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(54) Title: COPOLYMER HYBRID AEROGELS BASED ON ISOCYANATE - CYCLIC ETHER - CLAY NETWORKS

(57) Abstract: An aerogel according to the present invention is obtained by reacting silanol moieties on a surface of a clay; an isocyanate compound A; an isocyanate compound B; a cyclic ether compound; a solvent A; and a solvent B. Aerogels according to the present invention have good mechanical properties and good thermal insulation properties.

Copolymer hybrid aerogels based on isocyanate – cyclic ether – clay networks

TECHNICAL FIELD

The present invention relates to an aerogel obtained by reacting silanol moieties on a surface of a clay; an isocyanate compound A; an isocyanate compound B; a cyclic ether compound; a solvent A; and a solvent B. Aerogels according to the present invention have good mechanical properties and good thermal insulation properties.

BACKGROUND

Aerogels are synthetic porous materials discovered by Kistler while trying to replace the solvent of a wet gel to a gas without causing shrinkage. Since then, several different materials and drying techniques have been investigated in order to simplify production process and to modify aerogels to be suitable for different applications.

Traditional thermal insulators are vastly based on fiberglass, mineral wool, cellulose, extruded or expanded polystyrene and polyurethane foams. Despite their low manufacturing costs, these insulation materials have certain limitations in performance. Aerogels, on the other hand, are produced by a different process, which leads to materials with a well-developed nanostructure, having noticeably smaller pores than those present in the traditional insulators. For this reason, aerogels outperform traditional thermal insulation materials.

Global market for thermal insulation is driven by strong focus on energy savings and growing awareness of the importance of insulation to improve industrial, domestic and transportation efficiencies. In some applications, it is possible to use a thick insulator panel to reduce the heat transfer. However, other applications may require thinner insulating layers because of size limitations. In these cases, the thermal conductivity of the material has to be extremely low in order to get the same insulating properties with a thinner layer. Aerogels are lightweight materials that show the lowest thermal conductivity of the thermal insulators currently in the market. Thus, thickness of the insulating layer can be reduced compared to a traditional insulating material, while obtaining corresponding insulating properties. Additionally, in some cases and depending on the application, high mechanical properties are also required.

on silica) display very good thermal insulating properties, however, they are very brittle and present significant dustiness. Low mechanical properties of silica based aerogels are generally attributed to the well-defined narrow inter-particle necks. On the other hand, organic aerogels are robust and mechanically stable, which represents an advantage for many applications. However, their thermal insulating properties are not as good as those of silica based aerogels. Despite of their high thermal insulating properties, a slow commercialization has been observed for inorganic aerogels due to their fragility and poor mechanical properties.

Organic aerogels emerged in the 1990's, and are based on polymeric networks, which are formed by cross-linking organic building blocks in a solution to yield a gel. First organic aerogels were based on phenol-formaldehyde resins, which can also be used to prepare carbon aerogels by pyrolysis. Other important materials to form organic aerogels are polyimides, polyamides and polyureas. Currently, numerous aerogels have also been made from biopolymers such as cellulose. Although these materials are normally more durable and have better mechanical properties, they show worse thermal insulating performance than silica based aerogels.

Hybrid aerogels take advantage of both approaches. Up to date, there is a broad aerogel landscape based on different strategies to reinforce inorganic materials. Different attempts to combine the low thermal conductivity of inorganic aerogels with the good mechanical properties of organic aerogels have been described. For example, by cross-linking these silica aerogels with organic polymers or by post-gelation casting of a polymer coating over the entire internal porous surface of the wet-gel nanostructure. In this sense, silica based aerogels were reinforced with isocyanate by reacting the –OH functionalized surface of the silica particles with the isocyanate, obtaining polyurethane. By these means, the mechanical properties were increased up to 300 times over pure silica aerogels while the density multiplied by three. In a similar manner, amino-functionalized silica aerogels were cross-linked with isocyanate, obtaining a polyurea. These polymer cross-linked aerogels tried to combine good mechanical properties, while maintaining low thermal conductivity. In addition, polyimide based aerogels have been prepared with amino-functionalized polysilsesquiloxanes, providing materials with as high as or higher modulus than previously reported silica-reinforced materials. Another approach involves the cross-linking of clay powders with polymeric chains in order to obtain a self-standing structure, which can then

alkoxysiloxane reaction blends was carried out, obtaining inorganic materials with soft and hard segments.

Another strategy is to copolymerize different materials having different material properties together. Indeed, copolymerization of several polymers is a technique employed to improve the properties of the final polymeric network based on the combination of the properties of the different monomers taking place in the reaction. For example, the crosslinking of polyimide through urea linkages obtaining a copolymer of polyamide and urea. Crosslinked polyamide-urea aerogel have demonstrated to have increased flexibility compared to polyamide aerogel due to the presence of urea linkages. In addition, a low shrinkage was demonstrated. As a drawback, the synthesis requires customized reactants and implies several steps. Another example is the crosslinking of benzoxazines with other monomers to get polybenzoxazine-copolymer aerogels. Mixtures of benzoxazines and co-monomers such as epoxy resins, dianhydrides, dicarboxylic acids and diisocyanates have been synthetized. The resulting aerogels have reduced brittleness compared to neat polybenzoxazine aerogels. However, relative long reaction time and high temperatures are required to obtain these aerogels.

Different drying techniques have also been investigated to obtain porous structures from sol-gel chemistry (figure 1 illustrates the steps in the formation of an aerogel). These drying processes can be classified as sub- and supercritical drying techniques. The main method for subcritical drying is ambient drying, which requires selection of appropriate solvents and temperature conditions. The most effective drying method is supercritical drying, which overcomes the problems of the subcritical drying. The process takes advantage of removing the initial solvent by using a supercritical fluid. By these means, the capillary forces exerted by the solvent due to its evaporation are minimized, and structures with large internal void spaces are achieved.

Although all above strategies resulted in a remarkable enhancement of the properties of the aerogels, there is still a need for aerogels, which have excellent thermal insulation properties, while mechanical properties are improved.

SHORT DESCRIPTION OF FIGURES

Figure 1 illustrates the steps of the formation of an aerogel.

The present invention relates to an aerogel obtained by reacting silanol moieties on a surface of a clay; an isocyanate compound A; an isocyanate compound B; a cyclic ether compound; a solvent A; and a solvent B.

The present invention also relates to a thermal insulating material and/or an acoustic insulating material comprising an aerogel according to the present invention.

The present invention encompasses the use of an aerogel according to the present invention as a thermal insulating material and/or acoustic insulating material.

The present invention also encompasses a method for preparing an aerogel according to the present invention comprising the steps of: 1) adding a clay into the mixture of solvent A and solvent B and mixing at high shear rates; 2) dissolving a cyclic ether compound into the mixture prepared in step 1; 3) adding an isocyanate compound B and mixing; 4) adding an isocyanate compound A and mixing; 5) adding a catalyst, if present and mixing; 6) letting the mixture to stand in order to form a gel; 7) exchanging the solvent of said gel with a solvent; and 8) drying said gel by supercritical or ambient drying.

DETAILED DESCRIPTION OF THE INVENTION

In the following passages the present invention is described in more detail. Each aspect so described may be combined with any other aspect or aspects unless clearly indicated to the contrary. In particular, any feature indicated as being preferred or advantageous may be combined with any other feature or features indicated as being preferred or advantageous.

In the context of the present invention, the terms used are to be construed in accordance with the following definitions, unless a context dictates otherwise.

As used herein, the singular forms “a”, “an” and “the” include both singular and plural referents unless the context clearly dictates otherwise.

The terms “comprising”, “comprises” and “comprised of” as used herein are synonymous with “including”, “includes” or “containing”, “contains”, and are inclusive or open-ended and do not exclude additional, non-recited members, elements or method steps.

The recitation of numerical end points includes all numbers and fractions subsumed within the respective ranges, as well as the recited end points.

unless otherwise indicated.

When an amount, a concentration or other values or parameters is/are expressed in form of a range, a preferable range, or a preferable upper limit value and a preferable lower limit value, it should be understood as that any ranges obtained by combining any upper limit or preferable value with any lower limit or preferable value are specifically disclosed, without considering whether the obtained ranges are clearly mentioned in the context.

All references cited in the present specification are hereby incorporated by reference in their entirety.

Unless otherwise defined, all terms used in disclosing the invention, including technical and scientific terms, have the meaning as commonly understood by one of the ordinary skill in the art to which this invention belongs to. By means of further guidance, term definitions are included to better appreciate the teaching of the present invention.

The aim of the present invention is to provide an aerogel material that overcomes the fragility of the inorganic aerogels, while maintaining its good thermal insulation properties. In the method according to the present invention, the gelation is carried out by reacting polyisocyanates with cyclic ether groups and polyisocyanates with silanol moieties on a surface of a clay. The resulting co-polymeric 3D network shows a combination of the properties of organic and inorganic materials. Aerogels according to the present invention have a good thermal performance, together with adjustable mechanical properties and non-existent dustiness.

In addition, morphology of the aerogels according to the present invention can be modified, by adjusting the ratio of the chemistries used. For example organic aerogels based on isocyanate and cyclic ether polymer networks have a globular morphology, wherein said particles are of nanometric size. On the other hand hybrid aerogels obtained by reacting an isocyanate compound and a clay in a presence of a solvent show a fibrillary structure of interconnected nanometric fibres.

Furthermore, aerogels according to the present invention can be easily reinforced with different materials due to the mild gelation conditions needed to prepare them.

By the term “wet gel” is meant herein a gel, which is obtained after mixing and reacting the reagents, while the solvent has not yet been extracted by supercritical conditions.

gel under supercritical conditions.

An aerogel according to the present invention is obtained by reacting silanol moieties on a surface of a clay; an isocyanate compound A; an isocyanate compound B; a cyclic ether compound; a solvent A; and a solvent B.

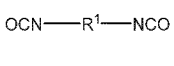
An isocyanate compound B reacts with the silanol moieties on a surface of a clay to form polyurethane components. Although, it may also form polyurea and polyisocyanurate components, however, in a lesser extent as a side reaction. On the other hand, an isocyanate compound A reacts with a cyclic ether compound to form a polyurethane, which is part of the copolymer hybrid network of the aerogel according to the present invention.

Figure 2 illustrates the formation of an aerogel according to the present invention. More specifically figure 2 illustrates how solution A and solution B are mixed in different volumetric ratios and subsequently a hybrid network of polyurethane and polyurea in a lesser extent is obtained.

Suitable isocyanate compound A and isocyanate compound B for use in the present invention are independently an aromatic isocyanate compound or an aliphatic isocyanate compound. Preferably, said isocyanate compound A is an aromatic isocyanate compound and said isocyanate compound B is an aliphatic isocyanate compound.

The reactivity of the aliphatic isocyanate compound B (aliphatic) to the epoxy compound is low, therefore, it is expected that most of isocyanate compound A (aromatic) is reacting with the epoxy, whereas most of the isocyanate compound B is reacting with the silanol moieties on a surface of a clay. However, the reaction of the aromatic isocyanate compound A to the clay is also possible, however only as a small side reaction.

Suitable isocyanate compound A and isocyanate compound B for use in the present invention are independently selected from the group consisting of



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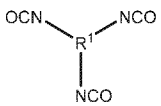

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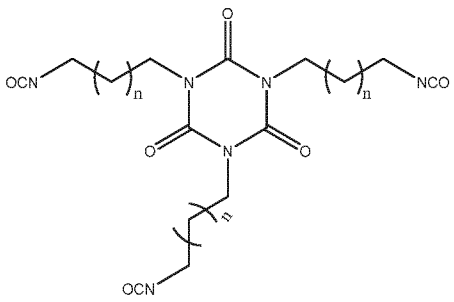

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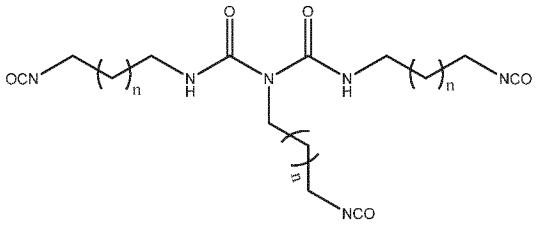

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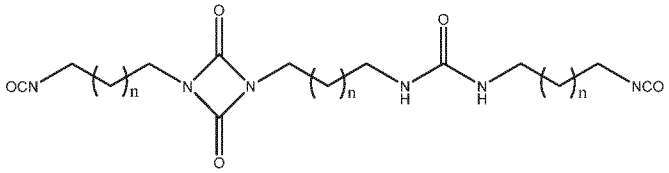

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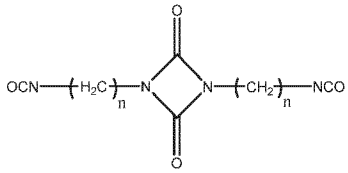
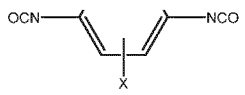


(8)

wherein R^1 is selected from the group consisting of a single bonded –O-, -S-, -C(O)-, -$S(O)_2$-, -$S(PO_3)$-, a substituted or unsubstituted C1-C30 alkyl group, a substituted or unsubstituted C3-C30 cycloalkyl group, a substituted or unsubstituted aryl group, a substituted or unsubstituted C7-C30 alkylaryl group, a substituted or unsubstituted C3-C30 heterocycloalkyl group and a substituted or unsubstituted C1-C30 heteroalkyl group and a combination of thereof; and an integer n is from 1 to 30;



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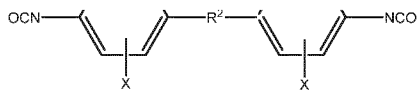

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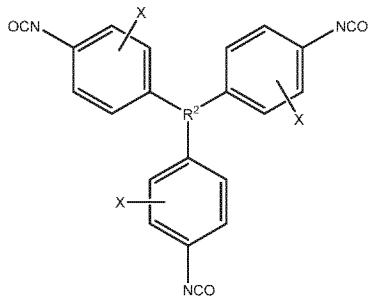

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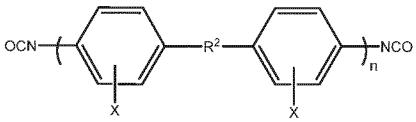
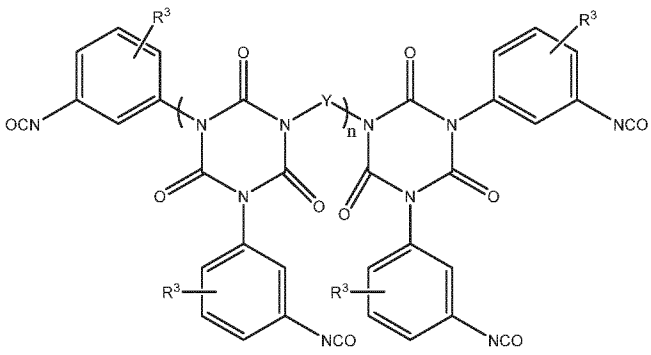
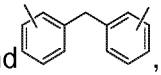


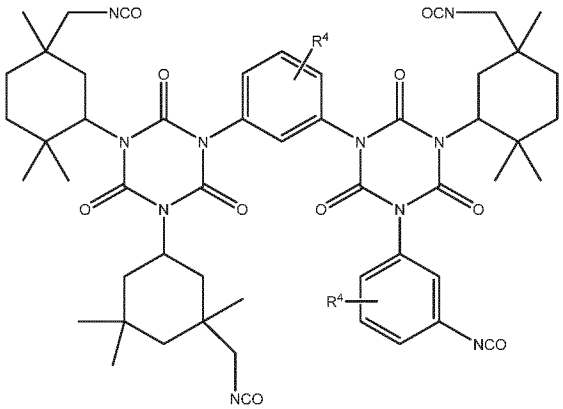
(12)

wherein X represents a substituent, or different substituents and are selected independently from the group consisting of hydrogen, halogen and linear or branched C1-C6 alkyl groups, attached on their respective phenyl ring at the 2-position, 3-position or 4-position, and their respective isomers, and R^2 is selected from the group consisting of a single bonded –O-, -S-, -C(O)-, -$S(O)_2$-, -$S(PO_3)$-, a substituted or unsubstituted C1-C30 alkyl group, a substituted or unsubstituted C3-C30 cycloalkyl group, a substituted or unsubstituted aryl group, a substituted or unsubstituted C7-C30 alkylaryl group, a substituted or unsubstituted C3-C30 heterocycloalkyl group and a substituted or unsubstituted C1-C30 heteroalkyl group from and a combination of thereof; and an integer n is from 1 to 30;



(13)

alkenyl, and Y is selected from the group consisting of  and  , and n is an integer from 0 to 3;



(14)

wherein R^4 is selected independently from the group consisting of alkyl, hydrogen and alkenyl.

Preferably isocyanate compound A and isocyanate compound B are independently selected from the group consisting of 1,3,5-tris(6-isocyanatohexyl)-1,3,5-triazinane-2,4,6-trione, 6-[3-(6-isocyanatohexyl)-2,4-dioxo-1,3-diazetidin-1-yl]hexyl N-(6-isocyanatohexyl) carbamate, 1,6-diisocyanatohexane, methylene diphenyl diisocyanate, 1-[bis(4-isocyanatophenyl)methyl]-4-isocyanatobenzene, 2,4-diisocyanato-1-methyl-benzene, oligomers of the above-mentioned and mixtures thereof.

More preferably isocyanate compound A is an aromatic isocyanate compound and selected from the group consisting of methylene diphenyl diisocyanate, 1-[bis(4-isocyanatophenyl)methyl]-4-isocyanatobenzene, 2,4-diisocyanato-1-methyl-benzene, oligomers of the above-mentioned and mixtures thereof; and isocyanate compound B is an aliphatic isocyanate compound and selected from the group consisting of 1,3,5-tris(6-isocyanatohexyl)-1,3,5-triazinane-2,4,6-trione, 6-[3-(6-isocyanatohexyl)-2,4-dioxo-1,3-diazetidin-1-yl]hexyl N-(6-isocyanatohexyl) carbamate, 1,6-diisocyanatohexane, oligomers of the above-mentioned and mixtures thereof.

Commercially available isocyanates for use in the present invention include, but are not limited to, Desmodur RE, Desmodur N3300, Desmodur N3200, Desmodur IL, and Desmodur HL from Bayer; Diphenylmethane 4,4'-diisocyanate (MDI) from Merck; and

Company.

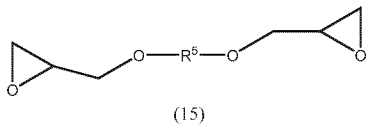
An aerogel according to the present invention has an isocyanate compound A content from 0.1 to 65% based on the weight of the solvent A, preferably from 1 to 40% and more preferably from 2 to 30%.

An aerogel according to the present invention has an isocyanate compound B content from 1 to 60% based on the weight of the solvent B, preferably from 2 to 40%, and more preferably from 5 to 25%.

These ranges are preferred because desired materials can be obtained: low thermal conductivity and shrinkage. In addition, the morphology of the material is different from aerogels described in the prior art. If the aerogel would exceed the quantity of isocyanate compound A or B, the obtained materials would have higher density in combination with too high thermal conductivity.

A cyclic ether compound reacts with the isocyanate compound A to form a urethane, which is part of the copolymer hybrid network of the aerogel according to the present invention. A suitable cyclic ether compound for use in the present invention is an epoxy compound or an oxetane compound.

When the cyclic ether compound is an epoxy compound, it is preferably selected from the group consisting of



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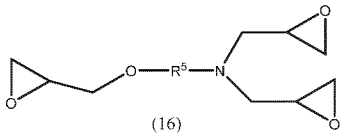

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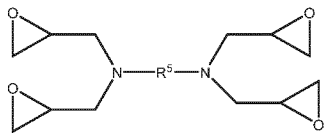

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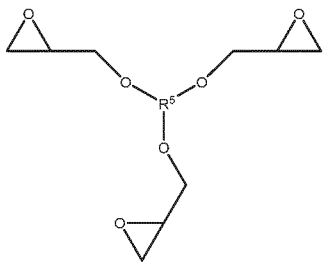

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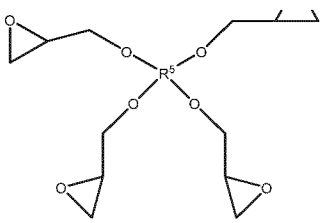

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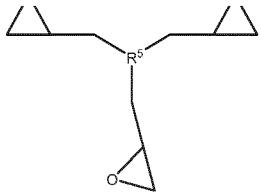

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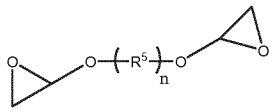
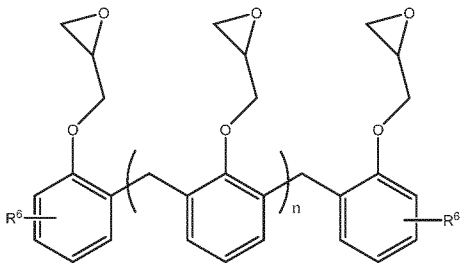


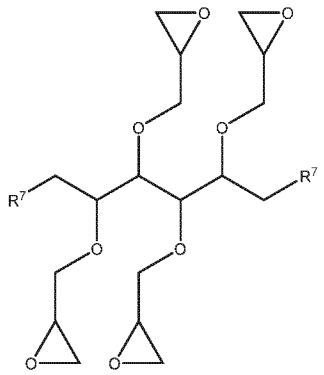
(21)

wherein R^5 is selected from the group consisting of a substituted or unsubstituted C1-C30 alkyl group, a substituted or unsubstituted C3-C30 cycloalkyl group, a substituted or unsubstituted aryl group, a substituted or unsubstituted C7-C30 alkylaryl group, a substituted or unsubstituted C3-C30 heterocycloalkyl group and a substituted or unsubstituted C1-C30 heteroalkyl group; and n is an integer from 1 to 30;



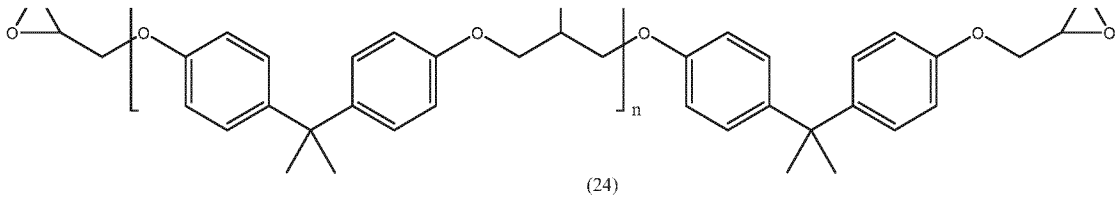
(22)

wherein R^6 is selected independently from the group consisting of hydrogen, halogen, alkyl and alkenyl; and n is an integer from 1 to 10;



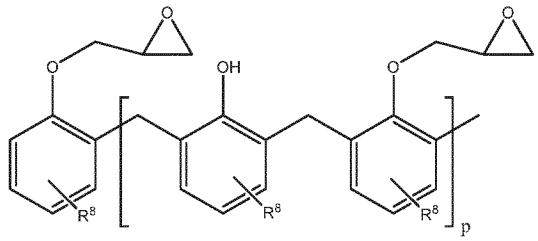
(23)

wherein R^7 is selected independently from the group consisting of hydrogen, hydroxyl,



(24)

wherein n is an integer from 0 to 16;



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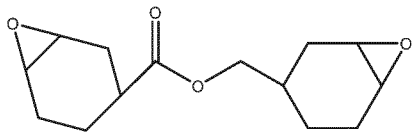
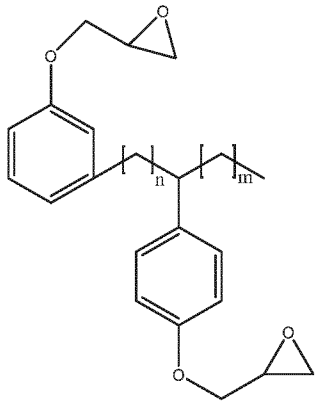
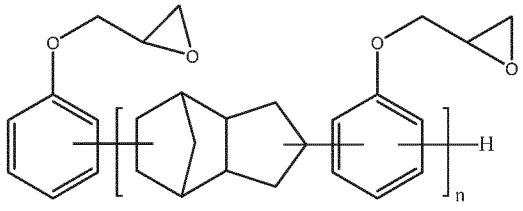


(26)

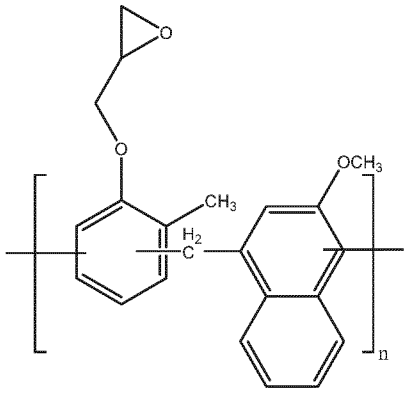


(27)

wherein R^8 represents a substituent or different substituents and is selected independently from a group consisting of hydrogen, halogen and linear or branched C1-C15 alkyl or alkenyl groups, attached to their respective phenyl ring at the 3-, 4- or 5-position and their respective isomers and p is an integer from 1 to 5; wherein n and m are integers from 1 to 10;

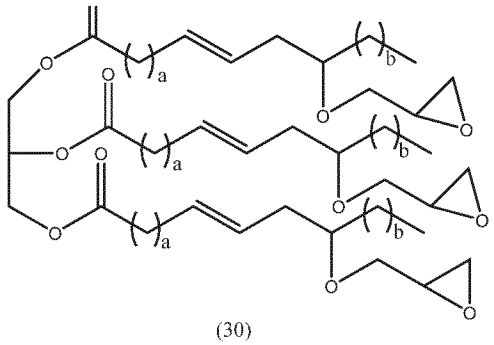


(28)



(29)

wherein n is an integer from 1 to 5;



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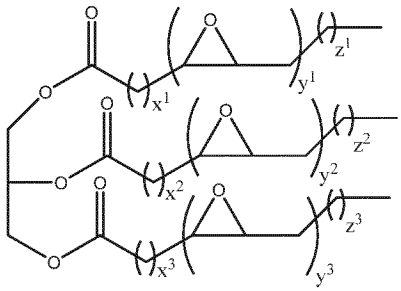

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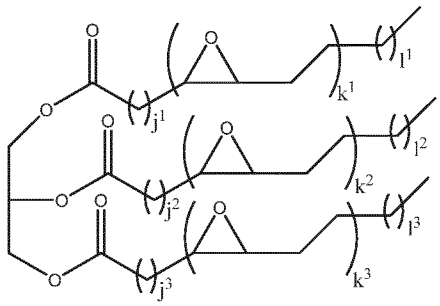


(32)

wherein a and b independently are from 1 to 12; wherein x^1, x^2, x^3 are independently from 1 to 26, y^1, y^2, y^3 are independently from 0 to 6, provided $y^1+y^2+y^3$ is at least 2 and z^1, z^2, z^3 are independently from 0 to 25; wherein j^1, j^2, j^3 are independently from 1 to 26, k^1, k^2, k^3 are independently from 0 to 6, provided $k^1+k^2+k^3$ is at least 2 and l^1, l^2, l^3 are independently from 0 to 25.

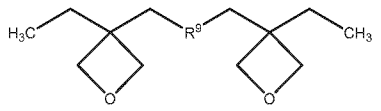
In a preferred embodiment compounds represented by formulae (31) or (32) may not have more than 28 carbon atoms in an individual chain, for e.g. in the chain containing x^1, y^1 and z^1, starting from the carbon of the carbonyl x^1, y^1 and z^1 have values such that the chain has no more than 28 carbon atoms.

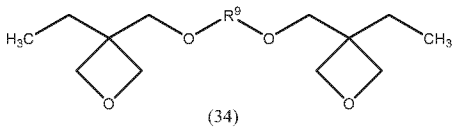
More preferably said epoxy compound is selected from the group consisting of N,N-diglycidyl-4-glycidyloxyaniline, sorbitol glycidyl ether-aliphatic polyfunctional epoxy resin, 4,4′-methylenebis(*N*,*N*-diglycidylaniline), 2-[[4-[2-[4-(oxiran-2-ylmethoxy)phenyl]propan-2-yl]phenoxy]methyl]oxirane and poly[(*o*-cresyl glycidyl ether)-co-formaldehyde].

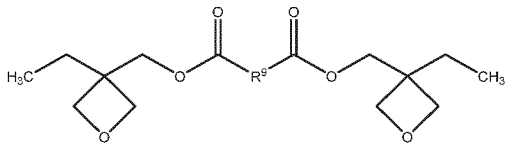
Suitable commercially available epoxy compounds for use in the present invention include, but are not limited to 1,4 butanediol diglycidyl ether (Erisys™ GE21), cyclohexandimethanol diglycidyl ether (Erisys™ GE22), ethylene glycol diglycidyl ether (Erisys™ EDGE), dipropylen glycol diglycidyl ether (Erisys™ GE23), 1,6 hexanediol diglycidyl ether (Erisys™

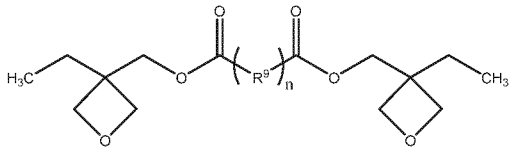
GE60), phenol novolac epoxy resins (Epalloy™ 8220, 8230, 8240, 8250, 8280, 8330, 8350, 8370), from CVC Thermoset resins; tetraglycidyl ether of 1,1,2,2-tetrakis(hydroxyphenyl)ethane (Araldite® XB-4399-3), N,N,N',N'-Tetraglycidyl-4,4'-methylenebisbenzenamine (Araldite® MY720), tris-(hydroxyl phenyl) methane-based epoxy resin (Tactix® 742), triglicidyl ether of meta-aminophenol (Araldite® MY0610, MY0600), triglicidyl ether of para-aminophenol (Araldite® MY0510, MY0500), bisphenol-A based epoxy resins (Araldite® GY6004, GY6005, GY9513, GY9580, GY9613, GY9615, GT6243, GT4248, GT6097, GT7072, Tactix® 123) and phenol novolac epoxy resins (Araldite EPN 1179, 1180) and Araldite® CY5622 from Huntsman; bisphenol-A based epoxy resins (D.E.R. ™ 317, 330, 331, 332, 337, 362, 383) and polypropylene glycol epoxy (D.E.R.™ 732, 736), phenol novolac epoxy resins (D.E.N.™ 425, 431, 438, 439, 440) from Dow Chemical, Cardolite (NC-547, NC-514 and NC-514S) from Cardolite; Epiclon (HP-5000, HP7200H and HP-9500) from DIC Corporation; castor oil triglycidyl ether (Erisys GE35) from CVC thermoset; CER 4221 from DKSH; epoxidized palm oil, epoxidized soybean oil (Vikoflex 7170) and epoxidized linseed oil (Vikoflex 7190) from Arkema.

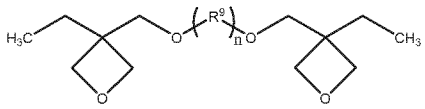
When the cyclic ether compound is an oxetane compound, it is preferably selected from the group consisting of


(33)


(34)


(35)


(36)


(37)

wherein R^9 is selected from the group consisting of a substituted or unsubstituted C1-C30 alkyl group, a substituted or unsubstituted C3-C30 cycloalkyl group, a substituted or unsubstituted aryl group, a substituted or unsubstituted C7-C30 alkylaryl group, a substituted or unsubstituted C3-C30 heterocycloalkyl group and a substituted or unsubstituted C1-C30 heteroalkyl group; and n is an integer from 1 to 30.

ethyl-3-oxetanylmethoxy)methyl]benzene and bis[1-ethyl(3-oxetanyl)]methyl ether.

Suitable commercially available oxetane compound for use in the present invention include, but are not limited to 1,4-bis[(3-ethyl-3-oxetanylmethoxy)methyl]benzene (Eternacoll OXBP), bis[(3-ethyl-3-oxetanyl)methyl]terephthalate (Eternacoll OXTP), bis[1-ethyl(3-oxetanyl)]methyl ether (Aron OXT 221), and 1,4-bis[(3-ethyl-3-oxetanylmethoxy) methyl]benzene (Aron OXT 121) from Toagosei America INC.

An aerogel according to the present invention has a cyclic ether content from 0.1 to 65% by weight of the weight of the initial solvent A, preferably from 1 to 40%, and more preferably from 2 to 30%.

An aerogel according to the present invention has an equivalent ratio of epoxy or oxetane groups to isocyanate groups of isocyanate compound A is 15:1 – 1:15, preferably 10:1 – 1:10, more preferably 5:1 – 1:5.

Preferred ratios are desired because obtained aerogels have a low thermal conductivity and less shrinkage. Aerogel obtained at higher ratios, such as 20:1 or 1:20 or 50:1 or 1:50, would contain more unreacted compounds.

An aerogel according to the present invention is obtained by reacting isocyanate compound B and silanol moieties on a surface of a clay to form a polyurethane component, which is part of the hybrid network of the aerogel according to the present invention. Although, it may also form polyurea and polyisocyanurate components, however, in a lesser extent.

Clays have a high impact in the final material properties, especially when they are in a delaminated state, as a very high aspect ratio is achieved. In addition, properly dispersed and aligned clay platelets have proven to be very effective in increasing stiffness. Therefore, clay based aerogels can combine both advantages from inorganic and organic materials. Low thermal conductivity and good mechanical properties are maintained, while dustiness is minimized.

Clays are a class of aluminosilicate minerals that are naturally hydrophilic. They contain several aluminosilicate platelets. Each platelet is formed by two silicate layers with an aluminium oxide layer sandwiched in between. Some aluminium atoms are replaced by magnesium, generating a global negative charge. Small ions such as Na^+, K^+, Ca^{2+}, etc., stay in the gallery between the platelets, counter-balancing the charge. In organoclays, these cations consist on quaternary ammonium salts with hydrocarbon substituents. The

stack the platelets together forming aggregates and tactoids.

When clays are put in contact with solvents or polymers, two main situations can be obtained: 1) intercalation, wherein the solvent or the polymer is located in between two different platelets; 2) delamination, where platelets are exfoliated and dispersed in a continuous solvent or polymer matrix. In order to favour delamination in the presence of solvents or hydrophobic polymers, clays can be organically modified. In such organoclays, the intergallery cations are replaced by quaternary alkyl ammoniums, increasing their compatibility with the organic systems.

According to the present invention, to achieve the network formed by the reaction between the silanol groups located on the surface of the clay and isocyanate groups of the isocyanate compound B, the clays must be delaminated prior to the reaction.

Delamination allows the silanol groups confined in-between the agglomerated platelets to react with isocyanates. Therefore, dispersion and delamination is a key step during the aerogel preparation process in order to achieve the desired aerogel. Moreover, only when a high degree of delamination is achieved the enhancement in the properties of the final material due to the presence of clays, is observed.

The clays suitable for use in the present invention are mainly organically-modified, in order to enhance clays' compatibility with non-aqueous media. However, non-modified clays may also provide aerogels in some non-aqueous solvents.

In the aerogels according to the present invention, the clay itself is helping to promote the formation of a strong 3D network of the aerogel through the crosslinking bridges. In order to get the proper supramolecular interaction to direct the gel formation, a good compromise between the clay, the reactive isocyanate compounds A and B, the reactive cyclic ether, the solid content and the solvent needs to be carefully designed.

Suitable clays for use in the present invention are phyllosilicate mineral species. Preferably, clay is selected from the group consisting of 2:1 laminar silicates, and more preferably from the subgroup of montmorillonite or sepiolite and mixtures thereof.

In a highly preferred embodiment, the clay is quaternary ammonium alkyl and/or aryl modified clay.

Preferred clays have a good dispersion and good solvent compatibility, which leads to

not limited to Tixogel VZ, Tixogel MPZ, Tixogel VP, Tixogel MP250, Cloisite 30B, Cloisite 10A, Cloisite 15, Cloisite 20, Cloisite 93, Cloisite 116, Optigel CL, Claytone AF, Claytone 40, Laponite EP, Laponite B, Laponite RD, Laponite RDS and Garamite 1958 from BYK; Nanocor I30P and Nanocor PGN from Nanocor; Pangel S9, Pangel W, Pangel 20B, Pangel 40B Pansil 400 from Tolsa.

An aerogel according to the present invention has a clay content from 0.5 to 30% by weight of the weight of the initial solvent B, preferably from 0.5 to 20% and more preferably from 0.5 to 10%.

If the clay content is less than 0.5% obtained gel with poor performance. On the other hand if the clay content is higher than 30% obtained gel would have higher density and too high thermal conductivity.

An aerogel according to the present invention is obtained in the presence of solvent A and solvent B. Solvent A and solvent B can be same or different solvents. Preferably, solvent A and solvent B are the same solvent.

Suitable solvents for use in the present invention are polar solvents, preferably aprotic polar solvents. Preferably solvent A and solvent B are a polar solvent, preferably a polar aprotic solvent. More preferably solvent A and solvent B are independently selected from the group consisting of dimethylacetamide (DMAc), dimethylformamide (DMF), 1-methyl-2-pyrrolidinone (NMP), dimethyl sulfoxide (DMSO), acetonitrile, acetone, methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK) and mixtures thereof.

An aerogel according to the present invention has a volumetric ratio of solution A to solution B from 10:1 to 1:10, preferably from 6:1 to 1:6, and more preferably from 3:1 to 1:3.

An aerogel according to the present invention may be obtained in the presence of a catalyst. The presence of the catalyst depends on the reaction conditions.

A catalyst is needed when the total solid content is below 20%, this is because the gelation time increases at lower solid contents. Although, in normal conditions a catalyst is used to speed up gelation time and control the reactivity.

Suitable catalyst for use in the present invention is selected from the group consisting of alkyl amines, aromatic amines, imidazole derivatives, aza compounds, guanidine derivatives and amidines, preferably said catalyst is selected from the group consisting of

methylimidazole, 4,4'-methylene-bis(2-ethyl-5-methylimidazole), 3,4,6,7,8,9-hexahydro-2H-pyrimido[1,2-a]pyrimidine, 2,3,4,6,7,8,9,10-octahydropyrimido [1,2-a]azepine, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), 1,4-diazabicyclo[2.2.2]octane (DABCO), 1,5-diazabicyclo[4.3.0]non-5-ene, quinuclidine, dibutyltin dilaurate (DBTDL) and mixtures thereof.

When a catalyst is present, the catalyst content is from 0.01 to 30% by weight of the total weight of isocyanate compound A and a cyclic ether compound, preferably from 0.1 to 20%, more preferably from 1 to 15%, and more preferably from 1 to 10%.

In order to improve the mechanical properties of the aerogels, different materials can be used as structural reinforcing agents. In order to reinforce the aerogels, the reinforcing agent is introduced in the synthesis once all the reactants have been dissolved, but before the gelation starts. This allows for a homogeneous distribution of the reinforcing agent in the system.

In another embodiment, the reinforcing agent may also be introduced in the synthesis before or during the addition of other reactants.

Therefore, an aerogel according to the present invention may further comprise at least one reinforcement agent, wherein said reinforcement agent is selected from the group consisting of fibres, particles, non-woven and woven fibre fabrics, fiber glass chopped strand mats, 3D structures and mixtures thereof.

More specifically suitable reinforcement agents may include honeycomb cores (based on aramid fibre or others), glass fibres, glass wool cellulose fibres, jute fibre fabrics, carbon black or others.

An aerogel according to the present invention has a solid content from 4 to 32%, based on total weight of the total initial solution, preferably from 5 to 20%, more preferably from 5 to 10%. In this context by total initial solution is meant the sum of solution A and solution B.

If the solid content is less than 4%, no gelation is observed and on the other hand if the solid content is above 32%, the thermal conductivity increases too much.

An aerogel according to the present invention has a thermal conductivity less than 75 mW/m·K, preferably less than 55 mW/m·K, more preferably less than 50 mW/m·K, and even more preferably less than 40 mW/m·K. Thermal conductivity is measured by means of

The thermal conductivity is measured by using a diffusivity sensor. The heat source and the measuring sensor are on the same side of the device. The sensors measure the heat that diffuses from the sensor throughout the materials. Diffusivity sensor method is appropriate for lab scale tests. The diffusivity sensor used was a C-Therm TCi (C-Therm Technologies).

The present invention allows to adjust thermal conductivity and compressive Young's modulus of the aerogel by varying the aerogel formulation variables. For instance, Table 1 illustrates the effect of varying the volumetric ratio.

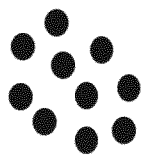
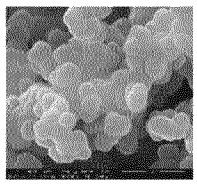
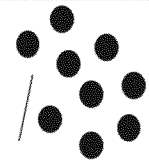
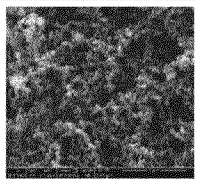
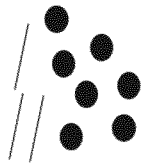
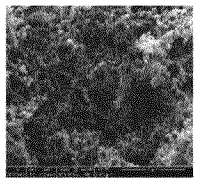
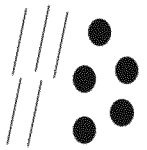
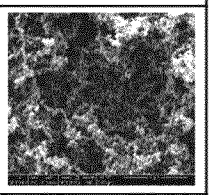
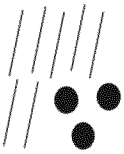
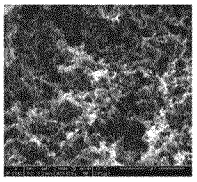
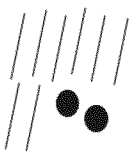
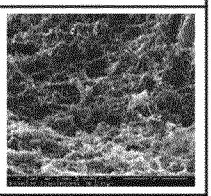
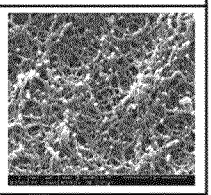
Volumetric ratio	*Thermal conductivity (mW/m·K)*	*Linear Shrinkage (%)*	*Density (g/cm^3)*	*Compressive Young's Modulus (MPa)*	*Morphology simplify schema*	*Morphology SEM (100.000X)*
Solution A	40.0	6.9	0.102	0.06		
3 to 1	39.7	10.9	0.162	0.49		
2 to 1	38.7	7.4	0.143	0.48		
1 to 1	38.4	7.2	0.116	0.56		
1 to 2	38.7	7.7	0.121	0.89		
1 to 3	39.7	9.4	0.124	1.23		
Solution B	41.7	21.2	0.192	7.24		

Table 1 above illustrates a comparison of copolymer hybrid aerogels obtained by mixing two different solutions, solution A and solution B at different volumetric ratios. The solution A is composed of an epoxy (Araldite MY0510) and an aromatic isocyanate (Desmodur RE)

total solution (solution A + solution B) is 12wt%.

Aerogels thermal conductivity decreases from 40.0 mW/mK for the aerogel obtained with 100% of solution A, to 38.4 mW/m·K, when 1/1 of volumetric ratio of solution A and solution B is used. The thermal conductivity of the aerogel increases up to 41.7 mW/mK, when 100% of solution B is used.

Aerogel shrinkage of copolymer hybrid aerogels decreased from 10.9% (3/1 volumetric ratio) to 7.2% when volumetric ratio of 1/1 is used. By increasing volume of solution B an increase in the linear shrinkage up to 21% is observed.

The aerogel morphology changes from a completely particle based morphology obtained when 100% solution A is used, to a mixed fibrillar and particle-like morphology, when a higher volumetric ratio of solution B is used.

An aerogel according to the present invention has a compressive Young's modulus more than 0.01 MPa, preferably more than 0.1 MPa, more preferably more than 15 MPa, and most preferably more than 30 MPa. Compression Young Modulus is measured according to the method ASTM D1621.

An aerogel according to the present invention has a bulk densities ranging from 0.01 to 0.8 g/cc. The bulk density is measured as the ratio of the mass weighted divided by the aerogel volume measured.

An aerogel according to the present invention has preferably a specific surface area ranging from 10 m^2/g to 300 m^2/g. Surface area is determined from N_2 sorption analysis at -196°C using the Brunauer-Emmett-Teller (BET) method, in a specific surface analyser Micromeretics ASAP 2000. High surface area values are preferred because they are indicative of small pore sizes, which may be an indication of low thermal conductivity values.

An aerogel according to the present invention has preferably an average pore size ranging from 5 to 50 nm. Pore size distribution is calculated from Barret-Joyner-Halenda (BJH) model applied to the desorption branch from the isotherms measured by N_2 sorption analysis. Average pore size was determined by applying the following equation: Average pore size = (4*V/ SA) wherein V is total pore volume and SA is surface area calculated from BJH. Porosity of the samples can also be evaluated by He picnometry.

because that allows obtaining high performance thermal insulation aerogels having very low thermal conductivity values.

An aerogel according to the present invention has an adjustable morphology comprising interconnected particles of nanometric size and fibrils of nanometric width, or both particles and fibrils are obtained. Table 1 illustrates how the morphology of the aerogel can be adjusted by changing volumetric ratios of components.

The preparation of aerogels is widely known and can be split in three main steps. Firstly, a sol-gel process, where the reactive monomers react to form oligomers and the supramolecular interactions between these oligomers with time generates the gel. The subsequent step involves a solvent exchange, where the initial solvent is replaced by fresh solvent one or more times in order to remove the impurities. And finally, a drying step, in which the removal of the solvent is carried out by minimizing stresses in the solid backbone to yield a material that has high porosity and low density. The drying step might be done via different techniques, which are usually classified as subcritical or supercritical. Figure 1 illustrates the steps in the general formation of an aerogel.

The main method for subcritical drying is room temperature drying, where the appropriate solvent is allowed to dry under ambient conditions. Although this procedure is relatively inexpensive, it entails some problems. When the original solvent in the gel is evaporated, capillary stress in the pores of the gel induces the struts of the pore network to collapse and the material shrinks. The density of the aerogel is increased and consequently a less insulating material is obtained. The most effective method, supercritical drying, overcomes these problems. The process takes advantage of removing the initial solvent by using a supercritical fluid. By these means, the capillary forces exerted by the solvent due to evaporation are minimized, and structures with large internal void spaces are achieved. The materials presented here can be dried by both procedures, ambient and supercritical drying, allowing the drying technique to be selected according to the application requirements.

Many of the properties of an aerogel according to the present invention can be adjusted by tailoring the production process. Bulk density is one good example of this, it can be adjusted simply by making a more or less concentrated precursor gel. The thermal conductivity of an aerogel can be also adjusted this way, since the thermal conductivity is related to density.

A method for preparing an aerogel according to the present invention comprises the steps

high shear rates;

2) dissolving a cyclic ether compound into the mixture prepared in step 1;

3) adding an isocyanate compound B and mixing;

4) adding an isocyanate compound A and mixing;

5) adding a catalyst if present and mixing;

6) letting the mixture to stand in order to form a gel;

7) exchanging the solvent of said gel with a solvent; and

8) drying said gel via supercritical or ambient drying.

Steps three and four, involving addition of isocyanate compounds A and B, can be done in any order, however, it is preferred that less reactive isocyanate compound is added first, meaning that the aliphatic isocyanate compound is added first and the aromatic isocyanate compound is added second.

The gelation step, step six, is carried out for the pre-set time and temperature. Gelation in the step six is preferably conducted at room temperature, although gelation in the method according to the present invention is done in the temperature from 20°C to 160°C, more preferably from 35°C to 155ºC. Gelation in the step six is achieved in most of the cases in less than 24 hours. Typically gelation time in the method according to the present invention is between 10 minutes and 48 hours, preferably between 10 minutes and 24 hours, more preferably between 10 minutes and 5 hours.

The solvent of wet gels is changed one or more times after the gelation in step seven. The solvent is exchanged gradually, and if required, to the preferred solvent for the drying process.

In one embodiment, the solvent is exchanged gradually as follows: 1) N,N-dimethylacetamide; 2) N,N-dimethylacetamide:acetone 3:1; 3) N,N-dimethylacetamide:acetone 1:1; 4) N,N-dimethylacetamide:acetone 1:3 5) acetone.

Solvent exchange time is from 12 hours to 96 hours in step seven, preferably from 24 hours to 72 hours.

Once the wet gel remains in the proper solvent in the step seven, it is dried in supercritical (CO_2) or ambient conditions in step eight obtaining an aerogel material. For example, if the obtained gels are dried in CO_2 the replacing solvent is acetone, whereas if the obtained gels

gel with CO_2 or other suitable solvents in their supercritical state. Due to this, capillary forces exerted by the solvent during evaporation in the nanometric pores are minimized and shrinkage of the gel can be reduced.

The supercritical state of a substance is reached once its liquid and gaseous phases become indistinguishable. The pressure and temperature at which the substance enters this phase is called critical point. In this phase, the fluid shows the low viscosity of a gas, and the high density of a liquid. It can effuse through solids like a gas and dissolve materials like a liquid. Considering an aerogel, once the liquid inside the wet gel pores reaches the supercritical phase, its molecules do not possess enough intermolecular forces to create the necessary surface tension that creates capillarity stress. Hence, the gel can be dried, minimizing shrinkage and possible collapse of the gel network.

Alternatively, wet gels can be dried at ambient conditions, in which the solvent is evaporated at room temperature. However, as the liquid evaporates from the pores, it can create a meniscus that recedes back into the gel due to the difference between interfacial energies. This may create a capillary stress on the gel, which responds by shrinking. If these forces are strong enough, they can even lead to the collapse or cracking of the whole structure. However, there are different possibilities to minimize this phenomenon. One practical solution involves the use of solvents with low surface tension to minimize the interfacial energy between the liquid and the pore. Hexane is usually used as a convenient solvent for ambient drying, as its surface tension is one of the lowest among the conventional solvents. Unfortunately, not all the solvents lead to gelation, which means that some cases would require the exchange of solvent from an initial one, required for the gel formation to a second one, mostly appropriate for the drying process.

It was found that very limited shrinkage of the final aerogel structure (compared to the initial volume of the wet gel) occurred in aerogels prepared by using the method according to the present invention. The shrinkage was approximately 5-10% for the samples dried by supercritical drying and 15-20% for the samples dried at ambient conditions.

Aerogels according to the present invention can be used as a thermal and/or acoustic insulating material.

The present invention also relates to a thermal and/or an acoustic insulating material comprising aerogels according to the present invention.

Aerogels according to the present invention may be used in a variety of applications such

automotive engines and electronic devices. Other potential applications for aerogels is as a sound absorption material and a catalyst support.

Aerogels according to the present invention according to the present invention can be used for thermal insulation in different applications such as aircrafts, space crafts, pipelines, tankers and maritime ships replacing currently used foam panels and other foam products, in car battery housings and under hood liners, lamps, in cold packaging technology including tanks and boxes, jackets and footwear and tents.

Aerogels according to the present invention according to the present invention can also be used in construction materials due to their lightweight, strength, ability to be formed into desired shapes and superior thermal insulation properties.

Aerogels according to the present invention according to the present invention can be also used as thermal insulation in storage and transportation of cryogens.

Aerogels according to the present invention according to the present invention can be also used as an adsorption agent for oil spill clean-up, due to their high oil absorption rate.

Aerogels according to the present invention according to the present invention can be also used in safety and protective equipment as a shock-absorbing medium.

EXAMPLES

Example 1: Copolymer hybrid aerogel reinforced with chopped glass fibres without catalyst

The calculation of the components content for the synthesis of the aerogels was based on the mixture of two different solutions, solution A and solution B. The volumetric ratio between solution A and B was 1:1. The solution A was composed of an epoxy (Araldite MY0510), solvent (acetone) and trifunctional aromatic isocyanate (Desmodur RE). This solution was prepared with an equivalent ratio epoxy/isocyanate of 1:1. The solution B was composed of an organically-modified clay (Tixogel VZ), solvent (acetone) and trifunctional aliphatic isocyanate (Desmodur N3300). The weight ratio isocyanate/clay was 10/3. The solid content of the total solution (solution A + solution B) was 27wt%.

For the preparation of a sample of 20 mL, 7.48 g of solvent (0.09 g of acetone in solution A and 7.39 g of acetone in solution B) was poured in a polypropylene speed mixer cup (50

beads (Zirmyl Y) to increase the shearing while mixing. The system was mixed in a speed mixer for three minutes at 3500 rpm. The ceramic beads were removed from the obtained dispersion and Araldite MY0510 (1.87 g) was added and manually stirred. Subsequently, Desmodur N3300 (0.63 g) was incorporated and manually stirred. Finally, Desmodur RE (8.35 g, containing 2.25 g of pure isocyanate) was added and manually stirred.

1wt% (based on the weight of the total initial solution, A and B) of chopped glass fibres with a length ranged from 0.5 to 2 cm was incorporated in the mixture and carefully distributed with a wooden spatula. The final mixture was left to gel in the same recipient in an oven at 45 °C overnight. The obtained gel was washed with acetone in several steps and subsequently dried via CO_2 supercritical drying (SCD). Table 2 summarizes the properties obtained for the aerogel.

Table 2

Solvent	***Density (g/cm^3)***	***Linear shrinkage (%)***	***Thermal conductivity (mW/m·K)***	***Compression Modulus** (MPa)***
Acetone	0.255	8.7	42.0	5.1

*Thermal conductivity measured with the C-Therm TCi according to the method described above.

**Mechanical properties determined in accordance with ASTM D1621

Example 2: Copolymer hybrid aerogel prepared at high temperature (155ºC)

The calculation of the components content for the synthesis of the aerogels was based on the two different solutions, solution A and solution B. The volumetric ratio between solution A and B was 1:1. The solution A was composed of an epoxy (Araldite MY0510), solvent (N,N-dimethylacetamide, DMAc), aromatic isocyanate (diphenylmethane 4,4'-diisocyanate, MDI) and catalyst (N,N-dimethylbenzylamine, DMBA). This solution was prepared with an equivalent ratio epoxy/isocyanate of 3:1. The solution B was composed of an organically-modified clay (Tixogel VZ), solvent (DMAc) and trifunctional aliphatic isocyanate (Desmodur N3300). The weight ratio isocyanate/clay was 10/3. The solid content of the total solution (solution A + solution B) was 19wt%.

A and 11.39 g of DMAc in solution B) was poured in a polypropylene container (120 mL) followed by the addition of Tixogel VZ (0.33 g) and 20 phr of grinding ceramic beards (Zyril Y) to increase the shearing while mixing. The system was mixed in a speed mixer for three minutes at 3500 rpm. The ceramic beads were removed from the dispersion and Araldite MY0510 (2.64 g) was added and manually stirred. Subsequently, Desmodur N3300 (1.10 g) was incorporated and manually stirred. MDI (1.09 g) was added to the dispersion and manually stirred. Finally, DMBA (0.75 g) was incorporated in the system and manually stirred.

The final mixture was left to gel in the same recipient in an oven at 155ºC for 1.5 hours. The solvent (DMAc) was changed to acetone in several steps: DMAc, DMAc/acetone 3:1, 1:1, 1:3 and acetone. The samples were dried via CO_2 supercritical drying (SCD). Table 3 summarizes the properties obtained for the aerogel.

Table 3

Solvent	***Density (g/cm3)***	***Linear shrinkage (%)***	***Thermal conductivity (mW/m·K)***	***Compression Modulus** (MPa)***
N,N-Dimethylacetamide	0.300	24.7	44.6	7.7

*Thermal conductivity measured with the C-Therm TCi according to the method described above.

**Mechanical properties determined in accordance with ASTM D1621

Example 3: Copolymer hybrid aerogel reinforced with carbon black

The calculation of the components content for the synthesis of the aerogels was based on the mixture of two different solutions solution A and solution B. The volumetric ratio between solution A and B was 1:1. The solution A was composed of an epoxy (Araldite MY0510), solvent (acetone), trifunctional aromatic isocyanate (Desmodur RE) and catalyst (1,4-diazabicyclo[2.2.2]octane, DABCO). This solution was prepared with an equivalent ratio epoxy/isocyanate of 1:1. The solution B was composed of an organically-modified clay (Tixogel VZ), solvent (acetone) and trifunctional aliphatic isocyanate (Desmodur N3300). The weight ratio isocyanate/clay was 10/3. The solid content of the total solution (solution A + solution B) was 7.5wt%

and 7.4 g of solvent in solution B) was poured in a polypropylene speed mixer cup (50 mL) followed by the addition of Tixogel VZ (0.19 g) and 20 phr of grinding ceramic beads (Zirmyl Y) to increase the shearing while mixing. The mixture was mixed in a speed mixer for three minutes at 3500 rpm. The ceramic beads were removed from the dispersion and Araldite MY0510 (0.184 g) was added and manually stirred. Desmodur N3300 (0.637 g) was incorporated and manually stirred. Desmodur RE (0.82 g, containing 0.22 g of pure isocyanate) was added to the dispersion and manually stirred. Finally, DABCO (0.04 g) was incorporated and manually stirred.

0.1wt% (based on the weight of the total initial solution, A and B) of carbon black was incorporated in the system and mixed in the speed mixer for three minutes at 3500 rpm. The final mixture was left to gel in the same recipient in an oven at 45ºC for two hours. The gel was washed with acetone in several steps and subsequently dried via CO_2 supercritical drying (SCD). Table 4 summarizes the properties obtained for the aerogel.

Table 4

Solvent	***Density (g/cm^3)***	***Linear shrinkage (%)***	***Thermal conductivity (mW/m·K)***	***Compression Modulus** (MPa)***
Acetone	0.134	23.0	37.0	1.23

*Thermal conductivity measured with the C-Therm TCi according to the method described above.

**Mechanical properties determined in accordance with ASTM D1621

Example 4: Copolymer hybrid aerogel reinforced with glass fibre fabrics

The calculation of the components content for the synthesis of the aerogels was based on the mixture of two different solutions, solution A and solution B. The volumetric ratio between solution A and B was 1:1. The solution A was composed of an epoxy (Araldite MY0510), solvent (acetone), trifunctional aromatic isocyanate (Desmodur RE) and catalyst (1,4-diazabicyclo[2.2.2]octane, DABCO). This solution was prepared with an equivalent ratio epoxy/isocyanate of 1:1. The solution B was composed of an organically-modified clay (Tixogel VZ), solvent (acetone) and trifunctional aliphatic isocyanate (Desmodur N3300).

A + solution B) was 7.5wt%.

For the preparation of a sample of 20 mL, 14.5 g of solvent (7.1 g of acetone in solution A and 7.4 g of acetone in solution B) was poured in a polypropylene speed mixer cup (50 mL) followed by the addition of Tixogel VZ (0.19 g) and 20 phr of grinding ceramic beads (Zirmyl Y) to increase the shearing while mixing. The system was mixed in a speed mixer during three minutes at 3500 rpm. The ceramic beads was removed from the dispersion and Araldite MY0510 (0.184 g) was added and manually stirred. Desmodur N3300 (0.637 g) was incorporated and manually stirred. Desmodur RE (0.82 g, containing 0.22 g of pure isocyanate) was added to the dispersion and manually stirred. Finally, DABCO (0.04 g) was incorporated and manually stirred.

25wt% (based on the weight of the total initial solution, A and B) of glass fibre fabrics (10 layers of fabric) was placed in the system. The final mixture was left to gel in the same recipient in an oven at 45ºC for two hours. The gel was washed with acetone in several steps and subsequently dried via CO_2 supercritical drying (SCD). Table 5 summarizes the properties obtained for the aerogel.

Table 5

Solvent	***Density (g/cm3)***	***Linear shrinkage (%)***	***Thermal conductivity (mW/m·K)***	***Compression Modulus** (MPa)***
Acetone	0.421	2.6	35.9	0.45

*Thermal conductivity measured with the C-Therm TCi according to the method described above.

**Mechanical properties determined in accordance with ASTM D1621

Example 5: Copolymer hybrid aerogel using difunctional and trifunctional isocyanates.

The calculation of the components content for the synthesis of the copolymer hybrid aerogels was based on the mixture of two different solutions of 10 ml each. The solution A was composed of an epoxy (Araldite MY0510), solvent (acetone), trifunctional aromatic isocyanate (Desmodur RE) and catalyst (1,4-diazabicyclo[2.2.2]octane, DABCO). This solution A was prepared with an equivalent ratio epoxy/isocyanate of 1:1. The solution B

isocyanate/clay was 10/3. The solid content of the total solution (solution A + solution B) was 26wt%.

For the preparation of a sample of 20 mL, 7.47 g of acetone (0.08 g of acetone in solution A and 7.39 g of acetone in solution B) was poured in a polypropylene speed mixer cup (50 mL) followed by the addition of 0.19 g Tixogel VZ and 20 phr of the grinding ceramic beads (Zirmyl Y) to increase the shearing while mixing. The mixture was stirred for three minutes at 3500 rpm. The ceramic beads were removed from the dispersion and 1.73 g of Araldite MY0510 is added and manually stirred. Then, 0.63g of Desmodur N3200 was incorporated and manually stirred. Finally, 7.73g of Desmodur RE (containing 2.09 g of pure isocyanate in ethyl acetate) was added to the dispersion, then 0.76 g of DABCO catalyst was incorporated and the solution was manually stirred.

The final mixture was left to gel in the same recipient at room temperature. The gel was formed in 5 minutes. Then gels were washed with solvents in several steps and subsequently dried via CO_2 supercritical drying (SCD). Table 6 illustrates measured properties of the obtained aerogel.

Table 6

Solvent	***Density (g/cm3)***	***Linear shrinkage (%)***	***Thermal conductivity (mW/m·K)***	***Compression Modulus** (MPa)***
Acetone	0.29	5.0	44.0	9.4

*Thermal conductivity measured with the C-Therm TCi according to the method described above.

**Mechanical properties determined in accordance with ASTM D1621

Example 6: Copolymer hybrid aerogel using a tetrafunctional epoxy and tetrafunctional isocyanate.

The calculation components content for the synthesis of the copolymer hybrid aerogels was based on the mixture of two different solutions, solution A and solution B. The volumetric ratio between solution A and solution B was 1:1. The solution A was composed of an epoxy (Erisys GE60), solvent (DMAc), isocyanate (Polurene HR), and TBD as a catalyst.

N3300). The weight ratio isocyanate/clay was 10/3. The solid content of the total solution (solution A+ solution B) was 15 wt%.

For the preparation of a sample of 20 mL, 15.36 g of DMAc (6.72 g of DMAc in solution A and 8.64 g of DMAc in solution B) was poured in a polypropylene speed mixer cup (50 mL) followed by the addition of 0.22 g of Tixogel VZ and 20 phr of the grinding ceramic beads (Zirmyl Y) to increase the shearing while mixing. The mixture was stirred for three minutes at 3500 rpm. The ceramic beads were removed from the dispersion and 0.8 g of Erisys GE60 was added and manually stirred. Then, Polurene HR (2.36 g, containing 1.18 g of pure HR in butyl acetate) was incorporated and manually stirred. Then, 0.74 g of Desmodur N3300 was incorporated and manually stirred. Finally, 0.019 g of the catalyst was added to the dispersion and manually stirred.

The final mixture was left to gel in the same recipient at room temperature for 5 hours. The resulting gel was washed stepwise in a mixture of Acetone 1:3 DMAc, Acetone 1:1 DMAc, Acetone 3:1 DMAc and Acetone, duration of each step was 24h, and using solvent three times the volume of the gel for each step. Subsequently the gel was dried via CO_2 supercritical drying (SCD).Table 7 illustrates measured properties of the obtained aerogel.

Table 7

Solvent	***Density (g/cm3)***	***Linear shrinkage (%)***	***Thermal conductivity* (mW/m·K)***	***Compression Modulus** (MPa)***
N,N-Dimethylacetamide	0.585	39.0	57.0	30

*Thermal conductivity measured with the C-Therm TCi according to the method described above.

**Mechanical properties determined in accordance with ASTM D1621

Example 7: Copolymer hybrid aerogel using epoxy/isocyanate equivalent ratio of 5:1

The calculation of the components content for the synthesis of the copolymer hybrid aerogels was based on the mixture of two different solutions of solutions, solution A and solution B. The volumetric ratio between solution A and solution B was 1:1. The solution A was composed of an epoxy (Araldite MY0510), solvent (acetone), isocyanate (Desmodur RE), and DMBA as a catalyst. The equivalent ratio epoxy/isocyanate was 5:1. The solution

trifunctional aliphatic isocyanate (Desmodur N3300). The weight ratio isocyanate/clay was 10/3. The solid content of the total solution (solution A + solution B) was 10wt%.

For the preparation of a sample of 20 mL, 14.27 g of acetone (6.88 g of acetone in solution A and 7.39 g of acetone in solution B) was poured in a polypropylene speed mixer cup (50 mL) followed by the addition of 0.189 g of Tixogel VZ and 20 phr of the grinding ceramic beads (Zirmyl Y) to increase the shearing while mixing. The mixture is stirred for three minutes at 3500 rpm. The ceramic beads were removed from the dispersion and 0.65 g of Araldite MY0510 was added and manually stirred. Then, Desmodur RE (0.58 g, containing 0.16 g of pure RE in ethyl acetate) was incorporated and manually stirred. Then, 0.63 g of Desmodur N3300 was incorporated and manually stirred. Finally, 0.161 g of the catalyst was added to the dispersion and also manually stirred.

The final mixture was left to gel in the same recipient for 24h at 40 °C. The gels were washed with Acetone in several steps and subsequently dried via CO_2 supercritical drying (SCD). Table 8 illustrates measured properties of the obtained aerogel.

Table 8

Solvent	***Density (g/cm3)***	***Linear shrinkage (%)***	***Thermal conductivity* (mW/m·K)***	***Compression Modulus** (MPa)***
Acetone	0.134	21.0	37.0	1.4

*Thermal conductivity measured with the C-Therm TCi according to the method described above.

**Mechanical properties determined in accordance with ASTM D1621

Example 8: Copolymer hybrid aerogel using oxetane

The calculation of the components content for the synthesis of the copolymer hybrid aerogels was based on the mixture of two different solutions, solution A and solution B. The volumetric ratio between solution A and solution B was 1:1. The solution A was composed of an oxetane (OXT-221), solvent (DMAc), isocyanate (Polurene KC), and TBD as a catalyst. The equivalent ratio oxetane/isocyanate was 1:1. The solution B was composed of an organically-modified clay (Tixogel VZ), solvent (acetone) and isocyanate (Desmodur

(solution A + solution B) was 15wt%.

For the preparation of a sample of 20 mL, 13.74 g (6.35 g of DMAc in solution A and 7.39 g of acetone in solution B) was poured in a polypropylene speed mixer cup (50 mL) followed by the addition of 0.189 g of Tixogel VZ and 20 phr of the grinding ceramic beads (Zirmyl Y) to increase the shearing while mixing. The mixture was stirred for three minutes at 3500 rpm. The ceramic beads were removed from the dispersion and 0.56 g of OXT-221 was added and manually stirred. Then, Polurene KC (2.74 g, containing 1.37 g of pure KC in butyl acetate) is incorporated and manually stirred. Then, 0.63 g of Desmodur N3300 was incorporated and manually stirred. Finally, 0.019 g of the catalyst was added to the dispersion and manually stirred.

The final mixture was left to gel in the same recipient for 3h at room temperature. The gels were washed with acetone 1:1 DMAc, acetone 3:1 DMAc and acetone, duration of each step was 24h, and using solvent three times the volume of the gel for each step. Subsequently the gel was dried via CO_2 supercritical drying (SCD). Table 9 illustrates measured properties of the obtained aerogel.

Table 9

Solvent	***Density (g/cm3)***	***Linear shrinkage (%)***	***Thermal conductivity* (mW/m·K)***	***Compression Modulus** (MPa)***
N,N-Dimethylacetamide/ Acetone	0.226	29	43.0	37

*Thermal conductivity measured with the C-Therm TCi according to the method described above.

**Mechanical properties determined in accordance with ASTM D1621

Example 9: Copolymer hybrid aerogel using volumetric ratio of 1 to 6

The calculation of the components content for the synthesis of the copolymer hybrid aerogels was based on the mixture of two different solutions A and B. The volumetric ratio between solution A and solution B was 1:6, solution A of 2.86 ml and solution B of 17.14 ml. The solution A was composed of an epoxy (Araldite MY0510), solvent (acetone), aromatic isocyanate (Desmodur RE), and 1,4-diazabicyclo[2.2.2]octane (DABCO) as a

and trifunctional aliphatic isocyanate (Desmodur N3300). The weight ratio isocyanate/clay in solution B was 10/3. The solid content of the total solution (solution A + solution B) was 10wt%.

For the preparation of a sample of 20 mL, 14.4 g of acetone (1.77 g of acetone in solution A and 12.67 g of acetone in solution B) was poured in a polypropylene speed mixer cup (50 mL) followed by the addition of 0.32 g of Tixogel VZ and 20 phr of the grinding ceramic beads (Zirmyl Y) to increase the shearing while mixing. The mixture was stirred for three minutes at 3500 rpm. The ceramic beads were removed from the dispersion and 0.11 g of Araldite MY0510 was added and manually stirred. Then, Desmodur RE (0.48 g, containing 0.13 g of pure RE in ethyl acetate) was incorporated and manually stirred. Then, 1.08 g of Desmodur N3300 was incorporated and manually stirred. Finally, 0.025 g of the catalyst was added to the dispersion and manually stirred.

The final mixture was left to gel in the same recipient for 24h at 40 ºC. The gels were washed with acetone in several steps and subsequently dried via CO_2 supercritical drying (SCD). Table 10 illustrates measured properties of the obtained aerogel.

Table 10

Solvent	***Density (g/cm3)***	***Linear shrinkage (%)***	***Thermal conductivity* (mW/m·K)***	***Compression Modulus** (MPa)***
Acetone	0.093	7.5	35.0	0.7

*Thermal conductivity measured with the C-Therm TCi according to the method described above.

**Mechanical properties determined in accordance with ASTM D1621

Example 10: Copolymer hybrid aerogel using a volumetric ratio of 2 to 1 and tetrafunctional epoxy

The calculation of the components content for the synthesis of the copolymer hybrid aerogels was based on the mixture of two different solutions, A and B. The volumetric ratio between solution A and solution B was 2:1, solution A of 13.3 ml and solution B of 6.7 ml. The solution A was composed of an epoxy (4,4,methylenebis N;N diglycidylaniline), solvent

an organically-modified clay (Tixogel VZ), solvent (acetone) and trifunctional aliphatic isocyanate (Desmodur N3300). The weight ratio of isocyanate/clay in solution B was 10/3. The solid content of the total solution (solution A + solution B) was 7.3wt%.

For the preparation of a sample of 20 mL, 14.4g of acetone (9.45 g of acetone in solution A and 4.94 g of acetone in solution B) was poured in a polypropylene speed mixer cup (50 mL) followed by the addition of 0.15 g of Tixogel VZ and 20 phr of the grinding ceramic beads (Zirmyl Y) to increase the shearing while mixing. The mixture was stirred for three minutes at 3500 rpm. The ceramic beads were removed from the dispersion and 0.27 g of 4,4′-Methylenebis(N,N-diglycidylaniline) was added and manually stirred. Then, Desmodur RE (1.03 g, containing 0.28 g of pure RE in ethyl acetate) was incorporated and manually stirred. Then, 0.492g of Desmodur N3300 was incorporated and manually stirred. Finally, 0.11 g of the catalyst was added to the dispersion and manually stirred.

The final mixture was left to gel in the same recipient at 45ºC for 5 hours. The gels were washed with acetone in several steps and subsequently dried via CO_2 supercritical drying (SCD). Table 11 illustrates measured properties of the obtained aerogel.

Table 11

Solvent	***Density (g/cm3)***	***Linear shrinkage (%)***	***Thermal conductivity* (mW/m·K)***	***Compression Modulus** (MPa)***
Acetone	0.0507	5.2	32.8	0.2

*Thermal conductivity measured with the C-Therm TCi according to the method described above.

**Mechanical properties determined in accordance with ASTM D1621

Example 11: Copolymer hybrid aerogel reinforced with honeycomb

The calculation of the components content for the synthesis of the aerogels is based on the mixture of two different solutions, A and B. The volumetric ratio between solution A and solution B was 1:2, solution A of 6.7 ml and solution B of 13.3 ml. The solution A was composed of an epoxy (Araldite MY0510), solvent (acetone), trifunctional aromatic isocyanate (Desmodur RE) and catalyst (DMBA). This solution was prepared with an equivalent ratio epoxy/isocyanate of 1:1. The solution B was composed of an organically-

(Desmodur N3300). The weight ratio isocyanate/clay for this solution was 10/3. The solid content of the total solution (solution A + solution B) was 11wt%. The honeycomb incorporated was based on aramid fibers and phenolic resin with a density of 48 kg%m^3 and a cell size of 4.8 mm.

For the preparation of a sample of 20 mL, 13.93 g of acetone (4.06 g of acetone in solution A and 9.87 g of acetone in solution B) was poured in a polypropylene speed mixer cup (50 mL) followed by the addition of 0.29 g of Garamite 1958 and 20 phr of the grinding ceramic beads (Zirmyl Y) to increase the shearing while mixing. The mixture was stirred for three minutes at 3500 rpm. The ceramic beads were removed from the dispersion and 0.24 g of Araldite MY0510 was added and manually stirred. Then, Desmodur RE (1.09 g, containing 0.29 g of pure RE in ethyl acetate) was incorporated and manually stirred. Then, 0.98 g of Desmodur N3300 was incorporated and manually stirred. Finally, 0.22 g of the DMBA catalyst was added to the dispersion and also manually stirred. Once the reactants were dispersed, the reinforcement, a honeycomb core based on aramid fibre and phenolic resin was incorporated.

The final mixture was left to gel in the same recipient in an oven at 45°C for two hours. The gel was washed with acetone in several steps and subsequently dried via CO_2 supercritical drying (SCD). Table 12 illustrates measured properties of the obtained aerogel.

Table 12

Solvent	***Density (g/cm^3)***	***Linear shrinkage (%)***	***Thermal conductivity* (mW/m·K)***	***Compression Modulus** (MPa)***
Acetone	0.09	3.7	39.1	67.7

*Thermal conductivity measured with the C-Therm TCi according to the method described above.

**Mechanical properties determined in accordance with ASTM D1621

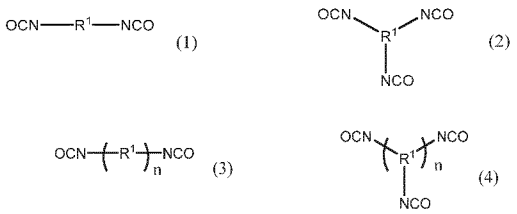
1. An aerogel obtained by reacting

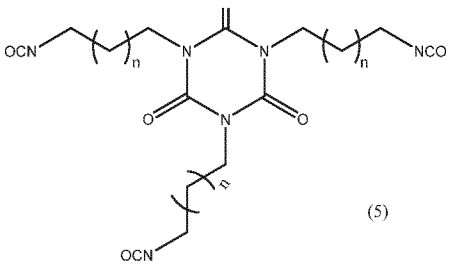
- silanol moieties on a surface of a clay;
- an isocyanate compound A;
- an isocyanate compound B;
- a cyclic ether compound;
- a solvent A; and
- a solvent B.

2. An aerogel according to claim 1, wherein said aerogel is obtained in the presence of a catalyst.

3. An aerogel according to claim 1 or 2, wherein said isocyanate compound A and isocyanate compound B are independently an aromatic isocyanate compound or an aliphatic isocyanate compound, preferably said isocyanate compound A is an aromatic isocyanate compound and said isocyanate compound B is an aliphatic isocyanate compound.

4. An aerogel according to any of claims 1 to 3, wherein said isocyanate compound A and isocyanate compound B are independently selected from the group consisting of





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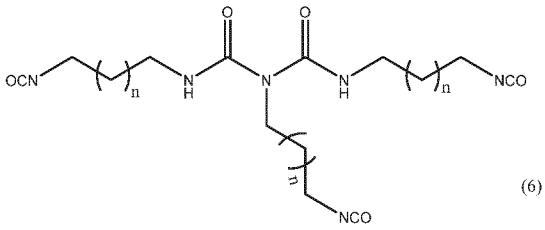

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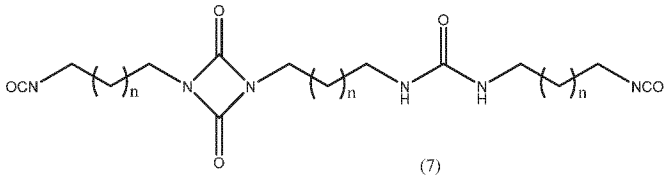
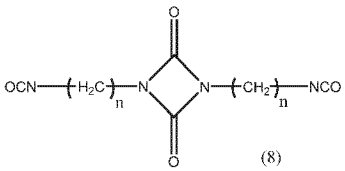
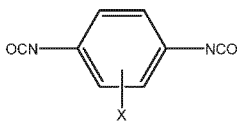


(7)

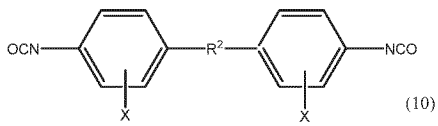


(8)

wherein R^1 is selected from the group consisting of a single bonded –O-, -S-, -C(O)-, -$S(O)_2$-, -$S(PO_3)$-, a substituted or unsubstituted C1-C30 alkyl group, a substituted or unsubstituted C3-C30 cycloalkyl group, a substituted or unsubstituted aryl group, a substituted or unsubstituted C7-C30 alkylaryl group, a substituted or unsubstituted C3-C30 heterocycloalkyl group and a substituted or unsubstituted C1-C30 heteroalkyl group and a combination of thereof; and an integer n is from 1 to 30;



(9)



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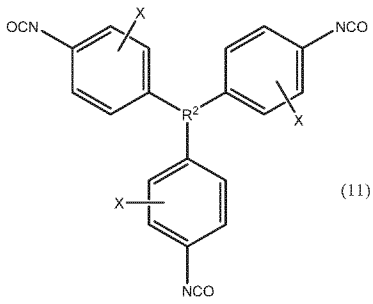

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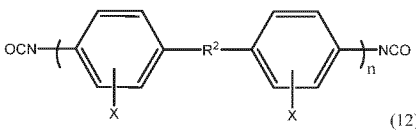
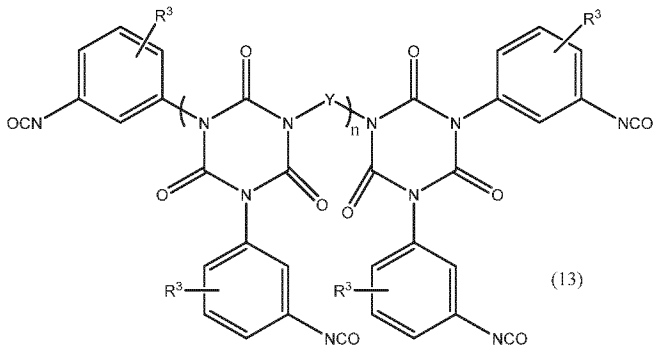
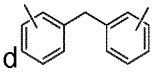
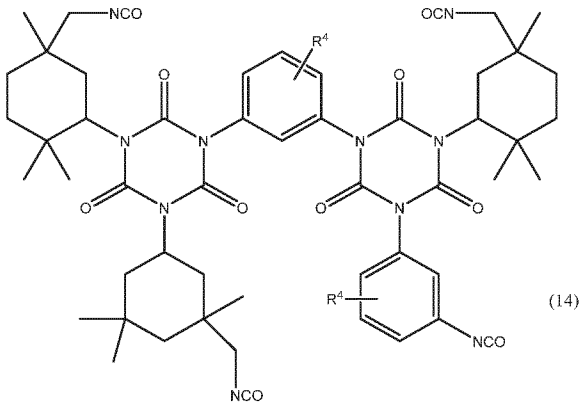


(12)

independently from the group consisting of hydrogen, halogen and linear or branched C1-C6 alkyl groups, attached on their respective phenyl ring at the 2-position, 3-position or 4-position, and their respective isomers, and R^2 is selected from the group consisting of a single bonded –O-, -S-, -C(O)-, $-S(O)_2-$, $-S(PO_3)-$, a substituted or unsubstituted C1-C30 alkyl group, a substituted or unsubstituted C3-C30 cycloalkyl group, a substituted or unsubstituted aryl group, a substituted or unsubstituted C7-C30 alkylaryl group, a substituted or unsubstituted C3-C30 heterocycloalkyl group and a substituted or unsubstituted C1-C30 heteroalkyl group from and a combination of thereof; and an integer n is from 1 to 30;


(13)

wherein R^3 is selected independently from the group consisting of alkyl, hydrogen and alkenyl, and Y is selected from the group consisting of  and  , and n is an integer from 0 to 3;

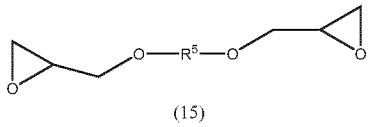

(14)

wherein R^4 is selected independently from the group consisting of alkyl, hydrogen and alkenyl,

preferably isocyanate compound A and isocyanate compound B are independently

isocyanatohexyl) carbamate, 1,6-diisocyanatohexane, methylene diphenyl diisocyanate, 1-[bis(4-isocyanatophenyl)methyl]-4-isocyanatobenzene, 2,4-diisocyanato-1-methyl-benzene, oligomers of the above-mentioned and mixtures thereof.

5. An aerogel according to any of claims 1 to 4, wherein said cyclic ether compound is an epoxy compound, preferably selected from the group consisting of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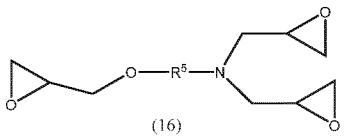
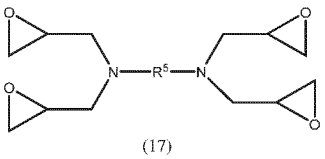

(16)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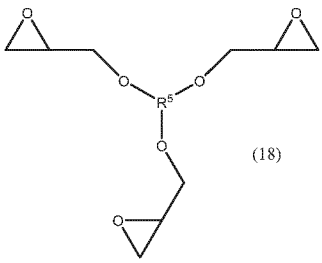
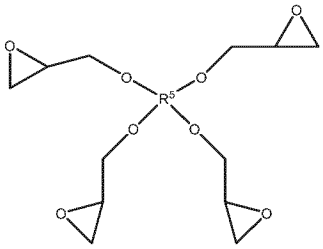

(18)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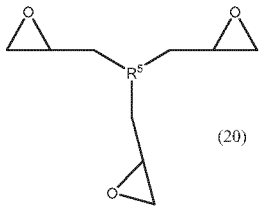
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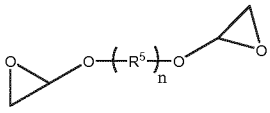
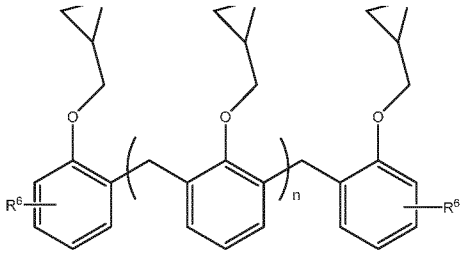
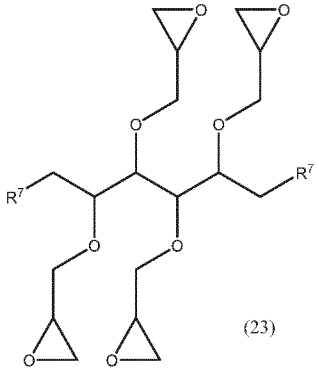

(21)

wherein R^5 is selected from the group consisting of a substituted or unsubstituted C1-C30 alkyl group, a substituted or unsubstituted C3-C30 cycloalkyl group, a substituted or unsubstituted aryl group, a substituted or unsubstituted C7-C30 alkylaryl group, a substituted or unsubstituted C3-C30 heterocycloalkyl group and a substituted or unsubstituted C1-C30 heteroalkyl group; and n is an integer from 1 to 30;



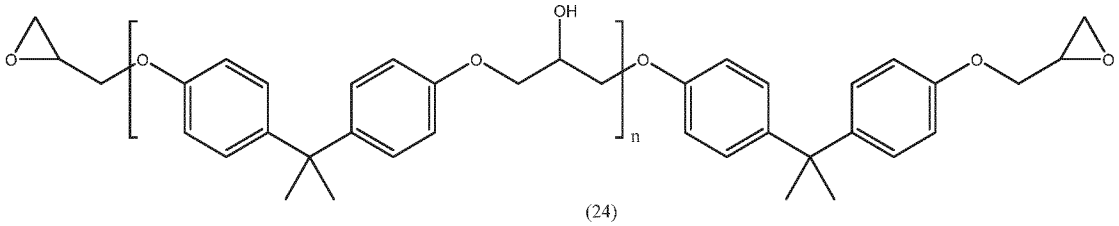
(22)

wherein R^6 is selected independently from the group consisting of hydrogen, halogen, alkyl and alkenyl; and n is an integer from 1 to 10;



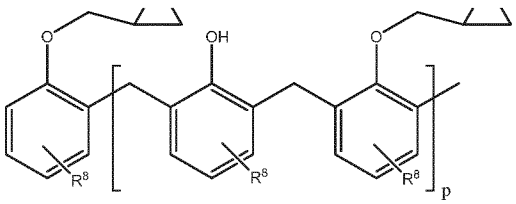
(23)

wherein R^7 is selected independently from the group consisting of hydrogen, hydroxyl, halogen, alkyl and alkenyl;



(24)

wherein n is an integer from 0 to 16;



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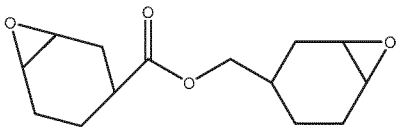
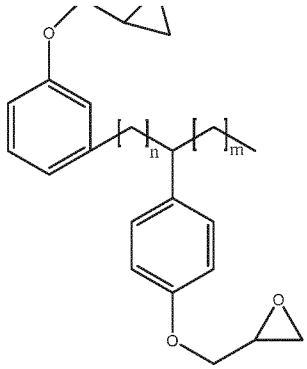
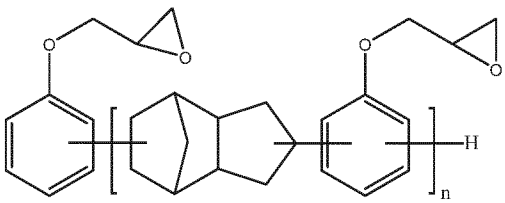


(26)

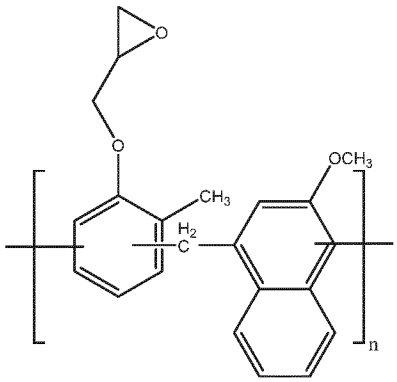


(27)

wherein R^8 represents a substituent or different substituents and is selected independently from a group consisting of hydrogen, halogen and linear or branched C1-C15 alkyl or alkenyl groups, attached to their respective phenyl ring at the 3-, 4- or 5-position and their respective isomers and p is an integer from 1 to 5; wherein n and m are integers from 1 to 10;

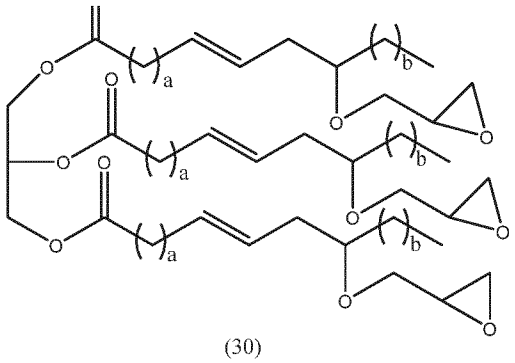


(28)



(29)

wherein n is an integer from 1 to 5;



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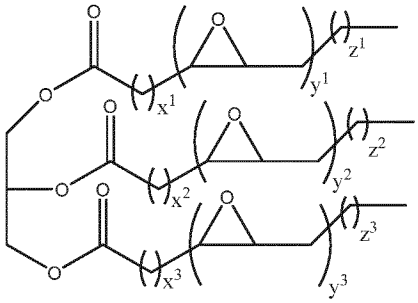
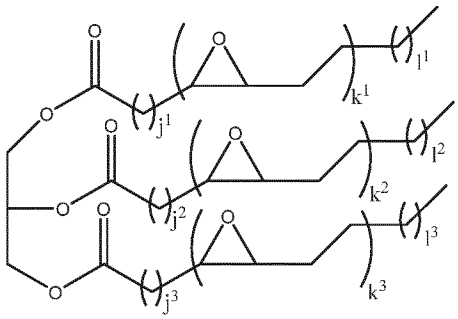


(31)

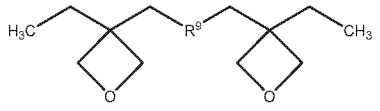


(32)

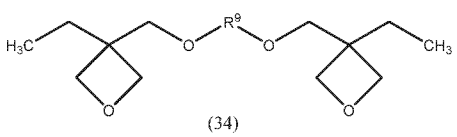
wherein a and b independently are from 1 to 12; wherein x^1, x^2, x^3 are independently from 1 to 26, y^1, y^2, y^3 are independently from 0 to 6, provided $y^1+y^2+y^3$ is at least 2 and z^1, z^2, z^3 are independently from 0 to 25; wherein j^1, j^2, j^3 are independently from 1 to 26, k^1, k^2, k^3 are independently from 0 to 6, provided $k^1+k^2+k^3$ is at least 2 and l^1, l^2, l^3 are independently from 0 to 25; and

more preferably said epoxy compound is selected from the group consisting of N,N-diglycidyl-4-glycidyloxyaniline, sorbitol glycidyl ether-aliphatic polyfunctional epoxy resin, 4,4′-methylenebis(*N*,*N*-diglycidylaniline), 2-[[4-[2-[4-(oxiran-2-ylmethoxy)phenyl]propan-2-yl]phenoxy]methyl]oxirane and poly[(*o*-cresyl glycidyl ether)-co-formaldehyde];

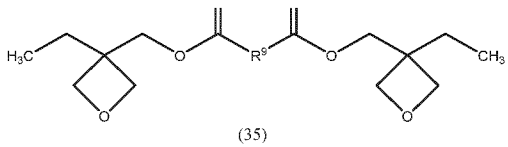
or said cyclic ether compound is an oxetane compound, preferably selected from the group consisting of



(33)



(34)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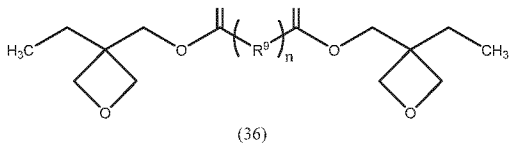
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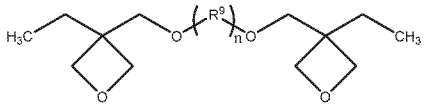
(37)

wherein R^9 is selected from the group consisting of a substituted or unsubstituted C1-C30 alkyl group, a substituted or unsubstituted C3-C30 cycloalkyl group, a substituted or unsubstituted aryl group, a substituted or unsubstituted C7-C30 alkylaryl group, a substituted or unsubstituted C3-C30 heterocycloalkyl group and a substituted or unsubstituted C1-C30 heteroalkyl group; and n is an integer from 1 to 30; and

more preferably said oxetane compound is selected from the group consisting of 1,4-bis[(3-ethyl-3-oxetanylmethoxy)methyl]benzene and bis[1-ethyl(3-oxetanyl)]methyl ether.

6. An aerogel according to any of claims 1 to 5, wherein said clay is phyllosilicate mineral species, preferably selected from the group consisting of 2:1 laminar silicates, and more preferably from the subgroup of montmorillonite or sepiolite and mixtures thereof.

7. An aerogel according to the any of claims 1 to 6, wherein said solvent A and solvent B are a polar solvent, preferably a polar aprotic solvent, more preferably solvent A and solvent B are independently selected from the group consisting of dimethylacetamide (DMAc), dimethylformamide (DMF), 1-methyl-2-pyrrolidinone (NMP), dimethyl sulfoxide (DMSO), acetonitrile, acetone, methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK) and mixtures thereof.

8. An aerogel according to the any of claims 2 to 7, wherein said catalyst is selected from the group consisting of alkyl amines, aromatic amines, imidazole derivatives,

benzyldimethylamine (DMBA), N,N-dimethyl-1-phenylmethanamine, 2-ethyl-4-methylimidazole, 2-phenylimidazole, 2-methylimidazole, 1-methylimidazole, 4,4'-methylene-bis(2-ethyl-5-methylimidazole), 3,4,6,7,8,9-hexahydro-2H-pyrimido[1,2-a]pyrimidine, 2,3,4,6,7,8,9,10-octahydropyrimido [1,2-a]azepine, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), 1,4-diazabicyclo[2.2.2]octane (DABCO), 1,5-diazabicyclo[4.3.0]non-5-ene, quinuclidine, dibutyltin dilaurate (DBTDL) and mixtures thereof.

9. An aerogel according to any of claims 1 to 8, wherein equivalent ratio of epoxy or oxetane groups to isocyanate groups of isocyanate compound A is 15:1 – 1:15, preferably 10:1 – 1:10, more preferably 5:1 – 1:5.

10. An aerogel according to any of claims 1 to 9, wherein clay content is from 0.5 to 30% by weight of the weight of the initial solvent B, preferably from 0.5 to 20% and more preferably from 0.5 to 10%.

11. An aerogel according to the any of claims 2 to 10, wherein catalyst content is from 0.01 to 30% by weight of the total weight of isocyanate compound A and an cyclic ether compound, preferably from 0.1% to 20%, more preferably from 1% to 15% and more preferably from 1% to 10%.

12. An aerogel according to any of claims 1 to 11, wherein isocyanate compound A content is from 0.1 to 65% based on the weight of the solvent A, preferably from 1 to 40% and more preferably from 2 to 30%; and isocyanate compound B content is from 1 to 60% based on the weight of the solvent B, preferably from 2 to 40% and more preferably from 5 to 25%.

13. An aerogel according to the any of claims 1 to 12, wherein said aerogel has a solid content from 4 to 32%, based on total weight of the total initial solution (solution A and solution B), preferably from 5 to 20, more preferably from 5 to 10%

A to solvent B is from 10:1 to 1:10, preferably from 6:1 to 1: 6, and more preferably from 3:1 to 1:3.

15. A thermal insulating material and/or an acoustic insulating material comprising an aerogel according any of claims 1 to 14.

16. Use of an aerogel according to the any of claims 1 to 14 as a thermal insulating material and/or acoustic insulating material.

17. Use of an aerogel according to claim 16 as a thermal insulating material for the storage of cryogens.

18. A method for preparing an aerogel according any of claims 1 to 14 comprising the steps of:

1) adding a clay into the mixture of solvent A and solvent B and mixing at high shear rates;

2) dissolving a cyclic ether compound into the mixture prepared in step 1;

3) adding an isocyanate compound B and mixing;

4) adding an isocyanate compound A and mixing;

5) adding a catalyst if present and mixing;

6) letting the mixture to stand in order to form a gel;

7) exchanging the solvent of said gel with a solvent; and

8) drying said gel by supercritical or ambient drying.

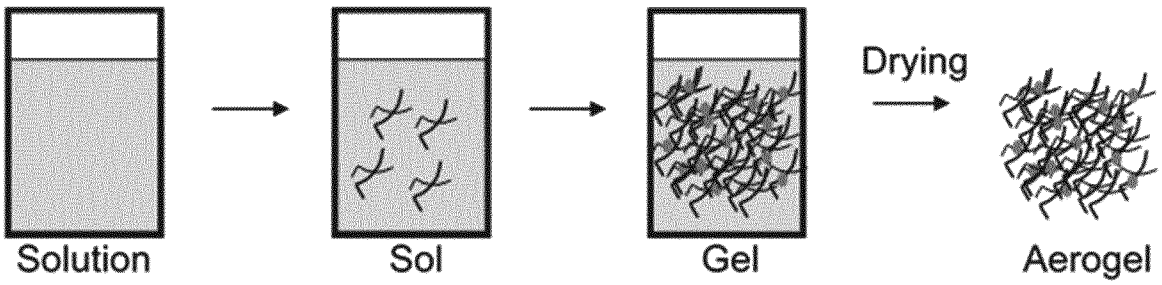
Solution
Sol
Gel
Drying
Aerogel

Fig. 1

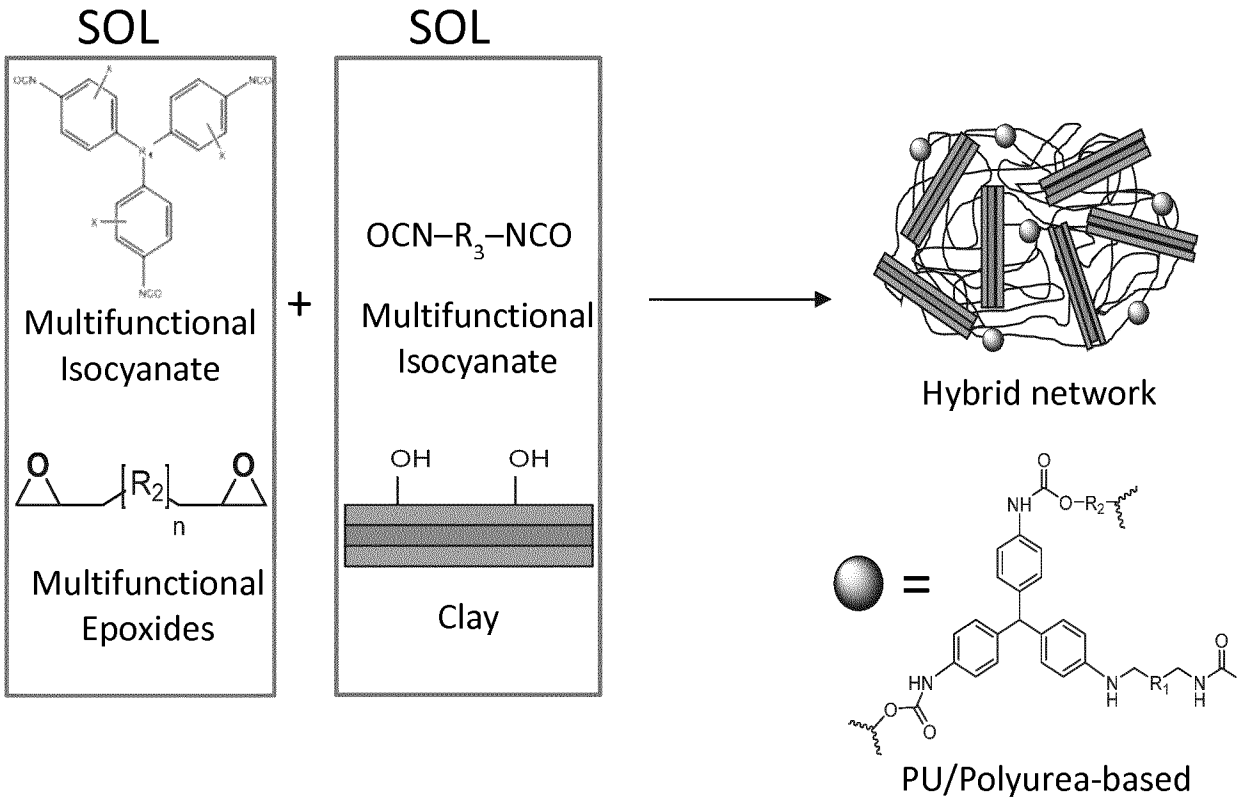
SOL
SOL
Multifunctional Isocyanate
+
OCN–R3–NCO
Multifunctional Isocyanate
OH
OH
Clay
Multifunctional Epoxides
Hybrid network
=
PU/Polyurea-based

Fig. 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/077136

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08G18/76 C08G18/79 C08G18/00
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08G

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2006/281825 A1 (LEE JE KYUN [US] ET AL) 14 December 2006 (2006-12-14) example 1 -----	1-18

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

☒ See patent family annex.

* Special categories of cited documents :

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

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

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
7 December 2017	05/01/2018

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

Information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2006281825 A1	14-12-2006	US 2006281825 A1	14-12-2006
		WO 2006135882 A2	21-12-2006