics, in biomedicine technology for implantable materials or drug carriers, for electrical capacitors, for catalytic surfaces and the like.

Also, composite materials can be important in mechanical constructions, e.g. in aeronautical or automotive engineering, in medical engineering, membrane technology and other fields of application. The use of composites allows for a combination of different materials having different physico-chemical properties, resulting in a composite material having completely new or at least improved properties. Thus, composites may show the same or a superior stability, biocompatibility and/or strength at less overall weight when compared to non-composite materials.

Composites may allow for an individual adjustment of material properties such as thermal or electrical isolation, the thermal coefficient of expansion, corrosive properties, absorption properties, or conductivity of thermal and/or electrical energy, conduction of acoustic noise, thermal or chemical resistance and the like, for example by suitably selecting the components from which the composite material is made. Porous composite materials find increasing attention in coating technology, e.g. for functionalizing materials with specific physical, electrical, magnetic or optical properties. Consequently, they can also be important in photovoltaic, sensor, catalytic or electrochromatic display technology.

Conventionally, porous composite materials are typically prepared by sintering methods. Powders comprising fibers, dendritic or spherically-formed precursor particles are pressed into molds or extruded and then subjected to a sinter process. In such materials, the rigidity of the material, the pore size and the surface area depends on the packaging density, the size, form and the composition of particles in the powders actually used.

One disadvantage of these methods may be that the adjustment of pore sizes is hardly controllable, and the mechanical properties can only be insufficiently tailored, especially in dependence of the pore size, the porosity degree or the surface area. Particularly, the parameters of the sintering process also have an influence on the strength, pore size and surface area of the porous materials. Typically, pore sizes may have to be later adjusted in additional processing steps, e.g. by deposition from the gas phase, electroplating or electroless plating for decreasing the size of large pores by adding further material in order to improve a homogeneous pore size distribution. These methods, however, lead to a reduction of the available surface in these porous materials. Other methods are based on spray-coating of pre-sintered porous materials with a slurry, subsequently drying and again sintering. These methods lead to a pore diffusion of the material from the slurry into the porous sintered structured and to an insufficient adhesion of the material deposed in the second processing step, particularly caused by different thermal coefficients of expansion and shrinking of the material.

In International Patent Application WO 04/054625, an already pre-sintered porous material is coated by powdered nanoparticle material and subsequently re-sintered. In International Patent Application WO 99/15292, porous fiber-containing composite structures are obtained from a dispersion of fibers with the use of binders and subsequent gasification of the mixture prior, during or after the sinter processing.

A further disadvantage of the above-described methods is that the sintering methods are typically performed at high temperatures, thus making it impossible to produce porous composites of polymers and inorganic and/or organic components if the sintering temperature is above the melting point of the polymer components. It

is, therefore, also a specific disadvantage of these methods that the material is processed in costly molding processes into a stable two- or three-dimensional structure, and typically only restricted forms are possible due to the brittleness of the materials.

Furthermore, the processing of the materials in accordance with conventional methods often requires several post-treatment processing steps, and the sintering process is, in essence, restricted to inorganic composites due to the conditions necessarily used.

Summary Of The Invention

There may be a need for the provision of porous composite materials having improved properties, particularly for materials which may be adapted in their physico-chemical properties to the specific requirements of the individual application field. Furthermore, there may be a need to additionally functionalize porous composite materials e.g. by a suitable combination of components, which may comprise specific electrical, dielectrical, magnetic or optical properties, for example semi conducting, ion conducting, magnetic or super conducting properties.

Furthermore, there may be a need for porous composite materials which may be produced in a cost efficient manner, avoiding high costs for energy consumption when applying high pressures and/or high temperatures. Furthermore, in powder-based sintering methods, flaws and imperfections in the material occur relatively often, i.e., the powder sintered materials often lack the desired homogeneity, particularly in the case of coatings.

It is one object of the present invention to provide, e.g., a porous composite material, for example based on organic and/or inorganic particles and inorganic and/or organic matrix materials, which can be easily modified in its properties. For example, the adjustment of the thermal coefficient of expansion, the electric, dielectric, conducting or semi-conducting and magnetic or optical properties and/or further physico-chemical properties may be facilitated by exemplary embodiments of the present invention.

A further object of the invention is the provision of, e.g., adjustable, preferably self organizing, network-like structural properties, e.g. allowing, on the basis of the same material, to produce any possible two- and three-dimensional structure as well as a fine structure, such as the individual adjustment of porosity, preferably substantially without deteriorating the chemical and/or physical stability of the material.

A further object of the invention is to provide, e.g., a material which may be used as a coating as well as a bulk material, having the desired properties.

A further object of the invention is, e.g., the provision of a method for the production of porous reticulated composite materials, which may be produced from cheap and in their properties broadly variable starting materials in a cost-efficient manner, preferably in only a few process steps.

A further object of the invention is, e.g., the provision of a method for the manufacture of porous composite materials which can allow an individual adjustment for example of the thermal coefficient of expansion, electric, dielectric, conductive, semi conductive, magnetic or optical properties

For example, these and other objects of the invention can be achieved by one exemplary embodiment of the present invention which provides a process for the production of porous composite materials comprising the following steps:

a) Providing a liquid mixture, comprising

i) at least one reticulating agent;

ii) at least one matrix material comprising at least one polymer; and

b) Solidifying the liquid mixture.

In further exemplary embodiments of the invention, the liquid mixture used in processes as described above may includes at least one solvent and may include at least one of a dispersion, suspension, emulsion or solution, or the liquid mixture may be substantially free of solvents.

In still further exemplary embodiments of the invention, the reticulating agents used in processes as described above may be in the form of particles, such as nano-

or microcrystalline particles, which may comprise at least two particle size fractions of the same or different material, the fractions differing in size by a factor of at least 1.1, or at least 2. Also, the reticulating agent may have a form selected from tubes, fibers or wires.

In still further exemplary embodiments of the invention, the reticulating agents used in processes as described above may include inorganic materials such as metals, metal compounds, metal oxides, semi conductive metal compounds, carbon species such as carbon fiber, graphite, soot, carbon black, fullerenes, or nanotubes; or the reticulating materials may include particulate organic materials or fibers made of organic materials such as polymers, oligomers or pre-polymers, for example a synthetic homopolymer or copolymer of an aliphatic or aromatic polyolefin, such as polyethylene or polypropylene; or a biopolymer.

In still further exemplary embodiments of the invention, the reticulating agents used in processes as described above may comprise at least one inorganic material in combination with at least one organic material, or a combination of at least one particulate material with at least one material having a form selected from tubes, fibers or wires.

In still further exemplary embodiments of the invention, the matrix materials used in processes as described above may include oligomers, polymers, copolymers or prepolymers, thermosets, thermoplastics, synthetic rubbers, extrudable polymers, injection molding polymers, or moldable polymers such as, for example, epoxy resins, phenoxy resins, alkyd resins, epoxy-polymers, poly(meth)acrylate, unsaturated polyesters, saturated polyesters, polyolefines, rubber latices, polyamides, polycarbonates, polystyrene, polyphenol, polysilicone, polyacetale, cellulose, or cellulose derivatives.

In still further exemplary embodiments of the invention, the liquid mixture used in processes as described above include further additives such as cross linkers, fillers, surfactants, acids, bases, pore-forming agents, plasticizers, lubricants, flame resistants, biologically active compounds, therapeutically active compounds, agents

for diagnostic purpose, or markers, and the liquid mixture may have, e.g., a total solids content of below 20 % by weight.

Furthermore, in exemplary embodiments of the invention, the reticulating agents used in processes as described above may be selected from materials capable of forming a network-like structure, and/or capable of self-orientation into a three dimensional structure.

In still further exemplary embodiments of the invention, the ratio of the reticulating agent(s) to the matrix component(s) in the liquid mixture used in processes as described above may be suitably selected such that a three-dimensional network in the solid phase is formed upon removal of the solvent or during a change in viscosity of the solvent-free mixture during solidification, for example by a phase separation between the solvent phase and the solids phase occurs during solidification.

In further exemplary embodiments of the invention, the solidification step used in processes as described above may include a thermal treatment, drying, freeze-drying, application of vacuum, e.g. evaporation of the solvent, or cross linking, wherein the cross linking may be induced chemically, thermally or by radiation.

In still another exemplary embodiment of the invention, the solidification step used in processes as described above may include a phase separation in the liquid mixture into a solids and a liquid phase, or precipitating the solids from the liquid mixture, for example before or by removal of the solvent, and/or by cross linking the matrix material.

In still further exemplary embodiments of the invention, the phase separation or precipitation used in processes as described above may be induced by an increase of the viscosity of the liquid mixture, which may be caused by, for example, cross linking, curing, drying, rapidly increasing the temperature, rapidly lowering the temperature, or rapidly removing the solvent .

In preferred exemplary embodiments of the invention, the matrix material used in processes as described above is substantially not decomposed during

solidification, so that, e.g. the reticulating agents are embedded in the polymeric matrix material in the final composite material.

In still further exemplary embodiments of the invention, the liquid mixture used in processes as described above may include at least one cross linker, which may be suitably selected such that cross linking during processing of the liquid mixture before the solidification step does essentially not lead to a viscosity change in the system, and/or the cross linking reaction essentially only starts during solidification.

In a still further exemplary embodiment of the invention, a process is provided wherein the reticulating agent includes at least one of soot, fullerenes, carbon fibers, silica, titanium dioxide, metal particles, tantalum particles, or polyethylene particles; the matrix material includes at least one of epoxy resins or phenoxy resins; the liquid mixture comprises an organic solvent; and the solidification includes removal of the solvent by a heat treatment, preferably a rapid removal. Optionally, the resulting solvent-free material may be subsequently heat treated in an inert atmosphere at temperatures up to 300 °C, substantially without decomposing the matrix material.

In still further exemplary embodiments of the invention, the porous composite material resulting from processes as described above may be impregnated, coated or infiltrated with therapeutically active agents, which can optionally be resolved or extracted from the material in the presence of physiologic fluids.

In a further exemplary embodiment of the invention a porous reticulated composite material or a porous coating is provided, which are obtainable by the processes as described above. Such materials may, in still further exemplary embodiments of the invention, be used for example for the manufacture of a medical device for therapeutic and/or diagnostic purposes, which may optionally comprise a marker for diagnostic purpose, or as a scaffold for tissue engineering in vivo or in vitro. For use as a scaffold, the composite material may be loaded with at least one of a microorganism, a viral vector, cells or living tissue.

In accordance with exemplary embodiments of the present invention, it was found that the degree of porosity as well as pore sizes in composite materials can be

selectively adjusted, e.g., by suitably selecting the amount and type of reticulating agents, their geometry and particle size as well as by, e.g., suitably combining different particle sizes of the reticulating agent and the matrix material.

Furthermore, it was found that, e.g. by suitably selecting the solidification conditions, a fine structuring of the material with regard to the degree of porosity, the pore size and the morphology may be selectively influenced. Additionally, it was found that by combining reticulating agents and a suitable matrix material, composite materials may be produced, the mechanical, electrical, thermal and optical properties thereof can be selectively adjusted, e.g., by the solids content of the reticulating agent and/or the matrix material in the liquid mixture, the type of solvent or solvent mixture, the ratio of reticulating agents to matrix material and/or by suitably selecting the materials according to their primary particle size and their structure and type.

Without wishing to be bound to any specific theory, it could be shown that for example by suitably selecting the conditions in the liquid mixture and particularly the conditions upon solidifying, the particles may be oriented in the form of a solid network essentially determining the porosity of the resulting composite material. In exemplary embodiments of the invention, the materials and processing conditions used may be selected such that the solids in the liquid mixture form a self-organizing network structure, e.g. a reticulated structure before and/or during the solidification step. Generally, it is assumed that suitably selected reticulating agents, For example mixtures of reticulating agents of different sizes and/or mixtures of reticulating agent particles with tubes, fibers or wires may have a strong tendency to self aggregate in the liquid mixture, and this may be further promoted for example by suitably selecting the matrix material, the solvent, if any, as well as certain additives.

Description Of The Figures

The following detailed description, given by way of example, but not intended to limit the invention solely to the specific embodiments described, may be best understood in conjunction with the accompanying figures, in which:

FIG. 1 shows a 50,000x magnification of the porous reticulated material layer of example 1.

FIG. 2 shows a SEM picture at 20,000x magnification of the material of example 2.

FIG. 3 shows a SEM picture at 20,000x magnification of the material of example 3.

FIG. 4 shows a SEM picture at 5,000x magnification of the material of example 4.

FIG. 5 shows a SEM picture at 20,000x magnification of the material of example 5.

FIG. 6 shows a SEM picture at 200x magnification of the porous composite material of example 6.

FIG. 7 shows SEM pictures (Fig. 7a at 100x magnification and 7b at 20,000x)of the material of example 7.

FIG. 8 shows a picture of the surface of the material of example 8

Detailed Description Of The Present Invention

In accordance with exemplary embodiment of the present invention process is provided, wherein a mixture capable of flowing is prepared comprising at least one reticulating agent, and at least one matrix material selected from polymers or polymer mixtures, which is subsequently solidified. The mixture can be a liquid mixture in the form of a dispersion, suspension, emulsion or solution, optionally comprising a solvent or solvent mixture.

In an exemplary embodiment of the invention, the mixture may be substantially free of any solvents and may utilize a liquid matrix material, which may be a material in molten state, i.e. a melt of the matrix material.

In the following, whenever the terms "liquid mixture" or "mixture capable of flowing" are used, it should be understood that these terms are used interchangeably and that they may encompass any mixture capable of flowing, either containing solvent or not, and regardless of its viscosity, i.e. the term also encompasses melts,

slurries or pasty materials having high viscosity, including substantially dry flowable powder or particle mixtures.

The liquid mixture may be prepared in any conventional way, e.g. by dissolving or dispersing solid components in at least one solvent or at least one matrix material in any suitable order, by mixing solids in dry state, optionally subsequently adding at least one solvent, by melting a matrix material and dispersing the at least one reticulating agent therein, optionally before adding at least one solvent, or by preparing a paste or slurry and subsequently diluting it with at least one solvent or a dispersion of other components in solvent.

In exemplary embodiments, at least one, optionally both, of the reticulating agent and the matrix material can be a synthetic material, i.e. a material which is not of natural origin. Particularly, extracellular matrix materials of biological origin may be excluded from any of the components of certain embodiments of the present invention. The reticulated material in exemplary embodiments of the invention may be a rigid, substantially non-elastic material.

Reticulating Agent

In the present invention, the term "reticulating agent" includes materials which can be oriented into a network or network like-structure under the conditions described herein for converting the liquid mixture into porous solidified composite materials. In exemplary embodiments of the invention, reticulating agents can include materials which are capable of self-orienting or promoting self-orientation into a network or network-like structure. A "network" or "network-like structure" within the meaning of the present invention can be any regular and/or irregular three-dimensional arrangement having void space, e.g. pores in it. The porous structure of the reticulated material may e.g. permit or promote ingrowth of biological tissue and/or proliferation into the material, and it can be for example used for storing and releasing active agents, diagnostic markers and the like.

The at least one reticulating agent may be selected from organic and/or inorganic materials of any suitable form or size or any mixtures thereof.

For example, the reticulating agent(s) may include inorganic materials like zero-valent metals, metal powders, metal compounds, metal alloys, metal oxides, metal carbides, metal nitrides, metal oxynitrides, metal carbonitrides, metal oxycarbides, metal oxynitrides, metal oxycarbonitrides, organic or inorganic metal salts, including salts from alkaline and/or alkaline earth metals and/or transition metals, including alkaline or alkaline earth metal carbonates, -sulphates, -sulfites, semi conductive metal compounds, including those of transition metals and/or metals from the main group of the periodic system; metal based core-shell nanoparticles, glass or glass fibers, carbon or carbon fibers, silicon, silicon oxides, zeolites, titanium oxides, zirconium oxides, aluminum oxides, aluminum silicates, talcum, graphite, soot, flame soot, furnace soot, gaseous soot, carbon black, lamp black, minerals, phyllosilicates, or any mixtures thereof.

Also, biodegradable metal-based reticulating agents selected from alkaline or alkaline earth metal salts or compounds can be used, such as magnesium-based or zinc-based compounds or the like or nano-alloys or any mixture thereof. The reticulating agents used in certain exemplary embodiments of the present invention may be selected from magnesium salts, oxides or alloys, which can be used in biodegradable coatings or molded bodies, including in the form of an implant or a coating on an implant, that may be capable of degradation when exposed to bodily fluids, and which may further result in formation of magnesium ions and hydroxyl apatite.

Certain reticulating agents may include, but are not limited to, powders, preferably nanomorphous nanoparticles, of zero-valent-metals, metal oxides or combinations thereof, e.g. metals and metal compounds selected from the main group of metals in the periodic table, transition metals such as copper, gold and silver, titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, manganese, rhenium, iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium or platinum, or from rare earth metals. The metal-based compounds which may be used include, e.g., organometallic compounds, metal alkoxides, carbon particles, for example soot, lamp-black, flame

soot, furnace soot, gaseous soot, carbon black, graphite, carbon fibers or diamond particles, and the like. Further examples include, metal containing endohedral fullerenes and/or endometallofullerenes may be selected, including those of rare earth metals such as cerium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, iron, cobalt, nickel, manganese or mixtures thereof, such as iron-platinum-mixtures or alloys. Magnetic super paramagnetic or ferromagnetic metal oxides may also be used, such as iron oxides and ferrites, e.g. cobalt-, nickel- or manganese ferrites. To provide materials having magnetic super paramagnetic, ferromagnetic or signaling properties, magnetic metals or alloys may be used, such as ferrites, e.g. gamma-iron oxide, magnetite or ferrites of Co, Ni, or Mn. Examples of such materials are described in International Patent Publications WO83/03920, WO83/01738, WO88/00060, WO85/02772, WO89/03675, WO90/01295 and W090/01899, and U.S. Patent Nos. 4,452,773, 4,675,173 and 4,770,183. The at least one reticulating agent can include any combination of the materials listed hereinabove and below.

Additionally, semi conducting compounds and/or nanoparticles may be used as a reticulating agent in further exemplary embodiments of the present invention, including semiconductors of groups II-VI, groups III-V, or group IV of the periodic system. Suitable group II-VI-semiconductors include, for example, MgS, MgSe, MgTe, CaS, CaSe, CaTe, SrS, SrSe, SrTe, BaS, BaSe, BaTe, ZnS, ZnSe, ZnTe, CdS, CdSe, CdTe, HgS, HgSe, HgTe or mixtures thereof. Examples of group III-V semiconductors include, for example, GaAs, GaN, GaP, GaSb, InGaAs, InP, InN, InSb, InAs, AlAs, AlP, AlSb, AlS, or mixtures thereof. Examples of group IV semiconductors include germanium, lead and silicon. Also, combinations of any of the foregoing semiconductors may be used.

In certain exemplary embodiments of the present invention, it may be preferable to use complex metal-based nanoparticles as the reticulating agents. These may include, for example, so-called core/shell configurations, which are described by Peng et al., Epitaxial Growth of Highly Luminescent CdSe/CdS Core/Shell

Nanoparticles with Photostability and Electronic Accessibility, Journal of the American Chemical Society (1997, 119: 7019 – 7029).

Semi conducting nanoparticles may be selected from those materials listed above, and they may have a core with a diameter of about 1 to 30 nm, or preferably about 1 to 15 nm, upon which further semi conducting nanoparticles may be crystallized to a depth of about 1 to 50 monolayers, or preferably about 1 to 15 monolayers . Cores and shells may be present in combinations of the materials listed above, including CdSe or CdTe cores, and CdS or ZnS shells.

In a further exemplary embodiment of the present invention, the reticulating agents may be selected based on their absorptive properties for radiation in a wavelength ranging anywhere from gamma radiation up to microwave radiation, or based on their ability to emit radiation, particularly in the wavelength region of about 60 nm or less. By suitably selecting the reticulating agents, materials having non-linear optical properties may be produced. These include, for example, materials that can block IR-radiation of specific wavelengths, which may be suitable for marking purposes or to form therapeutic radiation-absorbing implants. The reticulating agents, their particle sizes and the diameter of their core and shell may be selected to provide photon emitting compounds, such that the emission is in the range of about 20 nm to 1000 nm. Alternatively, a mixture of suitable compounds may be selected which emits photons of differing wavelengths when exposed to radiation. In one exemplary embodiment of the present invention, fluorescent metal-based compounds may be selected that do not require quenching.

In exemplary embodiments of the invention the at least one reticulating agent may include carbon species such as nanomorphous carbon species, for example fullerenes such as C36, C60, C70, C76, C80, C86, C112 etc., or any mixtures thereof; furthermore, multi-, double- or single walled nanotubes like MWNT, DWNT, SWNT, random-oriented nanotubes, as well as so-called fullerene onions or metallo-fullerenes, or simply graphite, soot, carbon black and the like.

Additionally, the reticulating agents may include organic materials like polymers, oligomers or pre-polymers; shellac, cotton, or fabrics; and any combinations thereof.

In some exemplary embodiments of the present invention the reticulating agent may comprise a mixture of at least one inorganic and at least one organic material.

Furthermore, the reticulating agents of all the materials mentioned herein may be selected among particles, i.e. substances having an essentially spherical or spherical-like irregular shape, or fibers. They may be provided in the form of nano- or microcrystalline particles, powders or nanowires . The reticulating agents may have an average particle size of about 1 nm to about 1,000 micrometer, preferably about 1 nm to 300 μm, or more preferably from about 1 nm to 6 μm. These particle sizes typically refer to all materials mentioned herein which may be used as reticulating agents.

The reticulating agents may comprise at least two particles of the same or different material, the particles thereof having a size differing by a factor of at least 2, or at least 3 or 5, sometimes at least 10. Without wishing to be bound to any specific theory, it is believed that a difference in particle size can further promote self-orientation of the reticulating agents under formation of a network structure.

In exemplary embodiments, the reticulating agents include a combination of carbon particles such as soot, carbon black or lamp black, with fullerenes or fullerene mixtures. The carbon particles may have an average size ranging from about 50 to 200 nm, e.g. about 90 to 120 nm. In a further exemplary embodiment, the at least one reticulating agent includes a combination of metal oxide particles such as silica, alumina, titanium oxide, zirconium oxide, or zeolites or combinations thereof, with fullerenes or fullerene mixtures. The metal oxide particles may have an average size ranging from about 5 to 150 nm, e.g. about 10 to 100 nm. In some exemplary embodiments the at least one reticulating agent may include a combination of at least one metal powder with metal oxide particles such as silica, alumina, titanium oxide, zirconium oxide, zeolites or combinations thereof. The metal oxide particles may

have an average size ranging from about 5 to 150 nm, e.g. about 10 to 100 nm, and the metal powder may have an average particle size in the micrometer range, e.g. from about 0.5 to 10 μm, or from about 1 to 5 μm. All these reticulating agents may be combined with e.g. epoxy resins as the matrix material, preferably thermally curable and/or cross linkable phenoxy resins.

Alternatively, the at least one reticulating agent can also be in the form of tubes, fibers, fibrous materials or wires, particularly nanowires, made of any of the materials mentioned above. Suitable examples include carbon fibers, annotates, glass fibers, metal nanowires- or metal microwares. Such forms of the reticulating agent can have an average length from about 5 nm to 1,000 micrometer, e.g. from about 5 nm to 300 μm, such as from about 5 nm to 10 μm, or from about 2 to 20 μm, and/or an average diameter from about 1 nm to 1 μm, e.g. from about 1 nm to 500 nm, such as from 5 nm to 300 nm, or from about 10 to 200 nm.

The particle sizes can be provided as a mean or average particle size, which may be determined by laser methods such as the TOT-method (Time-Of-Transition), which may be determined, e.g., on a CIS Particle Analyzer of Ankersmid. Further suitable methods for determining particle size include powder diffraction or TEM (Transmission-Electron-Microscopy).

In some exemplary embodiments solvent free mixtures may be used, wherein the matrix material may be, for example, a liquid prepolymer or a melt, i.e. a molten matrix material, which may be subsequently solidified by e.g. cross linking or curing,

In some exemplary embodiments, the reticulating agent and the matrix material do not comprise fibers or fibrous materials, and the resulting composite produced is substantially free of fibers.

In further exemplary embodiments, it may be advantageous to modify the reticulating agents e.g. to improve their dispersibility or wettability in solvents or the matrix material, in order to generate additional functional properties or increase compatibility. Techniques to modify the particles or fibers, if necessary, are well known to those skilled in the art, and may be employed depending on the requirements of the individual composition and the materials used. For example,

silane compounds like organosilanes may be used for modifying the reticulating agents. Suitable organosilanes and other modifying agents are for example those described in International Patent Application PCT/EP2006/050622 and US Patent application Serial No. 11/346,983 and these may be employed also in the embodiments in the present invention, as well as those substances defined therein and herein as cross linkers.

In exemplary embodiments of the present invention, the reticulating agents may be modified with at least one of alkoxides, metal alkoxides, colloidal particles, particularly metal oxides and the like. The metal alkoxides may have the general formula $M(OR)_x$ where M is any metal from a metal alkoxide which may, e.g., hydrolyze and/or polymerize in the presence of water. R is an alkyl radical comprising between 1 and about 30 carbon atoms, which may be straight, chained or branched, and x can have a value equivalent to the metal ion valence. Metal alkoxides such as $Si(OR)_4$, $Ti(OR)_4$, $Al(OR)_3$, $Zr(OR)_3$ and $Sn(OR)_4$ may also be used. Specifically, R can be the methyl, ethyl, propyl or butyl radical. Further examples of suitable metal alkoxides can include $Ti(isopropoxy)_4$, $Al(isopropoxy)_3$, $Al(sec\text{-}butoxy)_3$, $Zr(n\text{-}butoxy)_4$ and $Zr(n\text{-}propoxy)_4$.

Further suitable modifying agents may be selected from at least one of silicon alkoxides such as tetraalkoxysilanes, wherein the alkoxy may be branched or straight chained and may contain 1 to 25 carbon atoms, e.g. tetramethoxysilane (TMOS), tetraethoxysilane (TEOS) or tetra-n-propoxysilane, as well as oligomeric forms thereof. Also suitable are alkylalkoxysilanes, wherein alkoxy is defined as above and alkyl may be a substituted or unsubstituted, branched or straight chain alkyl having about 1 to 25 carbon atoms, e.g., methyltrimethoxysilane (MTMOS), methyltriethoxysilane, ethyltriethoxysilane, ethyltrimethoxysilane, methyltripropoxy-silane, methyltributoxysilane, propyltrimethoxysilane, propyltriethoxysilane, isobutyltriethoxysilane, isobutyltrimethoxy-silane, octyltriethoxysilane, octyltrimethoxysilane, which is commercially available from Degussa AG, Germany, methacryloxydecyltrimethoxysilane (MDTMS); aryltrialkoxysilanes such as phenyltrimethoxysilane (PTMOS), phenyltriethoxysilane, which is commercially

available from Degussa AG, Germany; phenyltripropoxysilane, and phenyltributoxysilane, phenyl-tri-(3-glycidyloxy)-silane-oxide (TGPSO), 3-aminopropyltrimethoxysilane, 3-aminopropyl-triethoxysilane, 2-aminoethyl-3-aminopropyltrimethoxysilane, triaminofunctional propyltrimethoxysilane (Dynasylan® TRIAMO, available from Degussa AG, Germany), N-(n-butyl)-3-aminopropyltrimethoxysilane, 3-aminopropylmethyl-diethoxysilane, 3-glycidyl-oxypropyltrimethoxysilane, 3-glycidyloxypropyltriethoxy-silane, vinyltrimethoxysilane, vinyltriethoxysilane, 3-mercaptopropyltrimethoxy-silane, Bisphenol-A-glycidylsilanes; (meth)acrylsilanes, phenylsilanes, oligomeric or polymeric silanes, epoxysilanes; fluoroalkylsilanes such as fluoroalkyltrimethoxysilanes, fluoroalkyltriethoxysilanes with a partially or fully fluorinated, straight chain or branched fluoroalkyl residue of about 1 to 20 carbon atoms, e.g., tridecafluoro-1,1,2,2-tetrahydrooctyltriethoxysilane, or modified reactive fluoroalkylsiloxanes which can be available from Degussa AG under the trademarks Dynasylan® F8800 and F8815; and any mixtures thereof. Furthermore, 6-amino-1-hexanol, 2-(2-aminoethoxy)ethanol, cyclohexyl-amine, butyric acid cholesterylester (PCBCR), 1-(3-methoxycarbonyl)-propyl)-1-phenylester or combinations thereof may also be used.

It should be noted, that, typically the above modification agents and silanes may optionally also be used as cross linkers, e.g. in a solidification step for curing/hardening the liquid mixture.

In a further exemplary embodiment, the at least one reticulating agent includes particles or fibers selected from polymers, oligomers or pre-polymeric organic materials. These particles or fibers may be prepared by conventional polymerization techniques producing discrete particles, e.g. polymerizations in liquid media in emulsions, dispersions, suspensions or solutions. Furthermore, these particles or fibers may also be produced by extrusion, spinning, pelletizing, milling, or grinding of polymeric materials. When the reticulating agent is selected from particles or fibers of polymers, oligomers, pre-polymers, thermoplastics or elastomers, these materials may be selected from homopolymers or copolymers as

defined herein below for use as matrix materials. These polymers may be used either as the matrix material, if not in particle or fiber form, or as a reticulating agent if used in particle or fiber form. Polymeric reticulating agents may be selected among those which can decompose at elevated temperatures, and may thus act as pore formers in the reticulated materials. Examples include polyolefins like polyethylene or polypropylene particles or fibers.

In an exemplary embodiment, the reticulating agent may include electrically conducting polymers, such as defined below as electrically conductive matrix materials.

In further exemplary embodiments of the present invention, the at least one reticulating agent may e.g. include polymer encapsulated non polymeric particles wherein the non polymeric particles may be selected from the materials mentioned above. Techniques and polymerization reactions for encapsulating the non-polymeric reticulating agent particles include any suitable polymerization reaction conventionally used, for example a radical or non-radical polymerization, enzymatic or non-enzymatic polymerization, for example a poly-condensation reaction. The encapsulation of reticulating agent particles can –depending from the individual components used- lead to covalently or non-covalently encapsulated reticulating agent particles. For combining with the matrix material, the encapsulated reticulating agents may be in the form of polymer spheres, particularly nanosize- or micro spheres, or in the form of dispersed, suspended or emulgated particles or capsules, respectively. For the manufacture of polymer encapsulated particles any conventional method can be utilized in the present invention. Suitable encapsulation methods and the materials and conditions used therefore are described, for example, in International Patent Applications PCT/EP2006/060783 and PCT/EP2006/050373 and US Patent Applications Serial No. 11/385,145 and 11/339,161, and these methods, materials and procedures may also be used in the embodiments of the present invention.

Suitable encapsulation methods are described, for example, in Australian Patent Application No. AU 9169501, European Patent Publication Nos. EP 1205492,

EP 1401878, EP 1352915 and EP 1240215, U.S. Patent No. 6380281, U.S. Patent Publication No. 2004192838, Canadian Patent Publication No. CA 1336218, Chinese Patent Publication No. CN 1262692T, British Patent Publication No. GB 949722, and German Patent Publication No. DE 10037656; and in the further documents cited in this context e.g. in International Patent Applications PCT/EP2006/060783 and PCT/EP2006/050373 as mentioned above.

The encapsulated reticulating agents may be produced in a size of about 1 nm to 500 nm, or in the form of micro particles having an average size ranging from about 5 nm to 5 μm. Reticulating agents may be further encapsulated in mini- or micro-emulsions of suitable polymers. The term "mini- or micro-emulsion" may be understood as referring to dispersions comprising an aqueous phase, an oil or hydrophobic phase, and one or more surface active substances. Such emulsions may comprise suitable oils, water, one or several surfactants, optionally one or several co-surfactants and/or one or several hydrophobic substances. Mini-emulsions may comprise aqueous emulsions of monomers, oligomers or other pre-polymeric reactants stabilized by surfactants, which may be easily polymerized, and wherein the particle size of the emulgated droplets can be between about 10 nm and 500 nm or larger.

Mini-emulsions of encapsulated reticulating agents can also be made from non-aqueous media, for example, formamide, glycol or non-polar solvents. Pre-polymeric reactants may comprise thermosets, thermoplastics, plastics, synthetic rubbers, extrudable polymers, injection molding polymers, moldable polymers, and the like, or mixtures thereof, including pre-polymeric reactants from which poly(meth)acrylics can be used.

Examples of suitable polymers for encapsulating the reticulating agents can include, but are not limited to, homopolymers or copolymers of aliphatic or aromatic polyolefins such as polyethylene, polypropylene, polybutene, polyisobutene, polypentene; polybutadiene; polyvinyls such as polyvinyl chloride or polyvinyl alcohol, poly(meth)acrylic acid, polymethylmethacrylate (PMMA), polyacrylocyano acrylate; polyacrylonitril, polyamide, polyester, polyurethane, polystyrene,

polytetrafluoroethylene; particularly preferred may be biopolymers such as collagen, albumin, gelatin, hyaluronic acid, starch, celluloses such as methylcellulose, hydroxypropyl cellulose, hydroxypropyl methylcellulose, carboxymethylcellulose phthalate; casein, dextranes, polysaccharides, fibrinogen, poly(D,L-lactides), poly(D,L-lactide coglycolides), polyglycolides, polyhydroxybutylates, polyalkyl carbonates, polyorthoesters, polyesters, polyhydroxyvaleric acid, polydioxanones, polyethylene terephthalates, polymaleate acid, polytartronic acid, polyanhydrides, polyphosphazenes, polyamino acids; polyethylene vinyl acetate, silicones; poly(ester urethanes), poly(ether urethanes), poly(ester ureas), polyethers such as polyethylene oxide, polypropylene oxide, pluronics, polytetramethylene glycol; polyvinylpyrrolidone, poly(vinyl acetate phthalate), shellac, and combinations of these homopolymers or copolymers; with the exception of cyclodextrine and derivatives thereof or similar carrier systems.

Other encapsulating materials that may be used include poly(meth)acrylate, unsaturated polyester, saturated polyester, polyolefines such as polyethylene, polypropylene, polybutylene, alkyd resins, epoxypolymers, epoxy resins, polyamide, polyimide, polyetherimide, polyamideimide, polyesterimide, polyesteramideimide, polyurethane, polycarbonate, polystyrene, polyphenol, polyvinylester, polysilicone, polyacetale, cellulosic acetate, polyvinylchloride, polyvinylacetate, polyvinylalcohol, polysulfone, polyphenylsulfone, polyethersulfone, polyketone, polyetherketone, polybenzimidazole, polybenzoxazole, polybenzthiazole, polyfluorocarbons, polyphenylenether, polyarylate, cyanatoester-polymere, or mixtures or copolymers of any of the foregoing.

In certain exemplary embodiments of the present invention, the polymers used to encapsulate the reticulating agents may comprise mono(meth)acrylate-, di(meth)acrylate-, tri(meth)acrylate-, tetra-acrylate- and pentaacrylate-based poly(meth)acrylates. Examples for suitable mono(meth)acrylates are hydroxyethyl acrylate, hydroxyethyl methacrylate, hydroxypropyl methacrylate, hydroxypropyl acrylate, 3-chloro-2-hydroxypropyl acrylate, 3-chloro-2-hydroxypropyl methacrylate, 2,2-dimethylhydroxypropyl acrylate, 5-hydroxypentyl acrylate, diethylene glycol

monoacrylate, trimethylolpropane monoacrylate, pentaerythritol monoacrylate, 2,2-dimethyl-3-hydroxypropyl acrylate, 5-hydroxypentyl methacrylate, diethylene glycol monomethacrylate, trimethylolpropane monomethacrylate, pentaerythritol monomethacrylate, hydroxy-methylated N-(1,1-dimethyl-3-oxobutyl)acrylamide, N-methylolacrylamide, N-methylolmethacrylamide, N-ethyl-N-methylolmethacrylamide, N-ethyl-N-methylolacrylamide, N,N-dimethylol-acrylamide, N-ethanolacrylamide, N-propanolacrylamide, N-methylolacrylamide, glycidyl acrylate, and glycidyl methacrylate, methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, amyl acrylate, ethylhexyl acrylate, octyl acrylate, t-octyl acrylate, 2-methoxyethyl acrylate, 2-butoxyethyl acrylate, 2-phenoxyethyl acrylate, chloroethyl acrylate, cyanoethyl acrylate, dimethylaminoethyl acrylate, benzyl acrylate, methoxybenzyl acrylate, furfuryl acrylate, tetrahydrofurfuryl acrylate and phenyl acrylate; di(meth)acrylates may be selected from 2,2-bis(4-methacryloxyphenyl)propane, 1,2-butanediol-diacrylate, 1,4-butanediol-diacrylate, 1,4-butanediol-dimethacrylate, 1,4-cyclohexanediol-dimethacrylate, 1,10-decanediol-dimethacrylate, diethylene-glycol-diacrylate, dipropyleneglycol-diacrylate, dimethylpropanediol-dimethacrylate, triethyleneglycol-dimethacrylate, tetraethyleneglycol-dimethacrylate, 1,6-hexanediol-diacrylate, Neopentylglycol-diacrylate, polyethyleneglycol-dimethacrylate, tripropyleneglycol-diacrylate, 2,2-bis[4-(2-acryloxyethoxy)phenyl]propane, 2,2-bis[4-(2-hydroxy-3-methacryloxypropoxy)phenyl]propane, bis(2-methacryloxyethyl)N,N-1,9-nonylene-biscarbamate, 1,4-cycloheanedimethanol-dimethacrylate, and diacrylic urethane oligomers; tri(meth)acrylates may be selected from tris(2-hydroxyethyl)isocyanurate-trimethacrylate, tris(2-hydroxyethyl)isocyanurate-triacrylate, trimethylolpropane-trimethacrylate, trimethylolpropane-triacrylate or pentaerythritol-triacrylate; tetra(meth)acrylates may be selected from pentaerythritol-tetraacrylate, di-trimethylolpropane- tetraacrylate, or ethoxylated pentaerythritol-tetraacrylate; suitable penta(meth)acrylates may be selected from dipentaerythritol-pentaacrylate or pentaacrylate-esters; as well as mixtures, copolymers or combinations of any of the foregoing. Biopolymers or acrylics may be preferably

used to encapsulate the reticulating agents in certain exemplary embodiments of the invention, e.g. for biological or medical applications.

Encapsulating polymer reactants may comprise polymerizable monomers, oligomers or elastomers such as polybutadiene, polyisobutylene, polyisoprene, poly(styrene-butadiene-styrene), polyurethanes, polychloroprene, natural rubber materials, gums such as gum arabica, locust bean gum, gum caraya, or silicone, and mixtures, copolymers or any combinations thereof. The reticulating agents may be encapsulated in elastomeric polymers alone, or in mixtures of thermoplastic and elastomeric polymers, or in an alternating sequence of thermoplastic and elastomeric shells or layers.

The polymerization reaction for encapsulating the reticulating agents can include any suitable conventional polymerization reaction, for example, a radical or non-radical polymerization, enzymatic or non-enzymatic polymerization, including poly-condensation reactions. The emulsions, dispersions or suspensions used may be in the form of aqueous, non-aqueous, polar or homopolar systems. By adding suitable surfactants, the amount and size of the emulgated or dispersed droplets can be adjusted as required.

The surfactants may be anionic, cationic, zwitter-ionic or non-ionic surfactants or any combinations thereof. Preferred anionic surfactants may include, but are not limited to, soaps, alkylbenzolsulphonates, alkansulphonates, olefinsulphonates, alkyethersulphonates, glycerinethersulphonates, α-methylestersulphonates, sulphonated fatty acids, alkylsulphates, fatty alcohol ether sulphates, glycerin ether sulphates, fatty acid ether sulphates, hydroxyl mixed ether sulphates, monoglyceride(ether)sulphates, fatty acid amide(ether)sulphates, mono- and di-alkylsulfosuccinates, mono- and dialkylsulfosuccinamates, sulfotriglycerides, amidsoaps, ethercarboxylicacid and their salts, fatty acid isothionates, fatty acid arcosinates, fatty acid taurides, N-acylaminoacid such as acyllactylates, acyltartrates, acylglutamates and acylaspartates, alkyloligoglucosidsulfates, protein fatty acid condensates, including plant derived products based on wheat; and alky(ether)phosphates.

Cationic surfactants suitable for encapsulation reactions in certain embodiments of the present invention may comprise quaternary ammonium compounds such as dimethyldistearylammoniumchloride, Stepantex® VL 90 (Stepan), esterquats, particularly quaternized fatty acid trialkanolaminester salts, salts of long-chain primary amines, quaternary ammonium compounds such as hexadecyltrimethyl-ammoniumchloride (CTMA-Cl), Dehyquart® A (cetrimonium-chloride, Cognis), or Dehyquart® LDB 50 (lauryldimethylbenzylammoniumchloride, Cognis).

Other preferred surfactants may include lecithin, poloxamers, i.e., block copolymers of ethylene oxide and propylene oxide, including those available from BASF Co. under the trade name pluronic®, including pluronic® F68NF, alcohol ethoxylate based surfactants from the TWEEN® series available from Sigma Aldrich or Krackeler Scientific Inc., and the like.

The reticulating agent can be added before or during the start of the polymerization reaction and may be provided in the form of a dispersion, emulsion, suspension or solid solution, or as solution of the reticulating agents in a suitable solvent or solvent mixture, or any mixtures thereof. The encapsulation process may comprise the polymerization reaction, optionally with the use of initiators, starters or catalysts, where an *in-situ* encapsulation of the reticulating agents in polymer capsules, spheroids or droplets may occur. The solids content of the reticulating agents in such encapsulation mixtures may be selected such that the solids content in the polymer capsules, spheroids or droplets is between about 10 weight % and about 80 weight % of active agent within the polymer particles.

Optionally, the reticulating agents may also be added after completion of the polymerization reaction, either in solid form or in liquid form. The reticulating agents can be selected from those compounds which are able to bind to the polymer spheroids or droplets, either covalently or non-covalently. The droplet size of the polymers and the solids content of reticulating agents can be selected such that the solids content of the reticulating agent particles ranges from about 5 weight % to about 90 weight % with respect to the total weight polymerization mixture.

In an exemplary embodiment of the present invention, the encapsulation of the reticulating agents during the polymerization can be repeated at least once by addition of further monomers, oligomers or pre-polymeric agents after completion of a first polymerization/encapsulation step. By performing at least one repeated polymerization step in this manner, multilayer coated polymer capsules can be produced. Also, reticulating agents bound to polymer spheroids or droplets may be encapsulated by subsequently adding monomers, oligomers or pre-polymeric reactants to overcoat the reticulating agents with a polymer capsule. Repetition of such processes can produce multilayered polymer capsules comprising the reticulating agent.

Any of the encapsulation steps described above may be combined with each other. In a preferred exemplary embodiment of the present invention, polymer-encapsulated reticulating agents can be further coated with release-modifying agents.

In further exemplary embodiments of the present invention, the reticulating agents or polymer encapsulated reticulating agents may be further encapsulated in vesicles, liposomes or micelles, or overcoatings. Suitable surfactants for this purpose may include the surfactants typically used in encapsulation reactions as described in above. Further Surfactants include compounds having hydrophobic groups which may include hydrocarbon residues or silicon residues, for example, polysiloxane chains, hydrocarbon based monomers, oligomers and polymers, or lipids or phosphorlipids, or any combinations thereof, particularly glycerylester such as phosphatidylethanolamine, phosphatidylcholine, polyglycolide, polylactide, polymethacrylate, polyvinylbuthylether, polystyrene, polycyclopentadienyl-methylnorbornene, polypropylene, polyethylene, polyisobutylene, polysiloxane, or any other type of surfactant.

Furthermore, depending on the polymeric shell, surfactants for encapsulating the polymer encapsulated reticulating agents in vesicles, overcoats and the like may be selected from hydrophilic surfactants or surfactants having hydrophilic residues or hydrophilic polymers such as polystyrensulfonicacid, poly-N-alkylvinylpyridinium-halogenide, poly(meth)acrylic acid, polyaminoacids, poly-N-vinylpyrrolidone,

polyhydroxyethylmethacrylate, polyvinylether, polyethylenglycol, polypropylene oxide, polysaccharides such as agarose, dextrane, starch, cellulose, amylase, amylopektine or polyethylenglycole, or polyethylennimine of a suitable molecular weight. Also, mixtures from hydrophobic or hydrophilic polymer materials or lipid polymer compounds may be used for encapsulating the polymer capsulated reticulating agents in vesicles or for further over-coating the polymer encapsulating reticulating agents.

Additionally, the encapsulated reticulating agents may be chemically modified by functionalization with suitable linker groups or coatings. For example, they may be functionalized with organosilane compounds or organo-functional silanes. Such compounds for modification of the polymer encapsulated reticulating agents are further described above.

The incorporation of polymer-encapsulated particles into the materials described herein can be regarded –without wishing to be bound to any particular theory- as a specific form of a reticulation agent. The particle size and particle size distribution of the polymer-encapsulated reticulating agent particles in dispersed or suspended form typically correspond to the particle size and particle size distribution of the particles of finished polymer-encapsulated particles. The polymer-encapsulated particles can be characterised in the liquid phase, e.g. by dynamic light scattering methods with regard to their particle size and monodispersity.

Furthermore, the particles used as the reticulating agents in the process of the present invention may be encapsulated in bio-compatible, preferably bio-degradable polymers. For example, the bio-compatible polymers mentioned herein as possible matrix materials may be used. These materials may also be directly used as reticulating agents, as discussed above.

In some exemplary embodiments, pH-sensitive polymers may be used for encapsulating reticulating agent particles or as the reticulating agent particle itself. For example, the pH-sensitive polymers mentioned herein as possible matrix materials may be used.. Furthermore, polysaccharides such as cellulose acetate-

phtalate, hydroxypropylmethylcellulose-phtalate, hydroxypropylmethylcellulose-succinate, cellulose acetate-trimellitate and chitosan may be used.

Temperature-sensitive polymers or polymers having a thermogel characteristic may also be used for encapsulating the reticulating agent particles or as the reticulating agent particle itself. Examples are mentioned below in the context of matrix materials.

The at least one reticulating agent can be combined with a matrix material in a suitable solvent before subsequently being converted into a porous reticulated composite material of the present invention.

Matrix material

In accordance with exemplary embodiments of the present invention, the at least one reticulating agent is combined with matrix materials, optionally in the presence or absence of a suitable solvent or solvent mixture, wherein the matrix materials may be combined with the selected reticulating agents or mixtures thereof to form the porous reticulated composite material.

The matrix material may include polymers, oligomers, monomers or pre-polymerized forms, optionally of synthetic origin, and the polymers may be the same as the polymeric materials mentioned above as suitable for reticulating agents or in the referenced documents for encapsulating the reticulating agents, as well as all substances which may be synthesized to pre-polymeric, partially polymerized or polymeric materials or which are already present as such materials, particularly also polymer composites. Polymer composites may already be present as nano-composites or may contain nanomorphous particles in homogeneously dispersed form, as well as substances which can be solidified from suspensions, dispersions or emulsions and which are suitable for forming a composite material with the selected reticulating agents. The polymers used may include thermosets, thermoplastics, synthetic rubbers, extrudable polymers, injection molding polymers, moldable polymers and the like or mixtures thereof.

Furthermore, additives may be added which improve the compatibility of the components used in producing the composite material, for example coupling agents like silanes, surfactants or fillers, i.e., organic or inorganic fillers.

In one exemplary embodiment, the polymer for use as the matrix material may include homopolymers, copolymers prepolymeric forms and/or oligomers of aliphatic or aromatic polyolefins such as polyethylene, polypropylene, polybutene, polyisobutene, polypentene; polybutadiene; polyvinyls such as polyvinyl chloride, polyvinylacetate, or polyvinyl alcohol, polyacrylates, such as poly(meth)acrylic acid, polymethylmethacrylate (PMMA), polyacrylocyano acrylate; polyacrylonitril, polyamide, polyester, polyurethane, polystyrene, polytetrafluoroethylene; particularly preferred are bio-compatible polymers as further defined herein; furthermore polyethylene vinyl acetate, silicones; poly(ester urethanes), poly(ether urethanes), poly(ester ureas), polyethers such as polyethylene oxide, polypropylene oxide, pluronics, polytetramethylene glycol; polyvinylpyrrolidone, poly(vinyl acetate phthalate), or shellac, and combinations of these.

In further exemplary embodiments, the polymer for use as the matrix material may include unsaturated or saturated polyesters, alkyd resins, epoxy-polymers, epoxy resins, phenoxy resins, nylon, polyimide, polyetherimide, polyamideimide, polyesterimide, polyesteramideimide, polyurethane, polycarbonate, polystyrene, polyphenol, polyvinylester, polysilicon, polyacetal, cellulose acetate, polysulfone, polyphenylsulfone, polyethersulfone, polyketone, polyetherketone, polyetheretherketone, polyetherketonketones, polybenzimidazole, polybenzoxazole, polybenzthiazole, polyfluorocarbons, polyphenylenether, polyarylate, cyanatoester-polymers, copolymers or mixtures of any of these.

Other suitable polymers for the matrix material include acrylics, e.g. mono(meth)acrylate-, di(meth)acrylate-, tri(meth)acrylate-, tetra-acrylate and pentaacrylate-based poly(meth)acrylates. Examples for suitable mono(meth)acrylates are hydroxyethyl acrylate, hydroxyethyl methacrylate, hydroxypropyl methacrylate, hydroxypropyl acrylate, 3-chloro-2-hydroxypropyl acrylate, 3-chloro-2-hydroxypropyl methacrylate, 2,2-dimethylhydroxypropyl acrylate, 5-hydroxypentyl

acrylate, diethylene glycol monoacrylate, trimethylolpropane monoacrylate, pentaerythritol monoacrylate, 2,2-dimethyl-3-hydroxypropyl acrylate, 5-hydroxypentyl methacrylate, diethylene glycol monomethacrylate, trimethylolpropane monomethacrylate, pentaerythritol monomethacrylate, hydroxy-methylated N-(1,1-dimethyl-3-oxobutyl)acrylamide, N-methylolacrylamide, N-methylolmethacrylamide, N-ethyl-N-methylolmethacrylamide, N-ethyl-N-methylolacrylamide, N,N-dimethylol-acrylamide, N-ethanolacrylamide, N-propanolacrylamide, N-methylolacrylamide, glycidyl acrylate, and glycidyl methacrylate, methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, amyl acrylate, ethylhexyl acrylate, octyl acrylate, t-octyl acrylate, 2-methoxyethyl acrylate, 2-butoxyethyl acrylate, 2-phenoxyethyl acrylate, chloroethyl acrylate, cyanoethyl acrylate, dimethylaminoethyl acrylate, benzyl acrylate, methoxybenzyl acrylate, furfuryl acrylate, tetrahydrofurfuryl acrylate and phenyl acrylate; di(meth)acrylates may be selected from 2,2-bis(4-methacryloxyphenyl)propane, 1,2-butanediol-diacrylate, 1,4-butanediol-diacrylate, 1,4-butanediol-dimethacrylate, 1,4-cyclohexanediol-dimethacrylate, 1,10-decanediol-dimethacrylate, diethylene-glycol-diacrylate, dipropyleneglycol-diacrylate, dimethylpropanediol-dimethacrylate, triethyleneglycol-dimethacrylate, tetraethyleneglycol-dimethacrylate, 1,6-hexanediol-diacrylate, neopentylglycol-diacrylate, polyethyleneglycol-dimethacrylate, tripropyleneglycol-diacrylate, 2,2-bis[4-(2-acryloxyethoxy)-phenyl]propane, 2,2-bis[4-(2-hydroxy-3-methacryloxypropoxy)-phenyl]propane, bis(2-methacryloxyethyl)N,N-1,9-nonylene-biscarbamate, 1,4-cycloheanedimethanol-dimethacrylate, and diacrylic urethane oligomers; tri(meth)acrylates may be selected from tris(2-hydroxyethyl)-isocyanurate-trimethacrylate, tris(2-hydroxyethyl)isocyanurate-triacrylate, trimethylolpropane-trimethacrylate, trimethylolpropane-triacrylate or pentaerythritol-triacrylate; tetra(meth)acrylates may be selected from pentaerythritol-tetraacrylate, di-trimethylopropan- tetraacrylate, or ethoxylated pentaerythritol-tetraacrylate; suitable penta(meth)acrylates may be selected from dipentaerythritol-pentaacrylate or pentaacrylate-esters; examples for polyacrylates are polyisobornylacrylate,

polyisobornylmethacrylate, polyethoxyethoxyethylacrylate, poly-2-carboxyethylacrylate, polyethylhexylacrylate, poly-2-hydroxyethylacrylate, poly-2-phenoxylethylacrylate, poly-2-phenoxyethylmethacrylate, poly-2-ethylbutylmethacrylate, poly-9-anthracenylmethyl methacrylate, poly-4-chlorophenylacrylate, polycyclohexylacrylate, polydicyclopentenyloxyethylacrylate, poly-2-(N,N-diethylamino)ethylmethacrylate, poly-dimethylaminoeopentylacrylate, poly-caprolactone 2-(methacryloxy)ethylester, polyfurfurylmethacrylate, poly(ethylene glycol)methacrylate, polyacrylic acid and poly(propylene glycol)methacrylate, as well as mixtures, copolymers and combinations of any of the foregoing.

Suitable polyacrylates also comprise aliphatic unsaturated organic compounds, e.g. polyacrylamide and unsaturated polyesters from condensation reactions of unsaturated dicarboxylic acids and diols, as well as vinyl-derivatives, or compounds having terminal double bonds. Examples include N-vinylpyrrollidone, styrene, vinyl-naphthalene or vinylphtalimide. Methacrylamid-derivatives include N-alkyl- or N-alkylen-substituted or unsubstituted (meth)acrylamide, such as acrylamid, methacrylamide, N-methacrylamide, N-methylmethacrylamide, N-ethylacrylamide, N,N-dimethylacrylamide, N,N-dimethylmethacrylamide, N,N-diethylacrylamide, N-ethylmethacrylamide, N-methyl-N-ethylacrylamide, N-isopropylacrylamide, N-n-propylacrylamide, N-isopropylmethacrylamide, N-n-propylmethacrylamide, N-acryloyloylpyrrolidine, N-methacryloylpyrrolidine, N-acryloylpiperidine, N-methacryloylpiperidine, N-acryloylhexahydroazepine, N-acryloylmorpholine or N-methacryloylmorpholine.

Further suitable polymers for use as the matrix material in the present invention include unsaturated and saturated polyesters, particularly also including alkyd resins. The polyesters may contain polymeric chains, a varying number of saturated or aromatic dibasic acids and anhydrides, or epoxy resins, which may be used as monomers, oligomers or polymers are suitable, particularly those which comprise one or several oxirane rings, one aliphatic, aromatic or mixed aliphatic-aromatic molecular structural element, or exclusively non-benzoid structures, i.e.,

aliphatic or cyclophatic structures with our without substituents such as halogen, ester groups, ether groups, sulfonate groups, siloxane groups, nitro groups, or phosphate groups, or any combination thereof.

In preferred exemplary embodiments of the invention, the matrix material may include epoxy resins, for example of the glycidyl-epoxy type, such as those equipped with the diglycidyl groups of bisphenol A. Further epoxy resins include amino derivatized epoxy resins, particularly tetraglycidyl diaminodiphenyl methane, triglycidyl-p-aminophenol, triglycidyl-m -maminophenole, or triglycidyl aminocresole and their isomers, phenol derivatized epoxy resins such as, for example, epoxy resins of bisphenol A, bisphenol F, bisphenol S, phenol-novolac, cresole-novolac or resorcinole, phenoxy resins, as well as alicyclic epoxy resins. Furthermore, halogenated epoxy resins, glycidyl ethers of polyhydric phenols, diglycidylether of bisphenol A, glycidylethers of phenole-formaldehyde-novolac resins and resorcinole diglycidylether, as well as further epoxy resins as described in US Patent No. 3,018,262, herewith incorporated by reference, may be used. These materials may be easily solidified or cured thermally or by radiation or cross linking.

Epoxy resins can be particularly preferred in combination with metal or metal oxide particles and combinations thereof as the reticulating agent. Also, in other exemplary embodiments, epoxy resins can be particularly preferred in combination with carbon particles and/or fullerenes as the reticulating agent.

In some exemplary embodiments of the present invention, the matrix material does not comprise cellulose or cellulose derivatives, or it may be substantially non-elastic, or the matrix material may be substantially free of fibers or particles.

The selection of the matrix material is not restricted to the materials mentioned above, particularly also mixtures of epoxy resins from two or several components as mentioned above may be used, as well as monoepoxy components. The epoxy resins may also include resins which may be cross linked via radiation, e.g. UV-radiation, and cycloaliphatic resins.

Further matrix materials include polyamides, like e.g. aliphatic or aromatic polyamides and aramides (nomex®), and their derivatives, e.g. nylon-6-

(polycaprolactam), nylon 6/6 (polyhexamethyleneadipamide), nylon 6/10, nylon 6/12, nylon 6/T (polyhexamethylene terephthalamide), nylon 7 (polyenanthamide), nylon 8 (polycapryllactam), nylon 9 (polypelargonamide), nylon 10, nylon 11, nylon 12, nylon 55, nylon XD6 (poly metha-xylylene adipamide), nylon 6/I , and poly-alanine.

Also, metal phosphinates or polymetal phosphinates as well as inorganic metal-containing polymers or organic metal-containing polymers such as, for example, metallodendrimers, metallocenyl polymers, carbosilanes, polyynes, noble metal alkynyl polymers, metalloporphyrine polymers, metallocenophanes, metallocenylsilane-carbosilane copolymers as mono, diblock, triblock or multiblock copolymers may be used, as well as poly(metallocenyldimethylsilane) compounds, carbothiametallocenophanes, poly(carbothiametallocenes) and the like, wherein this list of compounds is not exclusive and includes any combinations thereof.

In an exemplary embodiment, the matrix material may include electrically conducting polymers, such as saturated or unsaturated polyparaphenylene-vinylene, polyparaphenylene, polyaniline, polythiophene, poly(ethylenedioxythiophene), polydialkylfluorene, polyazine, polyfurane, polypyrrole, polyselenophene, poly-p-phenylene sulfide, polyacetylene, and monomers, oligomers or polymers or any combinations and mixtures thereof with other monomers, oligomers or polymers or copolymers made of the above-mentioned monomers. Conductive or semi-conductive polymers may have an electrical resistance from 10^{12} and 10^{12} Ohm·cm. Examples further include monomers, oligomers or polymers including one or several organic radical, for example, alkyl- or aryl-radicals and the like, or inorganic radicals, such as silicone or germanium and the like, or any mixtures thereof.

Polymers which comprise complexed metal salts may also be used as the matrix material. Such polymers typically comprise a oxygen, nitrogen, sulfur or halogen atom or unsaturated C-C bonds, capable of complexing metals. Without excluding others, examples for such compounds are elastomers like polyurethane, rubber, adhesive polymers and thermoplastics. Metal salts for complexation include transition metal salts such as $CuCl_2$, $CuBr_2$, $CoCl_2$, $ZnCl_2$, $NiCl_2$, $FeCl_2$, $FeBr_2$,

$FeBr_3$, CuI_2, $FeCl_3$, FeI_3, or FeI_2; furthermore salts like $Cu(NO_3)_2$, metal lactates, glutamates, succinates, tartrates, phosphates, oxalates, $LiBF_4$, and $H_4Fe(CN)_6$ and the like.

In some exemplary embodiments of the present invention, the matrix material may include biopolymers, bio-compatible or biodegradable polymers such as collagen, albumin, gelatin, hyaluronic acid, starch, celluloses such as methylcellulose, hydroxypropyl cellulose, hydroxypropyl methylcellulose, carboxymethylcellulose phthalate; casein, dextranes, polysaccharides, fibrinogen, poly(D,L-lactides), poly(D,L-lactide coglycolides), poly(glycolides), poly(hydroxybutylates), poly(alkylcarbonates), poly(orthoesters), poly(hydroxyvaleric acid), polydioxanones, poly(ethyleneterephthalates), poly(maleic acid), poly(tartaric acid), polyanhydrides, polyphosphazenes, poly(amino acids), or shellac.

Furthermore, the matrix material may be selected from oligomers or elastomers such as polybutadiene, polyisobutylene, polyisoprene, poly(styrene-butadiene-styrene), polyurethanes, polychloroprene, or silicone, and any mixtures, copolymers and combinations thereof. The matrix material may also be selected from pH-sensitive polymers such as, for example, poly(acrylic acid) and its derivatives, for example homopolymers such as poly(aminocarboxyl acid), poly(acrylic acid), poly(methyl-acrylic acid) and copolymers thereof; or may be selected from temperature-sensitive polymers, such as, for example poly(N-isopropylacrylamide-Co-sodium-acrylate-Co-n-N-alkylacrylamide), poly(N-methyl-N-n-propylacrylamide), poly(N-methyl-N-isopropylacrylamide), poly(N-n-propylmethacrylamide), poly(N-isopropylacrylamide), poly(N,-diethylacrylamide), poly(N-isopropylmethacrylamide), poly(N-cyclopropylacrylamide), poly(N-ethylacrylamide), poly(N-ethylmethyacrylamide), poly(N-methyl-N-ethylacrylamide), poly(N-cyclopropylacrylamide). Furthermore, suitable matrix material polymers having a thermogel characteristic include hydroxypropyl-cellulose, methyl-cellulose, hydroxypropylmethyl-cellulose, ethylhydroxyethyl-cellulose and pluronics® like F-127, L-122, L-92, L81, or L61.

The matrix material may be itself in a liquid form, e.g. a liquid prepolymer, a melt, polymer or a solution, dispersion, emulsion, and may be mixed with the at least one reticulating agent in the absence or presence of a solvent, or may be a solid.

Liquid mixture

In accordance with the invention, the at least one reticulating agent can be combined with the matrix material, optionally in the presence or absence of a suitable solvent or solvent mixture to form a mixture capable of flowing, e.g. a solution, suspension, dispersion or emulsion, or a melt, slurry, paste or flowable particle mixture. The liquid mixture may be substantially uniform and/or substantially homogenous. However, in most instances uniformity or homogeneity of the liquid mixture is not critical.

Suitable solvents may comprise water, sols or gels, or nonpolar or polar solvents, such as methanol, ethanol, n-propanol, isopropanol, butoxydiglycol, butoxyethanol, butoxyisopropanol, butoxypropanol, n-butyl alcohol, t-butyl alcohol, butylene glycol, butyl octanol, diethylene glycol, dimethoxydiglycol, dimethyl ether, dipropylene glycol, ethoxydiglycol, ethoxyethanol, ethyl hexane diol, glycol, hexane diol, 1,2,6-hexane triol, hexyl alcohol, hexylene glycol, isobutoxy propanol, isopentyl diol, methylethyl ketone, ethoxypropylacetate, 3-methoxybutanol, methoxydiglycol, methoxyethanol, methoxyisopropanol, methoxymethylbutanol, methoxy PEG-10, methylal, methyl hexyl ether, methyl propane diol, neopentyl glycol, PEG-4, PEG-6, PEG-7, PEG-8, PEG-9, PEG-6-methyl ether, pentylene glycol, PPG-7, PPG-2-buteth-3, PPG-2 butyl ether, PPG-3 butyl ether, PPG-2 methyl ether, PPG-3 methyl ether, PPG-2 propyl ether, propane diol, propylene glycol, propylene glycol butyl ether, propylene glycol propyl ether, tetrahydrofurane, trimethyl hexanol, phenol, benzene, toluene, xylene any of which may be mixed with dispersants, surfactants or other additives and mixtures of the above-named substances.

Readily removable solvents may be sometimes preferred, i.e. those which may be easily volatized. Examples include solvents having a boiling point below 120 °C, such as below 80°C, or even below 50 °C. The solvent or solvent mixture can be

used to facilitate effective dispersion of the solids, especially where uniform or homogenous liquid mixtures are preferred.

The solvent used in certain exemplary embodiments may further be selected from solvents mixtures thereof which are suitable for dissolving or swelling the matrix material or at least a part or the main component of the matrix material if this is a composite or mixture. Solvents which substantially completele dissolve the matrix material may be preferred in exemplary embodiments of the invention.

In accordance with exemplary embodiments of the invention, the liquid mixture may be in the form of a colloidal solution, solid solution, dispersion, suspension or emulsion, which comprises the at least one matrix material and the at least one reticulating agent. The skilled person may select the matrix material, the reticulating agent, the solvent and possible additives in order to produce for example an essentially stable and optionally homogeneous dispersion, suspension, emulsion or solution.

The dynamic viscosity of the liquid mixture comprising a solvent, e.g., a solution, dispersion, suspension or emulsion comprising the matrix material and the reticulated agent, can be at least about 10 to 99%, preferably 20 to 90%, or 50 to 90% below the viscosity of the matrix material at the application temperature of the liquid mixture before solidifying, preferably at about 25 °C,.

Where the mixture capable of flowing does not comprise a solvent, the temperature and/or composition of the liquid mixture or the matrix material can be selected such that the dynamic viscosity of the mixture capable of flowing free of any solvent is at least about 10 to 99%, preferably 20 to 90% or 50 to 90% below the viscosity of the matrix material at said temperature. Also, these values refer to the mixture substantially before any cross linking occurs or cross linkers are added, respectively. Viscosities may be measured by conventional methods, e.g. in a capillary viscosimeter or Brookfield apparatus.

Additionally, the individual combination of reticulating agents, the solvent and the matrix material can be selected such that the selected reticulating agents are wetted by the solvent, the matrix material or the liquid mixture. Optionally, the

reticulating agents may be modified with the use of suitable additives or surface modifiers as described above to increase there wettability, preferably to be essentially fully wetted.

Furthermore, the at least one reticulating agent and the matrix material may be combined in a specific weight or volume ratio to each other, e.g. in order to optimize the structure of the porous composites formed under the conditions used for solidifying the liquid mixture. The specific ratio of both components may depend on the molecular weight, the particle size and the specific surface area of the particles. The ratio used can be selected such that upon removal of the solvent during the solidification step or upon changing the viscosity of the matrix component, a phase separation into a solvent phase and a solids phase consisting of the matrix material and the reticulating agent can be achieved. The viscosity change can be achieved by changing the temperature to higher or lower values, or by the addition of cross linkers, specifically in solvent free systems.

This phase separation can facilitate the formation of a three-dimensional network of the solid phase e.g. by self orientation of the components used. In exemplary embodiments of the present invention, the volume ratio between the total volume of the reticulating agents and the total volume of the matrix material can range from about 20:80 to 70:30, preferably from 30:70 to 60:40, or from 50:50 to 60:40.

In exemplary embodiments of the invention, the solids content in the liquid mixture may be up to 90 % by weight, referring to the total weight of the liquid mixture, preferably up to 80%, or below 20 % by weight, referring to the total weight of the liquid mixture, preferably below 15 % by weight, e.g. below 10 % by weight or sometimes even below 5 % by weight.

Additives

With the use of additives, it is possible to further vary and adjust the mechanical, optical and thermal properties of the material, which can be particularly suitable for producing tailor-made coatings. Therefore, in some exemplary

embodiments of the present invention, further additives can be added to the liquid mixture.

Examples of suitable additives include fillers, further pore-forming agents, metals and metal powders, etc. Examples of inorganic additives and fillers include silicon oxides and aluminum oxides, aluminosilicates, zeolites, zirconium oxides, titanium oxides, talc, graphite, carbon black, fullerenes, clay materials, phyllosilicates, silicides, nitrides, metal powders, including transition metals such as copper, gold, silver, titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, manganese, rhenium, iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium or platinum.

Further suitable additives are cross linkers, plasticizers, lubricants, flame resistants, glass or glass fibers, carbon fibers, cotton, fabrics, metal powders, metal compounds, silicon, silicon oxides, zeolites, titan oxides, zirconium oxides, aluminum oxides, aluminum silicates, talcum, graphite, soot, phyllosilicates and the like.

Typical additives for cross linking include e.g. organosilanes such as tetraalkoxysilanes, alkylalkoxysilanes, and aryltrialkoxysilanes such those described above herein, and in International Patent Application PCT/EP2006/050622 and US Patent application Serial No. 11/346,983 and these may be employed also as cross linking additives in the embodiments in the present invention.

Further additives for wetting, dispersing and/or satirically stabilizing the components, or electrostatic stabilizers, theology or thixotropy modifiers, such as the various additives and dispersing aids sold under the trademarks Byk®, Disperbyk® or Nanobyk® by Byk-Chemie GmbH, Germany, or equivalent compositions from other manufacturers, may be added if necessary.

Emulsifiers may be used in the liquid mixture. Suitable emulsifiers may be selected from anionic, cationic, zwitter-ionic or non-ionic surfactants and any combinations thereof. Anionic surfactants include soaps, alkylbenzolsulphonates, alkansulphonates such as, sodium dodecylsulphonate (SDS) and the like, olefinsulphonates, alkyethersulphonates, glycerinethersulphonates, α-

methylestersulphonates, sulphonated fatty acids, alkylsulphates, fatty alcohol ether sulphates, glycerin ether sulphates, fatty acid ether sulphates, hydroxyl mixed ether sulphates, monoglyceride(ether)sulphates, fatty acid amide(ether)sulphates, mono- and di-alkylsulfosuccinates, mono- and dialkylsulfosuccinamates, sulfotriglycerides, amidsoaps, ethercarboxylicacid and their salts, fatty acid isothionates, fatty acid arcosinates, fatty acid taurides, N-acylaminoacids like acyllactylates, acyltartrates, acylglutamates and acylaspartates, alkyoligoglucosidsulfates, protein fatty acid condensates, particularly plant derived products based on wheat; and alky(ether)phosphates.

Cationic surfactants include quaternary ammonium compounds such as dimethyldistearylammoniumchloride, Stepantex® VL 90 (Stepan), esterquats, such as quaternized fatty acid trialkanolaminester salts, salts of long-chain primary amines, quaternary ammonium compounds like hexadecyltrimethyl-ammoniumchloride (CTMA-Cl), Dehyquart® A (cetrimoniumchloride, available from Cognis), or Dehyquart® LDB 50 (lauryldimethylbenzylammoniumchloride, available from Cognis).

The person skilled in the art may select any or several of such additives as necessary in order to produce a stable dispersion, suspension or emulsion in the liquid mixture.

Further to the reticulating agents used, additional fillers can be used to further modify the size and the degree of porosity. In some exemplary embodiments of the invention non-polymeric fillers are preferred. Non-polymeric fillers include any substance which can be removed or degraded, for example, by thermal treatment, washing out or other conditions, without adversely effecting the material properties. Some fillers can be dissolved in a suitable solvent and can be removed in this manner from the final material. Furthermore, non-polymeric fillers, which can be converted into soluble substances under the chosen thermal conditions, can also be applied. Non-polymeric fillers includes for example, anionic, cationic or non-ionic surfactants, which can be removed or degraded, e.g. under certain thermal conditions. Fillers can also include inorganic metal salts, particularly salts from

alkaline and/or alkaline earth metals, such as alkaline or alkaline earth metal carbonates, -sulphates, -sulphites, -nitrates, -nitrites, -phosphates, -phosphites, -halides, -sulphides, and -oxides. Further suitable fillers can include organic metal salts, e.g. alkaline or alkaline earth and/or transition metal salts, e.g. their formiates, acetates, propionates, malates, maleates, oxalates, tartrates, citrates, benzoates, salicylates, phthalates, stearates, phenolates, sulphonates, and amines as well as mixtures thereof.

In another exemplary embodiment of the present invention polymeric fillers can be applied. Suitable polymeric fillers can be those as mentioned above as encapsulation polymers, particularly in the form of spheres or capsules. Preferred examples include saturated, linear or branched aliphatic hydrocarbons, which can be homo- or copolymers, e.g. polyolefins such as polyethylene, polypropylene, polybutene, polyisobutene, polypentene as well as copolymers and mixtures thereof. Furthermore, polymer particles formed of methacrylates or polystearine as well as electrically conducting polymers as described herein above, e.g. polyacetylenes, polyanilines, poly(ethylenedioxythiophenes), polydialkylfluorenes, polythiophenes or polypyrroles can also be applied as polymeric fillers, e.g. for providing electrically conductive materials.

In the above-mentioned procedures, soluble fillers and polymeric fillers can be combined, which are volatile under thermal conditions used e.g. in the solidification step according to the invention, or can be converted into volatile compounds during a thermal treatment. In this way the pores formed by the polymeric fillers can be combined with the pores formed by the reticulating agents or other fillers to achieve an isotropic or anisotropic pore distribution, for example a hierarchical pore size distribution.

Suitable particle sizes of the non-polymeric fillers can be determined by a person skilled in the art depending on the desired porosity and/or size of the pores of the resulting composite material.

Suitable solvents, which can be used for the removal of the fillers or for cleaning steps, after solidification of the material, include, for example, (hot) water,

diluted or concentrated inorganic or organic acids, bases, or any of the solvents mentioned above herein. Suitable inorganic acids include, for example, hydrochloric acid, sulphuric acid, phosphoric acid, nitric acid as well as diluted hydrofluoric acid. Suitable bases include, for example, sodium hydroxide, ammonia, carbonate as well as organic amines. Suitable organic acids include, for example, formic acid, acetic acid, trichloromethane acid, trifluoromethane acid, citric acid, tartaric acid, oxalic acid and mixtures thereof.

Fillers can be partly or completely removed from the reticulated composite material depending on the nature and time of treatment with the solvent. The complete removal of the filler after solidification can be preferred.

Solidification

The solidification step typically depends on specific properties and composition of the liquid mixture use. Solidification may be achieved e.g. by thermal treatment, e.g. heating or cooling; variation of pressure, e.g. evacuation, flushing or ventilation, drying with gases, including inert gases, drying, freeze-drying, spray-drying, filtration, or chemical or physical curing or hardening, e.g. with the use of cross linkers, optionally combined with a thermal cross linking or radiation induced cross linking, or any combinations thereof.

Preferably, the solidification substantially occurs without decomposition of the matrix material or the combination of the at least one reticulating agent and matrix material, i.e. there is substantially no thermolysis or pyrolysis of the matrix material. The reticulating agents may be embedded in the matrix material.

A person skilled in the art can apply suitable conditions like temperature, atmosphere or pressure, depending on the desired property of the final composite material according to the invention and the components used, to ensure a substantially complete solidification.

In preferred exemplary embodiments of the invention, the solidification step may include a phase separation of the liquid mixture into a solids phase and a liquid phase, e.g. by precipitating the solids from the liquid mixture. Without wishing to be bound to any specific theory, it is believed that such a phase separation or

precipitations facilitates or even promotes the development of a reticulated structure in the resulting composite material. Such a development of the structure may preferably occur substantially before the solvents are removed, e.g. the phase separation or precipitation may be induced before removal of the at least one solvent.

In preferred solidification steps of exemplary embodiments of the invention, the phase separation or precipitation is induced by at least one measure including removal of the solvent(s), cross linking the matrix material, or increasing the viscosity of the liquid mixture.

The increase in viscosity of the liquid mixture may be induced by at least one measure including cross linking, curing, drying, rapidly increasing the temperature, rapidly lowering the temperature, or rapidly the removing solvent. "Rapidly" in this context means within less than 5 hours, preferably less than one hour, or within less than 30 minutes, 20 minutes, 15 minutes, 10 minutes, 5 minutes or even within less than 2 minutes or less than 1 minute after starting to apply this particular measure asmentioned above. The time period required will typically depend on the mass of the liquid mixture.

A thermal treatment may includes heating or cooling in a temperature range of from –78 °C to 500 °C, and may include heating or freezing, freeze-drying and the like.

The solvent can be removed from the liquid mixture before a thermal treatment. This may be achieved by filtration, or conveniently by a thermal treatment of the liquid mixture, e.g. by cooling or heating in the temperature range from about –200 °C to 300°C, e.g. in the range from about –100 °C to 200 °C, or in the range from about –50°C to 150°C, such as about 0°C to 100°C, or from about 50°C to 80°C. An evaporation of the solvents at room temperature or in a stream of hot air or other gases can also be used. Drying may be performed by spray drying, freeze drying or similar conventional methods.

The solidification treatment may also involve a thermal treatment at elevated temperatures, with or without prior removal of the solvent, typically from about 20 °C to about 4000 °C, or from about 100 °C to about 3500 °C, or from about 100

°C to about 2000 °C, e.g. from about 150°C to about 500 °C, optionally under reduced pressure or vacuum, or in the presence of inert or reactive gases.

Solidification without decomposing any of the components may be done at temperatures up to about 500 °C, however, in some exemplary embodiments of this invention it may also be preferred to partially or totally carbonize, pyrolize or decompose at least one of the constituents of the composite material during or after the solidification. This can be normally done at higher temperatures ranging from about 150 °C to about 4000 °C. Also, these high temperatures can be used in exemplary embodiments of the invention where an additional sintering step may be desired.

However, typically sintering steps at high temperatures, i.e. temperatures above 500 °C are not required and treatment steps involving decomposition of matter, e.g. pyrolysis or carbonization steps, are preferably avoided. The solidification step of exemplary embodiments of the invention may involve temperatures ranging from about 20 to 500 °C, e.g. from about 30 to 350 °C, such as from about 40 to 300 °C, or below 200 °C, e.g. from about 100°C to 190°C.

The solidification step can be further performed in different atmospheres e.g. inert atmosphere, such as nitrogen, SF_6, or noble gases such as argon, or any mixtures thereof, or in an oxidizing atmosphere comprising e.g. oxygen, carbon monoxide, carbon dioxide, or nitrogen oxide. Furthermore, the inert atmosphere can be blended with reactive gases, e.g. hydrogen, ammonia, C_1-C_6 saturated aliphatic hydrocarbons such as methane, ethane, propane and butane, or mixtures thereof.

In some exemplary embodiments of the invention, the atmosphere in the solidification step, particularly when thermally treating the liquid mixture, can be an oxidizing atmosphere such as air, oxygen or oxygen enriched inert gases. Alternatively, the atmosphere during the solidification treatment can be substantially free of oxygen, i.e. the oxygen content is below 10 ppm, or even below 1 ppm.

The solidification can also be performed by laser applications, e.g. by selective laser sintering (SLS), or radiation induced, e.g. when using UV- or gamma-radiation curing cross linkers.

It can be preferred to precipitate the solid components from a solvent based liquid mixture e.g. by thermal treatment, cross linking or by evaporating the solvent. For forming e.g. a substantially homogeneous porous structure in the resulting composite material and/or to promote a network-like or reticulated orientation of the particles in the liquid mixture a low viscosity can be preferred, as well as e.g. a rapid viscosity increase of the solid phase during the solidification step. This can be achieved by separating the solid phase from the solvent phase. In doing so, the temperature to be applied is typically dependent on the freezing point or the boiling point, respectively, of the solvent and the matrix material.

The solvent, in case of a solidification by increasing the temperature may have a boiling point from at least about 5 to about 200°C, such as about 30 to 200°C, or from about 40° to 100°C below the melting point of the matrix material, so that there is essentially no reduction of the viscosity of the matrix material, no melting or incomplete thermal decomposition of the matrix material or the reticulating agents during thermal treatment of the liquid mixture and/or during removal of the solvent.

In a preferred exemplary embodiment of the invention, the liquid mixture is solidified by a rapid, instantaneous lowering of the temperature. This can be done with liquid mixtures comprising a solvent or not. In a solvent based mixture, the solvent may have a boiling point from at least 10 to 100°C, preferably 20 to 100°C and particularly preferred 30 to 60°C above the melting point of the matrix material.

By manufacturing a dispersion, suspension, emulsion or solution at temperature conditions in the region of the melting point of the matrix material, preferably a polymer, the network of the reticulating agents may be formed by rapidly lowering the temperature, resulting in a rapid increase of the viscosity of the liquid mixture. To incorporate the reticulating agents in the matrix material, the solvent phase can be removed from the liquid mixture by a vacuum treatment.

Cross linkers can be added to the dispersions, suspensions or emulsions forming the liquid mixture. Cross linkers may include, for example, isocyanates, silanes, diols, di-carboxylic acids, (meth)acrylates, for example such as 2-hydroxyethyl methacrylate, propyltrimethoxysilane, 3-(trimethylsilyl)propyl

methacrylate, isophoron diisocyanate, polyols, glycerine and the like. Biocompatible cross linkers such as glycerine, diethylentriaminoisocyanate and 1,6-diisocyanatohexane, may be preferred e.g. when the liquid mixture is converted into the solid composite material at relatively low temperatures, e.g. below 100 °C.

The content and type of the cross linker can be suitably selected such that the cross linking during solidifying of the liquid mixture does not lead to a viscosity change of the system essentially, before the solid composite phase has formed by phase separation or evaporation of the solvent. Cross linking and may be interrupted components of the matrix material which are not already cross linked or only incompletely cross linked may be dissolved and removed by treating the system with suitable solvents, in order to modify the morphology and the overall structure of the composite material.

Further processing

The liquid mixture or the final composite material may be further processed in several ways, depending on the particular intended use.

For example, reductive or oxidative treatment steps may be applied in which the solidified material or coating is treated one or more times with suitable reducing agents and/or oxidizing agents, such as hydrogen, carbon dioxide, water vapor, oxygen, air, nitrous oxide or oxidizing acids such as nitric acid and the like and optionally mixtures of these, to modify pore sizes and surface properties. Activation with air can be one option, e.g. at an elevated temperature, such as from about 40°C to 1000°C, or from about 70°C to 900°C, or from about 100°C to 850°C, sometimes from about 200°C to 800°C, or at approximately 700°C. The composite material can be modified by reduction or oxidation or a combination of these treatment steps at room temperature. Boiling in oxidizing acids or bases may also be used to modify surface and bulk properties, where desired.

The pore size and pore structure can be varied according to the type of oxidizing agent or reducing agent used, the temperature and the duration of the activation. The porosity can be adjusted by washing out fillers that are present in the

composite material, as described above. These Fillers can include polyvinylpyrrolidone, polyethylene glycol, powdered aluminum, fatty acids, microwaxes or emulsions thereof, paraffins, carbonates, dissolved gases or water-soluble salts, which may be removed with water, solvents, acids or bases or by distillation or oxidative and/or non-oxidative thermal decomposition. Suitable methods of this are described in German Patent DE 103 22 187 and/or international Patent application PCT/EP2004/005277, for example, and may be applied here.

The properties of the material may optionally also be altered by structuring the surface with powdered substances such as metal powder, carbon black, phenolic resin powder, fibers, in particular carbon fibers or natural fibers.

The composite material may optionally also be subjected to a so-called CVD process (chemical vapor deposition) or CVI process (chemical vapor infiltration) in another optional process step in order to further modify the surface structure or pore structure and its properties. To do so, the material or coating can be treated with suitable precursor gases that release carbon at high temperatures, as conventionally used. Subsequent application of diamond-like carbon can be preferred here. Other elements may also be deposited by conventional methods in this way, such as silicon. Almost all known saturated and unsaturated hydrocarbons with sufficient volatility under CVD conditions may be used as the precursors to split off carbon. Suitable ceramic precursors include, for example, BCl_3, NH_3, silanes such as SiH_4, tetraethoxysilane (TEOS), dichlorodimethylsilane (DDS), methyltrichlorosilane (MTS), trichlorosilyldichloroborane (TDADB), hexadichloromethylsilyloxide (HDMSO), $AlCl_3$, $TiCl_3$ or mixtures thereof. By means of CVD methods, the size of pores in the material can be reduced in a controlled manner or the pores may even be completely closed and/or sealed. This makes it possible to adjust the sorptive properties as well as the mechanical properties of the composite material in a tailored manner. By CVD of silanes or siloxanes, optionally in mixture with hydrocarbons, the materials or coatings can be modified by formation of carbide or oxycarbide, so that they are resistant to oxidation, for example.

The materials or devices produced according to this invention can be additionally coated and/or modified by sputtering methods or ion implantation/ion bombardement methods. Carbon, silicon and metals and/or metal compounds can be applied by conventional methods from suitable sputter targets. For example, by incorporating silicon compounds, titanium compounds, zirconium compounds, or tantalum compounds or metals by CVD or PVD into the material, it is possible to form carbide phases which increase the stability and oxidation resistance.

Furthermore the composite material can be worked mechanically to produce porous surfaces. For example, controlled abrasion of the surface layer(s) by suitable methods can lead to modified porous surface layers. One option is cleaning and/or abrasion in an ultrasonic bath, where defects in the material and further porosity can be produced in a targeted manner by admixture of abrasive solids of various particle sizes and degrees of hardness and by appropriate input of energy and a suitable frequency of the ultrasonic bath as a function of treatment time. Aqueous ultrasonic baths to which alumina, silicates, aluminates and the like have been added, preferably alumina dispersions, may be used. However, any other solvent that is suitable for ultrasonic baths may also be used instead of or in combination with water.

Furthermore, by ion implantation of metal ions, in particular transition metal ions and/or non-metal ions, the surface properties of the material can be further modified. For example, by nitrogen implantation it is possible to incorporate nitrides, oxynitrides or carbonitrides, in particular those of the transition metals. The porosity and strength of the surface of the materials can be further modified by implantation of carbon.

The composite reticulated materials can be further modified e.g. by applying biodegradable and/or resorbable or non-biodegradable and/or resorbable polymers, optionally porous, for example in layer form or as an overcoat.

Furthermore, by optional parylenation of the composite reticulated material before or after any activation steps, the surface properties and porosity of the material can be further modified. The materials can be first treated with para-

cyclophane at an elevated temperature, usually approximately about 600°C, with a polymer film of poly(p-xylylene) being formed on the surface of the material. This film can optionally then e.g. be converted to carbon by known methods in a subsequent carbonization step.

If necessary, the reticulated material may be subjected to additional chemical and/or physical surface modifications. Cleaning steps to remove any residues and impurities that might be present may be provided here. For this purpose, acids, in particular oxidizing acids, or solvents may be used, but boiling in acids or solvents is preferred. Carboxylation of some materials can be achieved by boiling in oxidizing acids. Washing with organic solvents, optionally with application of ultrasound, optionally at elevated temperatures may also be used for further processing the reticulated/devices materials.

The reticulated materials/devices may be sterilized by conventional methods, e.g., by autoclaving, ethylene oxide sterilization, pressure sterilization or gamma-radiation. According to this invention, all the above steps may be combined or used with any of them and those described below.

Coatings or bulk materials of the porous reticulated material in or on the devices may be structured in a suitable way before or after solidification into the inventive composite material by folding, embossing, punching, pressing, extruding, gathering, injection molding and the like before or after being applied to the substrate or being molded or formed. In this way, certain structures of a regular or irregular type can be incorporated into the composite coating produced with the material according to this invention.

The reticulated material can be further processed by conventional techniques to provide a desired shape, or least a part thereof, e.g. by building molded paddings and the like or by forming coatings on any medical devices.

The composite materials can be produced in any desired forms. By applying multi-layered half-finished molded shapes, asymmetric constructions can be formed from the composite materials. The materials can be brought into the desired form by applying any appropriate conventional technique, including but not limited to casting

processes such as sand casting, shell molding, full mold processes, die casting, centrifugal casting, or by pressing, sintering, injection molding, compression molding, blow molding, extrusion, calendaring, fusion welding, pressure welding, jiggering, slip casting, dry pressing, drying, firing, filament winding, pultrusion, lamination, autoclave, curing or braiding.

Coatings of the composite reticulated material can be applied in liquid, pulpy or pasty form, for example, by painting, furnishing, phase-inversion, dispersing atomizing or melt coating, extruding, die casting, slip casting, dipping or as a hotmelt, for example directly from the liquid mixture before solidifying. Where the material is already in a solid state it may be applied on a suitable substrate by powder coating, flame spraying, sintering or the like, to form the medical device. Dipping, spraying, spin coating, ink-jet-printing, tampon and microdrop coating or 3-D-printing may be preferred for applying the liquid mixture into a substrate. The application of the liquid mixture may be done by means of a high frequency atomizing device, for example the one described in applicants International Patent Application PCT/EP2005/000041, or by print- or roller coating using a device as described in applicants International Patent Application WO 2005/042045. These devices and methods may also be used to further coat the medical device with any further agents, e.g. therapeutically or diagnostically active agents or further coatings as described herein below. A coating with the reticulated material can be manufactured for example in that a coating of the liquid mixture is applied to a medical device, dried and if necessary thermally treated.

Furthermore, coated devices can be obtained by a transfer process, in which the reticulated material is applied to the device substrate in the form of a prepared lamination. The coated devices can be dried, cured and afterwards the coating can be e.g. thermally treated or further processed. A coated medical device can also be obtained by suitable printing procedures, e.g. gravure printing, scraping or blade printing, spraying techniques or thermal laminations or wet-in-wet laminations. It is possible to apply more than one thin layer, for example to ensure an error-free composite film. By applying the above-mentioned transfer procedure, it is also

possible to form multi-layer gradient films from different layers of different sequences of layers, which, after the solidification can provide for gradient materials, in which the density of the reticulated material varies form place to place.

The liquid mixture can also be dried or thermally treated and then comminuted by conventional techniques, for example by grinding in a ball mill, or roller mill and the like. The comminuted reticulated material can be used as a powder, flat blank, a rod, a sphere, hollow sphere in different grainings and can be processed by conventional techniques into granulates or extrudates in various forms. Hot-pressure-procedures, if necessary with the use of suitable binders, can be used to form the medical device or parts thereof from the reticulated material.

Additional possibilities of processing can be the formation of powders by other commonly used techniques, for example by spray-pyrolysis, or precipitation or the formation of fibers by spinning-techniques, such as by gel-spinning.

Functionalization and use

By suitably selecting the components and the processing conditions, the processes described herein allow e.g. for the production of bioerodible or biodegradable materials, devices or coatings, or coatings and reticulated materials which are dissolvable or may be peeled of from substrates in the presence of e.g. physiologic fluids. For example, coatings may be produced, which may be used in the medical field for coronary implants such as stents, wherein the coating may comprise a therapeutically and/or diagnostically active agent.

The therapeutically and/or diagnostically active agent may be included in the composite materials as at least a part of the reticulating agent, the matrix material, as an additive or may be applied onto or into the composite reticulated material after solidification.

A diagnostically active agent may be a marker, contrast medium or radiopaque material, typically selected from materials having signaling properties, e.g. a material that produces a signal detectable by physical, chemical or biological detection methods. The terms “diagnostically active agent”, “agent for diagnostic purpose” and “marker” are synonymously used in the present invention. Suitable

examples for these materials are mentioned, in part, above as reticulating agents, and further suitable diagnostic agents having signaling properties are described in detail in applicants co-pending US Patent application Serial No. 11/322,694, and in International Patent Application PCT/EP2005/013732, and may be used in embodiments of the present invention as markers. Certain matrix materials may also have signaling properties and may therefore also serve as a marker or contrast medium. The composite reticulated material may be suitably modified to allow for a controlled release of the diagnostic agent.

Markers or agents having signaling properties can produce signals detectable by physical, chemical or biological detection methods such as x-ray, nuclear magnetic resonance (NMR), computer tomography methods, scintigraphy, single-photon-emission computed tomography (SPECT), ultrasonic, radiofrequency (RF), and the like. For example, metal based reticulating agents used as markers can be encapsulated in a polymer shell and thus cannot interfere with the composite material itself or a substrate upon which it is coated, e.g. an implant material, often also a metal, which may lead to electro corrosion or related problems. Coated implants may be produced with encapsulated markers, wherein the coating remains permanently on the implant.

If therapeutically active reticulating agents are used, these may be encapsulated in bioerodible or resorbable materials, optionally allowing for a controlled release of the active ingredient under physiological conditions. Also, coatings or composite materials can be obtained which, due to their tailor-made porosity, may be infiltrated or loaded with therapeutically active agents, which can be resolved or extracted in the presence of physiologic fluids. This allows e.g. for the production of medical devices or implants providing for a controlled release of active agents. Examples include drug eluting stents, drug delivery implants, drug eluting orthopedic implants and the like.

Also, the processes described herein may be used for producing optionally coated, porous bone and tissue grafts (erodible and non-erodible), optionally coated porous implants and joint implants as well as porous traumatologic devices like nails,

screws or plates, e.g. with enhanced engraftment properties and therapeutic functionality, with excitable radiating properties, e.g. for the local radiation therapy of tissues and organs.

Another reticulated material and/or a coating comprised thereof may be based on conductive fibers like carbon nanotubes that have high reflection and absorption properties of electromagnetic irradiation and therefore comprise shielding properties for e.g. electronic medical devices, such as metal implants or pacemakers and parts thereof.

Furthermore, carbon tube and nanofiber based porous reticulated materials with high specific surface areas and their specific thermal and anisotropic electric conductivity can be produced for use e.g. as actuators for micro- and macro-applications, also as thin film materials for the production of artificial muscles or actuating fibers and films.

Furthermore, in non-medical applications the processes described herein may be used e.g. for the production of sensors with porous texture for venting of fluids; porous membranes and filters for nano-filtration, ultrafiltration or microfiltration, as well as mass separation of gases. It is also possible to produce catalytic active porous materials with high specific surfaces containing covalently or non-covalently bound catalytic active agents like catalytic metals, enzymes or reactive agents for catalytic applications.

Porous composite material coatings with controlled reflection and refraction properties may also be produced for various purposes. Examples include the production of optical coatings with improved functional properties such as combination of electromagnetic shielding and/or electric conductivity and nano-porosity with high light transmittance and optical transparency, but anti-reflexive properties, e.g. for use as advanced touch screens, large area displays, flexible displays and solar voltaic collectors with high specific surface area.

Average pore sizes of the composite materials may be determined by SEM (Scanning Electron Microscopy), adsorptive methods like gas adsorption or mercury intrusion porosimetry, by chromatographic porosimetry. Porosity and specific

surface areas may be determined by N_2 or He absorption techniques, e.g. according to the BET method. Particle sizes, for example of the reticulating agents, may be determined for example on a CIS Particle Analyzer (Ankersmid) by the TOT-method (Time-Of-Transition), X-ray powder diffraction, laser diffraction, or TEM (Transmission-Electron-Microscopy). Average particle sizes in suspensions, emulsions or dispersions may be determined by dynamic light scattering methods. Solids contents of liquid mixtures may be determined by gravimetric methods or by humidity measurements.

The invention will now be further described by way of the following non-limiting examples.

Example 1

A homogeneous dispersion of soot, Lamp-Black (Degussa, Germany) having a primary particle size of 90 to 120 nm and a phenoxy resin (Beckopox® EP 401, Cytec) was prepared. First, a parent solution of methylethylketone (31 g), 3.1 g Beckopox® EP 401 and 0.4 g of glycerin (cross linker, Sigma Aldrich) was prepared. A soot paste was prepared from 1.65g Lamp Black and 1.65 g dispersing additive (Disperbyk® 2150, solution of a block copolymer in 2-methoxy-1-methylethylacetate, Byk-Chemie, Germany) under adding of portions of the methylethylketone/Beckopox® EP 401 parent solution. Subsequently, the paste was converted into a dispersion by adding the residual parent solution with the use of a Pentraulik® dissolver for 15 minutes to obtain a homogeneous dispersion. The dispersion had a total solids content of about 3.5%, which was determined by a humidity measurement device (Sartorius MA 50). The particle size distribution in the dispersion was D50 = 150 nm, which was determined by a laser diffractometer Horiba LB 550.

The dispersion was sprayed onto a steel substrate with an average surface area weight of $4g/m^2$. Immediately after spraying, the layer was dried with hot air for 2 minutes. Then, the sample was thermally treated in a nitrogen atmosphere in a

conventional tube furnace under a heating and cooling temperature ramp of 1.33 k/min up to maximum temperature Tmax of 280°C, which was held for 30 minutes. The sample resulting from this process was examined with scanning electron microscopy (SEM). In Figure 1, a 50,000x magnification of the resulting porous composite material layer having an average pore size of 100 to 200 nm is shown.

Example 2

A homogeneous dispersion made of soot, of Lamp-Black (Degussa, Germany) having a primary particle size of 90 to 120 nm and phenoxy resin (Beckopox® EP 401, Cytec) was prepared as in Example 1 above. Instead of using 1.65 g Lamp-Black, only 0.9 g Lamp-Black was used and 0.75 g of a fullerene mixture (Nanom Mix, FCC) were used. The amounts of all other components are identical to those used in Example 1 above. The resulting dispersion had a total solids content of about 3.4%, determined as mentioned in Example 1. The particle size distribution in the dispersion was D50 = 1 µm.

The resulting dispersion was sprayed onto a steel substrate with an average surface area weight of 3.8 g/m^2 and dried with hot air for 2 minutes. The samples were subjected to a thermal treatment as described above in Example 1. The resulting porous composite-coated steel substrate was examined with the use of scanning electron microscopy. Figure 2 below shows a SEM at 20,000x magnification of the resulting porous composite layer having a medium pore size of about 1 µm.

Example 3

The sample resulting from Example 2 was subjected to a 30-minute treatment in an ultrasonic bath in acetone at 35°C. Then, the samples were dried in a ordinary convection oven at 200°C for 2 hours. The SEM picture in Figure 3 shows a 20,000 x magnification of the spongy composite layer.

Example 4

A homogeneous dispersion was prepared as described in Examples 1 to 3 above. Instead of soot and/or fullerenes, carbon nanofibers with a medium length of about 2 µm and an average diameter of about 200 nm (Polytech) were used in

amount of 1.65 g. The resulting dispersion had a total solids content of about 3.6%. The dispersion was sprayed onto a steel substrate with a surface area weight of 4.2 g/m^2 and dried with hot air for 2 minutes.

Subsequently, the sample was thermally treated as described in Examples 1 to 3 above. Then, the samples were treated in an ultrasonic bath in acetone at 35°C for 30 minutes. After drying in an convention oven for 2 hours at 200°C, the samples were examined with scanning electron microscopy. Figure 4 below shows a SEM picture at 5,000x magnification of the resulting mesh or textile-like composite layer. The average pore size was about 2 μm.

Example 5

A homogeneous dispersion was prepared from the components using the same amounts as described in Example 1. However, instead of soot, 1.6 g silica (Aerosil R972, Degussa, Germany) was used. The dispersion had a total solids content of about 3.2%, and the average particle size distribution was D50 = 150 nm. The dispersion was sprayed onto a steel substrate with an average surface area weight of 3.3 g/m^2 and dried with hot air for 2 minutes. The thermal treatment was identical to that described in Example 1.

The scanning electron microscopy picture in Figure 5 at 20,000x magnification shows the resulting porous composite layer having an average pore size of 150 nm.

Example 6

A homogeneous dispersion of Tantalum nanoparticles (Sigma Aldrich) having a particle size distribution of D50 = 100 nm and Beckopox® EP 401 (Cytec) was prepared. A parent solution of Beckopox® EP 401 (0.59 g), 0.13 g of a liquid aliphatic polyisocyanate based on a low viscosity HDI trimer (Desmodur® N3600, Degussa) as the cross linker and solvent ethoxypropylacetate (EPA) 0.38 g was prepared, and a paste was prepared in a mortar from 0.98 g tantalum powder with the subsequent addition of portions of the parent solution. The dispersion had a total solids content of about 80%, determined as described above. The particle size distribution in the dispersion was at D50 = 200 nm.

The dispersion was dropped onto a magnesium substrate and dried with hot air for 2 minutes. Subsequently, a thermal treatment was carried out in conventional convection oven under a nitrogen atmosphere up to a maximum temperature Tmax of 280°C which was held for 30 minutes. The samples were examined with scanning electron microscopy. Figure 6 shows a SEM picture at 200x magnification of the porous composite of Example 6, having a medium pore size of 200 nm.

Example 7

1.87 g of a phenoxy resin (Beckopox EP 401 (Cytex) were placed in a mortar, and subsequently 0.635 g of tantalum particles having a medium particle size of about 3 μm (H.C. Stark) were added in portions and the mixture was ground to form a substantially homogeneous paste.

Separately, 0.626 g of titanium dioxide particles having a medium particle size of about 21 nm (Aeroxide P25, Degussa, Germany) were combined with 1.268 g of a dispersion aid (Dysperbyk P-104, Byk Chemie, Germany), ground to form a paste and then diluted to form a dispersion by adding 4.567 g of methylethylketone. The dispersion was combined with the homogeneous paste of tantalum particles in the phenoxy resin, and 0.649 g of ethoxypropylacetate, 0.782 g of glycerin (cross linker) as well as 0.057 g of polyethylene particles (Microscrub, average particle size about 150 μm, Impag Company) and 0.126 g of polyethylene oxide (MW 300,000, Sigma Aldrich) were added. The resulting mixture was homogenized in a swing mill (Retsch) at 25 kHz for 2 minutes in the presence of 3 steel balls having a diameter of 1 cm. The resulting dispersion was dropped with a pipette onto a circular blank made of titanium and dried for 30 minutes in a conventional air convection oven at about 50°C. Subsequently, the sample was thermally treated at about 300°C in a nitrogen atmosphere to completely cure the resin. The resulting material revealed microscopic pores having a size of about 100 to 200 μm, as shown in Figures 7a and b. Scanning electro-microscopy revealed smaller pores of a reticulated, sponge-like structure in combination with the microscopic pores, resulting in a hierarchical porosity, as shown in Figures 7a (100x magnification) and 7b (20,000x).

Example 8

As described above in Example 7, a tantalum-containing paste was produced, however with the use of Dysperbyk® 180 (Byk Chemie, Germany) as the dispersion aid, and combined with the titanium dioxide-containing dispersion, as described in Example 7. Subsequently, 0.649 g of ethoxypropylacetate, 0.782 g glycerine (cross linker) and 0.057 g of polyethylene particles (Microscrub, medium particle size of about 150 µm, available from Impag Company) and 0.126 g of polyethyleneoxide (MW 300,000, Sigma Aldrich) were added as fillers or porogenes, respectively. The resulting mixture was homogenized in a swing mill (Retsch) at 25 kHz for 2 minutes with 3 steel balls having a diameter of 1 cm. The resulting dispersion was dropped with a pipette onto a circular blank made of titanium and dried for 30 minutes at 50°C in a conventional air convection oven. The samples revealed a microscopically porous surface having a medium pore size of about 100 µm, as shown in Figure 8a. Figure 8b shows a 100-fold magnification thereof, clearly showing the simultaneous presence of macroscopic pores in a finely-structured reticulated material of microporous structure.

* * *

Having thus described in detail several exemplary embodiments of the present invention, it is to be understood that the invention described above is not to be limited to particular details set forth in the above description, as many apparent variations thereof are possible without departing from the spirit or scope of the present invention. The embodiments of the present invention are disclosed herein or are obvious from and encompassed by the detailed description and figures. The detailed description, given by way of example, is not intended to limit the invention solely to the specific embodiments described.

The foregoing applications and all documents cited therein or during their prosecution ("appln. cited documents") and all documents cited or referenced in the appln. cited documents, and all documents, references and publications cited or referenced herein ("herein cited documents"), and all documents cited or referenced

in the herein cited documents, together with any manufacturer's instructions, descriptions, product specifications, and product sheets for any products mentioned herein or in any document incorporated by reference herein, are hereby incorporated herein by reference, and may be employed in the practice of the invention. Citation or identification of any document in this application is not an admission that such document is available as prior art to the present invention. It is noted that in this disclosure and particularly in the claims, terms such as "comprises," "comprised," "comprising" and the like can have the broadest possible meaning; e.g., they can mean "includes," "included," "including" and the like; and that terms such as "consisting essentially of" and "consists essentially of" can have the broadest possible meaning, e.g., they allow for elements not explicitly recited, but exclude elements that are found in the prior art or that affect a basic or novel characteristic of the invention.

What is claimed is:

1. A process for manufacturing a porous composite material, the process comprising the following steps:

a) Providing a liquid mixture, comprising

i) at least one reticulating agent; and

ii) at least one matrix material comprising at least one organic polymer;

b) Solidifying the mixture.

2. The process of claim 1, wherein the liquid mixture is substantially free of any solvent.

3. The process of claim 1, wherein the liquid mixture includes at least one solvent.

4. The process of claim 3, wherein the liquid mixture includes at least one of a dispersion, suspension, emulsion or solution.

5. The process of any one of claims 1 to 5, wherein the reticulating agent is in the form of particles.

6. The process of claim 5, wherein the particles include nano- or microcrystalline particles.

7. The process of claim 6, wherein the particles have a mean particle size from 1 nm to 1,000 μm.

8. The process of claim 6, wherein the particles have a mean particle size from 1 nm to 300 μm.

9. The process of claim 7, wherein the particles have a mean particle size from 1 nm to 6 μm.

10. The process of any one of claims 1 to 9, wherein the reticulating agent comprises at least two particle size fractions of the same or different material, the fractions differing in size by a factor of at least 1.1.

11. The process of claim 10, wherein the fractions differ in size by a factor of at least 2.

12. The process of any one of claims 1 to 11, wherein the reticulating agent has a form selected from tubes, fibers or wires.

13. The process of claim 12, wherein the reticulating agent has an average length from 5 nm to 1,000 μm.

14. The process of claim 12, wherein the reticulating agent has an average length from 5 nm to 300 μm.

15. The process of claim 12, wherein the reticulating agent has an average length from 5 nm to 10 μm.

16. The process of claim 12, wherein the reticulating agent has and an average diameter from 1 nm to 1 μm.

17. The process of any one of claims 1 to 16, wherein the reticulating agent is selected from inorganic materials.

18. The process of claim 17, wherein the reticulating agent includes at least one of a metal, metal powder, metal compound, metal alloy, metal oxide, silicon oxide, zeolite, titanium oxide, zirconium oxide, aluminum oxide, or aluminum silicate, metal carbide, metal nitride, metal oxynitride, metal carbonitride, metal oxycarbide, metal oxynitride, metal oxycarbonitride, organic metal salt, inorganic metal salt, a semi conductive metal compound, such as MgS, MgSe, MgTe, CaS, CaSe, CaTe, SrS, SrSe, SrTe, BaS, BaSe, BaTe, ZnS, ZnSe, ZnTe, CdS, CdSe, CdTe, HgS, HgSe, HgTe, GaAs, GaN, GaP, GaSb, InGaAs, InP, InN, InSb, InAs, AlAs, AlP, AlSb, AlS, germanium, lead or silicon; metal based core-shell nanoparticle, glass, glass fibers, carbon, carbon fiber, graphite, soot, flame soot, furnace soot, gaseous soot, carbon black, lamp black, fullerenes, such as C36, C60, C70, C76, C80, C86, C112, nanotube, such as MWNT, SWNT, DWNT, random-oriented nanotubes, fullerene onions, metallo-fullerenes, metal containing endohedral fullerenes, or endometallofullerenes, talcum, mineral, organometallic compound, or metal alkoxide.

19. The process of claim 17, wherein the reticulating agent includes at least one of a magnetic, super paramagnetic, or ferromagnetic metal or alloy particle, including at least one of iron, cobalt, nickel, manganese, iron-platinum mixtures, iron-platinum alloys, metal oxides, such as iron oxide, gamma-iron oxide, magnetites or ferrites of iron, cobalt, nickel or manganese.

20. The process of any one of claims 1 to 16, wherein the reticulating agent is selected from particulate organic materials, or fibers made of organic materials.

21. The process of claim 20, wherein the organic materials include at least one of polymers, oligomers or pre-polymers; shellac, cotton, or fabrics.

22. The process of claim 21, wherein the polymers include at least one of a synthetic homopolymer or copolymer of an aliphatic or aromatic polyolefin, such as polyethylene or polypropylene; or a biopolymer.

23. The process of any one of claims 1 to 22, wherein the reticulating agent comprises at least one inorganic material in combination with at least one organic material.

24. The process of any one of claims 1 to 23, wherein the reticulating agent includes a combination of at least one particulate material with at least one material having a form selected from tubes, fibers or wires.

25. The process of any one of claims 1 to 24, wherein the matrix material includes at least one of oligomers, polymers, copolymers or prepolymers, thermosets, thermoplastics, synthetic rubbers, extrudable polymers, injection molding polymers, or moldable polymers.

26. The process of any one of claims 1 to 25, wherein the matrix material includes at least one of poly(meth)acrylate, unsaturated polyester, saturated polyester, polyolefines, polyethylene, polypropylene, polybutylene, alkyd resins, epoxy-polymers, epoxy resins, phenoxy resins, rubber latices, polyamide, polyimide, polyetherimide, polyamideimide, polyesterimide, polyesteramideimide, polyurethane, polycarbonate, polystyrene, polyphenol, polyvinylester, polysilicone, polyacetale, cellulose, cellulose derivatives,

cellulosic acetate, starch, polyvinylchloride, polyvinyl acetate, polyvinyl alcohol, polysulfone, polyphenylsulfone, polyethersulfone, polyketone, polyetherketone, polybenzimidazole, polybenzoxazole, polybenzthiazole, polyfluorocarbons, polytetrafluorethylene, polyphenylene ether, polyarylate, or cyanatoester-polymers.

27. The process of claim 25 or 26, wherein the matrix material is in liquid form.

28. The process of claim 3 or 4, wherein the solvent is capable of dissolving or swelling at least a part of the matrix material.

29. The process of claim 3 or 4, wherein the matrix material is soluble in the solvent.

30. The process of any one of claims 3 to 29, wherein the solvent includes at least one of polar, homopolar, protic or aprotic solvents such as alcohols, ethers, ketones, glycols, aliphatic hydrocarbons, aromatic hydrocarbons, or water.

31. The process of any one of claims 1 to 29, wherein the liquid mixture includes at least one further additive selected from cross linkers, fillers, surfactants, acids, bases, pore-forming agents, plasticizers, lubricants, flame resistants, biologically active compounds, therapeutically active compounds, agents for diagnostic purpose, or markers.

32. The process of any one of claims 3 to 31, wherein the viscosity of the liquid mixture is at least 10 to 99% below the viscosity of the matrix material.

33. The process of any one of claims 3 to 31, wherein the viscosity of the liquid mixture is 20 to 90% below the viscosity of the matrix material.

34. The process of any one of claims 3 to 31, wherein the viscosity of the liquid mixture is 50 to 90% below the viscosity of the matrix material.

35. The process of any one of claims 1 to 34, wherein the total solids content of the liquid mixture is below 20 % by weight, referring to the total weight of the liquid mixture.

36. The process of any one of claims 1 to 34, wherein the total solids content of the liquid mixture is below 15 % by weight, referring to the total weight of the liquid mixture.

37. The process of any one of claims 1 to 34, wherein the total solids content of the liquid mixture is below 10 % by weight, referring to the total weight of the liquid mixture.

38. The process of any one of claims 1 to 34, wherein the total solids content of the liquid mixture is below 5 % by weight, referring to the total weight of the liquid mixture.

39. The process of any one of claims 1 to 38, wherein the at least one reticulating agent is a material capable of forming a network-like structure.

40. The process of any one of claims 1 to 39, wherein the at least one reticulating agent is a material capable of self-orienting into a three dimensional structure.

41. The process of any one of claims 1 to 40, wherein the ratio of the reticulating agent(s) to the matrix component(s) in the liquid mixture is selected such that a three-dimensional network in the solid phase is formed upon removal of the solvent or during a change in viscosity of the solvent-free mixture during solidification.

42. The process of any one of claims 3 to 41, wherein the ratio of the reticulating agent(s) to the matrix material(s) is selected such that a phase separation between the solvent phase and the solids phase occurs during solidification.

43. The process of any one of claims 1 to 42, wherein the volume ratio between the total volume of the reticulating agent(s) and the matrix material(s) ranges from 20:80 to 80:20.

44. The process of any one of claims 1 to 43, wherein the solidification includes at least one of thermal treatment, drying, freeze-drying, application of vacuum, or cross linking.

45. The process of claim 44, wherein the cross linking is induced chemically, thermally or by radiation.

46. The process of any one of claims 1 to 45, wherein the solidification includes a phase separation in the liquid mixture into a solids and a liquid phase.

47. The process of any one of claims 1 to 46, wherein the solidification includes precipitating the solids from the liquid mixture.

48. The process of claims 46 or 47, wherein the phase separation or precipitation is induced before removal of the at least one solvent.

49. The process of claims 46 or 47, wherein the phase separation or precipitation is induced by removal of the at least one solvent.

50. The process of claims 46 or 47, wherein the phase separation or precipitation is induced by cross linking the matrix material.

51. The process of any one of claims 46 to 50, wherein the phase separation or precipitation is induced by an increase of the viscosity of the liquid mixture.

52. The process of claim 51, wherein the increase in viscosity is induced by at least one of cross linking, curing, drying, rapidly increasing temperature, rapidly lowering temperature, or rapidly removing solvent.

53. The process of claim 44, wherein the thermal treatment includes heating or cooling in a temperature range of from –78 °C to 500 °C.

54. The process of any one of claims 1 to 52, wherein the matrix material is substantially not decomposed during solidification.

55. The process of any one of claims 3 to 53, wherein the boiling point of the at least one solvent is at least 5 to 200°C below the melting point of the at least one matrix material.

56. The process of any one of claims 3 to 53, wherein the boiling point of the at least one solvent is at least 30 to 200°C below the melting point of the at least one matrix material.

57. The process of any one of claims 3 to 53, wherein the boiling point of the at least one solvent is at least 40 to 100°C below the melting point of the at least one matrix material.

58. The process of any one of claims 3 to 53, wherein the boiling point of the at least one solvent is at least 10 to 100°C above the melting point of the matrix material.

59. The process of any one of claims 3 to 53, wherein the boiling point of the at least one solvent is at least 20 to 100°C above the melting point of the matrix material.

60. The process of any one of claims 3 to 53, wherein the boiling point of the at least one solvent is at least 35 to 60°C above the melting point of the matrix material.

61. The process of any one of claims 1 to 60, wherein at least one of the reticulating agent, the matrix material or the solvent is selected such that upon rapidly decreasing the temperature of the liquid mixture the viscosity of the liquid mixture is increased, resulting in a phase separation, and then removing the solvent phase by vacuum treatment.

62. The process of any one of claims 1 to 61, wherein the liquid mixture includes at least one cross linker, which is suitably selected such that cross linking during processing of the liquid mixture before the solidification step does essentially not lead to a viscosity change in the system.

63. The process of claim 62, wherein the cross linking reaction essentially starts during solidification.

64. The process of claim 62, wherein the solidification includes an evaporation of the solvent.

65. The process of any one of claims 62 to 64, wherein the cross linking reaction is interrupted.

66. The process of claim 65, wherein not cross linked or incompletely cross linked material is subsequently removed from the reticulated material.

67. The process of any one of claims 62 to 66, wherein the cross linker includes at least one of isocyanates, silanes, diols, dicarboxylic acids, (meth)acrylates, 2-hydroxyethyl methacrylate, propyltrimethoxysilane, 3-(trimethylsilyl)propyl methacrylate, isophoron diisocyanate, or glycerine.

68. The process of any one of the previous claims, wherein

a) the reticulating agent includes at least one of soot, fullerenes, carbon fibers, silica, titanium dioxide, metal particles, tantalum particles, or polyethylene particles;

b) the matrix material includes at least one of epoxy resins or phenoxy resins;

c) the liquid mixture comprises an organic solvent; and

d) the solidification includes removal of the solvent by a heat treatment.

69. The process of claim 68, wherein the removal of solvent is performed rapidly.

70. The process of claim 68 or 69, wherein the solvent-free material is subsequently heat treated in an inert atmosphere at temperatures up to 300 °C, substantially without decomposing the matrix material.

71. The process of any one of claims 1 to 70, wherein the resulting porous composite material is impregnated, coated or infiltrated with at least one therapeutically active agent, which can be resolved or extracted from the material in the presence of physiologic fluids.

72. A porous reticulated composite material obtainable by the process of any of the previous claims.

73. A porous coating obtainable by a process of any one of claims 1 to 72.

74. The material or coating of any one of claims 72 or 73, having an average pore size of at least 1 nm.

75. The material or coating of any one of claims 72 or 73, having an average pore size of at least 5 nm.

76. The material or coating of any one of claims 72 or 73, having an average pore size of at least 10 nm.

77. The material or coating of any one of claims 72 or 73, having an average pore size of at least 100 nm.

78. The material or coating of any one of claims 72 or 73, having an average pore size from about 1 nm to about 400 μm.

79. The material or coating of any one of claims 72 or 73, having an average pore size from about 500 nm to 1000 μm.

80. The material or coating of any one of claims 72 or 73, having an average pore size from about 500 nm to about 800 μm.

81. The material or coating of any one of claims 72 to 80, having an average porosity from about 30 % to about 80 %.

82. The use of the material or coating of any one of claims 72 to 81, for the manufacture of a medical device for therapeutic and/or diagnostic purposes.

83. The use of claim 82, wherein the material or coating comprises a marker for diagnostic purpose.

84. The use of a material or coating of any one of claims 72 to 81, as a scaffold for tissue engineering in vivo or in vitro.

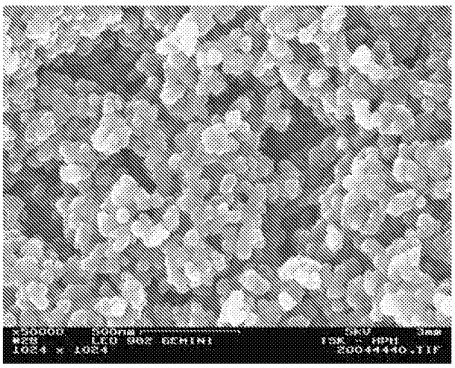
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Fig. 1

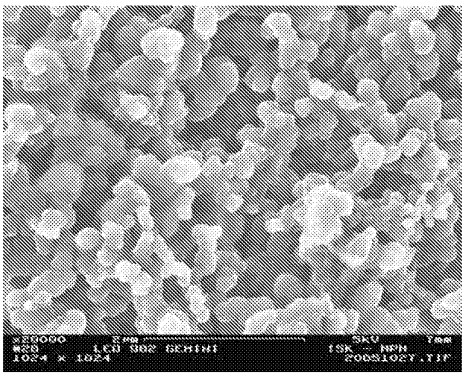
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Fig. 2

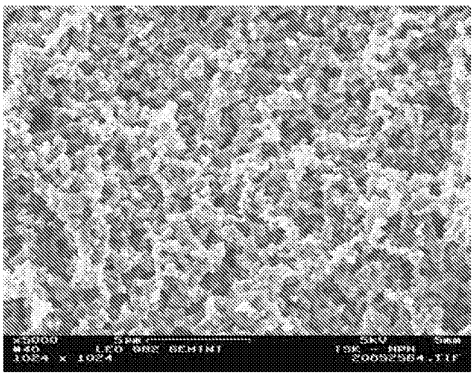

Fig. 3

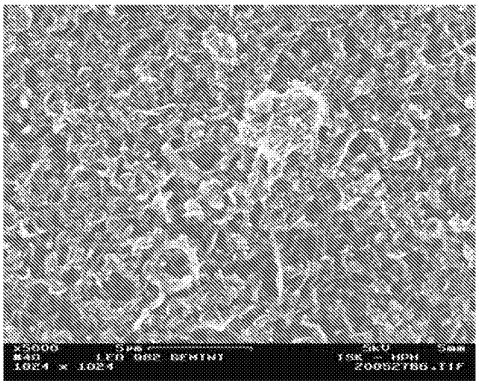

Fig. 4

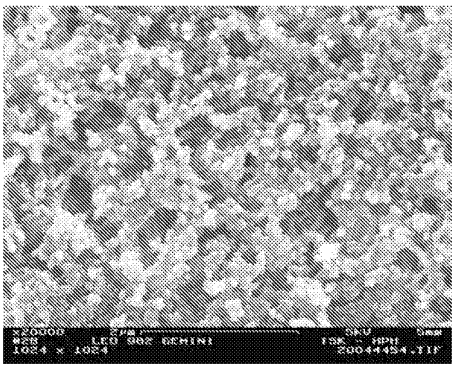
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Fig. 5

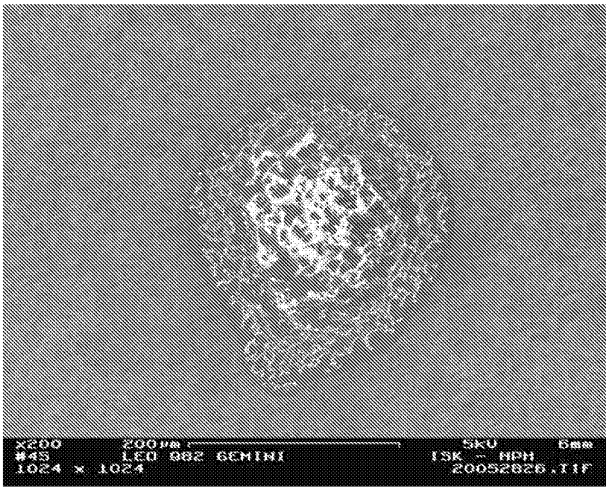
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Fig. 6

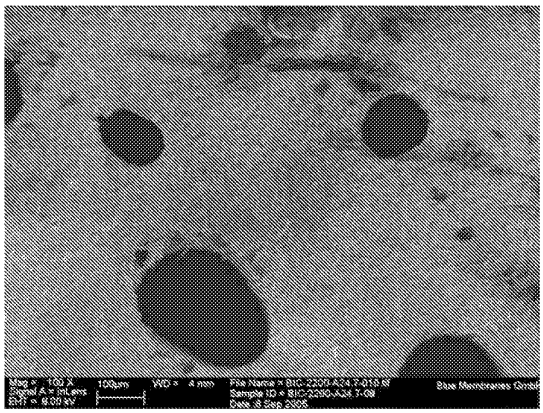
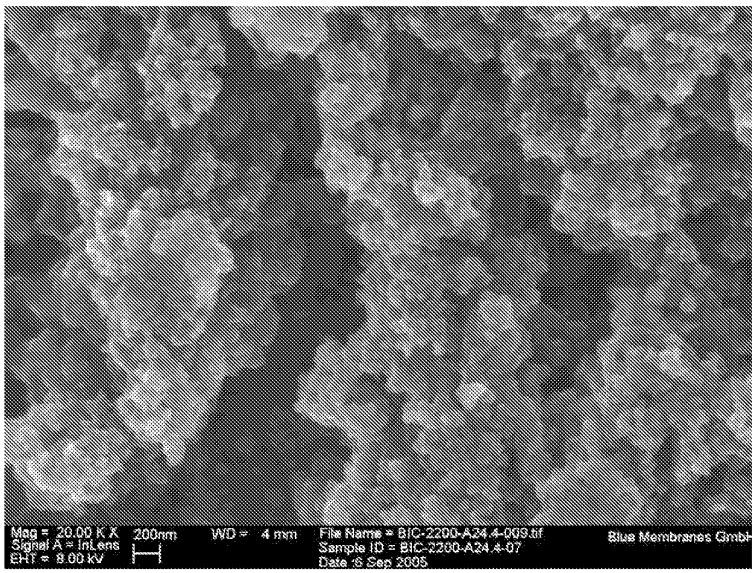


Fig. 7a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Date :6 Sep 2005
Blue Membranes GmbH

Fig. 7 b

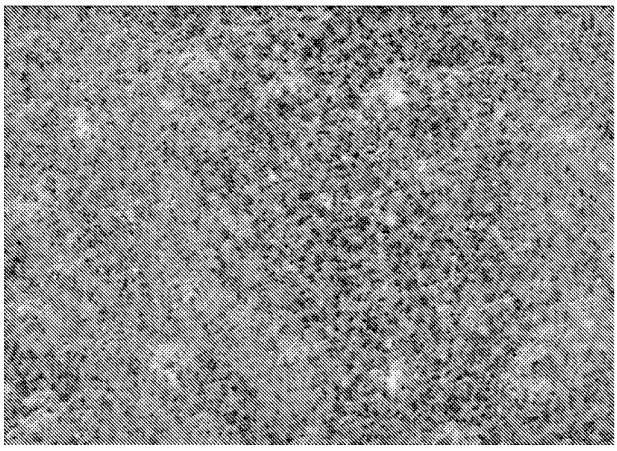

Fig. 8