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(54) Title: FLEXIBLE HYBRID AEROGELS PREPARED UNDER SUBCRITICAL CONDITIONS AND THEIR PREPARATION PROCESS

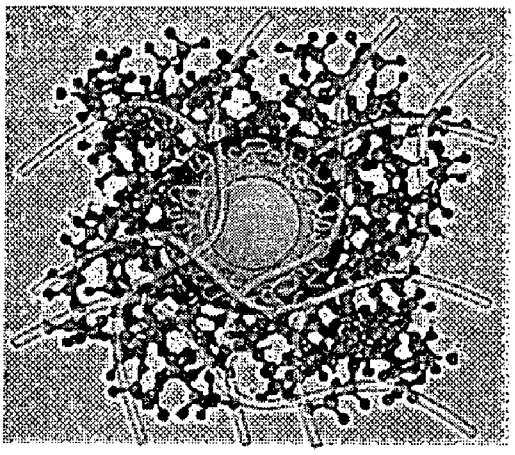

Figure 1

(57) Abstract: The present invention regards flexible aerogels, characterized by being hybrid organic-inorganic-fiber nanocomposites (1), designed to work as thermal insulators in transportation, building, textile or other industries. Their preparation procedure consists in coating textile fibers or mixtures of textile fibers, either organic or inorganic, with a hybrid aerogel of silica and polymer nanoparticles of low glass transition temperature, chemically bonded to the inorganic matrix. The coating is performed by the sol-gel process, immersing the fibers in a precursor mixture of the hybrid gel. By hydrolysis and condensation reactions wet flexible gels are formed, which are aged, washed and dried under subcritical conditions. The flexible aerogels, hereafter referred to as aerogel blankets, contain between 20 and 80 wt% of fiber, between 13 and 79 wt% of silica, between 0.2 and 40 wt% of polymer nanoparticles, have thicknesses between 1 and 80 mm, present thermal conductivities between 0.03 and 0.08 $W.K^{-1}.m^{-1}$, apparent densities between 100 and 165 $kg.m^{-3}$, surface densities between 2 and 4.5 $kg.m^{-2}$, are stable at atmospheric moisture and are hydrophobic.

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DESCRIPTION

Flexible hybrid aerogels prepared under subcritical conditions and their preparation process

Field of the invention

Technical field in which the invention is included

The present invention is included in the generic field of high performance thermal insulating materials and refers, more specifically, to flexible hybrid aerogels containing between 20 and 80 wt% of fiber, between 13 and 79 wt% of silica, and between 0.2 and 40 wt% of polymer nanoparticles, to a process for their preparation under subcritical drying conditions, and to its use in transportation, building, textile or other industries.

State of the art

The transportation, building and specific textile industries have particular demands regarding efficiency, environmental impact, flammability and flexibility of the thermal insulators (as described, for instance, on the ISO Standards - ICS 91.100.60, ISO 9774:2004, ISO 15831:2004, ISO 12576-1:2001 or ISO 13787:2003).

The conventional insulators do not meet simultaneously those requirements. For instance, the fabrication of rock wool involves high temperatures and the production of unwanted residues. Polystyrene, polyolefin and polyurethane based polymeric foams are flammable, non-biodegradable and use pollutant expansion agents such as fluorocarbonides, chlorofluorocarbonides or hydrocarbons.

A new class of very light, highly efficient and non-flammable materials was introduced in the market of high performance insulators in the 1980 decade. These are inorganic aerogels, as described for instance on patents US 3672833, US 6017505 or EP-A-0 171 722.

These aerogels are low density inorganic foams (10-300 $kg \cdot m^{-3}$), having a continuous pore network within a solid matrix, with characteristic diameters in the order of 10 nm. Such microstructure is responsible for high porosities (60-99% by volume) and surface areas (350-1100 $m^2 \cdot g^{-1}$), which makes them excellent thermal and acoustic insulators, with thermal conductivities in the order of 0.01-0.02 $W \cdot m^{-1} \cdot K^{-1}$ and acoustic impedance in the order of 10^3-10^6 $kg \cdot m^{-2} \cdot s^{-1}$.

The production of inorganic aerogels involves two main steps: the synthesis of a wet gel and its drying avoiding significant volume decrease. The synthesis by the sol-gel process is carried out starting from a colloidal solution (the sol) containing precursors of vitreous or ceramic materials, water, solvents and catalysts, which is placed in a mold. By hydrolysis and condensation reactions, the sol changes into a porous solid matrix, which remains immerse in the residual liquid, the gel. The wet gel is a monolithic body, essentially keeping the form and dimensions of the mold. In the silica case, the initial solution includes typically a silicon alkoxide, water, an alcohol and an acid or basic catalyst.

In the general sense, the term "aerogel" refers to a "dry gel containing above 50% by volume of air as a disperse phase", the drying not necessarily performed at temperatures and pressures above the critical point of the liquid to be removed. As a consequence, the drying techniques usually follow two approaches. In the first one, named supercritical drying, the wet gel is heated above the critical temperature of the solvent used as drying medium, in an autoclave that allows exceeding the critical pressure of the solvent. This process is described, for instance, in patents US 5962539, WO 92/03378 or EP-A-0 396076, or in paper [1]. In the second one, named subcritical drying, the wet gels are dried at atmospheric pressure and at temperatures close or slightly above the boiling point of the solvent used as drying medium. See for instance patents US 5705535 or US 5966832.

The supercritical approach is very efficient, since above the critical point there is no liquid/vapor interface at the pores of the gel matrix and, therefore, there are no capillary forces. The resulting dry gel undergoes only a small volume reduction (<15%) in relation to the wet gel, and the corresponding porosity loss is negligible. Although efficient, this is an expensive technique: on one hand due to the high pressures and/or temperatures usually involved in the process; on the other due to the need of relatively expensive equipment and to complex and long intermediate steps. Even when using supercritical extraction of carbon dioxide (with critical temperature of 31.06 °C), the drying pressure is still high (7.3 MPa), the compression equipment needed to liquefy the carbon dioxide and the cryogenic equipment to keep it in the liquid state are still very expensive (as described, for instance, in patents US 4610863 and US 5795557). Besides, the aerogels produced by this technique are extremely fragile and hydrophilic, and, in order to become stable to the atmospheric moisture, they need to undergo additional chemical treatments, usually releasing environmentally harmful products.

The subcritical approach is based on reducing the effect of capillary tensions developed during drying, which can be achieved by different ways: through a judicious choice of the drying medium, as described in patent US 5911658, by chemical modification of the internal surface of the pores of the wet gel, as described for instance in patent WO 94/25149, or by increasing the average dimension of the pores, as described for instance in patents US 4681615, WO 92/20623 and US 5023208.

Independently of the drying method, the high porosity of inorganic aerogels, which confers them unique insulating properties, is also responsible for their mechanical instability, since the transmission of tensions can only occur through the tenuous structure of the solid network. Their fragility, lack of flexibility and the possibility of releasing powders render transportation, handling and installation of

aerogel insulators difficult, restricting their potential applications.

To overcome the problem of powder release, the use of inorganic aerogels in the form of particles embedded in resins (see for instance patent US 6143400) or in foams (as described, for instance, in patents US 5124364 and US 6040375) was proposed. However, the organic resins and foams are flammable and reduce the insulating properties of the aerogel.

The improvement of the mechanical properties was achieved through hybrid inorganic-organic aerogels, either supercritically dried (see for instance patent US 20120175546), or subcritically dried (see for instance patent US 7737189). In some cases, this improvement allowed the production of flexible insulators based on hybrid aerogels. See, for instance, the use of modified silica precursors, which originate secondary aerogel particles able to bond to a polymer that reinforces the structure [2], or patent US 2011245359, where the co-condensation of a metallic oxide precursor with another precursor functionalized with organic groups is proposed, using an ethylenic cross-linking agent. Flexibility may also be attained by using hydrated silanes as precursors of the aerogel chain, as described, for instance, in KR 2010 0092683. However, the flexibility of these materials is limited and the production process also includes supercritical drying, suffering from the technical difficulties and high costs referred above.

For the production of insulating aerogel based fabrics or blankets there has been a number of approaches. One of them consists in the preparation of composite materials by mixing aerogel powder with fibers and/or resins. The fabrication process involves the prefabrication of the different ingredients. See, for instance, patents WO 2008 051029, KR 2009 0097747 or KR 2010 0098905. However, their preparation is expensive, since it demands large quantities of supercritical aerogel powder and the production process involves a significant number of steps.

Another approach consists in preparing nanocomposites in which the aerogel is formed interstitially within a fiber matrix. See, for instance, the paper by L. Zhang and co-workers [3], where the matrix is a cellulose gel made of fibrils with less than 10 nm in length, or patent US 6068882, where the matrix is made of low density fibers (silicon or aluminum carbonide), or even patent DE102009042526, where a nanoporous insulating material containing pyrogenic silicic acid, silica aerogel and precipitated silicic acid is electrostatically attached to the macrocavities of the fibers.

Another approach consists in using the aerogel structure as a matrix to incorporate a nanophase, typically fibers, which are added to the sol-gel precursor mixture, in order to reinforce the inorganic network. See, for instance, patents US 6087407 and US 20070154698A1, where the gel may be inorganic or organic and the fibers may be of glass or carbon.

The nanocomposites referred above are supercritically dried, with replacement of the residual liquid by carbon dioxide, involving all the problems associated with this type of drying.

The number of patents on insulating blankets with subcritical drying is very low. See, for instance, patent US 2010140840, which claims blankets containing commercial hydrophobic aerogel particles, evenly dispersed within a fibrous matrix, and patent CN 101671030, which involves a surface modification step of the fiber-silica aerogel composite material, after ageing and before washing and subcritical drying.

The possibility of using layers of different nature to produce high performance insulating blankets has also been considered in recent years. See, for instance, patents US 2007173157, WO 2008129281, US 2008307737, US 2008229704, KR 20100083543 (three fibrous layers bonded by an organic glue, where the third one is a non-woven fabric coated with silica aerogel powder), patent CN 101791881 (a sandwich with polytetrafluoroethylene external layers and a hydrophobic aerogel powder filling), patent JP 2010167685 (laminated formed by a sheet of aerogel with porosity

above 80%, coated on one face with a layer of resin or an inorganic fiber tissue impregnated with resin, and reinforced on the other face with a highly heat-resistant foil, the different layers being integrated by a mechanical coupling method), and patent US 2012168095 (a blanket intended for insulating blinds made of commercial aerogel granules bonded by polyester fibers between tissue layers that may be cellular, for instance polyester, the layers being glued, sewed or mechanically adapted).

In the present invention, an alternative production process is proposed for insulating blankets stable to atmospheric moisture, made of a silica/polymer particles/fiber hybrid nanocomposite aerogel, where the fibers are coated by the hybrid nanoaerogel synthesized *in situ*, the said aerogel being object of patent PT 103257/US 7737189, and subsequently dried under subcritical conditions. The flexible hybrid aerogel is henceforth named *AEROFLEX* or aerogel blanket. The possibility of producing the blankets as multilayers of alternating monolayers of non-modified and coated is also proposed.

Summary of the invention

The present invention refers to a new flexible, hybrid aerogel material under subcritical conditions. This nanostructured material is prepared by immersion of textile fibers into a precursor mixture of a hybrid gel of silica and polymer nanoparticles, whose dispersion in water is commonly named latex, in a mold. The textile fibers may be of an inorganic polymer, an organic polymer, or a mixture of the previous, in the form of woven fabric, non-woven fabric or foam. Upon the hydrolysis and condensation reactions the fibers are coated by the hybrid silica-latex gel. The preparation of the precursor mixture of the hybrid silica-latex gel, as well as the gelation reactions, are described in patent PT 103257/US 7737189, the compositions having been optimized for the production of blankets. The hydrophobicity of the material may be increased by

inclusion of additives in the precursor mixture of the hybrid silica-polymer nanoparticles gel, such as silanes, alkylsilanes, silazanes, long chain siloxanes, unsaturated or sulphurated alkyl chains, containing co-condensable groups with the silica oligomers, in a weight proportion between 0.05 and 20%. The wet gel blanket obtained by gelation is then aged in different media, with or without hydrophobizing additives, and subsequently washed and dried under temperature and pressure conditions below the critical point of the fluid to be extracted, in an atmosphere almost saturated in the washing solvent, in order to produce an aerogel.

The aerogel blanket is an inorganic-organic-fiber hybrid nanocomposite (1), which is flexible, stable at atmospheric moisture and hydrophobic, with apparent density between 100 and 165 $kg.m^{-3}$, surface density between 2 and 4.5 $kg.m^{-2}$ and thermal conductivity between 0.03 and 0.08 $W.K^{-1}.m^{-1}$. The flexible hybrid aerogel may have thickness between 1 and 80 mm and fiber content between 20 and 80 wt%, silica content between 13 e 79 wt%, and latex content between 0.2 and 40 wt%.

This material has applications as thermal insulator in several industries, and may be prepared in the form of a monolayer of flexible hybrid aerogel or of a laminated material consisting of different layers, alternating layers of flexible hybrid aerogel with layers of uncoated fiber.

Detailed description of the invention

The material described in the present invention consists of a high performance thermic insulator, composed of flexible hybrid aerogels prepared under subcritical conditions, designated aerogel blankets. These blankets are hybrid fiber-organic-inorganic nanocomposites (1), prepared by immersion of a textile fiber in a precursor mixture of an hybrid gel containing silica and low glass transition temperature polymer nanoparticles (latex) in a mold, allowing the coating of the fiber by gelification of the mixture. The blankets of wet gel are aged,

washed and dried under subcritical conditions, in an atmosphere of the washing solvent close to saturation. Solvent extraction is achieved with the gel in the mold, followed by removal of the aerogel from the mold.

The precursor mixture of the hybrid silica network and polymer nanoparticles is prepared by acid co-hydrolysis of an alcoholic dispersion of alcoxisilanes and colloidal polymer nanoparticles functionalized with trimethoxisilyl groups in the shell. The synthesis parameters for this mixture (conditions for catalysis of the hydrolysis and condensation reactions and method for the preparation of the latex) are described in the patent PT 103257/US 7737189 and were optimized for the production of blankets.

The textile fiber is composed of a polymer, that can be organic, inorganic or a mixture of the previous, can have different morphologies, including woven fabric, non-woven fabric or foam, and can be immersed in the precursor mixture of hybrid gel in different steps of the synthesis procedure: either during the acid hydrolysis, or during the basic polycondensation. Organic fibers can be pre-treated to become fire-resistant.

The ageing of the blankets is carried out at 60°C, in two steps. In the first step, the gel is left immersed in the residual liquid for a period of 12 to 48 hours. In the second step, the gel is immersed, during a period of 12 to 24 hours, in water or in a hydrophobizing mixture containing 5 to 20 wt% of additives such as silanes, alkylsilanes and silazanes.

Alternatively, the hydrophobicity of the material can be increased by incorporating 0.05 to 20 wt% of additives in the precursor mixture of silica hybrid gel and polymer nanoparticles mixture. The additives can be silanes, alkylsilanes, silazanes, long-chain siloxanes, or insaturated or sulfonated alkylic chains, containing groups that can be co-condensed with the silica oligomers.

The aerogel blankets can also be composed of several coated and uncoated fiber layers.

The flexible hybrid aerogels contain between 20 and 80 wt% of fiber, between 13 and 79 wt% of silica and between 0.2 and 40 wt% of polymer nanoparticles with diameter equal to, or lower than 100 nm. The resulting blankets have between 1 and 80 mm of thickness, apparent density between 100 and 165 $kg.m^{-3}$, surface density between 2 and 4.5 $Kg.m^{-2}$, thermal conductivity between 0.03 and 0.08 $W.K^{-1}.m^{-1}$, are stable to atmospheric moisture and hydrophobic.

The material of the present invention presents technological advantages when compared to commercially available insulators, as can be observed in Table 1, where some fundamental properties of blankets from different thermic insulators are compared.

Table 1: Comparison between some relevant properties of the present flexible hybrid aerogel (*AEROFLEX*) and those of other thermal insulators

Material	Apparent Density/ $kg.m^{-3}$	Thermal Conductivity at 50°C/$W.m^{-1}.K^{-1}$	Thickness for equivalent insulation/mm[1]	Surface Density/ $kg.m^{-2}$
Polyester veil	60	0.095	62.9	3.8
Polyester foam	12	0.06	39.7	0.5
Glass veil	100	0.042	27.8	2.8
Rock wool	100	0.068	45	4.5
Glass wool	80	0.040		
$AEROFLEX_{PETVeil}$[a]	125	0.048	31.8	4.0
$AEROFLEX_{GVeil}$[b]	165	0.041	27.1	4.5
$AEROFLEX_{PETFoam}$[c]	100	0.032	21.2	2.1
$AEROFLEX_{Multilayer}$[d]	125	0.035	23.1	2.9
Aerogel A[e]	180	0.020	13.3	2.4
Aerogel B[f]	170	0.017	11.3	1.9
Aerogel C[g]	110	0.015		
Aerogel D[h]	130	0.013		
Aerogel EZ[i]	130	0.017	11.3	1.5
Aerogel F[j]	70	0.025		

[1] Thickness normalized to a 45 mm rock wool layer
[a] Subcritical hybrid aerogel/Polyester veil (PET, 40-45 wt%)
[b] Subcritical hybrid aerogel/Glass veil (G, 40-55 wt%)
[c] Subcritical hybrid aerogel/Polyester foam (PET, 15-30 wt%)
[d] $AEROFLEX_{GVeil}$/$AEROFLEX_{PETVeil}$/Glass wool/$AEROFLEX_{PETVeil}$/$AEROFLEX_{GVeil}$
[e] Methylated silica/Glass fiber (G, 40-50 wt%)
[f] Methylated silica/Polyacrylonitrile fiber (PAN, 70-50 wt%)
[g] Methylated silica/fibers - for high temperatures
[h] Methylated silica/Polytetrafluoroethylene/Glass fiber (PTFE/G, 40-50 wt%)
[i] Silica/PET/Glass fiber (Silica, 40-50%/PET, 10-20%/G, 10-20 wt%)
[j] Methylated silica/PTFE/Nylon (Silica, 45-77 wt%/PTFE, 17-47 wt%/Nylon, 0-6 wt%)

The new product, described in this invention, is characterized by presenting lower thermal conductivities than the lower cost insulators (first four lines of Table 1) and lower densities than the higher cost insulators (last six lines of Table 1). It therefore represents a good compromise between the values of density and thermal conductivity, fundamental properties to considering the selection of an insulator blanket.

In terms of safety, the new product is non-toxic, non-flammable and stable at atmospheric conditions. The production technology uses green chemistry processes, with no environmental risks, allowing the recycling of all the used solvents.

Description of the Drawings

Figure 1 represents a scheme of the structure of the hybrid organic-inorganic-fiber nanocomposite (1) constituting the aerogel blankets, illustrating a slice network containing interpenetrated fibers and polymer nanoparticles.

Figure 2 represents the diagram of the synthesis of the flexible hybrid aerogels, or aerogel blankets, illustrating the following steps: a) Preparation of the polymer nanoparticles (PNPs) by emulsion polymerization, with addition of: n-bulyl methacrylate (BMA), n-butyl acrylate (BA) and ethylene glycol dimethacrylate (EGDMA); sodium dodecyl sulphate (SDS) surfactant; potassium persulfate (KPS) initiator; and trimethoxisilyl propyl methacrylate (MPS); b) Acid hydrolysis of the tetraetoxysilane (TEOS) precursor in 2-propanol in the presence of the PNPs; c) Basic condensation; d) Ageing; e) Washing; f) Drying in subcritical conditions, in an atmosphere almost saturated with the washing solvent, at 333 K.

Figure 3 presents laser scanning fluorescence confocal microscopy images (left) and optical microscopy images (right) of clean glass fiber veil before (A) and after coating with subcritical hybrid aerogel (B). Comparison between one glass fiber before and after being coated (C).

Examples

The following example describes the preparation, by the process proposed in the present invention, of silica/latex/fiber hybrid aerogel blanket containing 43 wt% of polyester fiber veil and 57 wt% of subcritical hybrid aerogel (containing 1 wt% of poly(butyl methacrylate-co- butyl acrylate) copolymer nanoparticles with 100 nm average diameter, surface modified with trimethoxisilyl groups).

The coating with hybrid aerogel is prepared by hydrolysis/ condensation of tetraethoxisylane (TEOS) in two steps, described in the patent PT 103257/US 7737189.

An aqueous dispersion of colloidal cross-linked polymer nanoparticles with 100 nm average diameter and trimethoxysilane groups in the shell is added, drop by drop, to a mixture of TEOS in 2-propanol (corresponding to a 1:4 molar ratio of TEOS:2-propanol), in order to obtain a mixture containing 35 wt% of TEOS, 0.1 wt% of polymer nanoparticles and 24 wt% of water (corresponding to a 1:8 molar ratio of TEOS:water). The reaccional mixture is acidified with chloridric acid (HCl) 0.1 N (corresponding to a 1:0.007 molar ratio of TEOS:HCl) and added to the fiber in a closed recipient, heated to 60°C and stirred at 120 rpm during 60 minutes. The reactional mixture is then neutralized with a mixture of ammonia (corresponding to a 1:0.014 molar ratio of TEOS:ammonia) in 2-propanol, using a volume that completely covers the fiber, and then left undisturbed to gelify, which takes about 7 minutes. The wet hybrid gel blanket is aged for 48 hours at 60°C: the first 24 hours in the residual liquid and the following 24 hours after the addition of an hydrophobizing hexadimethylsilazane (HMDZ) in 2-propanol (corresponding to a 1:0.02 molar ratio of TEOS:HMDZ), followed by addition of 1 M nitric acid (corresponding to a 1:0.35 molar ratio of HMDZ:nitric acid) to catalyze the hydrophobization reaction. The gel blanket is washed with 2-propanol at 60°C and dried in subcritical conditions, at 60°C

and atmospheric pressure, controlling the solvent evaporation, until the weight loss becomes insignificant.

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Date: February 13th, 2014

CLAIMS

1. Hybrid flexible aerogels, prepared under subcritical conditions, characterised in that they are hybrid organic-inorganic-fiber nanocomposites (1), constituted by a textile fiber coated with a hybrid aerogel of silica and polymer nanoparticles.

2. Hybrid flexible aerogels according to claim 1, wherein they contain between 20 and 80 wt% of fiber, between 13 and 79 wt% of silica, and between 0.2 and 40 wt% of polymer nanoparticles.

3. Hybrid flexible aerogels according to claims 1 and 2, wherein the polymer nanoparticles have low glass transition temperature and average diameter of 100 nm or less.

4. Hybrid flexible aerogels according to claims 1 to 3, wherein the textile fiber is an inorganic polymer, an organic polymer, or a mixture of the previous.

5. Hybrid flexible aerogels according to claims 1 to 4, wherein the textile fiber have different morphologies, including woven fabric, non-woven fabric, or foam.

6. Hybrid flexible aerogels according to claims 1 to 5, wherein organic fibers are pre-treated to make them non-flammable.

7. Hybrid flexible aerogels according to claims 1 to 6, wherein the thickness of the said aerogels is between 1 and 80 mm.

8. Hybrid flexible aerogels according to claims 1 to 7, wherein the said aerogels have apparent density between 100 and 165 kg.m^{-}3, surface density between 2 and 4.5 kg.m^{-2}, and thermal conductivity between 0.03 and 0.08 W.K^{-1}.m^{-1}.

9. Hybrid flexible aerogels according to claims 1 to 8, wherein the said aerogels are stable at atmospheric moisture and are hydrophobic.

10. Process of preparation of the aerogel blankets defined in claims 1 to 9, wherein the hybrid aerogel of silica and polymer nanoparticles is prepared by the sol-gel process in two steps, comprising the hydrolysis step catalyzed by a strong acid, and the polycondensation step catalyzed by an alkaline catalyst.

11. A process according to claim 10, wherein the hybrid gel precursor mixture is prepared in acidic alcoholic medium, by co-hydrolysis of a silicon alkoxide and polymer nanoparticles surface-functionalized with trimethoxysilyl groups.

12. A process according to claim 11, wherein the hybrid gel precursor mixture includes includes hydrophobising additives.

13. A process according to claim 12, wherein the additives include long chain siloxanes and unsaturated or sulphurated alkyl chains, containing groups co-condensable with silica oligomers.

14. A process according to claims 12 and 13, wherein the amount of additive in the hybrid gel precursor mixture is between 0.05 and 20 wt%.

15. A process according to claims 10 to 14, wherein the fibers are immersed in the hybrid gel precursor mixture during the acidic hydrolysis step or during the basic polycondensation step.

16. A process according to claim 15, wherein the fibers are immersed in the hybrid gel precursor mixture in a mold.

17. A process according to claims 10 to 16, wherein the hybrid wet gel blankets is aged in the mold at 60°C.

18. A process according to claim 17, wherein the ageing is carried out by keeping the hybrid wet gel immersed in the residual liquid for one period between 12 and 48 hours, followed by a period between 12 and 24 hours of immersion in water.

19. A process according to claim 17, wherein the ageing is carried out by keeping the hybrid wet gel immersed in the residual liquid for one period between 12 and 48 hours, followed by a period between 12 and 24 hours of immersion in a hydrophobization mixture containing silanes, alkyl silanes or silazanes.

20. A process according to claim 19, wherein the hydrophobization mixture contains between 5 and 20 wt% of additive.

21. A process according to claims 10 to 20, wherein the aged hybrid wet gel blankets are washed with a solvent.

22. A process according to claims 10 to 21, wherein the aged and washed hybrid wet gel blankets are dried under subcritical conditions, in an atmosphere that is almost saturated in the washing solvent.

23. A process according to claim 22, wherein the drying is carried out with the wet gel blanket in the mold, followed by removal of the aerogel blanket from the mold.

24. Use of the hybrid flexible aerogels defined in claims 1 to 9, characterised in that they are applied as thermal insulators, either in the form of aerogel blankets or laminates of alternating layers of uncoated fiber and flexible hybrid aerogel.

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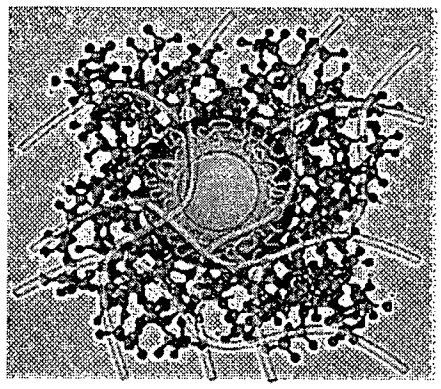

Figure 1

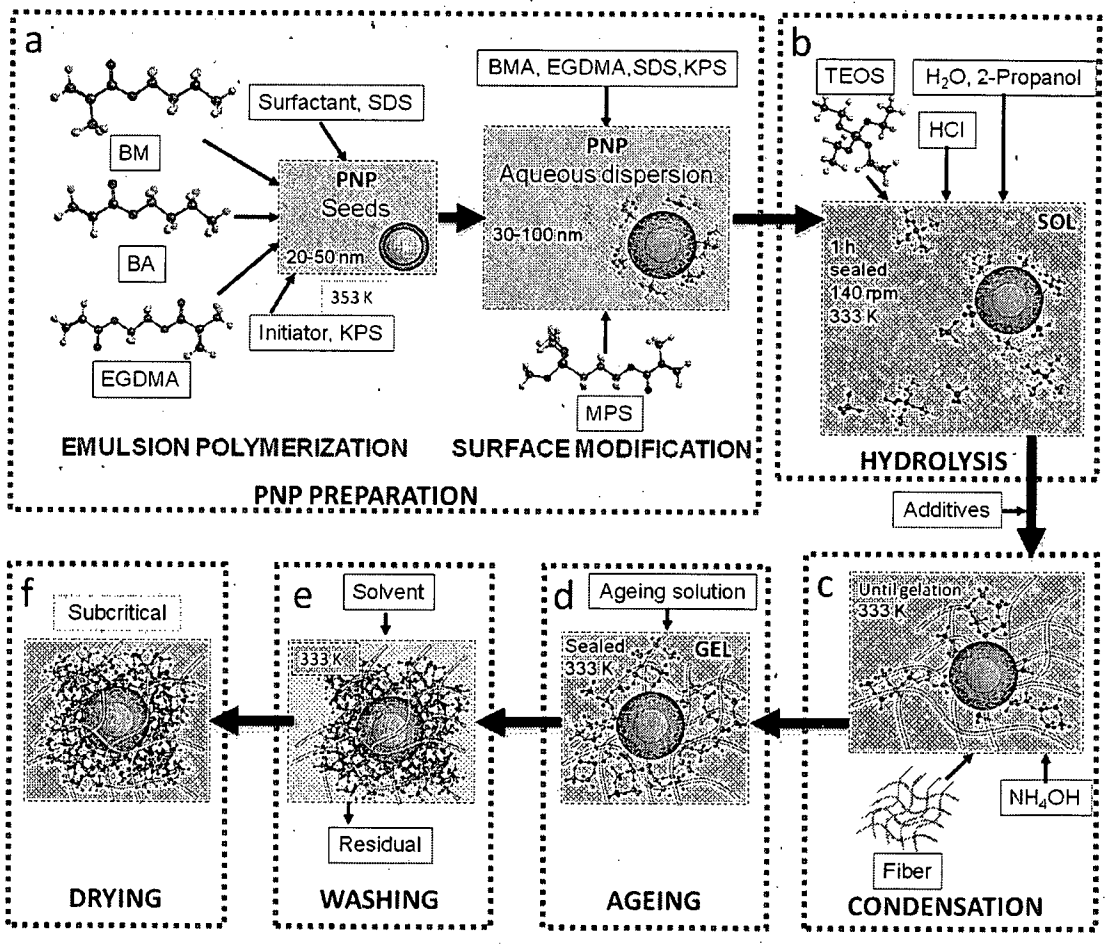

Figure 2

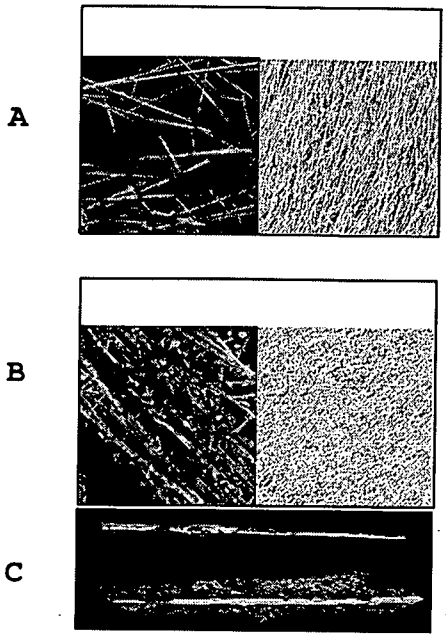

Figure 3

INTERNATIONAL SEARCH REPORT

International application No
PCT/PT2014/000012

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01J13/00 D06M11/79 D06M23/08 E04B1/78 F16L59/02
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)
B01J D06M E04B F16L

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2013/005842 A1 (EVANS OWEN R [US] ET AL) 3 January 2013 (2013-01-03) paragraph [0005] paragraph [0011] - paragraph [0016] paragraph [0034] - paragraph [0035] figure 2 -----	1-24
Y	WO 2006/107226 A1 (INST SUPERIOR TECNICO [PT]; GASPAR MARTINHO JOSE MANUEL [PT]; ILHARCO) 12 October 2006 (2006-10-12) cited in the application claims ----- -/--	1-24

[X] Further documents are listed in the continuation of Box C.

[X] 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

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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
3 June 2014	11/06/2014

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Fiocco, Marco

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Form PCT/ISA/210 (second sheet) (April 2005)

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	A. FIDALGO ET AL: "Hybrid Silica/Polymer Aerogels Dried at Ambient Pressure", CHEMISTRY OF MATERIALS, vol. 19, no. 10, 1 May 2007 (2007-05-01), pages 2603-2609, XP055028508, ISSN: 0897-4756, DOI: 10.1021/cm062962w the whole document -----	1-24
Y	US 2011/245359 A1 (CONDO PETER D [US] ET AL) 6 October 2011 (2011-10-06) cited in the application paragraph [0013] examples 9-12 -----	1-24
Y	JP 2010 167685 A (IMAE KOGYO KK) 5 August 2010 (2010-08-05) cited in the application abstract -----	24

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/PT2014/000012

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		US 2011245359 A1	06-10-2011
		WO 2010080239 A2	15-07-2010
JP 2010167685 A	05-08-2010	JP 5354266 B2	27-11-2013
		JP 2010167685 A	05-08-2010