

CONDUCTIVE POLYMERS AND POLYMER-DERIVED CERAMICS

RELATED APPLICATION

[0001] This application claims the benefit of Australian provisional patent application number 2023902235, filed 12 July 2023, the entire contents of which is incorporated herein by reference.

TECHNICAL FIELD

[0002] The present disclosure relates to resins for forming electrically conductive polymeric and/or polymer-derived ceramic (PDC) materials, the resins comprising: a photopolymerisable organosilicon monomer; and a conductivity additive. Also disclosed are electrically conductive polymeric and PDC materials, polymeric materials for forming electrically conductive PDC materials, and methods of formation of these materials.

BACKGROUND ART

[0003] The advent of 3D printing has assisted the production of polymeric articles, whereby a resin is printed to shape and polymerised to provide a polymeric article. This is owing to the ability of 3D printing to readily generate customised, complex, and three-dimensionally controlled geometries and article structures, that were difficult to achieve in the past using conventional casting and subtractive manufacturing techniques.

[0004] The advent of 3D printing has also assisted the production of ceramic articles. Using a preceramic resin, a 3D printed and polymerised preceramic polymer article may be converted into a polymer-derived ceramic (PDC) material. The common process for making PDC materials involves subjecting a preceramic polymer article to pyrolytic conditions at temperatures in excess of 1000 °C. This causes a thermally-induced conversion from organic to inorganic (i.e. ceramic) material and thermal decomposition of certain components of the preceramic polymer. Decomposition tends to release gases which may include carbon dioxide, carbon monoxide, methane, water and others. This tends to produce solid, non-porous PDC materials. 3D printing thus allows the more

efficient and tightly controlled manufacture of ceramic materials through the pre-shaping and polymerisation of a softer, more malleable preceramic resin before converting the shaped article into a hard ceramic material.

[0005] However, 3D printing is still in its infancy. Most 3D printing methods, especially for forming PDC materials, are limited to the use of direct ink writing (DIW) techniques and photopolymerisation-based techniques such as stereolithography, digital light projection, two-photon lithography, and volumetric printing stereolithography. These techniques which are restricted to specific resins which form only non-conductive polymeric and PDC materials, and they can be limited to the formation of relatively simple articles produced with low resolution.

[0006] 3D printing of conductive electrochemical devices is limited to Fused Deposition Modelling (FDM), DIW, and Selective Laser Sintering/Melting (SLS/M). FDM printing of electrochemical devices is usually based on graphene and polylactic acid (PLA) composite filaments. The printing method offers low resolution, is restrictive in resin component choice, produces only low conductivity articles, and PLA is hydrolytically unstable. DIW offers higher flexibility in resin components and produces higher conductivity articles than FDM but offers even lower resolution. SLS/M offers higher resolution, but is limited to only a few metals (generally stainless steel, titanium, and nickel) and require expensive printers and raw materials.

[0007] Conductive ceramic and polymeric material articles are widely used in various socio-economically important applications, such as sustainable energy production and storage, drug development, surgical and medical devices, environment and health monitoring, consumer products and engineering fields. Specific applications for conductive ceramic articles include resistors, semiconductors and superconductors in electronic circuits, gas sensors and heating elements. Most are metallic or semi-metallic. Their use arises from these ceramic materials generally being characterised by impressive thermal stability, chemical stability, and mechanical strength. Specific applications for conductive polymeric articles include semiconductors and supercapacitors in electronic circuits, chemical sensors, electromagnetic shielding and electrochemiluminescence.

Their use arises from polymeric materials generally being characterised by elasticity, biodegradability, non-brittle nature, and being soft to touch.

[0008] Accordingly, conductive polymeric and ceramic materials have impressive properties that are desirable to implement in many fields of endeavour, though limitations in their manufacture, especially by 3D printing techniques, prevents them from being adopted as broadly as may otherwise be possible.

[0009] It would thus be desirable to provide a resin that allows the production of conductive polymeric and/or ceramic materials, especially using 3D printing techniques that reduces or avoids one or more of the drawbacks outlined in the foregoing, and which may be utilised in new and existing applications.

SUMMARY

[0010] The present disclosure is predicated on the acquired knowledge that certain components used in a resin give rise to electrically conductive polymeric materials, and/or to conductive PDC materials formed using a step of pyrolysis of a polymeric material formed from the resin.

[0011] In an aspect, the present disclosure relates to a resin for forming an electrically conductive polymeric or polymer-derived ceramic (PDC) material, said resin comprising: a photopolymerisable organosilicon monomer; and a conductivity additive.

[0012] In another aspect, the present disclosure provides an electrically conductive polymeric or PDC material formed from a resin as described herein using a step of photopolymerisation.

[0013] In another aspect, the present disclosure provides an electrically conductive polymeric material comprising: a photopolymerised photopolymerisable organosilicon monomer; and a conductive substance.

[0014] In another aspect, the present disclosure provides a polymeric material for forming an electrically conductive PDC material, said polymeric material comprising: a photopolymerised photopolymerisable organosilicon monomer; and a conductivity additive.

[0015] In another aspect, the present disclosure provides an electrically conductive PDC material comprising: a pyrolysed preceramic polymer, said preceramic polymer comprising a photopolymerised photopolymerisable organosilicon monomer and a conductivity additive; and a conductive substance.

[0016] In another aspect, the present disclosure provides a method for forming an electrically conductive polymeric material, said method comprising subjecting a resin as herein described to photopolymerising conditions to form an electrically conductive polymeric material.

[0017] In another aspect, the present disclosure provides a method for forming an electrically conductive PDC material, said method comprising:

- a) subjecting a resin as herein described to photopolymerising conditions to form an optionally electrically conductive preceramic polymer; and
- b) subjecting the optionally electrically conductive preceramic polymer to pyrolytic conditions to form a conductive PDC material.

[0018] In another aspect, the present disclosure provides a polymeric material, an electrically conductive polymeric material, or an electrically conductive PDC material, formed by a method as described herein.

DESCRIPTION OF THE FIGURES

[0019] Figure 1 graphs electrical conductivity (S/m) against pyrolysis temperature (°C) of PDC materials containing conductivity additives graphene (uG), graphene oxide nanoplatelet (GO), and carbon nanotubes (CNT), prepared according to Examples 1/24 (uG), 2/23 (GO), 15/19 (CNT 1 wt%), 16/20/25 (CNT 2 wt%), 17/21/26 (CNT 3 wt%) and 18/22/27 (CNT 4 wt%) (with varying pyrolysis temperatures).

[0020] Figure 2 graphs porosity (BET surface area, m²/g) against pyrolysis temperature (°C) of PDC materials containing conductivity additives graphene (uG), graphene oxide nanoplatelet (GO), and carbon nanotubes (CNT), prepared according to Examples 1 (uG), 2/23 (GO), 15/19 (CNT 1 wt%), 16/20 (CNT 2 wt%), 17/21 (CNT 3 wt%) and 18/22 (CNT 4 wt%) (with varying pyrolysis temperatures).

[0021] Figure 3 is a) photograph of a carbon-enriched black glass electrode with interdigitated pillars, including an SEM image inset showing porosity, b) an additional SEM image showing porosity, for Example 1.

[0022] Figure 4 is a photograph of a carbon-enriched black glass electrode, including an SEM image inset showing porosity, for Example 2.

[0023] Figure 5 is a photograph of a polymer electrode with interdigitated pillars, including an SEM image inset showing porosity, for Example 3.

[0024] Figure 6 is a photograph of a silicon carbide and silicon oxycarbide composite ceramic electrode, including an SEM image inset showing porosity, for Example 4.

[0025] Figure 7 is photograph of a carbon-enriched black glass electrode, including an SEM image inset showing porosity, for Example 5.

[0026] Figure 8 is a photograph of a carbon-enriched black glass disc, including an SEM image inset showing porosity, for Example 9.

[0027] Figure 9 is a photograph of a carbon-enriched polydimethylsiloxane disc, including an SEM image inset showing porosity, for Example 10.

[0028] Figure 10 is a photograph of a carbon-enriched black glass electrode, including an SEM image inset showing porosity, for Example 11.

[0029] Figure 11 is a BET isotherm showing porosity, for Example 20.

[0030] Figure 12 BET isotherm showing porosity, for Example 21.

[0031] Figure 13 is an SEM image showing porosity, for Example 22.

[0032] Figure 14 is a) an SEM image showing porosity and b) a BET isotherm showing porosity, for Example 2.

[0033] Figure 15 is a BET isotherm showing porosity, for Example 18.

DETAILED DESCRIPTION

[0034] Polymeric materials are generally formed by a process which involves the polymerisation of a monomer contained within a resin; or in other words, are generally formed by subjecting a resin comprising a monomer to polymerising conditions. PDC materials are generally formed by a process which involves the pyrolysis of a preceramic

polymer; or in other words, are generally formed by subjecting a preceramic polymer to pyrolytic conditions. A preceramic polymer is a polymeric material formed when the resin is a preceramic resin containing a preceramic monomer. Generally speaking, during pyrolysis a preceramic resin is converted from an organic to an inorganic material.

[0035] Many polymeric materials are non-conductive or have an electrical conductivity that is too low for practical application. Similarly, many PDC materials are non-conductive or have an electrical conductivity that is too low for practical application.

[0036] The present disclosure is concerned with photopolymerisable monomers including preceramic monomers, photopolymerised polymeric materials including preceramic polymers, and PDC materials formed from preceramic polymers; from photopolymerised preceramic monomers. The present disclosure is concerned with resins which contain certain components as detailed herein, being at least a photopolymerisable organosilicon monomer and a conductivity additive, for forming electrically conductive polymeric and/or PDC materials. The present disclosure is also concerned with electrically conductive polymeric materials and electrically conductive PDC materials. The electrically conductive polymeric or PDC materials may generally be said to comprise a polymer or a ceramic material, respectively, and an electrically conductive substance; being a substance that confers electrical conductivity to the polymer or PDC material. The present disclosure is also concerned with resins for forming electrically conductive polymeric or PDC materials, and to polymeric materials for forming electrically conductive PDC materials, using at least a step of photopolymerisation. A resin for forming an electrically conductive polymeric or PDC material by photopolymerisation may generally be said to comprise at least one photopolymerisable monomer and a conductivity additive; being a substance for conferring electrical conductivity to a polymeric or PDC material formed from the resin. That is, the resins of the present disclosure find particular utility in forming electrically conductive polymeric or PDC materials using a step of photopolymerisation. The step of photopolymerisation as preferably performed as part of a 3D printing process. The present disclosure accordingly provides for 3D printed electrically conductive polymeric materials or for

electrically conductive PDC materials, formed using a step of photopolymerisation. The present disclosure also provides for electrically conductive polymeric materials and electrically conductive PDC materials which are porous, and microstructures of electrically conductive polymeric materials and electrically conductive PDC materials.

Definitions

[0037] Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by those of ordinary skill in the art. Although any methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present disclosure, preferred methods and materials are described. For the purposes of the present disclosure, a number of terms are defined throughout.

[0038] The term “electrically conductive” refers to the ability of a material to conduct electric current. A material may be determined to be electrically conductive by a measure of its “electrical conductivity”. “Electrical resistivity” is the converse of electrical conductivity and refers to the measure of an ability of a material to resist the conduction of electric current. A “conductivity additive” is a substance for conferring electrical conductivity to a material. The term “conferring electrical conductivity” refers to the ability of a substance contained within a material to increase the electrical conductivity of the material. A conductivity additive in a resin may itself be electrically conductive in the resin and in a polymeric or PDC material formed from the resin, or may not itself be electrically conductive in the resin, but may be conductive in a polymeric or PDC material formed from the resin, and may, in the process of the resin being converted into a polymeric or PDC material, be converted into a substance that is electrically conductive in that material. A conductivity additive that is electrically conductive in the resin and polymeric or PDC material formed from it may be referred to as a “conductive substance”. A conductivity additive that is not electrically conductive in the resin but is converted into an electrically conductive substance in the process of the resin being converted into a polymeric or PDC material may be referred to as a “pre-conductive substance”. Electrical

conductivity and electrical resistivity are experimentally determinable using methods known in the art. One known method is the four-point probe measurement which measures the conductivity and resistivity of a layer of a material. It generally uses four equidistant probes placed in a line in contact with the material and an electrical current is passed between the outermost probes. The innermost probes measure any drop in voltage as the current passes through the material. Electrical conductivity and resistivity are calculable from the applied current and voltage measurements. A four-point probe resistivity is generally provided as a sheet resistance in ohms per square and/or an electrical resistivity in ohms per metre. A four-point probe electrical conductivity is generally provided as a conductivity in siemens per metre.

[0039] A “polymeric material” is a material formed or formable by the polymerisation of at least one monomer. A “monomer” is a chemical species capable of polymerising to form a polymeric material. A “photopolymerised” polymeric material is a polymeric material formed using, either alone or with other steps of a method, a step of photopolymerisation. “Photopolymerisation” is light-induced polymerisation (either directly or by the use of a photoinitiator). A monomer which is capable of participating in photopolymerisation is “photopolymerisable”.

[0040] The present disclosure uses photopolymerisable organosilicon monomers. An “organosilicon” is a chemical compound with a chemical structure that contains silicon atoms covalently bonded to carbon atoms. A photopolymerisable organosilicon monomer is one which contains a photopolymerisable functional group.

[0041] The term “preceramic” refers to the ability of a material to be converted into a ceramic material using, either alone or with other steps of a method, a step of pyrolysis. Thus, a “preceramic polymer” is a polymeric material which is capable of being converted into a ceramic material using a method comprising a step of pyrolysis. In turn, a “preceramic resin” is a material containing at least one monomer which is capable of being converted into a preceramic polymer using a method comprising a step of polymerisation. Such a monomer of a preceramic resin may be referred to as a “preceramic monomer”. A “polymer-derived ceramic” (PDC) material is a manufactured

ceramic material formed by pyrolysis of a preceramic polymer.

[0042] A “green body” is a shaped article comprising a polymeric material, which may be subject to further processing steps, such as washing steps, and/or pyrolysis when the polymeric material is a preceramic polymer. A green body may be formed by shaping processes known in the art. Shaping processes particularly applicable to the present disclosure are 3D printing methods such as stereolithography, digital light projection, two-photon lithography, continuous liquid interface methods, direct ink writing and inkjet printing. These methods are generally known in the art.

[0043] A “microstructure” refers to a structure, being a physical feature or dimension, characterisable by a dimension of less than 1 mm and particularly by a dimension of between about 1 micron and less than 1 mm. For example, a microstructure may be characterised by one or more of the three principle dimensions of three-dimensional space (i.e. as is commonly represented by X-, Y- and Z- axis) of less than 1 mm. To use an example, a cylindrical protrusion from a surface with a height of 50 microns and a diameter of 50 microns may be described as being a microstructure, or a structure with dimensions within the microstructure range. A structure may also be a feature characterised by an absence of a substance (i.e. “negative feature”) – such as a cylindrical bore having a depth of 50 microns and a diameter of 50 microns. What distinguishes a microstructure from microscopic irregularities in a surface is the controlled formation or controlled arrangement of the microstructure, as distinct from random or irregular microscopic features. A microstructure may be a structure of a larger article, or macrostructure.

[0044] A “macrostructure” generally refers to a structure characterisable by a dimension of greater than or equal to 1 mm. For example, a polymeric or PDC material article may be characterised by one or more of the three principle dimensions of three-dimensional space (i.e. as is commonly represented by X-, Y- and Z- axis) of greater than or equal to 1 mm. The dimension may be from 1 mm to 100 mm, and preferably from 1 mm to 50 mm, more preferably from 1 mm to 10 mm. In the case of preceramic polymers, the dimensions of a green body may be larger than a PDC material formed by pyrolysis of

the green body by a factor accounting for a degree of shrinkage.

[0045] By “porous” or having “porosity” is meant the containing of pores. A “pore” is a space which is devoid of the solid material that makes up the material. Pores may be considered hierarchically in terms of pore size, as micropores, mesopores and macropores. A “micropore” refers to a pore with a diameter of less than 2 nm. A “mesopore” refers to a pore with a diameter of from 2 nm to 50 nm. A “macropore” refers to a pore with a diameter of from 50 nm to 100 micrometres. Macropores may further be considered as sub-, inter- and super-macropores, which refers to a macropore with a diameter of from 50 nm to 1 micrometre, from 1 micrometre to 10 micrometres, and from 10 micrometres to 100 micrometres, respectively. By “diameter” does not limit the shape of a pore and refers to the greatest axial dimension. Similarly, “microporous” refers to the containing of micropores, while “mesoporous” refers to the containing of mesopores, and “macroporous” refers to the containing of macropores. Pore size may be experimentally determinable using methods known in the art. Known methods include gas adsorption (including using a BET surface analyser), scanning electron microscopy and liquid intrusion (including mercury porosimetry). Similarly, porosity is directly related to specific surface area: the greater the porosity, the greater the specific surface area. Specific surface area is experimentally determinable using methods known in the art including gas adsorption (including using a BET surface analyser) and liquid intrusion (including mercury porosimetry).

Resins, Polymeric and PDC Materials

[0046] The applicability of the resins of the present disclosure to forming electrically conductive polymeric and PDC materials is surprising. Traditionally, it has been difficult to form polymeric and PDC articles, especially that are 3D printable, based on resins that contain more than a minor amount of non-polymerisable additives, as the additives tend to cause a reduction in the integrity of a polymeric and PDC material formed therefrom. Further, the production of electrically conductive polymeric and PDC materials, especially by 3D printing techniques, has not utilised photopolymerisation. In the present

disclosure, it has been found that the combination of the resin components including a photopolymerisable organosilicon monomer and conductivity additive as herein described, allows for the formation of electrically conductive polymeric and PDC materials including without, with reduced risk of, or to a lesser extent, breakdown of the material integrity.

[0047] In preferred embodiments, the electrically conductive polymeric materials have electrical conductivity of at least 0.1 $\mu\text{S/m}$, preferably at least 1 $\mu\text{S/m}$, preferably at least 10 $\mu\text{S/m}$, and preferably at least 30 $\mu\text{S/m}$, and may have electrical conductivity of at least 40 $\mu\text{S/m}$, at least 70 $\mu\text{S/m}$ or at least 100 $\mu\text{S/m}$. The electrical conductivity may be as high as 1 S/m, as high as 900 mS/m, as high as 800 mS/m, as high as 700 mS/m, as high as 600 mS/m, or as high as 500 mS/m. Any minimum and maximum may be combined without limitation. For example, expressed as a range, the electrical conductivity may be between 0.1 $\mu\text{S/m}$ and 1 S/m, 1 $\mu\text{S/m}$ and 800 mS/m, 10 $\mu\text{S/m}$ and 700 mS/m, 30 $\mu\text{S/m}$ and 500 mS/m, 70 $\mu\text{S/m}$ and 500 mS/m, or 100 $\mu\text{S/m}$ and 500 mS/m. Generally speaking, the greater amount of conductivity additive, the higher the electrical conductivity of the electrically conductive polymeric materials, and the greater electrical conductivity of the conductivity additive itself, or the conductive substance formed therefrom (in the case of a pre-conductive substance), the greater the electrical conductivity of the electrically conductive polymeric materials.

[0048] In preferred embodiments, the electrically conductive PDC materials have electrical conductivity of at least 0.1 $\mu\text{S/m}$, preferably at least 1 $\mu\text{S/m}$, preferably at least 10 $\mu\text{S/m}$, preferably at least 40 $\mu\text{S/m}$, preferably at least 70 $\mu\text{S/m}$ and preferably at least 100 $\mu\text{S/m}$. The electrical conductivity may be as high as 600 S/m, as high as 500 S/m, as high as 400 S/m, as high as 300 S/m, as high as 200 S/m, as high as 150 S/m, or as high as 100 S/m. Any minimum and maximum may be combined without limitation. For example, expressed as a range, the electrical conductivity may be between 0.1 $\mu\text{S/m}$ and 600 S/m, 1 $\mu\text{S/m}$ and 500 S/m, 10 $\mu\text{S/m}$ and 500 S/m, 40 $\mu\text{S/m}$ and 300 S/m, 70 $\mu\text{S/m}$ and 200 S/m, or 100 $\mu\text{S/m}$ and 150 S/m. Like for electrically conductive polymeric materials, generally speaking, the greater amount of conductivity additive, the higher the

electrical conductivity of the electrically conductive PDC materials, and the greater electrical conductivity of the conductivity additive itself, or the conductive substance formed therefrom (in the case of a pre-conductive substance), the greater the electrical conductivity of the electrically conductive PDC materials.

[0049] The resins of the present disclosure are applicable to the formation of polymeric and PDC microstructures, including microstructures of larger articles; of macrostructures. A principle finding of formation of microstructures in the formation of PDC materials is described in the specification for Australian provisional patent application number 2022901435 filed 27 May 2022, and PCT patent application number PCT/AU2023/050159 filed 8 March 2023, the disclosure of each of which is herein incorporated by reference in their entireties. The resins described herein are suited to be formed into polymeric and PDC microstructures, and particularly into PDC articles containing microstructures, because the resins when pyrolysed from a green body may undergo linear and volumetric shrinkage forming PDC materials that are smaller than the green bodies from which they are pyrolysed. This is because, during pyrolysis, a preceramic polymer will generally undergo a certain degree of linear and volumetric shrinkage as the material undergoes a thermally-induced conversion from organic to inorganic material and liquids and gases are expelled. The degree of shrinkage is controllable in one way by the use of resins characterised by differing degrees of polymerisation, and which contain, or form during post-polymerising processing steps, porosity. Generally speaking, the lower the degree of polymerisation the greater the degree of shrinkage during pyrolysis as unpolymerised monomer is expelled as liquids and gases. Similarly, the greater the porosity the greater the degree of shrinkage as the porous structure during pyrolysis allows a greater volume of liquids and gases to escape and the porous structure may then collapse into a smaller volume. This allows for the manufacture of PDC articles containing microstructures of a sub-resolution dimension; that is, smaller than the smallest practical resolution obtainable by the method used to form a green body. For example, many benchtop 3D printers have a lowest practical resolution (as determined by the properties of the resin printed, e.g. its viscosity etc.) of

about 500 microns. By exploiting the shrinkage potential of preceramic resins formulated according to the present disclosure, microstructures may be formed having a resolution of less. A principle utilisation of shrinkage in the formation of PDC materials is described in the specification for Australian provisional patent application number 2022901435 and PCT patent application number PCT/AU2023/050159 referenced above. Generally speaking, and for a similar reason, the electrical conductivity of electrically conductive PDC materials tends to be higher than that of electrically conductive polymeric materials containing the same amount of the same conductivity additive. One reason for this is believed to be that, like-for-like, electrically conductive PDC material contain a higher density of conductivity additive (per volume of material) than electrically conductive polymeric materials.

[0050] The resins of the present disclosure are applicable to the formation of porous polymeric and PDC materials. A principle finding of formation of porous PDC materials is described in the specification for Australian provisional patent application number 2022900557 filed 8 March 2022, and PCT patent application number PCT/AU2023/050161 filed 8 March 2023, the disclosure of each of which is herein incorporated by reference in their entireties. Porous polymeric and PDC materials may be formed from resins which contain porosity and which is maintained during polymerisation and pyrolysis, or which allow the introduction of porosity during polymerisation and/or pyrolysis. A resin may contain porosity by the inclusion of a porous substance in the resin, such as porous particles, which may remain porous in a polymeric or PDC material formed from the porous resin. Porosity may be introduced to a polymeric material during polymerisation of a resin which contains a particulate substance such as porous particles or a particulate conductivity additive. During polymerisation, crosslinks may be forced to form around the particulate substance creating pores. The degree of porosity is controllable by the porosity of a porous substance, and by the amount of porous substance included. Porosity may be introduced to a PDC material during pyrolysis of a preceramic polymer. The degree of porosity of a PDC material is controllable by the porosity of a porous substance, by the control of a maximum temperature during pyrolysis

that is below the temperature at which porosity in the material collapses, and by the use of resins characterised by differing degrees of polymerisation for unpolymerised monomers to burn off, by the use of two or more monomers characterised by different ceramic yields, and/or by adding a porogen to the resin which burns off during pyrolysis.

[0051] The applicability of the resins of the present disclosure to forming porous electrically conductive polymeric and PDC materials is surprising. As explained above, additives in a resin such as a porous substance tend to cause a reduction in the integrity of a polymeric and PDC material formed therefrom. Similarly, porosity results in a density reduction of a material and intuitively has the effect of reducing the integrity of a polymeric or PDC material. However, in the present disclosure, it has been found that certain components of the resin as herein described allow for the formation of porous electrically conductive polymeric and PDC materials. This is provided by photopolymerisable organosilicon monomers which tend to be one or both of highly reactive and stable, and which form polymeric materials characterised by one or both of a high degree of polymerisation and stability which counteracts the destabilising effect of the conductivity additive and porosity.

[0052] That said, generally speaking the porosity of the electrically conductive polymeric materials formable from the resins disclosed herein is characterised by an upper limit before the destabilising effects of the conductivity additive and porosity may outdo the stabilising effect of the photopolymerisable organosilicon monomers and the polymerised materials they form. Accordingly, generally speaking the porosity of the electrically conductive polymeric materials is characterised by an upper limit of about $150 \text{ m}^2/\text{g}$. This may be a porosity of between about $5 \text{ m}^2/\text{g}$ and $150 \text{ m}^2/\text{g}$, including $5 \text{ m}^2/\text{g}$, $10 \text{ m}^2/\text{g}$, $20 \text{ m}^2/\text{g}$, $30 \text{ m}^2/\text{g}$, $40 \text{ m}^2/\text{g}$, $50 \text{ m}^2/\text{g}$, $60 \text{ m}^2/\text{g}$, $70 \text{ m}^2/\text{g}$, $80 \text{ m}^2/\text{g}$, $90 \text{ m}^2/\text{g}$, $100 \text{ m}^2/\text{g}$, $110 \text{ m}^2/\text{g}$, $120 \text{ m}^2/\text{g}$, $130 \text{ m}^2/\text{g}$, $140 \text{ m}^2/\text{g}$, and $150 \text{ m}^2/\text{g}$. This includes when analysed by BET surface analysis which may be referred to as a BET specific surface area. This does not necessarily apply to electrically conductive PDC materials which may be characterised by a porosity which is above $100 \text{ m}^2/\text{g}$.

[0053] Porosity may be provided in the polymeric and PDC materials as micropores,

mesopores and/or macropores. Micropores may be provided by way of a porous substance in the resin. Mesopores may similarly be provided by way of a porous substance in the resin, and may be formed during polymerisation and/or pyrolysis. Macropores may be formed by porogen in the resin which is burnt off during pyrolysis. That said, macropores tend to be more destabilising than micropores and mesopores. Accordingly, in preferred embodiments, porosity is substantially provided by way of micropores and/or mesopores. Accordingly, in preferred embodiments, the PDC materials described herein are formed from preceramic polymers that contain only a small amount, or are substantially or effectively absent, of a porogen, as described further below.

[0054] The materials produced find utility in numerous engineering and scientific fields in which electrically conductive materials are employed, for example as electrodes including microelectrodes, catalyst supports, bipolar plates, electrocatalytic reactors, electrochemical devices.

Photopolymerisable Organosilicon Monomer

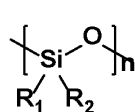
[0055] The present disclosure uses photopolymerisable organosilicon monomers which are organosilicon compounds that contain a photopolymerisable functional group.

Organosilicon Compound

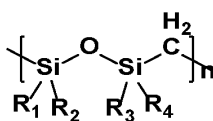
[0056] Turning firstly to the organosilicon compounds upon which the photopolymerisable organosilicon monomers are based, organosilicon compounds are generally based on a backbone chain structure of repeating silicon atom-containing motifs, and in that sense they are generally oligomeric or polymeric compounds. Examples applicable to the present disclosure include polysiloxanes, polycarbosiloxanes, polysilsesquioxanes, polycarbosilanes, polysilylcarbodiimides, polysilsesquicarbodiimides, polysilazanes, polysilsesquiazanes, polyborosilanes, polyborosiloxanes and polyborosilazanes. As silicon and carbon atoms are generally tetravalent, an organosilicon, including the backbone structure of polymeric organosilicons, is generally substituted with carbon-containing organic chemical groups.

By “substituted” in reference to an organosilicon is meant that any one or more hydrogen atoms bound to an atom under consideration is replaced, provided that the atom's valence is not exceeded and a stable compound results. Non-limiting examples of suitable substituents include those of the R-groups as defined below.

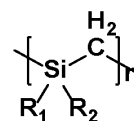
[0057] In preferred embodiments, the organosilicon compound upon which the photopolymerisable organosilicon monomers are based is selected from one or more of a polysiloxane, polycarbosiloxane, polycarbosilane, polysilylcarbodiimide and a polysilazane. Preferably, these organosilicon compounds have the following chemical structures of Formula 1, Formula 2, Formula 3, Formula 4 and Formula 5:



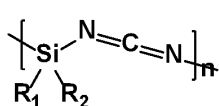
Formula 1



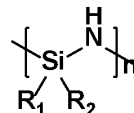
Formula 2



Formula 3



Formula 4



Formula 5

wherein:

n represents a backbone structure of repeating silicon atom-containing motifs and is independently an integer of from 2 to 15; and

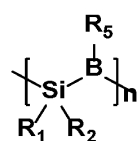
R₁, R₂, R₃ and R₄ are independently selected from the group consisting of H, a C₁-C₁₈ substituted or unsubstituted alkyl, a C₁-C₁₈ substituted or unsubstituted alkyl ether, a phenyl and a halide, independently for each integer of n, with the proviso that the pairs of R₁ and R₂ and R₃ and R₄ are not both H, alkyl ether or halide for every integer of n. Preferably, the pairs of R₁ and R₂ and R₃ and R₄ are not both H, alkyl ether or halide for any integer of n. Preferably, each of R₁ and R₂ and R₃ and R₄ are identical for every integer of n.

[0058] In Formulas 2, 3 and 5, the hydrogen atoms of the CH₂ and NH groups may also be substituted with one or more groups as defined for R₁. As stated above, an organosilicon is a chemical compound with a chemical structure that contains silicon

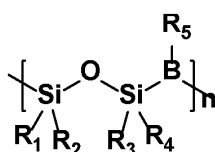
atoms covalently bonded to carbon atoms, which includes organosilicon monomers of Formulas 1 to 5 where n is an integer equal to 1. That is, in Formulas 1 to 5, n may independently be an integer of 1 or more, or from 1 to 15.

[0059] The organosilicon compound upon which the photopolymerisable organosilicon monomers are based may also be a polyoctahedral silsesquioxane, preferably selected from one or more of a polysilsesquioxane, polysilsesquicarbodiimide and a polysilsesquiazane substituted with one or more groups as defined for R₁. In other words, the polyoctahedral silsesquioxane may be substituted with one or more groups selected from the group consisting of a C₁-C₁₈ substituted or unsubstituted alkyl, a C₁-C₁₈ substituted or unsubstituted alkyl ether, a phenyl and a halide.

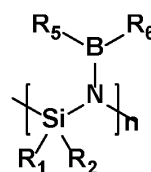
[0060] The organosilicon compound upon which the photopolymerisable organosilicon monomers are based may also be selected from one or more of a polyborosilane, a polyborosiloxane and a polyborosilazane having the following chemical structures of Formula 6, Formula 7 and Formula 8:



Formula 6



Formula 7



Formula 8

wherein:

n represents a backbone structure of repeating silicon atom-containing motifs and is independently an integer of from 2 to 15;

R₁, R₂, R₃ and R₄ are as defined above; and

R₅ and R₆ are independently selected from the group consisting of H, OH, a C₁-C₁₈ substituted or unsubstituted alkyl, a C₁-C₁₈ substituted or unsubstituted alkyl ether and a phenyl, independently for each integer of n. Like for R₁, R₂, R₃ and R₄, preferably R₅ and R₆ are identical for every integer of n.

[0061] As stated above, an organosilicon is a chemical compound with a chemical structure that contains silicon atoms covalently bonded to carbon atoms, which includes organosilicon compounds of Formulas 6 to 8 where n is an integer equal to 1. That is, in

Formulas 6 to 8, n may independently be an integer of 1 or more, or from 1 to 15.

[0062] In preferred embodiments, the organosilicon compound is selected from one or more of a polysiloxane, polycarbosiloxane and a polycarbosilane wherein n is independently an integer of from 2 to 5 and R₁, R₂, R₃ and R₄ are identical for every integer of n and independently selected from the group consisting of H, methyl and isobutyl, with the proviso that the pairs of R₁ and R₂ and R₃ and R₄ are not both H, and a polysilsesquioxane substituted with a group as defined for R₁ and preferably isobutyl.

[0063] In most preferred embodiments, the organosilicon compound is a polysiloxane wherein n is independently an integer of from 2 to 5 and R₁, R₂, R₃ and R₄ are identical for every integer of n and independently selected from the group consisting of H, methyl and isobutyl, with the proviso that the pairs of R₁ and R₂ and R₃ and R₄ are not both H.

Photopolymerisable Organosilicon Monomer

[0064] A photopolymerisable organosilicon monomer is an organosilicon compound as described above that is substituted to contain a photopolymerisable functional group, or in other words is an organosilicon compound as described above which contains a photopolymerisable functional group.

[0065] The photopolymerisable functional group may be substituted at one or more points of the organosilicon compound including, in the case of oligomeric or polymeric organosilicon compounds, at any point(s) along the backbone structure. Alternatively, or in addition, and especially in the case of oligomeric or polymeric organosilicon compounds, the photopolymerisable functional group may be terminally substituted, i.e., at one or more end groups of the backbone structure. By “substituted” in reference to a photopolymerisable organosilicon monomer is meant that any one or more non-polymerisable chemical groups of an organosilicon compound which is bound to an atom under consideration is replaced by a photopolymerisable functional group, provided that the atom valence is not exceeded and a stable compound results. Non-limiting examples of suitable substituents include those of the photopolymerisable functional groups defined below.

[0066] Accordingly, a photopolymerisable organosilicon monomer may be obtained by substituting any one or more of R₁, R₂, R₃ and R₄, or a terminal group(s), of an organosilicon compound describe above, with one or more of one or more types of photopolymerisable functional groups. Photopolymerisable functional groups of different “types” are those having different chemical structures. The type of photopolymerisable functional group(s) used is not particularly critical provided that it provides for photopolymerisation of the organosilicon monomer(s). One type of photopolymerisable functional group may be used, selected such that it reacts with itself, or alternatively two or more types of photopolymerisable functional groups may be used, selected such that they react with (i.e. are complementary to) each other. Alternatively, or in addition, photopolymerisable functional groups may be selected such that they react with a crosslinking agent added to the resin.

[0067] As described, photopolymerisable organosilicon monomers tend to be one or both of highly reactive and stable, and which form polymeric materials characterised by one or both of a high degree of polymerisation and stability. As in, a photopolymerisable organosilicon monomers may be highly reactive with itself or with another photopolymerisable monomer (optionally via a crosslinking agent) to form polymeric materials characterised a high degree of polymerisation, or may form a polymeric material characterised by high stability, or may be both highly reactive to form polymeric materials characterised by a high degree of polymerisation and which also forms a polymeric material characterised by high stability. The photopolymerisable organosilicon monomer may be selected based on a degree of polymerisation and/or stability that it forms in polymerising; or in other words, may be selected for forming a polymeric material that is characterised by a particular degree of polymerisation and/or stability.

[0068] By “degree of polymerisation” refers to the polymerisation yield, being the ratio of reacted (polymerised / crosslinked) polymerisable functional groups or monomers to unreacted (unpolymerised / uncrosslinked) polymerisable functional groups or monomers in a polymeric material (i.e. relative to what it is intended to polymerise with, for example itself and/or another monomer(s), including optionally via a crosslinker group). The

photopolymerisable organosilicon monomer may be selected for a high degree of polymerisation, being a polymerisation yield that is greater than 80% and even a “very high degree of polymerisation” that is greater than or equal to 90%, even greater than or equal to 95% or greater than or equal to 98%, and also includes “complete polymerisation” that is greater than or equal to 99% or practically detectably 100%. The photopolymerisable organosilicon monomer may similarly be selected for a “medium degree of polymerisation” being a polymerisation yield of between 60% and 80%. A medium degree of polymerisation is applicable particularly to high stability polymeric materials, but less-so otherwise. The photopolymerisable organosilicon monomers tend not to form polymeric materials characterised by a “low degree of polymerisation” being a polymerisation yield of less than or equal to 60%.

[0069] By “degree of stability” refers to an ability of a material to resist degradation. The photopolymerisable organosilicon monomer may be selected for a high degree of stability of itself and/or of a photopolymerised polymeric material formed using it.

[0070] A high degree of polymerisation is particularly applicable for forming comparatively dense polymeric and PDC materials, though the polymeric and PDC materials may be characterised by a comparatively lower porosity. A medium degree of polymerisation is particularly applicable for forming porous polymeric and PDC materials. A high degree of stability is applicable to assisting to counteract destabilising effects of the conductivity additive and/or porosity.

[0071] Selection of photopolymerisable organosilicon monomers based on degree of polymerisation and stability may generally be achieved through the selection of the photopolymerisable functional group.

[0072] The photopolymerisable functional group(s) may be selected from the group (or a group comprising a motif) consisting of a hydroxyl, epoxide, vinyl, allyl, ethynyl, thiol, glycidyl, acrylate and thiocyanate.

[0073] In preferred embodiments, the photopolymerisable functional group(s) is selected for ability to participate in thiol-ene, thiol-acrylate or acrylate photopolymerisation chemistry. It has been found that resins comprising certain components as described

herein including photopolymerisable monomer(s) which participate in thiol-ene chemistry are highly reactive and tend to form polymeric materials characterised by a high degree of polymerisation though the resins are comparatively less stable, while photopolymerisable monomer(s) which participate in acrylate chemistry tend to be comparatively more stable though are less reactive and may form polymeric materials characterised by a comparatively lower degree of polymerisation, while photopolymerisable monomer(s) which participate in thiol-acrylate chemistry tend to be comparatively more stable and may form polymeric materials characterised by a high degree of polymerisation. Accordingly, in preferred embodiments, the photopolymerisable organosilicon monomer comprises one or two types of photopolymerisable functional group, preferably selected from an allyl, vinyl, thiol and acrylate, more preferably thiol and acrylate, so as to participate in thiol-acrylate photopolymerisation chemistry. In preferred embodiments when another photopolymerisable monomer is included in the resin, the photopolymerisable organosilicon monomer comprises one type of photopolymerisable functional group, preferably selected as above, and is more preferably thiol or acrylate, while the other photopolymerisable organosilicon monomer comprises one type of photopolymerisable functional group which is complementary, preferably the other of thiol or acrylate.

[0074] Example optional crosslinking agents applicable to these embodiments are diacrylates and dithiols.

[0075] A photopolymerisable organosilicon monomer that is a preceramic monomer is characterisable by a ceramic yield. A “ceramic yield” refers to the mass of PDC material obtainable by pyrolysis, expressed as a percentage of the mass of the preceramic monomer (i.e. the mass of the converted PDC material as a percentage of the preceramic material). For example, a preceramic monomer when 10 g of PDC material is formed by pyrolysis of 11 g of preceramic monomer has a ceramic yield of $10/11 \times 100 = 91\%$.

[0076] A photopolymerisable organosilicon monomer may be present in the resin in an amount of at least about 15%, 20%, 25%, 30% or at least about 35% by weight of the preceramic resin and up to an amount of about 98%, 95%, 90%, or about 80% by weight

of the preceramic resin. A photopolymerisable organosilicon monomer may also be present in the preceramic resin in an amount of at least about 10%, 15%, 20%, 25% or at least about 30% by volume of the preceramic resin. The amount of the photopolymerisable organosilicon monomer may be not more than about 95%, 90%, 80%, 75% or not more than about 70% by volume of the preceramic resin. Any minimum and maximum can be combined without restriction. For example, the amount may be between 15% and 98% by weight of the preceramic resin, between 15% and 80% by weight of the composition etc. In some embodiments, the photopolymerisable organosilicon monomer may be present in an amount of at least about 60 wt% to about 95 wt%, preferably between about 65 wt% to about 90 wt%, and more preferably between about 70 wt% to about 85 wt%, say between 75 wt% and 80 wt%.

[0077] The ceramic yield of a preceramic monomer is a chemical property generally influenced by the chemical structure of the monomer. Methods for determining the ceramic yield of a preceramic monomer are known in the art and generally involve subjecting the preceramic monomer to pyrolysing conditions in a thermogravimetric analyser (TGA). Generally, in TGA the weight of a preceramic monomer is measured during pyrolysis as it undergoes conversion to a PDC material. The maximum pyrolysis temperature is usually at least about 600 °C and is often about 850 °C to ensure complete conversion to PDC material. Complete conversion is generally indicated by an experimentally-determined zero weight change between time points at the maximum pyrolysis temperature. A TGA may be capable of determining a starting weight and a final weight following pyrolysis, and from this the ceramic yield can be calculated. A detailed methodology is provided in the Examples. In preferred embodiments, ceramic yield is determined using this method, which may herein be referred to as “TGA₈₅₀ ceramic yield” or “TGA₈₅₀ method”, “850” representing the maximum temperature reached during the analysis.

[0078] Representative photopolymerisable organosilicon monomers are methacryloxypropyl terminated polydimethylsiloxane (ca. ceramic yield 18%), (mercaptopropyl) methylsiloxane homopolymer (c. 55% ceramic yield),

allylhydridopolycarbosilane, and vinylmethoxysiloxane homopolymer (ca. 50% ceramic yield). When only one photopolymerisable organosilicon monomer is present in the resin (mercaptopropyl) methylsiloxane homopolymer is preferred.

Other Monomers

[0079] The resins of the present disclosure may contain additional photopolymerisable monomers including a second and subsequent photopolymerisable organosilicon monomer and/or one or more photopolymerisable organic monomers. When a resin contains two or more photopolymerisable organosilicon monomers, a “first photopolymerisable organosilicon monomer” is synonymous with a “photopolymerisable organosilicon monomer” *simpliciter*, as described above, while a “second”, “third” etc. photopolymerisable organosilicon monomer may be referred to as such. The terms “first”, “second” etc. are not intended to imply an order or hierarchy, but simply to distinguish between photopolymerisable organosilicon monomers.

Second and Subsequent Photopolymerisable Organosilicon Monomer

[0080] A second photopolymerisable organosilicon monomer may be as described above in respect of the first photopolymerisable organosilicon monomer, though it will have a different chemical structure to the first photopolymerisable organosilicon monomer, whether that be by way of the backbone, substituents or photopolymerisable functional group.

[0081] That is, in preferred embodiments, a second photopolymerisable organosilicon monomer has a structure of Formula 1, Formula 2, Formula 3, Formula 4, Formula 5, Formula 6, Formula 7 or Formula 8, or is a polysilsesquioxane, polysilsesquicarbodiimide or a polysilsesquiazane as described above, substituted with one or more photopolymerisable functional groups as described above.

[0082] The second photopolymerisable organosilicon monomer may be selected based on a degree of polymerisation and/or stability of a polymeric material formed from a resin containing, as described above in respect of the first photopolymerisable organosilicon

monomer.

[0083] The photopolymerisable functional group of a second photopolymerisable organosilicon monomer need not be complementary to a photopolymerisable functional group of the first photopolymerisable organosilicon monomer. Rather, for a second photopolymerisable organosilicon monomer, one photopolymerisable functional group may be selected such that it reacts with itself under photopolymerising conditions, but not with a photopolymerisable functional group of the first photopolymerisable organosilicon monomer. Alternatively, or two or more types of photopolymerisable functional groups may be used, selected such that they react with (i.e. are complementary to) each other under photopolymerising conditions, but are not reactive with a photopolymerisable functional group of the first photopolymerisable organosilicon monomer. Alternatively, or in addition, photopolymerisable functional groups may be selected such that they react with a crosslinking agent added to the resin.

[0084] In preferred embodiments, the photopolymerisable functional group(s) of a second organosilicon monomer is selected such that it is complementary to a photopolymerisable functional group of the first photopolymerisable organosilicon monomer. In which case, the preferred photopolymerisable functional groups of a second photopolymerisable organosilicon monomer are selected from the group consisting of (with preferred photopolymerisable functional groups of the first photopolymerisable organosilicon monomer indicated in parentheses) a hydroxyl, epoxide, vinyl, allyl, ethynyl, thiol, glycidyl, acrylate, and thiocyanate.

[0085] In preferred embodiments, the photopolymerisable functional group(s) of a second photopolymerisable organosilicon monomer are selected for their ability to participate in thiol-ene, thiol-acrylate and acrylate photopolymerisation chemistry and accordingly, in preferred embodiments, a second photopolymerisable organosilicon monomer comprises one or two types of photopolymerisable functional group, preferably selected from an allyl, vinyl, thiol and acrylate, more preferably thiol and acrylate so as to participate in thiol-acrylate photopolymerization chemistry. In preferred embodiments when a first photopolymerisable organosilicon monomer is included in the resin, the first

photopolymerisable organosilicon monomer comprises one type of photopolymerisable functional group, preferably being a thiol, acrylate, allyl or vinyl and a second photopolymerisable organosilicon monomer comprises one type of photopolymerisable functional group being complementary thereto, preferably being a thiol, acrylate, allyl or vinyl.

[0086] The ceramic yield of a photopolymerisable organosilicon monomer will generally differ according to the chemical structure of the monomer and as such, because a second photopolymerisable organosilicon monomer is chemically different to the first, the ceramic yield of the second photopolymerisable organosilicon monomer will differ from that of the first. However, that is not to preclude the possibility that different photopolymerisable organosilicon monomers may happen to have the same ceramic yield, nor to preclude these embodiments from applicability to the present disclosure.

[0087] The ceramic yield of a second photopolymerisable organosilicon monomer may be similar or different to that of the first photopolymerisable organosilicon monomer. In some embodiments, the ceramic yield of the two monomers may differ by about 15% or less, being a difference of about 15%, 14%, 13%, 12%, 11%, 10%, 9%, 8%, 7%, 6%, 5%, 4%, 3%, 2%, 1% or less, including undetectably different. In some embodiments, the ceramic yield of the two monomers may differ by about 10% or less or about 5% or less. In some embodiments, the ceramic yield of the two monomers may differ by 5% or more, or 10%, 15%, 20%, 25%, 30%, 35%, 40%, 45%, 55% or more, or any integer therebetween to the limits of practical application. Preferably, the ceramic yield of the two monomers is about 15% or less as described above. The ceramic yield of a first photopolymerisable organosilicon monomer may be referred to as a “first ceramic yield” while the ceramic yield of a second photopolymerisable organosilicon monomer may be referred to as a “second ceramic yield”, and so on.

[0088] The inclusion of two photopolymerisable organosilicon monomers having different ceramic yields, especially when they differ by 5% or more, is applicable to embodiments for forming porous PDC materials and/or to embodiments which result in shrinkage as this leads to the formation of porosity during pyrolysis allowing a greater

volume of liquids and gases to escape. The porosity can then be made to collapse during pyrolysis providing high shrinkage.

[0089] The amount of a second photopolymerisable organosilicon monomer included in a resin may be such that the first and second photopolymerisable organosilicon monomers are present in a 1:1 ratio in respect of the photopolymerisable functional groups. Alternatively, one photopolymerisable organosilicon monomer may be present in excess relative to another, in respect of the photopolymerisable functional groups. This may be, for example, a ratio of between 1:1 to 1:10, or 1:1 to 1:5, or 1:1 to 1:3, or 1:1 to 1:2, such as 1:1, 1:1.1, 1:1.2, 1:1.3, 1:1.4, 1:1.5, 1:1.6, 1:1.7, 1:1.8, 1:1.9 or 1:2. An excess may be used for example to drive the polymerisation of the photopolymerisable organosilicon monomer present as the limiting reagent to a greater extent than may otherwise occur, though the excess may remain unpolymerised in the polymeric material formed. Remaining unpolymerised photopolymerisable organosilicon monomer may be removed for example during pyrolysis when the polymeric material is a preceramic polymer. In embodiments for forming a porous polymeric or PDC material, an excess may be used as a preference for the introduction of porosity upon its removal during pyrolysis.

[0090] The amount of the second photopolymerisable organosilicon monomer, when present in the resin, may be present in an amount of at least about 15%, 20%, 25%, 30% or at least about 35% by weight of the resin and up to an amount of about 80%, 75%, 70%, or about 65% by weight of the resin. The second photopolymerisable organosilicon monomer may also be present in the resin in an amount of at least about 5%, 10%, 15%, 20% or at least about 25% by volume of the resin. The amount of the second photopolymerisable organosilicon monomer may be not more than about 75%, 70%, 65%, 60% or not more than about 55% by volume of the resin. Any minimum and maximum can be combined without restriction. For example, the amount may be between 15% and 80% by weight of the resin, between 15% and 65% by weight of the resin etc.

[0091] When first and second photopolymerisable organosilicon monomer is present in the resin the preferred combinations are (mercaptopropyl) methylsiloxane homopolymer with methacryloxypropyl terminated polydimethylsiloxane and (mercaptopropyl)

methyilsiloxane homopolymer with vinylmethoxysiloxane homopolymer.

[0092] A third and subsequent photopolymerisable organosilicon monomer may be selected in the same way as the second photopolymerisable organosilicon monomers described above. When present, the third and subsequent photopolymerisable organosilicon monomer may be present in an amount of about 1 wt% to about 50 wt%, preferably between about 5 wt% to about 30 wt%, and more preferably between about 10 wt% to about 20 wt% of the resin.

[0093] When second and subsequent photopolymerisable organosilicon monomers are present, the photopolymerisable organosilicon monomers may, together with the first photopolymerisable organosilicon monomer, be present in the resin in a combined amount of at least about 30%, 40%, 50%, 60% or at least about 70% by weight of the resin and up to an amount of about 98%, 95%, 90%, or about 80% by weight of the resin. The photopolymerisable organosilicon monomers may also be present in the resin in a combined amount of at least about 10%, 15%, 20%, 25% or at least about 30% by volume of the resin. The amount of the photopolymerisable organosilicon monomers together may be not more than about 95%, 90%, 80%, 75% or not more than about 70% by volume of the resin. Any minimum and maximum can be combined without restriction. For example, the amount may be between 30% and 98% by weight of the resin, between 30% and 80% by weight of the composition etc. In preferred embodiments, the photopolymerisable organosilicon monomers may together be present in a combined amount of at least about 60 wt% to about 90 wt%, preferably between about 65 wt% to about 85 wt%, and more preferably between about 70 wt% to about 80 wt% of the resin.

Photopolymerisable Organic Monomer

[0094] A “photopolymerisable organic monomer” is an oligomeric or polymeric carbon-containing chemical compound which contains one or more photopolymerisable functional groups and which is other than the organosilicon monomers as described herein, or in other words is an oligomeric or polymeric organic compound that is substituted to contain one or more photopolymerisable functional groups and is other than the

organosilicon monomers as described herein.

[0095] Oligomeric and polymeric organic compounds are identifiable to those of skill in the art. They tend to be based on a backbone chain structure of repeating motifs containing covalent carbon-carbon bonds and carbon-hydrogen bonds, and often contain covalently-bonded heteroatoms such as oxygen, nitrogen and/or sulfur.

[0096] The photopolymerisable functional group may be substituted at two or more points of the organic compound including terminally substituted, i.e., at one or more end groups of the organic compound. One or more types of photopolymerisable functional groups may be selected as described above in respect of the first photopolymerisable organosilicon monomer and are preferably selected to be complementary to one or more photopolymerisable functional groups of one or more photopolymerisable organosilicon monomers. The photopolymerisable organic monomer is typically a silicon-free organic monomer.

[0097] The chemical structure of the backbone structure of a photopolymerisable organic monomer to which one or more photopolymerisable functional groups may be connected may be referred to as a “spacer group”. A photopolymerisable organic monomer may thus be represented by the following formula:



wherein Spacer is a spacer group, L is a photopolymerisable functional group, and n is an integer of greater than or equal to 1. In preferred embodiments, n is an integer of from 2 to 4, and is preferably 2. The spacer group may be based on an optionally branched backbone structure comprising repeat units of, for example ethylene, ethylene glycol, propylene, polypropylene glycol, ethylamine, propylamine, etc. and may thus be based on an optionally branched backbone structure comprising polyethylene, polyethylene glycol, polypropylene, polypropylene glycol, polyethyleneimine, and polypropyleneimine etc., respectively. The photopolymerisable functional groups are preferably terminally substituted. Preferably one type of photopolymerisable functional group is used. The photopolymerisable functional group is preferably selected for reactivity with the first photopolymerisable organosilicon monomer as described above

for the second photopolymerisable organosilicon monomer, and is thus preferably selected from a group, or a group containing a motif, selected from one or more of a hydroxyl, epoxide, vinyl, allyl, ethynyl, thiol, glycidyl, acrylate, and thiocyanate. In preferred embodiments, the reactive group is an allyl, a vinyl, a thiol or an acrylate so as to participate in thiol-acrylate photopolymerisation chemistry, e.g., with a photopolymerisable organosilicon monomer having a complementary photopolymerisable functional group.

[0098] Representative photopolymerisable organic monomers include polyethylene glycol diacrylate, polyethylene glycol dithiol, polyethylene glycol divinyl ether, and polyethylene glycol diallyl ether.

[0099] Photopolymerisable organic monomers tend to be more reactive, under photopolymerising conditions, with photopolymerisable organosilicon monomers than photopolymerisable organosilicon monomers tend to be with each other. A photopolymerisable organic monomer may thus be selected to increase the degree of polymerisation of a polymeric material formed from the resin, as compared to a resin subject to the same conditions and not containing that photopolymerisable organic monomer. This is one reason why photopolymerisable organic monomer is a preferred component of resins described herein.

[0100] A photopolymerisable organic monomer may be included in stoichiometric amounts equating to complete, or as near as possible complete, reactivity of the photopolymerisable functional groups of the photopolymerisable organosilicon monomer(s) and the photopolymerisable organic monomer. The photopolymerisable organosilicon monomers may be present in a 1:1 ratio with photopolymerisable organosilicon monomers in respect of the photopolymerisable functional groups.

[0101] Alternatively, an excess amount of photopolymerisable organic monomer or photopolymerisable organosilicon monomer may be used. This may be, for example, a ratio of between 1.01:1 to 2:1 of photopolymerisable organic monomer to photopolymerisable organosilicon monomer, or of photopolymerisable organosilicon monomer to photopolymerisable organic monomer, in respect of the photopolymerisable

functional groups. An excess may be used to drive the reaction towards complete reactivity of the photopolymerisable organosilicon monomer or the photopolymerisable organic monomer. This may leave unpolymerised monomer in the polymeric material formed, which may be removed, for example during pyrolysis when the polymeric material is a preceramic polymer. In embodiments for forming a porous polymeric or PDC material, an excess may be used for the introduction of porosity which may form upon removal of unreacted monomer during pyrolysis.

[0102] In terms of physical amounts, the amount of photopolymerisable organic monomer when present may be at least about 1%, 2%, 5%, 8% or 10%, 15%, 20%, 25%, 30% or at least about 35% by weight of the resin and up to an amount of about 80%, 75%, 70%, or about 65% by weight of the resin. Any minimum and maximum can be combined without restriction. For example, the amount may be between 1% and 80% by weight of the resin, between 15% and 65% by weight of the composition etc. Many photopolymerisable organic monomers are of lower molecular weight than photopolymerisable organosilicon monomers and as such, the physical amount will tend to be less than the photopolymerisable organosilicon monomer and tend to be between about 1% and 25% by weight of the resin, encompassing for example 1%, 2%, 5%, 8%, 10%, 12%, 15%, 18%, 20%, 22%, 24% and 25%.

Conductivity Additive

[0103] The resin of the present disclosure uses a conductivity additive being a substance for conferring electrical conductivity to a polymeric or PDC material formed from the resin, whether that being a conductive or a pre-conductive substance.

[0104] Conductivity additives are identifiable to persons skilled in the art in the context of the present disclosure. Conductivity additives include metals such as copper, gold, nickel, silver, aluminium, iron, platinum, mercury, tin, zinc, lead, tungsten and their alloys. Conductivity additives also include inorganic metal compounds such as oxides, nitrides, carbides, carbonitrides and silfides of metals, such as MXenes. Conductivity additives also include allotropes of carbon such as graphite, graphene and carbon nanotubes and

nanoplatelets, and carbon-containing inorganic substances including oxides, nitrides and silfides of allotropes of carbon and carbon-containing ceramic substances such as silicon carbide. Metals, their alloys, inorganic metal compounds, allotropes of carbon and carbon-containing ceramics are generally electrically conductive substances, while carbon-containing inorganic substances may be either electrically conductive substances or pre-conductive substances. For instance, graphene oxide is a pre-conductive substance in the exemplified preceramic resin embodiments described herein. During pyrolysis, graphene oxide tends to be reduced to graphene or graphite.

[0105] In preferred embodiments, the conductivity additive is selected from one or more of the group consisting of a metal, metal alloy, inorganic metal compound, allotrope of carbon, and carbon-containing inorganic substance. Preferably, the conductivity additive is an allotrope of carbon and/or a carbon-containing inorganic substance. Preferably, the conductivity additive is selected from the group consisting of graphene, graphene oxide, silicon carbide and carbon nanotube. Most preferred is carbon nanotube for highest electrical conductivity.

[0106] In preferred embodiments, the conductivity additive is a solid substance under the conditions used to form the resin and the polymeric or PDC material.

[0107] Preferably, the conductivity additive is a particulate substance. Particle sizes of up to 1 mm are useable with many 3D printing methods, while particle sizes of up to several millimetres are useable with many injection moulding methods. That said, smaller particles are preferred for improved rheological properties of the resin (especially for 3D printing) and improved distribution in the resin. Particles are also preferred for the introductions of porosity to a polymeric material or PDC material during polymerisation and pyrolysis of a resin as described above.

[0108] In some embodiments, the particles are microparticles. By “microparticles” is meant a plurality of particles having a particle size falling between 1 μm and 1 mm. It is common for particulate substances to be supplied with a specified particle size range which usually reflects that at least a majority portion of those particles have a size within that range. This may be described as a particle size distribution. The particles may be

predominantly within that particle size range (e.g., >95%, >99%) or entirely within the particle size range. Preferably, at least 90%, 95%, 98%, 99%, 99.5% and even 99.9% of microparticles included in the resin have a size falling within the particle size range. Preferably, the microparticles have a size of between about 1 μm to about 100 μm , preferably between about 1 μm and 50 μm , preferably between about 1 μm and 25 μm , and more preferably between about 1 μm and 15 μm .

[0109] In some embodiments, the particles are nanoparticles. By “nanoparticles” is meant a plurality of particles having a particle size falling under 1 μm . Preferably, at least 90%, 95%, 98%, 99%, 99.5% and even 99.9% of the nanoparticles included in the resin have a size of under 1 μm , preferably under 500 nm, under 200 nm and even under 100 nm. Preferably, the nanoparticles have a size of between about 1 nm to about 100 nm, preferably between about 1 nm and 25 nm, and more preferably between about 1 nm and 10 nm.

[0110] In some embodiments, the particles include both microparticles and nanoparticles, in which case the resin may be said to comprise particles wherein a plurality of particles have a particle size falling under 1 mm. In preferred embodiments, at least 90%, 95%, 98%, 99%, 99.5% and even 99.9% of the particles included in the resin have a size of between about 1 nm and 1 mm, between about 1 nm and 100 μm , between about 1 nm and 50 μm , between about 1 nm and 25 μm , or between about 1 nm and 15 μm . Methods for determining particle size and particle size distribution are known in the art and include small angle X-ray scattering, dynamic light scattering and transmission electron microscopy. Preferably, the particles size distribution is determined using transmission electron microscopy (TEM).

[0111] The conductivity additive may be present in the resin in an amount of at least about 0.1 wt%, 0.25 wt%, 0.5 wt%, 0.75 wt% or 1 wt% by weight of the resin. The conductivity additive may be present in the resin in an amount of at most about 50%, 40%, 30%, 20% or 10% by weight of the resin. Any minimum and maximum can be combined without restriction. In preferred embodiments, the conductivity additive is present in the resin in an amount of between 0.1 wt% and 50 wt%, preferably 0.25 wt% and 40 wt%,

preferably 0.5 wt% and 30 wt%, preferably 0.75 wt% and 20 wt%, preferably 1 wt% and 10 wt%, and preferably 1 wt% and 5 wt% by weight, for example 1 or 2 or 3 or 4 or 5 wt%, of the resin.

[0112] In the process of forming the resin, a conductivity additive may be added to other resin components neat or along with a dispersant. A dispersant is applicable for conductivity additives that are not readily dispersed in the other resin components; for example, not readily dispersible in the included photopolymerisable monomer(s). Carbon-containing inorganic substances for example, such as graphene oxide, may be provided along with a dispersant. Preferably the dispersant is volatile. Applicable dispersants include organic liquids (liquid under the conditions used to form the resin) such as methanol, ethanol, isopropanol, diethyl ether, acetone, tetrahydrofuran, hexane and other petroleum spirits, ethyl acetate, benzene, toluene, acetonitrile, chloroform, dimethyl sulfoxide, dimethylformamide, dichloromethane and butanone. The preferred dispersants are alcohols such as methanol, ethanol and isopropanol, and preferably ethanol. The dispersant may be at least in part removed in the process of forming the resin, using for example a drying step, prior to subjecting the resin to photopolymerising conditions. When the dispersant is also a porogen as described below, an amount of dispersant may be left remaining in the resin as a porogen. Preferably, at least a substantial portion of the dispersant is removed, preferably such that at most only trace amounts remain. That is, preferably between 95% and 100% of the dispersant is removed, preferably between 98% and 100%, preferably between 98% and 100% and preferably between 99% and 100% of the dispersant is removed. Drying steps are described further below.

Other Components

[0113] The resins of the present disclosure may contain additional components including a photopolymerisable crosslinking agent, structural particles, a porogen, free radical initiator, free radical inhibitor, photoblocker, 3D printing resolution agent, and colour.

Structural Particles

[0114] Structural particles may be included in the resin and used to advantage as they tend to result in a comparatively stronger polymeric or PDC materials formed from the resin, that is less prone to breakdown in the integrity of the material formed. This is particularly advantageous in the formation of PDC materials. In the formation of PDC materials from polymeric materials, the material is subject to stresses from e.g. gasses and liquids escaping. It is thought that structural particles assist to reduce the risk of breakdown of the material under stress. Structural particles that are porous may also be used to add porosity to a polymeric or PDC material. An added advantage is arising when forming PDC materials. It is believed that structural particles act as a scaffold about which polymeric material may shrink during the organic to inorganic conversion under pyrolytic conditions, which may create additional porosity.

[0115] A structural particle is generally a solid particulate substance included in the resin, that is other than a conductivity additive, that is not reactive with the other components (under the conditions used to form the resin, polymeric and PDC material as applicable) and remains in existence as a solid substance in a polymeric or PDC material formed from the resin. Structural particles are identifiable to persons skilled in the art in the context of the present disclosure.

[0116] As the preferred polymeric and PDC materials described herein are based on photopolymerisable organosilicon monomers, which at least in the case of PDC materials form silicon-based ceramic materials following pyrolysis, then the preferred structural particles are silicon-based ceramic particles. Examples include SiO_2 , Si_3N_4 , SiC , SiCN , SiCO , SiCNO , SiBCN , SiBCO , SiAlCN , and SiAlCO . In preferred embodiments, the ceramic particles are silica (SiO_2) particles.

[0117] The structural particles may be porous or non-porous. Non-porous structural particles assist to form denser polymeric or PDC materials. Porous structural particles may assist to add porosity to polymeric or PDC materials formed from the resin. Porous structural particles are typically microporous and/or mesoporous so as to provide micropores and mesopores in the polymeric or PDC material.

[0118] The structural particles may be of any size fit for purpose in a similar way as particulate conductivity additives, when particulate, may be sized as described above. In some embodiments, the structural particles are microparticles as defined and described above in respect of particulate conductivity additives. In other embodiments, the ceramic particles are nanoparticles as defined and described above in respect of particulate conductivity additives. In some embodiments, the ceramic particles include both microparticles and nanoparticles. In preferred embodiments, at least 90%, 95%, 98%, 99%, 99.5% and even 99.9% of the structural particles included in the resin are nanoparticles have a size of between about 1 nm to about 100 nm, preferably between about 1 nm and 50 nm, and more preferably between about 5 nm and 20 nm.

[0119] Structural particles may be present in the resin in an amount of at least about 0.5%, 1%, 2%, 5%, 8% or 10% by weight of the resin. When present, the amount of the structural particles is preferably not more than about 95%, 90%, 80%, 70%, 50% or 30% by weight of the resin. Any minimum and maximum can be combined without restriction. In preferred embodiments, structural particles when present are included in an amount of between about 0.5 wt% to about 20 wt%, preferably between about 1 wt% to about 15 wt%, more preferably between about 1 wt% to about 10 wt%, and especially 2 wt% to about 8 wt% of the resin.

Other Components

[0120] A “porogen” is a substance which when added to a resin is capable of escaping during pyrolysis of a preceramic polymer in the process of forming a PDC material. It is believed that porogens add porosity in the process of escaping by vacating a space which remains as a pore. A porogen is generally not reactive with the other components in the resin (under the conditions used to form the resin, polymeric and PDC material, as applicable). A porogen may be an organic or an inorganic compound. Preferably, the porogen is an organic compound which may be referred to as an “organic porogen”. Many organic porogens are volatile liquids such as the list of liquids provided above in respect of a dispersant. Other examples include cyclohexanol, dodecanol, 1,2-popanediol, water,

1-propanol, 1,4-butanediol, decane and decanol, and polyethylene glycols (PEG) such as PEG 200, PEG 400, and PEG 20,000. The inclusion of porogen in a resin may result in a polymeric or PDC material which is less electrically conductive than the same resin formed by the same process but which does not contain any porogen. This is due at least to the increased porosity of the material as a result of inclusion of porogen. Accordingly, when present, porogen may be present in an amount of up to about 10 wt%. Expressed as a range, porogen may be present in an amount of between about 1 wt% to about 10 wt%, preferably between about 1 wt% to about 7 wt%, and more preferably between about 1 wt% to about 5 wt%, of the resin. In preferred embodiments, porogen is not added to the resin. Preferably, the resin is detectably absent of porogen. Also in preferred embodiments, the PDC materials described herein are formed from preceramic polymers that are substantially or effectively absent of a porogen.

[0121] As explained above, the monomer(s) may react via a crosslinking agent. A crosslinking agent is a chemical species that comprises a crosslinker group and two or more photopolymerisable functional groups that react with (i.e. are complementary to) one or more of the photopolymerisable functional groups of any one or more of the photopolymerisable monomer(s) included in the resin, and is such that, after crosslinking has occurred, photopolymerisable functional groups of the photopolymerisable monomer(s) are crosslinked resulting in the crosslinker group in the structure of the polymeric material. When present, a crosslinking agent will generally be selected based on the photopolymerisable functional groups of the photopolymerisable organosilicon monomer(s), to have complementary photopolymerisable functional group(s) as described above. A crosslinking agent differs from a photopolymerisable organic monomer in that a crosslinking agent is not itself oligomeric or polymeric. Representative crosslinking agents include ethylene glycol diacrylate, ethylene glycol dithiol, ethylene glycol divinyl ether, ethylene glycol diallyl ether and hexanedithiol. In some preferred embodiments, a crosslinking agent is not added to the resin or in other words, the resin is absent of a crosslinking agent.

[0122] As the functional groups of the photopolymerisable organosilicon monomer(s)

are photopolymerisable, the resin may further comprise a free radical generator such as a photoinitiator which may catalyse the reaction of photopolymerisable functional groups. When present, a free radical generator may be in an amount of between about 0.01 wt% to about 20 wt%, preferably between about 0.1 wt% to about 5 wt%, and more preferably between about 0.2 wt% to about 1 wt% of the preceramic resin. Examples of photoinitiators include 2,2-dimethoxy-2-phenylacetophenone, 2-hydroxy-2-methylpropiophenone, camphorquinone, phenylbis (2,4,6-trimethylbenzoyl) phosphine oxide (BAPO), benzophenone and benzoyl peroxide. In preferred embodiments the photoinitiator is BAPO.

[0123] Examples of photoblockers include 2,5-Bis(5-tert-butyl-benzoxazol-2-yl)thiophene (BBOT), 4,4'-bis(benzoxazolyl)-cis-stilbene and 4,4-diamino-2,2-stilbenedisulfonic acid. In preferred embodiments the photoblocker is BBOT. When a photoblocker is included, the preferred photoblocker is 2,5-Bis(5-tert-butyl-benzoxazol-2-yl)thiophene (BBOT). When present, a photoblocker may be present in an amount of between about 0.01 wt% to about 20 wt%, preferably between about 0.1 wt% to about 5 wt%, and more preferably between about 0.2 wt% to about 1 wt% of the resin.

[0124] The resin may also further comprise a free radical inhibitor (also known as free radical scavenger). Examples include hydroquinone, methylhydroquinone, ethylhydroquinone, methoxyhydroquinone, ethoxyhydroquinone, monomethylether hydroquinone, propylhydroquinone, propoxyhydroquinone, tert-butylhydroquinone (TBHQ) and n-butylhydroquinone. In preferred embodiments the free radical inhibitor is tert-butylhydroquinone. When present, the free radical inhibitor may be present in an amount of about 0.01 wt% to about 20 wt%, preferably between about 0.05 wt% to about 5 wt%, and more preferably between about 0.1 wt% to about 2 wt% of the resin.

Representative Embodiments

[0125] Representative embodiments of the resins as herein described comprise a photopolymerisable organosilicon monomer and a conductivity additive, and optionally and independently the other components as follows:

- a) a second photopolymerisable organosilicon monomer;
- b) a photopolymerisable organic monomer;
- c) structural particles;
- d) a second photopolymerisable organosilicon monomer and a photopolymerisable organic monomer;
- e) a second photopolymerisable organosilicon monomer and structural particles;
- f) a photopolymerisable organic monomer and structural particles; or
- g) a second photopolymerisable organosilicon monomer, a photopolymerisable organic monomer and structural particles,

said components which may be as described herein, optionally any embodiment further comprising one or more of a crosslinking agent, a porogen, free radical initiator, free radical inhibitor, photoblocker, and 3D printing resolution agent, and colour.

Methods of the Disclosure

[0126] Methods of the present disclosure involve subjecting a resin as described herein to photopolymerising conditions to form an electrically conductive polymeric material. When it is intended to form a PDC material, then the photopolymerising conditions may form a pre-conductive polymeric material or a conductive polymeric material. In these embodiments, the polymeric material is a preceramic polymer, and the methods of the present disclosure may further involve subjecting a preceramic polymer to pyrolytic conditions to form an electrically conductive PDC material.

[0127] “Photopolymerising conditions” are conditions under which photopolymerisation reactions occur. Photopolymerisation reactions are typically photo-catalysed free radical reactions.

[0128] Resins may generally be formed by mixing the resin components together. All components of the resin may be placed together and subject to one mixing step, or the components may be added together in any particular order and mixed in between additions. In embodiments where a dispersant is used, a suspension of the conductivity

additive in a dispersant may be formed separately – or in other words, the conductivity additive may first be suspended in a dispersant – and the suspension may then be placed together with other components, preferably at least a photopolymerisable organosilicon monomer, and subject to a mixing step. Preferably at least a portion of the dispersant is removed prior to the resin being subjected to photopolymerising conditions. The removal of the at least a portion of the dispersant may be performed using a drying step such as by leaching, canulation, decanting and/or evaporation. As it is preferred that at least all but trace amounts of the dispersant is removed. Preferably removal of the dispersant is performed using evaporation, and preferably under a negative pressure i.e. vacuum.

[0129] The photopolymerisation conditions are preferably applied during a 3D printing process; that is, preferably the step of photopolymerisation is applied during a 3D printing process. A 3D printing process generally uses a 3D printing apparatus and comprises a shaping step where resin is deposited to form a shaped article, and a curing step where the deposited resin is subject to photopolymerising conditions to form a green body. The shaping and curing steps may be performed together or separately. That is, the deposited resin may be cured as it is deposited or during deposition, or the deposited resin may be cured after deposition and the shaped article is wholly formed. The present disclosure accordingly provides for 3D printed polymeric materials for electrically conductive polymeric or PDC materials; that is, polymeric materials for electrically conductive polymeric or PDC materials formed by a 3D printing process using a step of photopolymerisation.

[0130] “Pyrolytic conditions” are conditions including elevated temperatures under which pyrolysis occurs. “Pyrolysis” is the thermally-induced conversion of a preceramic polymer from organic to inorganic (i.e. PDC) material. Methods of pyrolysis are generally known to persons skilled in the art. Generally speaking, a preceramic polymer is placed in a cool furnace and the temperature is ramped-up to a maximum temperature and ramped down again. During pyrolysis, the inorganic material formed may exist in one or more material phases. Usually, the inorganic material may proceed through an amorphous phase and then, as the temperature increases, transitions to a crystalline phase. The

temperature at which this transition begins to occur may be referred to as the “phase transition temperature”. The phase that exists depends on the temperature to which the material is exposed. In other words, an amorphous or a crystalline PDC material may be formed by controlling the temperature. The phase transition temperature depends on the components of the resin. Similarly, for preceramic polymers which contain porosity, or are capable of forming porosity during pyrolysis, the porosity of the PDC material formed is similarly dependent on the temperature to which the material is exposed. That is, porosity tends to exist at lower pyrolysis temperatures until higher temperatures are reached which causes collapse of pores, reducing or eliminating porosity. The temperature at which pores detectably collapse may be referred to as the “porosity transition temperature”. Like for the material phase, a porous or a non-porous material may be formed by controlling the temperature. Typically, the phase transition temperature is higher than the porosity transition temperature, in which case amorphous porous materials and crystalline non-porous materials may selectively be formed by controlling the pyrolysis temperature. The following principles of pyrolysis temperature generally apply to the PDC materials in the context of the present disclosure:

- a) The photopolymerised monomer(s) of a preceramic polymer is begun to be converted to PDC material at about 300 °C and is essentially completely converted to PDC material when the temperature reaches about 600 °C.
- b) In PDC materials capable of forming porosity during pyrolysis, porosity begins to be formed as the material is converted to PDC material, being at about 300 °C, and maximum porosity is present at around the point of complete conversion to PDC material or at a temperature thereafter, and just prior to the temperature at which pores begin to collapse (the porosity transition temperature). This may be a temperature within the range of about 600 °C to about 1000 °C.
- c) As the temperature increases past the range of maximum porosity, pores begin to collapse, porosity is reduced, the PDC material begins to gain density and the electrical conductivity increases. By virtue of the inclusion

of the conductivity additive, the porosity transition temperature is generally at about or above 1000 °C. This contrasts with other PDC materials which generally speaking have a porosity transition temperature of less than 1000 °C or less than even 900 °C.

- d) The temperature may continue to be increased to the phase transition temperature. By virtue of the inclusion of the conductivity additive, the phase transition temperature is generally above 1400 °C, and may be above 1450 °C, and even 1500 °C. This contrasts with other PDC materials which generally speaking have a phase transition temperature of between 1300 °C and 1400 °C.

[0131] These principles are demonstrated in Figures 1 and 2 which compare the conductivity and porosity, respectively, of PDC materials of embodiments exemplified herein. In Figure 1, for PDC materials containing conductivity additives graphene, graphene oxide nanoplatelet, and carbon nanotubes, demonstrated is the trend that electrical conductivity increases with increasing pyrolysis temperature between 300 °C and 1000 °C and/or between 1000 °C and 1200 °C. Also demonstrated in Figure 1 with carbon nanotubes is the trend that the conductivity is greater in PDC materials containing a greater amount of conductivity additive. In Figure 2, for PDC materials containing conductivity additives graphene, graphene oxide nanoplatelet, and carbon nanotubes, demonstrated is the trend that porosity increases with increasing pyrolysis temperature up to the porosity transition temperature, here being at about 1000 °C, then decrease as the pyrolysis temperature increases, here shown to 1200 °C.

[0132] As many applications find benefit in electrically conductive PDC materials that are also porous, then in some embodiments preferably the maximum temperature of pyrolysis is less than the porosity transition temperature. That said, as electrical conductivity is greatest in materials having less porosity, then in some embodiments preferably the maximum temperature of pyrolysis is greater than the temperature of maximum porosity. By “maximum temperature” in this context is meant the maximum temperature reached during pyrolysis. Accordingly, in some preferred embodiments, the

maximum temperature of pyrolysis is between about 900 °C and 1200 °C. This may be a maximum temperature of about 900 °C, 950 °C, 1000 °C, 1050, 1100, 1150, or 1200 °C. In these embodiments, preferably, the maximum temperature of pyrolysis is between about 900 °C and 1100 °C, preferably between about 900 °C and 1150 °C, preferably between about 1000 °C and 1100 °C. It has been found that this temperature provides a balance of usable porosity and electrical conductivity.

[0133] If porosity is not required, then the maximum pyrolysis temperature may exceed the porosity transition temperature, though in preferred embodiments the maximum temperature is less than 1600 °C which is the temperature at which many PDC materials may start to approach their melting point. Accordingly, in these embodiments, the maximum temperature of pyrolysis may be between 1000 °C and 1600 °C, preferably between 1100 °C and 1600 °C and may be between 1300 °C and 1600 °C.

[0134] The maximum temperature of pyrolysis may be coupled with a minimum temperature of pyrolysis, which is preferably at least 300 °C for efficient conversion of organic to inorganic material.

[0135] The pyrolytic conditions may be characterised by a temperature ramp-up rate of no greater than 10 °C/minute for a period between the minimum and maximum pyrolysis temperatures, or in the whole period between the minimum and maximum pyrolysis temperatures, preferably the latter. A slower ramp-up rate is preferred for a period between the minimum pyrolysis temperature and the porosity transition temperature, or in the whole period between the minimum pyrolysis temperature and the porosity transition temperature, of no greater than 7 °C/minute, preferably no greater than 5 °C/minute, preferably no greater than 3 °C/minute, more preferably no greater than 2 °C/minute and most preferably no greater than 1 °C/minute. This may assist the formation of greater porosity and slow the rate at which liquids and gases are formed and escape from the material, reducing the risk of pressure build-up and breakdown in the PDC material integrity. In certain preferred embodiments, it may be even slower for a period, being no greater than 0.5 °C/minute or even no greater than 0.3 °C/minute. Expressed as a range, the temperature ramp-up rate may be, for a period between the minimum

pyrolysis temperature and the porosity transition temperature, or in the whole period between the minimum pyrolysis temperature and the porosity transition temperature, between 0.1 °C/min and 10 °C/min, between 0.1 °C/min and 7 °C/min, between 0.1 °C/min and 5 °C/min, between 0.2 °C/min and 3 °C/min, between 0.2 °C/min and 2 °C/min and preferably between 0.3 °C/min and 1 °C/min. Ramp-down rates may be similarly controlled as described for ramp up-rates, being generally of no greater than 10 °C/min, and may be slower for specific periods, for example between about 0.5° C/min and 1 °C/min or 2 °C/min.

[0136] Pyrolysis may be performed in an inert or a reactive atmosphere. A reactive atmosphere is generally characterised by the presence of a reactive gas; that is, a gas that is, under pyrolytic conditions, reactive to at least one component of the preceramic polymer material. Examples of reactive gases include oxygen, carbon dioxide, water (e.g. water vapour), methane, iodine, and ammonia. Air is an example of a reactive gas that contains oxygen, carbon dioxide and potentially water. An inert atmosphere is generally characterised by the absence of a reactive gas. An example of an inert environment is an environment of nitrogen gas or under vacuum. In preferred embodiments, pyrolysis is performed in an inert atmosphere, and preferably under vacuum.

[0137] The pyrolysis conditions may also include one or more hold times, at which the pyrolysis temperature is held at a specific temperature for a period of time. Examples of applicable points to use a hold time include at about or prior to the porosity transition temperature, and at about or prior to the phase transition temperature. A hold time may be for a period of time of between 30 and 300 minutes, or between 60 and 240 minutes, and any given hold time is preferably between 60 and 180 minutes.

[0138] The particular PDC material produced will generally arise from the identity of the photopolymerisable organosilicon monomer(s). Using the preferred photopolymerisable organosilicon monomers described herein, silicon-based PDC materials are generally produced which may be based on SiO, Si₃N₄, SiC, SiCN, SiCO, SiCNO, SiBCN, SiBCO, SiAlCN, SiAlCO, SiON and/or SiBN. The particular PDC material produced may also depend on the pyrolytic conditions used. For instance, the

presence of a reactive environment will generally influence the nature of the gases which escape from the material during pyrolysis and thus the nature of the PDC material produced. For example, pyrolysis of a preceramic polymer formed from a polysiloxane organosilicon monomer in an inert atmosphere will generally produce silicon oxycarbide ceramic material, whereas, pyrolysis of a preceramic polymer formed from a polysiloxane organosilicon monomer in a reactive air environment produces silica ceramic material because gases in air (e.g. O₂) undergo reactions with carbon atoms in the organosilicon backbone structure of the polysiloxane and escape as carbon-containing gases.

EXAMPLES

[0139] The TGA₈₅₀ method for determining ceramic yield of organosilicon monomers is as follows. A known amount of a photopolymerisable organosilicon monomer (preferably between 10 mg and 20 mg) was transferred to an alumina crucible approved for the thermogravimetric analyser in use. The crucible was placed in the analyser and its weight change with respect to time and temperature was studied as per the manufacturers' instructions. The sample crucible was subjected to a thermal cycle under nitrogen from room temperature to 850 °C and then back to room temperature. The sample was equilibrated at 30 °C for 30 minutes, and the resulting weight was tarred before increasing the temperature from 30 °C to 850 °C at a ramp rate of 1 °C/minute. The sample was further equilibrated at 850 °C for 60 minutes before cooling down from 850 °C to room temperature at a rate of 5 °C/min. The percentage change in weight of the sample during this thermal cycle is used to calculate the ceramic yield, where the percentage ceramic yield is calculated as $(1 - \text{sample weight lost}/\text{initial sample weight}) \times 100$.

[0140] A summary of the materials and pyrolytic conditions used for producing electrically conductive polymeric or PDC materials is given in Table 1.

Table 1. Materials and conditions used for producing electrically conductive polymeric and PDC material of Example 1 to 23, and the electrical conductivity of the material produced.

Ex.	Monomer(s)	Ceramic particles	Conductivity additive	Pyrolysis conditions	Electrical Conductivity
1	100 parts of (Mercaptopropyl) methylsiloxane homopolymer and 54.35 parts of Poly (ethylene glycol) diacrylate (average Mn 250)	SiO ₂ (porous), 5 wt%	Graphene particles, 2.3 wt%	T _{max} : 1000 °C; vacuum	465 mS/m
2	100 parts of (Mercaptopropyl) methylsiloxane homopolymer and 54.35 parts of Poly (ethylene glycol) diacrylate (average Mn 250)	SiO ₂ (porous), 5 wt%	Graphene oxide nanoplatelet, 4 wt%	T _{max} : 1000 °C; vacuum	16.5 mS/m
3	100 parts of (Mercaptopropyl) methylsiloxane homopolymer and 100 parts of methacryloxypropyl terminated polydimethylsiloxane	SiO ₂ (porous), 10 wt%	Graphene particles, 2 wt%	-	-
4	100 parts of (Mercaptopropyl) methylsiloxane homopolymer and 54.35 parts of Poly (ethylene glycol) diacrylate (average Mn 250)	SiC, 5 wt%		T _{max} : 1000 °C; vacuum	321 μS/m
5	100 parts of (Mercaptopropyl) methylsiloxane homopolymer and 100 parts of methacryloxypropyl terminated polydimethylsiloxane	SiO ₂ (porous), 5 wt%	Graphene particles, 2.5 wt%	T _{max} : 1000 °C; vacuum	80.7 mS/m
6	100 parts of (Mercaptopropyl) methylsiloxane homopolymer and 70 parts of vinylmethoxysiloxane homopolymer	SiO ₂ (porous), 5 wt%	Graphene particles, 2.3 wt%	T _{max} : 1000 °C; vacuum	52 mS/m
7	100 parts of (Mercaptopropyl) methylsiloxane homopolymer and 54.35 parts of Poly (ethylene glycol) diacrylate (average Mn 250)	SiO ₂ (non-porous), 4.5 wt%	Graphene particles, 2.3 wt%	T _{max} : 1000 °C; vacuum	-
8	100 parts of allylhydridopolycarbosilane and 50 parts of 1,6-hexanedithiol	SiC, 5 wt%		T _{max} : 600 °C; vacuum	-
9	100 parts of (Mercaptopropyl) methylsiloxane homopolymer and 54.35 parts of Poly (ethylene glycol) diacrylate (average Mn 250)	SiO ₂ (porous), 5 wt%	Carbon nanotubes, 5 wt%	T _{max} : 1000 °C; vacuum	124.7 S/m

10	100 parts of (Mercaptopropyl) methylsiloxane homopolymer and 54.35 parts of Poly (ethylene glycol) diacrylate (average Mn 250)	SiO ₂ (porous), 5 wt%	Carbon nanotubes, 5 wt%	-	356 mS/m
11	100 parts of (Mercaptopropyl) methylsiloxane homopolymer and 54.35 parts of Poly (ethylene glycol) diacrylate (average Mn 250)	SiO ₂ (porous), 5 wt%	Carbon nanotubes, 4 wt%	T _{max} : 600 °C; vacuum	6.1 S/m
12	100 parts of (Mercaptopropyl) methylsiloxane homopolymer and 54.35 parts of Poly (ethylene glycol) diacrylate (average Mn 250)	SiO ₂ (porous), 5 wt%	Carbon nanotubes, 4 wt%	-	36.2 mS/m
13	100 parts of (Mercaptopropyl) methylsiloxane homopolymer and 54.35 parts of Poly (ethylene glycol) diacrylate (average Mn 250)	SiO ₂ (porous), 5 wt%	Carbon nanotubes, 3 wt%	-	5.7 mS/m
14	100 parts of (Mercaptopropyl) methylsiloxane homopolymer and 54.35 parts of Poly (ethylene glycol) diacrylate (average Mn 250)	SiO ₂ (porous), 5 wt%	Carbon nanotubes, 2 wt%	-	33.4 uS/m
15	100 parts of (Mercaptopropyl) methylsiloxane homopolymer and 54.35 parts of Poly (ethylene glycol) diacrylate (average Mn 250)	SiO ₂ (porous), 5 wt%	Carbon nanotubes, 1 wt%	T _{max} : 600 °C; vacuum	256 mS/m
16	100 parts of (Mercaptopropyl) methylsiloxane homopolymer and 54.35 parts of Poly (ethylene glycol) diacrylate (average Mn 250)	SiO ₂ (porous), 5 wt%	Carbon nanotubes, 2 wt%	T _{max} : 600 °C; vacuum	1.04 S/m
17	100 parts of (Mercaptopropyl) methylsiloxane homopolymer and 54.35 parts of Poly (ethylene glycol) diacrylate (average Mn 250)	SiO ₂ (porous), 5 wt%	Carbon nanotubes, 3 wt%	T _{max} : 600 °C; vacuum	8.5 S/m
18	100 parts of (Mercaptopropyl) methylsiloxane homopolymer and 54.35 parts of Poly (ethylene glycol) diacrylate (average Mn 250)	SiO ₂ (porous), 5 wt%	Carbon nanotubes, 4 wt%	T _{max} : 600 °C; vacuum	16.5 S/m
19	100 parts of (Mercaptopropyl) methylsiloxane homopolymer and 54.35 parts of Poly (ethylene glycol) diacrylate (average Mn 250)	SiO ₂ (porous), 5 wt%	Carbon nanotubes, 1 wt%	T _{max} : 1000 °C; vacuum	360.5 mS/m

20	100 parts of (Mercaptopropyl) methylsiloxane homopolymer and 54.35 parts of Poly (ethylene glycol) diacrylate (average Mn 250)	SiO ₂ (porous), 5 wt%	Carbon nanotubes, 2 wt%	T _{max} : 1000 °C; vacuum	12.5 S/m
21	100 parts of (Mercaptopropyl) methylsiloxane homopolymer and 54.35 parts of Poly (ethylene glycol) diacrylate (average Mn 250)	SiO ₂ (porous), 5 wt%	Carbon nanotubes, 3 wt%	T _{max} : 1000 °C; vacuum	36.2 S/m
22	100 parts of (Mercaptopropyl) methylsiloxane homopolymer and 54.35 parts of Poly (ethylene glycol) diacrylate (average Mn 250)	SiO ₂ (porous), 5 wt%	Carbon nanotubes, 4 wt%	T _{max} : 1000 °C; vacuum	100.9 S/m
23	100 parts of (Mercaptopropyl) methylsiloxane homopolymer and 54.35 parts of Poly (ethylene glycol) diacrylate (average Mn 250)	SiO ₂ (porous), 5 wt%	Graphene oxide nanoplatelet, 4 wt%	T _{max} : 1200 °C; vacuum	32.55 S/m
24	100 parts of (Mercaptopropyl) methylsiloxane homopolymer and 54.35 parts of Poly (ethylene glycol) diacrylate (average Mn 250)	SiO ₂ (porous), 5 wt%	Graphene particles, 2.3 wt%	T _{max} : 1200 °C; vacuum	20.9 S/m
25	100 parts of (Mercaptopropyl) methylsiloxane homopolymer and 54.35 parts of Poly (ethylene glycol) diacrylate (average Mn 250)	SiO ₂ (porous), 5 wt%	Carbon nanotubes, 2 wt%	T _{max} : 1200 °C; vacuum	38 S/m
26	100 parts of (Mercaptopropyl) methylsiloxane homopolymer and 54.35 parts of Poly (ethylene glycol) diacrylate (average Mn 250)	SiO ₂ (porous), 5 wt%	Carbon nanotubes, 3 wt%	T _{max} : 1200 °C; vacuum	60 S/m
27	100 parts of (Mercaptopropyl) methylsiloxane homopolymer and 54.35 parts of Poly (ethylene glycol) diacrylate (average Mn 250)	SiO ₂ (porous), 5 wt%	Carbon nanotubes, 4 wt%	T _{max} : 1200 °C; vacuum	113 S/m

[0141] Example 1 – Conductive Ceramic: Carbon-Enriched Black Glass Electrodes

[0142] *A photopolymerisable organosilicon monomer + a photopolymerisable organic monomer + ceramic particles + graphene particles*

[0143] A resin was prepared by mixing 100 parts of (Mercaptopropyl) methylsiloxane homopolymer and 54.35 parts of Poly (ethylene glycol) diacrylate (average Mn 250) with 0.9 parts of phenylbis (2,4,6-trimethylbenzoyl) phosphine oxide and 0.8 parts of w/w tert-Butylhydroquinone (TBHQ). Porous silicon dioxide nanoparticles (spherical, 5-20 nm) (5% w/w) were added to this resin. Finally, 2.3 w/w% of micron-sized graphene particles (1.5 μm diameter) was added. The resin components were mixed thoroughly on a vortex mixer and sonication bath, and then the prepared resin was vacuumed for 15 minutes.

[0144] The resin was 3D printed using a digital light projection (DLP) printer, Miicraft Ultra, as per the manufacturer's standard operating procedure, to produce a 3D-printed electrically conductive green body.

[0145] The green body was pyrolysed under vacuum (12 mbar pressure) in a tube furnace. The pyrolysis was performed with a ramp rate of 1 °C/min from RT to 100 °C, followed by 0.2 °C/min from 100 °C to 600 °C. The furnace was held at 600 °C for 180 minutes, then up to 1000°C with a ramp rate of 1 °C/min which was held for 60 minutes. The furnace was then cooled from 1000 to 600 at a ramp rate of 1°C/min, and from 600 °C to 450 °C and then to 300 °C at a ramp rate of 2 °C/min. The furnace was held at 600 °C, 450 °C and 300 °C for 60 minutes each. It was finally cooled to RT at a ramp rate of 2 °C/min.

[0146] Figure 3 shows the produced 3D-printed and pyrolyzed carbon-enriched black glass electrodes with interdigitated pillars. The electrodes were found to be hierarchically porous as shown in the inset SEM image of Figure 3a), the SEM image of Figure 3b). The 4-point probe electrical conductivity test on the electrodes reported a sheet resistance of 4.3 k Ω /square, electrical resistivity of 2.15 Ω /m, and electrical conductivity of 465 mS/m.

[0147] Example 2 – Conductive Ceramic: Carbon-Enriched Black Glass Electrodes

[0148] *A photopolymerisable organosilicon monomer + a photopolymerisable organic monomer + ceramic particles + graphene oxide nanoplatelet*

[0149] A resin was prepared by mixing 100 parts of (Mercaptopropyl) methylsiloxane homopolymer and 54.35 parts of Poly (ethylene glycol) diacrylate (average Mn 250) with

0.9 parts of phenylbis (2,4,6-trimethylbenzoyl) phosphine oxide and 0.8 parts of w/w tert-Butylhydroquinone (TBHQ). Porous silicon dioxide nanoparticles (spherical, 5-20 nm) (5% w/w) were added to this resin. Finally, 4 w/w% of graphene oxide nanoplatelet (1 nm) was added. The resin components were mixed thoroughly on a vortex mixer and sonication bath, and then the prepared resin was vacuumed for 15 minutes.

[0150] The resin was 3D printed using a digital light projection (DLP) printer, Miicraft Ultra, as per the manufacturer's standard operating procedure, to produce a 3D-printed green body.

[0151] The green body was pyrolysed under vacuum (12 mbar pressure) in a tube furnace. The pyrolysis was performed with a ramp rate of 1 °C/min from RT to 100 °C, followed by 0.2 °C/min from 100 °C to 600 °C. The furnace was held at 600 °C for 180 minutes, then up to 1000 °C with a ramp rate of 1 °C/min which was held for 60 minutes. The furnace was then cooled from 1000 °C to 600 °C at a ramp rate of 1 °C/min, and from 600 °C to 450 °C and then to 300 °C at a ramp rate of 2 °C/min. The furnace was held at 600 °C, 450 °C, and 300 °C for 60 minutes each. It was finally cooled to RT at a ramp rate of 2 °C/min.

[0152] Figure 4 shows the produced 3D printed carbon-enriched black glass electrodes. The electrodes were found to be hierarchically porous as shown in the inset SEM image of Figure 4. Figure 14 shows a) an SEM image and b) a BET isotherm for the produced PDC material. The 4-point probe electrical conductivity test reported a sheet resistance of 121.2 kΩ/square, electrical resistivity of 60.6 Ω/m, and electrical conductivity of 16.5 mS/m.

[0153] Example 3 – Conductive Polymer

[0154] *First and second photopolymerisable organosilicon monomers + ceramic particles + graphene in ethanol dispersion*

[0155] A 2 w/w% graphene in ethanol dispersion was added in 40 parts to 100 parts of (Mercaptopropyl) methylsiloxane homopolymer. The components were mixed thoroughly on a vortex mixer and a sonication bath. To this mixture, 10 w/w% porous silicon dioxide nanoparticles (spherical, 10-20 nm) were added. The resulting mixture was placed in a vacuum oven at 30 °C for 12 hours to evaporate ethanol. The loss of ethanol was monitored using thermogravimetric analysis. Post-vacuum treatment, 100 parts of methacryloxypropyl terminated polydimethylsiloxane, 0.9 parts of phenylbis

(2,4,6-trimethylbenzoyl) phosphine oxide, and 0.8 parts of w/w tert-Butylhydroquinone (TBHQ) were added and mixed thoroughly on a vortex mixer and a sonicator bath. The prepared resin was vacuumed for 15 minutes.

[0156] The resin was 3D printed using a digital light projection (DLP) printer, Miicraft Ultra, as per the manufacturer's standard operating procedure, to produce a 3D-printed electrically conductive green body.

[0157] Figure 5 shows the produced 3D printed polydimethylsiloxane polymeric electrodes with interdigitated pillars. The electrodes were found to be hierarchically porous as shown in the inset SEM image of Figure 5.

[0158] Example 4 – Conductive Ceramic: SiC & SiOC Composite Electrodes

[0159] *A photopolymerisable organosilicon monomer + a photopolymerisable organic monomer + SiC particles*

[0160] A resin was prepared by mixing 100 parts of (Mercaptopropyl) methylsiloxane homopolymer and 54.35 parts of Poly (ethylene glycol) diacrylate (average Mn 250) with 0.9 parts of phenylbis (2,4,6-trimethylbenzoyl) phosphine oxide and 0.8 parts of w/w tert-Butylhydroquinone (TBHQ). Finally, 5 w/w% of silicon carbide nanoparticles (20 nm, laser synthesised) were added. The resin components were mixed thoroughly on a vortex mixer and sonication bath, and then the prepared resin was vacuumed for 15 minutes.

[0161] The resin was 3D printed using a digital light projection (DLP) printer, Miicraft Ultra, as per the manufacturer's standard operating procedure, to produce a 3D-printed electrically conductive green body.

[0162] The green body was pyrolysed under vacuum (12 mbar pressure) in a tube furnace. The pyrolysis was performed with a ramp rate of 1 °C/min from RT to 100 °C, followed by 0.2 °C/min from 100 °C to 600 °C. The furnace was held at 600 °C for 180 minutes, then up to 1000 °C with a ramp rate of 1 °C/min which was held for 60 minutes. The furnace was then cooled from 1000 °C to 600 °C at a ramp rate of 1°C/min, and from 600 °C to 450 °C and then to 300 °C at a ramp rate of 2 °C/min. The furnace was held at 600 °C, 450 °C and 300 °C for 60 minutes each. It was finally cooled to RT at a ramp rate of 2 °C/min.

[0163] Figure 6 shows the produced 3D printed silicon carbide and silicon oxycarbide composite electrodes. The electrodes were found to be hierarchically porous as shown in the inset SEM image of Figure 6. Their 4-point probe electrical conductivity test reported

a sheet resistance of 12.4 M Ω /square, electrical resistivity of 3.1 k Ω /m, and electrical conductivity of 321 μ S/m.

[0164] Example 5 – Conductive Ceramic: Carbon-Enriched Black Glass Electrodes

[0165] *A first photopolymerisable organosilicon monomer + a first photopolymerisable organosilicon monomer + ceramic particles + graphene particles*

[0166] A resin was prepared by mixing 100 parts of (Mercaptopropyl) methylsiloxane homopolymer (ca. 55% ceramic yield) and 100 parts of methacryloxypropyl terminated polydimethylsiloxane (ca. 18% ceramic yield) with 0.9 parts of phenylbis (2,4,6-trimethylbenzoyl) phosphine oxide and 0.8 parts of w/w tert-Butylhydroquinone (TBHQ). Porous silicon dioxide nanoparticles (spherical, 5-20 nm) (5% w/w) were added to this resin. Finally, 2.5 w/w% of graphene micron-sized particles were added to the resin. The resin components were mixed thoroughly on a vortex mixer and sonication bath, and then the prepared resin was vacuumed for 15 minutes.

[0167] The resin was 3D printed using a digital light projection (DLP) printer, Miicraft Ultra, as per the manufacturer's standard operating procedure, to produce a 3D-printed electrically conductive green body.

[0168] The green body was pyrolysed under a vacuum (12 mbar pressure) in a tube furnace. The pyrolysis was performed with a ramp rate of 1 °C/min from RT to 100 °C, followed by 0.2 °C/min from 100 °C to 600 °C. The furnace was held at 600 °C for 180 minutes, then up to 1000°C with a ramp rate of 1 °C/min which was held for 60 minutes. The furnace was then cooled from 1000 °C to 600 °C at a ramp rate of 1°C/min, and from 600 °C to 450 °C and then to 300 °C at a ramp rate of 2 °C/min. The furnace was held at 600 °C, 450 °C and 300 °C for 60 minutes each. It was finally cooled to RT at a ramp rate of 2 °C/min.

[0169] Figure 7 shows the produced 3D printed carbon-enriched black glass electrodes. The electrodes were found to be hierarchically porous as shown in the inset SEM image of Figure 7. The 4-point probe electrical conductivity test reported a sheet resistance of 24.7 k Ω /square, electrical resistivity of 12.4 Ω /m, and electrical conductivity of 80.7 mS/m.

[0170] Example 6 – Conductive Ceramic: Carbon-Enriched Black Glass Electrodes

[0171] *A first photopolymerisable organosilicon monomer + a first photopolymerisable organosilicon monomer + ceramic particles + graphene particles*

[0172] A resin was prepared by mixing 100 parts of (Mercaptopropyl) methylsiloxane homopolymer (ca. 55% ceramic yield) and 70 parts of vinylmethoxysiloxane homopolymer (ca. 50% ceramic yield) with 0.9 parts of phenylbis (2,4,6-trimethylbenzoyl) phosphine oxide and 0.8 parts of w/w tert-Butylhydroquinone (TBHQ). Porous silicon dioxide nanoparticles (spherical, 5-20 nm) (5% w/w) were added to this resin. Finally, 2.3 w/w% of micron-sized graphene particles (1.5 μm diameter) was added. The resin components were mixed thoroughly on a vortex mixer and sonication bath, and then the prepared resin was vacuumed for 15 minutes.

[0173] The resin was 3D printed using a digital light projection (DLP) printer, Miicraft Ultra, as per the manufacturer's standard operating procedure, to produce a 3D-printed electrically conductive green body.

[0174] The green body was pyrolysed under Vacuum (12 mbar pressure) in a tube furnace. The pyrolysis was performed with a ramp rate of 1 °C/min from RT to 100 °C, followed by 0.2 °C/min from 100 °C to 600 °C. The furnace was held at 600 °C for 180 minutes, then ramped up to 1000 °C with a ramp rate of 1 °C/min where it was held for 60 minutes. The furnace was then cooled from 1000 °C to 600 °C at a ramp rate of 1 °C/min, and from 600 °C to 450 °C and then to 300 °C at a ramp rate of 2 °C/min. The furnace was held at 600 °C, 450 °C, and 300 °C for 60 minutes each. It was finally cooled to RT at a ramp rate of 2 °C/min.

[0175] The 4-point probe electrical conductivity test reported a sheet resistance of 13.7 k Ω /square, electrical resistivity of 19.8 Ω /m, and electrical conductivity of 52 mS/m.

[0176] Example 7 – Conductive Ceramic: Ceramic Electrodes

[0177] *A photopolymerisable organosilicon monomer + a photopolymerisable organic monomer + ceramic particles + graphene particles*

[0178] A resin was prepared by mixing 100 parts of (Mercaptopropyl) methylsiloxane homopolymer and 54.35 parts of Poly (ethylene glycol) diacrylate (average Mn 250) with 0.9 parts of phenylbis (2,4,6-trimethylbenzoyl) phosphine oxide and 0.8 parts of w/w tert-Butylhydroquinone (TBHQ). Non-porous silicon dioxide nanoparticles (spherical, 10-20 nm) (4.5 % w/w) were added to the resin. Finally, 2.3 w/w% of micron-sized graphene

particles (1.5 μm diameter) were added to the resin. The resin components were mixed thoroughly on a vortex mixer and sonication bath.

[0179] The resin was 3D printed using a digital light projection (DLP) printer, Miicraft Ultra, as per the manufacturer's standard operating procedure, to produce a 3D-printed electrically conductive green body.

[0180] The green body was pyrolysed under vacuum (12 mbar pressure) in a tube furnace. The pyrolysis was performed with a ramp rate of 1 $^{\circ}\text{C}/\text{min}$ from RT to 100 $^{\circ}\text{C}$, followed by 0.2 $^{\circ}\text{C}/\text{min}$ from 100 $^{\circ}\text{C}$ to 600 $^{\circ}\text{C}$. The furnace was held at 600 $^{\circ}\text{C}$ for 180 minutes, then ramped up to 1000 $^{\circ}\text{C}$ with a ramp rate of 1 $^{\circ}\text{C}/\text{min}$ which was held for 60 minutes. The furnace was then cooled from 1000 $^{\circ}\text{C}$ to 600 $^{\circ}\text{C}$ at a ramp rate of 1 $^{\circ}\text{C}/\text{min}$, and from 600 $^{\circ}\text{C}$ to 450 $^{\circ}\text{C}$ and then to 300 $^{\circ}\text{C}$ at a ramp rate of 2 $^{\circ}\text{C}/\text{min}$. The furnace was held at 600 $^{\circ}\text{C}$, 450 $^{\circ}\text{C}$ and 300 $^{\circ}\text{C}$ for 60 minutes each. It was finally cooled to RT at a ramp rate of 2 $^{\circ}\text{C}/\text{min}$.

[0181] Example 8 – Conductive Ceramic: Ceramic Electrodes

[0182] *A photopolymerisable organosilicon monomer + a crosslinking agent + SiC particles*

[0183] A resin was prepared by mixing 100 parts of allylhydridopolycarbosilane and 50 parts of 1,6-hexanedithiol with 0.9 parts of phenylbis (2,4,6-trimethylbenzoyl) phosphine oxide and 0.8 parts of w/w tert-Butylhydroquinone (TBHQ). Finally, 5 w/w% of silicon carbide nanoparticles (20 nm, laser synthesised) were added. The resin components were mixed thoroughly on a vortex mixer and sonication bath, and then the prepared resin was vacuumed for 15 minutes.

[0184] The resin was 3D printed using a digital light projection (DLP) printer, Miicraft Ultra, as per the manufacturer's standard operating procedure, to produce a 3D-printed electrically conductive green body.

[0185] The green body was pyrolysed under vacuum (12 mbar pressure) in a tube furnace. The pyrolysis was performed with a ramp rate of 1 $^{\circ}\text{C}/\text{min}$ from RT to 100 $^{\circ}\text{C}$, followed by 0.2 $^{\circ}\text{C}/\text{min}$ from 100 $^{\circ}\text{C}$ to 600 $^{\circ}\text{C}$. The furnace was held at 600 $^{\circ}\text{C}$ for 180 minutes. The furnace was then cooled from 600 $^{\circ}\text{C}$ to 450 $^{\circ}\text{C}$ and then to 300 $^{\circ}\text{C}$ at a ramp rate of 2 $^{\circ}\text{C}/\text{min}$. The furnace was held at 450 $^{\circ}\text{C}$ and 300 $^{\circ}\text{C}$ for 60 minutes each. It was finally cooled to RT at a ramp rate of 2 $^{\circ}\text{C}/\text{min}$.

[0186] Example 9 – Conductive Ceramic

[0187] *A photopolymerisable organosilicon monomer + a photopolymerisable organic monomer + ceramic particles + carbon nanotubes*

[0188] A resin was prepared by mixing 100 parts of (Mercaptopropyl) methylsiloxane homopolymer and 54.35 parts of Poly (ethylene glycol) diacrylate (average Mn 250) with 0.9 parts of phenylbis (2,4,6-trimethylbenzoyl) phosphine oxide and 0.8 parts of w/w tert-Butylhydroquinone (TBHQ). Porous silicon dioxide nanoparticles (spherical, 5-20 nm) (5% w/w) were added to this resin. Finally, 5 w/w% of multi-walled carbon nanotube (3 ~ 12 μm) were added. The resin components were mixed thoroughly on a vortex mixer and sonication bath.

[0189] The resin was 3D printed using a digital light projection (DLP) printer, Miicraft Ultra, as per the manufacturer's standard operating procedure, to produce a 3D-printed electrically conductive green body.

[0190] The green body was pyrolysed under vacuum (0.3 mbar pressure) in a tube furnace. The pyrolysis was performed with a ramp rate of 1 °C/min from RT to 100 °C, followed by 0.2 °C/min from 100 °C to 600 °C. The furnace was held at 600 °C for 180 minutes, then up to 1000 °C with a ramp rate of 1 °C/min which was held for 60 minutes. The furnace was then cooled from 1000 °C to 600 °C at a ramp rate of 1 °C/min, and from 600 °C to 450 °C and then to 300 °C at a ramp rate of 2 °C/min. The furnace was held at 600 °C, 450 °C and 300 °C for 60 minutes each. It was finally cooled to RT at a ramp rate of 7 °C/min.

[0191] Figure 8 shows the produced 3D printed carbon-enriched black glass disc. The disc was found to be hierarchically porous as shown in the inset SEM image. The 4-point probe electrical conductivity test reported a sheet resistance of 24.6 Ω/square , electrical resistivity of 8 m Ω/m , and electrical conductivity of 124.7 S/m.

[0192] Example 10 – Conductive Polymer

[0193] *A photopolymerisable organosilicon monomer + a photopolymerisable organic monomer + ceramic particles + carbon nanotubes*

[0194] A resin was prepared by mixing 100 parts of (Mercaptopropyl) methylsiloxane homopolymer and 54.35 parts of Poly (ethylene glycol) diacrylate (average Mn 250) with 0.9 parts of phenylbis (2,4,6-trimethylbenzoyl) phosphine oxide and 0.8 parts of w/w tert-Butylhydroquinone (TBHQ). Porous silicon dioxide nanoparticles (spherical, 5-20 nm)

(5% w/w) were added to this resin. Finally, 5 w/w% of multi-walled carbon nanotube (3 ~ 12 μm) were added. The resin components were mixed thoroughly on a vortex mixer and sonication bath.

[0195] The resin was 3D printed using a digital light projection (DLP) printer, Miicraft Ultra, as per the manufacturer's standard operating procedure, to produce a 3D-printed electrically conductive polydimethylsiloxane polymeric material.

[0196] Figure 9 shows the produced 3D printed carbon-enriched polydimethylsiloxane polymeric disc. The disc was found to be hierarchically porous as shown in the inset SEM image. The 4-point probe electrical conductivity test reported a sheet resistance of 1.3 k Ω /square, electrical resistivity of 2.7 Ω /m, and electrical conductivity of 356 mS/m.

[0197] Example 11 – Conductive Ceramic

[0198] *A photopolymerisable organosilicon monomer + a photopolymerisable organic monomer + ceramic particles + carbon nanotubes*

[0199] A resin was prepared by mixing 100 parts of (Mercaptopropyl) methylsiloxane homopolymer and 54.35 parts of Poly (ethylene glycol) diacrylate (average M_n 250) with 0.9 parts of phenylbis (2,4,6-trimethylbenzoyl) phosphine oxide and 0.8 parts of w/w tert-Butylhydroquinone (TBHQ). Porous silicon dioxide nanoparticles (spherical, 5-20 nm) (5% w/w) were added to this resin. Finally, 4 w/w% of multi-walled carbon nanotube (3 ~ 12 μm) was added. The resin components were mixed thoroughly on a vortex mixer and sonication bath.

[0200] The resin was 3D printed using a digital light projection (DLP) printer, Miicraft Ultra, as per the manufacturer's standard operating procedure, to produce a 3D-printed electrically conductive green body.

[0201] The green body was pyrolysed under vacuum (0.3 mbar pressure) in a tube furnace. The pyrolysis was performed with a ramp rate of 1 $^{\circ}\text{C}/\text{min}$ from RT to 100 $^{\circ}\text{C}$, followed by 0.2 $^{\circ}\text{C}/\text{min}$ from 100 $^{\circ}\text{C}$ to 600 $^{\circ}\text{C}$. The furnace was held at 600 $^{\circ}\text{C}$ for 180 minutes. The furnace was then cooled from 600 $^{\circ}\text{C}$ to 450 $^{\circ}\text{C}$ and then to 300 $^{\circ}\text{C}$ at a ramp rate of 2 $^{\circ}\text{C}/\text{min}$. The furnace was held at 600 $^{\circ}\text{C}$, 450 $^{\circ}\text{C}$ and 300 $^{\circ}\text{C}$ for 60 minutes each. It was finally cooled to RT at a ramp rate of 7 $^{\circ}\text{C}/\text{min}$.

[0202] Figure 10 shows the produced 3D printed carbon-enriched black glass electrode. The electrodes were found to be hierarchically porous as shown in the inset SEM image of Figure 10. Their 4-point probe electrical conductivity test reported a sheet resistance

of 1.154 k Ω /square, electrical resistivity of 966.7 m Ω /m, and electrical conductivity of 6.1 S/m.

[0203] Example 12 – Conductive Polymer

[0204] *A photopolymerisable organosilicon monomer + a photopolymerisable organic monomer + ceramic particles + carbon nanotubes*

[0205] A resin was prepared by mixing 100 parts of (Mercaptopropyl) methylsiloxane homopolymer and 54.35 parts of Poly (ethylene glycol) diacrylate (average Mn 250) with 0.9 parts of phenylbis (2,4,6-trimethylbenzoyl) phosphine oxide and 0.8 parts of w/w tert-Butylhydroquinone (TBHQ). Porous silicon dioxide nanoparticles (spherical, 5-20 nm) (5% w/w) were added to this resin. Finally, 4 w/w% of multi-walled carbon nanotube (3 ~ 12 μ m) were added. The resin components were mixed thoroughly on a vortex mixer and sonication bath.

[0206] The resin was 3D printed using a digital light projection (DLP) printer, Miicraft Ultra, as per the manufacturer's standard operating procedure, to produce a 3D-printed electrically conductive polydimethylsiloxane polymeric material.

[0207] The 4-point probe electrical conductivity test reported an electrical resistivity of 27.5 Ω /m, and electrical conductivity of 36.2 mS/m.

[0208] Example 13 – Conductive Polymer

[0209] *A photopolymerisable organosilicon monomer + a photopolymerisable organic monomer + ceramic particles + carbon nanotubes*

[0210] A resin was prepared by mixing 100 parts of (Mercaptopropyl) methylsiloxane homopolymer and 54.35 parts of Poly (ethylene glycol) diacrylate (average Mn 250) with 0.9 parts of phenylbis (2,4,6-trimethylbenzoyl) phosphine oxide and 0.8 parts of w/w tert-Butylhydroquinone (TBHQ). Porous silicon dioxide nanoparticles (spherical, 5-20 nm) (5% w/w) were added to this resin. Finally, 3 w/w% of multi-walled carbon nanotube (3 ~ 12 μ m) were added. The resin components were mixed thoroughly on a vortex mixer and sonication bath.

[0211] The resin was 3D printed using a digital light projection (DLP) printer, Miicraft Ultra, as per the manufacturer's standard operating procedure, to produce a 3D-printed electrically conductive polydimethylsiloxane polymeric material.

[0212] The 4-point probe electrical conductivity test reported an electrical resistivity of 175 Ω /m, and electrical conductivity of 5.7 mS/m.

[0213] Example 14 – Conductive Polymer

[0214] *A photopolymerisable organosilicon monomer + a photopolymerisable organic monomer + ceramic particles + carbon nanotubes*

[0215] A resin was prepared by mixing 100 parts of (Mercaptopropyl) methylsiloxane homopolymer and 54.35 parts of Poly (ethylene glycol) diacrylate (average Mn 250) with 0.9 parts of phenylbis (2,4,6-trimethylbenzoyl) phosphine oxide and 0.8 parts of w/w tert-Butylhydroquinone (TBHQ). Porous silicon dioxide nanoparticles (spherical, 5-20 nm) (5% w/w) were added to this resin. Finally, 2 w/w% of multi-walled carbon nanotube (3 ~ 12 µm) were added. The resin components were mixed thoroughly on a vortex mixer and sonication bath.

[0216] The resin was 3D printed using a digital light projection (DLP) printer, Miicraft Ultra, as per the manufacturer's standard operating procedure, to produce a 3D-printed electrically conductive polydimethylsiloxane polymeric material.

[0217] The 4-point probe electrical conductivity test reported an electrical resistivity of 29.9 KΩ/m, and electrical conductivity of 33.4 uS/m.

[0218] Example 15 – Conductive Ceramic

[0219] *A photopolymerisable organosilicon monomer + a photopolymerisable organic monomer + ceramic particles + carbon nanotubes*

[0220] A resin was prepared by mixing 100 parts of (Mercaptopropyl) methylsiloxane homopolymer and 54.35 parts of Poly (ethylene glycol) diacrylate (average Mn 250) with 0.9 parts of phenylbis (2,4,6-trimethylbenzoyl) phosphine oxide and 0.8 parts of w/w tert-Butylhydroquinone (TBHQ). Porous silicon dioxide nanoparticles (spherical, 5-20 nm) (5% w/w) were added to this resin. Finally, 1 w/w% of multi-walled carbon nanotube (3 ~ 12 µm) were added. The resin components were mixed thoroughly on a vortex mixer and sonication bath.

[0221] The resin was 3D printed using a digital light projection (DLP) printer, Miicraft Ultra, as per the manufacturer's standard operating procedure, to produce a 3D-printed electrically conductive green body.

[0222] The green body was pyrolysed under vacuum (0.05 mbar pressure) in a tube furnace. The pyrolysis was performed with a ramp rate of 1 °C/min from RT to 100 °C, followed by 0.2 °C/min from 100 °C to 600 °C. The furnace was held at 600 °C for 180 minutes. The furnace was then cooled from 600 °C to 450 °C and then to 300 °C at a

ramp rate of 2 °C/min. The furnace was held at 450 °C and 300 °C for 60 minutes each. It was finally cooled to RT at a ramp rate of 7 °C/min.

[0223] The 4-point probe electrical conductivity test reported an electrical resistivity of 4 Ω/m, and electrical conductivity of 256 mS/m.

[0224] Example 16 – Conductive Ceramic

[0225] *A photopolymerisable organosilicon monomer + a photopolymerisable organic monomer + ceramic particles + carbon nanotubes*

[0226] A resin was prepared by mixing 100 parts of (Mercaptopropyl) methylsiloxane homopolymer and 54.35 parts of Poly (ethylene glycol) diacrylate (average Mn 250) with 0.9 parts of phenylbis (2,4,6-trimethylbenzoyl) phosphine oxide and 0.8 parts of w/w tert-Butylhydroquinone (TBHQ). Porous silicon dioxide nanoparticles (spherical, 5-20 nm) (5% w/w) were added to this resin. Finally, 2 w/w% of multi-walled carbon nanotube (3 ~ 12 µm) were added. The resin components were mixed thoroughly on a vortex mixer and sonication bath.

[0227] The resin was 3D printed using a digital light projection (DLP) printer, Miicraft Ultra, as per the manufacturer's standard operating procedure, to produce a 3D-printed electrically conductive green body.

[0228] The green body was pyrolysed under vacuum (0.05 mbar pressure) in a tube furnace. The pyrolysis was performed with a ramp rate of 1 °C/min from RT to 100 °C, followed by 0.2 °C/min from 100 °C to 600 °C. The furnace was held at 600 °C for 180 minutes. The furnace was then cooled from 600 °C to 450 °C and then to 300 °C at a ramp rate of 2 °C/min. The furnace was held at 450 °C and 300 °C for 60 minutes each. It was finally cooled to RT at a ramp rate of 7 °C/min.

[0229] The 4-point probe electrical conductivity test reported an electrical resistivity of 0.96 Ω/m, and electrical conductivity of 1.04 S/m. Brunauer-Emmett-Teller (BET) surface area analysis reported a surface area of 119.35 m²/g.

[0230] Example 17 – Conductive Ceramic

[0231] *A photopolymerisable organosilicon monomer + a photopolymerisable organic monomer + ceramic particles + carbon nanotubes*

[0232] A resin was prepared by mixing 100 parts of (Mercaptopropyl) methylsiloxane homopolymer and 54.35 parts of Poly (ethylene glycol) diacrylate (average Mn 250) with 0.9 parts of phenylbis (2,4,6-trimethylbenzoyl) phosphine oxide and 0.8 parts of w/w tert-

Butylhydroquinone (TBHQ). Porous silicon dioxide nanoparticles (spherical, 5-20 nm) (5% w/w) were added to this resin. Finally, 3 w/w% of multi-walled carbon nanotube (3 ~ 12 μm) were added. The resin components were mixed thoroughly on a vortex mixer and sonication bath.

[0233] The resin was 3D printed using a digital light projection (DLP) printer, Miicraft Ultra, as per the manufacturer's standard operating procedure, to produce a 3D-printed electrically conductive green body.

[0234] The green body was pyrolysed under vacuum (0.05 mbar pressure) in a tube furnace. The pyrolysis was performed with a ramp rate of 1 $^{\circ}\text{C}/\text{min}$ from RT to 100 $^{\circ}\text{C}$, followed by 0.2 $^{\circ}\text{C}/\text{min}$ from 100 $^{\circ}\text{C}$ to 600 $^{\circ}\text{C}$. The furnace was held at 600 $^{\circ}\text{C}$ for 180 minutes. The furnace was then cooled from 600 $^{\circ}\text{C}$ to 450 $^{\circ}\text{C}$ and then to 300 $^{\circ}\text{C}$ at a ramp rate of 2 $^{\circ}\text{C}/\text{min}$. The furnace was held at 450 $^{\circ}\text{C}$ and 300 $^{\circ}\text{C}$ for 60 minutes each. It was finally cooled to RT at a ramp rate of 7 $^{\circ}\text{C}/\text{min}$.

[0235] The 4-point probe electrical conductivity test reported an electrical resistivity of 117.5 m Ω/m , and electrical conductivity of 8.5 S/m. Brunauer-Emmett-Teller (BET) surface area analysis reported a surface area of 410.5 m $^2/\text{g}$.

[0236] Example 18 – Conductive Ceramic

[0237] *A photopolymerisable organosilicon monomer + a photopolymerisable organic monomer + ceramic particles + carbon nanotubes*

[0238] A resin was prepared by mixing 100 parts of (Mercaptopropyl) methylsiloxane homopolymer and 54.35 parts of Poly (ethylene glycol) diacrylate (average Mn 250) with 0.9 parts of phenylbis (2,4,6-trimethylbenzoyl) phosphine oxide and 0.8 parts of w/w tert-Butylhydroquinone (TBHQ). Porous silicon dioxide nanoparticles (spherical, 5-20 nm) (5% w/w) were added to this resin. Finally, 4 w/w% of multi-walled carbon nanotube (3 ~ 12 μm) were added. The resin components were mixed thoroughly on a vortex mixer and sonication bath.

[0239] The resin was 3D printed using a digital light projection (DLP) printer, Miicraft Ultra, as per the manufacturer's standard operating procedure, to produce a 3D-printed electrically conductive green body.

[0240] The green body was pyrolysed under vacuum (0.05 mbar pressure) in a tube furnace. The pyrolysis was performed with a ramp rate of 1 $^{\circ}\text{C}/\text{min}$ from RT to 100 $^{\circ}\text{C}$, followed by 0.2 $^{\circ}\text{C}/\text{min}$ from 100 $^{\circ}\text{C}$ to 600 $^{\circ}\text{C}$. The furnace was held at 600 $^{\circ}\text{C}$ for 180

minutes. The furnace was then cooled from 600 °C to 450 °C and then to 300 °C at a ramp rate of 2 °C/min. The furnace was held at 450 °C and 300 °C for 60 minutes each. It was finally cooled to RT at a ramp rate of 7 °C/min.

[0241] Figure 15 shows a BET isotherm for the produced PDC material. The 4-point probe electrical conductivity test reported an electrical resistivity of 60.5 mΩ/m, and electrical conductivity of 16.5 S/m. Brunauer-Emmett-Teller (BET) surface area analysis reported a surface area of 423.9 m²/g.

[0242] Example 19 – Conductive Ceramic

[0243] *A photopolymerisable organosilicon monomer + a photopolymerisable organic monomer + ceramic particles + carbon nanotubes*

[0244] A resin was prepared by mixing 100 parts of (Mercaptopropyl) methylsiloxane homopolymer and 54.35 parts of Poly (ethylene glycol) diacrylate (average Mn 250) with 0.9 parts of phenylbis (2,4,6-trimethylbenzoyl) phosphine oxide and 0.8 parts of w/w tert-Butylhydroquinone (TBHQ). Porous silicon dioxide nanoparticles (spherical, 5-20 nm) (5% w/w) were added to this resin. Finally, 1 w/w% of multi-walled carbon nanotube (3 ~ 12 μm) were added. The resin components were mixed thoroughly on a vortex mixer and sonication bath.

[0245] The resin was 3D printed using a digital light projection (DLP) printer, Miicraft Ultra, as per the manufacturer's standard operating procedure, to produce a 3D-printed electrically conductive green body.

[0246] The green body was pyrolysed under vacuum (0.05 mbar pressure) in a tube furnace. The pyrolysis was performed with a ramp rate of 1 °C/min from RT to 100 °C, followed by 0.2 °C/min from 100 °C to 600 °C. The furnace was held at 600 °C for 180 minutes, then ramped up to 1000 °C at a rate of 1 °C/min and held for 60 minutes. The furnace was then cooled from 1000 °C to 600 °C at a ramp rate of 1°C/min, and from 600 °C to 450 °C and then to 300 °C at a ramp rate of 2 °C/min. The furnace was held at 600 °C, 450 °C and 300 °C for 60 minutes each. It was finally cooled to RT at a ramp rate of 7 °C/min.

[0247] The 4-point probe electrical conductivity test reported an electrical resistivity of 2.8 Ω/m, and electrical conductivity of 360.5 mS/m. Brunauer-Emmett-Teller (BET) surface area analysis reported a surface area of 432.74 m²/g.

[0248] Example 20 – Conductive Ceramic

[0249] *A photopolymerisable organosilicon monomer + a photopolymerisable organic monomer + ceramic particles + carbon nanotubes*

[0250] A resin was prepared by mixing 100 parts of (Mercaptopropyl) methylsiloxane homopolymer and 54.35 parts of Poly (ethylene glycol) diacrylate (average Mn 250) with 0.9 parts of phenylbis (2,4,6-trimethylbenzoyl) phosphine oxide and 0.8 parts of w/w tert-Butylhydroquinone (TBHQ). Porous silicon dioxide nanoparticles (spherical, 5-20 nm) (5% w/w) were added to this resin. Finally, 2 w/w% of multi-walled carbon nanotube (3 ~ 12 μm) were added. The resin components were mixed thoroughly on a vortex mixer and sonication bath.

[0251] The resin was 3D printed using a digital light projection (DLP) printer, Miicraft Ultra, as per the manufacturer's standard operating procedure, to produce a 3D-printed electrically conductive green body.

[0252] The green body was pyrolysed under vacuum (0.05 mbar pressure) in a tube furnace. The pyrolysis was performed with a ramp rate of 1 °C/min from RT to 100 °C, followed by 0.2 °C/min from 100 °C to 600 °C. The furnace was held at 600 °C for 180 minutes, then ramped up to 1000 °C at a rate of 1 °C/min and held for 60 minutes. The furnace was then cooled from 1000 °C to 600 °C at a ramp rate of 1 °C/min, and from 600 °C to 450 °C and then to 300 °C at a ramp rate of 2 °C/min. The furnace was held at 600 °C, 450 °C and 300 °C for 60 minutes each. It was finally cooled to RT at a ramp rate of 7 °C/min.

[0253] Figure 11 shows a BET isotherm for the produced PDC material. The 4-point probe electrical conductivity test reported an electrical resistivity of 0.79 Ω/m , and electrical conductivity of 12.5 S/m. Brunauer-Emmett-Teller (BET) surface area analysis reported a surface area of 442.49 m^2/g .

[0254] Example 21 – Conductive Ceramic

[0255] *A photopolymerisable organosilicon monomer + a photopolymerisable organic monomer + ceramic particles + carbon nanotubes*

[0256] A resin was prepared by mixing 100 parts of (Mercaptopropyl) methylsiloxane homopolymer and 54.35 parts of Poly (ethylene glycol) diacrylate (average Mn 250) with 0.9 parts of phenylbis (2,4,6-trimethylbenzoyl) phosphine oxide and 0.8 parts of w/w tert-Butylhydroquinone (TBHQ). Porous silicon dioxide nanoparticles (spherical, 5-20 nm)

(5% w/w) were added to this resin. Finally, 3 w/w% of multi-walled carbon nanotube (3 ~ 12 μm) were added. The resin components were mixed thoroughly on a vortex mixer and sonication bath.

[0257] The resin was 3D printed using a digital light projection (DLP) printer, Miicraft Ultra, as per the manufacturer's standard operating procedure, to produce a 3D-printed electrically conductive green body.

[0258] The green body was pyrolysed under vacuum (0.05 mbar pressure) in a tube furnace. The pyrolysis was performed with a ramp rate of 1 °C/min from RT to 100 °C, followed by 0.2 °C/min from 100 °C to 600 °C. The furnace was held at 600 °C for 180 minutes, then ramped up to 1000 °C at a rate of 1 °C/min and held for 60 minutes. The furnace was then cooled from 1000 °C to 600 °C at a ramp rate of 1 °C/min, and from 600 °C to 450 °C and then to 300 °C at a ramp rate of 2 °C/min. The furnace was held at 600 °C, 450 °C and 300 °C for 60 minutes each. It was finally cooled to RT at a ramp rate of 7 °C/min.

[0259] Figure 12 shows a BET isotherm for the produced PDC material. The 4-point probe electrical conductivity test reported an electrical resistivity of 27.6 m Ω /m, and electrical conductivity of 36.2 S/m. Brunauer-Emmett-Teller (BET) surface area analysis reported a surface area of 419.01 m²/g.

[0260] Example 22 – Conductive Ceramic

[0261] *A photopolymerisable organosilicon monomer + a photopolymerisable organic monomer + ceramic particles + carbon nanotubes*

[0262] A resin was prepared by mixing 100 parts of (Mercaptopropyl) methylsiloxane homopolymer and 54.35 parts of Poly (ethylene glycol) diacrylate (average Mn 250) with 0.9 parts of phenylbis (2,4,6-trimethylbenzoyl) phosphine oxide and 0.8 parts of w/w tert-Butylhydroquinone (TBHQ). Porous silicon dioxide nanoparticles (spherical, 5-20 nm) (5% w/w) were added to this resin. Finally, 4 w/w% of multi-walled carbon nanotube (3 ~ 12 μm) were added. The resin components were mixed thoroughly on a vortex mixer and sonication bath.

[0263] The resin was 3D printed using a digital light projection (DLP) printer, Miicraft Ultra, as per the manufacturer's standard operating procedure, to produce a 3D-printed electrically conductive green body.

[0264] The green body was pyrolysed under vacuum (0.05 mbar pressure) in a tube

furnace. The pyrolysis was performed with a ramp rate of 1 °C/min from RT to 100 °C, followed by 0.2 °C/min from 100 °C to 600 °C. The furnace was held at 600 °C for 180 minutes, then ramped up to 1000 °C at a rate of 1 °C/min and held for 60 minutes. The furnace was then cooled from 1000 °C to 600 °C at a ramp rate of 1°C/min, and from 600 °C to 450 °C and then to 300 °C at a ramp rate of 2 °C/min. The furnace was held at 600 °C, 450 °C and 300 °C for 60 minutes each. It was finally cooled to RT at a ramp rate of 7 °C/min.

[0265] Figure 13 shows an SEM image for the produced PDC material. The 4-point probe electrical conductivity test reported an electrical resistivity of 9.9 mΩ/m, and electrical conductivity of 100.9 S/m.

[0266] Example 23 – Conductive Ceramic

[0267] *A photopolymerisable organosilicon monomer + a photopolymerisable organic monomer + ceramic particles + graphene oxide nanoplatelet*

[0268] A resin was prepared by mixing 100 parts of (Mercaptopropyl) methylsiloxane homopolymer and 54.35 parts of Poly (ethylene glycol) diacrylate (average Mn 250) with 0.9 parts of phenylbis (2,4,6-trimethylbenzoyl) phosphine oxide and 0.8 parts of w/w tert-Butylhydroquinone (TBHQ). Porous silicon dioxide nanoparticles (spherical, 5-20 nm) (5% w/w) were added to this resin. Finally, 4 w/w% of graphene oxide nanoplatelet (1 nm) was added. The resin components were mixed thoroughly on a vortex mixer and sonication bath, and then the prepared resin was vacuumed for 15 minutes.

[0269] The resin was 3D printed using a digital light projection (DLP) printer, Miicraft Ultra, as per the manufacturer's standard operating procedure, to produce a 3D-printed green body.

[0270] The green body was pyrolysed under vacuum (0.05 mbar pressure) in a tube furnace. The pyrolysis was performed with a ramp rate of 1 °C/min from RT to 100 °C, followed by 0.2 °C/min from 100 °C to 600 °C. The furnace was held at 600 °C for 180 minutes, then ramped up to 1200 °C at a rate of 1 °C/min and held for 60 minutes. The furnace was then cooled from 1200 °C to 600 °C at a ramp rate of 1°C/min, and from 600 °C to 450 °C and then to 300 °C at a ramp rate of 2 °C/min. The furnace was held at 600 °C, 450 °C, and 300 °C for 60 minutes each. It was finally cooled to RT at a ramp rate of 2 °C/min.

[0271] The 4-point probe electrical conductivity test reported an electrical resistivity of

30.7 mΩ/m, and electrical conductivity of 32.55 S/m. Brunauer-Emmett-Teller (BET) surface area analysis reported a surface area of 5.3 m²/g.

[0272] Example 24 – Conductive Ceramic

[0273] *A photopolymerisable organosilicon monomer + a photopolymerisable organic monomer + ceramic particles + graphene particles*

[0274] A resin was prepared by mixing 100 parts of (Mercaptopropyl) methylsiloxane homopolymer and 54.35 parts of Poly (ethylene glycol) diacrylate (average Mn 250) with 0.9 parts of phenylbis (2,4,6-trimethylbenzoyl) phosphine oxide and 0.8 parts of w/w tert-Butylhydroquinone (TBHQ). Porous silicon dioxide nanoparticles (spherical, 5-20 nm) (5% w/w) were added to this resin. Finally, 2.3 w/w% of micron-sized graphene particles (1.5 μm diameter) was added. The resin components were mixed thoroughly on a vortex mixer and sonication bath, and then the prepared resin was vacuumed for 15 minutes.

[0275] The resin was 3D printed using a digital light projection (DLP) printer, Miicraft Ultra, as per the manufacturer's standard operating procedure, to produce a 3D-printed green body.

[0276] The green body was pyrolysed under vacuum (0.05 mbar pressure) in a tube furnace. The pyrolysis was performed with a ramp rate of 1 °C/min from RT to 100 °C, followed by 0.2 °C/min from 100 °C to 600 °C. The furnace was held at 600 °C for 180 minutes, then ramped up to 1200 °C at a rate of 1 °C/min and held for 60 minutes. The furnace was then cooled from 1200 °C to 600 °C at a ramp rate of 1 °C/min, and from 600 °C to 450 °C and then to 300 °C at a ramp rate of 2 °C/min. The furnace was held at 600 °C, 450 °C, and 300 °C for 60 minutes each. It was finally cooled to RT at a ramp rate of 2 °C/min.

[0277] The 4-point probe electrical conductivity test reported an electrical resistivity of 47.9 mΩ/m, and electrical conductivity of 20.9 S/m.

[0278] Example 25 – Conductive Ceramic

[0279] *A photopolymerisable organosilicon monomer + a photopolymerisable organic monomer + carbon nanotubes*

[0280] A resin was prepared by mixing 100 parts of (Mercaptopropyl) methylsiloxane homopolymer and 54.35 parts of Poly (ethylene glycol) diacrylate (average Mn 250) with 0.9 parts of phenylbis (2,4,6-trimethylbenzoyl) phosphine oxide and 0.8 parts of w/w tert-Butylhydroquinone (TBHQ). Porous silicon dioxide nanoparticles (spherical, 5-20 nm)

(5% w/w) were added to this resin. Finally, 2 w/w% of multi-walled carbon nanotube (3 ~ 12 μm) were added. The resin components were mixed thoroughly on a vortex mixer and sonication bath.

[0281] The resin was 3D printed using a digital light projection (DLP) printer, Miicraft Ultra, as per the manufacturer's standard operating procedure, to produce a 3D-printed electrically conductive green body.

[0282] The green body was pyrolysed under vacuum (0.05 mbar pressure) in a tube furnace. The pyrolysis was performed with a ramp rate of 1 °C/min from RT to 100 °C, followed by 0.2 °C/min from 100 °C to 600 °C. The furnace was held at 600 °C for 180 minutes, then ramped up to 1200 °C at a rate of 1 °C/min and held for 60 minutes. The furnace was then cooled from 1200 °C to 600 °C at a ramp rate of 1 °C/min, and from 600 °C to 450 °C and then to 300 °C at a ramp rate of 2 °C/min. The furnace was held at 600 °C, 450 °C and 300 °C for 60 minutes each. It was finally cooled to RT at a ramp rate of 7 °C/min.

[0283] The 4-point probe electrical conductivity test reported an electrical resistivity of 26.4 m Ω /m, and electrical conductivity of 38 S/m.

[0284] Example 26 – Conductive Ceramic

[0285] *A photopolymerisable organosilicon monomer + a photopolymerisable organic monomer + carbon nanotubes*

[0286] A resin was prepared by mixing 100 parts of (Mercaptopropyl) methylsiloxane homopolymer and 54.35 parts of Poly (ethylene glycol) diacrylate (average Mn 250) with 0.9 parts of phenylbis (2,4,6-trimethylbenzoyl) phosphine oxide and 0.8 parts of w/w tert-Butylhydroquinone (TBHQ). Porous silicon dioxide nanoparticles (spherical, 5-20 nm) (5% w/w) were added to this resin. Finally, 3 w/w% of multi-walled carbon nanotube (3 ~ 12 μm) were added. The resin components were mixed thoroughly on a vortex mixer and sonication bath.

[0287] The resin was 3D printed using a digital light projection (DLP) printer, Miicraft Ultra, as per the manufacturer's standard operating procedure, to produce a 3D-printed electrically conductive green body.

[0288] The green body was pyrolysed under vacuum (0.05 mbar pressure) in a tube furnace. The pyrolysis was performed with a ramp rate of 1 °C/min from RT to 100 °C, followed by 0.2 °C/min from 100 °C to 600 °C. The furnace was held at 600 °C for 180

minutes, then ramped up to 1200 °C at a rate of 1 °C/min and held for 60 minutes. The furnace was then cooled from 1200 °C to 600 °C at a ramp rate of 1°C/min, and from 600 °C to 450 °C and then to 300 °C at a ramp rate of 2 °C/min. The furnace was held at 600 °C, 450 °C and 300 °C for 60 minutes each. It was finally cooled to RT at a ramp rate of 7 °C/min.

[0289] The 4-point probe electrical conductivity test reported an electrical resistivity of 16.7 mΩ/m, and electrical conductivity of 60 S/m.

[0290] Example 27 – Conductive Ceramic

[0291] *A photopolymerisable organosilicon monomer + a photopolymerisable organic monomer + carbon nanotubes*

[0292] A resin was prepared by mixing 100 parts of (Mercaptopropyl) methylsiloxane homopolymer and 54.35 parts of Poly (ethylene glycol) diacrylate (average Mn 250) with 0.9 parts of phenylbis (2,4,6-trimethylbenzoyl) phosphine oxide and 0.8 parts of w/w tert-Butylhydroquinone (TBHQ). Porous silicon dioxide nanoparticles (spherical, 5-20 nm) (5% w/w) were added to this resin. Finally, 4 w/w% of multi-walled carbon nanotube (3 ~ 12 μm) were added. The resin components were mixed thoroughly on a vortex mixer and sonication bath.

[0293] The resin was 3D printed using a digital light projection (DLP) printer, Miicraft Ultra, as per the manufacturer's standard operating procedure, to produce a 3D-printed electrically conductive green body.

[0294] The green body was pyrolysed under vacuum (0.05 mbar pressure) in a tube furnace. The pyrolysis was performed with a ramp rate of 1 °C/min from RT to 100 °C, followed by 0.2 °C/min from 100 °C to 600 °C. The furnace was held at 600 °C for 180 minutes, then ramped up to 1200 °C at a rate of 1 °C/min and held for 60 minutes. The furnace was then cooled from 1200 °C to 600 °C at a ramp rate of 1°C/min, and from 600 °C to 450 °C and then to 300 °C at a ramp rate of 2 °C/min. The furnace was held at 600 °C, 450 °C and 300 °C for 60 minutes each. It was finally cooled to RT at a ramp rate of 7 °C/min.

[0295] The 4-point probe electrical conductivity test reported an electrical resistivity of 8.8 mΩ/m, and electrical conductivity of 113.6 S/m. Brunauer-Emmett-Teller (BET) surface area analysis reported a surface area of 18.9 m²/g.

[0296] The above examples are only the preferred examples of the present disclosure. It shall be pointed out that various improvements and modifications could be made by those ordinarily skilled in the art without deviating from the principle of the present disclosure, which shall fall within the protection scope of the present disclosure.

[0297] It is to be understood that, if any prior art publication is referred to herein, such reference does not constitute an admission that the publication forms a part of the common general knowledge in the art, in Australia or any other country.

[0298] In the claims which follow and in the preceding description of the disclosure, except where the context requires otherwise due to express language or necessary implication, the word “comprise” or variations such as “comprises” or “comprising” is used in an inclusive sense, i.e. to specify the presence of the stated features but not to preclude the presence or addition of further features in various embodiments of the disclosure.

[0299] As used herein, except where the context requires otherwise due to express language or necessary implication, the articles “a” and “an” are used herein to refer to one or to more than one (i.e. to at least one) of the grammatical object of the article. By way of example, “an element” means one element or more than one element.

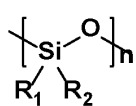
WHAT IS CLAIMED IS:

1. A resin for forming an electrically conductive polymeric or polymer-derived ceramic (PDC) material, said resin comprising: a photopolymerisable organosilicon monomer; and a conductivity additive.

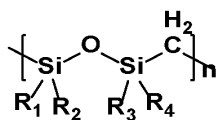
2. The resin according to claim 1, wherein the photopolymerisable organosilicon monomer is based on an organosilicon monomer selected from the group consisting of a polysiloxane, polycarbosiloxane, polysilsesquioxane, polycarbosilane, polysilylcarbodiimide, polysilsesquicarbodiimide, polysilazane, polysilsesquiazane, polyborosilane, polyborosiloxane and polyborosilazane.

3. The resin according to claim 1 or claim 2, wherein the photopolymerisable organosilicon monomer is based on an organosilicon monomer selected from the group consisting of:

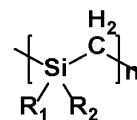
a) an organosilicon monomer having a chemical structure of Formula 1, Formula 2, Formula 3, Formula 4 or Formula 5:



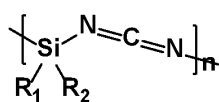
Formula 1



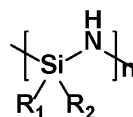
Formula 2



Formula 3



Formula 4



Formula 5

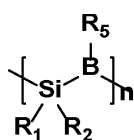
wherein:

n represents a backbone structure of repeating silicon atom-containing motifs and is independently an integer of from 2 to 15; and

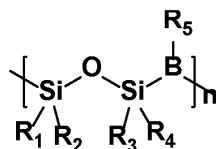
R₁, R₂, R₃ and R₄ are independently selected from the group consisting of H, a C₁-C₁₈ substituted or unsubstituted alkyl, a C₁-C₁₈ substituted or unsubstituted alkyl ether, a phenyl and a halide, independently for each integer of n, with the proviso that the pairs of R₁ and R₂ and R₃ and R₄ are not both H, alkyl ether or halide for every integer of n;

and

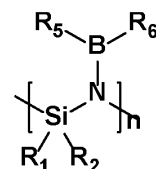
b) an organosilicon monomer having a chemical structure of Formula 6, Formula 7 or Formula 8:



Formula 6



Formula 7



Formula 8

wherein:

n represents a backbone structure of repeating silicon atom-containing motifs and is independently an integer of from 2 to 15;

R₁, R₂, R₃ and R₄ are as defined above; and

R₅ and R₆ are independently selected from the group consisting of H, OH, a C₁-C₁₈ substituted or unsubstituted alkyl, a C₁-C₁₈ substituted or unsubstituted alkyl ether and a phenyl, independently for each integer of n.

4. The resin according to any one of claims 1 to 3, wherein the photopolymerisable organosilicon monomer contains a photopolymerisable functional group selected from the group consisting of a hydroxyl, epoxide, vinyl, allyl, ethynyl, thiol, glycidyl, acrylate and thiocyanate.

5. The resin according to claim 4, wherein the photopolymerisable functional group is a thiol.

6. The resin according to any one of claims 1 to 5, wherein the conductivity additive is selected from the group consisting of a metal, metal alloy, inorganic metal compound, allotrope of carbon, and carbon-containing inorganic substance.

7. The resin according to any one of claims 1 to 6, wherein the conductivity additive is carbon nanotube.

8. The resin according to any one of claims 1 to 7, further comprising a

photopolymerisable organic monomer.

9. The resin according to claim 8, wherein the photopolymerisable organic monomer has the following formula:



wherein Spacer is a spacer group, L is a photopolymerisable functional group, and n is an integer of greater than or equal to 1.

10. The resin according to claim 9, wherein the photopolymerisable functional group is selected from the group consisting of a hydroxyl, epoxide, vinyl, allyl, ethynyl, thiol, glycidyl, acrylate and thiocyanate.

11. The resin according to claim 10, wherein the photopolymerisable functional group is an acrylate.

12. The resin according to any one of claims 8 to 11, wherein the photopolymerisable organic monomer is present in a 1:1 ratio with the photopolymerisable organosilicon monomers in respect of the photopolymerisable functional groups.

13. The resin according to any one of claims 1 to 12, further comprising structural particles.

14. The resin according to claim 13, wherein the structural particles are ceramic particles.

15. An electrically conductive polymeric or PDC material formed from a resin according to any one of claims 1 to 14 using a step of photopolymerisation.

16. An electrically conductive polymeric or PDC material according to claim 15, wherein the step of photopolymerisation is applied during a 3D printing process.

17. An electrically conductive polymeric material comprising: a photopolymerised

photopolymerisable organosilicon monomer; and a conductive substance.

18. The electrically conductive polymeric material according to any one of claims 15 to 17, having electrical conductivity of between 0.1 $\mu\text{S/m}$ and 1 S/m.

19. An electrically conductive PDC material comprising: a pyrolysed preceramic polymer, said preceramic polymer comprising a photopolymerised photopolymerisable organosilicon monomer and a conductivity additive; and a conductive substance.

20. The electrically conductive polymeric material according to any one of claims 15, 16 or 19, having electrical conductivity of between 0.1 $\mu\text{S/m}$ and 600 S/m.

21. A polymeric material for forming an electrically conductive PDC material, said polymeric material comprising: a photopolymerised photopolymerisable organosilicon monomer; and a conductivity additive.

22. An electrically conductive polymeric material, a polymeric material, or an electrically conductive PDC material according to any one of claims 15 to 21, wherein the polymeric material or preceramic polymer is 3D printed.

23. A method for forming an electrically conductive polymeric material, said method comprising subjecting a resin according to any one of claims 1 to 14 to photopolymerising conditions to form an electrically conductive polymeric material.

24. A method for forming an electrically conductive PDC material, said method comprising:

- a) subjecting a resin according to any one of claims 1 to 14 to photopolymerising conditions to form an optionally electrically conductive preceramic polymer; and
- b) subjecting the optionally electrically conductive preceramic polymer to pyrolytic conditions to form a conductive PDC material.

25. The method according to claim 23 or claim 24, wherein the photopolymerising conditions are applied during a 3D printing process.

26. A polymeric material, an electrically conductive polymeric material, or an electrically conductive PDC material, formed by a method according to any one of claims 23 to 25.